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Study on Polymer Modified Road Asphalt
Mixture

SUMMARY

Crumb rubber (CR) from scrap tires is further recycled, developed and taken into use of new tires, in tire-derived fuel, in construction and building material application and products, in agricultural uses, in activated carbon production and adsorption technology applications, recreational and sports applications and modified-asphalt production (i.e. in roofing and road pavement). Using polymer waste materials like crumb rubber and textile fiber (TF) from used tires, as well as plastics as modifiers in road asphalt mixture would foremost lessen additional road construction cost, increase the service life of asphalt pavement and in addition to that can be considered a great way to reduce environmental pollution.

The use of waste and virgin polymer modifiers on improving the engineering properties of asphalt binder has been identified by a number of previous researches. On the other hand, there are very few studies focused on the use of two different polymer modifiers as admixture additives in the improvements of road asphalt mixture. However, the formulation of ternary asphalt-additives blend composed of (CR : LDPE) and (CR : TF) couples, and quaternary asphalt additives-blend composed of (CR : LDPE : TF) triplets on the virgin asphalt to optimize the asphalt basic and rheological properties and to use the extrusion of two or three additives to obtain composite materials of them, as well as CR and TF in the form of single, may possibly be named novelty as there is no existing literature in this direction. In addition to that, in this study, broad investigations of the effects of binary, ternary and quaternary asphalt polymer blends on the reinforcements of the virgin asphalt binder are performed. Therefore, these laboratorial investigations in this direction demonstrate that workable polymer modified asphalt blends can be established with appropriate variables such as time of reaction, concentration levels of modifiers and ratios within each composite on the asphalt to improve engineering characteristics of the asphalt pavement material. The temperature of reaction is fixed at $180 \pm 2^\circ\text{C}$.

On one occasion, a technique implies a mixing process of virgin asphalt of (70/100) penetration grade with the single additives of low-density polyethylene (LDPE) commercially obtained, and crumb rubber (CR) and textile fiber (TF) derived from scrap tires each in a separate way at different concentrations of 3 wt% – 15wt%. While in



another technique, the mixing process involves virgin asphalt with composites of (CR:LDPE), (CR:TF) and (CR:LDPE:TF) separately. These composites are formally prepared in an extruder at different weight fractions. Then composites are cut into small pieces, subsequently were mechanically milled to obtain a less size of materials. Finally, binary, ternary and quaternary blends of asphalt and additives are prepared at 180 ± 2 °C with a high-speed mixing 3000 rpm for 60min.

The second part of the study implies the investigation of the effect of using grafted modifiers by the addition of maleic anhydride (MAH) on the basic and rheological properties of the asphalt binder. The process is carried out using a stainless steel batch reactor at 150 °C, 1500 rpm. The reaction was carried out under a nitrogen atmosphere for 60 min.

Basic physical and rheological properties measurements, as well as wheel track test (WTT), were studied. Test results show that the investigated properties of the virgin asphalt are improved by the addition of the additives. Thin layer chromatography coupled with flame ionization detector (TLC–FID), Fourier transform infrared spectroscopy, FTIR, Gel Permeation Chromatography (GPC/SEC), and scanning electron microscopy (SEM) techniques are used to follow the reactions occurring in two different types of asphalt modification method.

Keywords: *Asphalt, Polymer, Modification, Crumb rubber, Textile fiber, Tires, Rheology*

STRESZCZENIE

W niniejszej pracy przedstawiono wyniki badań dotyczące otrzymania i scharakteryzowaniem właściwości fizyko-chemicznych, reologicznych i użytkowych oraz stabilności podczas przechowywania nowej grupy lepiszczy polimerowo-asfaltowych modyfikowanych za pomocą polietylenu niskiej gęstości (LDPE), a także odpadowych materiałów polimerowych, w postaci granulatu gumowego (CR) i kordu tekstylnego (TF), uzyskiwanych w procesach recyklingu użytkowych opon samochodowych. Innowacyjność prowadzonych badań i ich przewaga nad znanymi już sposobami modyfikacji asfaltów polimerami polegała na wykorzystaniu w procesie modyfikacji asfaltu naftowego odpadowych modyfikatorów polimerowych przetworzonych w procesie wyłaczania do postaci granulatu oraz zastosowaniu bezwodnika maleinowego, który zaszczerpiony na asfalcie pełnił rolę kompatybilizatora mieszalności asfaltu i dodatków polimerowych.

Modyfikatory wykorzystane w pracy wytwarzane były z mieszanin złożonych z asfaltu użytego w ilości 10% mas. oraz odpowiednio granulatu gumowego, kordu tekstylnego i polietylenu, użytych w ilości 90% mas. W badaniach zastosowano również modyfikatory w postaci kompozytów trójskładnikowych (Asfalt:CR:TF oraz Asfalt:CR:LDPE) i czteroskładnikowych (Asfalt:CR:TF:LDPE), w których zastosowano różnych stosunek masowy poszczególnych komponentów.

Przetworzenie modyfikatorów polimerowych w procesie wyłaczania miało na celu wstępne ich zhomogenizowanie i spęcznienie asfaltem, a w przypadku modyfikatorów w postaci granulatu gumowego i kordu tekstylnego pozwoliło na częściową degradację ich struktury i przeprowadzenie w postać plastycznego granulatu. Dzięki temu mieszanie asfaltu z modyfikatorami polimerowymi było znacznie ułatwione, co w konsekwencji umożliwiło usprawnienie całego procesu modyfikacji i wpłynęło na uzyskanie lepiszczy polimerowo-asfaltowych charakteryzujących się polepszonymi właściwościami fizyko-chemicznymi, reologicznymi i aplikacyjnymi oraz stabilnością w warunkach ich magazynowania w podwyższonej temperaturze.

Słowa kluczowe: lepiszcza polimerowo-asfaltowe, modyfikacja asfaltu, odpady gumowe, kord tekstylny, recykling opon, właściwości reologiczne asfaltów.



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Finally, I wish to thank my family, my brothers and sisters and my great wife, for their endless love and unconditional support.

DEDICATION

This thesis is dedicated to:

My parents and my family for their love

My wife for her endless help and continuous support

My son

Abdullatif

for his sweet smile that gives me more energy to work

DECLARATION

The work described in this thesis was conducted at the Gdansk University of Technology, Department of Polymer Technology, between October 2012 and September 2017. I declare that the work is my own and has not been submitted for a degree of another university.

STRUCTURE OF THESIS

A concise introduction to the identification of the asphalt binder as an important material that has many applications, its history of application in road pavement construction, chemical composition, most failure modes and histories of polymer utilization in the reinforcement of asphalt mixtures are presented in **Chapter 1**. Also in this chapter, a section is dedicated to describing the problem of the study and the main objectives of the study. **Chapter 2** is focused on the different processes of asphalt modifications supported with a number of case studies carried out over the years with special attention paid towards the interaction theories of asphalt rubber. In **Chapter 3**, a number of publications and scientific reports from recent years and which are relevant to the asphalt modifications by using a variety of polymers are presented. **Chapter 4** is designed to provide details of the experiment studies, including the continuing phase (asphalt matrix) of 70/100 penetration grade and the modifier materials. Instruments involved in this study are covered in a separate section. The chapter also contains specific methods of sample formulations. **Chapter 5** reports data and results obtained from the sample analyses, which are conducted broadly in the laboratory. The chapter was tied up with the most important conclusions of this thesis.

LIST OF ACRONYMS

Characteristic	Meaning
A1	3 Percent of Crumb Rubber-modified Asphalt
A2	5 Percent of Crumb Rubber-modified Asphalt
A3	10 Percent of Crumb Rubber-modified Asphalt
A4	15 Percent of Crumb Rubber-modified Asphalt
AC	Asphalt Cement
AR	Asphalt Rubber
AASHTO	American Association of State Highway and Transportation Officials
ASTM	American Society for Testing and Materials
B1	3 Percent of Low-density Polyethylene-modified Asphalt
B2	5 Percent of Low-density Polyethylene-modified Asphalt
B3	10 Percent of Low-density Polyethylene-modified Asphalt
B4	15 Percent of Low-density Polyethylene-modified Asphalt
bPM-AS	Binary Polymer-modified Asphalt
C	Carbon
C1	3 Percent of Textile Fiber-modified Asphalt
C2	5 Percent of Textile Fiber-modified Asphalt
C3	10 Percent of Textile Fiber-modified Asphalt
C4	15 Percent of Textile Fiber-modified Asphalt
CR	Crumb Rubber
CRM-Asphalt	Crumb Rubber Modified Asphalt
CR-HMA	Crumb Rubber Hot-mix Asphalt

CRM	Crumb Rubber Modifier
CPP	Chlorinated Polypropylene
CTEBU	Center of Transportation Engineering of Bangalore University
D1	3 Percent of (3:1) Crumb Rubber : Low-density Polyethylene-modified Asphalt
D2	5 Percent of (3:1) Crumb Rubber : Low-density Polyethylene-modified Asphalt
D3	10 Percent of (3:1) Crumb Rubber : Low-density Polyethylene-modified Asphalt
D4	15 Percent of (3:1) Crumb Rubber : Low-density Polyethylene-modified Asphalt
DSR	Dynamic Shear Rheometer
DMS	Dynamic Mechanical Spectroscopy
DMA	Dynamic Mechanical Analysis
DTT	Direct Tensile Test
DSC	Differential Scanning Microscope
E1	3 Percent of (2:1) Crumb Rubber : Low-density Polyethylene-modified Asphalt
E2	5 Percent of (2:1) Crumb Rubber : Low-density Polyethylene-modified Asphalt
E3	10 Percent of (2:1) Crumb Rubber : Low-density Polyethylene-modified Asphalt
EVA	Ethylene-Vinyl Acetate
E4	15 Percent of (2:1) Crumb Rubber : Low-density Polyethylene-modified Asphalt
EVA-M-As	Ethylene-Vinyl Acetate-Modified Asphalt
EPDM	Ethylene-Propylene-Diene Monomer Rubber
F1	3 Percent of (3:1) Crumb Rubber : Textile Fiber-modified Asphalt

F2	5 Percent of (3:1) Crumb Rubber : Textile Fiber-modified Asphalt
F3	10 Percent of (3:1) Crumb Rubber : Textile Fiber-modified Asphalt
F4	15 Percent of (3:1) Crumb Rubber : Textile Fiber-modified Asphalt
FTIR	Fourier Transform Infrared
G1	3 Percent of (2:1) Crumb Rubber : Textile Fiber-modified Asphalt
G2	5 Percent of (2:1) Crumb Rubber : Textile Fiber-modified Asphalt
G3	10 Percent of (2:1) Crumb Rubber : Textile Fiber-modified Asphalt
G4	15 Percent of (2:1) Crumb Rubber : Textile Fiber-modified Asphalt
G'	Storage Modulus
G''	Loss Modulus
G*	Complex Shear Modulus
GMA	Glycidyl Methacrylate
GHG	Green House Gases
GPC	Gel Permeation Chromatography
GM-g-LDPE	Glycidyl Methacrylate-grafting- Low-density Polyethylene
H1	3 Percent of (3:1) Crumb Rubber : Low-density Polyethylene: Textile Fiber
H2	5 Percent of (2:1) Crumb Rubber : Low-density Polyethylene: Textile Fiber
H3	10 Percent of (2:1) Crumb Rubber : Low-density Polyethylene : Textile Fiber
H4	15 Percent of (2:1) Crumb Rubber : Low-density Polyethylene : Textile Fiber
H	Hydrogen
HDPE	High-density Polyethylene

HMA	Hot Mix Asphalt
I	CRM-g-MAH-Asphalt
IPPr	Isotactic Polypropylene
ITFT	Indirect Tensile Fatigue
j	LDPE-g-MAH-Asphalt
K	TF-g-MAH-Asphalt
L	CR:LDPE-g-MAH-Asphalt
LDPE	Low-density Polyethylene
LLDPE	Linear Low-density Polyethylene
M	CR:TF-g-MAH-Asphalt
MI	Modification indices
MSW	Municipal Solid Waste
Mw	Average Molecular Weight
MQ	Marshall Quotient
N	CR:LDPE:TF-g-MAH-Asphalt
N	Nitrogen
NCAT	National Center for Asphalt Technology
OGFC	Open Grade Friction Concrete
O	Oxygen
PE	Polyethylene
PP	Polypropylene
PS	Polystyrene
PVC	Polyvinyl Chloride
PET	Polyethylene Terephthalate

PPA	Poly-Phosphoric Acid
PG	Penetration Grade
PDI	Polydispersity Index
PMA	Polymer Modified Asphalt
PUF	Polyurethane Foam
qPM-AB	Quaternary Polymer-modified Asphalt
R²	Correlation Factor Coefficient
RAC	Recycled Asphalt Concretes
RAP	Reclaimed Asphalt Pavement
SBS-M-As	Styrene Butadiene Styrene Modified-Asphalt
SBS	Styrene Butadiene Styrene
SIS	Styrene-Isoprene-Styrene
SBR	Styrene-Butadiene-Rubber Random Copolymers
SB	Styrene-Butadiene Di-block Copolymers
S	Sulfur
SBS-M-As	Styrene Butadiene Styrene-Modified Asphalt
SAM	Stone Mastic Asphalt
S-w	Percentage of Swelling
SR	Stability Retained
SEM	Scanning Electron Microscope
TF	Textile Fibers
Tg	Transition Temperature
TEM	Transition Electron Microscope
TBEE	Triazole Borate Ester Ethanol



TBEO	Triazole Borate Ester Octanol
TFM-asphalt	Textile Fiber-modified Asphalt
TBEB	Triazole Borate Ester Butanol
TBEO_{SA}	Triazole Borate Ester-Sulphuric Acid
tPM-AB	Ternary Polymer-modified Asphalt
US-EPA	United States Environmental Protection Agency
WRAP	Waste and Resource Action Program
WMA	Warm Mix Asphalt
W_n	Number Average Molecular Weight
WTT	Wheel Tract Test
W1	Wet Weight of Modifiers
W2	Dry Weight After Swell
Zn	Zinc
η	Dynamic Viscosity
δ	Phase Angle

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DESCRIPTION OF THE STUDY

I. Problem Statement

The intended study can be described as follows. Roadways in all countries are believed to be one of the most important elements of infrastructure that can play an essential role in our daily lives and make it easy for people to travel overland and for all types of goods to be transported from one place to another. As a consequence, the nation economically will reach development and prosperity. Nevertheless, in some countries, cities' main streets and roadways are characterized with old deformed asphalt pavements due to a number of reasons, i.e. natural weather factor, uncontrolled traffic factor or a lack of frequent maintenance. Known solution to this problem is using of modified asphalt binders, which are unfortunately more expensive as ordinary asphalts and thus not available for some communities in developing countries.

From a different angle, the problem of the study can be described also on the basis of environmental concerns of a worldwide landfill disposal of polymer waste materials. The disposal of expired automobile tires and plastic substances randomly is considered one of the major causes of damage to our ecosystem and problem source to the health of all types of life alarmingly. Annually, a large volume of tires become exhausted and disposed of as wastes frequently seen on the sides of roads and highways, especially outside Europe and USA, where appropriate recycling technologies are not available.

The current research study is intended to investigate the utilization polyethylene wastes, crumb rubber and textile fibers obtained from scrap tires as asphalt binder modifiers to improve the engineering properties of asphalt binders.

II. Objectives of the Study

The aim of this research work is to provide basic and rheological properties for asphalt modification mixtures obtained with participation of plastic and rubber wastes.

Polymer waste materials such as scrap tires are creating costly disposal problems and using these materials are used as economical, environmentally sound and effective additives to improve the pavement performance, but there are still problems with maintaining their technological properties. The main objective of this research is to study the influence of polymer waste materials such as crumb rubber and textile fiber

obtained from scrap tires on the physical and rheological properties as well as applicability of asphalt mixtures. Therefore, the main objectives of this research work are as following:

1. Extensive review on usage of polymer waste materials for modifying asphalt, especially on rutting resistance of modified asphalt mixtures.
2. Development of a modified asphalt binder which is flexible and of good characteristics for road pavement applications.
3. Estimation of basic physical properties of asphalt binders modified by different materials and compared with the unmodified asphalt.
4. Estimation of the rheological characteristics of binders in dynamic shearing experiment in a wide range of temperatures.
5. Environmental importance of reduction of mass and volume of polymer waste materials when other recycling technology is not available.

III. Main Predictable Features of the Study

1. Crumb rubber and textile fiber wastes without any previous chemical treatment can be used for asphalt modification, it would contribute to the waste disposal problem.
2. Using recycling technology of used tires can be reducing huge amount of CO₂ emissions to the atmosphere (global warming reduction), caused by uncontrolled burning.
3. Since the modification process without chemicals addition is possible, it could be an eco-friendly technique. However, the three key benefits of polymer modified asphalt are economics, environment and engineering which is shortly called “EEE”.
4. From energy saving and economical point of view, a mobile mixing unit for asphalt-additives system can be used.
5. Encourage governmental and local administrations to deal with the waste tire and polymer problem to a greater extent.

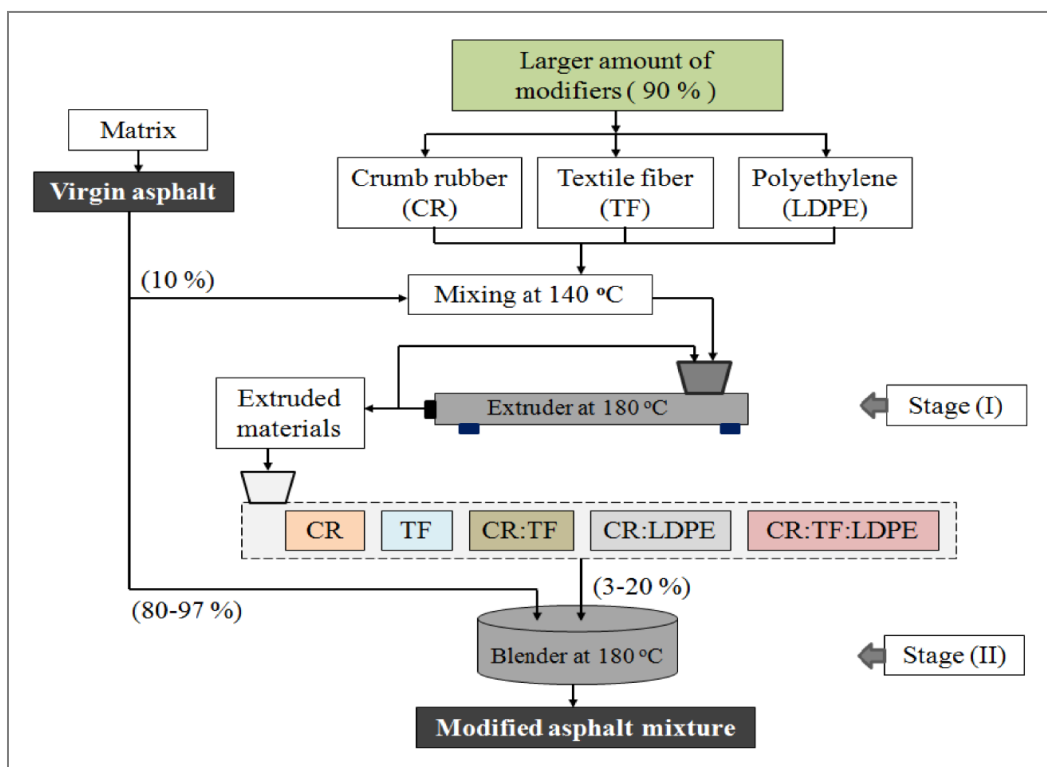
IV. Novelty of the Study

In this research study, an extruder was used to partially devulcanize crumb rubber and to mix it with textile fiber, both waste materials obtained from scrap tires, and/or with LDPE. The extruded materials (blends) were then used for asphalt modification.

The main points can be considered a novelty of this study are drawn as follows:

1. The use of textile fiber extracted from used tires as a novel modifier for asphalt modification.
2. The use of ternary asphalt-additives blend systems composed of (CR : LDPE) or (CR : TF) couples, and quaternary asphalt additives-blend system composed of (CR : LDPE : TF).
3. The use of extrusion technique for blending crumb rubber and textile fiber under partially devulcanization conditions.

Figure below highlights the novelty of this study. More details about the samples formulation are presented in chapter four (section. 4.3.1).



CHAPTER ONE

1. BACKGROUND

1.1 Definition and characteristics of Asphalt

The word “asphalt” is derived from the Greek word “asphaltos” meaning “secure”. Similarly the word “bitumen” originated from the Sanskrit word “jatu-krit” meaning “pitch creating”. In ancient times, asphalt was used as a mortar between bricks and stones, for ship caulking and as a water proofing material [1]. It was mainly used for adhesive applications where water-proofing properties were desired.

According to the Oxford English Reference Dictionary asphalt is defined as “a tar like mixture of hydrocarbons derived from petroleum naturally or by distillation and used for road surfacing and roofing” [1]. Asphalts are defined by the American Society for Testing and Materials (ASTM) as “dark brown to black cementations materials in which the predominant constituents are bitumen that occur in petroleum processing” [2]. According to the American Heritage Dictionary, asphalt is defined as “a brownish-black solid or semi-solid mixture of bitumen obtained from native deposits or as a petroleum byproduct, used in paving, roofing and water proofing” [1].

The petroleum by-product asphalt consists of a unique polymer-type network [3] and is mainly a thermoplastic material that softens when heated and on cooling regains its hard property. Asphalt also has visco-elastic nature [4] in that it exhibits the mechanical characteristics of viscous flow and elastic deformation over certain temperature ranges. According to Figure (1.1), it is shown that only about 10% of asphalt is used as roofing material for buildings, for humidity and leakage protection. Five percent is used in other applications such as thermal and acoustic insulation as well as corrosion protection components of paints and varnishes, etc., while the remaining 85% of the asphalt binder is commonly used by the paving industry [5].

Any improvement in service life of road pavement performance will be of a great economical advantage [1, 4, 6].

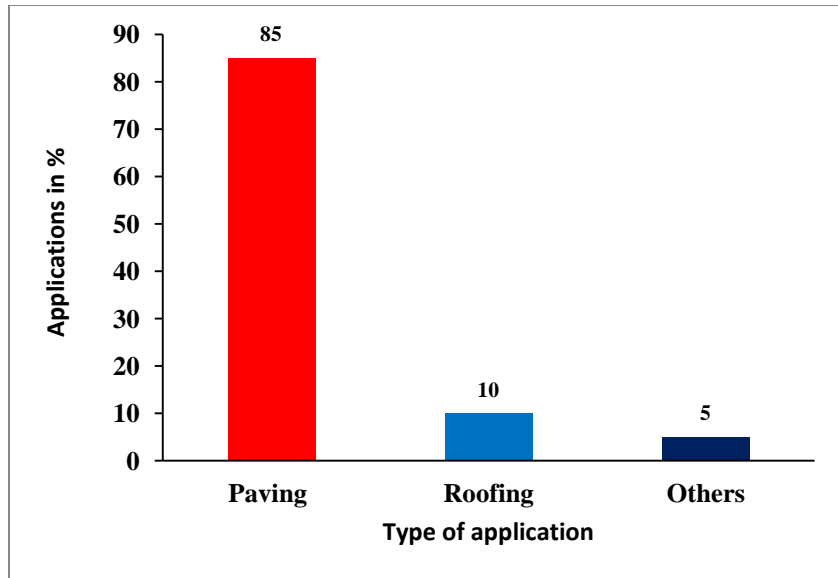


Fig.1.1: Asphalt application in paving, roofing, and others in percentage [5].

1.1.1. Historical Perspective of Asphalt

Asphalt is one of the oldest known engineering materials [1, 7]. It has been used for thousands of years in various ways, e.g. as adhesive, sealant, preservative, waterproofing agent and pavement binder [8]. The value and importance of asphalt started historically to emerge when the ancient Mesopotamians used asphalt to waterproof temple baths and water tanks. Also, the Phoenicians used it to caulk the seams of their merchant ships. In the days of the Egyptian Pharaohs, the people of Egypt used asphalt as mortar for rocks laid along the banks of the Nile to prevent erosion, and the infant Moses' basket was waterproofed with asphalt. The ancient Greeks were also familiar with asphalt. The Romans used it to seal their baths, reservoirs and aqueducts[4,9].

In terms of historical records, the first recorded application of asphalt as a road-construction material was in 625 B.C., in Babylon. The wide road in Paris city known as the Champs-Élysées received its first-time placement of large blocks of natural asphalt rocks in 1824. However, in terms of modern roads, the first construction of an asphalt road was in 1870 at Columbia University by the Belgian emigrant Professor Edward J. de Smedt, who called it "sheet asphalt pavement".

On 29th July 1870, the first sheet of Edward de Smedt's asphalt pavement was laid on William Street in Newark, New Jersey. He engineered a modern, "well-graded,"

maximum-density road asphalt. The first uses of this road asphalt were in Battery Park and on Fifth Avenue in New York City in 1872 (Figure 1.2) [9].

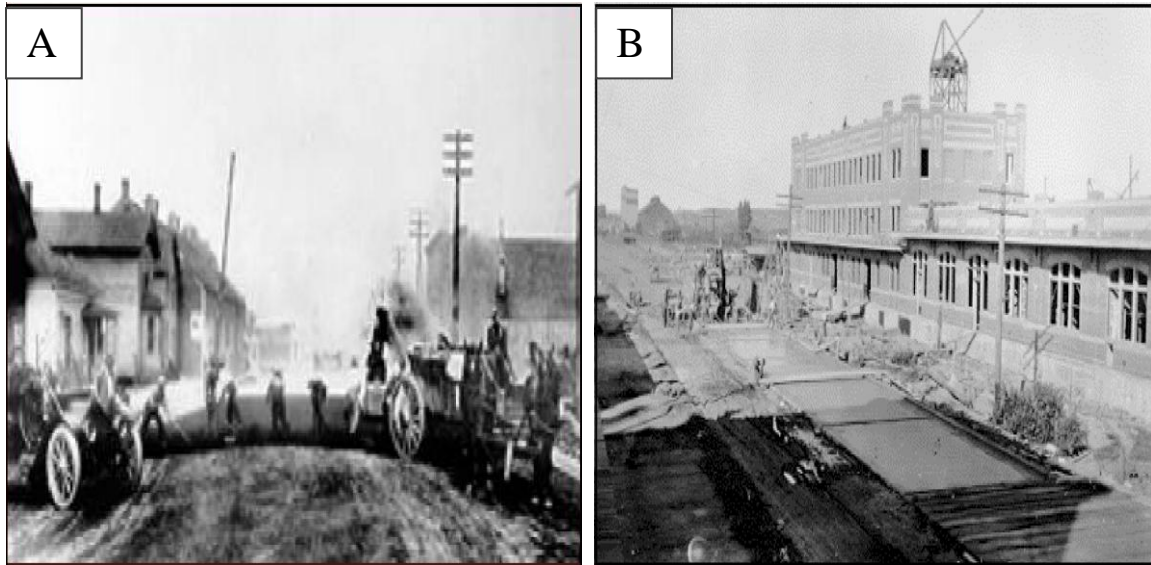


Fig.1.2: Pavement on a French highway in 1852 (A); Asphalt roads come to America in 1870 (B)[9].

1.1.2. Asphalt Production at Refineries

Asphalt is obtained at refining crude oil as presented in (Figure 1.3). At this process the crude oil is pumped from storage tanks, where it is kept at about 60°C , through a heat exchanger system where its temperature is increased to typically 200°C by exchanging heat gained from the cooling of newly produced products in the refining process. The crude oil is then further heated in a furnace to typically 300°C where it is partly vaporized into an Atmospheric Distillation Column. Here the physical separation of the components occurs. The lighter components rise to the top and the heavier components fall to the bottom of the column and pass through a second heat exchanger prior to treatment in a vacuum distillation column. Finally, asphalt is obtained by vacuum distillation or vacuum flashing of atmospheric residue from the vacuum distillation column. This is "straight run asphalt". This process is called asphalt production by straight run vacuum distillation which is using for asphalt pavement applications [4,10].

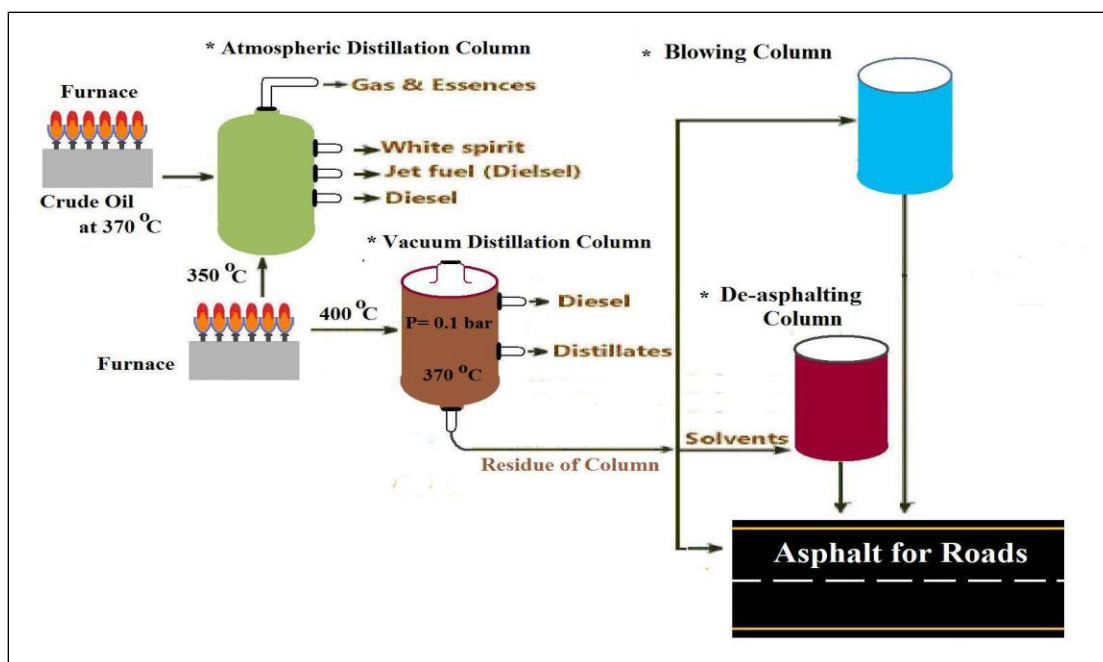


Fig. 1.3: Standard Asphalt Production Scheme [4,10].

1.1.3. Composition of the Asphalt

Characterization of asphalt can be accomplished by the study of its rheological properties. Rheology deals with flow (i.e. viscosity) and deformation at various rates and temperatures. Rheological properties of asphalt depend on the physical arrangement of the constituent molecules and this changes rapidly with temperature. Asphalt is a highly complex material that still is not characterized properly. Saturated and unsaturated aromatic as well as aliphatic compounds with up to an estimated 150 carbon atoms are the main components of asphalt, and usually the type of crude oil from which it was derived can make the difference in the composition of the asphalt [1].

Generally, the various molecular compounds within asphalt contain atoms of oxygen (O), nitrogen (N), sulphur (S) and others. However, asphalt is an organic substance and largely consists of about 82% - 86% by weight of carbon (C), up to 11% by weight of hydrogen (H), and about 6% by weight of sulphur (S), small amounts of oxygen (O) and nitrogen (N), and traces of metals like iron (Fe), nickel (Ni) and vanadium (V). The molecular weights of these constituent compounds vary from several hundred to many thousands [11]. The detailed composition of asphalt still commands a significant amount of attention from several research groups around the world. In

addition to the previous percentage mix of elements by weight, asphalt is composed also of a number of molecules such as paraffinics, naphthenics and aromatics with heteroatoms [12]. Globally, there is a huge number of types of crude oil produced. However, based on yield and quality, only a few of these can produce a suitable asphalt binder [12].

1.1.4. Main Chemical Components in Asphalt

Asphaltenes and maltenes are two major chemical constituents into which asphalts are often separated due to its complex composition. Maltenes can further be divided into three groups: saturates, aromatics, and resins [11, 13]. Figure 1.4 shows the representative structures of four chemical groups in asphalt. The complexity of the chemical structure, content of heteroatom, aromatic, and increase the molecular weight are in the order of saturates < aromatics < resins < asphaltenes [14]. Resins, which have polar character, are responsible for the adhesion and ductility of asphalt and also the dispersion action of the asphaltenes [15, 16]. While asphaltenes are responsible for the bulk of asphalt and oils, the asphalt components with the smallest molecular weight and the non-polar fraction has an influence on flow and viscosity properties [17].

The asphalt colloidal behavior is responsible for the rheological properties; it is demonstrated by a study conducted by Loeber and his colleagues [18]. In the study, they concluded that the rheological properties are reflection of the interaction of individual components. Furthermore, the fluctuation in one of these constitutions, such as asphaltenes, resins, aromatics, and saturates, would change the structure and rheological behavior of final asphalt binder.

The differences in percentages between asphaltenes and maltenes fractions of the asphalt are responsible for the ratio of viscous to elastic properties of asphalt and the performance of asphalt as a paving binder [15, 16]. Therefore, it can be said that when the ratio of asphaltenes to resins is high, an asphalt cement (AC) with high structural rigidity and elasticity is produced (low in phase angle and high in complex shear modulus), whereas the asphalt with an opposite ratio would result in AC with a high viscous behavior and higher softening point [11, 18].

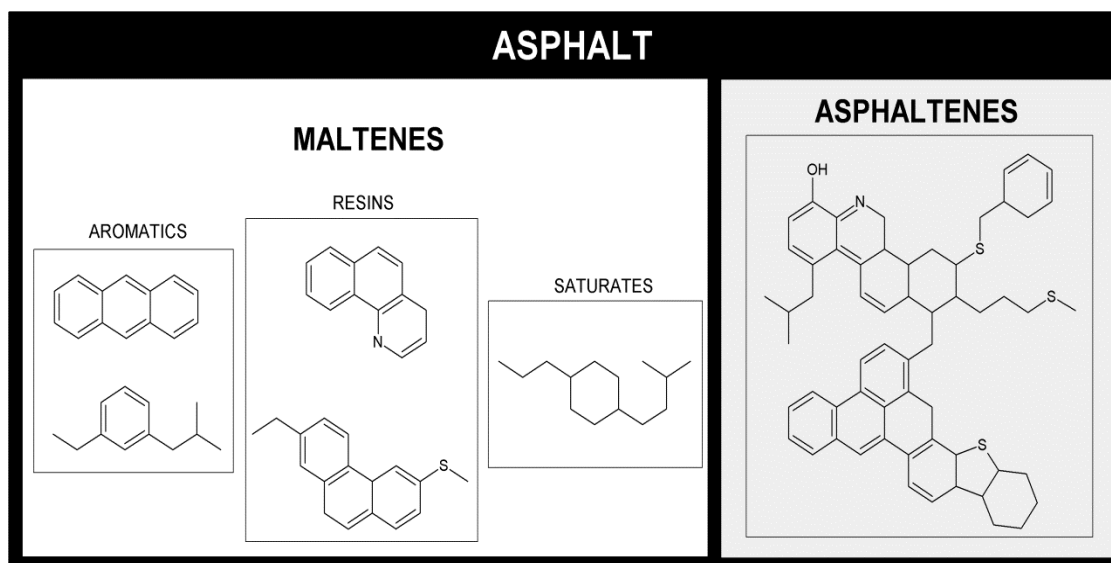


Fig. 1.4: Representative structures of asphalt main fractions[4, 14].

Resins have an intermediate molecular weight, they are semi-solid and their structure is formed by aromatic rings with side chains. Also, they have polar molecules which prevent asphaltene molecules from coagulating. The non-polar maltenes are components of asphalt with the smallest molecular weight and with a high proportion of side chains, compared to the amounts of rings. In general, asphaltenes produce the bulk of the asphalt while resins contribute to adhesion and ductility and maltenes influence flow and viscosity properties [18].

As mentioned above, the main components of asphalt are high molecular weight asphaltenes. These asphaltene micelles are dissolved in a lower molecular weight oily medium of maltene [19]. At a microscopic scale, each micelle is formed from asphaltenes with an absorbed sheath of high molecular weight aromatic resin stabilizers within an oily continuous phase. Therefore, any type of change in the quality of the resins fraction can directly affect the properties of the asphalt [4]. For example, if the quantity of resin is sufficiently aromatic with adequate solvating power, the asphaltenes are better peptized and possess good mobility within the asphalt. This is known as “sol-type” asphalt as presented by Figure 1.5 (left). In contrast, if the quantity of resins is insufficient and less aromatic, the asphaltenes will be less mobile and become clustered. This can create internal voids, which are filled with other constitution. This is called “gel-type” asphalt as presented by Figure 1.5 (right).

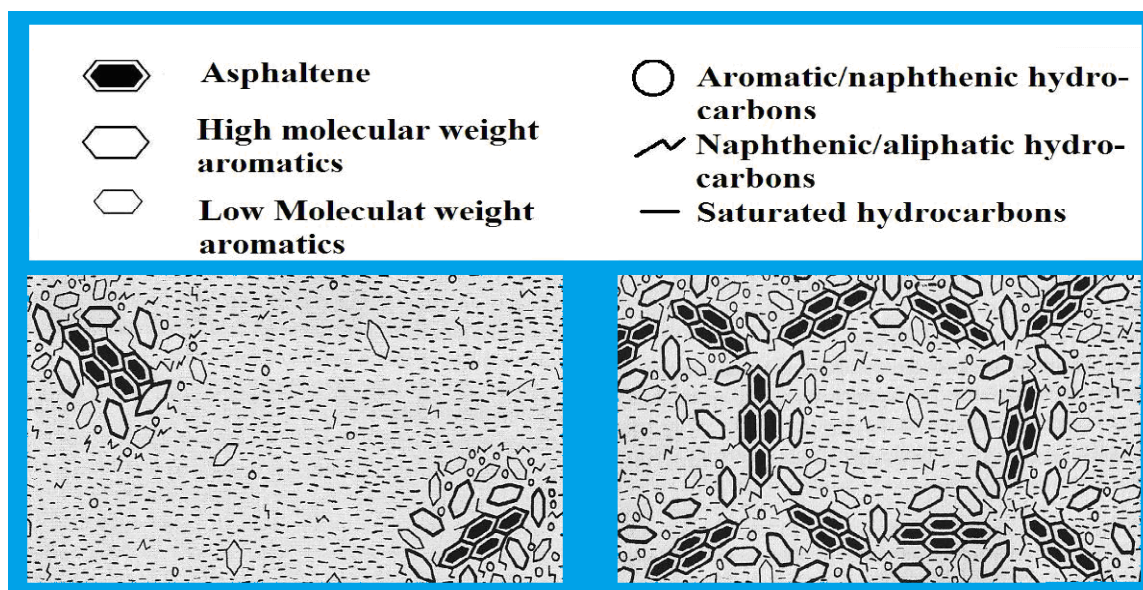


Fig. 1.5: Sol-type asphalt (left) and Gel-type asphalt (right) [1, 4, 20]

As final points, it can be concluded that this state of dispersion of the entire system can have a direct influence on the viscosity of the asphalt binder and thus the rheological performance (rutting and cracking resistance). The viscosity of saturates, aromatics and resins depends on their molecular weight distribution. Therefore, the viscosity of the asphalt binder increases as the molecular weight of the maltenes increases. In addition, as the saturate fraction increases, it decreases the solvating power of the maltenes fraction, as saturates are generally known to facilitate the precipitation of asphaltenes.

1.1.5. Rheological Properties Effects on Asphalt Performance

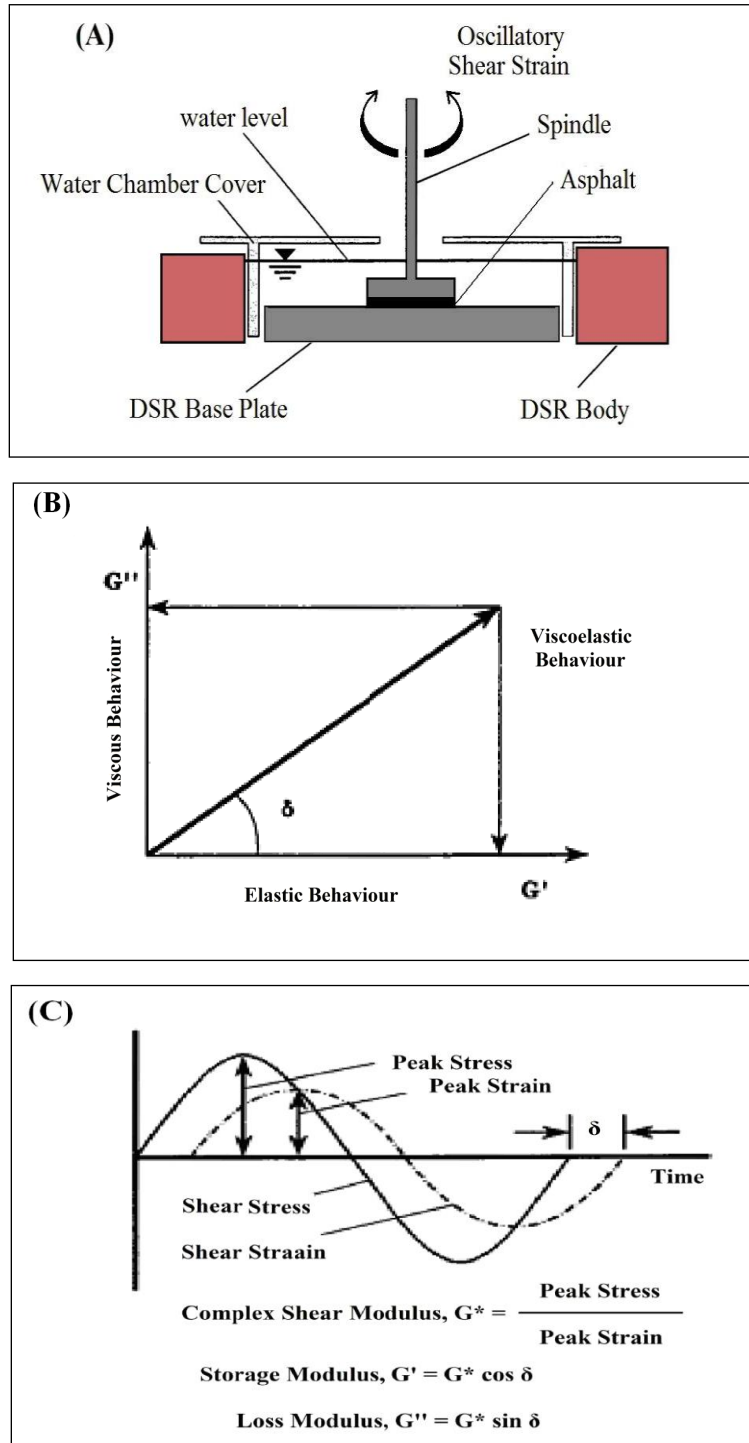
It is well known that asphalt is a visco-elastic material and such a property along with the asphalt's performance property as a road paving binder are considerably affected by the ratio between the main constituents of the asphalt binder, asphaltenes and maltenes [21]. Asphalts in roads are usually sensitive to the increased traffic volumes and vehicle loads due to their visco-elastic properties. As a result there is always a call to improve properties of virgin asphalts, particularly the resistance to permanent deformation, such as rutting and thermal cracking (will be explained in a later section). These two rheological properties are thought to affect the asphalt pavement performance [14].

There is a number of definitions applied to rheology as a science. One early definition implies that rheology is a part of a continuum mechanics and the study of material deformation [22]. Some researchers used the rheological properties as an indicator of the asphalt performance; at high temperature, such properties are related to the rutting of the asphalt; at intermediate temperatures impacts they are related to fatigue cracking, and at low temperature the properties are related to thermal cracking [23]. In another description of the rheological properties, it is indicated that the properties of asphalt binder are responsible for the asphalt pavement performance. Besides, there are several major distresses of road pavement. Since asphalt is a visco-elastic material, its rheological properties are very sensitive to temperature as well as the rate and magnitude of loading. It was also mentioned that the basic rheological properties can be used to evaluate and predict the asphalt pavement performance in the early stages [24].

Several parameters of asphalt samples such as complex shear modulus (G^*), dynamic viscosity (η), and phase angle (δ) can be calculated from data and results obtained from a number of tests [25]. They are available for fatigue characterization of asphalt binders. A special apparatus called dynamic shear rheometer (DSR) is very common in the evaluation of rheological properties of the asphalt binder. According to such laboratory binder tests, the characteristics of visco and elastic behavior of the asphalt at high and intermediate service temperatures can be achieved [26].

There are two basic rheological parameters; the first one is named the complex shear modulus (G^*) and the second one is named the phase angle (δ). The first (G^*), which provides a measure of the total resistance to deformation when the asphalt is subjected to shear loading, is composed of two components that have elastic and viscous features. The elastic-featured storage modulus (G') determines the energy stored in a sample during each loading while viscous-featured loss modulus (G'') determines the energy lost from a sample during each loading and are related to the (G^*) and to each other by means of the (δ), which is the phase lag between the shear stress and shear strain responses during the test, as presented in Figure 1.6.d. The $G^*/\sin \delta$ which refers to the loss modulus G'' also represents the rutting resistance parameter. An increase in G^* and a decrease in δ indicates the high elastic behavior of the material [25]. Testing arrangement

in the dynamic shear rheometer, viscoelastic behavior of asphalt and definitions of stiffness modulus from DSR tests are illustrated in Figure 1.6 [25].



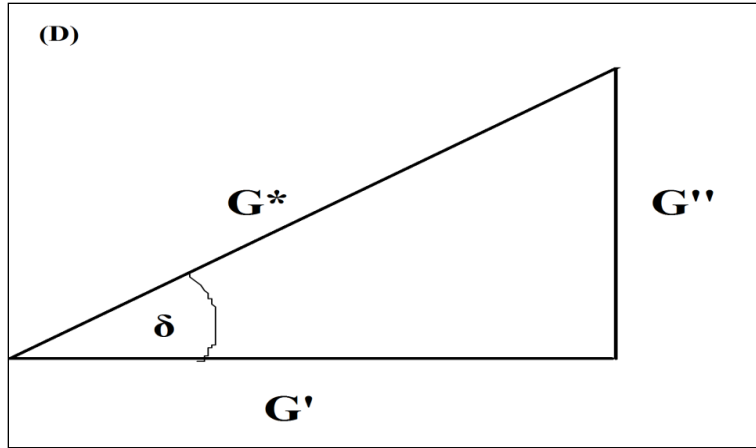


Fig.1.6: DSR-Testing: arrangement in DSR(A), viscoelastic behavior of asphalt(B), definitions of stiffness modulus(C), G^* , G' , G'' , and δ relationship(D)[25].

An investigative study was carried out using dynamic shear rheometer DSR test to evaluate the engineering properties of the crumb rubber modified asphalt (CRM-asphalt) at 67 °C and a frequency of 90 km/h car equivalent [27]. The results of the experiment showed an increase in G^* , G' , and G'' and a decrease in δ . It was concluded that the CRM-asphalt binder samples become less susceptible to permanent deformation or rutting. Besides, a relationship between the rheological parameters G^* , G' , G'' , and δ and softening point temperature (SPT) was present in terms of predicting physical-mechanical properties regardless of blending conditions.

Rheological characteristics of CRM-Asphalt binder were also experimentally studied by Navarro and his co-workers using a controlled stress Haake RS150 Rheometer [15]. The data obtained from their experiment displayed that the viscosities of the CRM-asphalt binder and the SBS-M-asphalt binder were higher than that of the virgin one. The data also displayed that CRM-asphalt binder with 9.0% CR by weight is similar to SBS-M-asphalt binder with 3.0% styrene-butadiene-styrene (SBS) by weight at -10.0 °C and 7.0% SBS by weight at 7.0 °C in regard to the visco-elastic property. They concluded that all attempted rubber modified asphalt samples had enhanced resistance to permanent deformation or rutting and also low-temperature cracking.

1.1.6. Asphalt Components and their Relation to the Rheology

The rheological properties of a certain asphalt binder can vary considerably according to the compositions of the asphalt binder. Some relevant observation was

recorded. For instance, the viscosity of asphalt binder would increase at a constant temperature as the amount of asphaltene increases. The asphalt softening point temperature is lowered by the increase of saturating compounds with a constant ratio of resin compounds to aromatic compounds percent. On the other hand, hardening and an increase in viscosity of the asphalt binder are observed as a result of an increase in amount of resin compounds. The last observation is the rheology of the asphalt binder, which is not affected by the increase in aromatic compounds at a constant ratio of saturating compounds to resin ones [28].

1.1.7. Most Failure Modes of Pavement Asphalt

Since the conventional road pavement technology become well recognized, many countries around the world, from time to time, face a problem with deterioration of their road structures represented in a number of pavement failures, such as the low temperature cracking, fatigue cracking, and rutting (or permanent deformation) at high temperatures, thus causing its quality and performance in pavement of roads to diminish. Acceleration in the rate of such incidents has been observed particularly in the last three decades.

Most failure modes usually encountered by pavement road designers are fractures and permanent deformations. A number of distresses are believed to be the main causes of such failures and they are as follows [1, 29, 30]. Rutting failure is one type which can be noticed in road constructed at regions of high-temperature conditions, such as in North African countries, where strain accumulates in the pavement and permanent deformation takes place in the form of ruts (tracks) on the surface of asphalt pavement Figure 1.7. These ruts occur as a result of heavy loads at low frequencies or high temperatures. This is often reduced by early repair planning. The second type of failure is called moisture damage. It is usually caused when the AC does not bond well with the aggregate and sand fractions. This lack of adhesion and cohesion between the main road pavement components becomes obvious in the presence of water (i.e. rain). In this case, and since the asphalt is hydrophobic and aggregate is hydrophilic, the asphalt mastic can be repelled from aggregates and sand fractions, resulting in random cracks in the surface of the pavement. Finally, the thermal cracking failure occurs mainly due to the frequent and long-term exposures of the road to extremely low temperatures in the winter seasons,

leading to road hardening and where thermal stresses exceed the strength of the materials, and the road pavement becomes cracked. The repeated thermal stresses below the design limit can also be a cause of thermal fatigue cracking failure (Figure 1.7). Another reason for thermal distress is the repetitive loading by heavy traffic during the freeze-thaw cycle, which is considered another cause of this failure. This mode of failure is observed usually due to the cyclic load of heavy trucks until road pavement is fractured and many random cracks show up.

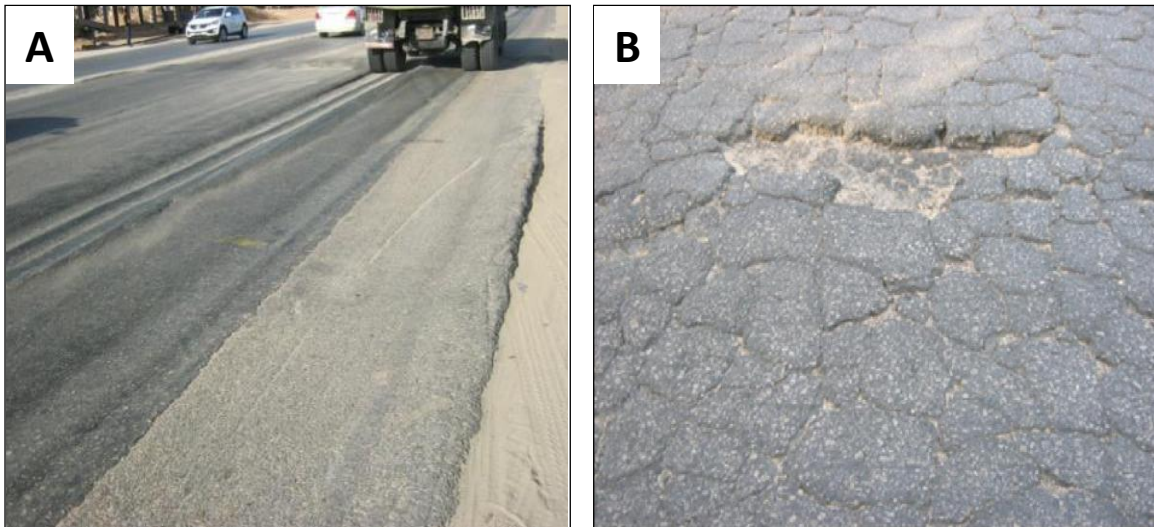


Fig. 1.7: Severe ruts in an asphalt pavement(A), Fatigue cracking(B) [Researcher camera]

1.2. Landfill Disposals of Expired Automobile Tires and Plastics

In recent years, one of the primary and global environmental concerns is the landfill disposals of expired automobile tires and plastics. Textile fiber and its landfill disposal also represent a hazard to the environment, yet with less intensity. At the end of 2007, about 128 million scrap tires remained in stockpiles in the United States [31]. In regard to waste tires, it was reported that the world's annual generation of this waste is about 1.5 billion waste tires [32] and the world annual consumption of plastic materials has increased from around 204 million tons in 2002 to nearly 300 million tons in 2013 [33].

Concerning polymer wastes, the highest component in quantity in municipal solid waste (MSW) stream is low-density polyethylene (LDPE) at about 23%, followed by 17.3% high density polyethylene (HDPE), 18.5% polypropylene (PP), 12.3% polystyrene

(PS), 10.7% polyvinyl chloride (PVC), 8.5% polyethylene terephthalate (PET) and, finally, 9.7% other types [34]. Table 1.1 shows types and quantities of polymers in MSW in the USA [35, 36].

Table 1.1: Types and quantities of Polymers in MSW in the USA

Type of Plastic	Quantity (Tons)
Low-density polyethylene (LDPE)	5,010,000
High density polyethylene (HDPE)	4,120,000
Polypropylene (PP)	2,580,000
Polystyrene (PS)	1,990,000
Polyethylene Terephthalate (PET)	1,700,000
Other	3,130,000

The landfill disposal of scrap tires of all types of automobiles is environmentally believed to cause serious problems for all ecosystem components (water, soil, air) all over the world. One of the potential hazards of uncontrolled tire landfills is fires (Figure 1.8). These, in turn, pose pollution problems first to atmospheric air by the release of volatile toxic gasses such as dioxins and polycyclic aromatic hydrocarbons and second to the water when the intense heat allows pyrolysis of oil and other toxic material to leach onto the soil profile reaching the underground water runoff [37, 38]. As a part of some extensive investigation conducted on the potential impacts of tire storage, it was reported that there is usually compound leach from the tires, which contaminates soil, groundwater, and surface water. It was also reported that burning of tires in the uncontrolled open air could cause the release of pyrolytic oils and other toxic compounds. These toxins will leachate into the soils and eventually reach groundwater. Large plumes of black smoke and other gaseous contaminants are also released into the air. Tire piles can pose another problem and becomes breeding sites for insects, rodents and other animals and creatures [38].



Fig. 1.8: Burning scrap tires at the open land [39].

At this point in time, there is also the availability of plastic wastes, which is enormous, as the plastic materials have become part and parcel of our daily life. Either they get mixed with the MSW or they are disposed over land areas. If they are not recycled, their present disposal approach may be by landfilling or incineration. However, both of those processes have significant impacts on the environment [40].

The chemical bonds of constituents in plastics make them very durable and resistant to the normal natural processes of degradation. Since the 1950s, it is estimated that around one billion tons of plastic have been discarded, and they may persist for hundreds or even thousands of years. The plastic gets mixed with water, does not disintegrate, and takes the form of small pellets, which causes toxicity and death of fish and many other aquatic animals that mistake them as food materials (Figure 1.9) [40, 41].



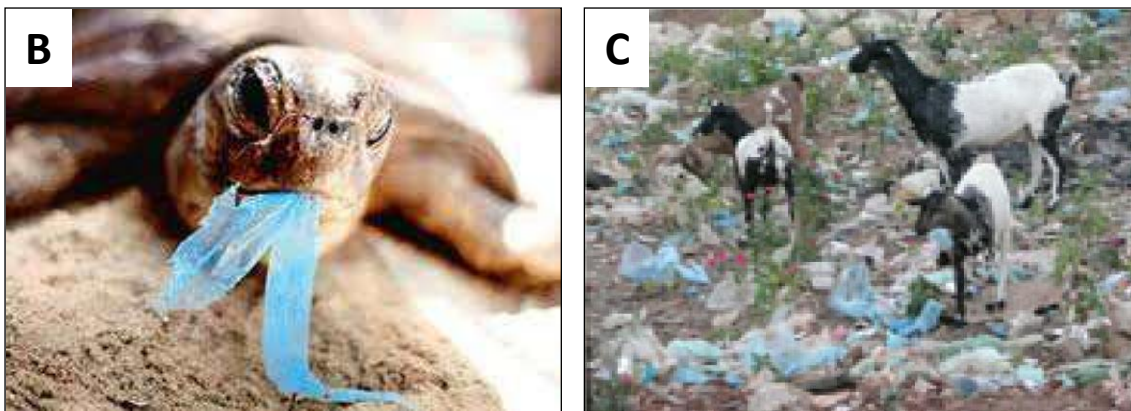


Fig. 1.9: Superficial water polluted with a mass of waste plastics (A), and an aquatic turtle and animals with plastics in their mouths (B and C)[40, 41].

Moreover, waste rubber plastics disposed of in the open land areas sometimes cause a fire in appropriate conditions because of their inflammable components, resulting in negative impacts on the atmospheric air and human health due to the toxic fume emissions. Besides, there are also pyrolytic components that can leachate into the soil, causing contamination and toxicity to soils, animals and humans when entering the food chain. The MSW disposal in the world primarily has three ways of dealing with waste and they are landfill, burning, and recycling.

Recycled polymers applied to asphalt pavement may be the best way to reduce large built up quantities of such wastes and simultaneously improve some engineering properties of asphalt binders. A research study was conducted to investigate the utilization of waste plastics and rubber tires as asphalt binder modifiers in the pavement of flexible highways. One conclusion from the study was that the project is not only to improve the engineering properties of asphalt binder but also to prevent the landfill disposal of such materials, collect them at low cost, and provide a solution to the global environmental problem imposed by the increased disposal of waste tires and plastics [42].

A large part of the scrap tire is converted to CRM. This modifier is a type of polymer and is used widely as an admixture with the paving asphalt binders for the improvement of performance properties of the road pavement asphalt. The use of the recycled polymers has been recognized for asphalt modification only in recent years [42 - 44]. In addition to its utilization as a recyclable material, the applications of CRM in the pavement field has also received great attention from environmentally conscious people

due to the environmental benefits of recycling scrap tires [45], which offered low-cost recycled resources and finally encouraged economics. From the material point of view, the automobile tire is made up of three main component materials: elastomeric compounds, fabrics, and steel, which could be separated and recycled [46].

1.3. Asphalt Modifiers

High-quality asphalt with improved properties from a very controlled refining process can be obtained from very few crude oils around the world. Therefore, in case road pavement construction engineers request asphalt with improved asphalt engineering properties, the next step implies property modification of crude asphalt binder. At the manufactory, this step can be done sometimes by air blowing or by the addition of fluxing agents or diluent oils. However, the first can make the asphalt final product harder and the later can make the asphalt softer [47]. Another bright technique that can usually be carried out as an alternative to improve the engineering properties of the asphalt binder is by the addition of modifiers such as crumb rubber (CR), textile fiber (TF), and commercial polymers. The oil shale company (TOSCO) was the first company that used poly-phosphoric acid (PPA) as a modifier in asphalt mixtures without air blowing. The other polymers that have been used together with PPA were ethylene-vinyl acetate (EVA), styrene butadiene styrene (SBS), styrene-isoprene-styrene (SIS), polyethylene (PE), polypropylene (PP), acrylonitrile-butadiene-styrene (ABS), amongst several others [47]. The blending is the most common method of modification [47]. Of all the additives (modifiers) in the world, the elastomeric additives comprise approximately 75%, the plastomeric additives 15% and the remaining 10% belongs to the rubber and other additives [6].

From the economic and environmental point of view, as well as the need to reduce the material cost of producing polymer-modified asphalt, drew the attention of asphalt producers to the possibility of using polymers derived from recycling as a modifiers of asphalt since, similarity in performance is found between recycled polymer and virgin polymers modified asphalt [15, 28]. Another main advantage of using polymer wastes as secondary materials in road pavement would prevent from additional road

construction cost in one hand and in other hand it would be a solution to minimize environmental pollution. It will also help to minimize the large volume of such wastes.

1.3.1. Crumb Rubber

Generally, crumb rubber (CR) is known as those rubber materials that have a particle size of 9.5 mm or less [48]. It becomes very well acknowledged that the improvement of the properties of virgin asphalts used in the road asphalt pavement construction is necessary to increase the design life and reduce the maintenance costs. The accomplishment of such aim in some occasions is carried out with the mix of these CR materials with virgin asphalt binders, which results in a product known as crumb rubber modified-asphalt binder (CRM-asphalt binder). The process implies the incorporation of CR mostly from scrap tires with virgin asphalt under certain conditions of time and temperature. The mixing technique of CR with asphalt binder is carried out by either one of the three processes and they are wet process, dry process and terminal blending [49].

The properties of CRM-asphalt binders produced by wet process depend basically on the characteristics of both CR and virgin asphalt used in the process [50]. For example, it was observed that the grain size distribution of CR used to produce the CRM-asphalt binders was one of the parameters that have a great influence on the physical properties of these modified binders. The influence of CR gradation on the behavior of CRM-asphalt binders can be related to the intensity of chemical reactions that occur between CR particles and virgin asphalt during the manufacturing process.

The crumb rubber (CR) from ground scrap tires can be produced by either one of the two common processes: (i) grinding process at ambient temperature or (ii) cryogenic process. The first basically involves tearing and crushing the old waste tires at the ambient temperature. Unwanted materials such as steel can be eliminated and extracted by special instruments [48].

1.3.1.1. Historical Perspective in Asphalt Crumb Rubber Blends

During the 1900's, the technique of using asphalt in pavements was first used on rural roads to prevent the rapid removal of dust from Water Bound Macadam due to the fast growth of automobiles. At initial stages, heavy oils were used as dust palliatives. The

estimations of the exact quantity of the heavy oil in the mix were performed by an eye judgment. The first formal method of mix design was called the Hubbard Field Method, which was actually developed on sand asphalt mixture. One limitation of this method, however, was the inability of dealing with mixtures with larger sized aggregate particles than dust. In 1927, a project engineer of the California Department of Highways named Francis Hveem developed the Hveem stabilometer. He did not have any previous experience in judging the required mix from its color; hence, he decided to measure various mixture parameters to find the optimum quantity of bitumen. He had used the surface area calculation concept, which was already in use at that time, to estimate the quantity of asphalt actually required. Then, just before the World War-II, Bruce Marshall developed the Marshall testing machine, which was adopted by the US Army Corps. of Engineers in the 1930's and subsequently modified in the 1940's and 50's [40].

The real role of rubber material in modifying the asphalt to obtain a material for use as joint sealers, patches and membrane started in the 1960's. After a number of attempts, a successful formulation was achieved by Charles H. MacDonald, a bureau of public roads employee. The story started when he was driving his car across the country inspecting highway material sources. He unexpectedly noticed a crack on the roof of his trailer. Then he tried to use asphalt to repair the crack and did not succeed. After a number of attempts, he thought he could repair the crack in one condition and that is to incorporate rubber with the asphalt [51]. In the 1960's and 1970's, after an extensive work with the addition of CR from automobile tires to hot mix asphalt (HMA) and only after thoroughly mixing them and allowing the reactants to react for a period of time, a new modified asphalt binder with improved engineering properties was obtained [52]. Since then, Charles H. MacDonald was known as the one who invented and developed the so-called "wet process", which was also called after him, the McDonald Process of formulating rubber modified asphalt. By 1968, the Arizona Department for Transportation in the USA began numerous and diverse research and development projects implying the mix of CR with asphalt binder to improve the engineering properties of asphalt for road pavement. By 1975, CR was successfully incorporated into HMA [52]. Later, in the 1980's, the Europeans began a research and study of the

development of newer polymer types and additives for use in asphalt binder modifications [52].

In the 1960's, the dry process was patented under the trade name "PlusRide" after being developed in Sweden and used in the United States for the first time in 1978. In the following years, many other technologies were developed based on some variations of the wet and dry processes. The generic dry process, chunk rubber asphalt concrete and continuous blending asphalt rubber are the recently developed technologies [53].

In addition to the top aims of developing asphalt binder with CR, environmental anxieties and the interest to find an alternative use for the huge piles of scrap tires and the enactment of interested environmental foundations emerged in 1991. Since that time asphalt technologists and rubber recycling entrepreneurs began looking to improve on the existing technologies available to add CR to asphalt pavement materials. Several new technologies have emerged and are being evaluated. The initial field test sections of CR asphalt mixture similar to McDonald technology were created in 1990. Additional technologies have been introduced since that time but have been largely under evaluation [52].

1.3.1.2. Processing of Crumb Rubber (CR)

1.3.1.2.1. Ambient Ground Rubber

The grinding process method has been widely adopted and is also the most productive. The final product is generally an irregular particle with a high specific surface. Working with granulators can result in more regular particles with lower specific surfaces [36, 53].

This type of CR is obtained by shredding and grinding (milling) the tire rubber at or above ordinary room temperature. This process produces a sponge-like surface on the granulated rubber crumbs, which have a considerably greater surface area for a given size particle than do cryogenically ground rubber particles. Increased surface area increases the reaction rate with hot asphalt. The Figure (1.10) is an example of a typical ambient scrap tire recycling plant. The process is called ambient, because all size reduction steps take place at or near ambient temperatures, i.e. no cooling is applied to make the rubber brittle [39].

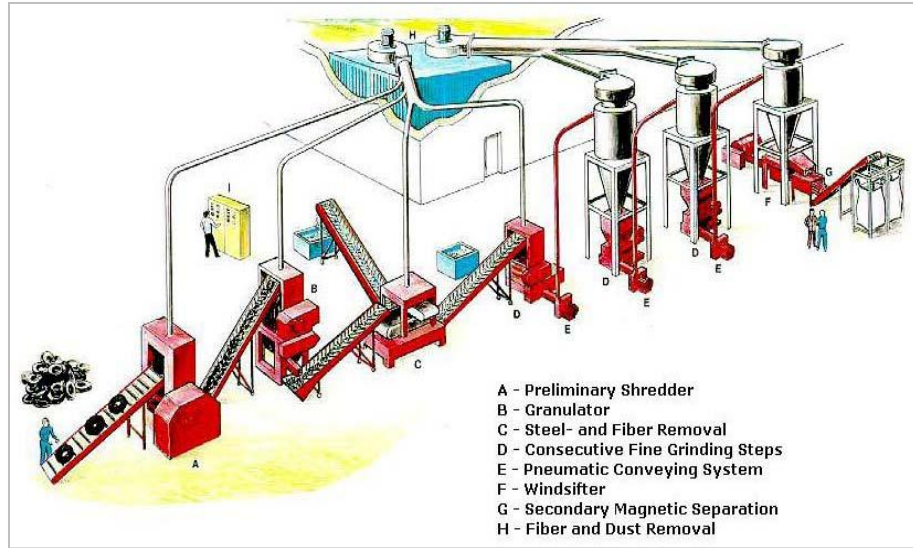


Fig. 1.10: Scheme of an ambient scrap tire processing plant [39].

1.3.1.2.2. Cryogenic Ground Rubber

In contrast, the cryogenic process is carried out at very low temperatures (-87°C to -198°C). In this case, the small sectors of scrap tires are dipped into liquid nitrogen so that the rubber becomes very brittle. Only then can the small sectors of the scrap tires be easily broken apart on a press, into the desired particle dimension. These particles of CR are more regular and have a lower specific surface than the ones obtained by the grinding process at an ambient temperature [36, 53]. The main disadvantage of cryogenic process is the cost for liquid nitrogen (LN_2) [39]. Figure (1.11) represent the scheme of a cryogenic scrap tire processing plant.

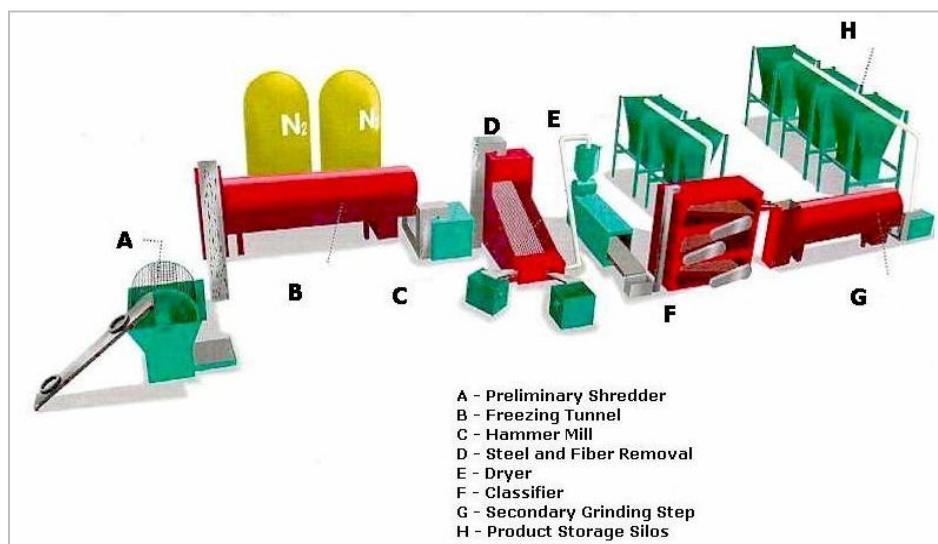


Fig. 1.11: Scheme of a cryogenic scrap tire processing plant [39].

This process produces CR particles with clean flat surfaces which, in turn, reduce the reaction rate with hot asphalt. According to the research by the Australian Road Research Board, this process produces undesirable particle morphology (structure) and generally gives lower elastic recovery compared to the ambient ground rubber. The comparisons between Ambient and Cryogenic Processing are shown in Table (1.2) and Table (1.3) [39, 54].

Table 1.2: The properties and benefits of ambient and cryogenically processing of crumb rubbers [54]

Physical property	Ambient Ground	Cryogenic Ground
Specific gravity	Same	Same
Particle Shape	Irregular	Regular
Fiber Content	0.5%	Nil
Steel Content	o.1%	Nil

Table 1.3: Comparison between Ambient and Cryogenic Processing [39, 54]

Parameter	Ambient	Cryogenic
Operating temp.	Ambient, max.120°C	Below -80 °C
Size reduction principle	Cutting, tearing, shearing	Breaking cryogenically embrittled rubber pieces
Particle morphology	Spongy and rough, high specific surface	Even and smooth, low specific surface
Particle size distribution	Relatively narrow particle size distribution, only limited size reduction per grinding step	Wide particle size distribution (ranging 10mm to 0.2mm) in just one processing step
Maintenance cost	Higher	Lower
Electricity consumption	Higher	Lower
LN2 Consumption	N/A	0.5-1.0 kg LN2 per kg tire input

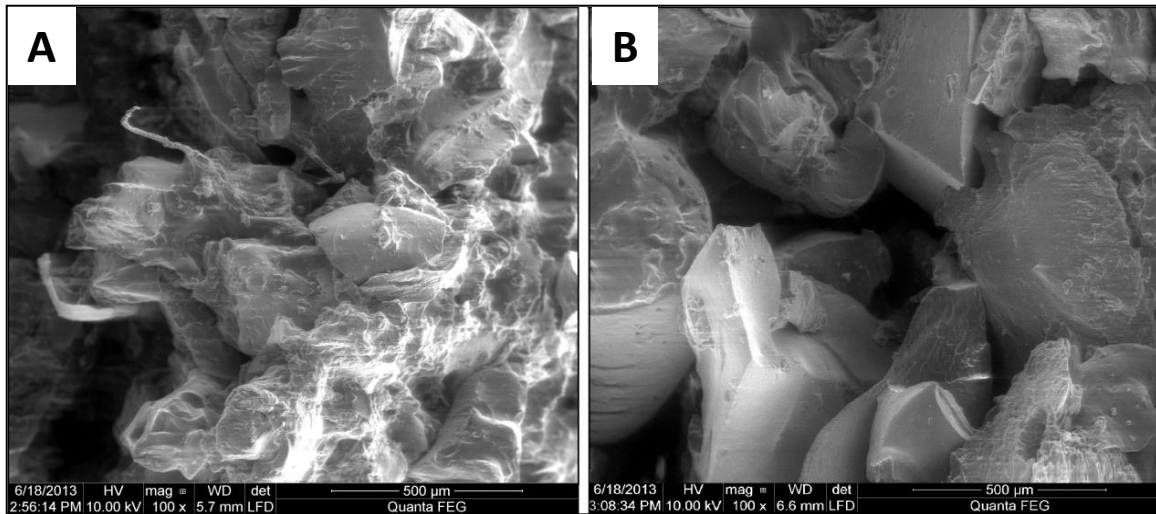


Fig. 1.12: SEM analysis of ambient CR (A) and cryogenic CR (B)[by researcher]

The following conclusions were drawn from a case study based on laboratory investigations conducted on the properties of CRM-asphalt binders as a function of CRM processing method (ambient vs. cryogenic) [54]. The CRM-asphalt binder was initially produced and then artificially aged through an accelerated aging process. The results from this study have indicated that the ambient CRM generally was found to be more effective in producing the CRM-asphalt binders that were more viscous and less susceptible to rutting and cracking. From test results, the following conclusions were also drawn. (i) The ambient CRM have resulted in higher viscosity values than the cryogenic CRM at the same percentage usage, and this was attributed to the increase in surface area and irregular shape of the ambient CRM. (ii) The ambient CRM was found to be more effective in producing the CRM-asphalt binders that were less susceptible to rutting at high pavement temperatures. (iii) The difference between ambient and cryogenic CRM was not found to have a significant effect on the $G^* \sin \delta$ of the CRM-asphalt binders at the 5% level. (vi) The CRM-asphalt binders produced with ambient CRM showed better resistance under low-temperature cracking than those with cryogenic CRM.

1.3.1.3. CR Variables that Influence the Properties of Rubberized Asphalt

1.3.1.3.1. Properties of Crumb Rubber

Choosing crumb rubber (CR) instead of any other common modifier for mix with asphalt binder depends on the desired properties of the modified asphalt binder for a

particular application. In addition, the choice is also determined to a certain extent by the cost of modification and the availability of the modifier [55], which are both greatly advantageous to CR when compared to, for instance, polymers.

Due to the huge generation of scrap tires as a result of rapid vehicle production, limitation of free disposal lands, and thus the emergence of a profound environmental problem, the recycling processes of these waste tires has been encouraged, and the production of CR from it has been found suitable for use as an asphalt modifier. Besides, the process offers other benefits such as the use of less complicated blending equipment. The polymer modified-asphalt binders (PM-asphalt binder) are usually produced with better properties, yet they are comparable to those of rubber modified-asphalt binders [55].

1.3.1.3.2. Components and Concentration of Crumb Rubber

CR of scrap tires actually is a blend of mainly synthetic rubber, natural rubber, carbon black, antioxidants, fillers, and extender type of oils, which are soluble in hot paving grade. There are two different methods in the use of CR in asphalt binders. The first one is by dissolving CR in the asphalt as a binder modifier. The second one is by substituting a portion of fine aggregates with ground rubber that does not completely react with asphalt [56]

A number of research studies concluded that CR content represents a significant factor in enhancing the performance properties of asphalt pavement resistance against deformation during construction and road services and the rheological properties of rubberized asphalt binders [55, 57, 58, 59]. At these investigations the increase in CR content was from 4.0 to 20.0%; as a result a number of properties, such as softening point, ductility, elastic recovery, viscosity, complex shear modulus, and rutting factor, were improved and also a linear increase was attained. This phenomenon could be explained by the absorption of CR particles with the lighter fraction oil of the asphalt, leading to an increase in CR particles through swelling during the blending process. The increase in CR content by 16% and 20% was unacceptable for asphalt pavement construction since they showed a corresponding increase in Brookfield viscosity value higher than (SRHP) Strategic Research Highway Program specification limits 3 Pa [11].

The increase in CR content within 18 – 22% showed a change in low-temperature performance that was of little significance within that range in affecting the tensile and fracture performance of the asphalt binder compared to varying the binder content between 6 and 9 percent by asphalt weight [56, 59]. It was found that the content of CR represents the most significant affecting factor followed by CR type and lastly the size of the particle according to an experimental study conducted by Liu and his coworkers [60].

1.3.1.3.3. Type and Particle Size of Crumb Rubber

Crumb rubber (CR) particle, made by shredding scrap tire, is graded and found in many sizes and shapes. To produce CR, initially it is important to reduce the size of the tires to small pieces (shreds). Commercially, there are four main classes of CR based on particle size: coarse 6.3 – 9.5 mesh; medium size 10 – 30 mesh; fine 40 – 80 mesh; and superfine 100 – 200 mesh as presented in Figure 1.13 [23].

The size of CR is thought to be as much a significant factor as mixing time and temperature in affecting the rubber depolymerization rate [61]. It was proved that superfine CR particles swell much faster than those larger in particle size due to a larger specific area and, therefore, give higher viscosities. Likewise, crumb rubber-modified asphalt (CRM-asphalt) produced from the smallest rubber particles will also have the fastest viscosity reduction in the heating process due to its fast swelling rate and thus a fast depolymerisation process. The factors that influence the viscosity of CRM-asphalt according to their order of significance are CR content, mixing temperature, rubber particle size, and mixing time; Liu, and his assistants [60] as well as Sun and Li [62] have stated it in one of their scientific literature.

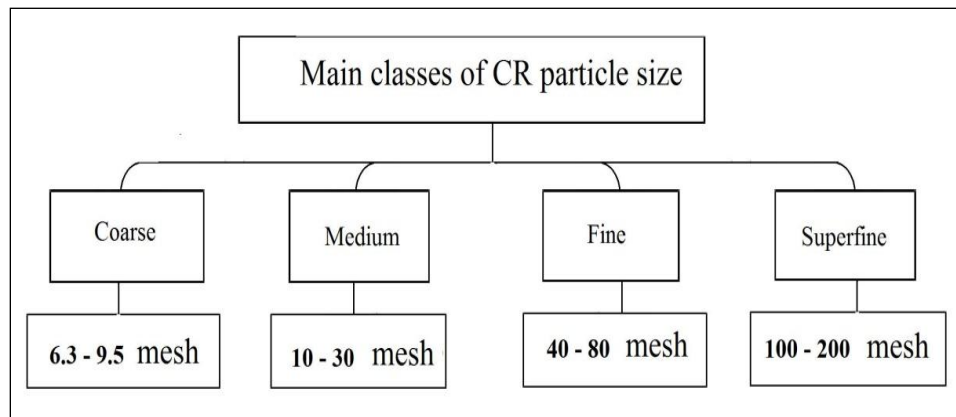


Fig. 1.13: The four main classes of CR particle sizes



Fig. 1.14: Recycled crumb rubber in particle size less than 0.8 mm [Researcher camera]

Generally, a small difference in the particles size of CR has no significant effect on CRM-asphalt blend properties. However, as stated above, the CR size can certainly make a big difference. Shen and his colleagues have carried out a study and reported that the particle size effect of CRM on high-temperature properties of CRM-asphalt binders was an influential factor in visco-elastic properties. In addition to that, it was found that the CR of the coarser type produced a modified asphalt binder with high shear modules. The increase in the content of CR in the asphalt blend has led to a decrease in the creep stiffness, which in turn led to modified asphalt with a better thermal cracking resistance [63].

In terms of interactions between the CRM and asphalt binder, it is strongly believed that the interaction of CR particles (of any particle size and shape mentioned above) with the asphalt binder is completed physically by the swelling of the CR particles caused by the absorption of light fractions into these particles and the stiffening of the residual binder phase [63, 64]. The swelling process limits the free space between the CR particles and causes a constriction of CR particle movement into the binder matrix. Compared to the coarser particles, the finer particles swell easily, thus developing a higher binder modification [63, 64]. The swelling capacity of CR particles is linked to the penetration grade of the binder, crude source, and the nature of the CR modifier [65]. Lower particle size unfortunately is available by using of expensive cryogenic process.

1.3.2. Polymers

The physical properties of a specific polymer are determined by the sequence and chemical structure of the monomers, its molecular weight, and molecular weight distribution. The addition of polymers to asphalt for the purpose of enhancing its properties over a range of different temperatures in paving applications was contemplated a long time ago [47].

There exist a number of reasons for polymers to be used as asphalt modifiers. They are as follows: to obtain softer blends at low service temperatures and reduce cracking, reach stiffer blends at high temperatures and reduce rutting, reduce viscosity at layout temperatures, increase the stability and the strength of mixtures, improve the abrasion resistance of blends, improve fatigue resistance of blends, improve oxidation and aging resistance, reduce structural thickness of pavements and, finally, reduce life costs of pavements [55].

Polymer characteristics, asphalt characteristics, mixing conditions, and compatibility of polymer with asphalt are the major factors that the properties of the final modified asphalt usually depend on when polymers are added to asphalt binders. Improvement in rutting resistance, thermal cracking, fatigue damage, stripping, and temperature susceptibility have made polymer modified-asphalt binders (PM-asphalt binders) to be a substitute for conventional asphalt in many paving and maintenance applications [58]. They are used whenever extra performance and durability are desired. In many cases, they generally are selected to cut down the life cycle costs [16].

1.3.2.1. Historical Perspective in Asphalt Polymer Blends

The following represent several studies concerning of the historical asphalt modifications which are previously supported and clarified by Zhu et al., (2014) in their extensive research study [8].

In the field of polymer modified-asphalt (PM-asphalt), synthetic polymers were not widely used until after World War II. One well-known early example is neoprene (polychloroprene) latex, which began to be increasingly used for asphalt modification in North America from the 1950s [66]. Today, widely used polymers for asphalt modification can be classified into two categories: plastomers and thermoplastic elastomers. Plastomers have a longer history of artificial synthesis than thermoplastic

elastomers. Most of the currently popular plastomers began to be produced commercially before 1960 [67]. However, only five years later, the thermoplastic elastomers was developed in the USA, and the first commercially acceptable product of that type was styrene-butadiene-styrene (SBS) [68].

The application of PM-asphalts was firstly used in roofing of buildings and then road pavement construction. In 1965, atactic polypropylene (APP), the by-product of isotactic polypropylene (IPP) manufacturing, was firstly used to modify asphalt for roofing in Italy and two years later was marketed [69]. However, SBS was not widely known and used only in the early 1970's in Europe. In contrast, widespread use of modified asphalt in roofing in the USA started in 1978. It was only around 1980 that American PM-asphalt manufacturing started [8, 69].

PM-asphalt for road construction with improved engineering properties was the patent of virgin asphalt and polyisobutylene in the early 1940's [70]. After that, especially after the invention of SBS as an asphalt modifier, a number of patents were applied for all over the world. During the 1970's, researchers proved that the addition of polymers, including plastomers and thermoplastic elastomers, could improve some properties of the asphalt binder, such as reducing temperature sensitivity or increasing the resistance to permanent deformation [8, 71 - 73]. In 1978, Chaffin and his assistants [74] reported the potential storage stability problems of asphalt modified with elastomers, but they also wrote that their field test sections constructed in Texas in 1976 were performing well.

At some stage in the 1980s, there was a great demand in establishing thin layer pavement roads, which drove researchers to more systematic investigations [75 - 77] regarding asphalt polymer modification. In this concern, Piazza and his coworkers [75] in 1980 through their research revealed the features of asphalt respectively modified by plastomers and thermoplastic elastomers. Later in 1982, Kraus [76] reported the swelling of elastomeric polymers in the asphalt. In 1983, a binder for pavement comprised of PE-M-asphalt was reported by Denning and his colleagues [77]; their work led to phase separation problems and higher manufacturing and compacting temperatures. Nevertheless, the results of more investigations [78, 79] into PE-M-asphalt were published in the several years that followed. Bowering [80] reviewed the necessity of

modifying asphalt with polymers in 1984 and claimed that the relatively high cost of PM-asphalt might be outweighed by the effects of reduced layer thickness and extended life of PM-asphalt pavements. The good resistance to aging and cracking of PM-asphalt after a two-year field test in California, USA, was reported by Reese and his team in 1989. They also claimed a need to perform further evaluations to be conclusive about the success of the modification [81].

Mechanical properties, rheology, temperature sensitivity, morphology, thermal behavior, storage stability and aging of different PM-asphalts were extensively investigated in the early 1990s [82 - 84]. Through these research studies, it was concluded that polymer modification resulted in some improved properties of asphalt, such as better elastic recovery, higher cracking resistance at low temperatures and higher rutting resistance at high temperatures of SBS-M-asphalt [85 - 87]. On the other hand, some drawbacks, such as the thermal instability and phase separation problems of some PM-asphalts, were demonstrated [82, 88]. From the mid-1990's on, the disadvantages of PM-asphalt were removed by the performance of many attempts. For example, Giavarini and his assistants (1996) [89] claimed that polyphosphoric acid (PPA) could help in improving the storage stability of PE-M-asphalt binder by changing the asphalt structure from sol type to gel type.

After the year 2000, the extensive investigations regarding PM-asphalts were divided into two fields. One field focused on the investigation of polymer modification mechanisms and its failure, and mainly on the microstructure, deformation, cracking, aging and fatigue of PM-asphalts. For example, in this field some researchers believe that asphalt has a heterogeneous colloid structure and the PM-asphalt binder should be investigated as a multiphase (polymers/Asphaltene/maltenes) visco-elastic emulsion [8, 90, 91], while some other researchers claim that asphalt is a homogeneous and continuous molecular solution based on their mutual solubility and that polymers result in good effects on PM-asphalt due to their partial solubility in asphalt [8, 92]. Some other authors think that asphaltenes are strongly polar components in asphalt, then the polarity of polymer modifiers has a significant influence on their compatibility with asphalt and the final storage stability of the resulting PMAs [8, 90], but some others believe asphaltenes are typical non-polar molecules from a chemical point of view [8, 93].

On the other hand, the second field of investigation was concerned with the attempts to overcome the disadvantages of PM-asphalts. Various ways were reported to remove PM-asphalt's drawbacks, including sulfur vulcanization [8, 94, 96], adding antioxidants [97-99], using hydrophobic clay minerals [100 - 102] and functionalization (including the application of reactive polymers) [8, 103, 104].

1.3.2.2. Popular Polymers for Asphalt Modification

After World War II ended, it was the beginning of synthetic polymers utilization in asphalt modifications. Over the years, researchers developed various polymer modifiers [8]. As mentioned previously, elastomers and thermoplastic elastomers are two classes of polymers most known for asphalt modification. As Stroup-Gardiner and Newcomb [105] reported, elastomers have little or no elastic component, which usually results in their quick early strength under load and the following permanent deformation or brittle failure. As for thermoplastic elastomers, they soften on heating, harden on cooling [106] and are able to resist permanent deformation by stretching under load and elastically recovering once the load is removed [8,105], which leads to their greater success than elastomers as asphalt modifiers. Generally, elastomeric polymers can improve rut resistance, but they are inferior to elastomers due to lack of significant improvements in fatigue resistance and cracking resistance[103]. In addition, elastomeric polymers cannot improve low-temperature performance of asphalt, while, elastomers can improve both fatigue resistance and cracking resistance, but it is limited to improve heat resistance [103]. Among asphalt modifiers, SBS was the best choice because it has the property of good dispersions (or appropriate solubility) in asphalt as well as the relatively excellent properties and the acceptable cost of final SBS modified asphalt [8, 107, 108]. The following represent some popular polymers used as asphalt additive systems [8, 105, 109, 110, 111]: 1) elastomers i. g. polyethylene (PE) and polypropylene (PP) the main advantage of both materials are good high-temperature properties and relatively low cost, while disadvantages include phase separation problems and limited improvement in elasticity, 2) thermoplastics, i.e. Styrene-butadiene-styrene (SBS) and Styrene-isoprene-styrene (SIS)—both polymers have reduced temperature sensitivity, increased stiffness, and improved elastic response, but the main disadvantages are low resistance to heat and oxidation, high cost and lack of compatibility with some asphalts. Some others like

styrene-butadiene-rubber random copolymers (SBR), styrene-butadiene di-block copolymers (SB) and ethylene-propylene-diene monomer rubber (EPDM) were also popular for asphalt modification [109, 110].

1.3.2.3. Benefits of Asphalt Polymer Blends

To be effective, when a polymer is blended with the asphalt binder, the PM-asphalt must increase its rutting resistance at high temperatures without rendering it too viscous for the mixing procedure or too brittle at low temperatures [89]. A suitable compatibility should be considered between the modifying polymer and the asphalt binder so as not to cause phase separation during the storage period, application and service. Besides, the polymer modifier (PM) must be cost effective, *i.e.* the polymer should improve the rheology and strength of the asphalt with which it is mixed in such a way that any increased road costs imposed by its use are recovered through performance and reduced resurfacing costs [111].

In regard to the blending process with the asphalt, polymer content ranges between 2 and 10% by weight; however, the most common proportions were about 5% or 6%, a few years ago. Nowadays the polymer content has been reduced to 2% or 3%. Due to environmental concern and cost of waste, they might be added in higher proportions or mixes of multiple polymers [111].

There is definitely a number of factors that affect the modification process of the asphalt binder with modifying polymer and they are polymer content, chemical composition, structure, average molecular weight, molecular weight distribution, degree of branching, crystallinity, etc. [111]. For example, for modifier SBS type block copolymers, enrichment in butadiene about 60% - 70% and the excess in molecular weights of the styrene fraction in more than 10,000 to obtain polystyrene (PS) rich domains [111, 112]. The main purpose of research study conducted by Ali and his associates [113] is to facilitate decisions concerning the effectiveness of modifiers in mitigating pavement distress and improving long-term overall pavement performance in actual field conditions, by utilizing short-term laboratory results and a mathematical prediction model. The modifiers investigated in their study were carbon black, neoprene latex, and polymer modified asphalt. The results of the study indicate that the effect of

the modifier on the paving mixture properties was insignificant at low temperatures (down to $-17\text{ }^{\circ}\text{C}$), but significant at high temperatures (up to $60\text{ }^{\circ}\text{C}$) where the synergistic effect of the modifier on the paving mixture was pronounced.

It was found that the nature of the polymer has an effect on the mixing process. The time required to achieve a homogeneous blend of the polymer and the asphalt will vary with the type of polymer, its molecular weight, and (for thermoplastic rubbers) with the chemical composition of the polymer. A higher molecular weight will give rise to longer blending times and vice versa [111]. In addition, the physical form of the polymer (i.e. powder, crumbs, and pellets) also has an effect on the blending process in two ways. The smaller the particle size of the polymer, the lesser it has to be reduced in order to achieve a good dispersion. In addition, since smaller particle size means larger surface area per unit mass of polymer, penetration of the asphalt binder and swelling of the polymer is facilitated, and thus more rapid dissolution is completed. Powdered polymers will, therefore, disperse and dissolve more rapidly than porous pellets [111].

A summary of the benefits and main reasons for using asphalt polymer blends for use in road constructions is as follows [4, 46, 47]: (1) obtaining softer blends at low service temperatures and reducing cracking, (2) obtaining stiffer blends at high temperatures and reducing rutting, (3) increasing the stability and the strength of mixtures, (4) improving the abrasion resistance and fatigue properties resistance of blends, and oxidation and aging resistance, (5) reducing structural thickness and life costs of pavements, (6) polymers can successfully improve the performance of asphalt pavements at almost all temperatures by increasing mixture resistance to fatigue cracking, thermal cracking and permanent deformation, (7) polymer modified asphalt binder also shows improved adhesion and cohesion properties. Thus, the use of polymer modifiers with a small proportion can actually improve the temperature susceptibility of the binder.

1.3.3. Fibers

1.3.3.1. Historical Perspective of Asphalt-Fiber Blend

The utilization of fibers in the improvement of some properties of materials other than the pavement asphalt binders started at ancient times in China when the Chinese constructed the famous great Chinese wall with clay earth mixed with fibers the arches

[114]. The idea of using fibers obtained from sources other than scrap tires to improve and reinforce the behavior of asphalt mixture is believed to have started in the early 1960s [115]. The fibers utilized included polyester fibers obtained from crude oil [116], asbestos fibers found in serpentine and amphibole rocks [117], cellulose fibers derived from natural products [118], carbon fibers [119], glass fibers [120], and nylon fibers [121]. Nevertheless, the fibers obtained from scrap tires started to receive great attentions in the last years, offering benefits to the environmental and low-cost recycled scrap tire resources.

An early known study of about 60 years ago at North Carolina in the USA was on the evaluation of placing coarsely-woven cotton layers between coats of asphalt. The attempt was aimed at strengthening the road surface and comforting the automobile riders [122]. The study concluded that the cotton has served both as a binder for the asphalt and waterproof blanket to restrain water from seeping through cracks and eroding the road base. Later, the study was applied on site in New Jersey and demonstrated very satisfying results [123].

1.3.3.2. Fibers from Scrap Tires

In addition to the sources of fibers mentioned above, generally, a scrap tire can also be a source of another unique substance that lately played a very important role in the modification of asphalt pavement binders. One of the major components that make up scrap tire is the body ply, which is made of fabric and rubber as shown in Figure 1.15.

The important body ply is made of a rubber layer, reinforcing fabric, and a second layer of rubber. The textile used in the early times was cotton; however, rayon, nylon, polyester, and Kevlar were among the new materials. Passenger tires typically have one or two body plies. Body plies give the tire structure strength. Truck tires, off-road tires, and aircraft tires have progressively more plies. The fabric cords are highly flexible but relatively inelastic [27]. According to the structural components, the tires in cars are composed of 5.0% textile fibers, while in truck textile fibers are entirely absent [46].

Although it is well acknowledged that the most popular asphalt modification technique is carried out by the addition of polymers [125, 126], it is also claimed that

among various modifiers for asphalt, textile fibers obtained from scrap tires are paid much attention due to their improving effects.

Early experimental researches have pointed to the TF's effect on the improvement of the asphalt engineering properties. It has been reported that fibers can increase the optimum asphalt content in the mixture design and prevent asphalt leakage due to its absorption of asphalt [127]. Others proved that fiber can also affect the viscoelasticity [128], improve the property of moisture susceptibility [129], creep compliance and rutting resistance [130], and reduce the reflective cracking of AC mixtures and pavements [131]. In some other literature, it was also reported that fibers were found to improve the low-temperature anti-cracking properties, fatigue life, and durability of AC mixtures [132]. Moreover, some research studies indicated that fibers can improve material toughness, tensile strength [120], dynamic modulus and elasticity [128]. Fibers can also increase the wear resistance of asphalt cement (AC) mixtures that are used as pavement wearing course [127].

On the other side, the addition of fibers to the asphalt binder may increase the air void of AC mixture, thereby requiring more compaction efforts to achieve the same density of unmodified AC mixture [128]. The main compositions of recycled textile fiber obtained from scrap tires in weight percent are 77.60% polyethylene-terephthalate (PET), 18.70% polyamide (PA), and 3.70% polypropylene (PP) [133].

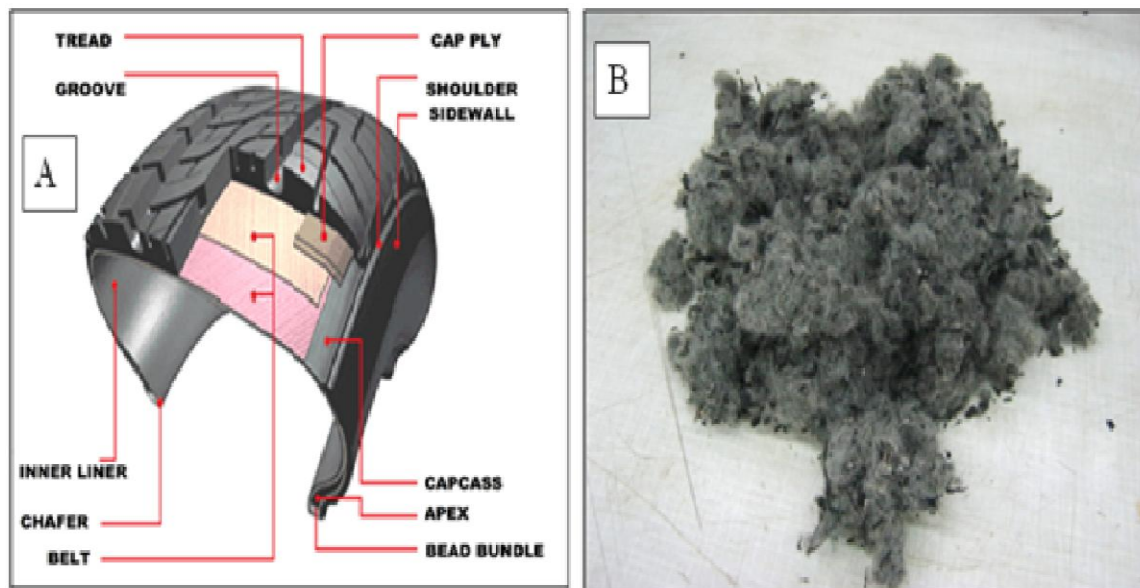


Fig.1.15: Tire structure(A) [46, 124],Textile fiber from used tires(B) [Researcher camera]

1.4. Cost Considerations of Asphalt Modifications for Pavement

From the economic point of view, the cost of any final product is very important to production companies. In regard to the asphalt binder productions, studies indicate that the cost of whole blending processes of either CRM or PM is considered to be higher in the production of final modified asphalt product than in the unmodified virgin asphalt. For that reason, the initial cost for asphalt modification by CR mixes can be 30% to 80% higher than that of the unmodified virgin asphalt. A number of production companies dealing with asphalt modification processes lately have suspended their business. The technology and usage of CR-HMA are limited to some distinctive companies. These companies, which continued their business of asphalt modification productions, have definitely an amazing vision; they looked into the life cycle cost. Pavement maintenance and rehabilitation strategies are very crucial factors and will affect the life cycle cost. It was easily proved from experience in states like California and Arizona. They have extensive experience with asphalt rubber mixes technology which has been shown to be very cost-effective for binders when properly produced and constructed [134]. It is sensible to consider the overall cost which implies that rubber-asphalt project is less than the unmodified asphalt project.

In 1994, a South African research center for road constructions demonstrated that the thickness of pavement using CRM-asphalt binders is reduced up to 50% using vehicle simulator. In addition to thickness reduction, it is also reported that the rates of pavement maintenance and rehabilitation strategies are usually lowered [135]. As a result, this definitely will save the national budget millions of dollars that is reported to be spent to compensate the rutting failures encountered in the road pavements [136].

Several studies concerning the economic and financial viability of asphalt modifications have been supported and clarified by Swapan and Ambarish (2012) in their technical report [137].

For example, it was reported that while the addition of polymeric material to asphalt has improved aging resistance and provided high elasticity to the asphalt binder, King and his colleague [138] found that such polymer-modified asphalt was able to withstand (4 – 10) times more loading than the virgin one and thus can last a longer period without any maintenance.

Furthermore, in terms of life cycle cost analysis, Kumar and his assistants [139] have concluded that their experimental work was found economically viable. They have proved that elastomers are better than plastomers and the weight loss in SBS-M-asphalt was lower than that in the virgin one as a sign of lower oxidative hardening, while it was reported by Valkering and his colleagues [140] that dynamic creep test predicted a better strain rate in PM-asphalt mixes. The team has also reported that the final PM-asphalt has had better physical properties (viscosity value and softening point), leading to the conclusion that the road pavement lasts longer, indicating better economic viability. Likewise, Collins and his coworkers [141] have found out from their laboratorial analysis that their final polymeric modified asphalt mix has been improved in terms of softening point, penetration, and elastic modulus and was, therefore, the most economically and financially viable option.

Overall, the addition of modifiers to the asphalt binder in order to improve the properties of the asphalt mixtures is usually successful which, in turn, reflects the increase in service life, reduce the maintenance cost and road pavement thickness [137].

CHAPTER TWO

2. CONTEMPORARY TECHNOLOGIES OF ASPHALT-RUBBER BLENDS

2.1. Benefits of Asphalt Modification by Crumb Rubber

In the field of crumb rubber modified asphalt, several case studies based on researches and experimental works and scientific reports referred to the benefit of using scrap tire rubbers in asphalt mixtures; it provides rubberized asphalt binder with better skid resistance, reduced fatigue cracking, improved resistance to rutting, improved tensile strength and toughness, longer pavement life and reduced maintenance costs compared with virgin mixtures. Rubberized asphalt shows better performances at high temperatures; they can be used in a variety of climate conditions and are more flexible at low and sub-zero temperatures, while the thickness of an asphalt layer can be reduced from 50 to 38mm. However, the potential benefits of CRM-asphalt techniques of using High-viscosity CRM-asphalt mixtures for use in road constructions are summarized as follows [46]: (1) increased viscosity that allows greater film thickness in paving mixes without excessive drain down or bleeding, (2) improved durability, (3) increased elasticity and resilience at high temperatures, (4) improved resistance to surface initiated, (5) improved fatigue properties, (6) reduced temperature susceptibility, (7) improved permanent deformation and aging and oxidation resistance, (8) low maintenance cost, (9) CRM-asphalt mixtures better pavement durability and performance, (10) CRM-asphalt also show reduced construction time due to thinner lifts, (11) reduced traffic noise, (12) improved safety due to better long-term color contrast for pavement markings because carbon black in the rubber acts as a pigment that keeps the pavement blacker longer, (13) reduction of road pavement thickness, (14) and, finally, savings in energy and natural resources by using waste products and not contributing to the stockpiles. The asphalt-rubber blending process used at the large scale is done in five steps as follows: I) asphalt transported to the heating tank for melting and then pumped into the blender, II) Crumb rubber transferred to the blender, III) Asphalt matrix blended with crumb rubber at high temperature around 180°C with a high speed of mixing at about 3000rpm, IV) modified asphalt pumped to the reaction vessel for complete reaction, V) and, finally, binder transported to plant and ready to use as shown in Figure 2.1. From energy saving and



economical point of view, the mobile modification unit can be use as shown in Figure 2.2. Such unit can also be solution for unstable modified asphalt.

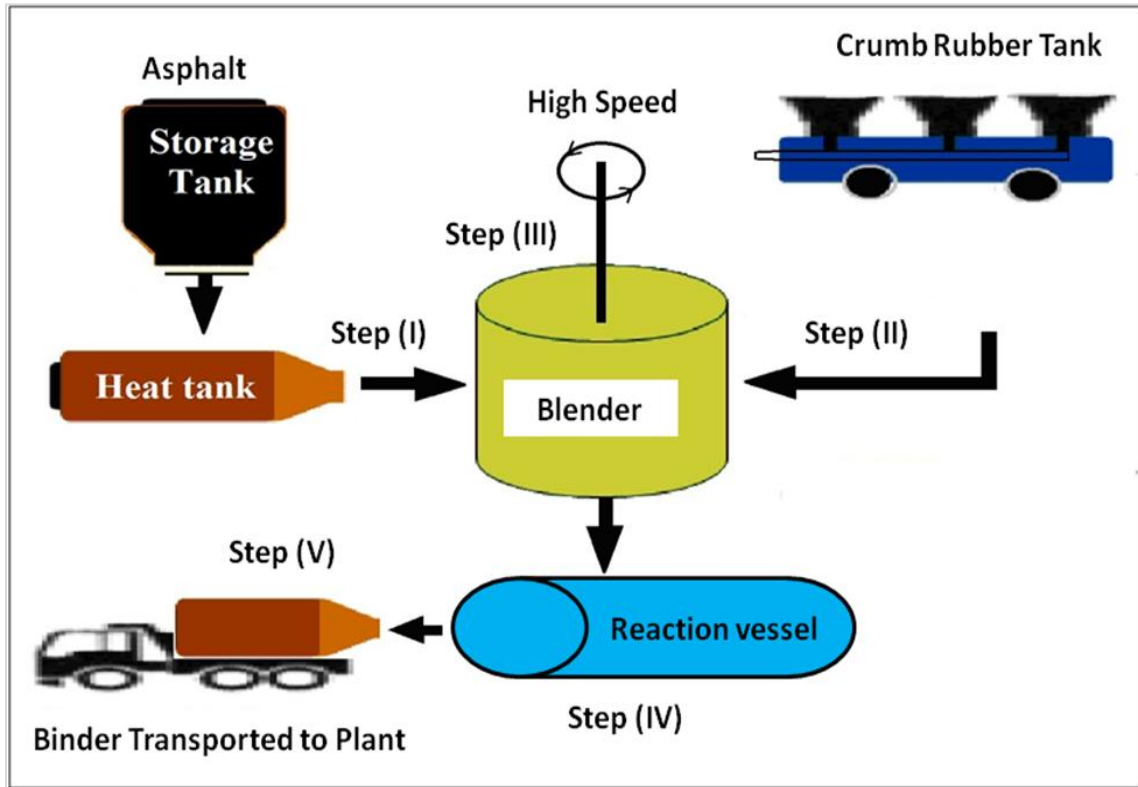


Fig. 2.1: Asphalt-Rubber blending process at a large scale

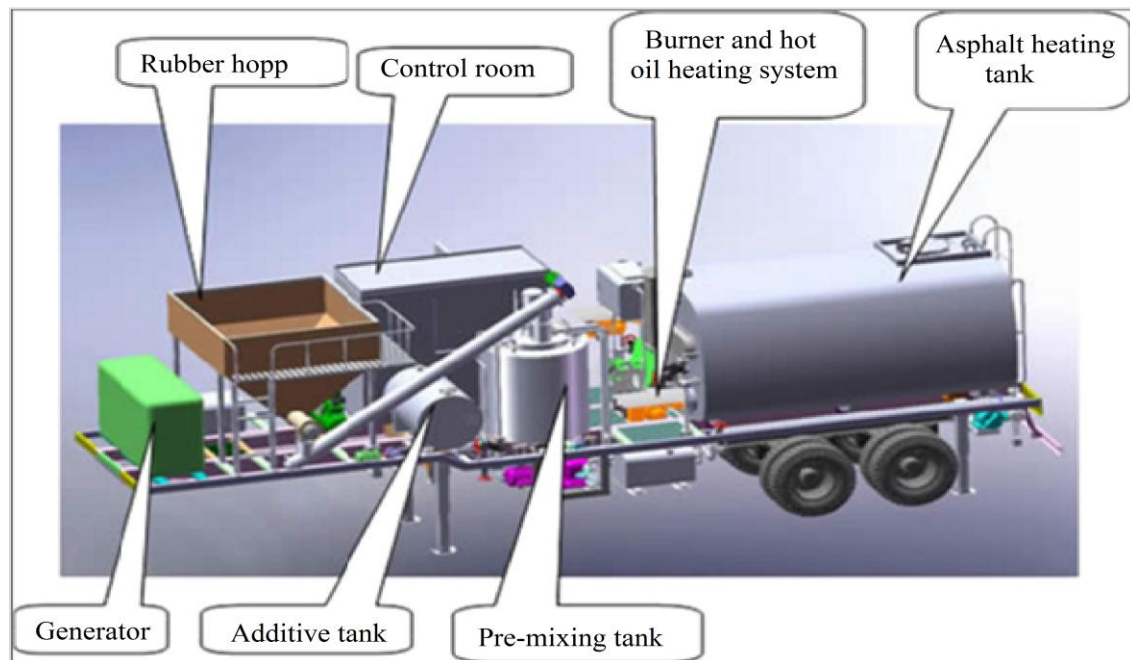


Fig.2.2: A mobile mixing unit for asphalt-additives system [46].

2.2. Processes of Asphalt Modifications with Crumb Rubber

Production of asphalt blends with tire rubber in the form of CR is traditionally established by mainly one of two common ways. The first one is called the wet process where CR particles are mixed with asphalt at elevated temperature prior to mixing with the hot aggregates as presented in Figure 2.3. The second type of CR processing is called dry process, where CR particles replace a small portion of the mineral aggregate in the asphalt mix before the addition of the asphalt as presented by Figure 2.4 [6].

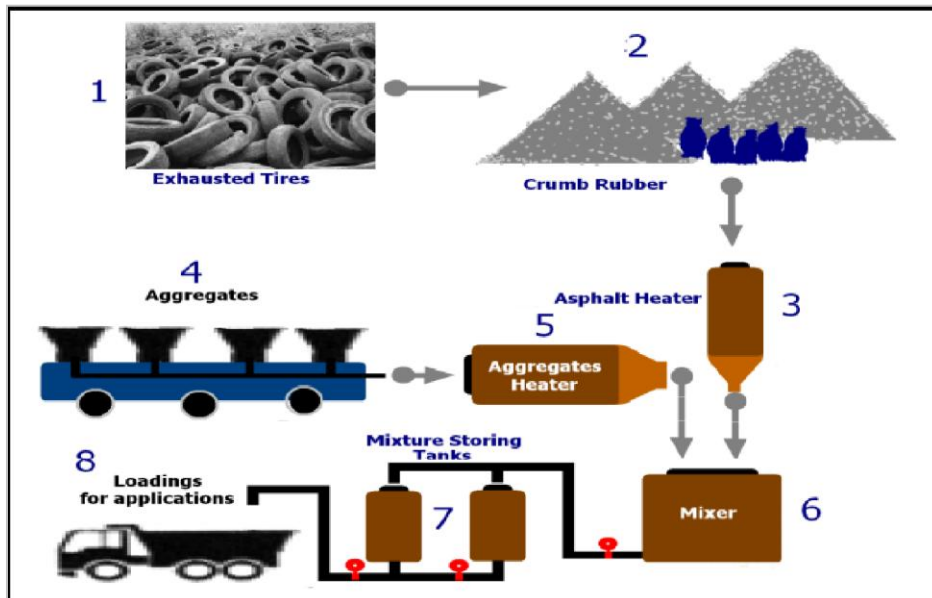


Fig. 2.3: Rubber-modified asphalt mixture by the wet process [6].

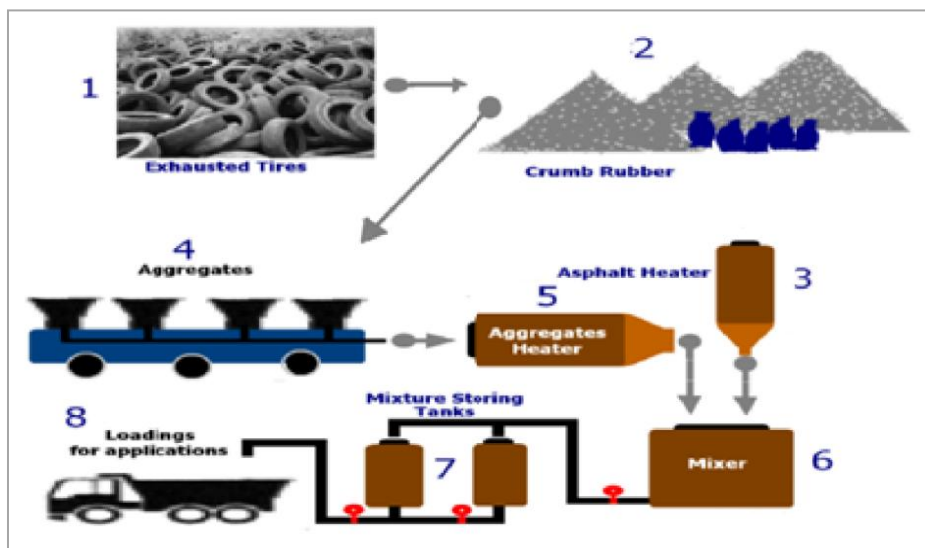


Fig. 2.4: Rubber-modified asphalt mixture by dry process [6]

Note: The arrows make the differences between fig. 2.3 and fig. 2.4

Explanation of numbers of top figures (Fig. 2.3 & 2.4)

- | | |
|-----------------------|---|
| 1- Whole tires | 2- Powder of waste tires |
| 3- Heat of Asphalt | 4- Aggregates |
| 5- Heat of aggregates | 6- Mixing bitumen with aggregates |
| 7- Storage of mixture | 8- Loading & transportation to the site |

2.2.1 The Wet Process

The binder produced from the wet process, or the McDonald process, is called asphalt rubber (Figure 2.3). It has been defined by the American Society for Testing and Materials (ASTM) as “A blend of asphalt cement, reclaimed tire rubber, and certain additives in which the rubber component is at least 15% by weight of the total blend and has reacted in the hot asphalt cement sufficiently to cause swelling of the rubber particles” [142].

In the wet process, asphalt is blended with a crumb rubber modifier (CRM) in a specialized blending unit at elevated temperatures (190 – 225°C), prior to mixing with aggregates, for a minimum of 45 min to promote the chemical interactions among the components of the interaction. During the blending process, CR grains swells and softens with the asphalt. This process is influenced by the blending temperature and time, the type of mechanical mixing, the size and texture of CR grains, the amount of CR, and the amount of aromatic component in the asphalt. CRM typically ranges from 18 to 22% by weight of the asphalt. Extender oils are sometimes used to reduce viscosity and promote the workability of the asphalt rubber as well as to increase the compatibility between the asphalt and CRM [47]. The diagram in Figure 2.3 shows production of asphalt rubber mixes using the wet process. An asphalt rubber mix is used primarily in open graded and gap graded HMA. It is also used in spray applications for seal coats and pavement inter-layers and as a crack sealant [143].

2.2.1.1. Advantage and Disadvantages of the Wet Process

The wet process can be utilized for recycling of any type, size, and shape of waste materials such as plastics and rubber. The disadvantages of the wet process are listed below [29]:

- a. Time consuming, which mean more energy for blending

- b. Powerful mechanical operations are required
- c. Additional cooling is required as improper additions of asphalt may cause air pockets in the road
- d. Maximum content level of waste plastic can be added at around 8%

2.2.1.2. Case Studies

According to laboratory tests concerning the application of the wet process of asphalt rubber mix [144, 145], it was concluded that CR particles retain a larger proportion of the asphalt compared with the aggregates, suggesting an interaction between the asphalt binder and CR particles. In another laboratory study conducted by Pais and his colleagues (2001) [146], they reported that tire rubber inclusions can modify a conventional HMA in terms of a flexural fatigue life since mixtures which include rubber treated using different processes (cryogenic or ambient) have shown greater fatigue life than conventional mixtures regardless of the void content. The last may vary from one mixture to another for the same category of asphalt. The examination of tensile strength characteristics of a dense asphalt macadam (DAM) mixes with CR by Punith, and his assistants (2002) [147] have revealed improved characteristics in terms of Marshall stability and indirect tensile strength at various temperatures under soaked and unsoaked conditions. Both of these properties increased as the CR percentage increased. For unsoaked conditions, in particular, the indirect tensile strength was higher compared with that of the soaked samples, while it decreased as temperature increased. Additionally, at high temperatures tensile strength was almost the same for both, the rubberized DAM mixture and the virgin asphalt, thus rubberized asphalt mixtures are expected to have a longer life than the conventional DAM.

Another study was carried out by Rahman and his coworkers (2004) [148] on dense, graded rubberized asphalt mixtures produced using the wet process, and containing (3–5)% CR by total aggregate weight. It was found that those mixtures are more susceptible to moisture damage compared with conventional mixtures while their stiffness reduced by 30–75%, depending on the CR content. However, when fine rubber particles (< 1.0 mm size) are added to the asphalt mixtures, they have produced mixtures with improved characteristics in terms of stiffness, resistance to permanent deformation,

and rut, whereas particles of such gradation were more effective than coarser ones as far as rutting resistance was concerned.

In the year 2005, Tortum and his team studied the effects of tire rubber and aggregate gradation, mixing and compaction temperature, tire rubber and binder ratio, and mixing time of asphalt mixtures [149]. They concluded that for specific conditions, rubberized asphalt mixtures performed better than the conventional mixture. Almost a similar conclusion was drawn by a pilot project conducted in Taiwan [150]. In this project two test sections were studied: the first section had a gap-graded design while the second had an open-graded design. The incorporation of CR showed that these mixtures can have equal or even better field density and smoothness than conventional mixtures. Field measurements and visual observations indicated that these mixtures performed well.

In fact, the CR addition technique to the asphalt using the wet process as a test project was conducted in Florida by Choubane and his assistants in 1999 [151] and was evaluated after 10 years. Results showed that crack resistance of surface mixtures was improved; another test project conducted using the dry process (described in the following section) resulted in more cracked areas. Since then, the use of rubberized asphalt has become more popular given the fact that it produces pavements with reduced noise pollution. This was first noted in Belgium in 1981, in a rubber HMA called “Drain Asphalt”. Other countries where rubberized asphalt mixtures have been used and where equal or lower traffic noise reduction levels have been reported include Canada (1991), England (1998), France (1984), Germany (1980), Austria (1988) and the Netherlands (1988). As a result, many states of the USA and other countries around the world have continued to use such mixtures [152, 153].

2.2.2. Hot-Mix and Warm-Mix Technologies

It was reported that about 299 million scrap tires are generated every year in the USA. Many state regulations penalize landfill disposal of these materials [153]. The incorporation of scrap tires in the asphalt binder is established by converting the scrap tires to CR. As mentioned previously, this CR will be added to asphalt before adding the asphalt to aggregate using the common wet process to produce HMA.

2.2.2.1. Case Studies

There has been a steady and increasing interest in using of CRM-asphalt binders in HMA pavements in the United States and other countries [23] Figure 2.5, due to the conclusions drawn from some investigative studies which have indicated that rubberized binders could produce asphalt pavements with a decreased traffic noise, reduced maintenance costs and improved resistance to rutting and cracking [154 – 156].

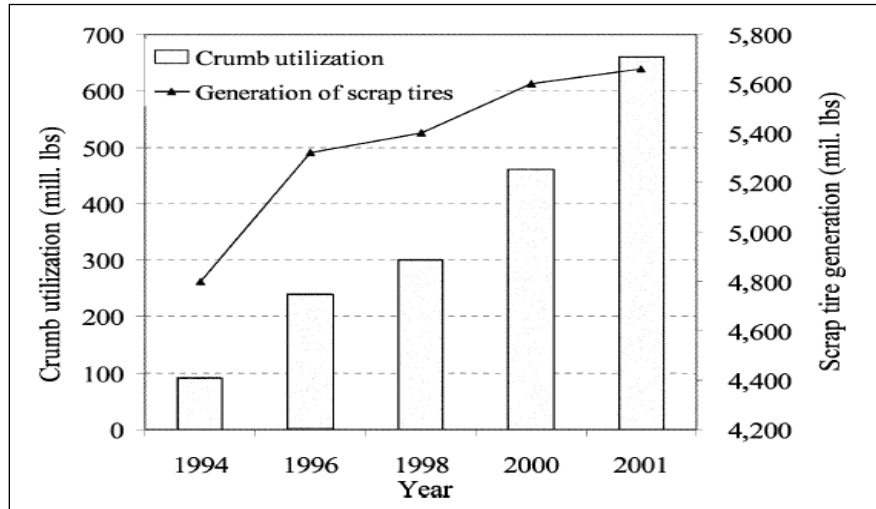


Fig. 2.5: Scrap tire utilization alternatives, [157]

However, the increase of CR content, unfortunately, produces an increase in flexibility, and the incorporation of the CR itself to the virgin asphalt binders can reduce the indirect tensile strength of modified mixtures [158]. Production of HMA at high temperatures can result in undesirable high-energy consumption [159], greenhouse gas (GHG) emissions, toxic fume and odor productions [113], and deteriorating inhabitants' locations. In addition, the high-temperature requirement results in shorter paving seasons, and longer cooling periods [160].

Alternatively, introducing warm mix asphalt (WMA) is known to provide decreased optimum mixing and compaction temperatures of the rubberized mixes and is expected to be comparable to those of conventional mixes. WMA was first originated in Europe in the mid-90s. WMA is mixed and compacted at temperatures lower than those of conventional HMA. Typically, the mixing and compaction temperatures of WMA range from 100 to 140°C in comparison with 150 to 180°C for HMA [161, 162].

It has been proven that WMA techniques can provide a number of benefits due to the lowered production temperatures. Although benefits can vary depending on the

specific warm mix additive being used, the potential benefits of WMA techniques are summarized as follows [162]: (i) improved compaction of asphalt mix, especially stiff mixes; (ii) increased use of reclaimed asphalt pavement; (iii) extension of paving seasons; (iv) night paving and longer haul distances; (v) reduction of asphalt oxidation for prolonged pavement life; (vi) less fuel consumption and energy costs; (vii) reduction of heat, odor, smoke and GHG at the plant.

However, in WMA some concerns have been reported regarding the durability of these mixtures due to the reduced mixing and compaction temperatures used in production. Several studies [157 – 159] have been conducted to determine the applicability of WMA techniques to paving operations and environmental conditions compared to the traditional HMA. One of the main concerns is the increased susceptibility of WMA to permanent deformation. For example, it is possible that the asphalt binder in WMA may not sufficiently harden at relatively low production temperatures and, hence, may develop higher post-construction densification or distortion under early-age traffic. Another concern is that WMA may have an increased tendency to moisture-induced damage. In WMA, aggregates are heated to relatively low temperatures and, therefore, may not thoroughly dry before they are mixed with the asphalt binder, thereby reducing the amount of binder absorbed into the aggregates.

Due to the different mechanisms of WMA preparation techniques, physical and chemical properties of the mixture can be altered, resulting in different short-term and long-term mechanical behaviors of the final product. Several researchers have evaluated the performance of WMA with regards to various physical pavement factors. For instance, in 2007, Prowell and his colleagues have reported similar performance for the emulsion-based WMA (Evotherm™ ET) and HMA surface mixes with the PG 67-22 base asphalt binder. However, laboratory tests indicated an increased moisture damage potential for WMA [163]. Another study has been carried out by Wasiuddin and his assistants (2007). The team has compared the performance of WMA with Sasobit and Aspha-Min additives. They have found out that Sasobit decreased the WMA rutting potential more significantly than the Aspha-Min additives. The addition of Sasobit could increase the high-temperature grading of the asphalt binder [164].

Later, Mallick and his coworkers (2008) have investigated the feasibility of using a WMA additive, Sasobit, with 75% reclaimed asphalt pavement (RAP) for producing a base course at a lower temperature. They have found that the performance of WMA with RAP was dependent on the stiffness of the combined (rejuvenated) binder in the mixture [165]. In addition, Lee and his assistants (2008) have investigated the performance properties of WMA binders (Aspha-Min and Sasobit) containing aged binder. They found that WMA additives might not have positive effects on the resistance to fatigue and thermal cracking when recycled binder was used in WMA [166]. However, Xiao and his coworkers (2010) have evaluated the rut depth, weight loss, and gyrations number of dry and conditioned specimens containing WMA's (Aspha-Min, Sasobit, and Evotherm™ 3G). The results indicated that the aggregate source affected the mix rutting potential most significantly, regardless of the additive and moisture content [167].

A series of studies have been conducted at the National Center for Asphalt Technology (NCAT) to evaluate the laboratory performance of asphalt mixtures with different WMA's; they were Evotherm™ 3G, Sasobit, and Aspha-min [168, 169]. Their major findings from several reports are summarized herein: (i) adding WMA additives improved the compatibility of the mixtures, (ii) application of either the warm-mix process did not affect the resilient modulus or increase the rutting potential of asphalt mixtures compared to control mixtures having the same PG binder, (iii) lower mixing and compaction temperatures for WMA may increase the potential for moisture damage. An anti-stripping agent may be added to yield an acceptable tensile strength ratio, (iv) based on the compaction and rutting results, a minimum field mixing temperature of 135°C and a minimum field compaction temperature of 121°C is recommended.

2.2.3. The Dry Process

In the dry process, as previously mentioned, CR is added to the aggregate in a hot mix plant operation prior to adding the asphalt. There is a relatively little reaction between the asphalt and CR in the dry process (Figure 2.4). In essence, CR replaces a portion of the aggregate. The dry process can be used in dense-graded, open-graded, or gap-graded HMA. The most commonly used dry process was developed and patented in the late 1960s in Sweden and in 1978 in the USA. The performance of pavements using

this process has met with mixed reviews and, as a result, the dry process is not widely used for modifying asphalt pavements [170].

2.2.3.1. Advantages and Disadvantage of the Dry Process

The advantages of the dry process are drawn as follows [29]. 1) Plastic is coated over the stone-improving surface property of aggregates. 2) Coating is easy and temperature required is the same as road laying temperature. 3) More than 15% of waste plastic can be used. 4) Flexible films of all types of plastic materials can be used. 5) No new equipment is required. 6) Asphalt bonding is stronger than normal. 7) There is no degradation of the road even 5-6 years after construction. 8) It can be practiced in all types of climatic conditions. The disadvantage of the process is that it is applicable only to thermoplastic waste materials.

2.2.3.2. Case Studies

Fernandes and his colleagues (2002), in one of their research projects, have concluded that CR in rubberized asphalt mixtures produced by the dry process has increased the elasticity of the mixture. It could enhance the bonding between the asphalt binder and aggregates, resulting in an increase in fatigue life and resistance to rutting, and it could lead to a reduction of the thermal and reflecting cracking of these mixtures [171].

Concerning the dry process, a number of scientific reports [172, 173] have revealed that the control of CR particles and asphalt interaction could not be done in an easy way since there was immediate mixing between aggregates and asphalt. When these mixtures were established correctly, such pavements were better for icy road conditions. Recent studies have also concluded that during mixing and transportation, CR particles reacted with asphalt, changing the properties, shape and rigidity of rubber; as a result, the performance of the asphalt mixture has also been changed [65, 139].

Studies on the effect of moisture on the mechanical properties of rubberized asphalt mixtures have shown that stiffness was reduced by the incorporation of CR particles (2 – 8mm) and that stiffness was decreased with increasing CR content. Reduction of stiffness was due to the creation of voids by CR particles in the mixture; as a result, more water penetrated into the matrix during saturation, giving a weaker structure. For rubberized asphalt mixtures, resistance to permanent deformation was found to decrease compared

with the control virgin asphalt mix in terms of strain rate because of the moisture conditioning; however, the presence of CR in the mixtures resulted in an increase in fatigue performance before moisture conditioning. Therefore, rubberized asphalt mixtures would result in better mechanical characteristics than the control virgin asphalt mixes during the early stages. It was reported that when rubberized asphalt mixtures are exposed to moisture for long periods, this enhanced performance would be reduced [140].

Another study was carried out by Kettab and Bali [174] indicating that when CR with particle size higher than 2 mm was added to asphalt mixtures the compaction and strength characteristics were improved as the CR fills the existing voids within the granular skeleton. Studies on CR asphalt mixtures produced by the dry process showed that the addition of CR at 10 – 15% by weight of the asphalt caused a reduction in penetration into asphalt and softening point. However, the viscosity of CRM-asphalt binder was increased with the increase of CR content from 10 – 15% and decreased as the temperature was elevated [173].

According to the conclusion of Fernandes and his colleagues (171), it was proved that rubberized dense asphalt mixtures have resulted in lower Marshall stability values than in virgin asphalt, while flowability increased with the increase of CR content. These mixtures, however, did not meet the requirements of the Brazilian standards. Besides, rubberized asphalt mixtures have also resulted in lower values of resilient modulus and tensile strength compared with virgin asphalt, while gradation of the CR has been found to have a small influence on the tensile strength. Reduction in resilient modulus has been higher as the size and content of CR increased, and mixtures with fine rubber particles ranging between 0.15 and 1.18mm in size at up to 2% (by weight of the total mix) have shown very good performance in terms of rutting resistance [152].

In Greece, a study was also conducted on CRM-asphalt binders using the dry process. However, the obtained results of the study did not meet the requirements of Hellenic Standards when mixtures contained CR at 1.0% (by weight of the aggregates) [173].

The extensive research and studies on both processes mentioned above led to a number of important conclusions. The main differences between these two processes include: (i) the size of CR; in the dry process, the size of CR is much coarser than in the

wet process, (ii) amount of CR; the dry process uses CR (2 to 4) times as much as the wet process, (iii) function of CR; in the dry process the CR acts more like an aggregate but in the wet process it acts more like the binder, and finally (iv) the ease of incorporation into the mix; in the dry process no special equipment are required while in the wet process special mixing chambers, reaction and blending tanks, and oversized pumps are required [175].

Accordingly, although the dry process has the advantages concerning the lower costs involved, the higher amount of rubber to be used, and the simple equipment involved, the process did not greatly attract researchers due to the irregular performance of some experiment sections built with it. Therefore, researchers have focused to a great extent on the wet process which usually presents more satisfactory results.

2.3. Interaction Theory of Asphalt –Rubber Blend

2.3.1. Physical Interaction Theory

Rubber, as a crosslinked polymer, is known to absorb some solvents and swell. The extent of swelling is dependent on the type of polymer as well as the nature, temperature and viscosity of the liquid; in our case it is the asphalt. The amount of liquefied asphalt diffused into the rubber depends on the compatibility with the asphalt and the shape and number of cross-links in the rubber. Furthermore, asphalt is a complex mixture of organic molecules, which include mainly hydrocarbon with minor amounts of oxygen, nitrogen, sulfur and other trace elements. When crumb rubber is added to the asphalt, it makes this composition even more complicated.

It is well acknowledged that the addition of a polymer to the asphalt binder may bring about improvements to the engineering properties of the asphalt. The question is how rubber molecules interact with the asphalt binder to produce, for instance, a PM-asphalt binder with enhanced stiffness; this is known to provide the final PM-asphalt binders with improved rutting resistance. In this case, it is believed that the asphalt rubber interaction is completed through physical interactions. In case of thermoplastic elastomers (SBR block copolymers) the process starts when rubber is immersed in the hot asphalt, and as a result some chain segments of rubber (or phases) will absorb the components of similar solubility and swell quickly. These particles of elastomers become

somehow cross-linked, preventing the particles from being completely dissolved in the liquefied asphalt binder. At this instant, with the addition of extra time of up to 90 min to the reaction, the liquefied asphalt penetrates into the internal matrix of the rubber, leading to more swelling; rubber particles might swell 3 – 5 times their original size [176] as shown in Figure 2.6. A number of factors were reported to influence the extent of rubber swelling in asphalt. The chemical nature of asphalt determines the equilibrium swell value, whereas the asphalt viscosity determines the rate of swelling [126, 177, 178], which increases as the viscosity of the liquefied asphalt decreases. The rate of asphalt penetration throughout the CR particles increases with the decrease in particle size [177, 178]. The solubility parameters of the asphalt components are an important factor that determines the compatibility of liquid and rubber [178].

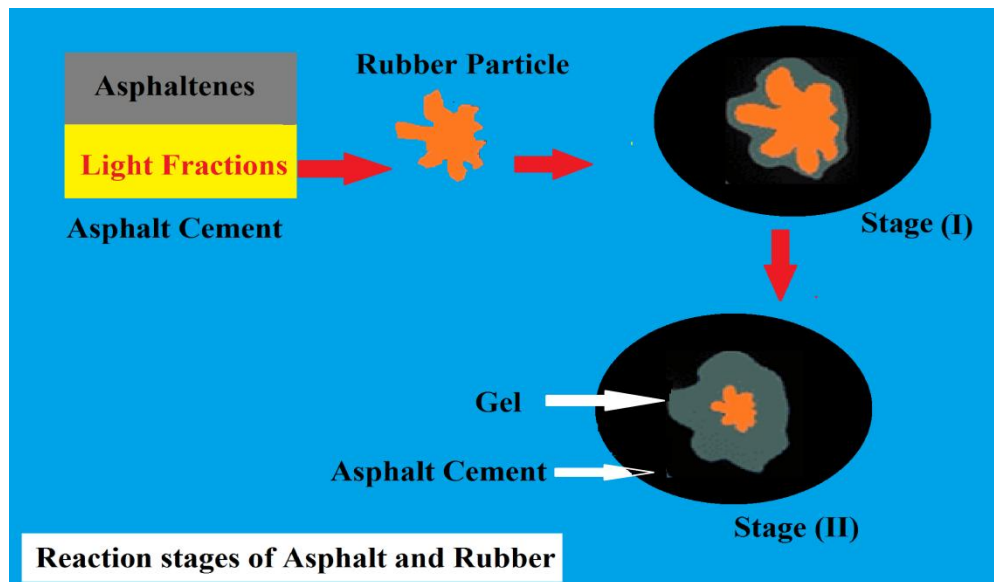


Fig. 2.6: Physical interactions between crumb rubber particles and asphalt [179]

Gawel and her colleagues [178] have found that the solubility parameters of the components for the asphalt used in their study as follows: saturates ($\lambda = 17.5$), aromatics ($\lambda = 18$), resins ($\lambda = 19.5$), and asphaltenes ($\lambda = 22.3$) were the most compatible with CRM obtained from scrap tires, which is primarily a combination of SBR ($\lambda = 17.5$) and natural rubber ($\lambda = 16.8$). The molecular weight of the asphalt components can be another significant factor determining the rate of interaction of the asphalt with the rubber. Stroup-Gadinear and his coworkers have concluded from viscosity testing that small molecular weight components of the asphalt binder are more interactive with the CR than

the heavier one [177]. Shen and Amirkhanian have confirmed that the swelling of CR particles due to the absorption of light fractions into it and the stiffening of the residual binder phase are the main mechanisms of the interaction [180]. The rate of swelling is variable and related to the CR content and asphalt composition [181].

2.3.2. Compatibility in Polymer Blending with Asphalt

In the field of asphalt polymer modification, as mentioned previously, although the interaction between the polymer and the asphalt binder is usually carried out by physical diffusion, there is some chemical reaction taking place in the process. Chemical modification of polymer modified asphalt aims to alter the typical chemical bonding between asphalt binder and rubber particles [11].

In chemical reactions between the asphalt and the polymer binder, sometimes some obstacles are found which limit asphalt's physical properties' improvements, such as aging resistance and storage stability [47, 182]. Therefore, researchers have attempted different ways of removing these obstacles, including sulfur vulcanization [95, 183], adding antioxidants [96, 97] and functionalization (or adding compatibilizers) [102, 184].

When adding a functionalized polymer to the asphalt binder, a specific interaction between asphalt and the polymers, such as hydrogen bonding, can take place. In addition, this can happen between the functional groups of the components of all blends. Therefore, when polymers with functional groups are blended, chemical compatibilization can occur, giving rise to the formation of *in-situ* copolymers due to the chemical reaction during processing [185]. A good example of a compatibilizer that reacts with asphalt binder is the a polymer grafted with maleic anhydride. The last appears to be responsible for the reaction observed when the polymer such as LDPE is mixed with hot asphalt. This type of copolymer reacts with asphalt to form a polymer-linked-asphalt system with improved performance properties [102, 185]. Four conditions have to be met in order to have reactive compatibilization to occur in blends of polymers [187], and they are: (1) sufficiently strong mixing to assure good dispersion, (2) presence of reactive functional groups capable of reacting in the interface of the polymers, (3) the reaction should occur within the residence time of the polymers in the extruder, and finally (4) stability of bonds formed for any further processing. The schematic interaction

between maleated asphalt and recycled LDPE was drawn as a part of study about the maleated asphalt-LDPE blends as shown in Figure (2.7)[186].

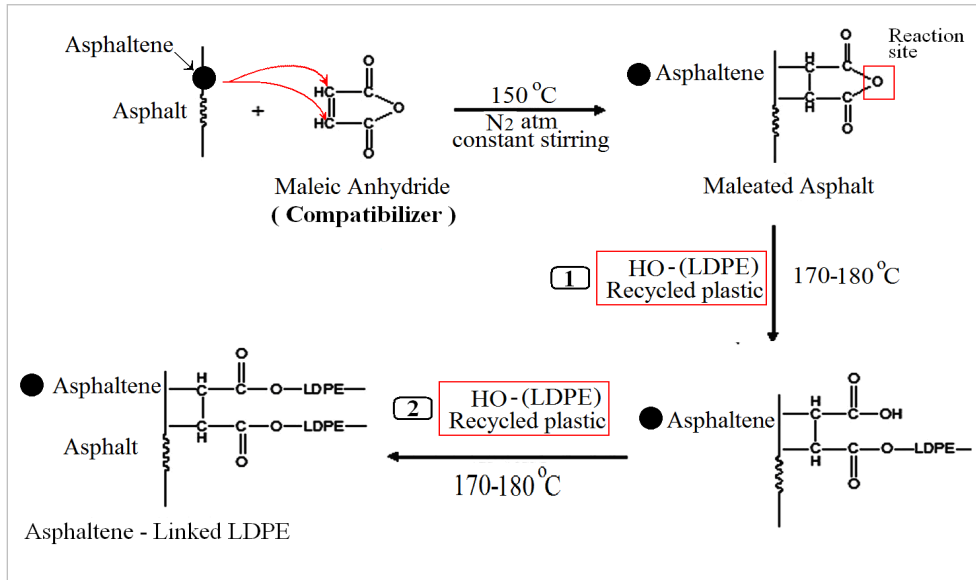


Fig. 2.7: Illustration of chemical interaction between asphaltene and recycled LDPE in the presence of maleic anhydride as a compatibilizer [186].

The enhancement of chemical reactions between CR and asphalt binder can be typically achieved with a grafting process. In this process, the surface of CR is modified by bulk polymerization of acrylic acid. It was found that such a process can also increase the viscosity and failure temperature of the CRM-asphalt binder. In addition, in this process better interactions with asphalt can be obtained [188]. It is reported that this can also result in a homogenous final product made of CRM-asphalt binder mix and thus improving the storage stability of the CRM-asphalt binder [189]. Storage stability of the final produced CRM-asphalt binder can also be highly improved by the addition of furfural activation agent [190]. Moreover, the improvement of storage stability can also be achieved by the addition of polymeric compatibilizer containing conjugated diene that reacts as a cross-linking agent [191].

Back in the early 1990's a research was carried out by Labib, M. E., and his team to achieve proper dispersion of CR particulates into asphalt and to make CR compatible modified asphalt with improved properties, both in high and low temperature properties, which can lead to reduction in the cracking, rutting, and unraveling tendencies of the CRMA pavement. The approach to the compatibility was to join the CR and asphalt molecules with small bi-functional molecules (compatibilizers). The CR compatible

asphalt was prepared from heating asphalt at 163°C, followed by the addition of the compatibilizer having the epoxy ring with a glycidyl backbone to the asphalt at continuous stirring. Then CR 6 – 15% was dispersed into the hot asphalt compatibilizer mixture with continuous stirring and heating. The use of a compatibilizer can enhance the solubility of CR into asphalt and improve the rheological properties of CRM asphalt. Modified compatible asphalt is advantageous over the ordinary one by having a wider useful temperature range. The use of modified compatible asphalt has the potential to prevent asphaltic pavement from unraveling and may increase the use of scrap tires. The content of compatibilizer used in asphalt is dependent on the source of asphalt [57].

Sulphur elements found in the asphaltenes and maltenes of the asphalt binder can be cross-linked to produce a macropolymer network. The achievement of this cross-link is done by the use of different grafting chemicals named polyphosphoric acid and a second additive known as Vestenamer. In turn, this causes the production of CRM-asphalt binder with better elastic properties at high temperatures and lower creep stiffness at low temperatures [192]. In addition to that, such processes can also lead to improvement in CRM-asphalt permanent deformation and thermal cracking resistance. [190]

The relatively strong hydrogen bonding can also take place as a part of the chemical interaction between polymer and the asphalt binder and is considered as a functionalizing agent added. Besides, the functional groups found as part of the chemical structure in the reactants can also be part of the interaction process [193]. As a result compatibilization between the polymer and the asphalt binder is enhanced and the chemical interaction is triggered, resulting in copolymers. A polymer such as ter-polymer comprising ethylene, butyl-acrylate and glycidyl meth-acrylate all together are assigned as EGA in Figure 2.8, representing a good model for such chemical interaction between the polymer and the asphalt binder. The EGA molecule is responsible for the reaction through its oxygen atom with the carboxylic group of the asphaltene.

In addition to the above, interaction enhancement between the asphalt binder and the modifying polymer can take place by the addition of elemental sulfur (S) to the blend. It was an aim of a study conducted to enhance the performance of tire CR and SBS-M-asphalt binder and to improve its storage stability. Wheel a tracking test was selected to

evaluate the effect of the vulcanized blend. Data obtained indicated that Marshal stability and resistance to plastic deformation of CR/SBS were increased after the addition of S. The best improvements were obtained at 4% CR/SBS and 1% sulfur (S). The improvement was attributed to the fact that the chemical bond that formed between the asphalt particles and S and cross-linking between rubber particles and S was so strong that it prevented a separation phase formation [193].

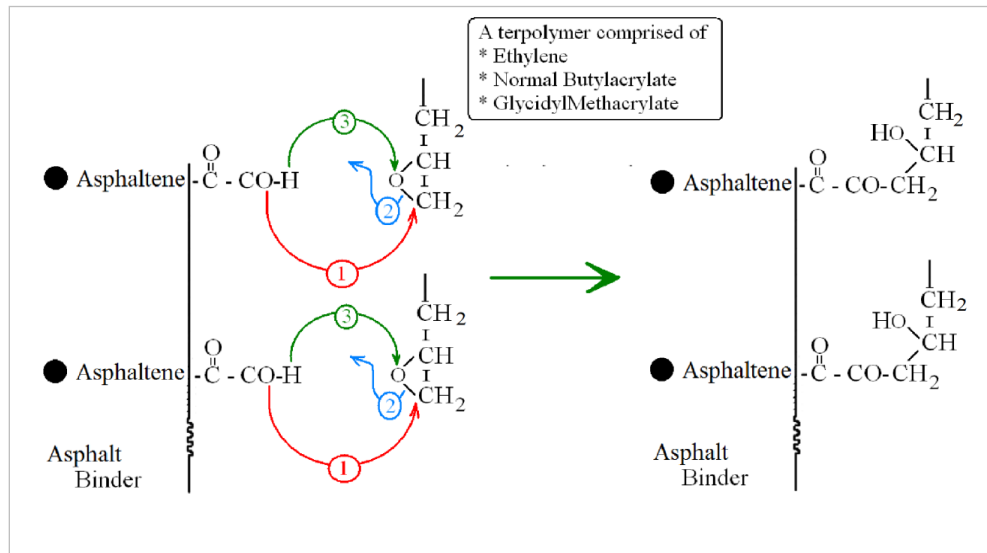


Fig. 2.8: Illustration of chemical interaction between the functionalizing terpolymer and the asphalt binder [111].

The performance of the final modified asphalt binder produced by either the physical or chemical reactions mentioned above can be affected by some external factors such as temperature and time of the reaction. Time reaction between the CR and asphalt binder is a very important factor that may change the properties of the final product, while the rate of the reaction can be effected by the temperature at which the reactants are blended. Most favorable temperature and time of reaction must be experimentally determined before real production of modified asphalt binder is initiated. It is advisable not to reach the flash point when attempting to accelerate the interaction between the CR particles and the asphalt binder constituents by increasing the temperature. Higher temperature and longer duration for reaction sometimes can have an adverse effect such as breakdown the mix [194].

In the case of CR of coarse particle shape and higher concentrations, when a modifier is blended with asphalt binder, the process needs a higher temperature [28].

However, at an extreme temperature and reaction duration time, an adverse effect can be observed. It is the depolymerization and random dispersion of the CR into the mix [195, 196]. One study has reported that increasing temperature beyond 200°C, will cause depolymerization and thus lead to the hardening of the final product. Depolymerization occurs slowly when the temperature is between 150°C and a little below 200 °C and starts to increase rapidly when close to or above 200 °C [197]. When considering these two factors, it can be said that the interaction process is unique and delicate. Likewise, between these two temperatures, viscosity initially increases rapidly, then reduces its pace, and subsequently decreases. At higher temperatures than 200 °C, viscosity reaches a maximum value within 5 min and decreases rapidly thereafter; it was a conclusion of Sun and Li's study [62]. The study also concluded that the CRM-asphalt that was mixed at 200 °C, its viscosity was 5% and at 223 °C was 41% higher than that at 177°C. In regard to the blending time, it was found that the viscosity of CRM-asphalt binder that was mixed for 5 min. has increased by 11%, and 46% at 480 min. On the other hand, the failure temperature between CRM-asphalt binder mixed at 177 °C and 200 °C was found to be negligible. Another study has demonstrated that the rate of swelling of CR particles increases as the temperature increases; but the extent of swelling decreases [198]. For a 10% CR mixture, a blending time of up to 60 minutes and a mixing temperature of up to 177 °C can contribute to a higher failure temperature and viscosity of binder at 135 °C [199]. Whereas, a shorter time of 15 minutes for a mixing process at 177 °C is suitable for 15% of medium to fine CR addition to fully interact with the asphalt binder, a conclusion drawn by Shen and Amirkhanian [63].

In a different study, it was demonstrated that a homogenous CRM-asphalt binder that has an enhanced performance can be achieved as an effect of shear rate reduction. It is suggested that this occurred by increasing the mixing temperature and mixing time [200].

CHAPTER THREE

3. CASE STUDIES ON ASPHALT MODIFICATIONS

3.1. Introduction

Asphalt has been modified by the incorporation of different additives in order to improve the engineering and road performance properties of the asphalt binder. As a result, a number of relevant publications and scientific reports have emerged. The publications have covered modification topics achieved by the use of scrap automobile tires and their constituents of rubbers, virgin polymer and fibers. Besides, some of these publications have expressed also some details on the use of some industrial polymeric wastes in such modifications, and the followings represent examples of some of these publications. Each type of polymer has its own associated physical properties. Consider these examples.

3.1.1. Case Studies on Commercial and Waste PM-Asphalt

Regarding the use of polymer waste material for asphalt applications, there are many modification processes and additives that are currently used in asphalt modifications such as styrene butadiene styrene (SBS)[201], styrene butadiene rubber (SBR)[11], low-density polyethylene (LDPE) [202], high density polyethylene (HDPE) [202, 203], polypropylene (PP) [204], ethylene-vinyl acetate (EVA) [205, 206], acrylonitrile-butadiene-styrene (ABS) [204], polyethylene terephthalate (PET) [207] and polyvinyl chloride (PVC) [208].

The SBS block copolymers and EVA are two polymeric materials widely used in asphalt property modification. They are recognized to improve low- and high-temperature behavior of asphalt, particularly at low concentrations ranging between 3.0 wt % to 5.0 wt %. [66]. SBS is known to increase the elasticity of the asphalt, much like a rubber band. Styrene butadiene rubber (SBR) latex polymers are another group of elastomeric polymers, which are also known to increase the ductility of asphalt cement [209, 210]. Today, although SBS has been probably the most appropriate polymer for asphalt modification as reported by a number of authors, SBS was proved with low aging resistance [209].

There are earlier findings of another study carried out by Button and Little (1998) [211] on the basis of stress-controlled fatigue testing at 20°C and 0°C. The study indicated that SBS-M-asphalt has exhibited a better fatigue property when compared to unmodified AC-5 Asphalt; the last is an ordinary virgin asphalt [40].

In 1991, Collins and his team work [141] found that SBS-M-asphalt mixes have longer lives than virgin asphalt mixes. The addition of SBS polymer to the asphalt binder also increases its resistance to low-temperature cracking.

Later in 1996, Adedeji A. and his coworkers [21] blended SBS with asphalt binder in the ratio of 0.0 to 96.0% by weight using two types of methods. The first was called solution casting, where stock solutions of the asphalt binder and SBS in non-selective solubilizing tri-chloroethane were all mixed. Whereas, the second was the melting process which involved the samples to be made in a batch mixer at 200 °C. The results showed that the asphalt binder had partially solubilized the poly-butadiene (PB) mid-block of the SBS polymer to produce saturated (PB) micro-domains network along with the macro-domains network of asphalt. The last was confirmed by stress relaxation tests and actually formed by phase separation of asphalt as large domains in a continuous matrix of SBS rich region, while its concentration varied from 10% to 90%. The macro-network will break down as the asphalt composition exceeds 90%. Examination by transition electron microscope (TEM) of the interior of SBS-rich regions discovered the micro-domains of asphalt-swollen PB mid-block with swollen PS micro-domains, which its shape was transformed from short cylinders to spheres. Dynamic mechanical spectroscopy (DMS) and differential scanning calorimetry (DSC) analysis indicated a systematic increase in the PB glass transition temperature (T_g) and a negligible change in the T_g of the PS as the asphalt content increased. They concluded that tri-block copolymers that can form a macro-network at low concentration seem to be more desirable for highway pavement modifications.

Near the beginning of seeking engineering properties' improvements to the asphalt binder, a study conducted by Shukla and Jain (1984) [212] has focused on the effect of wax-asphalt pavement binder in improving some of its properties upon the addition of 4.0% EVA, 6.0% SBS and 8.0% of resins. According to their results, they concluded that the blending has led to a reduction of susceptibility to high temperature,

bleeding at high temperature and brittleness at a low temperature of the final modified asphalt.

Very late in 2011, Mjthab and her assistants [213] carried out a research work on blending of EVA modifier with asphalt. They indicated in their conclusion that EVA modifier has essentially stiffened the asphalt binder and thereby made the asphalt more resistant to traffic loading and rutting, particularly at higher road temperatures during the hot summer seasons when asphalt surfaces were at higher risk of softening and rutting under traffic. At the end of their research, their final product of EVA-M-asphalt became much like a hard plastic and, therefore, the product was considered a plastomer.

Recycled EVA was aimed for asphalt binder modifications by a study of García-Morales and his assistants [205]. The modification of asphalt with such a modifier has led to very satisfying results. In their work, the studied concentrations ranged from 0 to 9% by weight. The results have proved that the recycled EVA can increase the binder viscosity at higher service temperatures, with consequent benefits on road performance, such as resistance to rutting. However, the asphalt viscosity at the production and application temperatures proved to be sufficiently low for its adequate use in pavements even at concentrations as high as 9% by weight.

Modification of asphalt with synthetic commercial polymer modifier incorporation can be considered also as a solution to improve the engineering properties of the asphalt binder. In this regard, PE, the most popular plastic material in the world, has been found to be one of the most effective polymer additives for asphalt modification. It is a semi-crystalline material with excellent chemical resistance, good fatigue, good wear resistance and low price.

In addition to its original benefit of improving the engineering properties of the asphalt, LDPE was also used widely in asphalt mixtures as an aggregate replacement. It was reported that Marshall Stability was increased by 250%, and mix density was reduced by 15% with the replacement of 30% LDPE in the form of aggregate particles with the size of 2.36 – 5.0mm during modification of asphalt production [207].

In 2007, Awwad and Sheeb [202] investigated the improvement of asphalt properties when mixed with commercial PE. Their study was carried out to determine the best type of PE to be used and its proportion. HDPE and LDPE were two types of PE

added to coat the aggregate of the asphalt binder blend. Data analysis proved that ground HDPE modifier provided better engineering properties. The recommended proportion of the HDPE modifier was 12% by weight of the asphalt content. It was also found that HDPE increases the stability, reduce the density and slightly increase the air voids and the voids of mineral aggregate.

Despite the fact that modification of asphalt with synthetic commercial polymer modifiers is considered a solution to improve the engineering and physical properties of the final PM-asphalt binder, the approach to PM-asphalt binders usually increases the cost of asphalt [214]. In this case, polymeric wastes combine the advantage of reducing cost as well as management problem for asphalt industries and producing a modified asphalt pavement binder with improved engineering properties [6, 57, 133, 141, 215].

In this regard, a study on the effect of PE on the modified asphalt properties was conducted by Fuentes-Audén and his coworkers [44]. They concluded that PE concentration incorporation in the asphalt matrix was up to 5 wt %; otherwise, the resulting viscosity would reduce the processability of the mixture. Furthermore, the addition of recycled PE has promoted a better resistance to rutting, cracking and to thermal fatigue.

An experimental work was carried out by Zoorob and Suparma [216] on the use of recycled plastics composed predominantly of PP and LDPE as modifiers blended with the asphalt binder. They reported that such modifiers have led to an increase in durability and improvement of fatigue life. They also used the recycled plastic composed of LDPE with a DAM. The LDPE was found to replace 30.0% of 2.36 – 5.0mm aggregates, reduced the density by 16.0%, and increased the Marshall Stability by 250.0%.

Another study focused on the use of reclaimed polyethylene obtained from LDPE carry bags as an additive for asphalt modification. Based upon the experimental results of this study, the following conclusions were drawn. (i) The flexural stiffness of the PE-modified mixtures was found to be comparatively higher than the virgin mixtures, whereas the dissipated energy and phase angle of the PE-modified asphalt mixtures were found to be comparatively lower than virgin mixtures. (ii) Fatigue life of the PE-modified mixtures increased by 2.5 times when compared with virgin mixtures. (iii) The thickness

of the PE-modified asphalt mixture for a given traffic is substantially lower than the virgin mixture for a given practical thickness of granular bases [217].

In 1992, Jain and his coworkers have reported that by mixing 2% PE with 80/100 grad penetration asphalt mixture, the fatigue life of asphalt binder increased by 10 times [217].

In a different aim, recycled LDPE in a size ranging between 0.30 and 0.92mm has replaced by 15.0% weight aggregates in asphalt binder for road pavement construction. It was estimated by Qadir and Imam [218] to double the Marshall quotient (MQ) and increase the stability retained (SR) by 15.0%, implying an improvement in resistance to rutting and water.

In another investigation due to the low compatibility of LDPE and asphalt, Glycidyl methacrylate (GMA) was used to improve compatibility between LDPE modifier and asphalt matrix. According to the results obtained, the GMA-g-LDPE modified asphalt had better elastic and rutting performance. In addition, temperature sensitivity and fatigue properties of asphalt mixture were both improved in asphalt investigation [207].

In other investigations, the influence of HDPE-modified asphalt mixture obtained by various blending time, blending temperature and HDPE level content on the Marshall Stability, flow and Marshall Quotient was the main purpose of the research work was done by Sinan and Emine (2004). Asphalt binder in this study was prepared by blending the HDPE in 4-6% and 8% by asphalt mass. Besides, three different mixing temperatures and times were considered in this study. They are 145°C, 155°C and 165°C, for 5 min, 15 min and 30 min, respectively. Results of this study concluded that 4% waste HDPE at 165°C has more resistance to permanent deformation. Moreover, among all blending times, 30 min of blending period showed the best result were when Marshall Quotient (MQ) increased by 50% compared to virgin mix [203].

The effect of HDPE in powder form as asphalt modifier on the permanent deformation of asphalt mixture using Marshall design parameters and creep behavior were at the center of the study conducted by Sinan and his coworkers [219]. Virgin asphalt was blended with the HDPE contents of 1-4% by asphalt weight at a mixing temperature of 185°C for 1 hr. Results of this study showed that the addition of 3%

HDPE led to an increase of 57% in Marshall quotient (MQ). In addition, the use of 2% HDPE decreased the permanent strain by 34% and increased the creep stiffness by 52%.

Asphalt modified by mixing with thermoplastic polymer namely LLDPE, HDPE, and PP at 120 rpm, mixing temperature was kept between 160 and 170°C for 1 hr. The contents of PP, LLDPE, and HDPE used were 0.5, 1.0, 2.0, 2.5, 3.0, and 5.0% by weight of the blend. Results of softening point temperature (SPT) values obtained showed there is no grade difference in the SPT for PMA up to 1.5% content of polymer in asphalt binder as compared to virgin asphalt. PP offered a better blend in comparison with HDPE and LLDPE. The viscosity of virgin asphalt was also enhanced with the addition of polymers. The pseudo-plastic behavior was more prominent for HDPE and LLDPE than PP. Finally, the best results in this study were obtained when polymer content was kept below 3% [220].

Casey and his colleagues [204], in their research work, concluded that waste HDPE and LDPE were the most promising recycled materials that can be used for asphalt modification when compared with recycled PET, PVC, and ABS. They had expected better results to be obtained with ABS and pointed out that a concentration of 4% was the ideal concentration of recycled HDPE and LDPE used as additives in the asphalt binder.

Comparably, a research work done by Costa and his assistants [221] was intended to evaluate the possible advantages of modifying the asphalt binder with different plastic wastes HDPE, LDPE, EVA, ABS, and CR in order to improve the properties of the asphalt binders. The performance of modified binders with those mentioned recycled polymers was compared with the virgin asphalt and the one of a commercial modified binder. The characterization of the different asphalts modified with 5% of each one of the studied polymers demonstrated that it is possible to obtain similar properties, or even better than those of commercial modified asphalt. In fact, it was observed that SBS, HDPE and EVA are the most promising polymers to increase the softening point of the modified binder; HDPE and EVA are the polymers with higher influence in the penetration test results; SBS, EVA, and CR presented the best performance in relation to resilience; all modified asphalts, excluding those with ABS and CR, only reach the proper viscosity to produce asphalt mixtures near or above 180°C, including the commercial asphalt; HDPE, LDPE, and EVA have a good dispersion in the asphalt,

whereas SBS, ABS and CR are difficult to be melted in the asphalt. This phenomenon was related to the viscosity of used modifiers, which were affecting their flowability and dispersibility in asphalt matrix.

Elastomers provide the elastic component of the asphalt binder stiffness at high temperatures and loading. In contrast, plastomers provide an increase in the binder's stiffness at high temperature and loading but without an increase in the elastic component of the binder [222]. Generally, plastomeric polymers can improve rutting resistance, but they are inferior to elastomers due to the lack of improvements in fatigue resistance, cracking resistance and low-temperature performance. However, elastomers are limited to improving heat resistance [103, 223].

Asphalt binders containing epoxy polymers are used to improve some properties of the asphalt binder. For instance, the paving layer on the steel bridge deck endures larger deformation and higher temperatures. Therefore, some polymers were used to prepare modified asphalt binders for such purpose. However, neither plastomeric nor elastomeric modified asphalt can change the thermoplastic nature of asphalt; in other words, they cannot prevent the flow of asphalt mixture at high temperatures [102, 103, 224].

For resolving the above-mentioned problems, in 2009, Jainying and his colleagues [103] carried out a laboratory study using asphalt binders and epoxy resin elastomers in combination. Epoxy-M-asphalt is prepared by mixing asphalt binder with a certain percentage of SBS copolymers. Next, an appropriate amount of curing agent (the ratio of 7.5:10 by mass of curing agent to epoxy resin was used) were added into the blend and mixed. Then, the desired amount of a preheated epoxy resin was added to the blend. Epoxy asphalts with 10, 20, 30, 40, and 50 wt% epoxy resin (including curing agent) were prepared respectively. Results have shown that asphalt in epoxy asphalt has little effect on the optimum ratio of curing agent to epoxy resin. Fluorescent microscope indicated that epoxy resin was dispersed in asphalt when the epoxy resin content was less than 30% by weight. The epoxy asphalt began forming network structures when 30% by weight epoxy resin was blended with asphalt. In addition, the epoxy resin phase gradually became the principal phase with epoxy resin contents continuously increasing. Epoxy asphalt can be cured not only at 120°C but also at 60°C. The initializing viscosity of epoxy asphalts was about 600–800 mPa s; it was not more than 2 Pa.s for 60 min at

120°C. The change of viscosity attained was due to the appropriate epoxy asphalt mixture blending and compacting. Mechanical properties showed the increase of tensile strength when the contents of epoxy resin were more than 30 wt % due to the formation of continuous network structures in epoxy asphalt. But the elongation at break of epoxy asphalt decreased as epoxy resin concentration increased.

Research work done by Araujo et al., 2012 [225] have studied the comparative aging of a conventional asphalt binder and styrene-butadiene-styrene (SBS) modified asphalt binders under the effect of weathering. The samples of asphalt binder were exposed to cycles of xenon radiation, moisture, and temperature. As a result, they concluded that the oxidation resistance of SBS modified asphalt was higher than the conventional asphalt binder which are evaluated by using the weathering test and FTIR analysis. They also found that for SBS modified asphalt binder, the aromatic content increased with the time of exposure in the weathering chamber.

In this trend, dealing with the utilization of waste plastics as asphalt binder modifier, Vasudevan along with his assistants [226] have studied the utilization of waste polymers at production of flexible road pavement materials. In the presented study, the authors coated the stone aggregates with molten waste plastics. As a result, they concluded that the coating of aggregates with plastics have reduced the porosity, absorption of moisture, and improved soundness. They also found out that the use of waste plastics for flexible pavement was one of the best methods for easy disposal of waste plastics.

At the center of transportation engineering of Bangalore University (CTEBU), a team carried out a research on the possible use of processed plastic bags as additives in asphalt concrete mixes. The properties of the modified asphalt were compared with virgin asphalt and it was observed that the penetration and ductility values of the modified asphalt have decreased with the increase in the proportion of the plastic additives, up to 12 % by weight. Therefore, the life of the pavement surfacing course using the modified asphalt is also expected to increase substantially in comparison with the use of virgin asphalt [227].

Shredded waste plastics were also used as modifiers in asphalt pavement material by Bindu and Beena (2010) [228]. They have studied the stabilization of the stone mastic

asphalt (SMA) mixture. The final product was subjected to performance tests, including Marshall stability, tensile strength, and compressive strength tests. They were conducted by varying asphalt percentages by weight of aggregates between 6.0 and 8.0%, and by varying plastic percentages between 6.0 and 12.0%. According to the results obtained, they found that 10.0% by wt of plastic was the most effective amount recommended to improve the performance of the SMA mixture.

3.1.2 Case Studies of CR-Modified Asphalt

Although polymer incorporation to the asphalt binders leads to improvements in properties of final PM-asphalt binder, they usually increase the cost of asphalt. Plastic solids such as PE and PPr, which comprise the major constituents, obtained either from fresh/commercial raw materials or municipal/industrial solid wastes, were not all compatible with the asphalt binder. Hence, alternatives were explored, extensively investigated, studied and reported in a variety of international literature.

Several studies referring to the benefit of using crumb rubber (CR) extracted from scrap tires in asphalt mixtures were performed; it provides rubberized asphalt with reduced fatigue cracking, improved resistance to rutting, improved tensile strength and toughness, longer pavement life and reduced maintenance costs compared with conventional asphalt mixtures [229 - 232].

Rubberized asphalt mixtures show better performance at high temperatures, can be used in a variety of climate conditions and are more flexible at very low temperatures. This advantage can also be achieved when the thickness of the modified asphalt layer is reduced from 50 to 38 mm [233]. As a result, rubberized asphalt concrete is cost effective; it is reported that it saves as much as \$22 000 per lane mile over conventional asphalt projects [234]. The CR modification asphalt projects can consume large quantities of scrap tires in a positive manner, preserving the environment from pollutions.

Chui-Te Chiu and Li-Cheng Lu (2007) have used rubberized asphalt which was produced by blending CR of (i) 30% of a coarse type, (ii) 20% of a fine type with asphalt binder for SMA. They found out that CRM-SMA mixtures were not significantly different from conventional SMA in terms of moisture susceptibility. However, it showed better rutting resistance than that of a conventional dense graded mixture [235].

A set of laboratorial tests were carried out using CR modifier (obtained by ambient grinding) blended with conventional asphalt commercially named CAP-50/70. From the tests performed in the laboratory, the following were concluded. (i) The penetration decreased as the amount of rubber increased up to 21% for only 60 min reaction time, then the heavier of 21% was varied due to the increase of viscosity. (ii) Up to 21% CR amount, the softening point increased and was similar for 30, 45 and 60 min reaction time. (iii) The resilience results were influenced mainly by the amount of CR added, and the reaction time had no influence in the change of asphalt properties; on the other hand, the addition of CR increased the elasticity. (iv) In a major way, the amount of CR added has influenced the viscosity of the final product and exceeded the standards when more than 21% was added [236].

Shankar and Prasad (2009) [237] have studied the blend of CRM-asphalt (commercially assigned CRMA 55) at specified temperatures. Marshall's mix design was carried out by changing the modified asphalt content at constant optimum CR content and subsequent tests have been performed to determine the different mix design characteristics. This has also been done for the conventional asphalt 60/70 type. Results showed very much improved characteristics when compared with the virgin asphalt and once again at reduced optimum modified binder content (5.67%).

Lately, another study was conducted by Ganapathi and his coworkers (2012) [238] on recycling of CR tires and LDPE blend on SMA by use of the dry process. The study was planned to reduce pollutions from waste tire disposals and to investigate the benefits of stabilizing the SMA using CR and LDPE in 15% and 30% by wt of asphalt, respectively. SMA had an optimum dosage of the additives of a combination of 30% (combination with 30% CR & 70% LDPE) by weight of the asphalt. Results of tensile strength test have found their ratio values to be in the range of 85 – 94%, which is more than 85% as specified for an SMA mixture. Generally, results revealed that the addition of CR and LDPE to SMA using the dry process could improve the engineering properties of SMA mixture, and the CR content has added a significant effect on long-term performance.

The study of Rokade S. (2012) [239] was achieved through the use of waste plastics; LDPE and CR blended with asphalt using the dry process and the wet process,

respectively. The study involved the use of the Marshal Method of asphalt mix design to determine the different mix of LDPE and CR and their effect on the design characteristics. Results have revealed that the Marshal Stability value, which is the strength parameter of semi-dense asphalt concrete, has increased by 25% as LDPE and CR increased. The density of the mix has also increased in both cases when compared with ordinary commercial asphalt, providing more stable and durable mix for the flexible pavements. Results and values of air voids, voids in mineral aggregate and voids filled with asphalt were found out to be within the required specifications. Researchers concluded also that plastics and CR will be of great benefits particularly to those hot and extremely humid climate countries. It was also worth mentioning that in the modified process (dry process) waste plastics were coated over aggregate. This was assumed to bring about a better binding between the asphalt and coated aggregates due to the increase in bonding and area of contact. This will, therefore, lead to a decrease in voids, preventing the moisture absorption and oxidation (by air/water) of the asphalt.

Tortum and his colleagues (2005) [149] have studied the effects of CR and aggregate gradation, mixing and compaction temperature, CR, and binder ratio, and mixing time on asphalt mixtures. They concluded that for specific conditions, rubberized asphalt mixtures performed better than the conventional asphalt mixture.

In another laboratory study, Pais and his colleagues (2001) [146] reported that CR inclusions can modify a conventional hot mix asphalt (HMA) in terms of flexural fatigue life since mixtures that include those that are CR-treated using different processes (cryogenic or ambient) show greater fatigue life than conventional mixtures. This is regardless of the void content, which may vary from one mixture to another for the same category of asphalt.

Nuha Mashaan and her assistants (2010) [240] have run different investigations of the asphalt binder properties as a function of various blending times, temperatures, and CR percentages. The final CRM-asphalt binders were produced through an accelerated un-aged binder process by using penetration, viscosity, and softening point tests. The results from this study showed the following. (i) Blending interaction times and blending interaction temperatures for CRM-asphalt binders have effects on the binder properties. (ii) The longer time and high temperature for the interaction of CRM-asphalt binders

result in an increase in viscosity and softening point. (iii) The CRM percentage decreased the penetration, which would enhance CRM-asphalt binder stiffness, asphalt binder consistency, and resistance to flow, which led to improved rutting resistance. However, this study has found that a control binder of 80/100 grad penetration had little change of the binder properties as a function of interaction blending conditions.

Once more, Nuha Mashaan with almost the same preceding assistance (2011) [55], has blended CR with asphalt binder in order to investigate the effect of various CR content on the physical and rheological properties as well as the rutting resistance of CRM-asphalt binder. The CRM-asphalt binder was prepared at a blending temperature of 180 °C for 60 min. The results showed that the elastic recovery values have increased from 16.38% for the virgin binder to 94.5% for the 20% CRM-asphalt binder. While the penetration degree has decreased as the quantity of CR increased up to 20%. The average reduction in the penetration value of final CRM-asphalt binder was between 16.5% and 61% with respect to the CR content ranging between 4% and 20%. Results of rheology showed that when CR content increased from 4% to 20%, the G^* , $G''/\sin\delta$ also increased from 28% to 87%, and 29% to 82%. The average reduction in the phase angle of CRM-asphalt binder was from 6 to 48% as CR content increased from 4% to 20%. However, at 20% CR content, the G' and G'' of the CRM-asphalt binder were increased by 64% and 74%, respectively.

Rubberized asphalt binders were also prepared by mixing 80/100 penetration-grade asphalt with various contents of fine grain CR [241]. Three percentages of CR were used; they are 3%, 9%, and 15% by weight of asphalt. The rubberized-bitumen was prepared at blending temperature and speed of 150°C and 250rpm, respectively, for 120 min. The main experimental approach of this study is focused on the determination of certain characteristics and properties of a CRM-asphalt as compared to virgin asphalt. Results of this study showed that all properties of final CRM-asphalt binders were improved by the addition of finer CR. Softening point, viscosity, and the complex shear modulus were increased as the CR content increased in the binder, while penetration and phase angle (δ) values were decreased as compared with the virgin asphalt. The softening point as an example was increased from 46°C for virgin asphalt to 54°C, 55°C, and 58°C with 3%, 9%, and 15% of CR, respectively.

Jeong and his coworkers have studied asphalt modification by blending of both 10% and 20% of CR. The experimental laboratory test was conducted in order to test viscosity and rutting factor ($G^*/\sin \delta$) values. The results showed that the 20% CR addition increased the viscosity and stiffness by 550% and 225%, respectively [242].

In the last few years, production of polyurethane foam (PUF) has been rapidly increasing worldwide. Because PUF has a very wide range of applications, including shoe production. It was reported that 17% of shoe content is PUF. In 2011, China alone produced about 7.5 million tons of PU, which generate a large amount of waste. So far in many countries, particularly in developing countries, the management of this waste still involves open area disposal by burning [243]. However, landfill disposal and pollution problems, stockpiling taking up a lot of area, problem of the storage, and effect on the living environment are the main disadvantages of PUF waste. Recycling of PUF as a feedstock for asphalt modification could be the best solution to landfill and pollution problems of such waste.

A novel study carried out by Sulyman et al. (2016) investigated the feasibility of using scrap polyurethane foam (PUF) obtained from a production process and post-consumed shoes and crumb rubber (CR) obtained from used tires as singular additives composed of binary asphalt-polymer blend and admixture additives composed of ternary asphalt-polymer blend. The experiments were carried out at a reaction temperature of 210°C with a high-speed mixing of 6000 rpm for 60min in dose percentages of (5 - 15 wt%). Three different weight fractions of ternary asphalt polymer blends composed of CR:PUF-modified asphalt, which are 25:75, 50:50, and 75:25, respectively, were studied. Basic and rheological properties of modified and unmodified asphalt samples were investigated. The results and data obtained showed that investigated properties of binary and ternary asphalt-polymer blends were improved, and the modifier type and its content levels played an important role in the experiments. Based upon the experimental results of this study, the following conclusions are drawn. 1) Fifteen percent was the best content level for both CR and PUF as well as CR:PUF admixture. 2) Temperature sensitivity decreased by 57%, 77%, and 72% for 15%CR, 15%PUF, 15% (75%CR:25%PUF) respectively. 3) Viscous flow results showed that the viscosity at 60°C was increased by 8-16 times at low shear rates and by 2-4 times at high shear rate in dependence on the

modifier types, while PUF-Modified-asphalt shows the highest viscosity at high shear rates. 4) Complex modulus (G^*) and rutting resistance parameter ($G^*/\sin \delta$) also increased by 5-9 times more than virgin asphalt, while phase angle(δ) was decreased by (5-10) times less than virgin asphalt. 5) An increase in complex modulus and a decrease in phase angle indicates high elastic behavior of the asphalt binder, which decreases the permanent deformation [243].

Rubber pavement association found that using CR in open-graded mixture binder could decrease tire noise by approximately 50% [244].

According to Mashaan and Karim (2013), the main factor in the increase in the physical and rheological properties of rubberized asphalt can be attributed to modifier (i.e. crumb rubber) content, regardless of modifier type and size, as well as the temperature of the reaction. Their studies concluded that the increase in reaction temperature corresponded to the increase in G^* , G' , G'' and softening point values and a decrease in δ [58].

3.1.3 Case Studies on Recycled PET and Fiber-Modified Asphalt

PET, the most abundant plastic waste material collected for recycling from the household waste stream as mentioned by Waste and Resource Action Program (WRAP) survey [245], may be used as an additive and modifier for asphalt binder. This was investigated by a number of researchers and many reports and scientific studies on this subject were published in recent years.

In 2012, Moghaddam and Karim [207] investigated the effects of adding waste PET particles to the asphalt mixture. The results of the study showed that PET reinforced asphalt mixtures to have had a higher stability value in comparison with the virgin one. In terms of the convenient quantity of the PET to be added, it was noted that the optimum value in case of stability was 0.4% PET. Moreover, adding higher amounts of PET into the mixture increased the flow values. In contrast, the stiffness of the mixture was decreased, yet fatigue life was increased by adding a higher amount of PET.

Earlier in 2010, Kalantar and his colleagues [246] investigated the possibility of using PET as polymer additives in asphalt mix. The binders were prepared by mixing the PET in amounts of 2%, 4%, 6%, 8%, and 10% by weight of optimum asphalt at 150°C. The results showed better resistance against permanent deformations and rutting when

compared to the virgin asphalt binder. The results also showed that the addition of PET to asphalt increased the softening point value, and as the higher PET content increased, the softening point temperature increased. This phenomenon indicated that the resistance of the binder to the effect of heat was increased and it would reduce its tendency to soften in hot weather.

In order to evaluate the effect of PET waste on the properties of stone mastic asphalt (SMA), Ahmadinia and his associates (2012) [247] have blended PET waste with asphalt mixture for assessments of the engineering properties of SMA. The weight percentage of PET was used from 0% to 10% by the interval of 2%. The mechanical properties of asphalt mixes were calculated and assessed with laboratory tests. The results showed that the appropriate amount of PET was found to be 6% by weight of asphalt.

Additionally, the incorporation of PET also has a significant positive effect on the properties of SMA such as increasing viscosity and stiffness of asphalt at normal service temperatures. However, all applied amounts of PET additives did not increase the elasticity of asphalt significantly, and on heating, they do not perform satisfactorily [248].

The application of waste PET in the form of granules pellet of 3.0 mm size was part of a study carried out by Hassean and his assistants [249]. They blended the waste PET as a partial fine aggregate with an asphalt binder (from 60/70 penetration grade asphalt and 12.5mm aggregate grading) at 140-180°C and then compacted it using Marshall hammer with 50 blows on each side. The results obtained in this study proved that the aggregate replacement of 20% fine aggregate of 2.36 - 4.75mm by volume with PET granulates of 5% total weight of the asphalt mixture was the effective use to get the highest Marshall Quotient with the lowest flow and the highest of stability. In addition, PET has been found to be the most effective polymer additives due to its low glass transition temperature and semi-crystallinity [250].

A study was performed in Nantes in France, which showed that fiber-modified mixtures have maintained the highest percentage of voids compared with unmodified asphalt and two elastomer-modified mixtures. The study concluded that a better drainage and, therefore, a decrease in susceptibility to moisture-related distress was attained [251]. Polyester and polypropylene fibers were the main fiber precursors for the reinforcement on crack resistance in asphalt mixture. The last was tested for modulus of elasticity

leading to an increase of 50 – 100 %, implying an increase in toughness; however, fracture energy and tensile strength were not significantly affected by the aforementioned fibers [252]. The polyester and polypropylene fibers were again the precursors used to modify the asphalt binder. Simpson and his colleagues have conducted such a research. The results of their research have implied that mixtures containing polypropylene fibers were found to have higher tensile strengths and resistance to cracking. In contrast, none of the fiber-modified mixtures showed resistance to moisture induced, freeze/thaw damage. They did not show any improvements in stripping potential either. A thermal cracking test was significantly demonstrated by polyester fiber and polymer asphalt mixture, whereas, it was not by polypropylene asphalt mixtures. The addition of the polypropylene to the asphalt binder has also decreased rutting potential as measured by repeated load deformation testing. The solution to asphalt mixture performance is a uniform distribution of fibers in a composite mixture [253].

The department of transportation in Ohio state in the USA has published a standard for the use of polypropylene fibers in high-performance asphalt concrete [254]. Polypropylene fibers have been used by Yi and McDaniel in order to reduce reflection cracking in an asphalt overlay. It was observed that crack intensities were less on the fiber-modified overlay sections and sections in which the pavement had been cracked and sealed before the overlay were found to have less reflection cracking when fibers were used in either the base or binder layers.

Based on the extensive research carried out by scientists and experts in this field, asphalt mixture improvements have included other modifiers. In this regard, cellulose fibers were also part of this issue. The cellulose fibers were added to the asphalt binders to study their effect on bleeding, void content reduction, abrasion, and drainage in porous asphalt. Cellulose fibers in the mixture allowed asphalt contents to be increased while drastically decreasing bleeding of the binder. Results showed no changes in either void content or abrasion after adding cellulose fibers. Sections of roads containing fibers retained the same drainage quality over six months, while the drainage time doubled in sections without fibers [254].

An investigation has been conducted by Stuart and his coworkers [255] to study asphalt mixtures with four different modifiers: a loose cellulose fiber, a palletized

cellulose fiber, and two polymers. The binder drain-down and resistance to rutting, low-temperature cracking, aging and moisture damage are the tests that were analyzed on all mixtures. Drain-down tests proved that all mixtures with fibers drained significantly less than those with polymers or the virgin asphalt. Fiber modified mixtures were the only ones to meet test specifications for drain-down. The virgin samples were found to have excellent resistance to rutting and no significant difference was observed between them and mixtures. Low temperature and moisture damaging results were inconclusive. Finally, polymer modified mixtures were found to have better resistance to aging.

Another research was conducted by Partl and his associates [256] using various cellulose fiber quantities in a study of SMA. The analysis focused on thermal stress restrained specimen tests and indirect tensile tests. It was found that increasing mixing temperature and duration has led to a good distribution of fibers and prevented to some extent the usual clumping of these fibers. It was concluded that SMA with cellulose fiber did not significantly improve the mix based on the two tests conducted, and the poor distribution of fibers may be behind the missed improvement.

Later, Selim and his team [257] studied the mixing of cellulose fibers in SMA for the assessments of binder drain-down, moisture susceptibility (reported as tensile strength ratio), static creep modulus and recovery efficiency. Fibers were added to virgin asphalt binders and another to polymer-modified binders. The results have proved dramatic improvement of binder drain-down in all mixtures containing cellulose fibers. In contrast, the mixtures with only virgin asphalt and fibers showed the highest indirect tensile strength. The tensile strength ratio has contributed in damaging all the mixtures tested after conditioning compared to polymer modified mixtures with fibers that showed the lowest tensile strength and resistance to moisture. However, variable, statistical analyses proved that creep modulus and recovery efficiency were better only in mixtures containing fibers and virgin asphalt binders.

The addition of cellulose fiber materials to recycled asphalt concretes (RAC) was a part of supplemented study which was carried out by Su K. Yoshitaka [258]. The results indicated that basic performances of RAC in terms of resistance to rutting, moisture susceptibility, and cracking, as well as its durability, were all improved. It was

concluded that RAC with modified asphalt binder at the recycling rate of 70% is recommended as a balanced result.

Stone mastic asphalt (SMA) was developed in Germany in the 1960s and has been used in European countries for more than 20 years [259, 260]. Cellulose fibers and mineral fibers are two types of commonly used fiber modifiers. They have been widely used in different kinds of asphalt mixtures, especially in SMA; it is a type of HMA with open grade friction concrete (OGFC) [250, 261].

In 2004, a comparison study was carried out by Putman and Amirkhanian [122] to investigate the performance of SMA mixtures containing waste CR from used tires, and carpet fibers with commonly used cellulose in one occasion and polyester fibers in the other. The results indicated a significant improvement in the toughness of the mixtures, but no significant difference in permanent deformation or moisture susceptibility was found.

Polyester fibers are usually used when strong and durable reinforcements of asphalt-fiber mastics are needed at higher temperatures, as it was reported by Shih and Kuei [116]. The influence of polyester and cellulose fiber additives on the engineering properties of asphalt was also investigated by the couples. They have found that good adhesion between the polyester fibers and asphalt enhanced the load-carrying ability of asphalt-fiber mastics.

The type of mixing or the process involved in the production of very effective asphalt road pavements is a very important factor in determining the final product properties. In 1987, an available report implied the successful application of BoniFibers™; it is the trade name for polyester fibers of 6mm length manufactured in the city of Tacoma, United States of America, and supplied to blend with asphalt. The report stated that in order to assure uniform distribution of BoniFibers™ throughout the asphalt concrete, BoniFibers™ must be added to the aggregate at the beginning of the dry-mix cycle which lasts at least 15 s and preferably 30 s [16].

In another study which was carried out on fatigue properties of polypropylene (PP) fiber modified asphalt mixtures [262], it was reported that the mixtures with polypropylene fiber had considerably more fatigue life in comparison with virgin mixture.

The addition of waste tire cord mesh with different contents (0, 1, 2, 3 and 5% by total asphalt weight) was investigated for fatigue and rutting characteristics of asphalt pavement. It was illustrated that the tire thread mesh improves fatigue and rutting properties of asphalt pavement, and a sample containing 3% of tire cord mesh showed the best result [263].

Another research program looked at the effect of glass fiber with different contents (0.1, 0.2, 0.3, 0.4 and 0.5% by weight of mix) in a study of SMA. Mixes were evaluated with dynamic creep and repeated load indirect tensile tests. The results showed that the use of glass fiber had a significant effect on fatigue life of mixes while fatigue life increased by about 28.2, 37.2 and 44.4% at fiber contents of 0.1, 0.2, and 0.3, respectively [263].

Jahromi and Khodaii, (2008) used various carbon fiber contents (0.1, 0.2, 0.3, 0.4 and 0.5% by wt). The effect of carbon fiber contents on the fatigue life of mixtures was the main purpose of the study. Indirect tensile fatigue test (ITFT) was conducted using constantly repeated stress of 350 kPa. It was illustrated that using mixtures with carbon fiber showed great promise when the fatigue lives increased about 28.2%, 37.2%, and 44.4% with the addition of 0.1%, 0.2%, 0.3% carbon fiber, respectively [264].

CHAPTER FOUR

4. EXPERIMENTAL METHOD

4.1. Materials

In this chapter, the four main raw materials used in this study are described. Initially, the asphalt type of 70/100 penetration grade produced by the Russian Crude Oil Company was supplied by Lotos Company from Poland. Its physical properties and chemical constituents were listed in Table 4.1 and Table 4.2 respectively.

Table 4.1: The basic physical properties of asphalt70/100.

Physical properties	Unit	Value	Physical properties	Unit	Value
Ring & Ball softening point	°C	47.0	Ductility at 25 °C	cm	>100
Penetration degree at 25°C	dmm	85.0	Elastic recovery	%	5.0
Viscosity at 160 °C	dPa.s	0.56	Bulk density	g/cm ³	1.0296
Solubility in toluene	%	99.9	Frass breaking point	°C	-11

Table 4.2: Chemical constituents of asphalt70/100.

Chemical constituents of Asphalt	Quantity, wt%
Sat – Saturates (Aliphatic compounds)	6.8
Aromatics	64.2
Resins	16.2
Asphaltene – (high molecular weight)	12.7

Then, low-density polyethylene (LDPE) was obtained commercially from Lyondell Basell Industries in Poland, with Malen E FGAN, 18-D003 index, a density of 0.92 g.cm⁻³, and a melt flow rate index of (0.2 - 0.35) g.10 min⁻¹. Crumb rubber (CR) was obtained from polish scrap tires of cars, with particle size less than 0.8 mm, and a bulk density of 1.25g/cm³. The CR was formulated and supplied by Orzeł Company in Poland. After that, it is the textile fibers (TF) that were obtained and collected by extraction from the same type of scrap tires. Maleic anhydride (MAH) purchased from Aldrich Company for chemicals (made in Germany), with greater than 99.0% purity, was used as received (C₄H₂O₃). Finally, Toluene and Dichloromethane with high purity (99.5%) as solvents were purchased from POCh Company in Poland.

4.2. Instruments

An automatic Penetrometer, model, PNR12, was used to measure the penetration point according to the European Standard, PN-EN1426 test. In this test, the samples



(virgin and modified asphalt) was initially thermostated in a water bath at 25°C for 60 min., then the penetration of a standard needle is allowed to penetrate vertically into each sample was measured, under a specified load of 100 g and loading time, at a fixed temperature of 25°C, and the measured value is reported in units of 0.1mm. Figure 4.1 simply shows the asphalt penetration test. The penetration test can be considered as an indirect measurement of the viscosity of asphalt at a temperature of 25°C [25, 265].

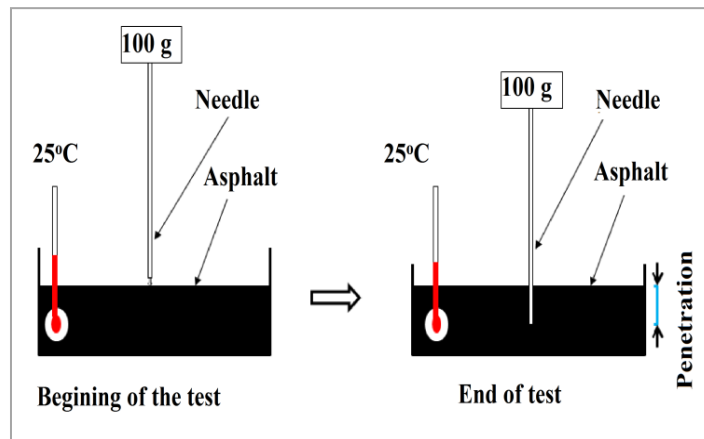


Fig. 4.1: Asphalt penetration test.

Ring and ball softening point test was carried out on all samples according to the PN-EN 1427. In this test, disks of the samples were cast in shouldered rings, and then the sample were trimmed to remove excess asphalt. Next, samples were placed in a rings holder and immersed in bath liquid (water bath when softening points is below 80 °C, and glycerol bath when softening points is above 80°C, Then the special rings were placed on the samples (placed in rings) and bath was heated at a constant rate of 5°C min⁻¹. When the samples surrounding the balls touched the bottom plate of rings holders, the softening temperature of asphalt was recorded as shown in Figure (4.2).

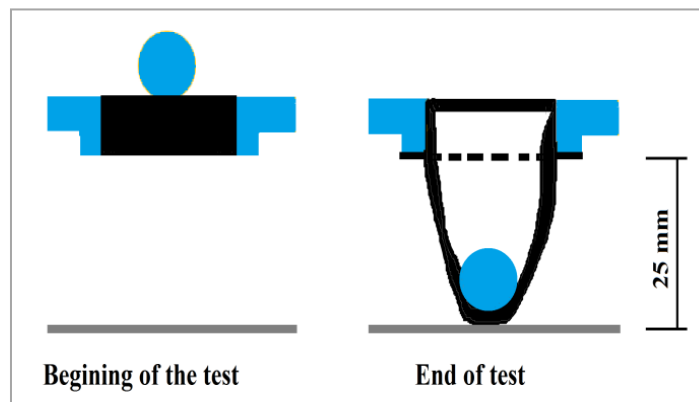


Fig. 4.2: Represent the softening point test of asphalt

Viscosity is the measure of the resistance to flow of a liquid and is defined as the ratio between the applied shear stress and the rate of shear strain. The rotational viscometer test method is presently considered to be the most practical means of determining the viscosity of asphalt, since the instrument allows the testing of a wide range of asphalts over a wide range of temperature [25]. In this study, the viscosities of the samples were determined by Digital Readout Rotational Viscometer, model viscotester 2 Plus, HAAKE Inc.

Storage stability of the samples was tested according to PE-EN 13399 test. The test was carried out as follows: each sample of the studied product was separately poured into an aluminum tube of 37 mm in diameter, 173 mm in height, and sealed. Next, it was stored vertically at $180 \pm 2^{\circ}\text{C}$ for 72 hours. Then, the tube was subjected to freezing at 5°C for 24 hr to completely solidify. Finally, the tube was cut horizontally into three equal parts. The top and bottom ends of the tubes were then melted into separate small beakers and analyzed for its softening point temperature using ring and ball method. The good storage stability of the sample implies that the difference between softening point temperature of the top and the bottom parts of the tube could be less than or equal to 2°C . Storage stability is considered a very important parameter for initial properties on modified asphalt, especially for transportation.

The ductility test was conducted according to PE-EN 13589. It provides a measure of tensile properties of asphalt materials. Simply, it measures asphalt binder's ductility by stretching a standard-sized briquette of asphalt binder to its breaking point at 25°C . The stretched distance in centimeters at breaking is then called as ductility. The main characteristics of the test are known with a number of facts [265]: (1) modified asphalt's indirect resistance to tension, (2) change of length in modified asphalt at a rate of 5cm/min, (3) it is conducted with constant temperature of 25°C .

The elastic recovery of the asphalt binder is conducted in a ductilometer at a temperature of typically 25°C (other temperatures can be used) according to PE-EN 13398. It is especially applicable to asphalt binders modified with thermoplastic elastomers (can also be used with other asphalt binders that generate only small recovery). The main characteristics of the test are the following [265]: (1) It is a basic test of the elasticity of the asphalt when modified. (2) Asphalt's heating temperature equals to

175 – 185 °C, depending on the tire rubber percentage. (3) Air temperature equals to 18 – 22°C. (4) Water temperature typically equals to 25°C. (5) Lengthen rate: 5cm/min. (6) Lengthen the sample till 10 cm, then cut and after 60 min, recovery is measured and expressed as a percentage (%) at a length of 20 cm. Automatic Breaking Point Analyzer, IWS-BPA (IWS Messtechnik GmbH).

The Frass breaking point of the modified asphalt at the best level of modification were measured. A sample of asphalt was weighed on a flat standard steel plaque. The plaque and the asphalt were gently heated up to form a uniform film of asphalt on the plaque. Then the plaque was put on a flat and horizontal surface to ensure the uniformity of the asphalt film and covered with a watch glass. The tests were carried out using the apparatus mentioned in the PN-EN 12593:2009 test procedure.

Dynamic temperature sweep test of modified and unmodified asphalt, in the linear viscoelastic range, were carried out in a controlled-stress rheometer RS-600 from Haake (Germany), using a plate-and-plate geometry 20 mm diameter and 1mm gap at a constant frequency of 10 rad/s and a temperature range of 30 – 100°C. Rheological parameters, such as storage modulus (G'), loss modulus (G''), phase angle (δ), and complex shear modulus (G^*) were estimated.

Tensor 27 Bruker model of Fourier transform infrared (FTIR) Spectroscopy, was used in this study to obtain the IR spectra of the modified asphalt. Measurements were done using the ATR technique (Attenuated Total Reflection) applying the zinc selenide and diamond base optics. Samples were analyzed in spectral range of 550 - 4000 cm^{-1} , with test parameters of 2 cm^{-1} resolution; 64 is the number of scans, and 4 mm is for spectral beam diameter. The surface morphology of modified asphalt blend samples are researched by using a Zeiss EVO 40 scanning electron microscope (SEM), which enabled an examine the phase distribution in modified asphalt blends. The SEM power was 20 kV.

The Thin Layer Chromatography or TLC on rods chromarods S II (silica gel) coupled with flame ionization detector – TLC-FID (analyzer latroscan, latron Labs, Japan) used for the analysis of the modified asphalt with the additives by separating the compounds in the mixture. TLC was used to help determining the number and the identities of components in the modified asphalt mixture. TLC consisted of three main

steps: (i) Spotting, where the asphalt mixture was dissolved in a 0.01 g/ml dichloromethane solvent and the additive powder left over was filtered from the liquor, (ii) Development involved placing the bottom of the TLC plate into a shallow pool of a development solvent, which then let to travel up the plate for a certain time, where it reached the highest point. Thereafter, the procedure was stopped for the next step, (iii) Visualization of the compounds was carried out using the FID with a hydrogen volumetric flow rate of 150 ml/min, air volumetric flow rate of 1.8 L/min with an injected volume at 1 μ l.

Gel Permeation Chromatography (GPC/SEC) is a method which are used for the analysis of the influence the used modifiers for molecular weight distribution of modified asphalt. Many studies have been conducted in efforts to connect the GPC outputs to the performance properties. Merck-Hitachi LaChrom series GPC equipment with computerized software, columns: 2 x LiChrogel PS MIX, 5 μ m, 250X7 mm (MERCK, Germany). 100 mg of binder samples were dissolved in 10 ml of tetrahydrofuran (THF < 0.05% H₂O, Sigma-Aldrich). A total of 50 μ l of the solution was injected into the column at a flow rate of 0.7ml/min and columns temperature were kept at 30°C in a column oven (LaChrom L-7350). UV detection was at 350 nm.

Thermo-gravimetric experiments were recorded on a TA instrument (SDT Q500) operating under nitrogen gas with a flow rate of 50 cm³ min⁻¹ through a furnace. Samples were about 10 mg in weight, varying the heating rate of 20°C min⁻¹ and temperature range of 50 - 600°C.

Wheel track rutting test was applied to determine the resistance of the asphalt concrete which are prepared from asphalt mixtures against permanent deformation at critical temperatures and under loading similar to how the pavement surface was applied. In this study, the rutting test was evaluated according to wheel tracking PE-EN12697-22. Materials used in the HMA, as well as mix ratios and particle sizes of aggregates used for these mixtures, are later presented in chapter Five (section:5.8). Mixing and compaction temperatures were 140°C for the mixtures with virgin asphalt binder and 160°C for those containing PM-asphalt binders. The wheel track test was conducted at a temperature of 60°C, an applied load equivalent to 700 N, specimen thickness of 60 mm, wheel diameter of 200 mm and a width of 50 mm.

4.3. Methods

4.3.1. Sample Formulations

Asphalt modification were performed using rubber-asphalt (CRM-Asphalt) and textile fibers-asphalt (TFM-Asphalt) modifiers, which were prepared by the extrusion process of mixture containing asphalt and crumb rubber or textile fibers. In the process of obtaining the CRM-Asphalt modifiers in the first stage 10 wt % asphalt was added to 90 wt% CR and heated at 140°C, while mixed mechanically to ensure complete wetting of the rubber grains by asphalt. Then, the mixture was cooled to room temperature for 3 hours. Next, CRM-Asphalt mixture was extruded at 180 °C by using laboratory single-screw extruder from Brabender (model GMF 106/2). In a similar way, the extruded TFM-asphalt mixtures were obtained by addition of 10 wt% virgin asphalt to 90 wt% of textile fiber (TF) at 140 °C, then cooled to room temperature for 3hr. Then, the amount of TFM-Asphalt mixture was extruded at 180°C.

The preparation of composite materials of CR:LDPE, CR:TF and CR:LDPE:TF were also performed by extrusion at weight fractions of 3:1, 2:1, 1.5:1 and 1:1 for both of CR:LDPE, CR:TF, while the third composite material of CR:LDPE:TF was obtained at a weight fraction of 3:0.5:0.5. Once again, it must be born in mind that all nine samples were used as asphalt modifiers and prepared by the same steps as mentioned above (addition of 10 wt% virgin asphalt to 90 wt% of each modifier, and similarly, they were mixed and heated at the same conditions mentioned above). The composite materials were mechanically milled to obtain a form of a granulate.

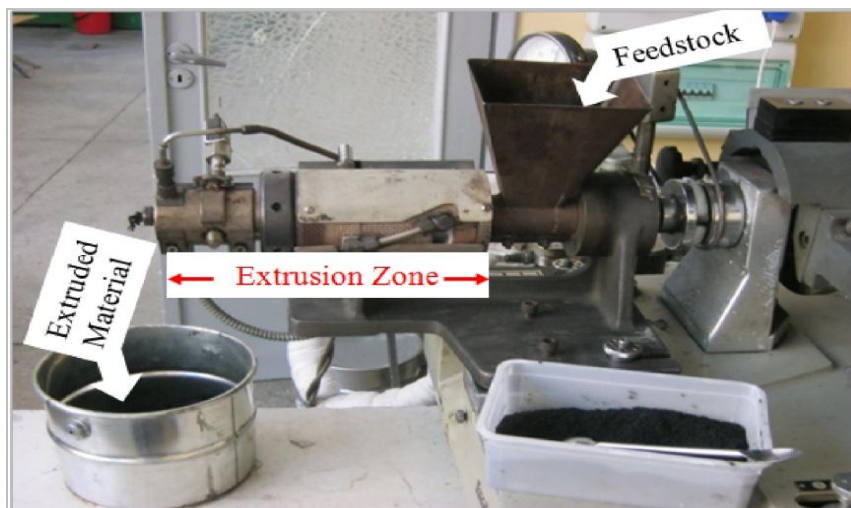


Fig 4.3: Single screw extruder used for obtaining of used modifiers[Researcher camera]



4.3.2. Preparation of Asphalt Binders (Binary, Ternary, and Quaternary)

Table 4.3-A: Modifiers and their codes and contents involved in asphalt binder blending for singular modifiers

Blends No.	Polymer content (wt%)	Blends No.	Polymer content (wt%)
Virgin	0.0 %	B3	10 % LDPE
A1	3 % CR	B4	15 % LDPE
A2	5 % CR	C1	3 % TF
A3	10 % CR	C2	5 % TF
A4	15 % CR	C3	10 % TF
B1	3 % LDPE	C4	15 % TF
B2	5 % LDPE	---	---

Table 4.3-B: Modifiers and their codes, contents, and ratios involved in asphalt binder blending for admixture modifiers

Admixture composites					
Blends No.	Polymer content (wt%)	Weight fraction	Blends No.	Polymer content (wt%)	Weight fraction
D1	3 % (CR:LDPE)	3:1	F3	10 % (CR:TF)	3:1
D2	5 % (CR:LDPE)	3:1	F4	15 % (CR:TF)	3:1
D3	10 % (CR:LDPE)	3:1	G1	3 % (CR:TF)	2:1
D4	15% (CR:LDPE)	3:1	G2	5 % (CR:TF)	2:1
E1	3 % (CR:LDPE)	2:1	G3	10 % (CR:TF)	2:1
E2	5 % (CR:LDPE)	2:1	G4	15 % (CR:TF)	2:1
E3	10 %(CR:LDPE)	2:1	H1	3 %(CR:LDPE:TF)	3:0.5:0.5
E4	15 %(CR:LDPE)	2:1	H2	5 % (CR:LDPE:TF)	3:0.5:0.5
F1	3 % (CR:TF)	3:1	H3	10 %(CR:LDPE:TF)	3:0.5:0.5
F2	5 % (CR:TF)	3:1	H4	15 %(CR:LDPE:TF)	3:0.5:0.5

In this part of the study, the above-prepared extruded samples were used as raw materials for the modification of asphalt binder. Generally, the blending procedures were performed in an open batch reactor using a homogenizer (IKA, Germany), in two approaches. The first modified asphalt binder was prepared by the addition of a singular CR, TF, and LDPE in each run at percentage ratios of 3% – 15% by weight to the asphalt binder; it was called a binary type of blend since it contained only one modifier and the



asphalt binder. In contrast, the other approach was carried out by blending multiple additives once in the form of CR:LDPE and another time in the form of CR:TF. In either of these cases, the whole blend was called a ternary type of blend since it contained two modifiers at once along with the asphalt binder. Finally, the multiple additives added to the asphalt binder could also be in the form of CR:LDPE:TF and in this case it was identified as a quaternary blend; it contained the three modifiers at once as a composite material along with the asphalt binder. Table 4.3-a and Table 4.3-b represented the modifiers and their codes from A1 to H4, content, and ratios involved in asphalt binder blending in this study.

In the case of a binary polymer modified asphalt binder which was briefly labeled (**bPM-AB**), the preparation steps started with keeping the virgin asphalt in an oven at about 180°C for 1hr. Next, only 500 g of the asphalt was added to the reactor at 180 ± 2 °C with an initial mixing speed of 1500 rpm, followed by the addition of only one of the three modifiers CR, LDPE, and TF, separately at percentage ratios of 3, 5, 10, and 15% by weight of asphalt. Only then is the mixing speed of 3000 rpm applied for another 60 min. Again, for the sake of simplicity, and to make the repetitive and enormous different samples more comprehensible, each sample with a different modifier weight fraction within one type of modified-asphalt binder was assigned a code. For instance, starting with CRM-asphalt binder and a ratio of 3.0% wt of asphalt, it was denoted A1. Likewise, this was applied for the LDPEM-asphalt binder and as well as for the TFM-asphalt binder, which were assigned B and C, respectively.

In the case of ternary polymer modified-asphalt binders (**tPM-AB**), the extruded runs of CR:LDPE at weight fractions of 3:1 and 2:1 were added to the melt virgin asphalt at 180 ± 2 °C and 3000 rpm for 1 h to produce eight modified samples assigned the following letters D1, D2, D3, and D4; E1, E2, E3, and E4, respectively.

Similarly, the runs of extruded CR:TF at weight fractions of 3:1 and 2:1 were added to the melt virgin asphalt at 180 ± 2 °C and 3000 rpm for 1 h to produce eight modified samples. However, these eight samples were assigned the following letters: F1, F2, F3, and F4; G1, G2, G3, and G4, respectively. Finally, the quaternary polymer modified asphalt binders (**qPM-AB**) implied the extruded samples of CR:LDPE:TF at a weight fraction of 3:0.5:0.5 to be added to the melt asphalt at 180 ± 2 °C and 3000 rpm

for 1 hr to produce the last four modified asphalt samples assigned the following letters H1, H2, H3, and H4. Figures 4.4 and 4.5 represent the experimental procedure used in this study and the binary, ternary, quaternary system respectively.

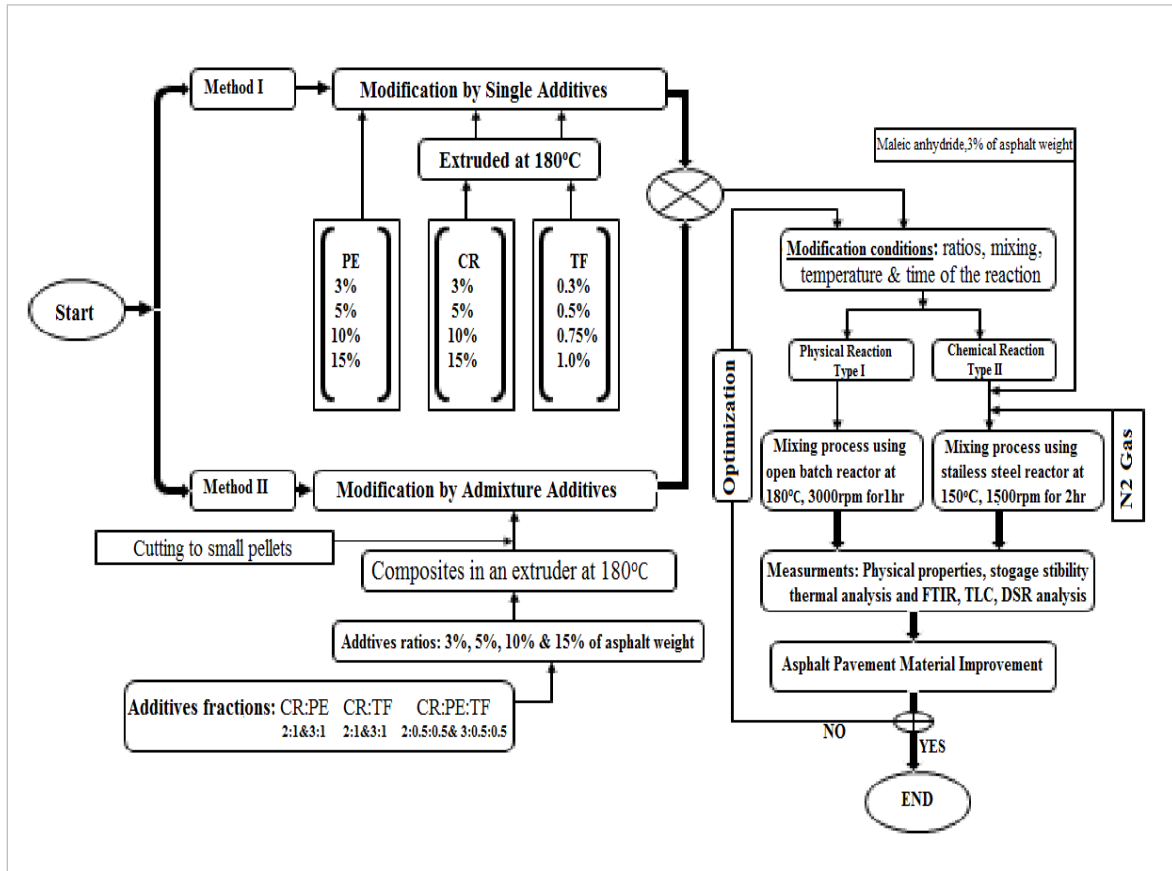


Fig. 4.4: Procedure flowchart involved in this study

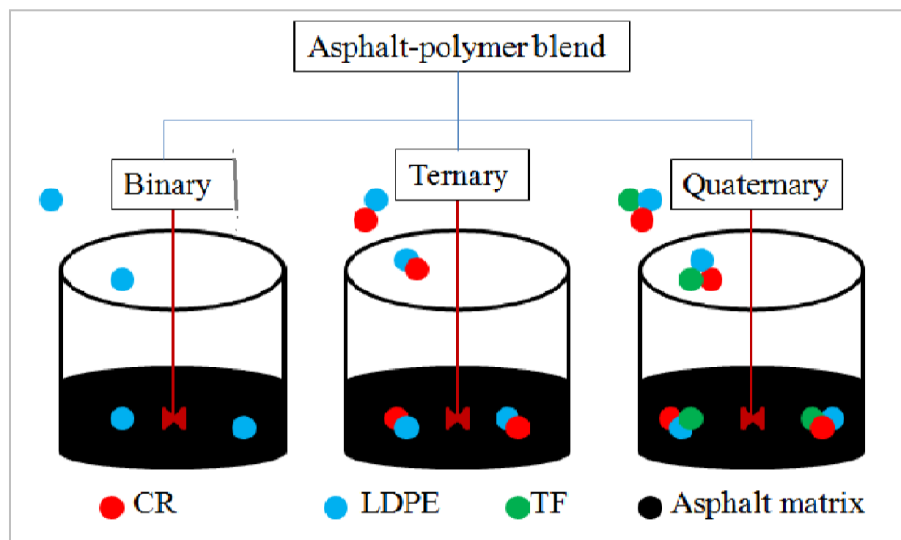


Fig. 4.5: Asphalt-polymer blends system

4.3.3. Preparation of Maleated Modifiers—Asphalt System

The process of maleated asphalt preparation was carried out in a wide-mouthed glass flask fitted with a mechanical stirrer, a reflux condenser (warm water refluxing, 75–80°C), N₂ cylinder for N₂ gas purge, and a thermocouple as shown in Figure 4.5. First, the reactor loaded with asphalt was heated at 180 °C while N₂ gas was purged for the whole process. MAH was added into the reactor (3 : 100, wt.) at a lower temperature. The whole mixture was stirred for 30 min keeping the temperature at 120 °C to carry out the maleation reaction of asphalt. Then, 10% sample of each composited admixture additive, single pure CR as well, and 5% of both singular additives of LDPE and TF (best content level with the best results selected from first part of the study) was poured into the reactor and temperature was raised to 180 °C subsequently for 1 hr. Finally, the end product of each blend was designated as component I (for CRM-asphalt + MAH), J (for LDPEM-asphalt + MAH), K (for TFM-asphalt + MAH), L (for (CR:LDPE)M-asphalt + MAH) M (for (CR:TF)M-asphalt + MAH), and N for ((CR:LDPE:TF)M-asphalt + MAH) to be compared with their non-maleated relevant M-asphalt samples and also with the virgin asphalt sample.

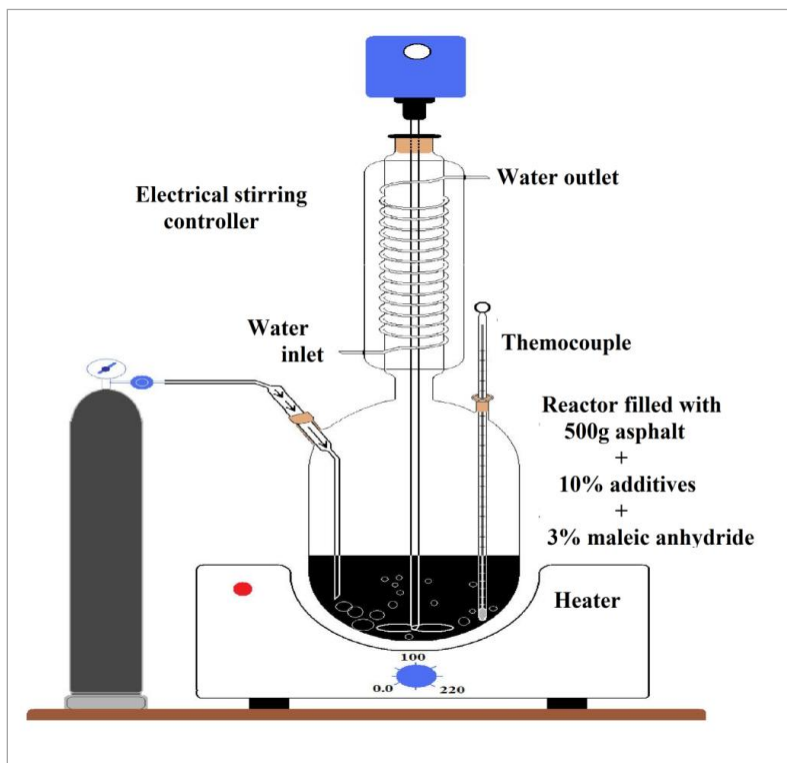


Fig. 4.6: Set up involved in sample preparation of mealated asphalt

CHAPTER FIVE

5. RESULTS AND DISCUSSION

5.1. Characteristics of Materials

5.1.1. Elemental Analysis of Textile Fiber (TF)

Table 5.1 lists the typical chemical composition of TF obtained from scrap tires by the application of wavelength dispersive X-ray fluorescent spectrometer (WDXRF) for inorganic elements and FLASH 2000 CHNS/O analyzer for CHNO. The chemical analysis of scrap tires has revealed that tire-derived textile is characterized by high zinc content of 0.76%. The high content of such element is probably attributed to the zinc oxide added as an activator in the process of vulcanization; the element is recognized with an environmental impact [266].

Table 5.1: Elemental analysis of tire-derived textile (%)

Elements	Values, wt%	Elements	Values, wt%
C	64.60	Zn	0.76
H	6.60	Fe	0.62
N	4.40	S	0.50
O	17.0	Si	0.27

5.1.2. Scanning Electron Microscope (SEM) of Textile Fiber (TF)

It is well known that natural and synthetic polymeric materials such as cotton, polyester, nylon, polypropylene, among others are involved in the composition of most of the fibrous waste [267].

The use of Scanning Electron Microscope (SEM) showed that textile fiber derived from scrap tires was not a pure textile material; it was a mixture of rubber and textile (Figure 5.1-A). It was believed that TF was still containing a small portion of rubber material and a small portion of steel, thus the characteristics were different from the synthetic textile material, which was usually free of any impurities. As a result, the next step has implied the removal of these CR within TF by simply stroking the TF mechanically, providing almost a clean TF as presented in Figure 5.1-B.

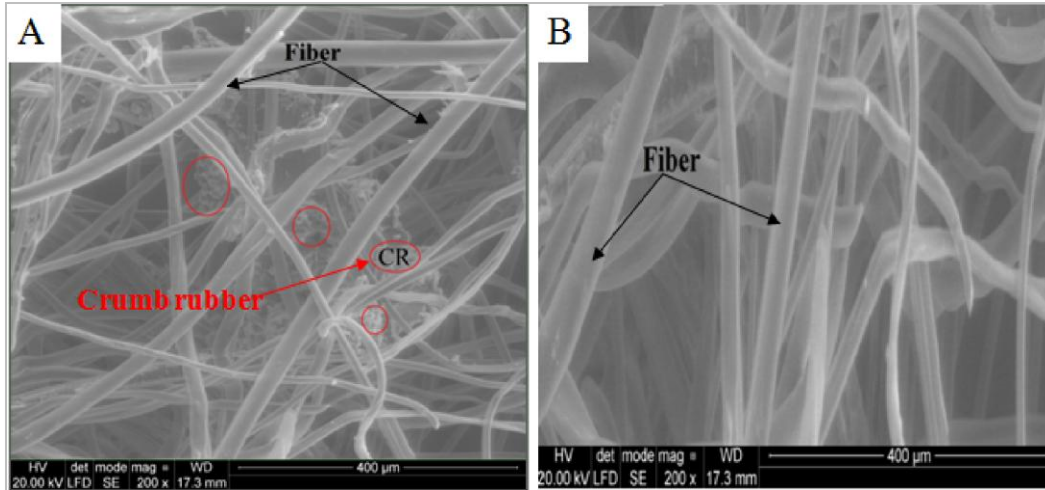


Fig. 5.1: SEM of TF with CR(A) and TF after removal of CR particles (B)

5.1.3. Scanning Electron Microscope (SEM) of CR

Based on particle size, CR are identified as those rubbers having particle size equal to or less than 9.5 mm (3/8 inch) [48]. In accordance to the photo taken by a normal photographic camera (Figure 5.2, A), the CR involved in this study had a particle size of almost 0.8 mm. Morphology of the CR was provided by SEM.

From Figure 5.2-B, SEM analysis presented satisfactory evidence to the granulated CR as they had an irregular and sponge-like surface, which provides considerably a greater surface area for a given size particle. It seems that the process of CR formulation is carried out using ambient grinding. Any increase in surface area increases the reaction rate with hot asphalt [39]. Figure 5.3 shows the composite material of CR and LDPE made by an extruder machine with specifications mentioned in previous chapter. These irregularly shaped composite materials were preserved as asphalt modifiers for future use after being cut into small pieces and then mechanically milled to less size. While, figure 5.3-A, shows the CR after extrusion process.

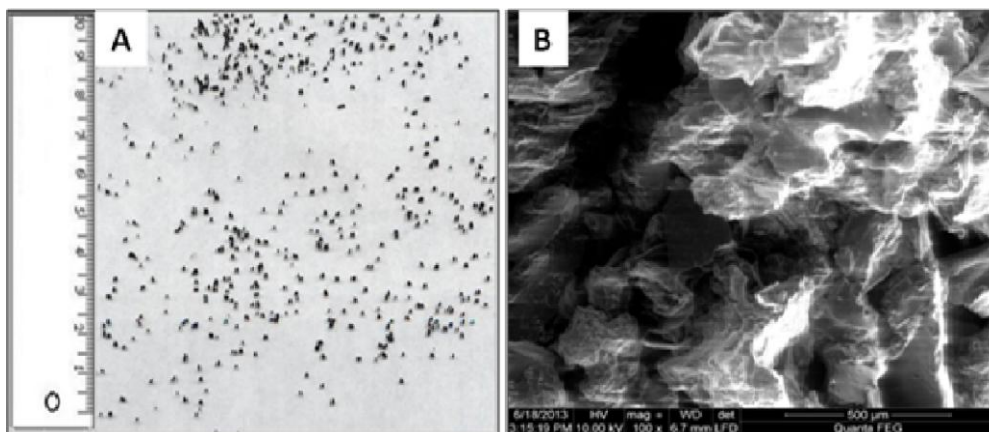


Fig. 5.2: Particles of CR with less than 0.8 mm (A) and SEM of CR (B)

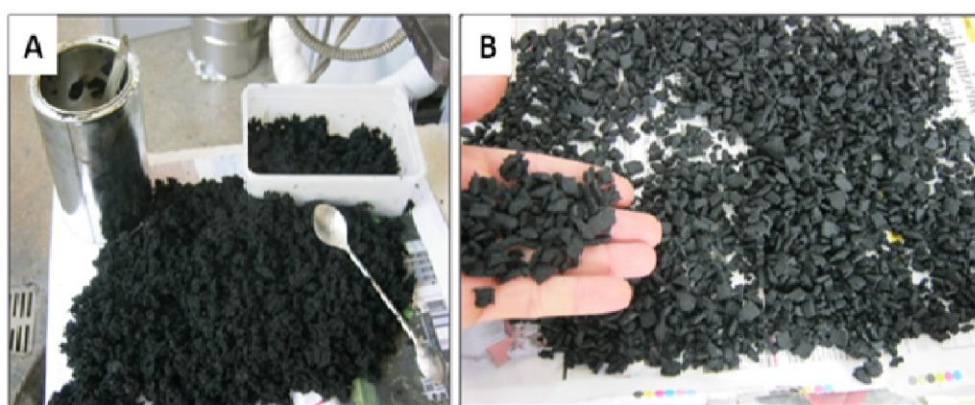


Fig. 5.3: Extruded materials of CR (A) and CR:LDPE (B)

5.1.4. FTIR of Raw Materials Used in the Study

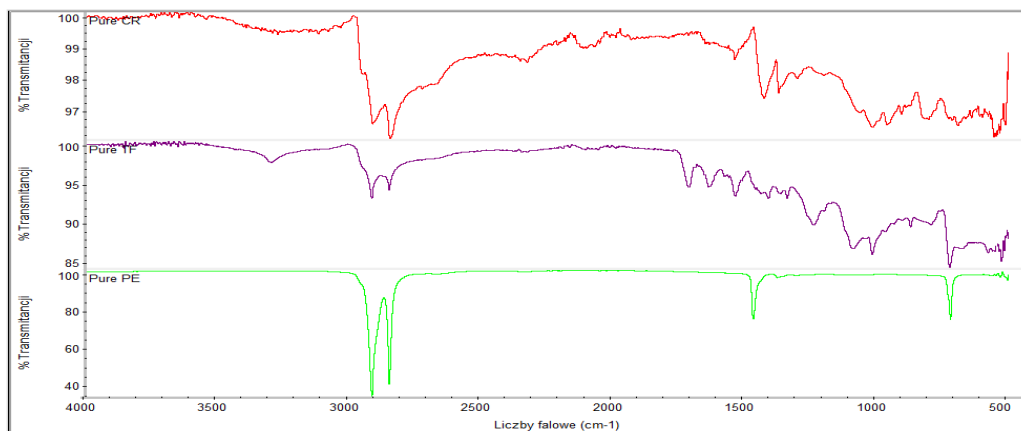


Fig. 5.4: FTIR spectra of raw materials used; they were CR, TF and LDPE

FTIR can be used as a means of comparing the starting material of any of the modifiers involved in the study with the final M-asphalt, which may also be compared to the virgin asphalt. As a result, there is a clear picture of whether or not there is a



successful blending. Besides, it can be described as the fingerprint of the final modified asphalt by evaluating the changes in the spectra associated with particular final modified asphalt product with certain frequencies ranges: such as S=O functional group and C-H chemical bond in aromatics signified with a peak at 1020 cm^{-1} ; SO from oxidation at a peak equals to 1108 cm^{-1} ; an easter (R-COOR) functional group with a peak at 1262 cm^{-1} ; C=C in aromatics at 1618 cm^{-1} ; C=O in carbonyl at 1702 cm^{-1} ; and -OH in polymers (i.e R-OH) at 3258 cm^{-1} [25, 268]. Research work was conducted by Negulescu et al. (2006) [269] utilizing FTIR to analyze SBS copolymer modified asphalt cement. In the study, the researchers used FTIR method to gain a relative understanding of oxidation, which is directly related to asphalt binder aging.

Figure 5.4 shows the spectra of all three modifiers CR, LDPE, and TF involved in this study as asphalt binder modifiers. Peaks at 1460 and 1376 cm^{-1} are related to aliphatic $-\text{CH}_2-$ and $-\text{CH}_3-$ in all modifiers. Bands at 1600 cm^{-1} may be associated with C=C of aromatics in TF and CR. A band at 1700 cm^{-1} is associated with C=O of carbonyl in TF. Peaks with shoulders at $2800\text{ cm}^{-1} - 2900\text{ cm}^{-1}$ perhaps are associated with C=O of stretching band in both CR and TF modifiers which are related to SBR for . Finally, broad and semi-broad peaks at $3200-3250\text{ cm}^{-1}$ are attributed to -OH functional groups in polymers; CR and TF are types of polymeric materials. According to the chemical nature of textile fiber, band at 1700 are associated to (C=O) , related to mixture of both PET ester and polyamide because are the main composition, while related to SBR for crumb rubber from car tires which is the main component.

5.1.5. Virgin and Modified Asphalt Samples



Fig. 5.5: Morphological differences between virgin and modified asphalt

The temperature needed for the blending of asphalt binder with polymer modifiers such as crumb rubber is generally between 190°C and 218 °C [46]. The morphology of both virgin asphalt and the M-asphalt binder used in this study are shown in figure 5.5 left and right, respectively.

The above Figure (5.5, left) shows the virgin asphalt type of 70/100 penetration grade with physical properties and chemical constituents listed in Table 4.1 in section 4.1. The virgin asphalt seems a sticky, dark brown and highly viscous liquid or semi-solid. Besides, the virgin asphalt visibly has a smooth surface as compared with the modified one. After blending with the polymer modifier at a certain temperature, the studied final M-asphalt binder visibly seems to change in texture and to be heterogeneous as the swelled particles of the polymer give rough form to the end product (Figure 5.5, right).

5.2. The Effect of Blending Time on Softening Point of Modified Asphalt Binder

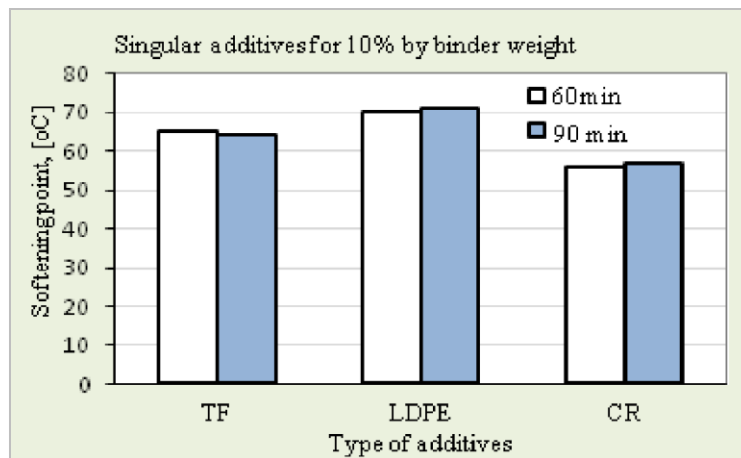


Fig. 5.6: Effect of blending time of singular modifiers on SPT

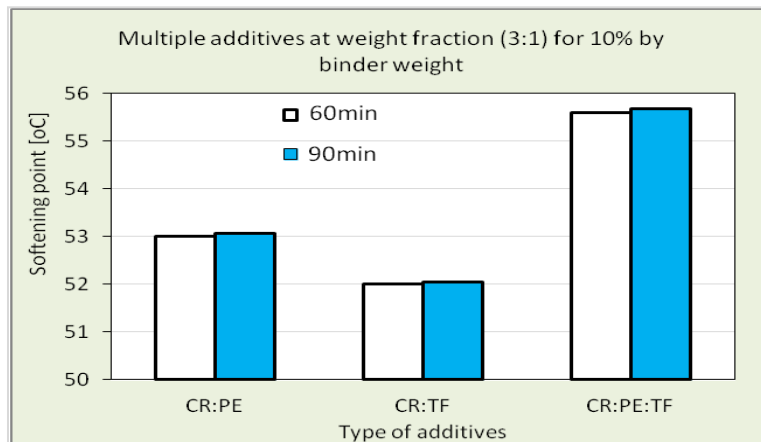


Fig. 5.7: Effect of blending time of pair and tertiary modifiers on SPT

The current study investigated the blending time effect of 60 min and 90 min in the case of singular additives and composite admixture additives on some properties; SPT test was chosen as a typical test for the other physical properties represented by P-Deg and viscosity (Figures 5.6 and 5.7). The obtained results showed that there were no significant differences in the softening point results at the two blending times of 60 min and 90 min; they were illustrated in Figures 5.6 and 5.7, respectively. As a result, it was found that the two studied blending times have no much effect, although, it was thought that due to the unique and delicate interaction process and the number of parameters involved, it was important that the blending process of asphalt with CR be handled with precaution and care; time is one factor that must be considered. Mashaan and Karim (2013) have both confirmed this result when they studied the effect of blending times of 30 min and 60 min on rheological properties of the modified asphalt by CR [58]. Furthermore, there are several investigations showing that the blending time ranging from 15 min to 90 min had no significant effect on the physical and rheological properties of the modified asphalt binder and its virgin type [55, 270, 271]. Soon-Jae Lee et al. (2006) also reported that the longer blending time in the control binder was found to have little effect on an increase in the high-temperature viscosity of the binder tested. The longest blending time, 480 minutes, resulted in an average increase of 6% [272]. Shen and Amirkhani (2005) reported that 15 minutes blending time was adequate to produce good blends incorporating up to 15 percent rubber, and increasing the blending time to 45 minutes would not have any adverse effect on the blended properties. This can be represented by the relatively consistent high temperature test results at different blending times [180]. Similar results have also been shown by other authors. In an experimental study, Mashaan et al. (2011) found that the blending time has an insignificant effect in case of 30 and 60 min on rheological properties of rubberized asphalt [57]. Paulo and Jorge (2008) also investigated the effect of blending conditions (temperature and time) on penetration, softening point and resilience modulus tests. Results of that study showed that there was no significant effect for three blending times 45, 60 and 90 min on modified binder properties, although, there was a tendency for blending time effect to become constant between 60 and 90 min [236].

5.3. Basic Physical Properties of Modified Asphalt Binders

The traditional empirical tests that are used to characterize asphalt are conducted at different regions of the temperature response of asphalt are Fraass breaking point (brittleness range), penetration (semi-solid range), softening point (beginning of fluidity range, and viscosity (fluidity range) [25]. The penetration grade of asphalt are traditionally specified by the consistency tests of penetration and softening point [25].

In this study, the effects of extruded crumb rubber (CR) and textile fiber (TF), and commercial low-density polyethylene (LDPE) as singular additives and composite admixture additives on basic physical properties of asphalt mixture include modification index (MI), softening point temperature (SPT), penetration degree (P-Deg) , and viscosity test, where established and very satisfying data were obtained.

5.3.1. Modification Indices for Softening Point and Penetration

The modification indices for SPT and P-Deg for asphalt modification were determined using Equation (5-1)[25], and are presented in Figures (5.8 to 5.11). The data obtained in these figures are simply intended to describe the quality of modifications and to improve the understanding of the modification process in terms of an index, rather than to present a relationship between modification versus polymer content relationship, but merely [25]. A similar phenomenon was recorded with modification index for penetration degree values.

$$\text{Modification Index (MI)} = P_{\text{modified}} / P_{\text{virgin}} \dots \dots \dots (5-1)$$

Where: P_{modified} = Physical properties such as SPT and P-Deg

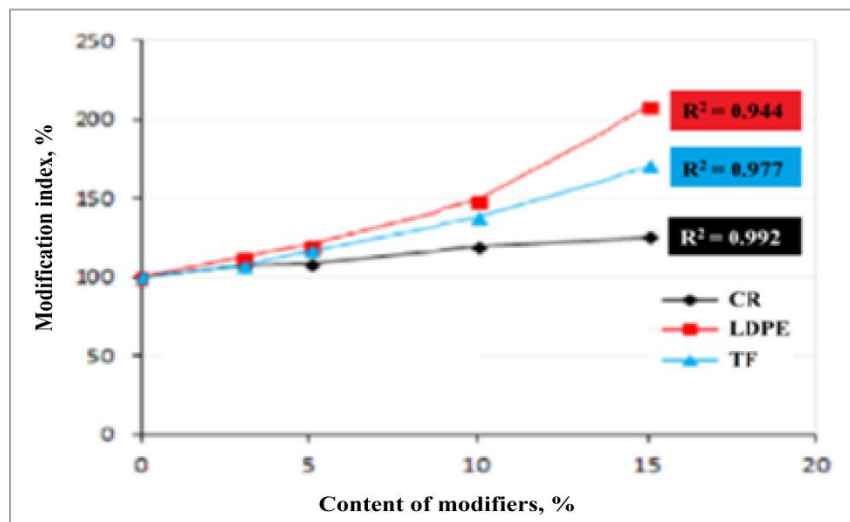


Fig. 5.8: Modification indices for SPT of final modified asphalt binder

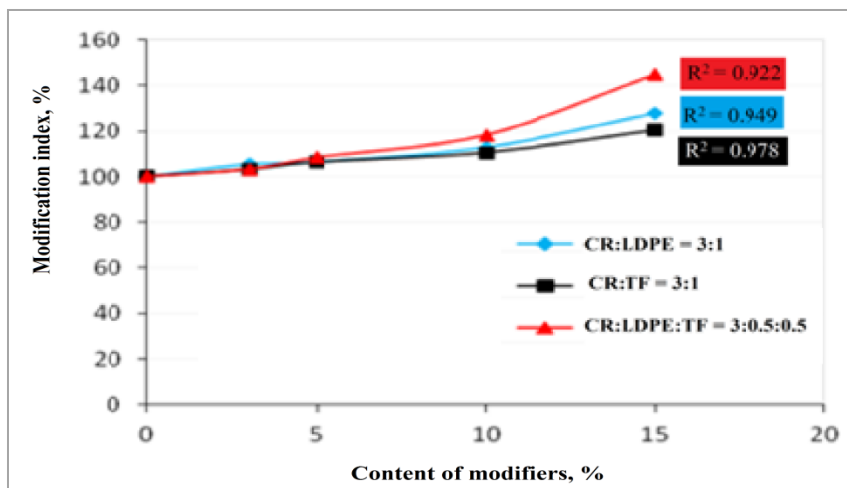


Fig. 5.9: Modification indices for SPT for modified asphalt binder

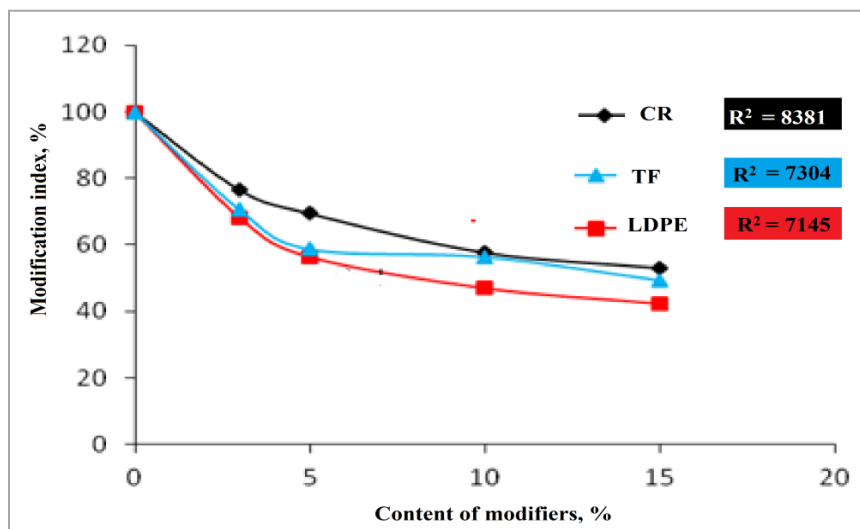


Fig. 5.10: Modification indices for P-Deg of modified asphalt binder

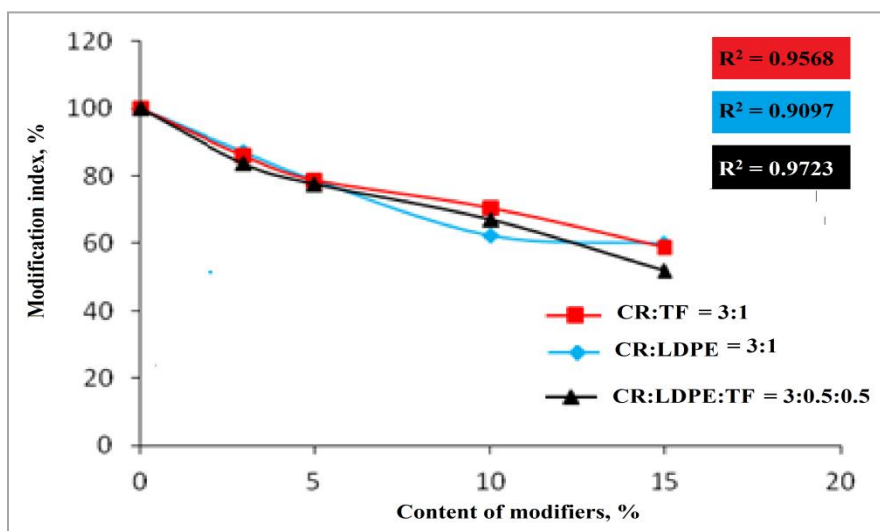


Fig. 5.11: Modification indices for penetration of modified asphalt binder

Considering the three different modifiers of CR, LDPE, and TF, the CRM-asphalt and TFM-asphalt showed relatively consistent increases in SPT as the modifier contents increased from 3% to 15%. However, for the LDPEM-asphalt, the increase is relatively minor, approximately 120% at the 3% polymer level but showed a sharp increase at 10% content level, being approximately 148%, followed by a slight reduction in the slope of the increase to be approximately 208% at the 15% polymer content level. A similar relationships were also reported in literature [25], by the addition of SBS and EVA at content levels of 3-7% to asphalt mixtures.

5.3.2. Effect of Modifier Type and Its Content Level on Softening Point

Table 5.2: The effect of modifier types and their contents on SPT of the M-asphalt binder

Blends No.	SPT, °C	MI, (%)	Blends No.	SPT, °C	MI, (%)
Control	47.0	100	E1	49.8	106
A1	50.3	107	E2	52.0	111
A2	51.0	109	E3	62.3	133
A3	56.0	119	E4	70.0	149
A4	59.0	126	F1	48.5	103
B1	53.0	113	F2	50.0	106
B2	56.5	120	F3	52.0	111
B3	70.0	149	F4	56.7	121
B4	98.0	209	G1	49.7	106
C1	50.5	107	G2	50.0	106
C2	54.7	116	G3	53.0	113
C3	65.0	138	G4	61.0	130
C4	80.0	170	H1	48.5	103
D1	49.5	105	H2	50.9	108
D2	50.0	106	H3	55.6	118
D3	53.0	113	H4	68.0	145
D4	60.0	128	-----	-----	-----

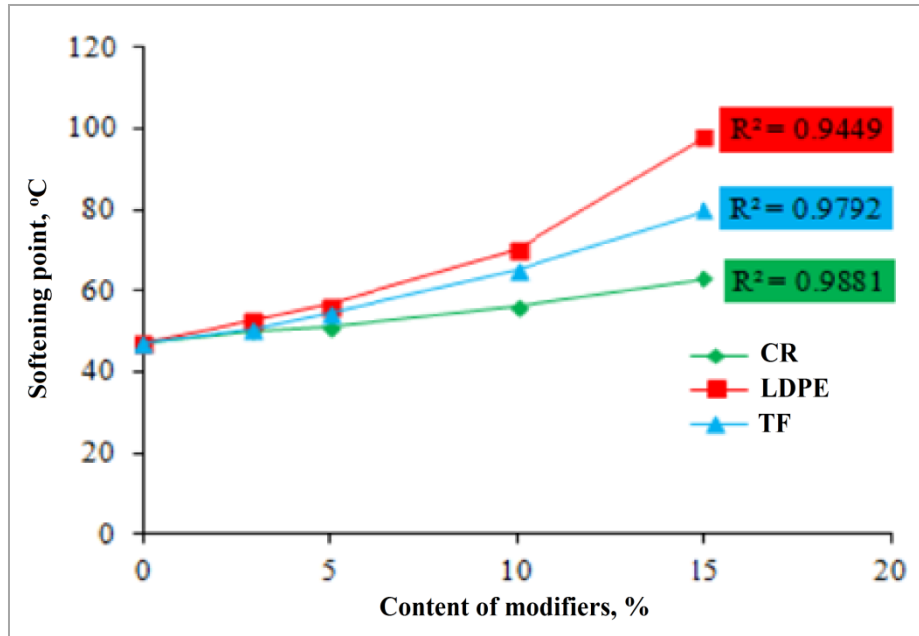


Fig. 5.12-a: Relationships between softening point temperature and contents of singular modifiers of modified asphalt binders

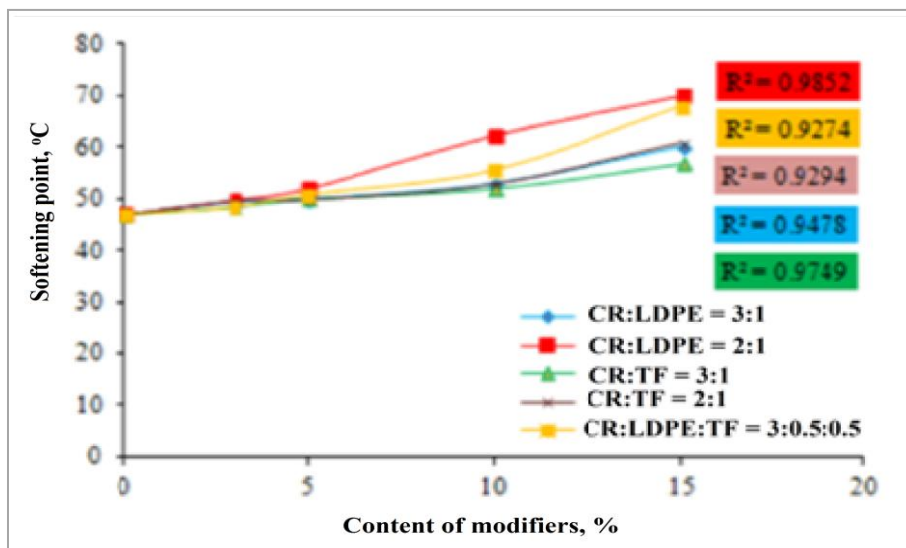


Fig. 5.12-b: Relationships between SPT and contents of pair modifiers of CR:LDPE and CR:TF and of a tertiary modifier of CR:LDPE:TF

The Ring and Ball softening point method is an indicator of the material stiffness and referred to the measurement of temperature at which the substance attains a particular degree of softening under specified condition of the test [273]. Blending of asphalt binder with CR, LDPE, and TF in one approach as singular additives and on another approach as composite admixture pairs of CR:LDPE and CR:TF additives and on a third approach as

an admixture tertiary of CR:LDPE:TF additive at ratios of 3:1, 2:1, and 3.0:0.5:0.5 for each, respectively, in concentrations level of 3.0-15.0% has been carried out. Their effect on SPT has been investigated and the data obtained are represented in Table 5.2.

Figure 5.12-a shows that there are significant differences in SPT for M-asphalt binder by those three singular modifiers at the four studied levels of concentration as compared to virgin asphalt. From evaluating the modification indices (see Equation 5-1 in section 5.3.1) for the singular additives to the asphalt binder, these four levels of concentrations of the three singular modifiers have increased SPT by 107%, 109%, 119%, 126%; 113%, 120%, 149%, >209%, and finally 107%, 116%, 138%, and 170%.

From Figure 5.12, it can be observed also that the least variation in SPT along with consistency for all ratios achieved by CR has been corroborated almost exactly with the results obtained by the Federal Highway Administration [274]. Nuha and her colleagues have reported that the increase in CR content between 4 and 20% in the asphalt was favorable due to its linear increase effect on SPT of the final CRM-asphalt binder. This outcome has been clarified by the fact that CR particle absorption occurred with the lighter fractions oil of the asphalt binder [11]. Generally, it was found that the content of CR was the most important affecting factor as compared to the type and size of the CR which come later [60].

Modified asphalt binder by the addition of CR usually shows, as expected, better results (Figure 5.8) concerning physical properties such as SPT. In addition to the above clarifications, this may also be attributed to the close chemical similarities between CR constituents (i.e. synthetic rubber, natural rubber, carbon black, fillers, and extended types of oils) and asphalt, as both of them are hydrocarbonous materials that provide a high attraction and strong bonding among the constituent molecules of both CR powder and asphalt binder. Besides, the small particle sizes of the rubber powder (< 0.8 mm) and their softnesses are also factors that may contribute to the bonding between both CR and asphalt since it provides a higher surface area as pointed out in some literature [275]. As a result, it is believed that this will afford the final M-asphalt binder resistance to permanent deformation (rutting and cracking), fatigue and temperature resistance [276].

Comparatively, figure 5.12-b illustrated the results of the effects of four composite pair additives and only one composite tertiary additive on SPT of the M-

asphalt. The figure above showed that there were consistent increases in the SPT of the M-asphalt samples by the four level concentrations of all studied modifiers as compared to the virgin asphalt binder. From figure 5.13, it can be seen clearly that the SPT of the M-asphalt binder was increased at a slow rate as the modifier ratio increased from 0.0% to 5.0%. However, an insignificant difference up to the level of concentration of 5.0% was clearly observed among them. At this level of concentration, modification indices of the five modifiers were 106%, 111%, 106%, 106%, and 108% respectively.

Unlike the pair CR:TF modifier in a ratio of 2:1, CR:TF modifier in a ratio of 3:1, and CR:LDPE modifier in a ratio of 3:1, which all had modification indices of 130%, 121%, and 128% at 15% level of concentrations, respectively, the pair CR:LDPE modifier in a ratio of 2:1 and the tertiary CR:LDPE:TF modifier in a ratio of 3:0.5:0.5 have enhanced higher effects on SPT such that the increases were proved sharp and more rapid with modification indices of 149% and 145%. Therefore, it was assumed that those two modifiers may have an adverse effect on the resistance to permanent deformation.

Remarkably, a close relation in terms of their effect on the SPT property of the M-asphalt binder can be observed when adding CR:LDPE in a ratio of 3:1 as shown in Figure 5.13. It seemed that the increase in the amount of CR in the composite pair of CR:LDPE (from 2:1 to 3:1) was responsible for increasing the SPT of the M-asphalt, which was further confirmed when increasing the amount from 1:1 ratio to 1.5:1 ratio at 10% level of concentration. A preceding part of the study implied the use of those ratios (1:1 and 1:1.5) for all composite pair modifiers.

The above can be explained from a different point of view. The rate of STP increased by the addition of CR:LDPE in a ratio of 2:1 was in a higher mode reaching 70.0 °C at 15.0% and a modification index of 149% than the addition of CR:LDPE of a lower amount of LDPE 3:1 which has a modification index of 128%. The lowering in the amount of LDPE was more favorable when the least variation of SPT for CR:LDPE M-asphalt needed to be accomplished. This piece of information was corroborated by [220] when they investigated the rheological properties of M-asphalt by use of LDPE, HDPE, and PP. CR was believed to be more effective in a way that influenced the blending process in two ways. The small particle size of the CR had probably achieved a good dispersion; these particles have a large surface area per unit mass, which also means

asphalt penetration and CR swelling were facilitated. Semi-powder CR was dispersed and dissolved more rapidly than porous pellets [7].



Fig. 5.13: Softening point test

5.3.3. Effect of Modifier Type and its Content Level on the Penetration

Table 5.3: The effect of modifier types and their content on penetration of the binder

Blends No.	PP, dmm	MI,%	Blends No.	PP, dmm	MI, (%)
Control	85	100	E1	70	82
A1	65	76	E2	62	73
A2	59	69	E3	49	58
A3	49	58	E4	45	53
A4	45	53	F1	73	86
B1	58	68	F2	67	79
B2	43	51	F3	60	71
B3	40	47	F4	50	59
B4	36	42	G1	70	82
C1	60	71	G2	66	78
C2	50	59	G3	59	69
C3	48	56	G4	47	55
C4	42	49	H1	71	84
D1	74	87	H2	66	78
D2	67	78	H3	57	67
D3	53	62	H4	44	52
D4	51	60	-----	-----	-----

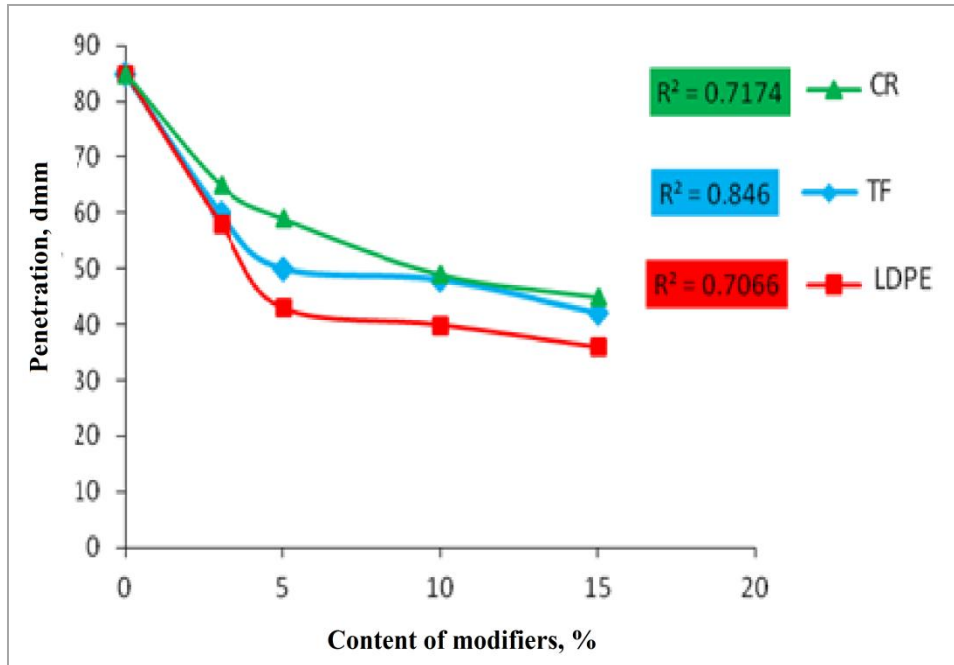


Fig. 5.14-a: Penetration vs. contents of singular modifiers of modified asphalt binders

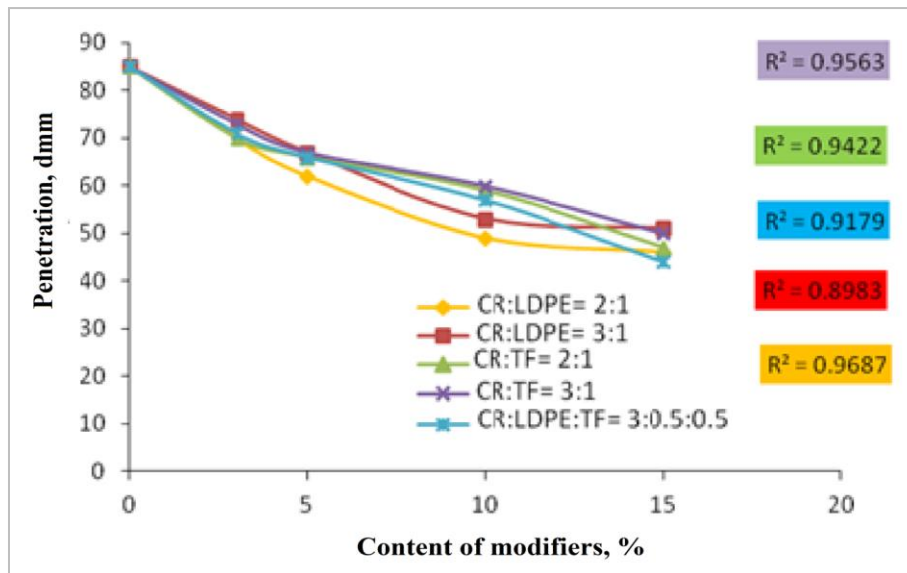


Fig. 5.14-b: Penetration vs. contents of pair modifiers and a tertiary modifying asphalt

The penetration test is considered the most widely used method of measuring the consistency of the asphalt binders at a given temperature. It is a means of classification rather than a measure of quality [220, 277].

Figure 5.14-a shows the effects of CR, LDPE, and TF additions as singular modifiers, while figure 5.15 shows the effects of CR:LDPE and CR:TF additions as composite admixture pair modifiers in both the ratios mentioned along with the effect of

a composite admixture tertiary CR:LDPE:TF addition on P-Deg as a second basic property of the M-asphalt binder. From both figures 5.14-a and 5.14-b, it can be observed obviously that penetration values decreased continuously and sharply from 85 dmm as an initial value of virgin asphalt to 59 dmm, 43 dmm, 50 dmm, 67 dmm, 62 dmm, 67 dmm, and 66 dmm at 5.0% dose of each aforementioned modifier added to the asphalt binder. These values have led to modification indices of 69%, 51%, 59%, 78%, 73%, and finally 78% (Table 5.3). This outcome definitely showed that the hardness of the final M-asphalt was increased. Whiteoak (1990) attributed the cause to the use of the molecular weight of the additive; the higher in molecular weight, the higher in P-Deg decrease. It was obvious from the observation that thermoplastics such as LDPE have more influence on the penetration with the increase in the viscosity of the asphalt [278].

In spite of the findings, considering the least percentages of additives which profoundly achieved an early differentiation in penetration is at less than or equal to 3.0% of all pure singular modifiers of CR, LDPE, and TF (Figure 5.14), at approximately 5.0% for an admixture of both pair modifiers CR:LDPE in a ratio of 3:1 and CR:LDPE in a ratio of 2:1 and, finally, at 5.0% for the tertiary modifier CR:LDPE:TF in a ratio of 3.0:0.5:0.5 (Figure 5.15). This end result was in compliance with the results of another work conducted by Noor and her colleagues (2011) when they investigated SPT and P-Deg in regard to the effect of LDPE, HDPE and PP modifiers additions on virgin asphalts [220]. The authors conclude that the addition of such additives are usually accompanied by the decrease in PP while SPT is usually increased (an inverse relationship).

Next, penetration in all cases considered in this study has continued to decrease almost in equivalent rates until 10.0% additions. However, as the level of concentrations of additives were further increased >10%, one could obviously observe a semi-sharp decline in a higher rate of penetration with the addition of CR:LDPE pair modifier in a ratio of 2:1, leading to a final modification index of 53%. A steady decrease in a slower rate of penetration was dominant at the addition of CR:LDPE pair modifier in a ratio of 3:1, providing a modification index of 50% and making it more favorable. The lower values shown by penetration as CR content increases indicated that the asphalt binder becomes stiff and more viscous [57].

Likewise, it seemed over again that the increase in the amount of LDPE was characterized with stiffness effects in the admixture of pair CR:LDPE modifier from a ratio of 3:1 to 2:1 and would be responsible for the high decrease in P-Deg compared with the flexibility effects of CR. This was conforming with the results of a singular addition of LDPE to the asphalt. In regard to these concentration additions mentioned as best effective on viscosity, penetration continued to decrease from 85 dmm at 0.0% modifier additions almost with consistency and slowly with the same rate up to the addition of 5.0% content of LDPE, TF and 10.0% content of CR, CR:LDPE and CR:LDPE:TF.

In contrast, penetration in all other cases where TF was mixed to form a quadric or a tertiary modified asphalt binder, values of P-Deg continued to decrease almost in higher rates beyond the addition of 10.0% weight, leading to modification index of 52% in respect to the quadric binder and between 50% and 59% in respect to tertiary binder. This indicated that the addition of CR as a singular additive or both CR with LDPE or with TF in any ratio would make the final M-asphalt harder and more consistent. It was reported that such an outcome would be suitable in one way since it improved the M-asphalt against permanent deformation such as rutting. However, it may lead to the production of a stiffer asphalt and thus reduce the resistance to fatigue cracking [276, 279]. This can be evaluated at a later stage of this study by performance tests. The hardening of the M-asphalt was attributed to the fact that since the melting temperature of polyethylene (i.e. LDPE) are below 160°C, at a mixing temperature of 180°C the polyethylene would absorb some oil and release low molecular weight fractions into the asphalt which increases the viscosity of the final modified asphalt [280]. Therefore, at the end of the mixing process, viscosity increases, and by the time final modified asphalt cools, a stiff and hard modified asphalt is formed.

Benefit can be obtained from the hardening of the asphalt because the blending increases the stiffness of the material and thus the load spreading capabilities of the structure but it can also lead to fretting or cracking [272].



Fig.5.15: Penetration measurement device

5.3.4. Effect of Modifier Type and Its Content Level on Viscosity Values

Table 5.4: The effect of modifier types and its content on viscosity

Blends No.	Viscosity(dPa.s)	Blends No.	Viscosity(dPa.s)
Control	0.54	E1	1.3
A1	1.0	E2	4.0
A2	2.0	E3	6.0
A3	5.0	E4	10.0
A4	12.0	F1	1.8
B1	4.0	F2	3.0
B2	5.0	F3	10.0
B3	10.0	F4	12.0
B4	>23	G1	2.0
C1	2.0	G2	4.0
C2	5.0	G3	10.0
C3	7.0	G4	14.0
C4	>17.0	H1	0.98
D1	0.85	H2	3.0
D2	3.0	H3	9.0
D3	6.0	H4	>21
D4	8.0	-----	-----

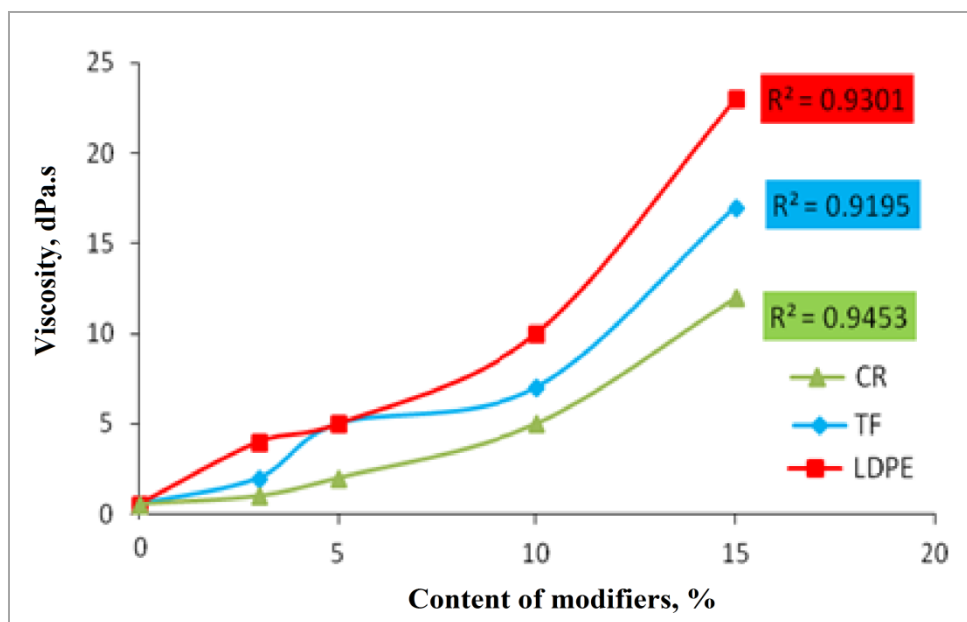


Fig.5.16: Viscosity vs. contents of singular modifiers of modified asphalt binders

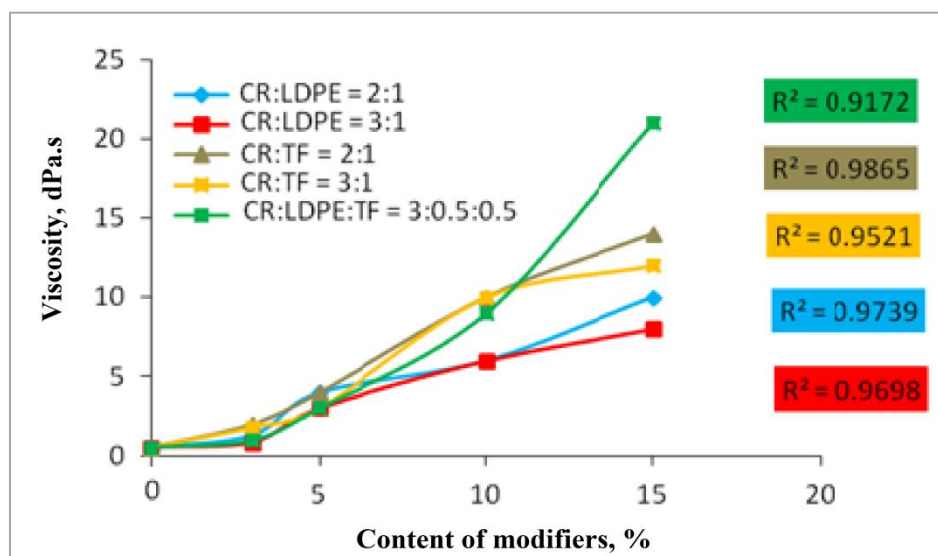


Fig.5.17: Viscosity vs. contents of pair modifiers of modified asphalt binders

The term “viscosity” is a gauge flow resistance of the asphalt and also refers to the fluid property of the asphalt cement. At the application temperature, viscosity greatly influences the potential of the resulting paving mixes [11]. At a low temperature, asphalt exhibits elastic behavior, while at a high temperature, it exhibits a viscous behavior. It is well known that M-asphalt binders are usually more viscous than virgin ones [281]. The

viscosity of the final M-asphalt binder was carried out by using the viscometer with specifications mentioned in chapter three.

Results obtained from testing the effect of singular CR, LDPE, and TF modifiers, composite pair CR:LDPE modifiers in ratios of 3:1 and 2:1 and a tertiary CR:LDPE:TF modifier with various levels of concentrations on viscosity for each of the asphalt blends are listed in Table 5.4.

The results proved that the viscosity of the modified asphalt blend with the singular CR, LDPE, and TF additives and the composite pair CR:LDPE additives and the pair CR:TF additives, in both weight fractions of 2:1 and 3:1 for each, were increased as the content of those additives increased in a higher manner than with the virgin asphalt.

From the graph in Figure 5.16, it can be proved that the singular LDPEM-asphalt and TFM-asphalt binders have shown the most variation in viscosity with 5.0 dPas similarly for both singular modifiers at 5.0% and with 7 dPas and 10 dPas at 10.0% weight of the virgin asphalt, respectively, meeting the findings found elsewhere [56, 57, 217]. Besides, from the graph in Figure 5.16, it can also be observed that the variation in regard to the effect of singular CR and TF additives on the viscosity of the final M-asphalt binder can be considered as the best at the level of concentration 3.0% of additives or less. These values will definitely approve and support the investigated modified asphalt for mix with aggregates [282].

In contrast, the composite pair of CR:LDPE modifier in ratios of 3:1 and 2:1, when blended with the virgin asphalt under the experimental conditions (Figure 5.17), both showed a less variation in viscosity at all concentration levels, especially at 5.0% and less (and as the other modifiers). As the percentage of admixture additives (of both ratios) increased further to 10.0%, they both resulted in an equal viscosity value of 6.0 dPa.s. The subsequent increase in the percentage of both admixture additives to the virgin asphalt has made a clear variation with a lower rate particularly by the pair CR:LDPE modifier in a ratio of 2:1. It appeared that the increase in CR quantity within the admixture additive was perhaps responsible for lowering the viscosity of the final M-asphalt product, implying that the CR was the dominant factor in having the best acceptable viscosity results. This can be well evident and supported by results illustrated in Figure 5.16.

The relation between the singular TF, the composite pair of CR:TF, and the composite tertiary of CR:LDPE:FT additives and the viscosity of the final product of M-asphalt binder was also illustrated in Figures 5.16 and 5.17. From the figures, one can clearly observe that the increase in quantities of any of the studied additives at any studied ratios has increased the viscosity of the M-asphalt binder, which is usually the case as mentioned elsewhere [281]. Concerning the singular TF additive, when it was added at 3% to 15% weight of the virgin asphalt binder, the viscosity value has been increased at a fast rate from 2.0 to 17.0 dPa.s

Nevertheless, the increase in the amount of TF (as a ratio from 1:3 to 1:2) with respect to the CR and its addition in higher percentages of weight of the asphalt binder has increased the viscosity at a higher rate from 2.0 dPa.s and 1.8 dPa.s at 3.0% addition, respectively, to 10.0 dPa.s at 10.0% weight for both. Thereafter, it seemed that the addition at 15.0% weight of them was not significantly effective, that they have raised the viscosity to 14.0 dPa.s and 12.0 dPa.s, respectively. The variations were made clear and observed at 10.0% weight. As result, this would lead to the fact that TF can be named as more responsible for affecting the viscosity values, particularly up to 10.0% addition by weight to the virgin asphalt binder (Table 5.4).

5.3.5. Enhancement Assessments (Confirmation step)

Table 5.5: Additional weight fraction in ratio for the composite materials

Physical Properties	Weight Fractions of Composite Materials at 10% wt.					
	PE:CR 1 : 1	PE :CR 1 : 1.5	TF:CR 1:1	TF:CR 1:1.5	PE:TF:CR 0.5:0.5:1	PE:TF:CR 0.5:0.5:1.5
SPT, °C	65.0	63.0	56.0	54.4	57.0	56.3
P-Deg, dmm	37.0	40.0	56.0	58.0	54.0	55
V, dPas	10.0	6.0	12.0	11.3	11.8	10.4

In an additional step, the experimental study has involved the assessment of studying the effect of low weight fractions of the composite admixtures pair CR:LDPE, CR:TF additives in ratios of one time 1:1 and another time 1.5:1 for each, respectively, and a tertiary CR:LDPE:TF additive in ratios of one time 1:0.5:0.5 and another time

1.5:0.5:0.5 at only 10% level of concentration on the physical properties of the final modified asphalt binder. The physical properties included SPT, P-Deg, and viscosity. The results obtained are listed in Table 5.5.

However, the data obtained of all modifiers mentioned above at their indicated weight fractions proved insignificant effects on the physical properties of the final M-asphalt binder. Therefore, the weight fractions in ratios of all studied composite modifiers (the paired and the tertiary modifiers) were worth improvement to raise to 2:1 and 3:1 instead of 1:1 and 1:1.5 for each pair modifier and to 3.0:0.5:0.5 instead of 1.5:0.5:0.5 and 1.5:0.5:0.5 for the tertiary modifier as have been illustrated throughout the study (preceding and following sections).

5.3.6. Storage Stability Test

Table 5.6: Ring and ball softening point of the storage stability test of final modified asphalt with singular additives

Storage stability							
Blends	Softening point Temp. °C			Blends	Softening point Temp. °C		
	SPT _{Top}	SPT _{Bottom}	Δ T		SPT _{Top}	SPT _{Bottom}	Δ T
A1	46.4	49.6	3.2	B3	98.0	74.0	24.0
A2	48.0	54.0	6.0	C1	50.0	48.3	3.0
A3	49.8	59.8	10.0	C2	52.0	48.0	4.2
B1	74.0	54.0	20.0	C3	55.0	47.0	7.0
B2	80.0	56.4	23.6	-----	----	----	----

Table 5.7: Ring and ball softening point of the storage stability test of final modified asphalt with composite admixture additives

Storage stability							
Blends	Softening point Temp. °C			Blends	Softening point Temp. °C		
	SPT _{Top}	SPT _{Bottom}	Δ T		SPT _{Top}	SPT _{Bottom}	Δ T
D1	47.2	50	1.4	F3	50.0	56.0	6.0
D2	50.0	51.6	3.0	H1	48.6	51.8	3.2
D3	52.0	57.8	5.8	H2	50.5	54.0	3.5
F1	47.6	51.8	4.2	H3	55.4	60.5	5.1
F2	48.0	53.0	5.0	----	----	----	----

It is very fundamental that the M-asphalt binder has satisfactory storage stability when the expensive M-asphalt binder modification unit is not close to the asphalt plant. The storage stability test was conducted according to EN 13399. It is the phase separation that is related to the storage stability of the M-asphalt sample; the difference between the softening point of the top portion and softening point of the bottom portion of the M-asphalt sample should not differ by more than 2°C [186]. The storage stability values of all modified asphalt samples considered in this study were compared with those of the virgin asphalt.

During handling and storage, chemical compatibility relating to a stable homogenous blend is considered very important. The modifier (i.e. polymers) must be chemically stable at the standard asphalt processing temperatures. The definition of compatibility is the ability of a polymer to remain distributed in the asphalt without phase separation occurring. However, the degree of compatibility varies by asphalt and by type and grade of the modifier used in the formulation of the M-asphalt binder. Compatibility also varies with the concentration of the modifier. The higher the concentration of the modifier means the lower the degree of compatibility between the modifier and the asphalt binder. Should total incompatibility occur, this could result in segregation and even gelling [111, 182, 277, 283].

As shown in Table 5.6, significant differences in SPT occurred in asphalt samples modified with LDPE at all studied levels of concentrations of additive (3-10)%. In contrast, CR and TF showed better and more favorable data results in this regard with 3.0–7°C and SPT difference at all additives level of concentrations ($\leq 10\%$). As each singular additive level of concentration increased, the SPT became higher. This has been proved again even when admixture of a composite pair of CR:LDPE and CR:TF additives were involved in a ratio of 3:1 for both at levels of concentration range of 3%–10%. The increase in SPT difference beyond 5°C as shown in Table 5.6 and Table 5.7 would suggest a substantial phase separation between the additive involved in the blend of (i.e. CR, TF, LDPE or CR:LDPE, CR:TF, or even CR: LDPE : TF) modifiers, with the asphalt leading to less storage stability. It was also reported that the poor storage stability of some modified asphalt binders usually results from the poor compatibility between the modifier and the asphalt binder, which is controlled mainly by the modifier's or asphalt's

different properties such as density, molecular weight, polarity and solubility [284]. In the case of the LDPE modifier, the poor storage stability of its final LDPEM-asphalt binder can be attributed to the absence of the intrinsic non-polarity and non-aromaticity nature of the LDPE, which reflects its low solubility with the asphalt binder dispersion medium, which is characterized by polarity and aromaticity nature [277, 283].

From the data in Tables 5.6 and 5.7, it seemed that the presence of CR would enhance suitable physical/chemical interaction between the asphalt binder and the modifier, and its final product as a singular additive was considered to have a better high-temperature storage stability than the LDPE, which is perhaps related to the miscibility of the whole blend. This was also corroborated by the findings of the study and analysis of chemically-grafted PE with maleic anhydride as asphalt modifiers [214]. The idea of utilizing such compatibilizer would be the center of the second part of this study in a subsequent section.

In case of testing the ternary M-asphalt made of CR:TF modifier in a ratio of 3:1 and a quaternary M-asphalt binder made of CR:LDPE:TF in a ratio of 3:0.5:0.5, the differences in SPT between the top and bottom sections of the tube measured according to the rule of isolation degree measurements were very close to the recommended value of 4.0 °C [279] at a level of concentration of 5.0 % weight of the asphalt binder. This would suggest that freshly prepared asphalt binders can be stored at room temperature for a long time and then melted again when pavement of roads needed to be achieved. However, beyond these percentage weights, the differences in SPT between the top and bottom sections of the tube have become larger, reaching 6.0 °C and 5.8 °C respectively, which contrarily would suggest the occurrence of a substantial phase separation between the additive CR:TF or the CR:LDPE:TF and the asphalt binder, leading to less stability in storing. This also highlights the need for an improvement when storage is necessary before paving application.

In some cases, the occurrences of phase separation in the stored final M-asphalt product is due to the differences in solubility parameter and density between the modifier and asphalt binder. Haiying and his colleagues confirmed such a failure when they worked on a modification of asphalt binder using SBS [285]. However, the team succeeded in attaining final M-asphalt binder with good storage stability when they

initially grafted the SBS with meth-acrylic acid by γ -ray irradiation. Then they successfully ran the modification process. Procedure of measurement of storage stability is shown in Figure 5.18.

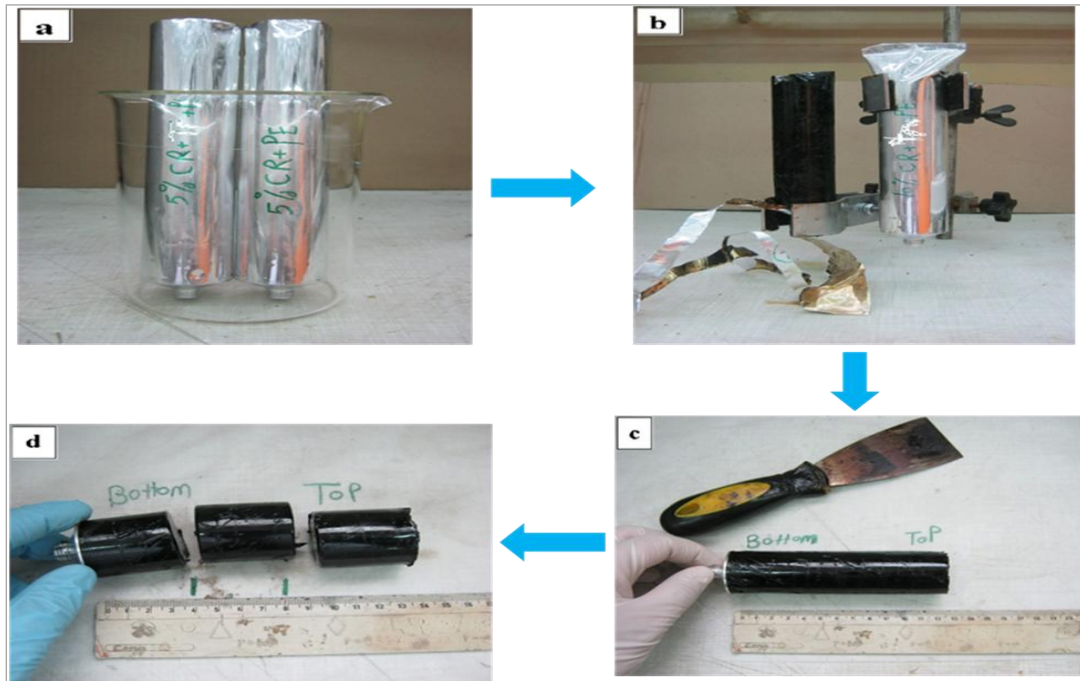


Fig.5.18: Steps involved for storage stability test in this study

5.3.7. Ductility Test

Table 5.8: Ductility as a function of different quantities of singular and composite admixture additives

Blends No.	Ductility (cm)	Blends No.	Ductility (cm)
A1	93.0	D1	95.0
A2	86.0	D2	83.0
A3	50.0	D3	77.0
A4	19.5	D4	25.0
B1	88.0	F1	90.0
B2	30.0	F2	83.0
B3	6.00	F3	75.0
B4	0.01	F4	24.0
C1	80.0	H1	96.0
C2	58.0	H2	80.0
C3	30.0	H3	66.0
C4	10.0	H4	23.0

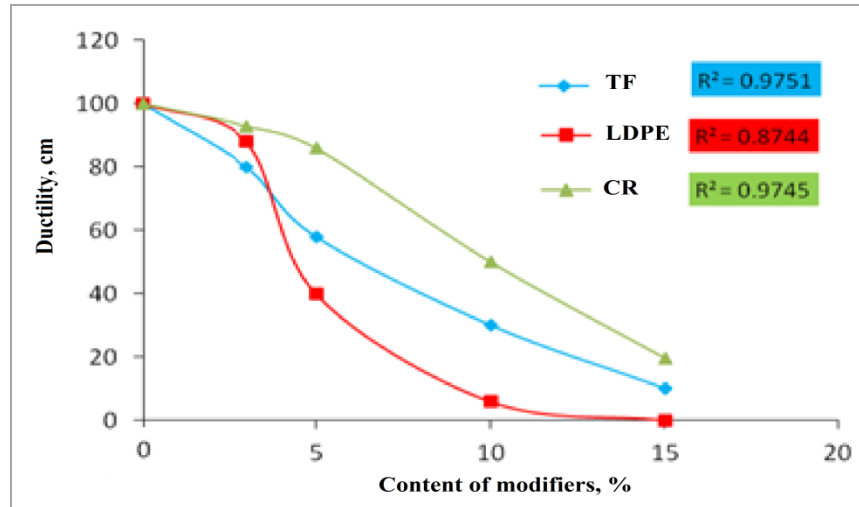


Fig. 5.19: Effect of CR and LDPE, TF contents on ductility of the asphalt binder

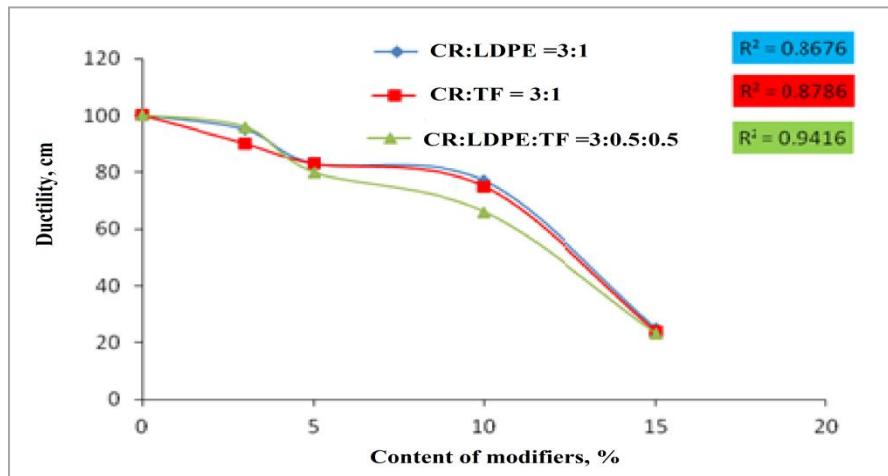


Fig. 5.20: The effect of composite additive contents on ductility of the asphalt binder

Ductility test of the final modified asphalt binder provides a measure of tensile properties of the asphalt materials. It is a measure of a distance to which the examined final M-asphalt binder will elongate before breaking [57]. The ductility results were conducted at 25 °C for different singular CR, LDPE, and TF modifier contents in one occasion as shown in Figure 5.19. Ductility results were also conducted at 25 °C for different pair CR:LDPE and CR:TF modifiers contents at different ratios of 2:1 and 3:1 on another occasion and a tertiary CR:LDPE:TF modifier content at a ratio of 3:0.5:0.5 on a third occasion as shown in Figure (5.20). From Figure 5.19, it can be noticed that ductility of the final M-asphalt binder by any of the singular additives dramatically decreased as the CR, TF, and LDPE contents increased with high correlation factor

coefficient (R^2), which are respectively 0.9754, 0.9751, and 0.8744. According to the obtained results, it can be concluded that CR modification of the final asphalt binder resulted in the highest ductility among the other modifiers, thus leading to the best rutting resistance. CR can be considered most favorable when dealing with modification of asphalt binders for pavement application. This result can corroborate with the study findings obtained by Nuha Mashaan and her coworkers (2011) [55]. They have concluded that finer CR particles resulted in higher ductility elongation and also that toughness would increase as CR content increased. But they stated that the modified asphalt binder was susceptible to decomposition and oxygen absorption. There were problems of low compatibility because of the high molecular weight. Furthermore, from the figure, it appeared that the high content of CR and also TF (from 3% to 15%) was linear and had a constant effect on the M-asphalt binder under elongation tensile force with correlation factors mentioned above. Authors related the explanation of these results to the physical interaction during the blending process.

Nevertheless, TF could have more preference as an asphalt modifier over the other modifier of LDPE. Perhaps, there are significant similarities between TF and CR in terms of chemical structure and classification as thermo-plastics. Fibers are a type of polymers; they seemed like rubbers, known to absorb solvents such as asphalt, in this case, and diffuse into those types of materials causing swelling. TF indicates compatibility with the asphalt solvent and, therefore, enhances cross-linking between components [125].

Based on the results in Table 5.9 and their illustration in Figure 5.20, it can be concluded that all studied composite pair admixtures along with the tertiary one used as asphalt modifiers have provided final M-asphalt product with improved ductility, especially when the percentage weight of the additives were equal or less than 10.0% weight of the asphalt binders. At this percentage weight of $\geq 10.0\%$, the effect of TF seemed to be significant when mixed as a composite to form a pair CR: TF modifier and a tertiary CR:LDPE:TF modifier in a ratio of 3:0.5:0.5, leading to ductility value of approximately up to 75 and 65 cm and correlation factors of 0.8786 and 0.9416 respectively at the studied conditions.

5.3.8. Elastic Recovery Test

Table 5.9: Elastic recovery as a function of different quantities of additives

Blends No.	Elastic Recovery, (%)	Blends No.	Elastic Recovery (%)
A1	10.0	D1	15.0
A2	24.0	D2	30.0
A3	38.0	D3	44.0
A4	75.0	D4	50.0
B1	21.0	F1	16.0
B2	42.0	F2	32.0
B3	51.0	F3	45.0
B4	84.0	F4	52.0
C1	23.0	H1	7.0
C2	38.0	H2	25.0
C3	40.0	H3	48.0
C4	79.0	H4	62.0

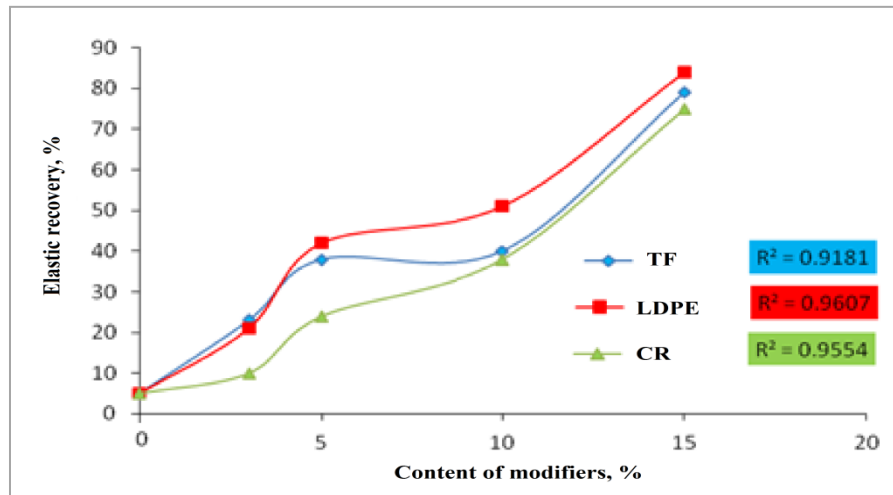


Fig. 5.21: The effect of single additive contents on the ER of the asphalt binder

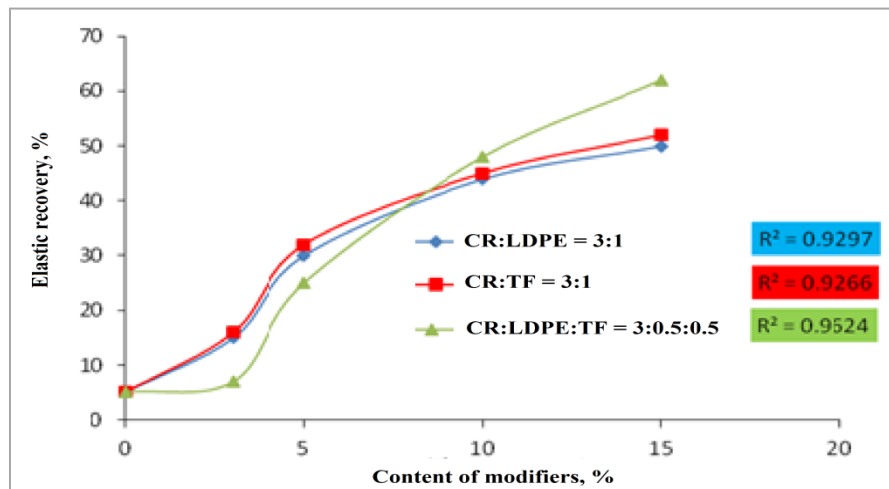


Fig. 5.22: The effect of composite additive contents on the ER of the asphalt binder

The elastic recovery or, as it is sometimes called, “elasticity”, describes the ability of asphalt binder to elongate when the tension is applied and to recover its original shape when the tension is released. In pavement construction material, the indication of permanent deformation is to use the degree of elastic recovery [66]. The property is important in describing the quality of any polymer (i.e. CR, LDPE, TF) involved as a modifier in asphalt binders. It is also important in the selection and evaluation of rutting resistance and fatigue, a conclusion of Jensen and Abdelrahman study [286].

The results of the elastic recovery as a function of different quantities of singular additives CR, LDPE, TF and composite admixture additives CR:LDPE, CR:TF, and CR:LDPE:TF are shown in Table 5.9.

Figure 5.21 has shown the effect of singular, CR, LDPE and TF additives on the elastic recovery at levels of concentrations of the additives (3, 5, 10, and 15wt%). The increase in additive content in the asphalt binder blend at the experimental conditions appeared to have a significant effect on the final product of the M-asphalt binders’ elastic recovery. The elastic recovery of the final product increased from 5.0% to almost 75.0% and 84.0% as the additives of CR and LDPE content increased to 15.0% weight with high R^2 value of 0.9554 and 0.9607, respectively, and to almost 79.0% as the additives of TF content increased from 0.0% weight (virgin asphalt) to 15% weight with a correlation factor of 0.9181. In another study, results showed that the elastic recovery values have increased from 16.38% for virgin asphalt to 94.5% for the 20% CRM-asphalt binder. The penetration degree has decreased as the content level of CR increased up to 20 wt% [57].

Figure 5.22 shows the results of the elastic recovery in percentage versus the content and the type of the composite additives. From the figure, it is found that the content and the type of the composite additives are two main factors that affect the elasticity of the final modified asphalt products. The percentage in elastic recovery increases as the content of the three composite additives increase, reaching 50.0%, 52.0%, and 62.0% with R^2 values of 0.9297, 0.9266, and 0.9624 for CR:LDPE, CR:TF, and CR:LDPE:TF respectively as compared to the initial value of 5.0% elastic recovery of the virgin asphalt. It seemed that when asphalt binder was blended with polymer modifiers, the recovery in elasticity was not expected to be complete, and when the applied stress was removed, the M-asphalt binder lost its ability in attaining its original

position, resulting in permanent deformation to some extent. The quantity and the type of polymers are two factors that may have an influence on the amount of such failure. Nuha and her coworkers (2011) have reported that a significant enhancement on the elastic recovery was demonstrated by the M-asphalt binders. However, the ductility of the same final M-asphalt binder was decreased as compared to the virgin asphalt binder [55, 57].

5.3.9. Fraas Breaking Point Test

Fraass breaking point is defined as the temperature at which a break or a crack appears on the thin layer of asphalt coating the steel plaque. The plaque is subjected to successive flexions under determined cooling conditions [287].

The breaking point was measured for all asphalt modifications at only the best level content of modifiers. It was decreased from -11°C for virgin asphalt to -15°C , -12°C , -12°C for components A3, B2, and C2 respectively. On the other side, it was found that the breaking point was decreased to -14°C for both components D3 and F3, while the breaking point was decreased to -13°C for component H3.

5.3.10. Studies of Swelling Rate of Modifiers in the Liquid Media

The swelling tests were carried out at room temperature in liquid media using pure toluene with the purity of (99.5%). The system was carried out as follows. Four kinds of modifiers were measured for swelling test with an initial amount of exactly 1.0 g of each modifiers. Three separate samples of each kind of modifiers were kept into empty tea bags, then they were soaked in the liquid media using 12 containers glass of 100ml toluene and closed. After a given time, the modifiers were taken off the liquid, following an evaporation process of solvent. The mass of the modifiers was measured during 210 min. The extent of swelling was estimated as the percentage of modifiers mass increment after a set time immersion in the media by the following equation.

$$S-w \% = (W1 - W_2 / W_2) \times 100 \dots\dots\dots (5-2)$$

Where: W1= wet weight of modifiers(g), W2 = raw dry weight (g)



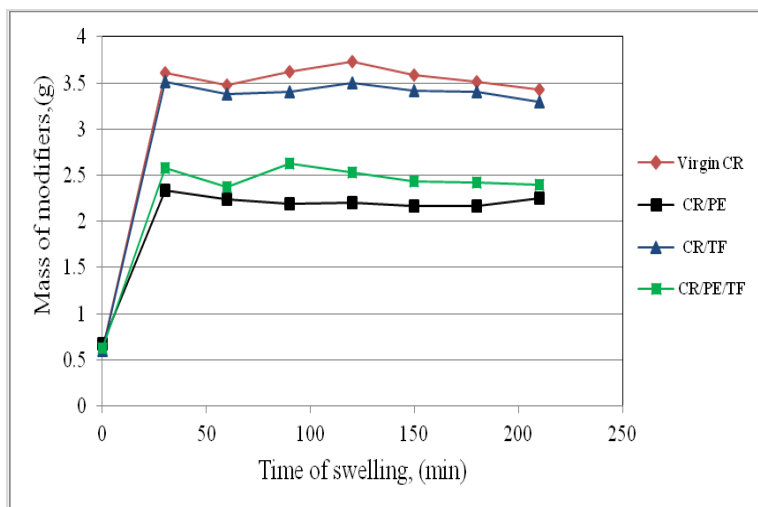


Fig. 5.23. Swelling rate of modifiers in solvent media at room temperature

From Figure 5.23, it can be seen clearly that the rate of modifiers swelling depended principally on the type of modifier (in addition to the rubber properties such as rubber particle size, surface area, and porosity). Equilibrium was established after approximately 100 min for all modifiers considered in this part of the study. The average percentage of the swelling calculated from the above Equation 5-2 are: 489.7 % for CR; 466.7 % for CR:TF; 223.8 % for CR:LDPE; and, finally, 323.6 % for CR:LDPE:TF. After Swelling studies of the modifiers in liquid asphalt media at high temperature are necessary to support this study. Irena and his team have demonstrated that the extent of swelling (the percentage of rubber mass increase) was greater when the rubber content in asphalt was lower. Their findings suggest that it was only those asphalt components occurring comparatively in small amounts that were responsible for CR swelling [178]. Maximum swelling percentage of extrusion CR was found to be 530% which is the highest value.

5.4. Gel Permeation Chromatography Analysis (GPC)

In blends, molecular weight occurs not as a discrete value but as a distribution. This means that to accurately assess the molecular weight distribution of a asphalt-polymer blend it is to estimate how many particles there are at every weight in the distribution. There are two characteristic values are describing the molecular weight distribution as follows [288]: i) the number average molecular weight, abbreviated to M_n , ii) weight average molecular weight (M_w). The value of M_n influences the

thermodynamic properties of the molecule and determined by measuring the molecular weight of N molecules, summing the weights, and dividing the results by N , reading.

$$M_n = \sum_i (N_i M_i) \div \sum_i (N_i) \text{ [g/mol] } \dots\dots (5-3)$$

When: N_i is the number of molecules with a molecular weight M_i . Alternatively, the weight average molecular weight M_w is obtained by multiplying the molecular weight values of each fraction by the respective mass fraction, as following:

$$M_w = \sum_i (m_i M_i) \div \sum_i (m_i) \text{ [g/mol] } \dots\dots(5-4)$$

When: M_i denotes the total weight of molecules with molecular weight M_i .

The M_w value is always greater than the M_n value unless the polymer is completely monodisperse. M_w affects many of the physical properties of polymers, and is the most often quoted molecular weight average. The ratio of M_w to M_n is used to calculate the polydispersity index (PDI). It is an indicator for the width of the molecular weight distribution. E.g., if all molecules of a sample exhibit the same molecular weight, with $M_w = M_n$ the polydispersity index becomes equal to one indicating that only molecules with one length are present [288]. The broader the molecular weight distribution, the larger the PDI [288].

The obtained values for M_w , M_n , and PDI are given in Table 5.10. From the Table, it can be seen clearly that the molecular weight distribution had two maximums to corroborate with Irena and his team's findings [178]. That was evident of the existence of two distinct types of asphalt particle aggregates in the solution [289]. From the molecular weight distribution of sample analysis, it was clear and commonsensical that the modified asphalt is richer in higher molecular weight components than virgin asphalt; there were similar results reported by Gawel and her colleagues [178].

Gawel and her team [178] have found that of the nonpolar components in the asphalt binder, the linear aliphatic chains possess a great tendency towards penetrations into rubber particles, which suggest that these components have good compatibility with the linear polymeric skeleton of CR. This was reasonable to explain the obtained results where 5% CR, followed by 5% CR:LDPE:TF and 5% CR:LDPE, had the highest values. This is explained by the higher molecular mass of the polymer molecules, resulting according to Equation (5-4) in higher M_w values [288].

Table. 5.10: Molecular weight distribution, number average molecular weight and polydispersity index of modified and unmodified asphalt.

Blends No.	M_w	M_n	PDI
Virgin asphalt	1205	430	2.802
A2	2404	559	4.303
B2	1823	527	3.461
C2	1695	551	3.078
D2	1984	573	3.460
F2	1665	528	3.155
H2	2088	570	3.664

5.5. Tine Layer Chromatography-flame Ionization Detection: TLC-IDF

5.5.1. Asphalt Fractional Composition

In this study, the obtained data in Table 5.11 illustrate the TLC analysis of both virgin asphalt and the modified asphalt binders at the best content level of additives for different modifications. One of the main key factors that influence the properties of asphalt-additive interactions is the asphalt chemical components [178].

Table 5.11: Components of modified and virgin asphalt binders

Blend sample	Components (wt%)				
	Saturates	Aromatics	Resins	Asphaltenes	As-/Res
Control	6.8	64.2	16.2	12.7	0.784
A3	6.4	62.3	14.0	17.3	1.23
B2	6.1	62.5	13.4	18.0	1.34
C2	5.2	60.7	14.4	19.3	1.34
D3	6.2	63.1	13.2	18.5	1.40
F3	6.1	63.8	12.7	17.5	1.38
H3	4.2	58.2	14.8	22.7	1.53

In Table 5.11, results of the final M-asphalt binders with the studied additives have indicated that saturates, a component with small a molecular weight, were decreased in concentration. This can be explained on the basis that saturates can easily be absorbed by i.e TFs (exist in the form of a single or composite additive) due to the function of surface physical absorption.

Resins, as naturally polar components, provide the asphalt binder with adhesive properties and ductility; they also act as dispersing agents for the asphaltenes [25, 278,

290]. However, the differing percentages between asphaltenes and maltenes fraction (Resins, saturates, aromatics) determines the viscous-elastic properties of M-asphalt binder [291, 292]. The complexity, content of heteroatom, aromatic, and increase of molecular weight are in the order of sat. < Arom. < Res. < Aasphs. [4, 14, 293]. An increase in one of these constitutions would change the structure and rheological behavior of the asphalt binder. According to the results in Table 5.11, it can be clearly noticed that the asphaltene concentrations increased when all tabulated additives were used as an asphalt modifier. However, the ratio of Asphs/Res was high in all tabulated additives. These results corroborate with the findings of Loeber and his assistants [18], who concluded in their report that asphalt with high Asphs/Res ratio led to a modified binder with more rigidity and elasticity (low in phase angle and high in complex shear modulus). This is unlike the case of asphalt with high Res/Asphs ratio, which has led to high viscous behavior, higher SPT, and lower penetration value.

Resins are polar molecules that act as peptizing agents to prevent asphaltenes molecules from coagulating, which may happen if the quantity of resin is sufficiently aromatic with adequate solvating power. This is known as a “sol-type” asphalt. However, if the quantity of resins is insufficient and less aromatic, the asphaltenes will be less mobile and become clustered. This can create internal voids which are filled with other constitutions. This is called “gel-type” asphalt. The lightest molecular weight materials are the nonpolar oils “Aromatics”. Oils generally have a high proportion of chains as compared to the number of rings. Resins and oils are referred to collectively as maltenes.

This state of dispersion of the entire system has a direct influence on the viscosity of the asphalt cement and thus the rheological performance (rutting and cracking resistance). The viscosity of saturates, aromatics and resins depend on their molecular weight distribution. Viscosity increases as the molecular weight of the maltenes increases. As the saturate fraction increases, it decreases the solvating power of the maltene fraction, as saturates are generally known to facilitate the precipitation of asphaltenes.

A simple way to increase the asphalt cement high temperature performance grade is through the formation of a partial or complete gel structure. A gel is defined as a material with an infinite zero or low shear viscosity and a stiffness approaching zero. Gels display

significant elasticity, delayed elasticity and non-linear visco-elastic behavior [294]. Before the beam exposure of a bitumen film, the surface appears to be flat and featureless. However, after the film has been exposed, a network entanglement of strands is visible. It is hypothesized that the electron beam volatilizes the low molecular weight oils in the asphalt by localized heating and thereby reveals the asphaltenes and resins after the upper surface layer of oil has been removed [293], as presented in figure(5.24)

In general, asphaltenes produce the bulk of the asphalt while resins contribute to adhesion and ductility and oils influence flow and viscosity properties [295]. According to the microstructure and the colloidal system, asphaltenes are diffused into an oily matrix of maltenes, encased by a shell of resins whereby its thickness varies with the temperature that is being tested [296]. Thus, asphalt composition and temperatures are strongly dependent on the mechanical properties, the microstructure of asphalt, the degree of aromatisation of the maltenes and the concentration of asphaltenes [296, 297].

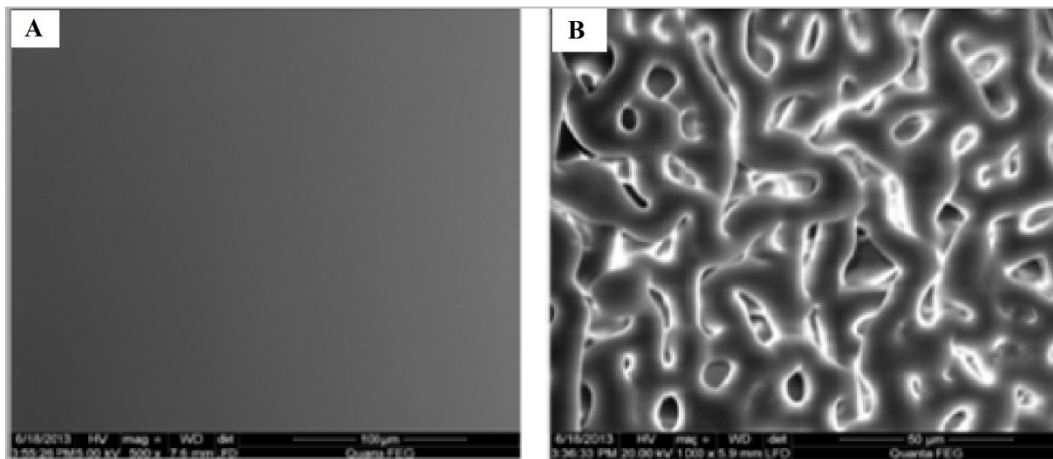


Fig.5.24. SEM: Image of the virgin asphalt before beam exposure (A) and after longer beam exposure.

5.6. Thermal Analysis (TGA)

Thermal stability of the M-asphalt binder is examined on the basis of percentage weight loss at different temperatures from TGA thermo-gram and compared to that of virgin asphalt. The thermo-gravimetric curves of the final binary asphalt binder and ternary and quaternary asphalt binders at the best level of concentrations are shown in Figure 5.26 (a) and Figure 5.26 (b), respectively. From both figures, it can be seen that the decomposition of all samples has similar trends. There were no weight loss

percentages for all samples until a temperature of 320°C. However, there was a sharp weight loss percentage only around 380°C, which then reached completion at a temperature of approximately 475°C. The residue weight of about 7% of the total weight of the virgin asphalt sample is recorded at 500°C. Whereas, the residue weight, which remained at the temperature of 500°C for the modified asphalt, was little higher; it was recorded at a range of 7.62% - 20% depends on the modifier's type.

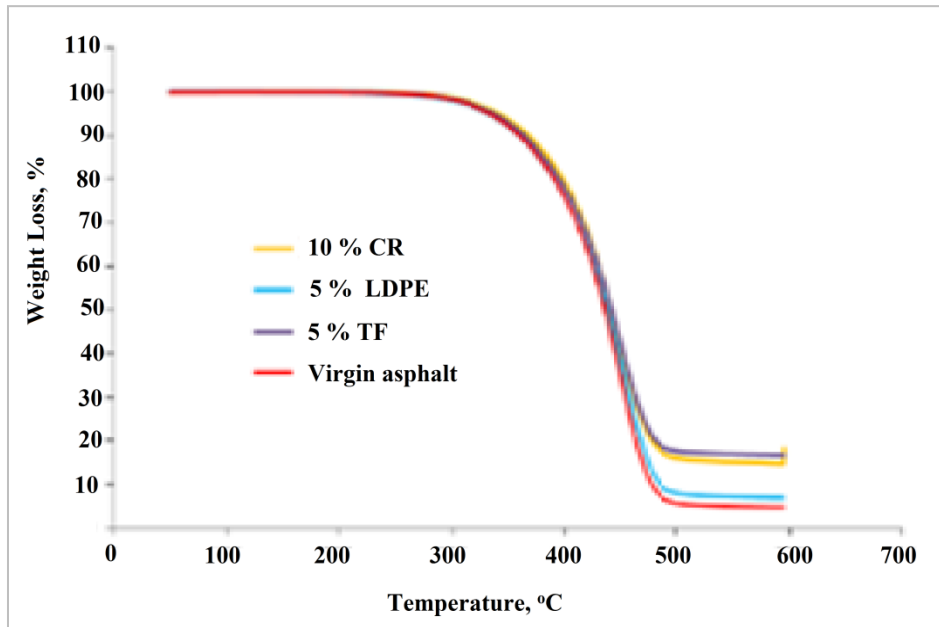


Fig. 5.25: TGA-analysis of modified asphalt by singular modifiers

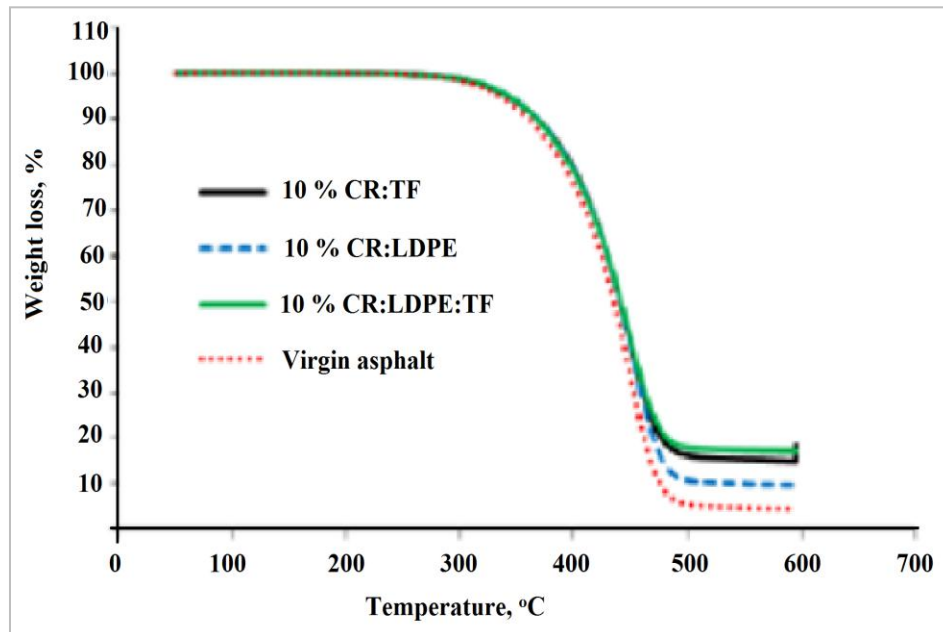


Fig. 5.26: TGA-analysis of modified asphalt by admixture modifiers

5.7. Rheological Characterization

Rheology is a very powerful tool for characterizing and quantifying asphalt binders' properties. It has been well established that the rheological properties of asphalt binder affect the pavement performance [298]. Dynamic visco-elastic properties also referred generally to the responses of a material to periodically varying strains or stresses [299].

In this study, the rheological properties of the different final M-asphalt binders with singular additives of CR, LDPE, and TF composite pairs of CR:LDPE and CR:TF additives and finally with a composite tertiary of CR:LDPE:TF additive at a concentration level of 10% weight of the asphalt binder was studied and the results were presented in the Figures 5.27 and 5.28. The concentration level of 10% has led to the best results concerning the basic properties and was thus further investigated for the study of rheological properties of the final M-asphalt binder. The measure of G' , G'' and $\tan \delta$ were conducted at a temperature range from 30 to 100°C for all intended modifiers. However, the G^* and the temperature sensitivity were both evaluated arithmetically using Equations 5 - 5 and 5 - 6 below, respectively.

5.7.1. Temperature Sweep Test

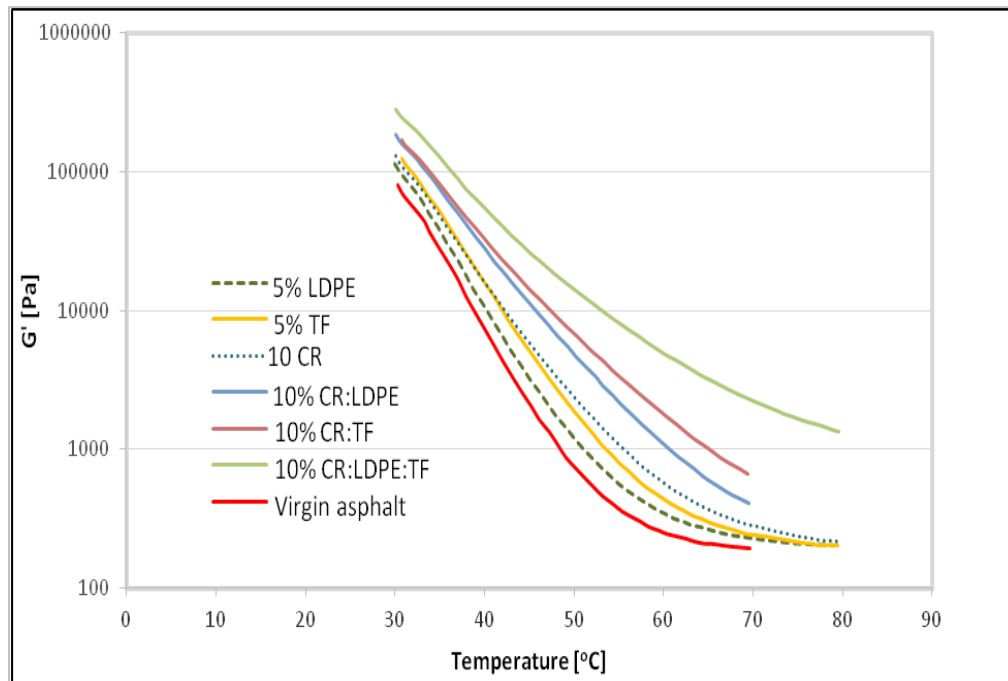


Fig. 5.27: Storage modulus G' of polymer modified asphalt.

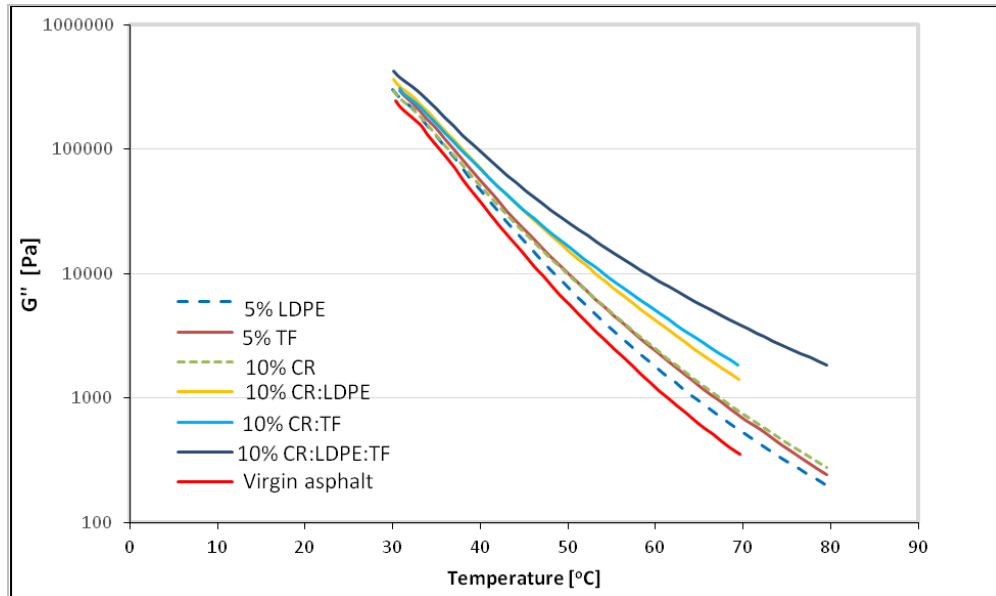


Fig. 5.28: Loss modulus G'' of polymer modified asphalt

Dynamic temperature sweep tests were performed at temperatures of a range between 30 – 80 °C for the six studied M-asphalt binders and the results were shown in Figures 5.27 and 5.28. Virgin asphalt binder, which has been included as a reference, shows a G' and G'' decrease as temperature increases. As a consequence, the viscous feature prevails over the elastic property at the whole range of temperature intended for study. In addition to the previous outcome, viscous flow can appear at the highest temperatures. From these figures, a similar trend can be seen apparently for every one of the studied M-asphalt binders although significantly higher values of the elastic and viscous moduli are found. However, the 10% (CR:LDPE:TF)M-asphalt binders present excellent differences and have shown higher values of G' and G'' in comparison with all other studied blends at the proposed temperature range.

It was very important to underline that for the same substance in the whole proposed temperature range, the obtained values of G'' of virgin asphalt have always been higher than G' . In addition to the above data, Figures 5.25 and 5.26, respectively, have also demonstrated that values of G' and G'' of the M-asphalt are higher than those of the same parameters with respect to the virgin asphalt all along the proposed temperature range.

As a conclusive point, the number of modifiers and the nature of each one of them probably has been capable of showing an obvious significant effect on both G' and G'' as

shown in the aforementioned figures. The decreases in the values of G' and G'' reflect the polymer modifier's nature as a primary control factor along with the temperature of the blending conditions for the polymeric asphalt binder. However, it was reported that any increase that might occur in G' and G'' could have resulted from the oxidation processes of the asphalt components [57].

The DSR results have led to the fact that at the studied intermediate and high temperature (30 – 80°C), both G' and G'' of all M-asphalt binders undergo a remarkable linear decrease, though being clearly higher than the corresponding to the virgin asphalt. As a result, the final quaternary asphalt blend was the least susceptible to temperature as the number and nature of polymer was blended. Such effects resulted in an improvement of the asphalt performance at intermediate and high in-service temperatures. The improvement in binder thermal susceptibilities can no doubt be achieved by adding polymeric modifiers. From the figures, it can also be concluded that the G' , G'' values of all M-asphalt blends at the best concentration level has been increased at all temperature ranges. For example-At a temperature of 60 °C, the storage modulus (G') increased from 244 Pa for virgin asphalt to 558 Pa, 552 Pa, 550 Pa, 1040 Pa, 998 Pa, and 1710 Pa for M-asphalt binders assigned A3, B2, C2, D3, F3 and H3, respectively, while the loss modulus (G'') was increased from 1150 Pa for virgin asphalt to 2310 Pa, 2383 Pa, 2370 Pa, 4030 Pa, 3231 Pa and 4835 Pa for the same above M-asphalt binders, respectively. Similar outcomes have been reported in early publications by Carrera and his team [300] and Navarro and his team [301].

The absolute value of G^* and temperature sensitivity (G^*_{30}/G^*_{60}) were calculated according to the Equations 5-5 and 5-6, respectively [302], and their results were given in Tables 5.12 and 5.13 at a temperature of 30°C and 60°C, respectively. The temperature dependence of G^* is seen to be reduced for all studied M-asphalt binders, compared to the control virgin asphalt binder. The reduction in temperature susceptibility and the increase in elasticity of the M-asphalt binders indicate a greater degree of intermolecular association within the final material (i.e. M-asphalt binder) [302, 303].

$$\text{Complex modulus } |G^*| = \sqrt{(G')^2 + (G'')^2} \dots\dots\dots (5-5)$$

$$\text{Temperature sensitivity} = (G^*)_{30^\circ\text{C}} / (G^*)_{60^\circ\text{C}} \dots\dots\dots (5-6)$$

$$\text{Tan } (\delta) = G'' / G' \dots\dots\dots (5-7)$$

The parameter ($\text{Tan } \delta$) was used as a measure of the relative elasticity of the asphalt binders intended for this study, and the ratio of $G^*_{30^\circ\text{C}} / G^*_{60^\circ\text{C}}$ was used as a measure of temperature sensitivity. Thus, the lower the value of $\text{Tan } \delta$ means the more elastic the system, and the lower the ratio of $G^*_{30^\circ\text{C}} / G^*_{60^\circ\text{C}}$ means the lower the temperature sensitivity of the system [303].

Table 5.12: Temperature sensitivity as a function of complex shear modulus G^* for polymer modified asphalt at 30°C

Blends No.	Modulus (Pa) at 30°C , and (10 rad s^{-1})			
	G'	G''	$\text{Tan } \delta$	G^*
Control	81150	244500	3.0	257615
A3	125000	298000	2.30	323154
B2	131033	296333	2.20	324010
C2	113500	303000	2.60	323560
D3	186500	366500	1.90	411223
F3	128000	307000	2.39	332615
H3	169000	308500	1.82	351757
H4	282666	427333	1.51	512360

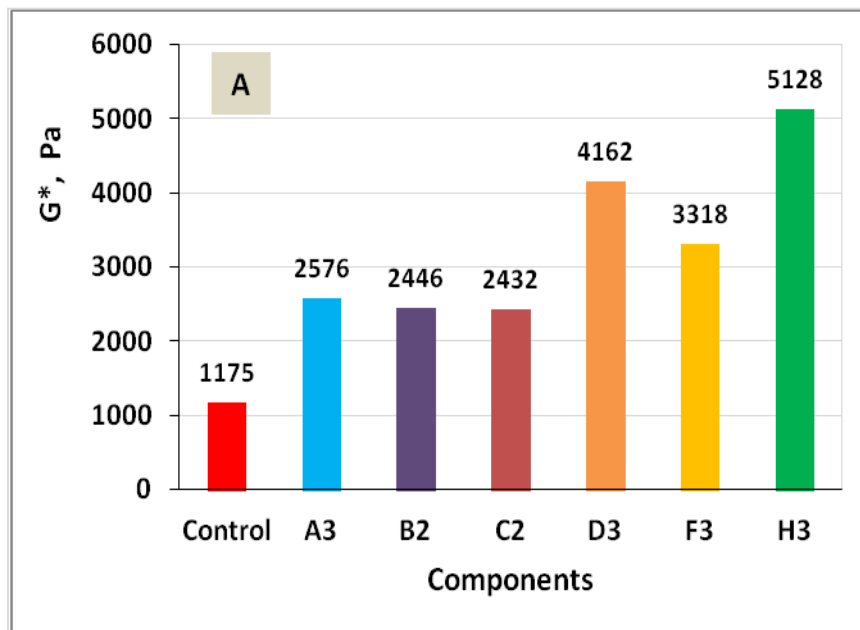
Table 5.13: Temperature sensitivity as a function of complex shear modulus G^* for polymer modified asphalt at 60°C

Blends No.	Modulus (Pa) at 60°C , and (10 rad s^{-1})				G^*_{30} / G^*_{60}
	G'	G''	$\text{Tan } \delta$	G^*	
Control	244	1150	4.7	1175	219
A3	558	2310	4.1	2576	125
B2	552	2383	4.3	2446	132
C2	550	2370	4.3	2432	133
D3	1040	4030	3.8	4162	98
F3	998	3231	3.2	3381	98
H3	1710	4835	2.8	5128	68
H4	4773	8686	1.8	9911	51

In addition to the above and according to DSR test results shown in Tables 5.11 and 5.12, all additives used as modifiers with the asphalt binder result in an increase in G^* values. The lower value of G^* means the asphalt binder is softer, and it can deform without developing large stresses as Samsuri and his group pointed out in their publication [304]. All additives also result in a decrease in $\text{Tan } \delta$ values of the virgin asphalt at 60°C and frequency of 10 rad s^{-1} . Lower values in phase angle (δ) means that the asphalt binder is more elastic than viscous and it will recover to its original condition

without dissipating energy. In addition, it was found that at high temperature low δ is favorable since this reduces permanent deformation [305]. Generally, these results enhance the mechanical properties of the final M-asphalt binder as compared to the virgin one. Furthermore, the values derived from the above parameters in Table 5.12.b show that the additives blended with asphalt binders increase the rutting resistance parameter $G^*/\sin \delta$ of virgin asphalt. From the obtained results illustrated in Figures 5.29.a and 5.29.b, it can be seen clearly that H3 prevailed over all the other M-asphalt blenders and creates the most increase in each DSR parameter values.

An additive from the thermoplastic elastomer family such as SBS, when added as a modifier to the asphalt blender, is well known to enhance high-temperature stability [306, 307] and increase the rutting resistance values by increasing G^* values of asphalt binder [108]. Another study was carried out to investigate the rheological properties of final products made of four novel boron-containing additives as asphalt modifiers. They were synthesized chemically, and the yielded components were abbreviated as “(TBEE), (TBEB), (TBEO), and (TBEOSA)”. According to DSR test results performed in this study, it was concluded that all additives increased G^* and decreased the δ values of virgin asphalt at 64°C. Besides, the additives also increased the rutting resistance $G^*/\sin \delta$ of virgin asphalt, and TBEOSA created more increase in the ratio of 49.6% at a temperature of 64°C [308].



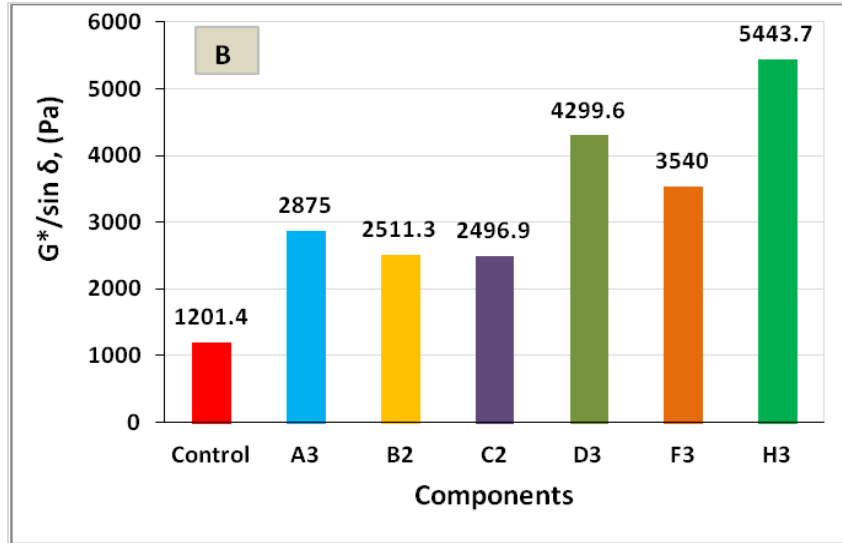


Fig. 5.29: Complex modulus (A), and rutting resistance (B) at 60°C

5.7.2. Viscous Flow Test

Viscosity property is a direct indicator of the stiffness of the asphalt binder. When aggregates are coated with asphalt binder and compacted in road pavement, the properties of the asphalts directly influence the resulting stiffness of the compacted mixture prior to use as a paving binder in road construction. The rate of shear is one of the factors that alter the rheological behavior (viscosity) of the asphalt.

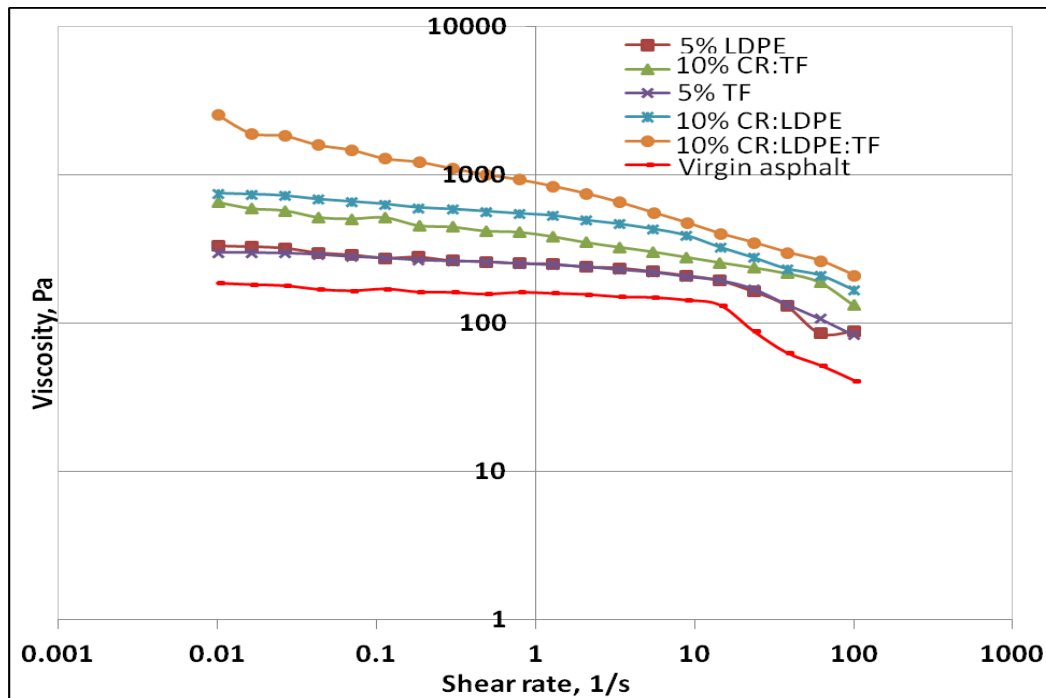


Fig.5.30: Relationships between viscous flow and shear rate at 60°C

In this part of the study, the M-asphalt samples prepared were subjected to different shear rates ($\dot{\gamma}$) in order to study dynamic viscosity (η) at 60°C. The viscous flow behavior (η) at 60°C for the best level of concentrations of the added modifiers assigned B2, C2, D3, F3 and H3 has been studied, and the results were presented in Figure 5.30. Results of component A3 is not presented in the figure. As a reference value, viscosity at 60°C for the virgin asphalt used has also been included. It can be observed that the virgin asphalt exhibits a lower viscosity than all modified asphalt binders, as has been reported elsewhere by other authors [309, 310]. It can also be observed that the virgin asphalt sample and the other M-asphalt binders show a quasi-constant in the value of viscosity in the entire range of shear rates ($\dot{\gamma}$) studied.

Initially, it is important to underline that the virgin asphalt binder showed typical Newtonian behavior over almost the whole shear rate ($\dot{\gamma}$) range. Whereas, the addition of any of the six different types of modifiers to the asphalt binder has led to a slow increase in η of the blends at low shear rate ($\dot{\gamma}$), especially those measured at less 1 s⁻¹, depending on the type and the amount of additives (Table 2 in section: 5.6). It is believed that the fluid phase surrounding the particles of the added modifiers is characterized by a very high viscosity (above 1 Pa s), then the viscous forces, created by the fluid on the particles upon the beginning of flow are so big, making the interactions among particles negligible, not leading to long-range structures, and particles will then act as inert suspended ones [291]. Besides this piece of information, one should expect that the presence of particles would increase the flow resistance of the product and the increase of the viscous dissipation in the liquid was necessitated by the adhesion of the fluid at the particle-liquid interface [291]. From Figure 5.30, a similar result can also be discovered where the M-asphalt binder blended with the modifier H3 had the highest rise in viscosity at low shear rate ($\dot{\gamma}$). It can be concluded that polymer addition to the asphalt binder can result in changing the rheological behavior of these systems from Newtonian to non-Newtonian fluids. Similarly, such results can be comparable to these obtained by Carrera and his team (2010) [300], who investigated the effect of processing on the rheological properties of polyurethane/urea asphalt binders. Another literature has pointed out to the fact that the rubber will absorb the lighter fractions of the asphalt (maltene fraction) more

readily [311], causing the proportion of asphaltene in the residual binder to increase and thus a change in its rheological properties occurs.

In addition, it can be part of a conclusion that the viscosity of all studied blends seems to follow a Newtonian type of behavior at the low shear rate range ($\dot{\gamma}$), as shown in Figure 5.30. Thus, the rheological behavior was typically of a viscous response.

5.8. FTIR of Modified Asphalt Binders

The functional groups, on the asphalt mixture analyzed by FT-IR . the FT-IR transmission spectra in the range of 400-4000 cm^{-1} for the modified and unmodified asphalt mixture which shown in Figure (5.31). The functional groups involved in the absorption were as follows: Peaks at 1457 and 1376 cm^{-1} are related to aliphatic $-\text{CH}_2-$ and $-\text{CH}_3-$ in all binders. Bands at 1600 cm^{-1} perhaps are associated with $\text{C}=\text{C}$ of aromatics. Peaks with shoulders at 2850 cm^{-1} - 2920 cm^{-1} the aliphatic C-H group [225]. Between 450 cm^{-1} and 900 cm^{-1} , there is a number of broad overlapping bands which are superimposed. They cannot, therefore, be described in terms of simple motion of specific functional groups or chemical bands. From the figure it is clearly that the virgin and modified asphalt have similar typical absorption peaks. But the peak values are different. The peak changes by the shifting in the range of 1330 cm^{-1} - 1750 cm^{-1} means the increase of aromatics in the asphalt mixture. In the range 720 cm^{-1} – 867 cm^{-1} the peak of modified asphalt is a little bit lower than that of the virgin asphalt. This may be caused by decreasing of saturate. Also, these finding of changes observed in the spectra, indicated that mass transfer between modifiers and asphalt exists. One more concede that the interaction between the admixture additives and virgin asphalt compositions becomes stronger compared with the singular additives. Similar outcomes have been reported by Ying et al., (2010) [312], and Araujo et al., (2012) [225] when they investigated interaction between asphalt and rubber powder, and SBS modified asphalt binder respectively.

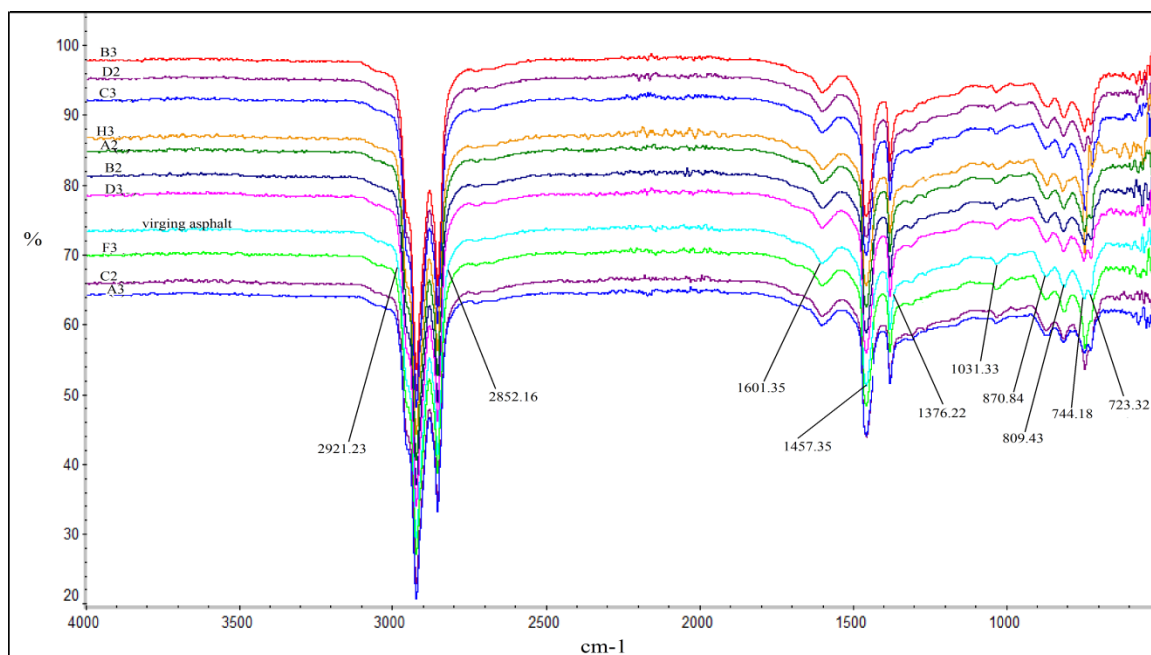


Fig. 5.31 : FTIR of virgin asphalt and modified asphalt by different components

5.9. Results of Wheel Track Test (WTT)

The idea of this test is to determine the final M-asphalt product's resistance against permanent deformation at critical temperature and under loading in a similar way to what occurs to the pavement road [136]. In this study, the rutting test was evaluated according to the EN12697-22 test. The materials used in the hot mix asphalt, mix ratios and particle sizes of aggregates used for the asphalt mixtures are shown in Table 5.14. Mixing with a compaction temperature of 140°C was applied for the mixtures with virgin asphalt, while a temperature of 160°C was applied for those containing PM-Asphalts. The test of wheel track was conducted at a temperature of 60°C, applied load equivalent of 700 N, specimen thickness of 60mm, wheel diameter of 200mm, and width of 50mm.

The effect of M-asphalt binder on asphalt mixture to resist rutting is shown in Figure 5.33. It can be seen that the addition of modifiers assigned D2, F2, and H2 to asphalt binder has reduced the rutting depth of asphalt mixture after 9000 cycle, respectively, to 54.48%, 44.82% and finally 57.93% compared to virgin asphalt binder. This outcome provides a proof to the claim that most modifiers possess high power in reducing permanent deformation of the asphalt mixture at different stresses.

The addition of polymer modifiers to the asphalt may cause increases in stiffness and viscosity of the final modified asphalt. Improving both of these features in modified



asphalt can lead considerably to a reduction in the rate of rut depth. From the obtained results, it can be concluded that temperature, stresses, and the content of modifiers are very important factors having an effect on rut depth test. From table 5.15, the average slope was found to be 0.26, 0.26 and 0.19 for CR:LDPE, CR:TF and CR:LDPE:TF respectively in a ratio weight of 5% of asphalt binder, which was less than that for the virgin mix (0.90). This outcome agrees to a great extent with the conclusion drawn by Shfabakhsh and his colleagues (2014) when they investigated the effect of adding waste rubber powder to the rutting performance of asphalt mixtures [136]. Another work has investigated the effect of CR, CR/SBS and CR/SBS/S on the asphalt binder. The obtained results showed that the rutting depth was reduced to 23.5%, 38.5% and 56.4% [193]. Laboratory wheel track test is presented by Figure (5.34).

Table 5.14. Materials used in hot mix asphalt for rutting test and their specifications

Material	Content, (wt%)
Coarse aggregate 11/16 – crushed granite	15.1
Coarse aggregate 8/11 – crushed granite	15.1
Coarse aggregate 5/8 – crushed granite	15.1
Coarse aggregate 2/5 – crushed granite	19.8
Fine aggregate 0/2 – crushed	12.3
Fine aggregate 0/2 – natural	12.3
Filler – limestone	4.7
Asphalt	5.6

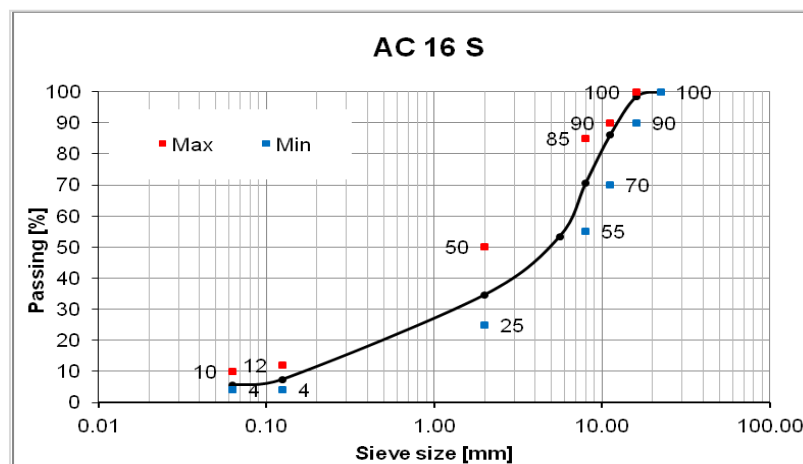


Fig.5.32: Aggregate gradation curves

Table. 5.15: Results of wheel track test: Ruth depth, slope, and rutting reduction at a temperature of 60°C, applied load 700 N, and 9000 cycle.

Asphalt binder	Ruth depth, mm	Slope	Ruth depth reduction, %
D2	6.6	0.26	54.48
F2	8.0	0.26	44.82
H2	6.1	0.19	57.93
Virgin asphalt	14.5	0.90	---

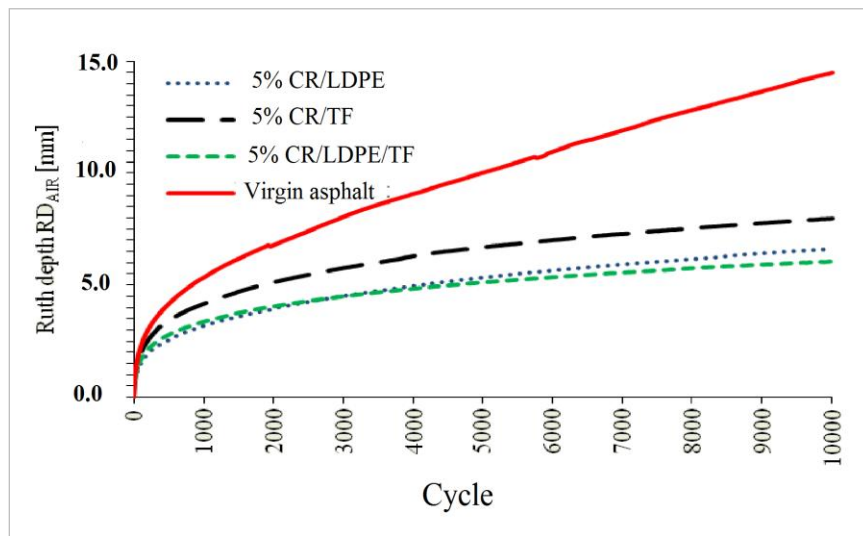


Fig. 5.33: Ruth depth as a function of cycle at 60°C and applied load 700 N.



Fig.5.34: Schematic view of the laboratory wheel track test

5.10. The Effect of Maleic Anhydride Additions

Table 5.16: Modifiers and their assigned letters, involved in asphalt binder blending at the most favorable concentration level.

Blends No.	Blend content	Blends No.	Blend content
Virgin	100% Asphalt	L	(CR:LDPE)-g-MAH-asphalt
I	CRM-g-MAH-Asphalt	M	(CR:TF)-g-MAH-asphalt
J	LDPE-g-MAH-Asphalt	N	(CR:LDPE:TF)-g-MAH-asphalt
K	TF-g-MAH-Asphalt	---	---

Despite the large number of polymeric products, the suitability of having few types of them to achieve better asphalt pavement performances are rare. Besides, the major concern of asphalt/polymer blends is their lack of stability during a prolonged storage at high temperature. Therefore, the current section is intended to investigate the basic and rheological properties of the asphalt binder using grafted modifiers by the addition of the monomer maleic anhydride (MAH).

The effect of MAH addition as an asphalt binder compatibilizer was targeted as a second scope of this study to evaluate the basic and rheological properties of the final M-asphalt blends. According to the preparation process of maleated M-asphalt binders, which were presented formerly in chapter four (section 4.3.2), the final product of each blend was designed and shortly assigned a letter as follows: I for (CRM-g-MAH-Asphalt), J for (LDPE-g-MAH-asphalt), K for (TF-g-MAH-asphalt), L for (CR:LDPE-g-MAH-asphalt), M for (CR:TF-g-MAH-asphalt), and finally N for (CR:LDPE:TF-g-MAH-asphalt) as presented in Table 5.16. The values obtained from evaluating these maleated M-asphalt binder products were subsequently compared with their relevant non-maleated M-asphalt samples and the virgin asphalt sample as well.

5.10.1. The effect of MAH on the Properties of the Virgin Asphalt

Table 5.17-a: Effect of 3% MAH on physical properties of the virgin asphalt

a. Basic properties			
Property	Unit	Value	Modification index (%)
Softening point (SPT)	°C	49.6	105.5
Penetration (P-Deg)	dmm	57.0	76
Viscosity	dpa.s	2.0	370
Ductility	cm	100.0	---
Elastic recovery	%	10.0	200
Storage stability (ΔT)	°C	0.5	---

Table 5.17-b: Effect of 3% MAH on rheological properties of the virgin asphalt

b. Rheological parameters			
Property	Unit	Value	Modification index (%)
G' at 30°C	Pa	92,000	---
G'' at 30°C	Pa	300,000	---
G' at 60°C	Pa	460	---
G'' at 60°C	Pa	2000	---
G^* at 30°C	Pa	313789	---
G^* at 60°C	Pa	2052	---
Tan δ	---	4.0	---
Tem. Sensitivity	---	158	---

Results obtained from assessing the effect of 3.0% MAH additions to the virgin asphalt binder under the studied conditions are summarized in Table (5.17-a) and Table (5.17-b). In all cases, it can be observed clearly that the addition of MAH has affected most basic properties in a way that it has increased the values of SPT and viscosity and reduced the values of P-Deg as compared to those values of the virgin asphalt. The modification indices for SPT, viscosity, and P-Deg, of the maleated asphalt were recorded as 105.5%, 370% and 76%, respectively, in agreement with other data mentioned elsewhere [186]. Some authors have attributed these positive results to the “reaction involving the active MAH double bond and condensed aromatic ring systems in the asphalt” [302, 303, 311]. Due to this interaction, the addition of MAH to the virgin asphalt binder also has improved the storage stability of the final blend as compared to the non-maleated ones and virgin asphalt binder; such a conclusion is in agreement with the one made by Vargas and her colleagues [313]. The improved property of viscosity of the maleated asphalt binders indicates that the addition of MAH to the M-asphalt is favorable for producing less temperature sensitive asphalt binders [186].

The data in Table (5.17) also show that the addition of 3.0% MAH has produced a significant increase in the elastic recovery of the final maleated asphalt blend. The work done by Singh and his team (2013) have supported a similar trend that when the level of MAH is increased the elastic recovery is also increased, and the 2% wt % MAH addition showed superior behavior than the blend containing 1 wt % MAH [186]. It is also clear from Table 5.17 that MAH modification has significantly reduced $\tan \delta$ which, in the field, should result in increased cohesion of these binders, relative to the virgin, at higher temperatures. Also, The reduction in temperature susceptibility and increased elasticity of the MAH modified asphalt by the addition of MAH indicate a greater degree of intermolecular association within the material, compared to the virgin [303].

Yang and his coworkers' results obtained from the direct tensile test (DTT) implied that the reaction mechanism of MAH and asphaltenes does not lie in the opening of anhydride but in the special reaction between the double bond of MAH or the whole MAH molecule and asphaltenes [290]. The same authors, however, find it hard to conclude that the exact mechanism is reached either by Diels-Alder, alternating copolymerization or charge transfer mechanism as they proposed. But they reported that they are sure that the reaction is a 2-order reaction when they reacted through Diels-Alder mechanism.

Another research work have reported that, the most likely reaction route is a Diels–Alder reaction involving the active maleic anhydride double bond and condensed aromatic ring systems in the bitumen. Given that the anhydride ring opens during the reaction, the end result is the introduction of two carboxylic acid sites to the bitumen molecule involved. The new acid groups are able to hydrogen bond to polar groups on other bitumen molecules, giving rise to the observed changes in physical properties discussed above [303]. The possible mechanisms of reaction between asphalt and maleic anhydride are presented in Figure 5.35 [290].

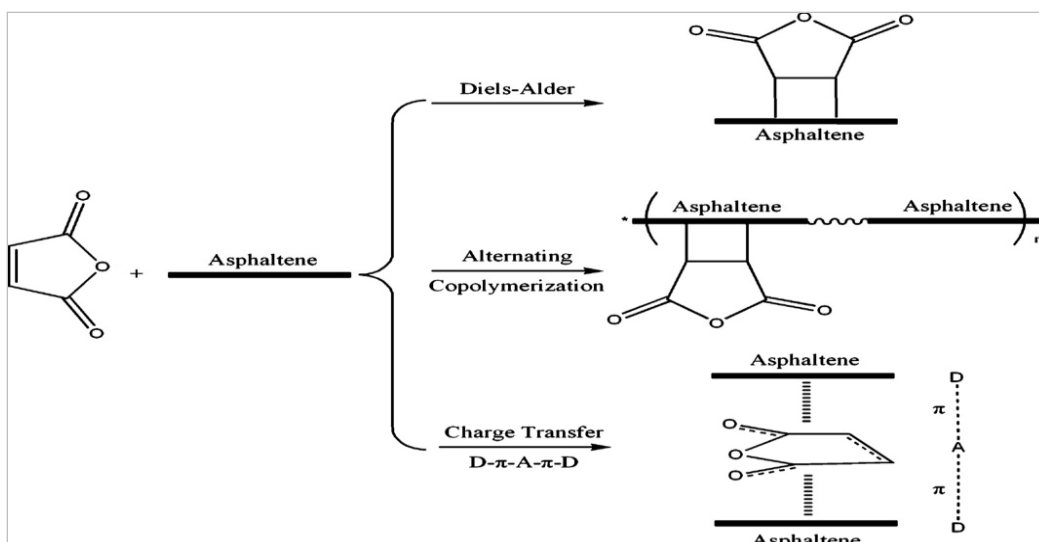


Figure 5.35: Possible mechanisms of reaction between asphalt and maleic anhydride [290].

5.10.2. The Effect of MAH on the Properties of the M-asphalt Binders

Table 5.18: Effect of 3% MAH on the Properties of the M-asphalt Binders

Property	Unit	Blends No.					
		I	J	K	L	M	N
Softening point	°C	58.0	59.0	56.0	59.6	61.6	62.0
Penetration	dmm	44.0	40.0	44.0	42.0	34.0	40.0
Viscosity	dPa.s	6.8	5.4	5.8	7.9	11.3	13.0
Ductility	cm	13.2	86.9	65.0	13.3	10.0	13.1
Elastic recovery	%	24.0	8.0	32.0	41.0	50.0	23.0
Storage stability	°C	6.0	12	3.5	4.1	4.5	3.1
SPT index	%	123	125	119	126	131	132
Penetration index	%	51	47	51	49	40	47

In addition to the above section, the effects of MAH additions on the properties of the M-asphalt binders with the studied additive modifiers I to N are summarized in Table 5.17. It can be obviously noticed that all studied basic and rheological properties tabulated above and related to the M-asphalt binders which were designed in six different components and assigned the following letters (I, J, K, L, M and N), were significantly affected by the addition of MAH. Accordingly and from the results obtained in this part

of the study, it can be concluded that all basic physical properties of the M-g-MAH-asphalt binders have been improved by the addition of 3.0% of MAH. Likewise, the phase separation, which is related to the storage stability of the M-asphalt binders and considered a problem of many M-asphalt binders, is also improved by the incorporation of MAH as a compatibilizer.

For the LDPE-g-MAH-asphalt blend, the difference in the SPT of its top and bottom parts was reduced to 18 °C when compared with 23°C for non-grafted LDPE asphalt blend. A similar study was carried out by Vargas and his assistants (2013) who through their study confirmed that the grafted PE in asphalt blends resulted in a better dispersion of the discrete polymer phase in the asphalt phase than the non-grafted PE. Very good stability results were obtained for blends containing grafted PE, especially HDPE-g-MAH blend. The addition of LDPE and HDPE-g-MA to the asphalt binder was sufficient to modify the mechanical behavior of the asphalt. The HDPE-g-MAH blend showed a large compatibility with asphalt and led to enhanced and better mechanical properties [313]. Storage stability was also highly improved by the addition of MAH to the M-asphalt mixture. It is reported elsewhere that the improvement of storage stability can be achieved by the addition of polymeric compatibilizer to the asphalt mixture modification, such as MAH [186, 214], acrylic acid [188], and epoxy ring with a glycide backbone [57]. The content of the compatibilizer used in asphalt mixture is dependent on the source of the asphalt [57].

In some cases, the modifier added to the asphalt binder can play a double role; a modifier additive that improves the basic properties of the final M-asphalt binder and also functions at the interface to create a chemical bridge between the reinforcement and the asphalt matrix. In other words, such agent improves the interfacial adhesion when one end of the molecule is joined to the reinforcement surface and the functionality at the other end reacts with the asphalt phase. The utilization of recycled polyurethane foam (PU) for asphalt modifications can represent a demonstrative example according to some scientific works in literature reported elsewhere [243, 314].

5.10.3. FTIR Analysis of Final Maleated M-Asphalt Blends

Singh and his coworkers represented the reaction mechanism of MAH with recycled LDPE as shown in chapter two (section. 2.3.2)

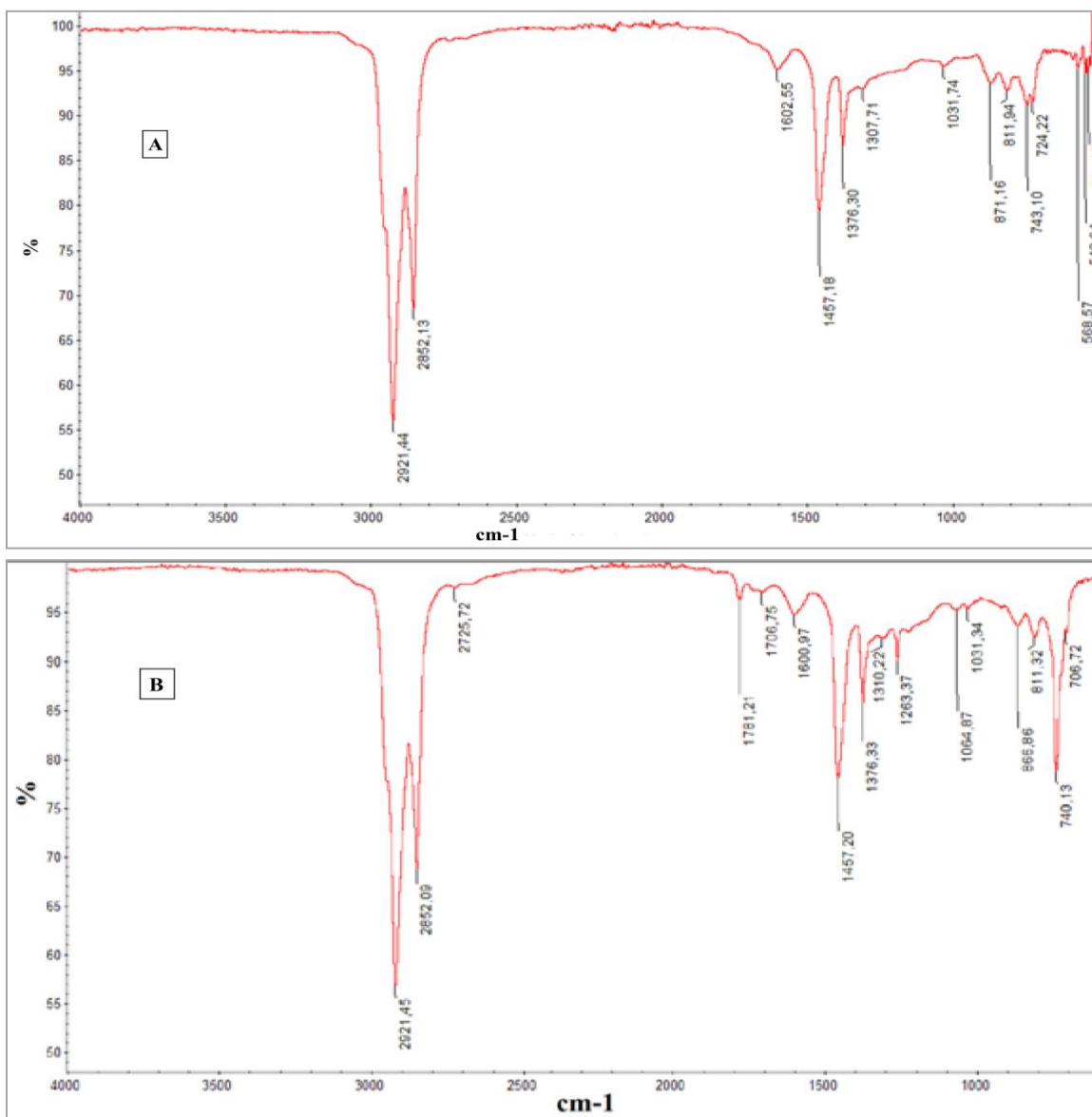


Fig. 5.36-b: Results of FTIR analysis of virgin asphalt (A), and Mated asphalt-additives system (B)

The maleic anhydride grafting on the polymer chains was confirmed by FTIR spectra. The FTIR spectra of MAH grafted polymers are shown above in Figure 5.36. The spectra show a number of peaks of MAH-asphalt blend and the two reaction mixtures were observed in the bands of $1500 - 1700 \text{ cm}^{-1}$. These bands were recognized to be characteristic peaks of aromatic compounds in general. As a consequence, it is an indication of the fact that reactions between MAH grafting agent and the asphalt binder occurred, and the cyclic anhydride was retained during the reaction. The cyclic anhydride

peaks are shown by the spectra and ascribed by an absorption peak at 1781 cm^{-1} . The spectrum of the asphalt binder has no peak from 2000 cm^{-1} to 1700 cm^{-1} . Similar results of modified asphalt with maleic anhydride and dicarboxylic acids has been reported by Herrington et al., (1999) [303].

5.10.4. TLC- Analysis of Maleated Asphalt-Additives System

Table. 5-19: Components of maleated asphalt and modified asphalt binder with MAH

Blends No.	Component, wt%				% of Asphaltens/Resins
	Saturate	Aromatics	Resins	Asphaltens	
Control	6.8	64.2	16.2	12.7	0.78
I	4.5	60.6	14.2	20.6	1.45
J	5.1	61.2	14.7	19.0	1.29
K	4.4	60.7	14.4	20.1	1.39
L	3.6	54.9	18.3	22.9	1.25
M	6.9	60.1	15.7	17.2	1.09
N	4.9	56.6	18.3	20.3	1.10

In this study, the data and results obtained from the TLC analysis of both virgin asphalt (control) and the maleated asphalt-additives system assigned I, J, K, L, M, and N are shown in Table 5.19. The table represents the chemical components of the modified asphalt and their changes in percentages (%) as due to the reaction and/or interactions that occurred by the additives within the final modified asphalt products via MAH.

The tabulated values of the final maleated asphalt-additive system have shown a similar trend as with the M-asphalt binders. The data indicated that almost all the three components of maltenes (saturates, resins & aromatics) were decreased in concentration, while the asphaltenes were increased.

Likewise in the part related to M-asphalt binders without the use of MAH, the incorporation of a grafting agent such as MAH has led the final maleated asphalt-additives system having a high Asphs/Res ratio. This outcome leads to a final Maleated-g-M-asphalt binder with more rigidity and elasticity (low in phase angle and high in complex shear modulus).

5.10.5. Rheological Analysis

5.10.5.1. Viscous Flow



Dynamic viscosity (η) at 60°C as a function of shear rate ($\dot{\gamma}$) of maleated-g-M-asphalt binders named as component N, I, L, M, J, and K, at the best level of concentration (10.0 %wt) compared to virgin asphalt are shown in Figures (5.37) and (5.38), respectively. In Figure 5.37, the virgin asphalt shows typical Newtonian behavior over almost the whole shear rate range. The diverse increase in dynamic viscosity (η) of blends at low shear rate depends on the type of polymer modifiers. Component N shows the highest rise in viscosity at a low shear rate compared with the other components: I, L, and M, at the same level of concentration, as seen in Figures (5.38-a to 5.38-d) respectively. On the other hand, component J shows higher than component K at 5.0 %wt level of concentration as seen in Figures (5.38-e) and (5.38-f) respectively.

In comparison to the first part of the study where no MAH was involved, it can be concluded that the blends prepared by the addition of MAH in asphalt blends enhanced the viscosity at the whole range of shear rate in a higher manner than before the addition of MAH to the M-asphalt blends. It was recorded that the viscosity at low shear rate of components named N, I, L, M, J and K were found to be 19400 Pa.s, 4270 Pa.s, 2760 Pa.s, 2280 Pa.s, 790 Pa.s and 559 Pa.s, respectively, compared to 3400 Pa.s, 1000 Pa.s, 893 Pa.s, 814 Pa.s, 530 Pa.s and 468 Pa.s for components named H3, A3, D3, F3, B2 and C2, respectively, while 167Pa.s for virgin asphalt was recorded. On the other hand, shear stress (τ) was increased from 4900 Pa for virgin asphalt to 10,000 Pa for both components J, K and in the range of 30,000 to 55,000 Pa for components I, L, M, and N, respectively, by using MAH grafting agent. The defenses in shear stress in the M-asphalt samples depend on the level of concentration and type of polymer.

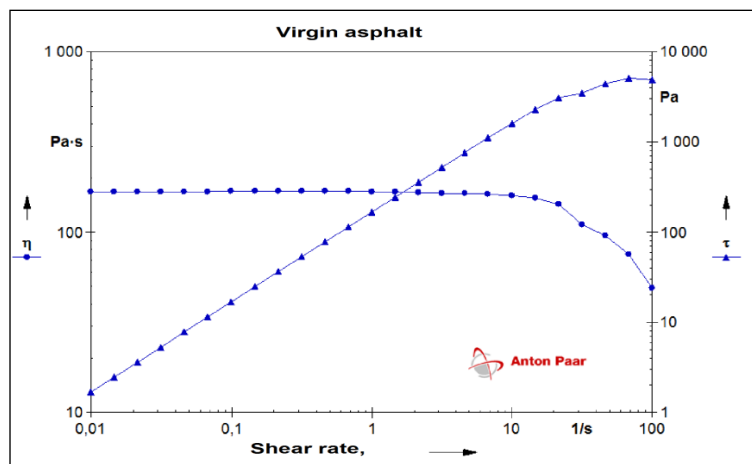


Fig. 5.37: Viscosity and shear rate relationships for virgin asphalt

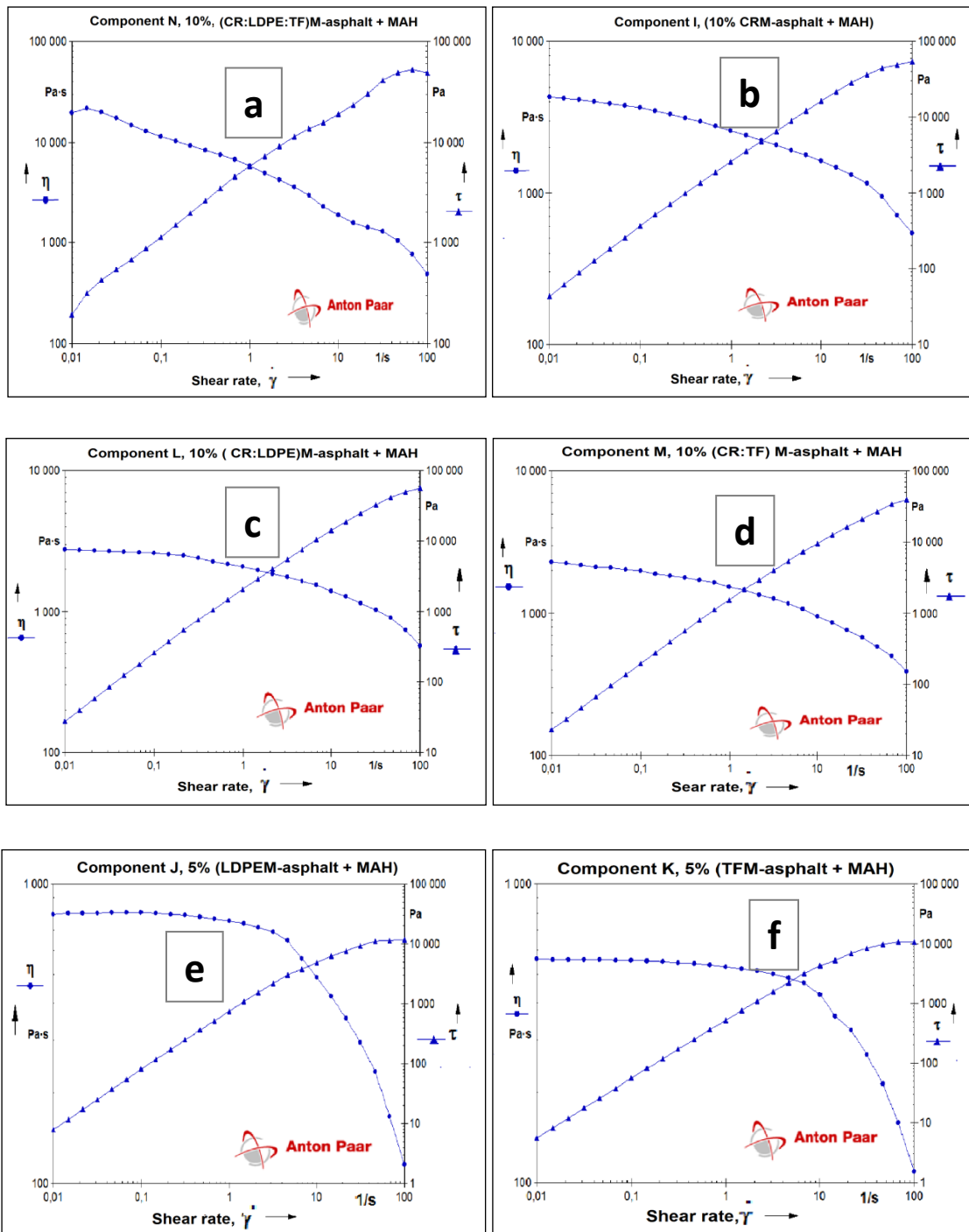


Fig. 5.38: Viscosity and shear rate relationships for component N (a), component I (b), component L (c), component M (d), component J (e) and component K (f).

5.10.5.2. Temperature Sweep

Maleic anhydride was used for increasing of cross-linking of the polymer-asphalt molecules and hence the elasticity of PMA. In general, polymer-grafted systems display

higher elasticity in comparison to the non-grafted moieties [313]. At the best content level selected from the first part of the study, the G' , G'' were examined at a frequency (ω) of 10 rad.s^{-1} and showed in Figures (5.40-a) to (5.40-f) compared with the virgin asphalt which is presented in figure (5.39) . From the figures, it can be concluded that at all temperature ranges, the (G'), (G'') has been increased compared to the non-grafted polymer-asphalt system, which is preferred for hot climates. Hence, the component N (10% CR:LDPE:TF-g-MA) is expected to have the best high-temperature resistance to permanent deformations (rutting), while $\tan \delta$ was decreased by the addition of polymer to asphalt mixture. Data obtained in the figures has been summarized in Table 5.19.

From figure 5.39 it can be clearly seen that the elastic modulus (G') behaviour with the temperature has two parts for the virgin asphalt. For temperatures below $80 \text{ }^\circ\text{C}$, G' decreases with the increase of temperature, but at 80°C the elastic behaviour of asphalt reaches the minimum value of G' which is very low value, due to high value of the viscous modulus (G'') which decreases regularly as the temperature increases up to $90 \text{ }^\circ\text{C}$, then reaches the minimum value and does not change with the temperature increase. While, δ was recorded the highest values at the low and the high temperature compared with all modified blends, and the maximum value of δ ($\approx 90^\circ$) is reached at $\approx 100 \text{ }^\circ\text{C}$. These finding of changes observed in the figures, indicated the improvements of asphalt by the addition of all modifiers. For modified blends, the maximum value of δ are reached at ($80\text{-}90 \text{ }^\circ\text{C}$) dependence on the type of modifiers. For temperatures below 80°C , the difference between G' and G'' increases, but for temperatures above 80°C the stabilization of G' at the minimum value and does not change with the temperature increase and continuous decrease of G'' reduces the difference between them specially for the components N, J, and L. Similar results were also reported in literature [293].

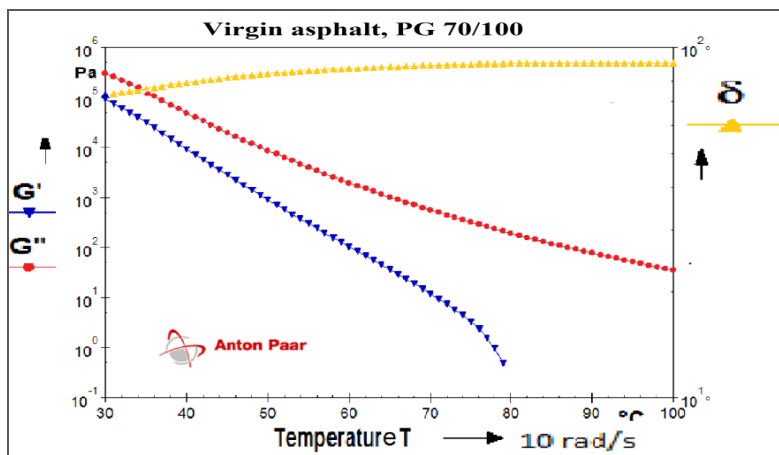
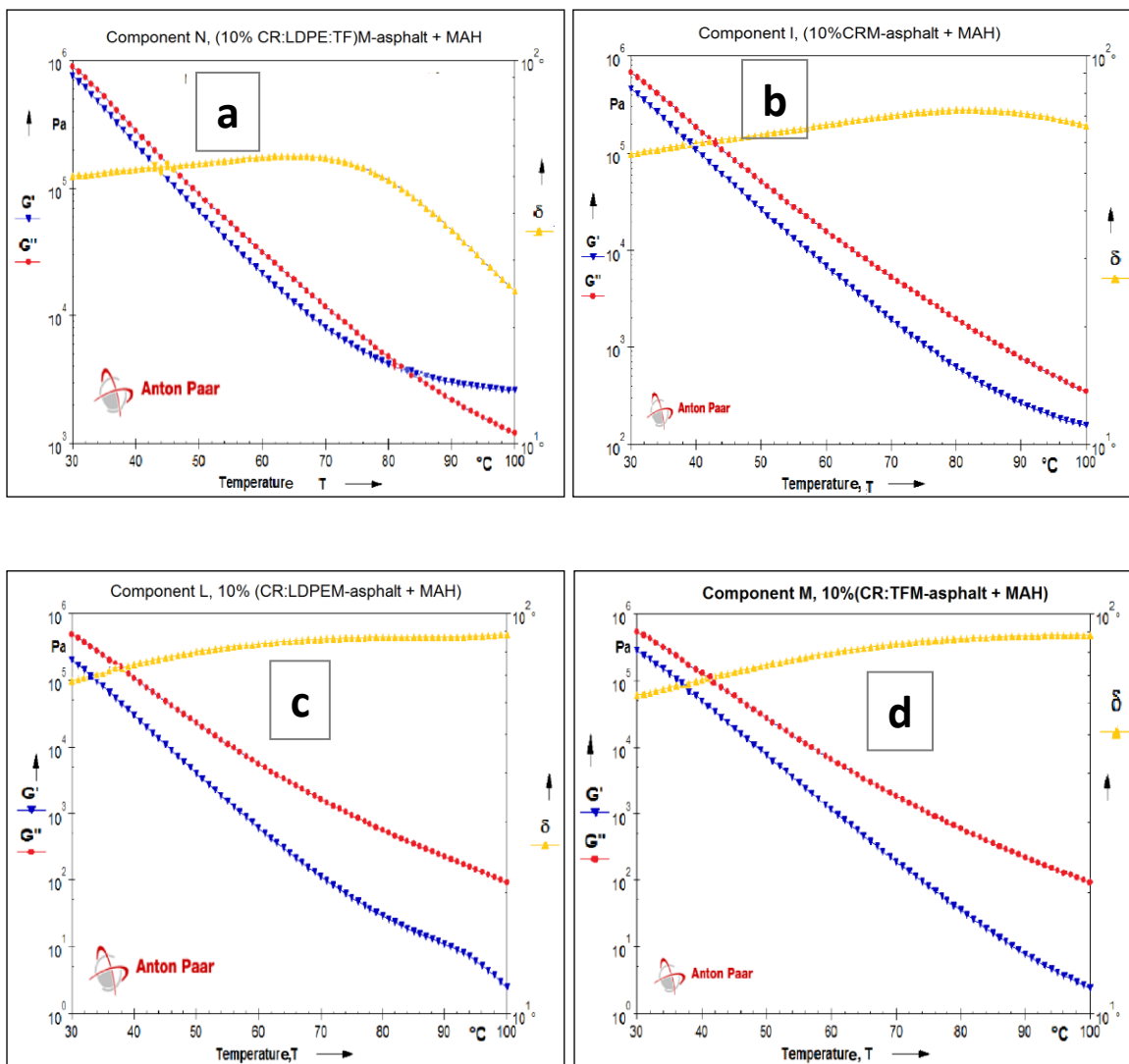


Fig.5.39: Temperature sweep test of virgin asphalt.



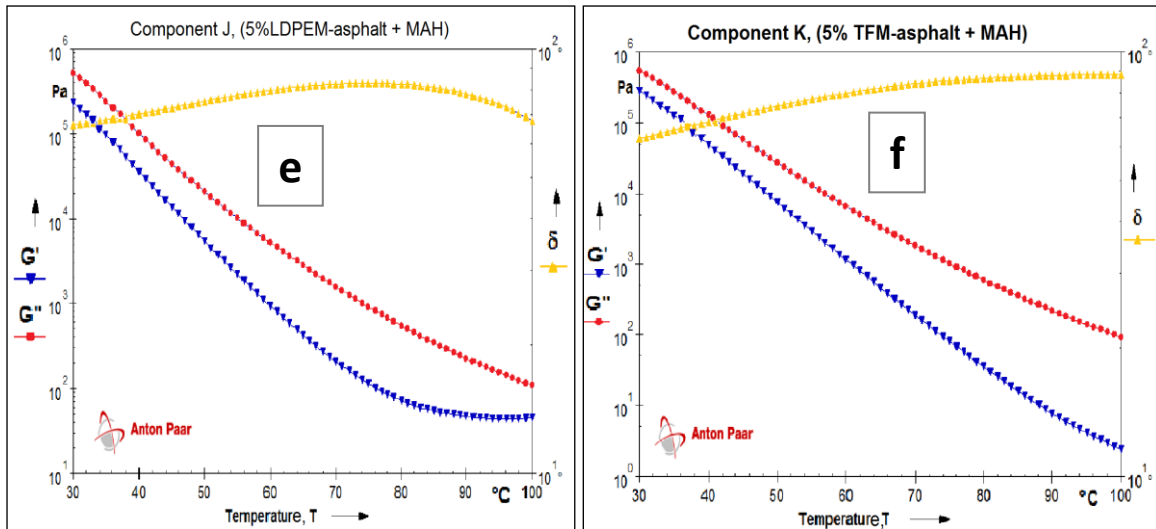


Fig.5.40: Temperature sweep test of component N (a), component I (b), component L (c), component M (d), component J (e) and component K (f).

The absolute value of G^* at 30°C and 60°C was calculated according to Equation (5.4). Data obtained are given in Table 5.19 and 5.20.

Table 5.20. Results of DSR at 10 rad/s and temperatures of 30°C

Blends No.	Modulus (Pa) at 30 °C		
	G'	G''	G^*
I	450000	673000	808040.2
J	392000	557000	877496.4
K	280000	540000	608276.2
L	194000	476000	479937.2
M	456000	709000	879022.7
N	750000	890000	1140175.4

Table 5.21. Results of DSR at 10 rad/s and temperatures of 60°C

Blends No.	Modulus (Pa) at 60 °C			Temp. sensitivity = $(G^*)_{30}/(G^*)_{60}$
	G'	G''	G^*	
I	6830	15700	17122.1	47.2
J	4490	12600	13376.1	65.6
K	1150	6400	6502.4	93.5
L	2410	10300	10328.0	46.7
M	5600	15000	16011.2	54.9
N	21000	31600	38164.3	30.0

In addition to the above results, the G^* of the modified and virgin asphalt mixture are identified for each binder at a frequency of 10 rad/s and a temperature of 60°C. From Tables 5.20 and 5.21, it can be seen that the G' values of the modified asphalt mixtures were highly increased compared to the virgin asphalt mixture. It is also an indication of a slight enhancement in the elastic property of the binder. It was reported elsewhere [302] that the G' values of modified asphalt binders were found to be 9-45 times higher than those of the control sample. In accordance with that, and as can be seen in Figures 5.41-a, all components had an increase in the binder G^* values. Rutting resistance parameter $G^*/\sin \delta$ related to all those components is shown in Figure 5.41-b. While all additives have improved the rutting resistance of initial virgin asphalt, the component N had the greatest value.

It can be concluded that the addition of MAH as a compatibilizer to the asphalt modification process with other additives such as components J highly enhances the DSR test. From some literature, results of DSR proved that asphalts containing polyethylene-grafted-MAH (P-M-asphalt binder) were better in interaction with the asphalt phase than non-grafted LDPE and HDPE, due to the higher dispersion of the amorphous content of such polymer into the binder matrix. Rutting resistance was also enhanced [214].

In a similar approach, Yu-Hsun Nien and his coworkers (2008) have involved asphalt paving material containing chlorinated polypropylene (CPP) through a wet mix process. Results and data analysis, some of which were obtained by using DSC, revealed that phase separation occurring in asphalt iso-tactic polypropylene blend (asphalt-iPP) has disappeared because of the amorphous property of the CPP with 26% by weight of chlorine; this showed more compatibility, led to a higher viscosity in terms of higher temperature to get Newtonian behavior and also display superior rutting resistance to avoid permanent deformation at high temperature. [315, 215]

In this current study, it is similar to component I that the enhancement of the chemical reactions between CR and asphalt binder can be typically achieved with a grafting process by the addition of MAH. Besides, it was found that such process of HAM grafting can improve the failure temperature of the CRM-asphalt binder. In addition, in this system better interactions with asphalt can be obtained [188]. It is

reported that this can also result in a homogenous final product made of CRM-asphalt binder mix and thus improve the storage stability of the binder [189].

It is clear from Table 5.21 that the temperature dependence of (G^*) is examined to be reduced for the MAH-modified asphalt mixtures, compared to the virgin asphalt and modified asphalt additives without MAH. It is also that the MAH modification system has significantly reduced $\tan \delta$. It is an indication that in the field it should result in increased cohesion of these binders in comparison to the virgin asphalt, at higher temperatures [303]. Comprehensive data and results obtained in this study of the main basic and rheological properties are tabulated in Tables 5.21 and 5.22 respectively. From these Tables, a comparison between polymer modified asphalt system and polymer-grafted-maleic anhydride modified system at the best concentration level can comprehensively be made.

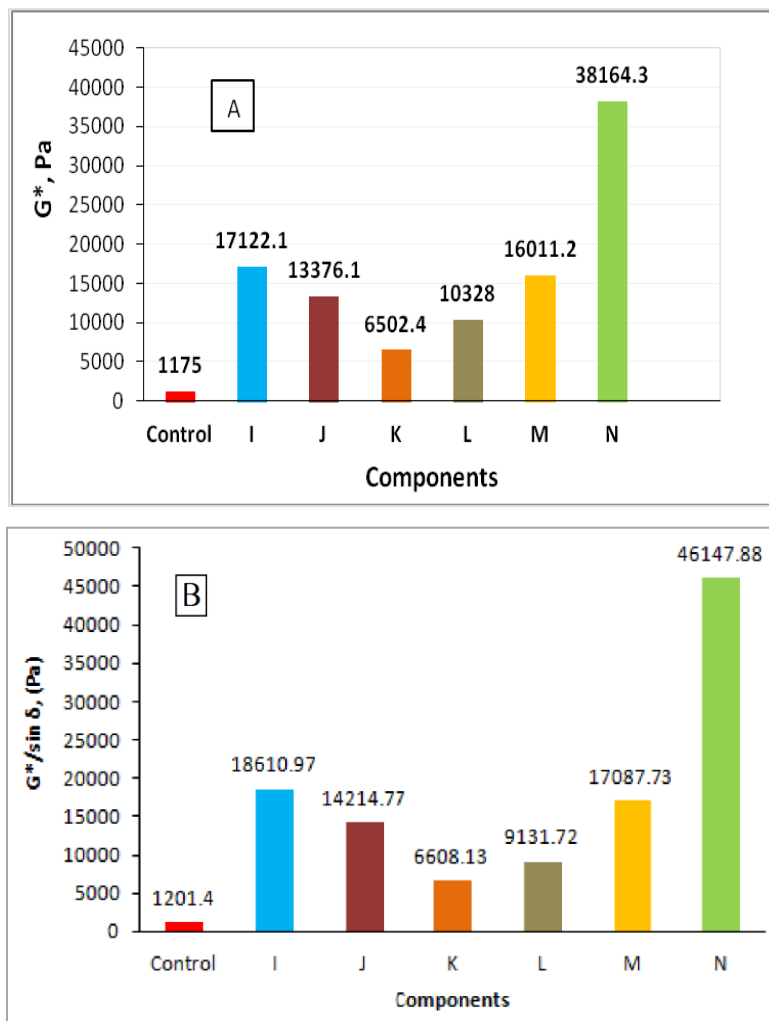


Fig. 5.41: DSR results: G^* (a), and $G^*/\sin \delta$ (b) at 60°C

Table 5.22: A comparison among values of all intended properties of final modified asphalt blenders without MAH compatibilizer

Properties	Unit	(I) Blend Components (modified asphalt without MAH)						
		"Control"	Singular Modifiers			Composite Modifiers		
		Virgin Asph.	A3	B2	C2	D3	F3	H3
SPT	°C	47	56	56.5	54.7	53	52	55.6
P-Deg	dmm	85	49	43	50	53	60	57
V	dPas	0.54	5	5	5	6	10	9
MI of SPT	%	100	119	120	116	113	111	118
MI of P-Deg	%	100	58	51	59	62	71	67
ST	°C	-	10	23	4.2	5.8	6.0	5.1
Ductility	cm	100	50	30	58	77	75	66
ER	%	5	38	42	38	44	45	48
G'	Pa	244	558	552	550	1040	998	1710
G''	Pa	1150	2310	2383	2370	4030	3231	4835
G^*	Pa	1175	2576	2446	2432	4162	3381	5128
Tan (δ)	--	4.7	4.1	4.3	4.3	3.8	3.2	2.8
$G^* / \sin(\delta)$	Pa	1201	2875	2511	2496	4299	3540	5443
T.S	--	219	125	132	133	98	98	68

Table 5.23: A comparison among values of all intended properties of final modified asphalt blenders with MAH compatibilizer

Properties	Unit	(II) Blend Components (modified asphalt With MAH)						
		"Control"	Singular Modifiers			Composite Modifiers		
		Asphalt	I	J	K	L	M	N
SPT,	°C	47	58	59	56	59.6	61.6	62
P-Deg,	dmm	85	44	40	44	42.0	34.0	40
V	dPa.s	0.54	6.8	5.4	5.8	7.9	11.3	13
MI of SPT	%	100	123	125	119	126	131.0	132
MI of P-Deg	%	100	51	47	51	49.0	40	47
ST	°C	-	6.0	12.0	3.5	4.1	4.5	3.1
Ductility	cm	100	13.2	86.9	65	13.3	10.0	13.1
ER	%	5	24	8	32	41	50	23
G'	Pa	244	6830	4490	1250	1200	5600	21000
G''	Pa	1150	15700	12600	5900	5530	15000	31600
G^*	Pa	1175	18610	133761	6502	10328	16011	38169
Tan (δ)	---	4.7	2.3	2.8	4.7	4.6	2.70	1.5
$G^* / \sin(\delta)$	Pa	1201	5565	14214	6605	19304	17087	46147
T.S	---	219	47.2	65.6	93.5	46.7	54.9	30

5.11. SEM Analysis of Virgin and Modified Asphalt Binders

Another important part of the study is the evaluation of the morphology of the studied M-asphalt binders by use of a fluorescence microscope to characterize the distribution and fineness of additives dispersed in the asphalt matrix. The additives were as follows. Singular additives of 10% CR, 5% LDPE, and 5% TF which were assigned A3, B2, and C2; composite pairs of 10% CR:LDPE additive and 10% CR:TF additive assigned D3 and F3, respectively; a composite tertiary of 10% CR:LDPE:TF assigned H3. These results were compared to those of additives-g-maleic anhydride-asphalt binders, which however were assigned I, J, and K for the singular-g-MAH-M-asphalt binders, L, M, for the composite pairs-g-MAH-M-asphalt binders and, finally, N for the composite tertiary-g-MAH-M-asphalt, respectively.

This analysis was done to observe the phase distribution of the additives in asphalt matrix at the same experimental conditions, as well as the effect of MAH addition to asphalt-additives system. The SEM results were shown in figures (from 5.42 to 5.47).

Figure (5.42-a) showed the micrograph of A3 final binder coated on a thin slide, which demonstrated that particles were partially separated from the asphalt matrix. However, from Figure (5.42-b) and in the case when 3.0% of MAH was added to the modification process by CRM, it can be seen that the phase separation has improved at the same time and temperature conditions.

Next, Figure (5.43-a) showed the micrograph of B2 final binder. It demonstrated that LDPE particles were clearly dispersed in a dark asphalt phase in the form of small spherical particles indicating the existence of very low interfacial adhesion between the two phases and both the modifier and the asphalt binder are strongly immiscible [312]. Similar results were obtained by Pei-Hung and his colleagues (2010) when they blended LDPE with asphalt in a content level of 5%. However, it was suggested that the use of LDPE at less than 5% probably would be the best choice [214]. The authors also concluded that the phase distributions in all of 5% of polyethylene in the form of LDPE/asphalt or HDPE/asphalt and PE-graft-maleic anhydride -asphalt micrographs illustrated critical phase separation that may refer to the aggregation of polymer chains to crystallize in the asphalt matrix as the polymer additive content up to 5% [214].

Figure (5.43-b) displayed a better dispersion of LDPE-g-MAH into the asphalt phase. Similar results were obtained by other authors [186]. However, Figures (5.44-a) and (5.44-b) illustrates that the SEM image of 5% TF-asphalt blend exhibits more compatibility with the asphalt matrix than other additives. Better results were obtained by blending admixture composite additives with asphalt matrix Figures (5.45-5.47). The grafting agent MAH has played an important role in improving phase separation between asphalt matrix and polymer modifiers due to trigger compatibility by chemical interaction between asphaltene components of the asphalt binder and polymer modifiers.

In addition to the above description, during handling and storage, chemical compatibility related to a stable homogenous blend is considered very important. The modifier must be chemically stable at the standard asphalt processing temperatures. The definition of compatibility is the ability of a polymer to remain distributed in the asphalt without phase separation occurring. However, the degree of compatibility varies by chemical and physical properties of the modifier that was used to the modification of asphalt binder. Compatibility also varies with the concentration of the modifier. A higher concentration of the modifier means a lower degree of compatibility between the modifier and the asphalt binder [277].

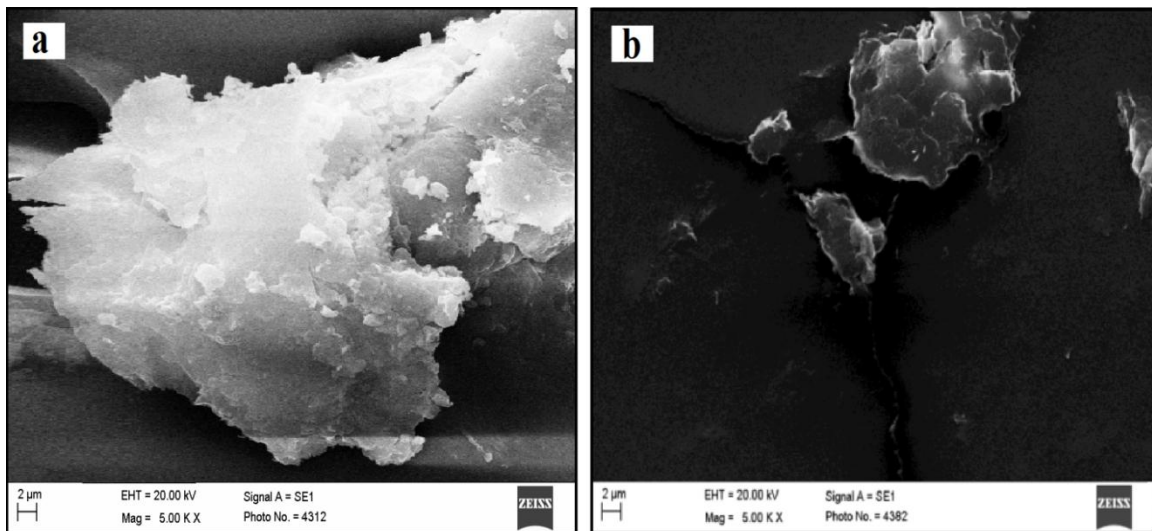


Fig. 5.42: CR-M-asphalt (a), CR-g-MAH-modified asphalt (b)

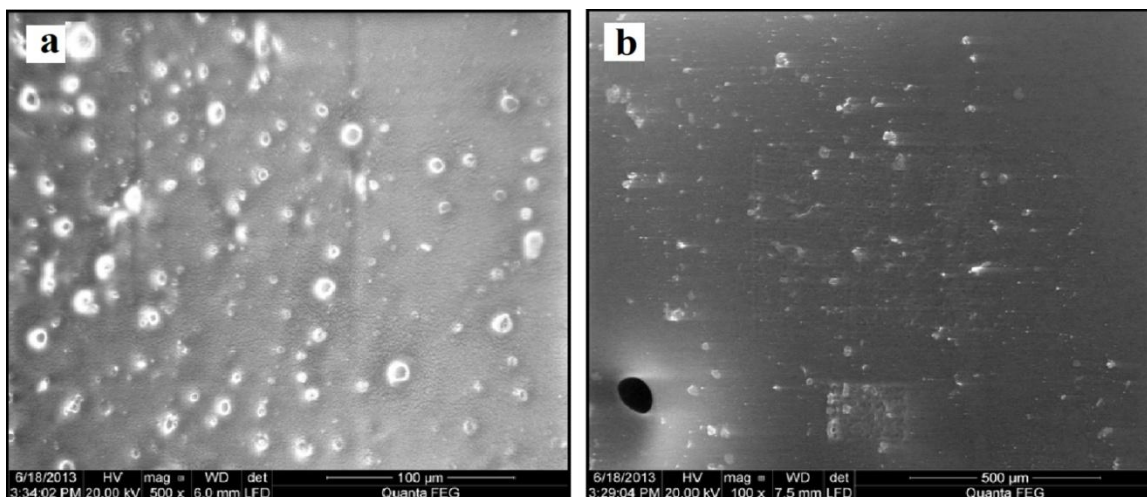


Fig.5.43: LDPE- M- asphalt (a), LDPE-g-MAH-modified asphalt (b)

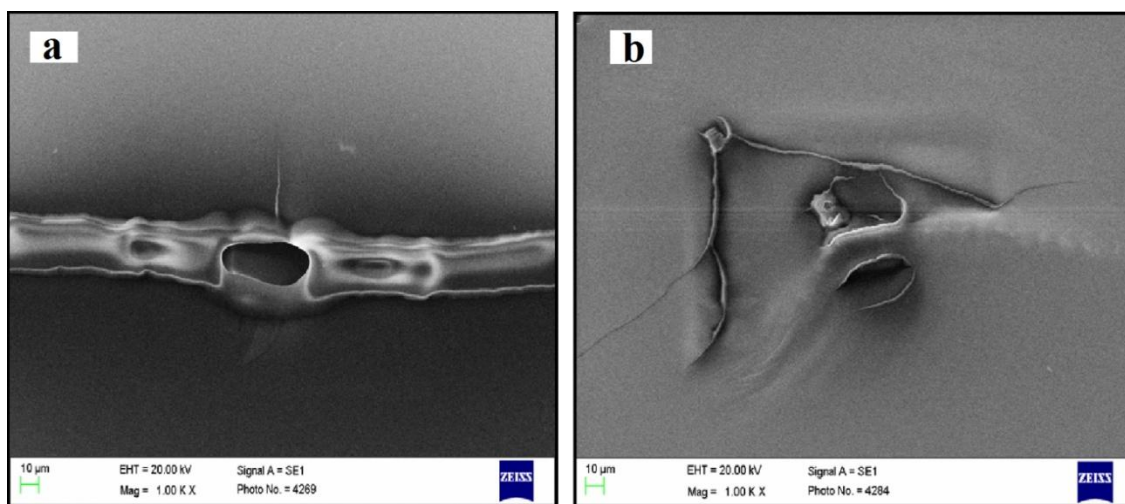


Fig.5.44. TF-Modified asphalt (a), TF-g-MAH-modified asphalt (b)

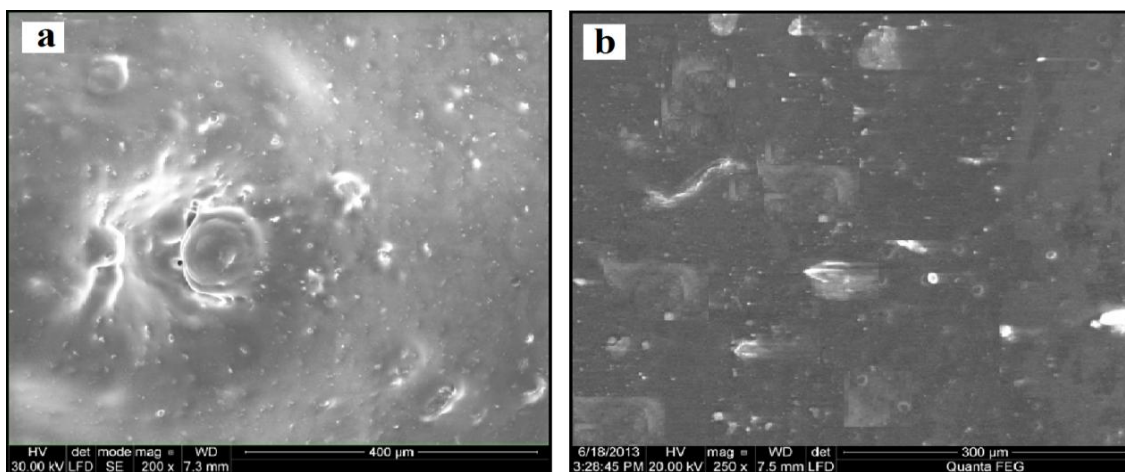


Fig. 5.45: (CR:LDPE)-M-asphalt (a), (CR:LDPE)-g-MAH-M asphalt (b)

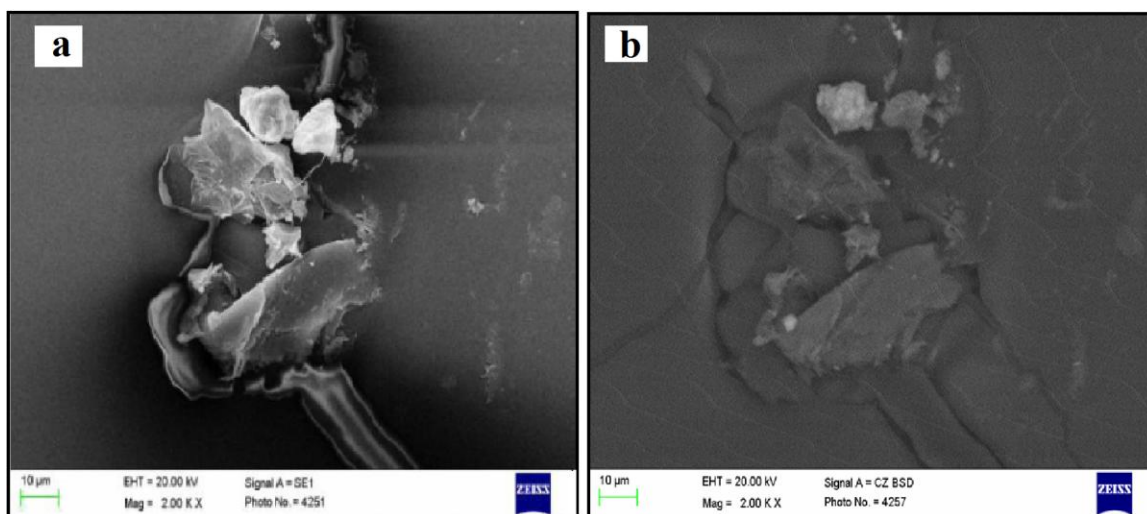


Fig. 5.46: CR:TF-M-asphalt (a), CR:TF-g-MAH-Modified asphalt (b)

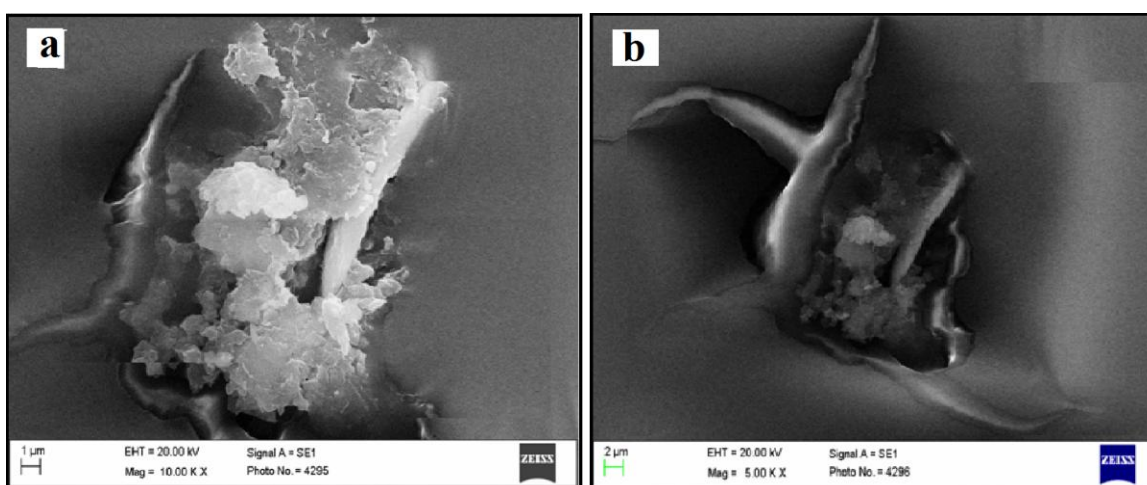


Fig. 5.47: (CR:LDPE:TF)-M-asphalt (a), (CR:LDPE:TF)-g-MAH-M-asphalt (b)

CHAPTER SIX

6.1. CONCLUSION

As expected, the applications of modifiers such as recycled CR, TF, and commercial LDPE in modifications of asphalt binders have significantly proven to improve characteristics of asphalt binders. Basic physical properties such as softening point, penetration degree, viscosity, and rheological properties such as loss modulus, storage modulus, complex modulus, and phase angle were among these characteristics. This subsequently improves the rutting resistance, resilience, and fatigue cracking resistance of asphaltic mixes. In order to achieve a superior and balanced modified

asphalt binders by the intended modifiers CR, LDPE, TF in terms of high and low-temperature properties, factors such as the mixing time, temperature, characteristics, and concentration levels of the modifiers and ratio of blends among modifiers when used as composites must be considered, since these are the factors that govern the resulting performance of asphaltic mixes.

Concerning the part of the study related to the maleation of the asphalt binders, the results have indicated that maleated asphalt can be effectively employed as an alternative to virgin asphalt in minimizing the phase separation via its coupling with CR, LDPE, and TF and, consequently, the improved performance of maleated M-asphalt blends during storage/application. The increase in the degree of maleation leads to increasing viscoelastic properties of the resulting blend systems. Using maleated asphalt, the recoverable blends composed of recycled CR and TF as well as virgin LDPE exhibited adequate softening point and low-temperature flexibility.

Based upon the experimental results of this study, the following major conclusions were drawn:

1. The results of the study show that CR and TF obtained from used tires without any previous use of chemical treatment can be successfully used as asphalt modifiers.
2. The best content level was found to be 10% by weight for components A, D, F, and H, respectively, while 5% for both components B and C.
3. In case of composite materials composed CR:LDPE, CR:TF, and CR:LDPE:TF, the best weight fraction was found to be 3:1.
4. Modifier type and its content levels were playing the major factors on the process of asphalt polymer blends.
5. Modification index in percentage for softening point was found to be 119%, 120%, 116%, and 113%, 111%, and 118% for components A3, B2, C2, D3, F3, and H3, respectively, while modification index for penetration values were found to be 58%, 51%, 59%, 62%, 60%, and 57%, respectively.
6. Ductility of modified asphalt decreased from 100cm for virgin asphalt to 50cm, 30cm, 58cm, 77cm, 75cm, and 66cm for components A3, B2, C2, D3, F3, and H3, respectively, while elastic recovery were increased from 5% for virgin asphalt to

38%, 42%, 38%, 44%, 45%, and 48% for components A3, B2, C2, D3, F3, and H3, respectively.

7. The rates of swelling were increased in the range of 2.2-5.3 times, depending on the modifier types, while the extrusion of CR shows the highest swelling rate.
8. Breakpoint at the best content level was decreased from -11°C for virgin asphalt to -15°C for component A3, -12°C for both components B2 and C2, while -14°C for both components D3 and F3, and -13°C for component H3.
9. According to the TGA analysis, there is no change in the decomposition behavior of all modified asphalt samples compared to the control sample.
10. From the first part of the study “without maleic anhydride addition”, the rheological behavior parameters, which are elastic component G' and viscous component G'' , were improved at the whole range of temperature, for instance at a temperature of 60°C the rate of increasing is estimated to be in the range of 2.25 to 7.0 times for G' and 2.0 to 4.20 times for G'' , while complex modulus G^* and rutting resistance parameter $G^*/\sin \delta$ were ranged of 2.07 to 4.36 times and 2.08 to 4.53 times, respectively, at the same temperature dependent on the modifier types. Phase separation has been improved by the addition of MAH.
11. The viscosity has been enhanced at the whole range of shear rate. At a low shear rate, the enhancing rates were found to be in the range of 2.80 to 20.35 times higher than for virgin asphalt.
12. Ruth depth was tested at 60°C , 9000 cycle and applied load of 700N for only components D, F, and H, at content level of 5%. According to the results and data obtained, the Ruth depth was reduced by 54.48%, 44.82%, and 57.93%, respectively.
13. From a compatibility point of view, the addition of maleic anhydride in asphalt blends enhanced the viscosity at the whole range of shear rate; for instance, at a low shear rate the enhancing rates were found to be in the range of 3.34 to 59.69 times, which is depending on the modifier types.
14. After addition of maleic anhydride, the rheological behavior parameters were improved at the whole range of temperature; for instance, at 60°C the rate of increase is estimated to be in the range of 2.46 to 86.07 and 4.78 to 27.47 for G' and G'' , respectively. G^* and $G^*/\sin \delta$ were in the range of 4.71 to 32.48 times and 4.63 to

38.41 times, respectively. On the other hand, $\text{Tan } \delta$ was decreased from 4.7 up to 2.8, depending on the modifier types.

15. As a result, and from an environmental and economic point of view, the use of both CR and TF, instead of virgin polymers, is a possible and preferable recycling method for these wastes, as it results in cost saving, lower energy consumption, and lower environmental pollution, as well as reduction of mass and volume of solid waste.
16. It is also possible to imagine the possibility of disposing of waste plastics such as low-density polyethylene bags within road asphalts, since similarity in performance is found between recycled polymers and virgin polymer modified asphalt.
17. Admixture additive modified asphalt sometimes has remarkable advantages over single modifiers at the same total content with respect to the storage stability and rheological properties.
18. The addition of small amounts of expensive virgin polymer like polyethylene to larger amounts of cheaper materials like crumb rubber or textile fiber obtained from recycled tires can be a cost-effective system.

Finally, I believe, being the author behind the preparation of this thesis, that the widespread use of the M-asphalt technologies by the incorporation of CR, LDPE, and TF in the form of binary, ternary and quaternary asphalt polymer blends within the road pavement industry is very advisable. In fact, the several benefits provided to the asphalt pavement performance and to the overall sustainability of the infrastructure are so evident that it is strongly advised to consider M-asphalt binder technologies using the intended modifiers as a first option to the asphalt binder currently used in road pavements. Companies, road authorities, etc., have to evaluate if it is convenient to use in particular the ternary and quaternary asphalt-polymer blend technology, which considered novelty and proved to provide several benefits. In particular, it allows roadway designers to reduce pavement failures faced after constructions due to the proven properties of M-asphalt, and it reduces the heavy burden on the environment created by the land-filling disposal of the solid wastes such as exhausted automobile tires and others made of LDPE. However, the technology presents some challenges such as the need for suitable blending and mixing equipment, the cost of such equipment and the degree of difficulty in preparing asphalt mix design.

REFERENCES

- [1] **Kanabar Amit (2010)** Physical and Chemical Aging Behavior of Asphalt Cement from Two Northern Ontario Pavement, *A Thesis Submitted to the Department of Chemistry in Conformity with the Requirement for the Degree of Master of Science*, Queen's University, Kingston-Ontario-Canada.
- [2] **American Society for Testing and Materials** *Annual Book of ASTM Standards*, Section 4, Construction, Volume 4.03 Road and Paving Materials, Pennsylvania, **1998**.
- [3] **Freemantle M. (1999)**. *Chem. Eng. News*, 77(47) 81.
- [4] **Read J. and Whiteoak D. (2003)** *The Shell Bitumen Handbook*, fifth edition; Hunter, R. N. (Ed.); Thomas Telford: London.
- [5] **Available online at:** <http://www.bitumina.co.uk/whatisbitumen.html>
- [6] **Mavridou S., Oikonomou N., A. Kalofotias (2010)** Integration of End-of-Life Tires in the Life Cycle of Road Construction "ROADTIRE". Thessaloniki, December 2010.
- [7] **Morgan P., Mulder A. (1995)**. *The Shell Bitumen Industrial Handbook*. Surrey: Shell Bitumen.
- [8] **Zhu J., Birgisson B., Kringos N. (2014)** Polymer Modification of Bitumen: Advances and Challenges. *European Polymer Journal*, 54: 18-38, available online at <http://dx.doi.org/10.1016/j.eurpolymj>
- [9] **Asphalt History:** Available online at: <http://www.simivalleyasphalt.com/id15.html>
- [10] **Available online at:** <http://www.bitumina.co.uk/bitumen-production.html>
- [11] **Mashaan N. S., Asim H.A., Mohamed R.K., and Mahrez A. (2014)** A Review on Using Crumb Rubber in Reinforcement of Asphalt Pavement, *The Scientific World Journal*, Vol. 2014, Article ID 214612, Hindawi Publishing Corporation.
- [12] **Mclean J.D. and Kilpatrick P.K. (1997)** Comparison of Precipitation and Extrography in the Fractionation of Crude oil Residue, *Energy and Fuel*, II (3): 570-585.
- [13] **American Standard Test Methods (ASTM) International (ASTM) (2009)** Standard Test Methods for Separation of Asphalt into Fractions, *Annual Book of ASTM standards*, D 4124 – 01, *Road and Paving Materials*; Vesicles Pavement Systems, 04.03, West Conshohocken, Pennsylvania, USA.
- [14] **Claudy P., Letoffe J.M., King G.N., Planche J.P., and Brule B (1991)** Characterization of Paving Asphalt By Differential Scanning Calorimetry, *Fuel Science and Technology International*, 9: 71-92.
- [15] **Navarro F.J., Partal P., Martinez-Poza F., Valecia C., and Gallegos C. (2002)** Rheological Characteristics of Ground Tire Rubber-Modified Bitumens, *Chemical Engineering Journal*, 89: I-3, 53-61.
- [16] **Lewandoski L.H. (1994)** Polymer Modification of Paving Asphalt Binders, *Rubber Chemistry and Technology*, 67(3): 447-480.



- [17] **Krebs R.D. and Walker R.D. (1971)** *Highway Materials*, McGraw-Hill, New York, NY, USA.
- [18] **Loeber L., Muller G., Morel J., and Sutton O. (1998)** Bitumen in Colloid Science: A Chemical, Structural and Rheological Approach, *Feul*, 77(13): 1443-1450.
- [19] **Girdler, R.B. (1965)** *In Proceeding of the Association of Asphalt Paving Technologists*, 34: 45.
- [20] **Roberts F.L., Kandhal P.S., Brown E.R., and Dunning R.L. (1989)** Investigation and Evaluation of Ground Tire Rubber in Hot-Mix Asphalt. Alabama, USA: NCAT Auburn University.
- [21] **Adedeji A., Grunfelder T., Bates F. S., Macosko C. W., Stroup-Gardiner M. and Newcomb D.E. (1996)** Asphalt Modified By Tri-Block Copolymer: Structures and Properties, *Polymer Engineering & Science*, 36(12): 1707–1723.
- [22] **Vinogradov G.V. and Malkin A. Ya (1980)** Rheology of Polymer, Report No. 145, Moscow Department of Transportation.
- [23] **Bahia H. and Davies R. (1994)** Effect of Crumb Rubber Modifiers (CRM) on Performance-Related Properties of Asphalt Binders, *Proceedings of the Association of Asphalt Paving Technology* 63: 414-449.
- [24] **Anderson D.A. (1994)** Binder Characterization, Strategic Highways Research Program, SHRP-A-369.
- [25] **Airey G.D. (1997)** Rheological Characterization of Polymer Modified and Aged Bitumen's, PhD Thesis, University of Nottingham, UK.
- [26] **Farag K. M. H. (2010)** Evaluation of Fatigue Resistance for Modified Asphalt Concrete Mixtures Based on Dissipated Energy Concept, *PhD Thesis, Technical University of Darmstadt*.
- [27] **Anderson D.A., Christensen D.W., Roque R., and Robyak R.A. (1992)** Rheological Properties of Polymer-Modified Emulsion Residue, *ASTM STP 1108*, pp. 20-34.
- [28] **Navarro F. J., Partal P., Mart´inez-Boza F. J. and Gallegos C. (2007)** Influence of Processing Conditions on the Rheological Behavior of Crumb Tire Rubber-Modified Bitumen, *Journal of Applied Polymer Science*, 104(3): 1683–1691.
- [29] **Gawande A., Zamare G., Renge V.C., Tayde S., and Bharskale G. (2012)** An Overview on Waste Plastic Utilization in Asphaltting of Roads., *Engineering Research and Studies Journal*, 3(2): 1-5.
- [30] **Rutting and Fatigue Specifications for Asphalt**, accessed (November 2010) at <http://www.engr.wisc.edu/centers/wsmtl/WSMTL-WEB-pg02P-NEWS-Delgadillo.html>
- [31] **Scrap Tire Markets in the United States” Rubber Manufacturers Association” 9th Biennial Report(May 2009)** Washington, DC. <http://www.rma.org>

- [32] **Sudha R. and Rajesh A. (2014)** Recycling of Scrap Tires. *International Journal of Materials Science and Application*, 3(5): 164-167.
- [33] **Europe Plastics – The Fact 2014/2015: An Analysis of European Latest Plastics Production, Demand and Waste Data**, Brussels – Belgium: Plastic Europe, 2013.
- [34] **Association of Plastics Manufacturers in Europe (APME) (2004)** Plastic Recovery in Western Europe. < www.plasticeurope.org >
- [35] **Rafat Siddique A., Jamal Khatib B, Inderpreet Kaur (2008)** Use of Recycled Plastic in Concrete: A Review, *Waste Management*; 28: 1835–1852.
- [36] **Subramanian P.M. (2000)** Plastic Recycling and Waste Management in the US. *Resource, Conservation and Recycling*; 28: 253-263.
- [37] **Kiresten Norquay (July 2004)** End of Life Tire Management: Storage Options, *Final Report for the Ministry of the Environment*, MWH New Zealand Ltd., Project No. 801/008288.
- [38] **EEC (Environmental Engineering and Contracting, Inc.) (23rd September 2002)** Tire Pile Fires: Prevention, Response, Remediation, Santa Ana California, USA.
- [39] **Reschner K. (2008)** Scrap Tire Recycling: A Summary of Prevalent Disposal and Recycling Methods, Berlin, Germany, K.Reschner@EnTire-Engineering.de
- [40] **Biswanath Prusty (2012)** Use of Waste Polyethylene in Bituminous Concrete Mixes, *Department of Civil Engineering, NIT Rourkela, National Institute of Technology, Roukela-769008(ODISHA)*.
- [41] Available online at: www.Plastic-Pollution.org
- [42] **Mui E.K., Lee V.C., Cheung W.H., and McKay G. (2008)** Kinetics Modeling of Waste Tires Carbonization. *Energy Fuel*, 22: 1650-1657.
- [43] **Rozada F., Otero M., Moran A., and Garcia A. (2005)** Activated Carbons from Sewage Sludge and Discarded Tires: Production & Optimization. *J. Hazard. Mater.* 124: 181-191.
- [44] **Fuentes-Auden C., Sandoval J.A., Jerez A., Navarro F.J., Martinez-Boza F. and Partal P. (2008)** Evaluation of Thermal and Mechanical Properties of Recycled Polyethylene Modified Bitumen. *Polym. Test.* 27: 1005-1012.
- [45] **Xiao F., Amerikanian S.N., and Putman B. (2006)** Laboratory Investigation of Dimensional Changes of Crumb Rubber with Asphalt Binder, *Proceedings of Asphalt Rubber Conference, California Palm Springs 2006*, pp. 693-715.
- [46] **Davide Lo Presti (2013)** Recycled Tire Rubber Modified Bitumens for Road Asphalt Mixtures: A literature review, *Construction and Building Materials*, 49: 863–881.
- [47] **Kalantar Z. N., Karim M. R., Mahrez A. (2012)** A Review of Using Waste and Virgin Polymer in Pavement, *Construction and Building Materials*, 33, 55-62.

- [48] **Sunthonpagasit N., Duffey M. (2004)** Scrap Tires to Crumb Rubber Feasibility Analysis for Processing Facilities, *Resource Conservation and Recycling Journal*, 40: 281-299.
- [49] **Takallou H.B. and Takallou M.B. (2003)** Effects of Mixing Time and Temperature on the Visco-elastic Properties of Asphalt Rubber Binder, *Asphalt Rubber 2003 – Proceedings*, Brazil, pp: 589-602.
- [50] **Dantas Neto, S.A. (2004)** Evaluation of the Properties of Binders and Mixes Modified with Crumb Rubber from Used Tires. (In Portuguese) *PhD Thesis, University of Brasilia, Department of Civil and Environmental Engineering, Brazil*.
- [51] **Winter, R.E. (1989)** The Conception of Development of Asphalt Rubber, *Presented at the National Seminar on Asphalt Rubber*, Kanass City Missouri-USA.
- [52] **Huffman J.E. (1980)** Sahuaro Concept of Asphalt Rubber, *Presented at the First Asphalt Rubber User Producer Workshop*, Scotsdate Arizona-USA.
- [53] **Puerto Rico Highway and Transportation Authority, PHTA (1994)** Feasibility of Using Crumb Rubber in Hot-Mix Asphalt Pavement Application in Puerto Rico, Final Report.
- [54] **Clean Washington Center, CWC (1998)** Best Practices in Scrap Tires and Rubber Recycling-Ambient versus Cryogenic Grinding, *Clean Washington Center, Best Practices*, BP-T203-04.
- [55] **Mashaan N. S., Ali A.H., and Abdelaziz M. (2011)** Effect of Blending Time and Crumb Rubber Content on Properties of Crumb Rubber Modified Asphalt Binder. *International Journal of Physics Science*, 6(9): 1289-21293.
- [56] **Mahrez A. (1999)** Properties of Rubberized Bitumen Binder and its Effect on the Bitumenous Mix (M.S. Thesis) Faculty of Engineering, University of Malaya, Kuala Lumpur, Malaysia.
- [57] **Labib M.E., Memon G.M., and Cholla B.H. (1996)** Compatabilizers for Crumb Rubber Modified Asphalt, Orlando, pp: 1209 – 1213.
- [58] **Mashaan N. S., and Karim M.R. (2013)** Investigating the Rheological Properties of Crumb Rubber Modified Bitumen and its Correlation with Temperature Susceptibility, *Material Research Journal*, 16(1): 116–127.
- [59] **Hossian M., Swartz S., and Hoque E. (1999)** Fracture and Tensile Characteristics of Asphalt-Rubber Concrete, *Journal of Materials in Civil Engineering*, 11(4): 287-294.
- [60] **Liu S., Cao W., Fang J., and Shang S. (2009)** Variance Analysis and Performance Evaluation of Different Crumb Rubber Modified (CRM) Asphalt, *Construction and Building Materials*, 23(7): 2701-2708.
- [61] **Leite L.F.M., and Soares B.G. (1999)** Interaction of Asphalt with Ground Tire Rubber, *Petroleum Science and Technology*, 17:(9-10) 1071–1088.
- [62] **Sun D.Q., and Li L.H. (2010)** Factors Affecting the Viscosity of Crumb Rubber-Modified Asphalt,” *Petroleum Science and Technology*, 28(15): 155–1566.

- [63] **Shen J., Amirkhanian S., Xiao F., and Tang B. (2009)** Influence of Surface Area and Size of Crumb Rubber on High Temperature Properties of Crumb Rubber Modified Binders, *Construction and Building Materials*, 23(1): 304-310.
- [64] **Abdelrahman M.A., and Carpenter H. (1999)** Mechanism of Interaction of Asphalt Cement with Crumb Rubber Modifier, *Transportation Research Record*, No.1661, 106-113.
- [65] **Airey G.D., Rahman M.M., and Collop A.C. (2003)** Absorption of Bitumen into Crumb Rubber Using the Basket Drainage Method, *International Journal of Pavement Engineering*, 4(2): 105-119.
- [66] **Yildirim Y. (2007)** Polymer modified asphalt binders. *Construction and Building Materials*; 21(1): 66-72.
- [67] **Utracki., L.A. (1995)** History of Commercial Polymer Alloys and Blends. *Polymer Engineering and Science*; 35(1): 2-17.
- [68] **Legge N.R. (1987)** Thermoplastic Elastomers. *Rubber Chemistry and Technology*; 60(3): 83-117.
- [69] **Johnson R. (1987 April 16-17)** History and Development of Modified Bitumen. In: Proceedings of the 8th Conference on Roofing Technology, Gaithersburg, Maryland. Rosemont, Illinois: National Roofing Contractors Association, 81-84.
- [70] **Anderson A.P., Nelson W.K. (1940 April 16)** Shell Development Company, Assignee. Bituminous Composition. United States patent US 2197461.
- [71] **Rostler F.S., White R.M., and Cass P.J. (1972)** Modification of Asphalt Cements for Improvement of Wear Resistance of Pavement Surfaces. Washington, D.C.: Federal Highway Administration; Report No.: FHWA-RD-72-24 Final Rpt.
- [72] **Zenke, G. (1976)** On the Use of Polymer-Modified Bitumen in Asphalt Mixes. *Stationaere Mischwerk*; 10(6): 255-264.
- [73] **Kameau G., Duron M. (1976)** Influence of Static and Sequenced Elastothermoplastic Copolymers on the Mechanical Properties of Bituminous Mixtures. Bulletin de Liaison des Laboratoires des Ponts et Chaussées; (18): 135-139.
- [74] **Chaffin C.W., O'Connor D.L., and Hughes, C.H. (1978)** Evaluation of the Use of Certain Elastomers in Asphalt. Washington, D.C.: *Federal Highway Administration*; Report No.: FHWA-TX-78180-1F Final Rpt.
- [75] **Piazza S., Arcozzi A., and Verga C. (1980)** Modified Bitumens Containing Thermoplastic Polymers. *Rubber Chemistry and Technology*; 53(4): 994-1005.
- [76] **Kraus G. (1982)** Modification of Asphalt by Block Polymers of Butadiene and Styrene. *Rubber Chemistry and Technology*; 55(5): 1389-1402.
- [77] **Denning J.H. and Carswell J. (1983)** Assessment of Novophalt as a Binder for Rolled Asphalt Wearing Course. Crowthorne, England: *Transport and Road Research Laboratory*; 1983. Report No.: TRRL Laboratory Report 1101.
- [78] **Milkowski, W. (1985)** Catalytic Modification of Road Asphalt by Polyethylene. *Journal of Transportation Engineering*; 111(1): 54-72.

- [79] Jew J., Shimizu J.A., Svazic M., and Woodhams R.T. (1986) Polyethylene-Modified Bitumen for Paving Applications. *Journal of Applied Polymer Science*; 31(8): 2685-2704.
- [80] Bowering R.H. (1984 August 27 – 28) Modified Bitumens. In: *Proceedings of the Australian Asphalt Pavement Association Conference 84*, Members Conference; Hobart, Tasmania. Kew, Victoria: Australian Asphalt Pavement Association.
- [81] Reese R. and Predoehl N.H. (1989 September) Evaluation of Modified Asphalt Binders - Interim report. Washington, D.C.: Federal Highway Administration; Report No.: FHWA/CA/TL-89/15.
- [82] Wardlaw K.R., Shuler S. (eds.) (1992) Polymer Modified Asphalt Binders. Philadelphia, Pennsylvania: *American Society for Testing and Materials*.
- [83] Aglan, H. (1993) Polymeric Additives and Their Role in Asphaltic Pavements. Part I: Effect of Additive Type on the Fracture and Fatigue Behavior. *Journal of Elastomers and Plastics*; 25(4): 307-321.
- [84] Bahia H.U. and Anderson D.A. (1993 March 22-24) Glass Transition Behavior and Physical Hardening of Asphalt Binders (with discussion) In: Asphalt Paving Technology, *Journal of the Association of Asphalt Paving Technologists*; Austin, Texas. St. Paul, Minnesota: Association of Asphalt Paving Technologists; 93-129.
- [85] Valkering C.P. and Vonk W. (1990 August 26-31) Thermoplastic Rubbers for the Modification of Bitumens: Improved Elastic Recovery for High Deformation Resistance of Asphalt Mixes". In: *Proceedings of the 15th Australian Road Research Board (ARRB) Conference*; Darwin, Northern Territory. Vermont South, Victoria: Australian Road Research Board; 1-19.
- [86] Krutz N.C., Siddharthan R., and Stroup-Gardiner M. (1991) Investigation of Rutting Potential Using Static Creep Testing on Polymer-Modified Asphalt Concrete Mixtures. Transportation Research Record: *Journal of the Transportation Research Board*; 1317: 100-108.
- [87] Stock A.F. and Arand W. (1993 March 22-24) Low Temperature Cracking in Polymer Modified Binders. In: Asphalt Paving Technology: *Journal of the Association of Asphalt Paving Technologists*; Austin, Texas. St. Paul, Minnesota: Association of Asphalt Paving Technologists; 23-53.
- [88] Lu X., Isaacson U., and Ekblad. J. (1999) Phase Separation of SBS Polymer Modified Bitumens: *Journal of Materials in Civil Engineering*; 11(1): 51-57.
- [89] Giavarini C., De Filippis P., Santarelli M.L., and Scarsella M. (1996) "Production of Stable Polypropylene-Modified Bitumens. *Fuel*; 75(6): 681-686.
- [90] Lesueur D. (2009) The Colloidal Structure of Bitumen: Consequences on the Rheology and on the Mechanisms of Bitumen Modification. *Advances in Colloid and Interface Science*; 145(1-2): 42-82.
- [91] Lesueur D., Gérard J.F., Claudy P., Létoffé J.M., Martin D., Planche J.P. (1998) Polymer Modified Asphalts as Viscoelastic Emulsions. *Journal of Rheology*; 42(5): 1059-1074.



- [92] Redelius P. (2004) Bitumen Solubility Model Using Hansen Solubility Parameter. *Energy & Fuels*; 18(4): 1087-1092.
- [93] Redelius P. (2009) Asphaltenes in Bitumen, What They Are and What They Are Not. *Road Materials and Pavement Design*; 10(sup1): 25-43.
- [94] Wen G., Zhang Y., Zhang Y., Sun K., Fan Y. (2002) Improved Properties of SBS-Modified Asphalt With Dynamic Vulcanization. *Polymer Engineering & Science*; 42(5): 1070-1081.
- [95] Wen G., Zhang Y., Zhang Y., Sun K., Chen Z. (2001) Vulcanization Characteristics of Asphalt/SBS Blends in the Presence of Sulfur. *Journal of Applied Polymer Science*; 82(4): 989-996.
- [96] Ouyang C., Wang S., Zhang Y., and Zhang Y. (2006) Improving the Aging Resistance of Styrene-butadiene-Styrene Tri-Block Copolymer Modified Asphalt by Addition of Antioxidants. *Polymer Degradation and Stability*; 91(4): 795-804.
- [97] Li Y., Li L., Zhang Y., Zhao S., Xie L., and Yao S. (2010) Improving the Aging Resistance of Styrene-Butadiene-Styrene Tri-Block Copolymer and Application in Polymer Modified Asphalt. *Journal of Applied Polymer Science*; 116(2): 754-761.
- [98] Dessouky S., Contreras D., Sanchez J., Papagiannakis A.T., and Abbas A. (2013) Influence of Hindered Phenol Additives on the Rheology of Aged Polymer-Modified Bitumen. *Construction and Building Materials*, 38: 214-223.
- [99] Ouyang C., Wang S., Zhang Y., Zhang Y. (2005) Preparation and Properties of Styrene-Butadiene-Styrene Copolymer/Kaolinite Clay Compound and Asphalt Modified with the Compound. *Polymer Degradation and Stability*; 87(2): 309-317.
- [100] Ouyang C., Wang S., Zhang Y., Zhang Y. (2006) Thermo-Rheological Properties and Storage Stability of SEBS/Kaolinite Clay Compound Modified Asphalts. *European Polymer Journal*; 42(2): 446-457.
- [101] Yu J., Wang L., Zeng X., Wu S., Li B. (2007) Effect of Montmorillonite on Properties of Styrene-Butadiene-Styrene Copolymer Modified Bitumen. *Polymer Engineering Science*; 47(9): 1289-1295.
- [102] Yvonne Becker, Müller A.J., Rodriguez Y. (2003) Use of Rheological Compatibility Criteria to Study SBS Modified Asphalts. *Journal of Applied Polymer Science*; 90(7): 1772-1782.
- [103] Jianying Yu, Peiliang Cong and Shaopeng Wu (2009) Laboratory Investigation on the Properties of Asphalt Modified with Epoxy Resin, *Journal of Applied Polymer Science*, 113: 3557 – 3563.
- [104] Fu H., Xie L., Dou D., Li L., Yu M., Yao S. (2007) Storage Stability and Compatibility of Asphalt Binder Modified by SBS Graft Copolymer". *Construction and Building Materials*; 21(7): 1528-1533.
- [105] Stroup-Gardiner M., and Newcomb D.E. (1995 Sept.) Polymer Literature Review. St. Paul, Minnesota: Minnesota Department of Transportation; Report No.: MN/RC-95/27.

- [106] **Isacsson U. and Lu X. (1995)** Testing and Appraisal of Polymer Modified Road Bitumens – State of the Art. *Materials and Structures*; 28(3): 139-159.
- [107] **Lu X. (1997)** Polymer Modified Road Bitumens, [Doctoral dissertation]. Stockholm: *KTH Royal Institute of Technology*.
- [108] **Chen J.S., Liao M.C., and Shiah M.S. (2002)** Asphalt Modified by Styrene-Butadiene-Styrene Tri-Block Copolymer: Morphology and Model. *Journal of Materials in Civil Engineering*; 14(3): 224-229.
- [109] **Zhang F. and Yu J. (2010)** The Research for High-Performance SBR Compound Modified Asphalt. *Construction and Building Materials*; 24(3): 410-418.
- [110] **Pérez-Lepe A., Martínez-Boza F.J., Gallegosa C., Gonzálezb O., Muñoz M.F., Santamaría A. (2003)** Influence of the Processing Conditions on the Rheological Behavior of Polymer-Modified Bitumen. *Fuel*; 82(11): 1339-1348.
- [111] **Yvonne Becker, Maryro P. Méndez, Yajaira Rodríguez (2001)** Polymer modified asphalt. *Vision Tecnológica*; 9(1):39-50.
- [112] **Lewandowski L. H. (1994)** Polymer Modification of Paving Asphalt Binders, *Rubber Chemistry and Technology*, 67 (3): 447.
- [113] **Ali N., Zahran S., Trogdon J., Bergan A. (1994)** A Mechanistic Evaluation of Modified Asphalt Paving Mixtures, *Canadian Journal of Civil Engineering*, Vol. 21, No. 6 : pp. 954-965, DOI: 10.1139/194-101.
- [114] **Hongu T. and Philips G. (1990)** New Fibers Ellis Horwood Series in Polymer Science and Technology. New York: Springer.
- [115] **Mahrez A., Karim M., Katman H. (2003)** Prospect of Using Glass Fiber Reinforced Bituminous Mixes. *J. East Asia Soc. Trans Studies*. 5: 794-807.
- [116] **Shiuh J. and Kuei-Yi L. (2005)** Mechanism and Behavior of Bitumen Strength Reinforcement Using Fibers. *J. Mater. Sci.*, 40: 87-95.
- [117] **Majoryl L. (1986)** Introductory Textile Science. 5th ed. Holet, Rinehart and Winston Pub.
- [118] **Decoene Y. (1990)** Contribution of Cellulose Fibers to the Performance of Porous Asphalts. *Trans. Res. Rec.* 1265: 82
- [119] **Chung, D. (1994)** Carbon Fiber Composite, Newton (USA): Butterworth-Heinmaenn Publishing.
- [120] **Bruce R.W. (2003)** The Pavement Performance and Life-Cycle Cost Impacts of Carbon Fiber Modified Hot Mix Asphalt, *MS Thesis*, Michigan Technological University, 2003.
- [121] **Joon S., Rust J.P., Hamouda H., Kim Y. (2005)** Fatigue Cracking Resistance of Fiber-Reinforced Asphalt Concrete. *Tex. Res.* 75(2): 123-128.
- [122] **Putman B.J. and Amirkhanian S.N. (2004)** Utilization of Waste Fibers in Stone Matrix Asphalt Mixtures. *Resour Cons Recycl.* 42: 265–74.

[123] NJDH (New Jersey Division of Highways) (1976) Reflection Cracking in Bituminous Overlays. *Technical Report*.

[124] Checkthatcar.com. <http://www.checkthatcar.com>

[125] James E. Mark, Burak Erman, and Fredrick R. Eirick (1994) Science and Technology of Rubber, Academic Press Inc.

[126] Rahman M.M. (2004) Characterisation of Dry Process Crumb Rubber Modified Asphalt Mixtures. *Thesis submitted to the University of Nottingham for the degree of Doctor of Philosophy*. s.l.: University of Nottingham, School of Civil Engineering; 2004.

[127] Hassan H.F., Oraimi S.A., Taha R. (2005) Evaluation of Open-Graded Friction Course Mixture Containing Cellulose Fibers Styrene Butadiene Rubber Polymer, *J. Mater. Civil. Eng.* 17: 416-422.

[128] Peltonen P. (1991) Wear and Deformation of Characteristics of Fiber Reinforced Asphalt Pavements. *Construct Build Mater*; 5: 18–22.

[129] Wu S, Ye Q, Li N. (2008) Investigation of Rheological and Fatigue Properties of asphalt mixtures containing polyester fibers. *Construct Build Mater*, 22: 2111–5.

[130] Tapkın S. (2008) The effect of polypropylene fibers on asphalt performance. *Build Environ.* 43: 1065–71.

[131] Lee S.J., Rust J.P., Hamouda H., Kim Y.R., Borden R.H. (2005) Fatigue Cracking Resistance of Fiber-Reinforced Asphalt Concrete. *Textile Res J.* 75: 123–8.

[132] Chen JS, and Lin KY. (2005) Mechanism and Behavior of Bitumen Strength Reinforcement Using Fibers. *J Mater Sci.* 40: 87–95.

[133] Sulyman M., Haponiuk J. and Formela K. (2016) Utilization of Recycled Polyethylene Terephthalate (PET) in Engineering Materials: A Review, *International Journal of Environmental Science and Development*, Vol. 7, No. 2.

[134] The Department of Civil and Structural Engineering (2006) The Use of Recycled Vehicle Tire on Road Paving in Hong Kong, *A thesis Submitted in Partial Fulfillment of the Requirement for the Degree of Master of Philosophy*, The Hong Kong Polytechnic University.

[135] State of California Department of Transportation (Jan 2003) Asphalt Rubber Usage Guide, *Material Engineering and Testing Service-MS # 5*, Sacramento, CA 95819-4612.

[136] Shfabakhsh G.H., Sadeghnejad M., Sajed Y. (2014) Case Study of Rutting Performance of HMA Modified with Waste Rubber Powder. *Construction Materials Journal*, 1: 69-76.

[137] Swapan K. Bagui and Ambarish G. (2012) “Economic and Financial Analysis for Polymer Modified Bitumen”. *Malaysian Journal of Civil Engineering*, 24(1): 96-106.

[138] King G.N., Muncy H.C., and Pruhomme J.B. (1986) Polymer Modified Binder’s Effect on Mix Properties. *Journal of the Association of Asphalt Paving Technologies*, 55: 519-540.

- [139] **Kumar P., Chandra S., and Bose S. (2004)** Rheology of Polymer Modified Bitumen. *Highway Research Bulletin 71*, Indian Roads Congress, pp.119-135.
- [140] **Valkering C.P., Lancon D.J.L., Dehilster E., and Stocker D.A. (1990)** Rutting Resistance of Asphalt Mixes Containing Non-Conventional and Polymer Modified Binders. *Journal of the Association of Asphalt Paving Technologies*, 596: 590-609.
- [141] **Collins J.H., Bouldin M.G., Gelles R. and Berker (1991)** Improvement Performance of Paving Asphalt by Polymer Modification: *Pro. Asso. Asphalt Paving Techol.*, 60:43
- [142] **ASTM (American Society for Testing and Materials) (2005)** *International Annual Book of Standards*, D 8 Definitions.
- [143] **Larry Santucci, PE (2009)** Rubber Roads: Waste Tires Find a Home, Pavement Technology Update, *Technology Transfer Program*, 1(2)
- [144] **Airey G.D., Collop A.C. and Singleton T.M. (2001)** Rheological and Cohesive Properties of Bitumen Cured in Crumb Rubber, In *Proceedings of the International Symposium of Concrete Technology*, University of Dundee, Eds R.K. Dhir, M.C. Limbachiya and K.A. Paine, *Recycling and Reuse of Used Tires*, 281–298.
- [145] **Oikonomou N. and Mavridou S. (2009a)** The Use of Waste Tire Rubber in Civil Engineering Works, in *Sustainability of Construction Materials*, Edited by Jamal Khatid, Chapter 9: 213-238, Woodhead Publishing.
- [146] **Pais J.C., Sousa J.B., Saam R., and Pereire P.A.A. (2001)** Effect of Crumb Rubber Origin on Asphalt Hot Mix Laboratory Performance, In *2nd International Symposium on Maintenance and Rehabilitation of Pavements and Technological Control*, 29 July – 1 August 2001, Auburn, AL, USA, PP. 1 – 10.
- [147] **Punith V.S., Thyagaraj M.N. and Veeraragavan A. (2002)** Studies on Tensile Strength Characteristics of Dense Bituminous Macadam Mix with Crumb Rubber as Modifier, In *Proceedings of the 3rd International Conference on Bituminous Mixtures and Pavements*, Thessaloniki, Greece, pp. 547–556.
- [148] **Rahman M.M., Airey G.D and Collop A.C. (2004)** Laboratory Investigation to Assess Moisture Sensitivity of Dry Process CRM asphalt Mixtures, In *Proceedings of the International Conference Organized by the Concrete and Masonry Research Group*, Kingston University - London, Eds. M.C. Limbachiya and J.J. Roberts, *Sustainable Waste Management and Recycling: Used-Post-Consumer Tyres*, Thomas Telford, pp. 151–162.
- [149] **Tortum A., Celik C., and Aydin A.C. (2005)** Determination of the Optimum Conditions for Tire Rubber in Asphalt Concrete, *Building and Environment*, 40, 1492–1504.
- [150] **Chiu C.-T. (2008)** Use of Ground Tire Rubber in Asphalt Pavements: Field Trial and Evaluation in Taiwan, *Resources, Conservation and Recycling*, 52(3) 522–532.
- [151] **Choubane B., Sholar G.A., Musselman J.A., and Page G.C. (1999)** Ten-Year Performance Evaluation of Asphalt-Rubber Surface Mixes, *Transportation Research Record*, 1681, 10–18.



[152] <http://www.ruberpavement.org>

[153] **Putman B.J., Thompson J.U., Amirkhanian S.N. (2005)** High-Temperature Properties of Crumb Rubber Modified (CRM) Asphalt Binders, *Proceeding of Fourth International Conference on Maintenance and Rehabilitation of Pavements and Technological Control (MAIREPAV4)* Belfast, Northern Ireland.

[154] **Huang B., Mohammad L.N., Graves P.S., and Abadie C. (2002)** Louisiana Experience with Crumb Rubber-Modified Hot-Mix Asphalt Pavement, *Transportation Research Record: Journal of the Transportation Research Board*, No. 1789, 1-13.

[155] **Lee S.-J., Amirkhanian S., Putman B.J., and Kim K.W. (2007)** Laboratory Study of the Effects of Compaction on the Volumetric and Rutting Properties of CRM Asphalt Mixtures, *Journal of Materials in Civil Engineering, ASCE*, 19(12): 1079-1089

[156] **Liang R.Y. and Lee S. (1996)** Short-Term and Long-Term Aging Behavior of Rubber Modified Asphalt Paving Mixtures, *Transportation Research Record: Journal of the Transportation Research Board*, No. 1530, 11-17.

[157] **Blumenthal M. and Serumgard J. (1999)** Overview of Scrap Tire Management and Markets in the United States, *A Meeting of the Rubber Division in Orlando, Florida, September 1999*, by the American Chemical Society.

[158] **Xiao F.P. and Amirkhanian S.N. (2007)** Resilient Modulus Behavior of Rubberized Asphalt Concrete (RAC) Mixtures Containing Reclaimed Asphalt Pavement (RAP), *Road Materials and Pavement Design* (in press).

[159] **Amirkhanian S. and Corley M. (2004)** Utilization of Rubberized Asphalt in the United States: An Overview. *Proceedings of the 4th International Symposium on Advanced Technologies in Asphalt Pavements*, South Korea, 3-13.

[160] **Imad L. Al-Qadi, Jongeun Baek, Zhen Leng, Hao Wang, Matthew Doyen, Jeff Kern and Steven L. Gillen (2012)** Short-Term Performance of Modified Stone Matrix Asphalt (SMA) Produced with Warm Mix Additives, A Report of the Findings of Early-Age Deformation/Rutting of Modified Stone Matrix Asphalt (SMA) Produced with Warm Mix Additives Project, Illinois Center for Transportation, USA.

[161] **Chandra Kiran Kumar Akisetty (2008)** Evaluation of Warm Asphalt Additives on Performance Properties of Crumb Binders and Mixtures, *A Dissertation Presented to the Graduate School of Clemson University in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy in Civil Engineering*, P. 13.

[162] **Chowdhury A. and Button J.W. (2008)** A Review of Warm Mix Asphalt, Report 473700-00080-1, *Texas Transportation Institute*, College Station, Texas.

[163] **Prowell B.D., Hurley G.C., and Crews E. (2007)** Field Performance of Warm-Mix Asphalt at National Center for Asphalt Technology Test Track, *Transportation Research Record*, No. 1998, Transportation Research Board, Washington, D.C., pp. 96-102.

[164] **Wasiuddin N.M., Selvamohan S., Zaman M.M., and Guegan M.L. (2007)** Comparative Laboratory Study of Sasobit and Aspha-Min Additives in Warm-Mix

Asphalt, *Transportation Research Record*, No. 1998, Transportation Research Board, Washington, D.C., pp. 82-88.

[165] **Mallick R.B., Kandhal P.S., and Bradbury R.L. (2008)** Using Warm-Mix Asphalt Technology to Incorporate High Percentage of Reclaimed Asphalt Pavement Material in Asphalt Mixtures, *Transportation Research Record*, No. 2051, Transportation Research Board, Washington, D.C., pp. 71-79.

[166] **Lee SJ, Akisetty CK, Amirkhanian SN. (2008)** The Effect of Crumb Rubber Modifier (CRM) on the Performance Properties of Rubberized Binders in HMA Pavements, *Constr. Build. Mater. J.*, 22(7): 1368–76.

[167] **Xiao F., Amirkhanian N., and Putman B. (2010)** Evaluation of Rutting Resistance in Warm-Mix Asphalts Containing Moist Aggregate, *Transportation Research Record*, No. 2180, Transportation Research Board, Washington, D.C. pp. 75-84.

[168] **Hurley G. and Prowell B.D. (2006)** Evaluation of Evotherm® for Use in Warm Mix Asphalt, NCAT Report 06-02, National Center for Asphalt Technology, Auburn University, Auburn, Alabama.

[169] **Brown E.R., Haddock J.E., Maliack R.B. and Lynn A.T. (1977)** Development of a Mixture Design Procedure for Stone Matrix Asphalt (SMA), NCAT Report No. 97-3.

[170] **Santucci P.E.L. (2009)** Rubber Roads: Waste Tires Find a Home, Pavement Technology Update, *Pavement Technology Program*, Vol. 1(2).

[171] **Fernandes Jr. J.L., Bertollo S.A.M., Bernucci L.L.B., and E. deMoura (2002)** Laboratory Evaluation of Dense Asphalt Mixtures Modified with Addition of Rubber, In *3rd International Conference on Bituminous Mixtures and Pavements*, J&A Publishers, Thessaloniki, Greece.

[172] **Rubber Rise Asphalt** [online]. Available: <http://www.rubberisedasphalt.org>

[173] **Khalid H.A. and Artamendi I. (2002)** Exploratory Study to Evaluate the Properties of Rubberized Asphalt Modified Using the Wet and Dry Processes, *3rd International Conference on Bituminous Mixtures and Pavements*, J & A Publishers, Thessaloniki, Greece, pp. 15 – 25.

[174] **Kettab R. and Bali A. (2004)** Modified Bituminous Concrete Using Rubber Powder, In *Proceedings of the International Conference organized by the Concrete and Masonry Research Group*, Kingston University, London, Thomas Telford, pp.163 – 170.

[175] **Freddy L. Roberts, Prithvi S. Kandhal, E. Ray Brown and Robert L. Dunning (1989)** Investigation and Evaluation of Ground Tire Rubber in Hot Mix Asphalt, National Center for Asphalt Technology, *NCAT Report* No. 89-3.

[176] **Massucco, J. (1994)** Asphalt Rubber a Federal Perspective. *Proceedings of the Third Material Engineering Conference. New Materials and Methods of Repair*, San Diego, p 467.

[177] **Stroup-Gardiner M., Newcomb D.E., and Tanquist B. (1993)** Asphalt-Rubber Interactions. *Transportation Research Record*. National Academy Press: Washington, D.C., 1417: 99

[178] **Gawel I., Stepkowski R., and Czechowski F. (2006)** Interaction Between Rubber and Asphalt, *Ind. Eng. Chem. Res.*, 45: 3044-3049.

[179] www.rubberpavements.org

[180] **Shen J., Amirkhanian S. (2005)** The Influence of Crumb Rubber Modifier (CRM) Microstructure on High Temperature Properties of Crumb Rubber Modified Binders, *International Journal of Pavement Engineering*, 6(4): 265-271.

[181] **Ould-Henia M. and Dumont A.-G. (2006)** Assessment of the Rheological Properties of Asphalt Rubber Binder and its Residual Phases, *In: Sousa JB, editor. Asphalt Rubber 2006 Conference*. Palm Springs, CA: Consulpav: 931-948.

[182] **Polacco G., Stastna J., Biondi D., Zanzotto L. (2006)** Relation Between Polymer Architecture and Nonlinear Viscoelastic Behavior of Modified Asphalts. *Current Opinion in Colloid & Interface Science*; 11(4): 230 - 245.

[183] **Wen G., Zhang Y., Zhang Y., Sun K., and Fan Y. (2002)** Rheological Characterization of Storage-Stable SBS-Modified Asphalts. *Polymer Testing*; 21(3): 295-302.

[184] **Yeh P.H., Nien Y.H., Chen J.H., Chen W.C., Chen J.S. (2005)** Thermal and Rheological Properties of Maleated Polypropylene Modified Asphalt. *Polymer Engineering & Science*; 45(8): 1152-1158.

[185] **Wang Q., Liao M., Wang Y., and Ren Y. (2007)** Characterization of End-Functionalized Styrene-butadiene-styrene Copolymers and Their Application in Modified Asphalt. *Journal of Applied Polymer Science*; 103(1): 8-16.

[186] **Singh B., Lokesh K., Gupta M., and Chauhan G. S. (2013)** Polymer-Modified Bitumen of Recycled LDPE and Maleated Bitumen, *J. Appl. Polym. Sci.* DOI: 10.1002/app.36810.

[187] **Kanyer R.E. (1999)** Sulfur in Oil Asphalt and Polymer Composition and Process, *Marathon Ash and Petroleum LLC*.

[188] **Kocevski S., Yagneswaran S., Xiao F., Punith V.S., Smith Jr. D.W., and Amirkhanian S. (2012)** Surface Modified Ground Rubber Tire by Grafting Acrylic Acid for Paving Applications, *Construction and Building Materials*, 34(3): 83-90.

[189] **Mull M.A., Stuart K., and Yehia A. (2002)** Fracture Resistance Characterization of Chemically Modified Crumb Rubber Asphalt Pavement, *Journal of Materials Science*, 37(3): 557-566.

[190] **Shatanawi K.M., Biro S., Geiger A., and Amirkhanian S.N. (2012)** Effects of Furfural Activated Crumb Rubber on the Properties of Rubberized Asphalt, *Construction and Building Materials*, 28(1): 96-103.

[191] Cheng G., Shen B., and Zhang J. (2011) A Study on the Performance and Storage Stability of Crumb Rubber-Modified Asphalts, *Petroleum Science and Technology*, Vol. 29, No. 2, pp: 192–200.

[192] Yadollahi G. and Sabbagh Mollahosseini H. (2011) Improving the Performance of Crumb Rubber Bitumen by Means of Poly Phosphoric Acid (PPA) and Vestenamer Additives, *Construction and Building Materials*, Vol. 25, No. 7, pp: 3108–3116.

[193] Ghaly N.F. (2008) Effect of Sulfur on the Storage Stability of Tire Rubber Modified Asphalt, *World Journal of Chemistry*, 3(2): 42-50.

[194] Benjamin C., Jorge V. P., and David D. (1994) Feasibility of Using Crumb Rubber Modified in Hot-Mix Asphalt Pavement Applications in Puerto Rico. *Final Report Submitted to Puerto Rico Highway and Transportation Authority*, Puerto Rico Transportation Technology Transfer Center, University of Puerto Rico Mayaguez Campus.

[195] Chehovits J.G. (1989) Design Methods for Hot Mix Asphalt-Rubber Concrete Paving Materials, presented at the *National Seminar on Asphalt-Rubber*.

[196] Lalwani S., Abushihada A., and Halasa A. (1982) Reclaimed Rubber Asphalt Blends Measurement of Rheological Properties to Assess Toughness, Resiliency, Consistency and Temperature Sensitivity, *Journal of the Association of Asphalt Paving Technologists*, 51: 562–579.

[197] Takallou H. D. (1991) Mix Design Guidelines for Rubber Modified Asphalt Concrete, *Tak Associates, Portland, Ore, USA*.

[198] Green E.L. and Tolonen W.J. (1977) The Chemical and Physical Properties of Asphalt-Rubber Mixtures, *Tech. Rep. ADOT-RS-14 (162)* Arizona Department of Transportation.

[199] Jeong K.D., Lee S.J., Amirkhanian S.N., and Kim K.W. (2010) Interaction Effects of Crumb Rubber Modified Asphalt Binders, *Construction and Building Materials*, 24(5): 824–831.

[200] Billiter T.C., Chun J.S., Davison R.R., and Bullin J.A. (1997) Investigation of the Curing Variables of Asphalt Rubber Binder, *Petroleum Science and Technology*, 15(5-6): 445–469.

[201] Hamed F.K.M. (2010) Evaluation of Fatigue Resistance for Modified Asphalt Concrete Mixture Based on Dissipate Energy Concept. [Ph.D. Thesis], Technische Universitat Darmstadt, Darmstadt, Germany, 2010.

[202] Awwad M.A. and SHbeeb L. (2007) The Use of Polyethylene in Hot Asphalt Mixtures, *American Journal of Applied Sciences*, Vol. 4, no. 6, pp: 390-396.

[203] Hınısliođlu S. and Ađar E. (2004) Use of Waste High Density Polyethylene as Bitumen Modifier in Asphalt Concrete Mix,” *Materials Letters*, Vol. 58, No. 3-4, pp: 267–271.

[204] Casey D., McNally C., Gibney A., and Gilchrist M.D. (2008) Development of a Recycled Polymer Modified Binder for Use in Stone Mastic Asphalt, *Resources Conservation and Recycling*, Vol. 52, No. 10, pp: 1167–1174.



- [205] **García-Morales M., Partal P., Navarro F.J., Martínez-Boza F., Gallegos C., González O., and Munoz M.E. (2004)** Viscous Properties and Microstructure of Cycled EVA Modified Bitumen, *Fuel*, Vol. 83, No. 1, pp: 31-38.
- [206] **Isaacson U. and Lu X. (1999)** Characterization of Bitumens Modified with SEBS, EVA and EBA Polymers, *Journal of Materials Science*, Vol. 34, pp: 3737–3745.
- [207] **Moghaddam T.B, and Karim M.R. (2012)** Properties of SMA Mixtures Containing Waste Polyethylene Terephthalate, *World Academy of Science, Engineering and Technology*, 6: 612–622.
- [208] **Kalantar Z.N., Karim M.R., and Mahrez A. (2012)** A Review of Using Waste and Virgin Polymer in Pavement, *Construction and Building Materials*, Vol. 33, pp: 55–62.
- [209] **Airey G.D. (2003)** Rheological Properties of Styrene Butadiene Styrene Polymer Modified Road Bitumen, *Fuel*, 82: 1709-1719.
- [210] **Sadeghpour Galooyak S., Dabir B., Ehsan Nazarbeygi A., and Moeini A. (2010)** Rheological Properties and Storage Stability of Bitumen/SBS/Montmorillonite Composites, *Constr. Buil. Mater.*, 24: 300-307.
- [211] **Button J.W. and Little D.N. (1998)** Additives Have Potential to Improve Pavement Life (Roads and Bridges: USA)
- [212] **Shukla R.S. and Jain P.K. (1984)** “Improvement of Waxy Bitumen by the Addition of Synthetic Rubbers, Polymer and Resins. *Highway Research Bulletin*, Indian Roads Congress, Delhi) pp: 17 – 28.
- [213] **Mjthab E. I., Hussien A. K., Al-Layla N. M. (2011)** Evaluation of the Properties and Storage Stability of EVA Polymer Modified Asphalt, *J. Edu. & Sci.*, 24(3): 321-328.
- [214] **Pei-Hung Yeh, Yu-Hsun Nien, Wei-Chyum Chen, Wen-Tsung Liu (2010)** Evaluation of Thermal and Viscoelastic Properties of Asphalt Binders by Compounding with Polymer Modifiers, *Polymer Composites*.
- [215] **Sulyman M., Sienkiewicz M., and Haponiuk J. (2014)** Asphalt Pavement Material Improvement: A Review, *International Journal of Environmental Science and Development*, Vol. 5, No. 5.
- [216] **Zoorob S.E. and Suprama L.B. (2000)** Laboratory Design and Investigation of the Properties of Continuously Graded Asphalt Concrete Containing Recycled Plastics Aggregates Replacement (Pastiphalt) *Cement Concrete Composite*, 22: 233-242.
- [217] **Punith V.S., Veeraragavan A., and Amirkhanian S. N. (2011)** Evaluation of Reclaimed Polyethylene Modified Asphalt Concrete Mixtures, *International Journal of Pavement Research and Technology*, Vol.4 No.1.
- [218] **Qadir A. and Imam M. (2005)** Use of Recycled Plastic Waste Aggregates as a Partial Substitution Material in Pavement Structure, In *Proceedings of the International Symposium on Pavement Recycling*.

- [219] **Sinan H., Hatice N.A., Osman U.B. (2005)** Effect of High Density Polyethylene on the Permanent Deformation of Asphalt Concrete. *Indian Journal of Engineering & Material Sciences*, vol. 22, pp. 456-460.
- [220] **Noor Zainab Habib, Ibrahim Kamaruddin, Madzalan Napiah and Isa Mohd Tan. (2011)** Rheological Properties of polyethylene and Polypropylene Modified Bitumen. *International Journal of Civil and Environmental Engineering*, 3 (2).
- [221] **Costa L.M.B., Silva H.M.R.D., Oliveira J.R.M., and Fernandes S.R.M. (2013)** Incorporation of waste plastic in asphalt binders to improve their performance in the pavement, *Int. J. Pavement Res. Technol*, Vol. 6, No. 4, pp: 457-464.
- [222] **Patrick Lavin, P.E. (2003)** Binder Performance, Published Online in Winter Haven, Fla accessed at: www.ARR-MAZ.com
- [223] **Vlachovicova Z., Wekumbura C., Stastna J., and Zanzotto L. (2007)** Creep Characteristics of Asphalt Modified by Radial Styrene-Butadiene-Styrene Copolymer, *Constr. Build. Mater. J.*, 21(3): 567-577.
- [224] **Wong W.G., Haifeng Han, Guiping He, Kelvin C.P. Wang and Weimin Lu (2004)** Rutting Response of Hot Mix Asphalt to Generalized Dynamic Shear Moduli of Asphalt Binder, *Const Buil Mater J.*, 18(6): 399-408.
- [225] **Araujo M., Lins V., Pasa V., Fonseca C. (2012)** Infrared Spectroscopy Study of Photodegradation of Polymer Modified Asphalt Binder, *Journal of Applied Polymer Science*, Vol. 125, 3275-3281.
- [226] **Vasudevan R., Nigam S.K., Velkennedy R., and Sundarakannan B. (without a year)** Utilization of Waste Polymers for Flexible Pavement and Easy Disposal of Waste Polymers, in *Proc. International Conference on Sustainable Solid Waste Management*, Chennai, India, pp. 105-111.
- [227] **Justo C.E.G. and Veeraragavan A. (2002)** Utilization of Waste Plastic Bags in Bituminous Mix for Improved Performance of Roads, Centre for Transportation Engineering, Bangalore University, Bangalore, India.
- [228] **Bindu C.S. and Beena K.S. (2010)** Waste Plastics as a Stabilizing Additive in Stone Mastic Asphalt, *International Journal of Engineering and Technology*, 2(6): 379-387.
- [229] **Khosla N.P. and Trogdon J.T. (1990)** Use of Ground Rubber in Asphalt Paving Mixtures, *Technical Report, Department of Civil Engineering*, North Carolina State University, Raleigh.
- [230] **Goulias D.G. and Ali A.H. (1998)** Asphalt Rubber Mixture Behavior and Des Process, *Journal of Testing and Evaluation*, 26(4): 306-314, American Society of Testing Materials, West Conshohocken, PA.
- [231] **Goulias D.G and A. Ntekim (2001)** Durability of Asphalt Mixtures with Recycled Tire Rubber, *Journal of Solid Waste Technology and Managements*, 27(3 & 4): 170-174, Philadelphia, PA.

[232] **Soon-Jae Lee, Chandra K. Akisetty and Serji N. Amirkhanian (2008)** The Effect of Crumb Rubber Modifier (CRM) on the Performance Properties of Rubberized Binders in HMA Pavements, *Constr. and Build. Mater. J*, 22: 1368–1376

[233] Available online at: <http://www.ruberizedasphalt.org>

[234] Available online at: <http://ladpw.org/epd/tirerecycling/RAC-REAS.cfm>

[235] **Chui-Te Chiu, Li-Cheng Lu (2007)** A Laboratory Study on Stone Matrix Asphalt Using Ground Rubber, *Constr. and Build. Mater. J.*, Vol. 21(5) pp: 1027-1033.

[236] **Paulo A.A. Pereira and Jorge C. Pais (2008)** Laboratory Optimization of Continuous Blend Asphalt Rubber, In *Proceedings of the 3rd European Pavement and Asset Management EPAM 3*. Coimbra, 2008, Vol. 1, pp: 1-12.

[237] **Shankar S., Prasad C.K. (2009)** Evaluation of Rutting Potential for Crumb Rubber Modified Bitumen in Asphaltic Mixes, *Emirates Journal for Engineering Research*, 14(2): 91-95.

[238] **Ganapathi Malarvizhi, N. Senthul and C. Kamaraj (2012)** A Study on Recycling of Crumb Rubber and Low-density Polyethylene Blend on Stone Matrix Asphalt, *Inter J. Sci. Res.*, 2(10)

[239] **Rokade S. (2012)** Use of Plastic and Waste Rubber Tires in Flexible Highway Pavement. *International Conference on Future Environment and Energy*, 28: IACSIT Press, Singapore

[240] **Mashaan N. S., Mohd R. Karim, Asim H. Ali and Mahrez Abdul Aziz (2010)** Influence of Blending Interaction of Crumb Rubber Modified Bitumen on Pavement Properties, In *Proceeding of Malaysian Universities Transportation Research Forum and Conferences 2010 (MUTRFC2010)*, Universiti Tenaga Nasional. ISBN 978-967-5770-08-1 43

[241] **Abdelaziz Mahrez and Mohamed Rehan Karim. (2001)** An Investigation on the Rheological Properties of Rubberized Bitumen, *Proceedings of the Eastern Asia Society for Transportation Studies*, Vol. 3(1).

[242] **Jeong K. D., Lee S. J., Amirkhanian S. N., and Kim K.W. (2010)** Interaction Effects of Crumb Rubber Modified Asphalt Binders, *Construction and Building Materials*, Vol. 24, no. 5, pp:824–831.

[243] **Sulyman M., Haponiuk J., Sienkiewicz M. (2016)** Utilization of Recycled Polyurethane Foam and Ground Tire Rubber for Asphalt Modifications: Basic and Rheological Properties, *2nd World Congress and Expo on Recycling July (25-27) Berlin, Germany*.

[244] **Mashaan N. S., Asim H. A., Mohamed R. K. and Mahrez A. (2012)** An Overview of Crumb Rubber Modified Asphalt, *International Journal of the Physical Sciences Vol. 7(2) pp: 166 - 170*, DOI: 10.5897/IJPSX11.007.

[245] **Waste and Resource Action Programme (WRAP) (2007)** Annual local authorities plastics collection survey.”

- [246] **Kalantar Z.N. (2010)** Properties of Bituminous Binder Modified with Waste Polyethylene Terephthalate, Presented at Malaysia Universities Transportation Research Forum and Conferences, Universiti Tenaga Nasional.
- [247] **Ahmadinia E., Zargar M., Karim M.R., Abdelaziz M. (2012)** Performance Evaluation of Utilization of Waste Polyethylene Terephthalate (PET) in Stone Mastic Asphalt, *Construction and Building Materials*, Vol. 36, pp: 984–989.
- [248] **Koide H., Tomon M., and Sasaki T. (2002)** Investigation of the Use of Waste Plastic as an Aggregate for Lightweight Concrete, *Sustainable Concrete Construction*, London, pp: 177–186.
- [249] **Hassean A. and Ganjidoust H. (2005)** Use of Plastic Waste (Polyethylene Terephthalate) in Concrete Mixture as Aggregates Replacement. *Journal of Waste Management and Research*, 23:(4) 322-327.
- [250] **Jabarin A.S. (1996)** Polyethylene Terephthalate Chemistry and Preparation, *The Polymeric Materials Encyclopedia*, CRC Press Inc.
- [251] **Serfass J. and Samanos J. (1996)** Fiber-Modified Asphalt Concrete Characteristics, Applications and Behavior, *J Assoc Asph Pav Tech*, 65: 193-230.
- [252] **Jenq Yeou-Shang, Liaw C., and Pei Liu (1993)** Analysis of Crack Resistance of Asphalt Concrete Overlays: A Fracture Mechanics Approach. *Trans Res. Rec.*, 1388: 160-166.
- [253] **Simpson Amy L. and Mahboob C. (1994)** Case Study of Modified Bitumenous Mixtures:Somerset, Kentucky. In: *Proceedings of the Third Material Engineering Conference*, ASCE: p. 88-96.
- [254] **Cleven M.A. (2000)** Investigation of the Properties of Carbon Fiber Modified Asphalt Mixtures, MSc Thesis, Department of Civil Engineering Michigan Technological University.
- [255] **Stuart Kevin D. and Malmquist P. (1994)** Evaluation of Using Different Stabilizers in US route 15 (Maryland) Stone Matrix Asphalt. *Trans Res Rec*: 1454: 48-57.
- [256] **Partl N., Vinson T, and Hicks R. (1994)** Mechanical Properties of Stone Mastic Asphalt In: Proceedings of the Third Materials Engineering Conference, ASCE, pp: 849-858.
- [257] **Selim Ali A., Taha R., and Bayomy (1994)** Laboratory Performance of Quartzite Based Stone Matrix Asphalt Mixtures (SMAM) In: *Proceeding of the Third Materials Engineering Conferences*, ASCE, pp: 635-642.
- [258] **Su K. Yoshitaka (2008)** Examination of Fiber-added Recycled Asphalt Concretes for Surface Course in Airport Pavements. In: *First International Conference on Transportation Infrastructure*, Beijing – China.
- [259] **Asi M.I. (2006)** Laboratory Comparison Study for the Use of Stone Matrix Asphalt in Hot Weather Climates, *J Constr Build Mater.*, Vol. 20, pp: 982–989.
- [260] **Schmiedlin R.B. (1988)** Stone Matrix Asphalt: The Wisconsin Experience, *Trans. Res. Record: J. Trans. Res. Board*, pp: 34-41.

- [261] Süreyya T., Halit O., and Atakan A. (2007) Investigation of Rutting Performance of Asphalt Mixtures Containing Polymer Modifiers, *Constr Build Mater*, Vol. 21, No. 2.
- [262] Huang H., White TD. (1996) Dynamic Properties of Fiber-Modified Overlay Mixture. *Trans. Res. Rec.*, 1545:98-104.
- [263] Moghaddam T. B., Karim M. R., Abdelaziz M. (2011) A Review on Fatigue and Rutting Performance of Asphalt Mixes, *Scientific Research and Essays*. Vol. 6(4) pp: 670-682.
- [264] Jahromi S., Khodaii A. (2008) Carbon fiber reinforced asphalt concrete. *Arab J Sci Eng*. 33:335-64.
- [265] Athanasios Kalofotias, PRESTE, Sofia Mavridou, Elias Aloupis and Nikolaos Oikonomou, LBM (2011). *Report on Rheological Characteristics of Rubberized Asphalt Binder*, Integration of End-of-Life Tires in the Life Cycle of Road Construction
- [266] Radvanska Agáta. (2012) Textile Recovery from Scrap Rubber Tires, 2nd International Conference Manufacturing Engineering & Management 2012, pp: 149-150, ISBN 978-80-553-1216-3
- [267] Wang1 Y., Zhang Y., Polk1 M., Kumar S., and Muzzy J. (2003) Recycling of Carpet and Textile Fibers, *Plastics and the Environment Handbook*, Edited by A. L. Andrady, John Wiley & Sons, New York, Chapter 16, pp: 697-725.
- [268] Benjamin F. B., Baoshan H., Xiang S., Brad C. M. (2014) Investigation of Reclaimed Asphalt Pavement Blending Efficiency Through GPC and FTIR, *Construction and Building Materials* 50, pp: 517–523.
- [269] Negulescu I, Mohammad L, Daly W, Abadie C, Cueto R, Duranga C. (2006) Chemical and Rheological Characterization of Wet and Dry Aging of SBS Copolymer Modified Asphalt Cements: Laboratory and Field Evaluation. *J Assoc Asphalt Paving Technol*;75:267–318.
- [270] Moreno F., Rubio M.C. and Martinez-Echevarria M.J. (2010) Analysis of Digestion Time and the Crumb Rubber Percentage in Dry-Process Crumb Rubber Modified Hot Bituminous Mixes. *Construction and Building Materials*. 25:2323-2334. <http://dx.doi.org/10.1016/j.conbuildmat>
- [271] Putman B.J., Thompson J.U. and Amirkhanian S.N. (2005) High Temperature Properties of Crumb Rubber Modified Binders. In: *Proceedings of the Mairepav 4th international Symposium: Maintenance and Rehabilitation of Pavements and Technological Control*; Belfast, Northern Ireland. pp: 1-9.
- [272] Soon-Jae Lee, Serji N. Amirkhanian, Khaldoun Shatanawi (2006) Effect of Crumb Rubber on the Aging of Asphalt Binders, *Asphalt Rubber*: <http://www.clemson.edu/ces/arts/AR2006>
- [273] ASTM D36 (2009) Standard Test Method for Softening Point of Bitumen (Ring & Ball Apparatus) American Society for Testing and Material, *ASTM International Standards Worldwide*, Volume 04.03, Road and Paving Materials; Vehicle-Pavement Systems.

- [274] **US Department of Transportation, Federal Highway Administration (1993)** Crum Rubber Modifier Design Procedures and Construction Practices, Workshop Notes PHWA-SA-93-011, Design Procedures and Construction Practice.
- [275] **Bashar A.M., Saadoun O.A. (2009)** Asphalt Pavement Materials Improvement by Powder Crumb Tire Rubber, *Journal of Pure Sciences, Al-Anbar University*, Vol. 3, No. 3, ISSN. 1991- 8941. (Translated from Arabic to English)
- [276] **Richard S., Kenji H., Akinori K., and Kenichi K. (2004)** The Effect of TIRE Rubber Type on Asphalt-Rubber Binders. Adapted from <http://www.library.jsce.org.jp/jsce/open/00035/2004/59-5/59-5-0559.pdf>
- [277] **ASTM, American Society for Testing and Materials (1998)** ASTM D5-73 Standard test method for penetration of bituminous materials. *Annual Book of ASTM Standards*, 04(03) Philadelphia 19103-1187.
- [278] **Whiteoak, D. (1990)** The Shell Bitumen Handbook, Shell Bitumen Surrey, UK.
- [279] **Zahra N. Kalantar (2010)** Properties of Bituminous Binders Modified With Waste Polyethylene Terephthalate, *Proceedings of Malaysian Universities Transportation Forum and Conferences (MUTRF2010)*, University Tenaga Nasional. ISBN 978-967-5770-08-1.
- [280] **Yousefi A.A., Ait-Kadi A., and Roy C. (2000)** Effect of Used Tri-Derived Pyrolytic Oil Residue on the Properties of Polymer-Modified Asphalt, *Fuel*, 70: 975-986.
- [281] **Aflaki S. and Tabatabaee N. (2008)** Proposals for Modifications of Iranian Bitumen to Meet the Climatic Requirements of Iran. *Journal of Construction and Building Materials*, 2(1): 1-10.
- [282] **Warren R.S., and McGennis R.B. (1995)** Superpave Asphalt Binder Test Methods: An Illustrate Overview, US Asphalt Institute, Washington D.C.
- [283] **Jiqing Zhu. (2016)**, Storage Stability and Phase Separation Behaviour of Polymer-Modified Bitumen: Characterization and Modeling, *Doctoral Thesis Submitted to the Department of Civil Engineering, School of Architecture and the Built Environment, KTH Royal Institute*, Sweden.
- [284] **Akmal N., Usmani AM (1999)** Application of Asphalt Containing Materials, *Polym News*, 24:136-140.
- [285] **Haiying F., Leidong X., Daying D., Linfan L., Ming Y., and Side Y. (2007)** Storage Stability and Compatibility of Asphalt Binder Modified by SBS Graft Copolymer, *Construction and Building Materials*, 21: 1528-1533.
- [286] **Jensen W. and Abdelrahman M. (2006)** Crumb Rubber in Performance Graded Asphalt Binder. Final Report SPR-01.Nebraska. Department of Roads, University of Nebraska – Lincoln, 05: 585.
- [287] **Ali A. Yousefi (2004)** Rubber-Polyethylene Modified Bitumens,” *Iranian Polymer Journal*, 13(2): 101-112.
- [288] **Stangl K., Jager A., Lackher R. (2006)** Micostructure-based Identification of Bitumen Performance, *Road Materials and Pavement Deign*, pp: 111-142.



- [289] **Dabir B., Nematy M., Mehrabi E.A., and Sahimi M. (1996)** Asphalt Flocculation and Deposition III. The Molecular Weight Distribution. *Fuel*, 75: 1633.
- [290] **Yang Kang, Fei Wang, and Zhiming Chen (2010)** Reaction of Asphalt and Maleic Anhydride: Kinetics and Mechanism, *Chem. Eng. J.* 164: 230-237.
- [291] **Navarro F.J., Partal P., Mart´inez-Boza F., Valencia C., and Gallegos C. (2002)** Rheological Characteristics of Ground Tire Rubbermodified Bitumens, *Chemical Engineering Journal*, 89(1–3): 53–61.
- [292] **Lewandowski L.H. (1994)** Polymer Modification of Paving Asphalt Binders, *Rubber Chemistry and Technology*, 67(3): 447–480.
- [293] **Elvira Joana Ferreira Peralta.(2009)** Study of the Interaction between Bitumen and Rubber, *A Thesis Submitted to the Department of Civil Engineering in Conformity with the Required for the Degree of Doctoral*, University of Minho.
- [294] **Simon A. M. Hesp. (2013)** Quality Assurance Testing of Asphalt Containing Waste Engine Oil, *International Journal of Pavements Conference*, Sao Paulo, Brazil.
- [295] **Krebs R.D. and Walker R.D. (1971)** Highway Materials, McGraw-Hill, New York, NY, USA.
- [296] **Navarro F.J., Partal P., Garcia-Morales G. (2009)** Bitumen Modification with Reactive and Non-Reactive (Virgin And Recycled) Polymers: A Comparative Analysis, *Journal of Industrial and Engineering Chemistry*, 15(4): 458–464.
- [297] **Widyatmoko I. and Elliott R. (2008)** Characteristics of Elastomeric and Plastomeric Binders in Contact with Natural Asphalts, *Construction and Building Materials*, 22(3): 239–249.
- [298] **Chetana Joshi, Amit Patted, Archana M.R., Anad M. S. Amarnath (2013)** Determining the Rheological Properties of Asphalt Binder Using Dynamic Shear Rheometer (DSR) for Selected Pavement Stretches, *International Journal of Research In Engineering and Technology*, IC-RICE Conference, available at <http://www.ijret.org>
- [299] **Kramer. O. and Ferry. J.D. (1978)** Dynamic Mechanical Properties. In Science and Technology of Rubber (ed. F.R. Eirich.), Academic Press, New York.
- [300] **Carrera V., Partal P., Garc´ia-Morales M., Gallegos C., and P´erez-Lepe A. (2010)** Effect of Processing on the Rheological Properties of Poly-urethane/urea Bituminous Products. *Fuel Processing Technology Journal*, 91:1139-1145.
- [301] **Navarro F.J., Francisco P.P., Martinez-Boza J., and Gallegos C. (2010)** Novel Recycled Polyethylene/Ground Tire Rubber/Bitumen Blends for Use in Roofing Applications: Thermo-Mechanical Properties, *Polymer Testing* 29: 588-595.
- [302] **Lu X. and Isacsson U. (1997)** Rheological Characterization of Styrene-Butadiene-Styrene Copolymer Modified Bitumens. *Construction and Building Materials*, 11(1): 23-32.
- [303] **Herrington P., Wu Y., Forbes M. (1999)** Rheological Modification of Bitumen with Maleic Anhydride and Dicarboxylic Acids, *Fuel*, 78, 101-110.

- [304] Samsuri A. and Karim M. R. (1997) Effect of Temperature of Mixing and Heat Aging on the Physical Properties of Rubberized Bitumen. *Conference on the Use of Rubberized Bitumen in Road Construction*.
- [305] Maccarrone S., Holleran G., and Gnaseelan G.P. (1994) Properties of Polymers Modified Binders and Relationship to Performance. *Proceedings, 17th ARRB Conference*, Part 3, 123-139.
- [306] Cortizo S.M., Larsen O.D., Bianchetto H., and Alessandrini L.J. (2004) Effect of the Thermal Degradation of SBS Copolymers During the Ageing of Modified Asphalts. *Polymer Degradation and Stability*, 86, 275-282.
- [307] Weizhen S., Peng Y., Kaifu H., Kejian L., Daosheng L., Feng Y., and Yi W. (2001) The Study of Producing SBS Modified Asphalt by Using Liaoshu High Viscous Crude Oil. *Petroleum Science and Technology*, 19, 1187-1196.
- [308] Oruc S., Yilmaz B., and Sancak K. (2015) Effect of Boron-containing Additives on Rheological Properties of Asphalt Binder, *Road Materials and Pavement Design*, <http://dx.doi.org/10.1080/14680629.2015.1120228>
- [309] Chipps J.F., Davison R.R., and Glover C.J. (2001) A Model for Oxidative Ageing of Rubber-Modified Asphalts and Implications and Performance Analysis. *Energy Fuel*, 15: 637-647.
- [310] Navarro F.J., Partal P., Martinez-Boza F., & Crispulo G. (2002) Rheological Characteristics of Ground Tire Rubber-Modified Bitumens, *Chem Eng. J.* 89: 53-61.
- [311] Blow C.M. (1971) *Rubber Technology and Manufacture*, Institution of the Rubber Industry, London-UK.
- [312] Ying G., Rongji G. (2010) Interaction Theory of Asphalt and Rubber, *Journal of Wuhan University of Technology-Mater. Sci. Ed.*, DOI:10.1007/s1 1595-010-0107-y.
- [313] Vargas M.A., Vargas M.A., Antonio S., and Manero O. (2013) "Asphalt/Polyethylene Blends: Rheological Properties, Microstructure and Viscosity Modeling," *Construction and Building Materials*. 45. pp, 243-250.
- [314] Carrera V., Cuadri A.A., Garcia-Morales M., and Partal P. (2014) The Development of Polyurethane Modified Bitumen Emulsions for Cold Mix Application, *Material and Structures*, DOI 10.1617/s11527-014-0408-2.
- [315] Yu-Hsun Nien, Yeh P.-H., Chen W.-C., Liu W.-T., and Chen J.-H. (2008) Investigation of Flow Properties of Asphalt Binders Containing Polymer Modifiers. Wiley Inter Science. [online]. Available: <http://www.interscience.wiley.com>



AUTHOR ACHIEVEMENTS

1. Conferences Participation

- 4th World Congress and Expo on Recycling 25-27/July/2017, Rome - Italy. "Student ambassadors".
- 177th International Conference on Environmental Science and Development 16 - 17/May/2017, Warsaw-Poland. "Acceptance"
- 2nd World Congress and Expo on Recycling 25-27/July/2016, Berlin - Germany. "Oral presentation"
- 6th International Conference "Advanced in Petroleum and Gas Industry and Petrochemistry", May 19-24, 2014, Lviv, Ukraine. Poster presentation.
- 2nd International Conference and Exhibition on Materials Science and Engineering, October 7-9, 2013, Las Vegas, USA. "Poster presentation"

2. Publications During PhD Study in the Field of Polymer Technology

- Sulyman M., Haponiuk J., Sienkiewicz M. Novel Recycled Polyurethane Foam/ Crumb Rubber/ Asphalt Blends: Physical Properties and Rheology, 2016. *Conference*.
- Sulyman M., Haponiuk J., Formela K. Utilization of Recycled Polyethylene Terephthalate (PET) in Engineering Material: A Review, *International Journal of Environmental Science and Development*, DOI: 10.7763/IJESD.2016.V7.749.
- Sulyman M., Sienkiewicz M., Haponiuk J. Asphalt Pavement Materials Improvement: A Review, *International Journal of Environmental Science and Development*, Vol. 5. No. 5, 2014, DOI: 10.7763/IJESD.2014.V5.525.
- Sulyman M., Sienkiewicz M., Haponiuk J. New Study on Improved Performance of Paving Asphalt by Crumb Rubber and Polyethylene Modifications, *Material Sci. Eng.*, 2 : 4, 2013. DOI: 10.4172/2169-0022.1000133.

3. Publications During PhD Study in the Field of Environmental Sciences:

- Sulyman M., Namiesnik J., Gierak A. Low-Cost Adsorbents Derived from Agricultural By-products/Wastes for Enhancing Contaminant Uptakes from Wastewater: A Review, *Pol. J. Environ. Stud.* Vol. 26, No. 2, 2017, 479-510, DOI: 10.15244/pjoes/66769, IF 0.790.
- Sulyman M., Namiesnik J., Gierak A. Adsorptive Removal of Aqueous Phase Crystal Violet Dye By Low-Cost Activated Carbon Obtained from Date Palm (L.) Dead Leaflets. *Engineering and Protection of Environment*, 19(4), DOI: 10.17512/ios.2016.4.14.
- Sulyman M., Namiesnik J., Gierak A. Utilization of New Activated Carbon Derived from Oak Leaves for Removal of Crystal Violet from Aqueous Solution, *Pol. J. Environ. Stud.*, Vol. 23, No. 6, DOI: 10.15244/pjoes/26764, IF. 0.790.