



Waste tire rubber as low-cost and environmentally-friendly modifier in thermoset polymers – A review

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ABSTRACT

Nowadays, waste tire rubber (WTR) management is a growing and serious problem. Therefore, research works focused on the development of cost-effective and environmentally-friendly methods of WTR recycling are fully justified. Incorporation of WTR into polymer matrices and composite materials attracts much attention, because this approach allows sustainable development of industrially applicable waste tires recycling technologies. Generally, utilization of WTR as a filler for polymer composites noticeably reduces materials costs, while suitable modification/functionalization of WTR may significantly enhance the performance of plastics and rubbers. This work aims to summarize the literature reports related to the thermoset/WTR composites based on various matrices such as: polyurethanes, epoxy and other resins. It particularly focuses on compatibilization strategies in thermosets/WTR systems and their impact on the chemistry and physical interfacial interactions between thermoset matrix and WTR filler phase, what significantly affecting performance properties of prepared materials. Moreover, future trends and limitation related to thermoset/WTR composites development are discussed.

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1. Introduction

Waste tires management is currently generating environmental, social, and economic problems, which is an enormous challenge for scientists and industry representatives for decades (Price and Smith, 2006; Schnecko, 1998; Stevenson et al., 2008). Regardless of existing legislation, the accumulation of used tires at landfills is still an issue, and the satisfactory industrially applied solution has not been found. The reason for this phenomenon is a complex physical and chemical structure of waste tires, which is

Abbreviations: CTBN, carboxyl terminated butadiene-acrylonitrile copolymer; DMA, dynamic mechanical analysis; DSC, differential scanning calorimetry; DTG, differential thermogravimetric curves; EG, expandable graphite; FTIR, Fourier-transform infrared spectroscopy; MDI, 4,4'-methylene bis(phenyl isocyanate); MUF, melamine-urea-formaldehyde; PU, polyurethane; SEM, scanning electron microscopy; TDI 2,4, toluene 2,4-diisocyanate; TDI 2,6, toluene 2,6-diisocyanate; WTR, waste tire rubber; XPS, X-ray photoelectron spectroscopy.

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different depending on its purpose (increased performance, service life, safety, noise reduction, etc.) and the manufacturer (unknown composition due to the confidential data). Moreover, a three-dimensional cross-linked structure, which was obtained via irreversible vulcanization process, makes the waste tires a non-biodegradable residue resistant to many external factors (Thomas et al., 2016).

Commonly applied method of waste tire rubber (WTR) management is energy recovery (Kandasamy and Gökalp, 2014). Whole or scrap tires are used as fuel in cement kilns, paper mills, or power plants. It is a relatively safe method, however, due to the environmental, financial (expensive furnaces) and efficiency (increasing amount of waste tires) issues, different solutions are required.

Finding a feasible and cost-effective method for recycling of waste tire rubber is of paramount importance. Nowadays, the most common action in terms of rubber recycling is grinding as a result of which a ground tire rubber is obtained. Waste tire rubber (WTR) may be subjected to different types of reclaiming processes (Bockstal et al., 2019). In the ideal process, C-S and/or S-S bonds have to be broken without affecting hydrocarbon backbone chains. However, in most cases, the energy delivered to the process is higher than bonds energies of C-C (which is higher than C-S and

S-S bonds energies), resulting in main chain scission (Formela et al., 2016). Although such processes seem to be very promising in obtaining new material with unique properties, the procedure is commonly complicated and hard to transfer to industrial-scale.

The most popular solution to material recycling of waste rubber is to combine WTR with a polymeric material which can flow under certain conditions so that it could be shaped into different products.

In general, incorporation of fillers into polymeric matrices is aimed to achieve two primary goals. The first one is associated with the lowering of materials' cost, which is very popular in the case of products that are not required to meet very high criteria related to their mechanical or thermal performance (Dixit et al., 2017). The second goal is to enhance various materials' parameters, e.g., tensile strength, toughness, or sound absorption properties (De Leon et al., 2016). The application of WTR particles into polymer matrices can be easily classified into both of these trends. Regarding price, ground tire rubber is generally cheaper than compounds used for the manufacturing of epoxy resins, polyurethanes (PU), and other thermoset plastics even if prior modification or functionalization of WTR particles is considered. Seghar et al. (2019) indicated that the cost of grinding rubber is approximately 120 €/ton for particles of 1–3 mm size, while for particles smaller than 0.8 mm increase to 300 €/ton.

In Table 1, there are presented example costs of materials used for the manufacturing of various thermoset plastics and costs of WTR, based on data available for the products in the polish market. It is clear that the application of WTR particles can be used in all cases for lowering of thermosets based materials' costs, what fully justified research and development in this field.

2. Compatibilization strategies in thermosets/WTR systems

WTR particles, as mentioned above, may also be used to provide desired properties to thermoset plastics. In the case of highly cross-linked polymers, e.g., epoxy, polyester, or melamine resins, incorporation of WTR is aimed mainly at the enhancement of their toughness (Ratna and Banthia, 2004). Due to the high elasticity of rubber particles, their presence may also beneficially influence the impact or flexural strength of materials. Previous research works showed that incorporation of WTR particles into pavement structures and other concrete-based materials enhances their sound absorption properties (Maderuelo-Sanz et al., 2013; Paje et al., 2010), so it could be the issue also in case of polymer composites.

Nevertheless, incorporation of WTR particles into the polymer matrix often results in deterioration of mechanical performance, which is associated with the insufficient interfacial interactions between matrix and filler (Ramarad et al., 2015). Enhancement of these interactions can be realized by the addition of proper compatibilizer, modification, or functionalization of WTR particles.

The first approach is often used in the case of non-polar polymers, which do not contain functional groups in their structures. It includes the introduction of compatibilizer, which shows good miscibility with the polymer matrix and simultaneously may

create interactions with filler particles. One of the most popular examples is the incorporation of polyethylene or polypropylene grafted with maleic anhydride or glycidyl methacrylate (Wang et al., 2003). Nevertheless, such an approach is most often used for thermoplastic matrices, where compatibilizer can be well mixed with matrix during melt compounding.

In the case of thermosets, more popular is the second approach, including the modification of filler particles. Thermosets and compounds used for their manufacturing, before curing, often have in their structure high content of functional groups, as presented in Fig. 1, unlike, e.g., polyolefins, so they can bond chemically with introduced fillers during hardening (Aoudia et al., 2017). However, electrostatic interactions, e.g., through hydrogen bonds, are also possible and enhanced comparing to polyolefins. However, unmodified WTR particles are rather non-polar and contain very few functional groups on their surfaces. Therefore, it is very beneficial to introduce various functional groups on the surface of rubber particles, which may enhance the interfacial interactions between the continuous and dispersed phases. This approach is realized in the case of polymer/WTR composites by grafting various compounds on the surface of rubber particles or partial devulcanization of particles' surface, which results in the generation of reactive, functional groups (de Sousa et al., 2017; Fuhrmann and Karger-Kocsis, 1999). Moreover, it changes the dispersion and distribution of WTR particles inside the polymeric matrix. Generally, there are two approaches to embed monomers onto the surface of a solid sample – physisorption and covalent attachment, as presented in Fig. 2 (Zhao and Brittain, 2000). In the case of physisorption, block copolymers are being absorbed onto an appropriate substrate with one block actively interacting with the WTR particle and the other block weakly interacting with the substrate. The covalent attachment can be done by “grafting to” or “grafting from” methods. In the first method, a suitable substrate is selected to react with the functional groups present on the WTR surface, while “grafting from” involves surface initiation (e.g., plasma or glow-discharge) and consecutive polymer growth (Zhao and Brittain, 2000).

The grafting process can be designed and controlled by the selection of proper monomers. Depending on the molecular structure, length, and a number of the side chains of applied monomer, the properties of the product may be tailored as required (Fan and Lu, 2011b). However, it must be pointed out that the presence of carbon black (strong radical scavenger) in the composition of waste tire rubber may hinder the process, so it is essential to create some unique reactive points before grafting (Tsubokawa et al., 1988).

Devulcanization is associated with partial destruction of the three-dimensional network responsible for the structure and performance of rubber materials, as presented in Fig. 3. In order to break chemical bonds in rubber, the proper amount of mechanical, thermal, or chemical energy needs to be provided. The main devulcanization methods can be divided into chemical (Anu Mary et al., 2016), mechanical and thermomechanical (Seghar et al., 2019), ultrasonic (Asaro et al., 2018), microwave (Formela et al., 2019) and other, e.g., biological (Tatangelo et al., 2016) or with using supercritical CO₂ (Mangili et al., 2014).

It is also worth to mention that mechanical and thermomechanical devulcanization of WTR is usually performed in the air atmosphere, which results in the partial oxidation of the devulcanized surface of particles. As a result, except breakdown of sulfuric bridges, the generation of various functional groups, whose presence may later enhance the interfacial interactions between WTR filler and polymer matrix (Adhikari et al., 2000).

Moreover, many literature reports indicate that some of the additives, e.g., accelerators can migrate from the partially devulcanized WTR to the polymer matrix, which is noticeably facilitated

Table 1
Materials' costs of popular thermosetting plastics and WTR.

Material	Producer	Average price, €/kg
Epoxy resin system	Organika Sarzyna S.A.	4.9
Polyester resin system	Organika Sarzyna S.A.	3.0
Polyurea resin system	Neotex S.A.	9.3
Polyurethane system	Dow	3.0
Waste tire rubber	Grupa Recykl S.A.	~0.2*

* Depends of WTR particles size.

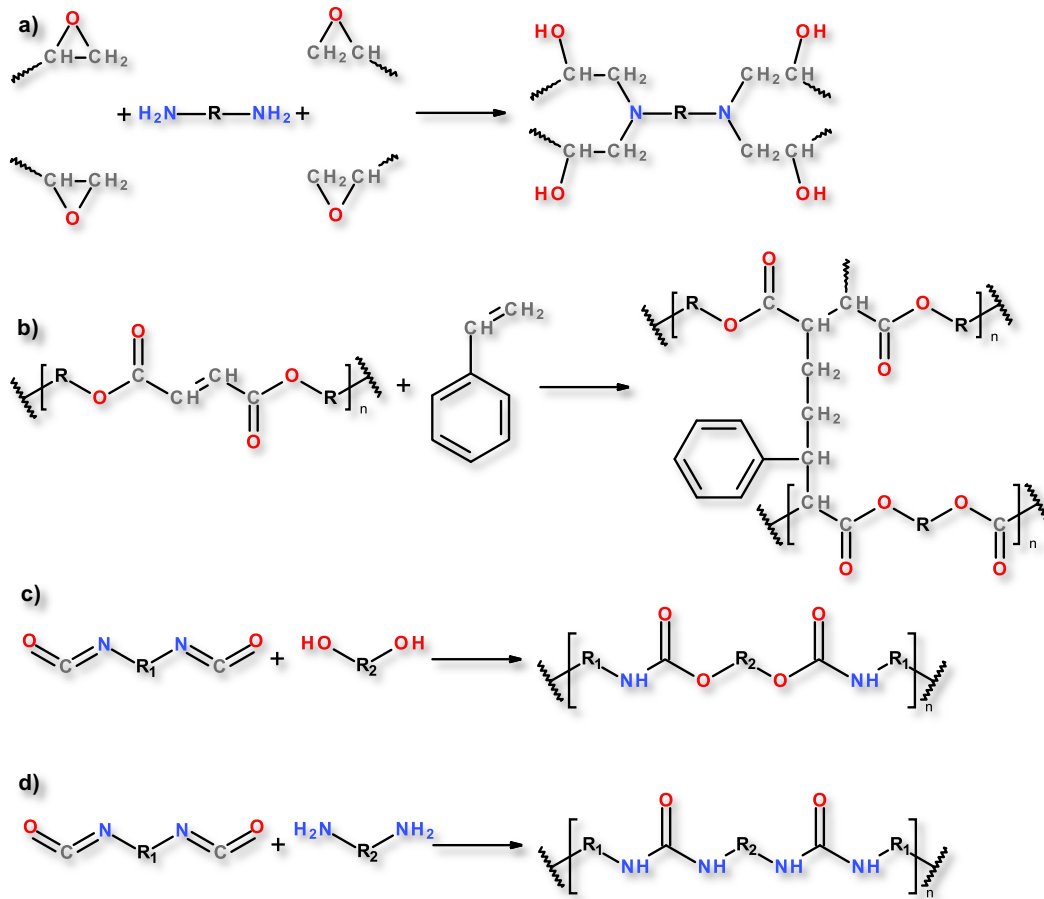


Fig. 1. General reaction schemes of (a) epoxy hardening, (b) polyester resins hardening, (c) polyurethane and (d) polyurea synthesis (Carragher, 2003).

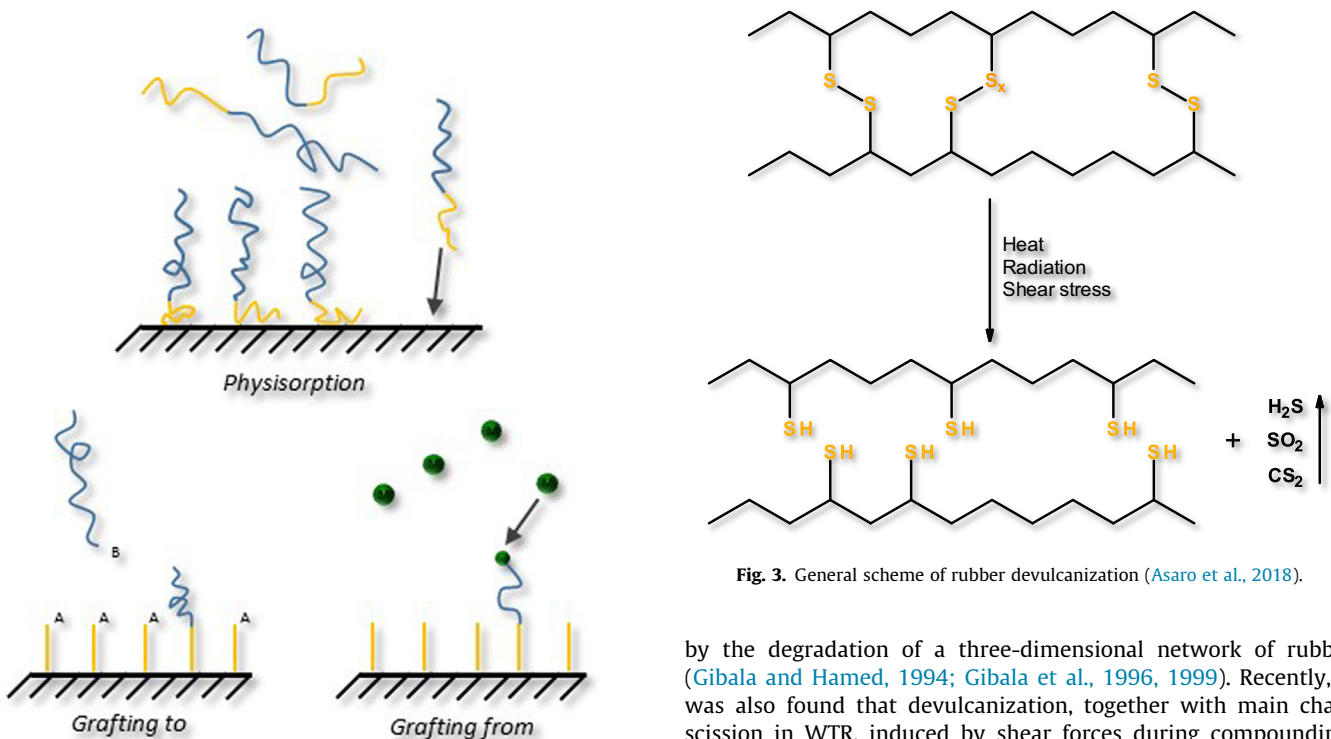


Fig. 3. General scheme of rubber devulcanization (Asaro et al., 2018).

Fig. 2. Possible mechanisms of the introduction of functional groups onto the surface of WTR particles (Zhao and Brittain, 2000).

by the degradation of a three-dimensional network of rubber (Gibala and Hamed, 1994; Gibala et al., 1996, 1999). Recently, it was also found that devulcanization, together with main chain scission in WTR, induced by shear forces during compounding, resulted in the migration of carbon black to the polymer matrix, which enhanced tensile properties of selected polymer composites. The phenomenon of rubber components migration during WTR

treatment is schematically presented in Fig. 4 (Formela and Haponiuk, 2014; Song et al., 2018).

Summarizing various treatment methods of WTR particles before preparation of thermoset-based composites, as well as the incorporation of compatibilizers, is a promising approach aimed at enhancing the interfacial interactions between the matrix and WTR filler phases (Piszczczyk et al., 2015a). In the following sections of this paper, different reports associated with the incorporation of WTR, as well as treated WTR particles into thermoset polymer matrices, have been discussed.

3. Performance properties of thermosets/WTR composites

In this subchapter the impact of WTR particles and their further modification/functionalization on performance properties of thermosets/WTR composites as a function of used the matrix was comprehensively described.

3.1. Solid polyurethanes

Polyurethanes are very versatile materials used in many different branches of industry. They are valued for their durability and abrasion resistance, but mostly for the possibility of engineering of their properties by the adjustment of chemical composition. Solid polyurethanes are often used in applications characteristic for rubbers. Therefore the combination of these two types of materials has already been investigated (Desai et al., 2001; Kalkornsurapranee et al., 2012; Tan et al., 2008). One step further is towards the preparation of environmentally friendly materials is the incorporation of waste rubber into the manufacturing of polyurethane materials. Literature reports suggest that incorporation of 15 wt% of previously treated rubber particles into solid polyurethane results in the composite showing similar properties to those of pure polyurethane and may even enhance some of them, e.g., coefficient of friction (De, 2001). Such an effect is associated with the above mentioned possible reactions between components used in the manufacturing of polyurethanes and functional groups present on the surface of rubber particles. In Fig. 5, there is presented a general scheme of possible reaction between a diisocyanate and WTR particle-containing hydroxyl and carboxyl groups on the surface, as a result of devulcanization and oxidation or related to carbon black content.

Sułkowski et al. (2004, 2006) and Danch et al. (2004, 2005) performed extensive thermogravimetric and dynamic mechanical analysis of polyurethanes highly filled with waste rubber particles. Authors prepared composites with different polyurethane

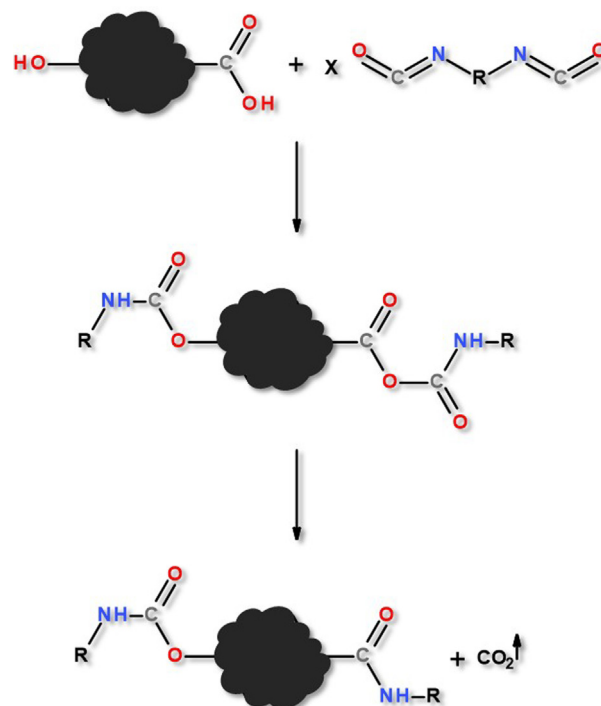


Fig. 5. General scheme of possible reactions between isocyanates and devulcanized WTR particles.

prepolymers based on different isocyanates: 4,4'-methylene bis (phenyl isocyanate) (MDI), toluene 2,4-diisocyanate (TDI 2,4) and toluene 2,6-diisocyanate (TDI 2,6) and polyoxypropylene. Mechanical properties of composites varied, depending on the applied prepolymer and its composition, hence on the segment structure of the polyurethane matrix. Nevertheless, despite the PU type, incorporation of WTR resulted in the decrease of hardness and a slight increase of elasticity. Such effect was ascribed to the possible reactions between isocyanate groups of the prepolymer and functional groups present on rubber particles, which was also suggested by differential scanning calorimetry (DSC).

Incorporation of rubber particles also resulted in the deterioration of thermal stability, which could be associated with the lower decomposition temperature of an oil fraction present in the rubber. The Authors also used differential thermogravimetric curves (DTG)

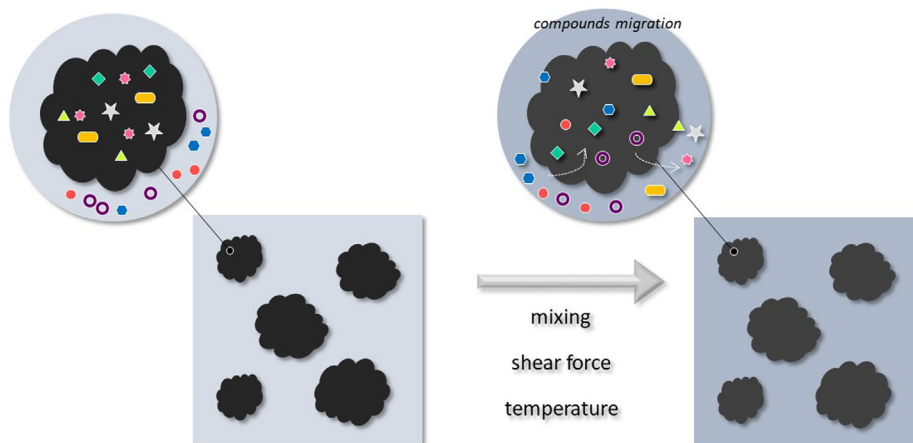


Fig. 4. Migration of additives from treated WTR to the polymer matrix (Formela and Haponiuk, 2014; Song et al., 2018).

to determine the values of activation energies. Differences between values determined experimentally and calculated from the data for raw materials suggested possible reactions between polyurethane prepolymers and functional groups present on the surface of rubber particles, which confirms the assumptions based on DSC results. Such effect was also corroborated by the results of dynamic mechanical analysis (DMA), which indicated shifts on the loss tangent-temperature dependence curves, which were associated with stress relaxation behavior changing with the type of applied prepolymer. It indicated a generation of different intermolecular structures at the interphase when various prepolymers were introduced. Based on the presented results, the Authors confirmed that among analyzed materials, the most stable composites, with the greater extent of reactions between phases, were obtained from MDI-based prepolymer, which except linear structure showed the highest value of free isocyanate groups.

Černý and Jančář (2016) investigated the effect of content (~20–90 wt%) and particle size distribution of WTR on the structure and properties of polyurethane-urea/WTR composites. Microscopic analysis of prepared samples revealed that the introduction of WTR particles up to 65 wt% led to a drop of porosity of the material, which initially was ~57% for neat polyurethane-urea. Only for the fraction with the smallest particle size, the inflection point, when porosity started to rise, was observed for lower rubber content of 48 wt%. Such an effect was related to stronger interactions due to the higher surface area of particles. Based on porosity measurements, the Authors also determined interspace filling of composites, which was maintained at a quite similar level up to 65 wt% of WTR. For higher WTR contents, the interspace filling was drastically decreased independently of particle size, which was due to the aggregation of rubber particles. Such effect, combined with relatively high viscosity of prepolymer, resulted in the situation when the reacting mixture was unable to fill space between WTR particles. Tensile properties of prepared composites were also investigated, and similar dependences were observed. Up to 65 wt% of rubber (48 wt% for smaller particle size), the enhancement of tensile modulus and tensile strength was noted. Further increase in filler content led to the deterioration of materials' performance. The Authors related the mechanical properties to the interspace filling, and the coefficient of determination was 0.83 and 0.93 for tensile modulus and tensile strength, respectively, when linear dependence was assumed. Presented results confirm the crucial impact of porosity and proper adhesion between matrix and filler on the performance of composite materials.

Strakšys et al. (2018) prepared PU-based composites with three types of waste rubber: ground tire rubber from passenger car tires, whole tread buffings from truck tires, and sieved tread buffings from truck tires. As a binder for rubber particles, PU resin with varying content of hardener was used. The appearance and morphology of samples were directly associated with the particle size and aspect ratio of applied filler, as well as the content of rubber particles. For higher content of filler, PU binder was unable to fill up all voids and properly wet all particles, which resulted in less smooth surface and morphology with a high share of empty voids. Such a phenomenon noticeably affected the mechanical performance of composites. At higher concentrations of fillers, the integrity of the composite was lower, and the continuity of material was too low to provide sufficient strength. Tensile strength, tensile modulus, and elongation at break were decreasing with the lowering of PU content in composites. A similar effect was observed for compressive properties, however, in that case, too high PU content, exceeding 40 wt%, was unfavorable and led to a deterioration of compressive strength. Moreover, the Authors also determined the optimal curing temperature for the analyzed set of rubber particles and the PU matrix as 60 °C, which provided the best tensile and compressive performance.

3.2. Polyurethane foams

Polyurethane foams are a very versatile group of materials, which can be simply divided into flexible and rigid foams. Due to the differences between the properties of these two types of foams, the incorporation of WTR particles has a different target.

Flexible polyurethane foams, as a group of materials, are very perspective for the incorporation of WTR, due to the multiplicity of their applications (Piszczczyk et al., 2015b). They are commonly used in furniture, automotive, packaging, and construction industries. Moreover, they are often used in applications, for which the cost of the material is one of the most critical factors, so the incorporation of relatively low-cost WTR could result in beneficial cost reduction and noticeably enhance the attractiveness for potential users. Except for economic factor, the application of WTR in flexible polyurethane foams may be aimed at enhancement of damping properties, both in terms of mechanics and acoustics, adjustment of hardness and resilience (Shan et al., 2013a). Previous works showed that waste rubber particles could be efficiently used in the manufacturing of sound absorbers for a broad absorption spectrum (Pfretzschner and Rodriguez, 1999).

Incorporation of WTR particles into polyurethane systems increases the systems' viscosity, which inhibits the volumetric expansion of foams and simultaneously leads to the rise of apparent density (Shan et al., 2013b).

Cachaço et al. (2013) investigated the properties of flexible polyurethane foams filled with WTR, which could be applied as compression-absorbing buoys. As a result of the noticeable increase of apparent density with the incorporation of recycled rubber, modified foams showed noticeably higher modulus and compressive strength. Authors stated that foams with rubber content of 200 wt% could absorb the compressive stress analogously to commercially used buoys.

Gayathri et al. (2013) analyzed the influence of WTR on the structure and performance of flexible foamed PU/WTR composites. Just as in the above-mentioned works, the apparent density of material was noticeably enhanced with the addition of WTR particles. The cellular structure of the material was hardly affected by WTR, cell size showed very similar values to unmodified foam, while cell wall thickness was increased by ~10%. The Authors indicate that this increase led to the enhancement of the tensile strength of the material with the addition of WTR. Compressive strength was also increased as a result of the rise of apparent density, which is typical for porous materials. Moreover, incorporation of WTR particles enhanced the thermal stability of the material, especially above 250 °C, and noticeably increased the sound absorption coefficient for the frequencies exceeding 150 Hz, even by 45%.

Despite some positive effects of WTR incorporation into flexible, foamed PU matrix, the Authors also indicate the possibility of enhancement of interfacial interactions by modification of WTR particles. However, there are very few works associated with the impact of WTR treatment on the structure and performance of flexible, foamed PU/WTR composites.

This topic was investigated by Piszczczyk et al. (2015b). Incorporation of both neat and auto-thermally reclaimed WTR increased foams' apparent density, which was associated with the higher viscosity of system and lower level of volumetric expansion during foaming. For composites filled with unmodified WTR, the increase of apparent density led to the simultaneous enhancement of compressive strength, which is typical for porous materials. However, in the case of foams with devulcanized rubber, the mechanical performance was deteriorated. Such effect may be related to the attenuation of polyurethane structure due to the competitiveness between hydroxyl groups of polyols and hydroxyl (as well as other functional groups generated during reclamation of WTR) groups

present on the surface of WTR particles, for the reaction with isocyanates. Due to the weakening of the polyurethane matrix, the cellular structure of foam was also affected, which can be seen in Fig. 6. In general, possible interactions between WTR filler and isocyanates should be taken into consideration when manufacturing PU/WTR composites and the isocyanate index applied in formulation needs to be adjusted.

Zhang et al. (2013) performed a mechano-chemical devulcanization of WTR in the pan-mill reactor. Such treatment resulted in noticeable changes in the WTR particles' structure. As determined by XPS analysis, oxygen content in WTR was increased by over 40% due to the oxidation reactions. Sol fraction increased from 8.6 to 27.7 wt%, which pointed to the breaking of the cross-linked structure after milling. Moreover, average particle size was reduced from ~250 to ~60 μm , which, together with partial devulcanization and development of the specific surface area, should noticeably promote the compatibility with foamed polyurethane matrix. Subsequently, the Authors incorporated from 10 to 30 wt % of untreated and devulcanized WTR into flexible PU foams. Regarding cellular structure, unmodified WTR particles showed poor compatibility with the PU matrix, which resulted in the disruption of cell morphology and less regular structure with larger cell size. On the contrary, the structure of composites containing modified WTR was more uniform and well defined, which was ascribed to the surface activation of WTR during devulcanization. Such effect contradicts the observations of Piszczyk et al. (2015b). However, it can be associated with the higher isocyanate index applied by Zhang et al. (2013) – around 1.2 instead of 1.0. As a result, the number of isocyanate groups present in the system during polymerization and foaming was enough to generate fully developed polyurethane structure and simultaneously react with functional groups present on the surface of devulcanized WTR particles, which resulted in better compatibility of system comparing to samples containing unmodified WTR. The Authors investigated also acoustic properties of prepared composites. Results indicate that recycled rubber itself has a higher sound absorption coefficient than conventional flexible PU foams. Therefore, the application of WTR resulted in the enhancement of this parameter in the whole analyzed range of frequencies. Mechano-chemical treatment of WTR noticeably improved sound absorption of resulting composites, which was related to the compatibility of the phases. Comparing to neat PU foam, the application of 30 wt% of devulcanized WTR led to the 133% increase of sound absorption coefficient at the frequency near 1000 Hz. Such a phenomenon can be associated with the damping properties of rubber, which were improved by the partial devulcanization and loss of elastic properties.

Summarizing, the proper treatment of WTR particles together with the adjustment of foams' formulations considering possible

reactions of isocyanates with functional groups resulting from devulcanization of rubber particles, may result in many beneficial changes in composites' structure and performance (Subramaniyan et al., 2013). Therefore, it should be considered by the scientific environment as the essential further direction of research related to flexible foamed PU/WTR composites.

In the case of rigid polyurethane foams, cross-linked materials, used mainly as thermal insulation, application of WTR may be aimed at enhancement of mechanical performance, especially compressive strength and brittleness as well as cost reduction. In theory, incorporation of rubber particles may also have a positive influence on thermal insulation materials, since natural rubber has lower thermal conductivity coefficient than solid polyurethane (~160 vs. ~220 mW/(m·K)) (Hejna et al., 2017; Sandberg and Bäckström, 1979). Nevertheless, in order to achieve such an effect, the cellular structure of foamed PU/WTR composites should be adjusted to provide the best insulation properties, and no such investigations have been described in the literature yet.

Piszczyk et al. (2015a, 2015c) investigated the impact of content and applied WTR type on the structure and properties of fully petrochemical and crude glycerol-based rigid polyurethane foams. The Authors used neat, unmodified ground tire rubber and modified during thermo-mechanical devulcanization. In both cases, WTR particles were introduced into the polyol mixture. As a result, a noticeable decrease of volumetric expansion during foaming was observed, which was associated with higher viscosity of polyol mixture, as well as chemical reactions occurring between isocyanates and functional groups present on the surface of WTR particles. Such effect was more pronounced in the case of foams containing devulcanized WTR particles and was confirmed by measurements of the temperature inside foam during the reaction, which was lowered due to the lower extent of exothermic reaction leading to the generation of urethane groups. In the case of devulcanized rubber particles, more functional groups able to react with isocyanates were present on their surface, which enhanced interfacial interactions, but simultaneously weakened the polyurethane matrix. Also, the migration of carbon black into the PU matrix was observed, which can be seen in Fig. 7.

As a result, a significant increase of apparent density was observed, which simultaneously enhanced the compressive strength of composites, which is typical for porous materials. It was associated with higher mobility of polymer chains due to lower cross-link density of the foam, expressed by the decrease of glass transition temperature with the addition of WTR particles.

The microscopic analysis also revealed some disruption of foams' cellular structure, an increase of average cell size and the open cells' content, which was associated with the above mentioned chemical reactions and too big particle size, which did not

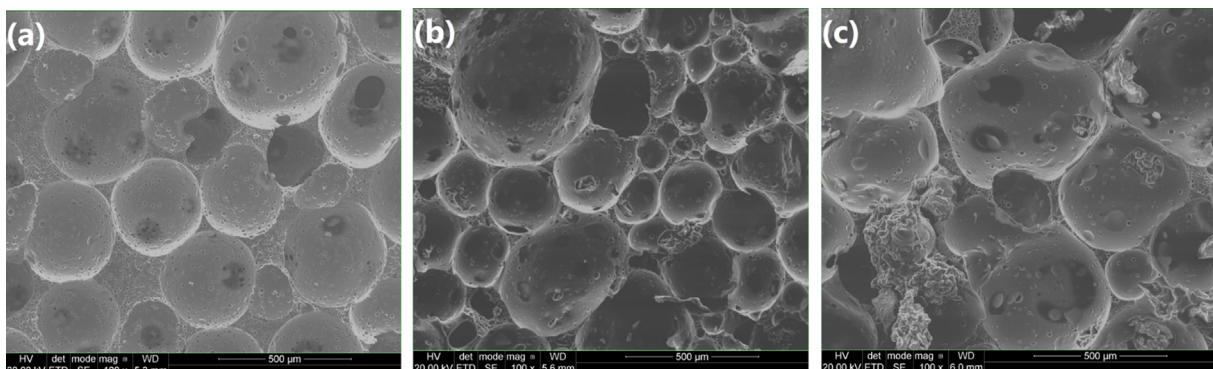


Fig. 6. SEM images of (a) reference PU foam, (b) foam containing 30 pbw (parts by weight) of unmodified WTR and (c) foam containing 30 pbw of devulcanized WTR (Images from (Piszczyk et al., 2015b)).

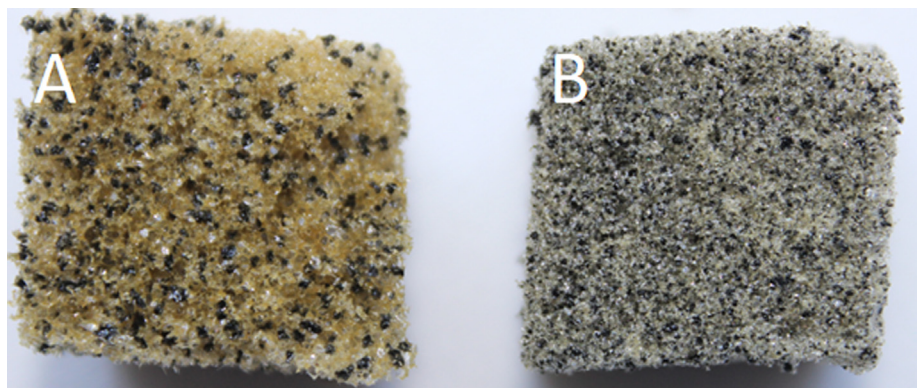


Fig. 7. Effect of carbon black migration on the appearance of rigid polyurethane foams filled with: A – untreated WTR and B – devulcanized WTR (Images from (Piszczczyk et al., 2015a)).

lead to nucleation effect, often observed when solid particles are introduced into the polymer matrix. In work (Formela et al., 2017), authors adjusted foams' formulations and incorporated WTR with smaller particle size, which allowed the reduction of average cell size without noticeable disruption of cellular structure, as presented in Fig. 8. In theory, such effect, combined with lower thermal conductivity of rubber comparing to solid PU, should have a beneficial influence on the thermal insulation properties, which are very important for the application of rigid PU foams. However, it was not investigated by authors.

For rigid polyurethane foams used as thermal insulation material, an essential parameter is the flammability of a studied product, which is associated with law regulations related to fire safety, which is becoming more and more strict. To the best of our knowledge, so far, only one paper was published, which discussed the flammability of foamed PU/WTR composites. Ryszkowska et al. (2018) applied expandable graphite (EG) and commercially applied organophosphorus compound – Fyrol PNX as flame retardants for semi-rigid polyurethane composites filled with 25 wt% of waste rubber particles. Incorporation of 5 wt% of Fyrol PNX and 25 wt% of EG increased by limiting oxygen index from 18.8 to 20.4 and 25.2%, respectively, while their combination led to the value of 25.0%. Cone calorimeter tests also showed very beneficial results, especially when composites were modified with expandable graphite. Application of this flame retardant decreased the value of total heat released from 20.8 to 8.6 MJ/m², while its combination with Fyrol PNX had an even, more substantial effect and led to 6.7 MJ/m². Also, values of heat release rate, parameter essential for the assessment of fire safety, were noticeably

decreased, even by 68%, when analyzed flame retardants were used. It is crucial that the application of flame retardants did not show unfavorable influence on the cellular structure of foams and their ability to absorb the energy. Presented results show immense potential for the reduction of PU/WTR composites' flammability, and this topic should be further analyzed in a more detailed way, especially considering potential applications of such materials.

Summarizing, we firmly believe that further works associated with the incorporation of waste rubber particles into foamed polyurethane matrices should be focused on the adjustment of foams' cellular structure, which is crucial for the performance of this group of materials.

3.3. Epoxy resins

Epoxy resins are one of the most popular thermosetting polymers, often used as coatings, adhesives, or various construction and composite materials reinforced with fibrous or particle fillers. They show excellent adhesion, chemical and heat resistance, good electrical insulating properties, as well as high mechanical properties. Nevertheless, for some applications, they show, like many other thermosetting polymers, unsatisfactory toughness, which limits their applications and encouraged researchers to investigate the toughening of epoxies (Yee and Pearson, 1986). The most common approach is the incorporation of various elastomers into epoxy matrices, therefore considering ongoing environmentally-friendly trends, the application of WTR seems to be a promising solution.

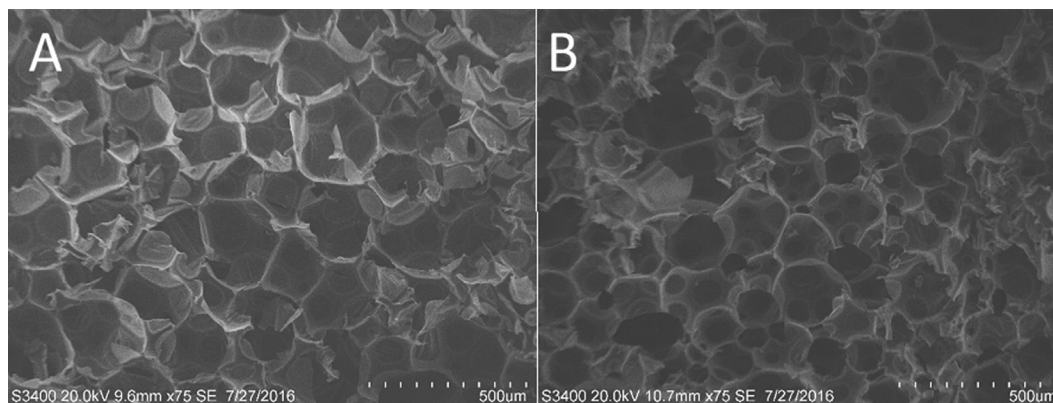


Fig. 8. The cellular structure of rigid polyurethane foam: A – without WTR and B – after addition of 20 parts by weight of WTR (right side) (Images from (Formela et al., 2017)).

Valášek et al. (2013) analyzed the influence of WTR content (5–30 wt%) on the structure and properties of epoxy-based composites. Incorporation of WTR particles into the epoxy matrix slightly affected the density of the material and resulted in air inclusions created during mixing, hence generated porosity at the level of 2–5%. The hardness of composites was linearly decreasing with the addition of rubber from 87 Sh D for neat epoxy to ~80 Sh D for 30 wt% content of WTR filler. Tensile testing of materials, together with microscopic analysis of samples, indicated very weak interfacial interactions and cohesive failure of samples during tension. As a result of poor compatibility, tensile strength decreased from 44.6 MPa for neat epoxy to 14.5 MPa for 20 wt% content of WTR. Further addition of rubber did not show a significant influence on the tensile performance of studied materials. Similar dependence was noted for elongation at break.

Aliabdo et al. (2015) incorporated WTR particles of different size and geometry into epoxy resin matrix and investigated their physical, mechanical as well as thermal and sound insulation properties. Authors used WTR resulting from the mechanical cutting of truck tires and two fibrous fractions obtained during retreading the tires, differing with particle size. In the case of compressive performance, the application of fibrous particles with larger size resulted in the most elastic behavior among analyzed materials, and the material was able to withstand multiple compression cycles. For bigger, fibrous particles, stress was transferred by the rubber phase, which resulted in higher elasticity of composite. On the contrary, for thermal and acoustic insulation properties, the most beneficial properties were observed for materials filled with WTR characterized by the smallest particle size and most regular shape. Such properties provided the best distribution of filler in the epoxy matrix, which led to the lowest values of thermal conductivity and sound attenuation coefficients. Application of WTR resulted in the values of 0.20 W/(m·K) and 1.60 dB/mm, respectively, while for fibrous WTR particles, coefficients show values of 0.30 W/(m·K) and 0.98 dB/mm.

As mentioned above, a very beneficial approach is the modification of WTR particles with various chemicals, which was used by Fuhrmann and Karger-Kocsis (1999). The Authors performed photochemical grafting of methacrylic acid onto WTR particles and then introduced them into the epoxy matrix. The effects of modification were compared with untreated WTR. Independently of WTR type, the addition of 10 wt% of WTR filler resulted in the decrease of materials' stiffness expressed by a 15% drop of Young's modulus. Simultaneously, the increase of impact strength was observed, which is one of the main goals of incorporation of WTR into epoxy matrices (Karger-Kocsis et al., 2012). However, in case of impact strength, noticeable differences in the level of enhancement, hence in the compatibility of the composites were observed. Incorporation of unmodified WTR particles resulted in a 15% increase of impact strength, while grafting of WTR leads to the 55% increase of this parameter. The Authors suggest that more substantial effect could be observed for smaller particle size.

Kaynak et al. (2001) investigated the toughening of epoxy resin with five types of surface-treated WTR particles because of the incompatibility of the hydrophilic matrix and hydrophobic fillers. Applied treatments and their impact on fracture toughness of epoxy resin are summarized in Table 2.

Based on the results obtained for samples modified with vinyltriethoxysilane, the Authors adjusted the content of silanes in other modifications as 2 wt%. It can be seen that the application of 3-aminopropyltriethoxysilane led to noticeably higher values of fracture toughness comparing to other silanes, which may be associated with the presence of the amine group in its structure. Another type of applied modifier was acrylic acid, which was used separately and in combination with benzoyl peroxide. It can be seen that the application of benzoyl peroxide noticeably enhanced

Table 2

Modifications of WTR particles applied in work (data (adapted from Kaynak et al., 2001)).

Rubber content,%	Rubber modification	Fracture toughness, MPa·m ^{1/2}
0	Reference sample	0.98 ± 0.23
5	Vinyltriethoxysilane, 1 wt%	1.12 ± 0.11
5	Vinyltriethoxysilane, 2 wt%	1.13 ± 0.06
5	Vinyltriethoxysilane, 4 wt%	1.06 ± 0.12
5	Vinyltriethoxysilane, 2 wt% + oxygen plasma treatment	1.02 ± 0.13
5	3-Aminopropyltriethoxysilane, 2 wt%	1.43 ± 0.25
5	Acrylic acid, 5 wt%	1.26 ± 0.08
5	Acrylic acid, 5 wt% and benzoyl peroxide, 0.25 wt%	1.54 ± 0.19
25	Acrylic acid, 5 wt% and benzoyl peroxide, 0.25 wt%	1.05 ± 0.04
25	3-Aminopropyltriethoxysilane, 2 wt%	1.05 ± 0.05

the performance of epoxy-based composites, which was associated with the radicals generated during the decomposition of peroxide, leading, e.g., to polymerization of acrylic acid on the surface of rubber particles. Additionally, it should be pointed out that benzoyl peroxide as an additive can enhance the devulcanization of WTR (Rooj et al., 2011; Sabzekar et al., 2015).

For both types of modifiers, an increase of rubber content in epoxy did not result in enhancement of its toughness, though its value was still higher than for unmodified epoxy. However, despite the achieved toughening effect, the same modifications caused noticeable deterioration of other mechanical parameters, e.g., impact toughness, elastic modulus or tensile strength, which was proven in other work of mentioned research group (Sipahi-Saglam et al., 2001). For the better investigation of toughening mechanisms, scanning electron microscope (SEM) images of interfaces between matrix and filler after fracture were presented. After analysis, the Authors suggested that the main mechanism was a crack deflection by rubber particles, often expressed as blunting of the crack tip. As a secondary mechanism was noted to shear deformation and slight debonding, which were ascribed to the strength of matrix-filler interface. Such assumptions were confirmed in their further works (Celikbilek et al., 2004; Kaynak et al., 2003).

One step forward in understanding the mechanism of epoxy toughening with the incorporation of rubber particles is the work of Bagheri et al. (1997). They investigated the combined impact of commercially available surface-treated recycled rubber particles (VISTAMER™ R-4200) and carboxyl terminated butadiene-acrylonitrile copolymer (CTBN) on the performance of the epoxy resin. The main goal of the study was the investigation of synergistic toughening of epoxy with two types of rubber, which were incorporated separately and in 3:1, 1:1 and 1:3 ratios in the total amount of 10 wt%. The addition of 10 wt% of waste rubber resulted in the 17% increase of fracture toughness, while its substitution by CTBN resulted in the 220% increase. Based on these results and the rule of mixture, the Authors tried to predict the values of fracture toughness for applied combinations of two types of rubber. For equal share and excess of waste rubber, results were slightly lower than expected but close to predicted values. However, the combination of waste rubber with CTBN in the ratio of 1:3 resulted in the synergistic effect and a 237% increase of fracture toughness, which noticeably exceeded predicted value. Such a synergistic effect in rubber-toughened polymers, when two types of rubber with varying particle sizes were incorporated, was also observed in other work (Pearson and Yee, 1991). According to Chen and Jan (1992), larger particles are inducing shear deformation of composite in the front of crack, while the smaller particles, dispersed between larger ones are toughening the shear bands. Bagheri

et al. (1997) confirmed these findings by analysis of microscopic images of crack zones. As a result of described synergistic effects, crack tip was not linearly “bridged” along with the large rubber particles but spread and branched, therefore stress concentration was lower, and fracture toughness of material was enhanced, as presented in Fig. 9 (Bagheri et al., 2009). Similar results, e.g., similar toughening mechanisms and synergistic effect for 3:1 ratio of butadiene-acrylonitrile copolymer to recycled rubber particles were later observed also by Abadyan et al. (2012a, 2012b). However, in their works, the amine-terminated butadiene-acrylonitrile copolymer was used.

Boynton and Lee applied the same modifiers of epoxy resin (waste rubber particles and CTBN) in their work (1997). They applied modifiers in a total amount of 6 wt%. Sole incorporation of waste rubber and CTBN enhanced fracture toughness by 5 and 87%, respectively, while their combination in 1:2 ratio led to a 114% increase of this parameter. Moreover, the Authors analyzed the influence of waste rubber particles’ average diameter on the fracture performance of epoxy-based composites. The increase of particle size from 75 to 250 μm resulted in the 15% increase of fracture toughness and a 146% increase comparing to neat epoxy resin. However, a further increase of particle size to 425 μm resulted in a slight deterioration of mechanical performance. The Authors suggested toughening with an increase of particle size could be associated with the increasing distance between waste rubber particles, which required more energy to generate the propagating fracture path.

As mentioned above, except chemical grafting of WTR particles’ surface, another method for enhancement of interfacial interactions between the epoxy matrix and WTR filler is its partial devulcanization (Aoudia et al., 2017). Such treatment results in the breakage of sulfur bridges, often followed by oxidation of rubber surface and generation of functional groups, which can react with functional groups present in the structure of thermosets.

Irez et al. (2018, 2019) combined chemical treatment of waste rubber particles with microwave devulcanization and incorporated modified waste rubber into the epoxy matrix. Before microwave devulcanization, rubber particles were treated with 2% vinyltriethoxysilane, acrylic acid, and toluene. Increasing rubber content led to the enhancement of flexural stress and modulus, as well as fracture toughness of the material. Such effect was the result of a well-developed interface between the rubber particles and epoxy resin, due to applied treatment, as revealed by microscopic analysis.

Recently, Aoudia et al. (2017) investigated the impact of microwave treatment of WTR on the structure and properties of epoxy-based composites containing 10 wt% of the modifier. In Table 3, there are presented applied parameters of microwave devulcanization and swelling degree of treated WTR.

Spectra obtained by Fourier-transform infrared spectroscopy (FTIR) analysis of devulcanized rubber indicated various changes in the chemical structure of WTR after microwave treatment, e.g., the effective and selective breaking of C-S and S-S bonds, which points to devulcanization of rubber or formation of sulfone and sulfoxide groups, which indicate oxidative degradation of rubber occurring along with devulcanization. Moreover, for a longer time of treatment and higher values of microwave power degradation of the main polymer chain occurred, what was expressed by the decrease in the intensity of signals associated with the presence of C-C bonds. Presented results of swelling tests and calculated values of devulcanization degree confirmed the results of FTIR analysis indicating the successful rupture of sulfur bridges. Such changes in chemical structure noticeably improved interfacial interactions between WTR filler and epoxy matrix, which led to a 20% enhancement of flexural stress and strain at break. Nevertheless, when too much energy was applied to sample (values exceeding 1250 J/kg), improvement of mechanical properties was significantly lower, which was ascribed to the following degradation/decomposition of WTR. Moreover, significant toughening of the epoxy matrix was observed, which was associated with enhancement of interfacial interactions between matrix and filler, confirmed by SEM analysis of failure surfaces.

A similar type of epoxy resin was used by Müller et al. (2018) as a matrix for plasma-treated WTR particles. The applied modification had a very beneficial influence on the wettability of rubber particles and noticeably enhanced the compatibility of the composite, which was observed on SEM micrographs. Such a phenomenon had led to 20–40% enhancement of tensile strength for the incorporation of 5–30 vol% of WTR particles. Samples containing modified rubber particles were also subjected to 30 cycles of degradation consisting of the exposition to 70 °C and 90% relative moisture for 16 h, –40 °C for 3 h and 70 °C and 50% relative moisture for 5 h. After that, mechanical performance and microstructure of samples were analyzed to determine the impact of degradation on the quality of interfacial interactions. Noticeable differences were observed in the case of microscopic fracture surface analysis. Without degradation, samples showed good compatibility and adhesion of matrix and WTR filler. Nevertheless, after degradation, partial delamination occurred, and voids were observed at the interface, which facilitated the pull-up of filler particles from the matrix during tensile tests. The Authors also analyzed the changes in the fracture surfaces with the addition of rubber particles. The addition of filler changed the character of fracture surfaces from cohesive to adhesive, which was related to the incorporation of an additional phase. Moreover, the increase of rubber content increased the thickness and uniformity of the adhesive layer on fracture surfaces.

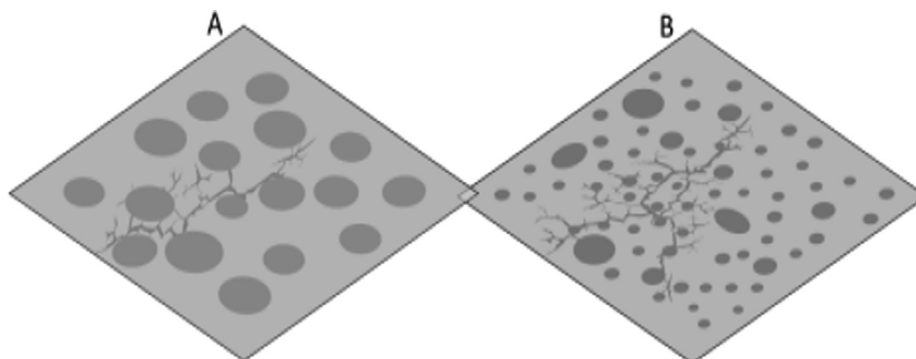


Fig. 9. Crack propagation mechanism of epoxy-WTR composites when (a) WTR with one particle size and (b) two types of WTR with varying particle size were applied (Based on (Bagheri et al., 2009)).

Table 3

Parameters of microwave devulcanization applied in work (Data (adapted from Aoudia et al., 2017)).

Sample	Time of treatment, s	Microwave power, W	Specific energy, J/kg	Swelling degree, %
1	15	350	540	54.99
2		500	772	61.52
3		650	1003	57.00
4		750	1157	85.53
5		900	1389	63.22
6	60	350	2160	71.26
7		500	3086	73.05
8		650	4012	75.18
9		750	4630	75.67
10		900	5556	78.14

Incorporation of ground tire rubber into epoxy resins may be aimed not only at toughness enhancement but also at the introduction of functional groups responsible for curing of epoxy, like in case of the study presented by Fan and Lu (2011a). The Authors who modified waste rubber particles by surface grafting of poly(amidoamine), which was performed by polymerization of methyl methacrylate on the surface of rubber particles followed by five cycles of amidation of terminal ester groups and Michael addition of methyl acrylate to amino groups on the surface, as presented in Fig. 10.

The Authors analyzed the impact of Michael addition cycles' number on the structure of the modified rubber. According to the results of FTIR and X-ray photoelectron spectroscopy (XPS), the increase of the amino groups' content on the surface of rubber was significantly lower compared to theoretical values. Nevertheless, the degree of grafting was enough to provide a strong hydrophilic character of rubber surface, which was confirmed by noticeably enhanced suspension stability in water compared to unmodified rubber. Moreover, the Authors proved that due to the much higher amino group density in comparison to conventional curing agents, poly(amidoamine) grafted rubber particles turned out to be effective curing agent for epoxy resin.

3.4. Other resins

In one of the first works related to polyester resin/WTR composites, Rodriguez (1988) investigated the impact of particle size, various silane treatment, and WTR content on the properties of unsaturated polyester resin. Among applied silane modifiers of WTR were N-2-aminoethyl-3-aminopropyltrimethoxysilane, 3-amino-propyltriethoxysilane, *p*-aminophenyl-triethoxysilane, and methyltrimethoxysilane. In general, all modifications of WTR particles' surface resulted in the elongation of gel time, which was associated with the additional reactions occurring during polymerization. Such effect was also ascribed to the presence of carbon black, which acts as a retardant of cobalt-accelerated polymerization reactions. All applied modifications of the WTR surface resulted in the 63–90% increase of composites' tensile strength and 95–228% increase of their tensile modulus. Nevertheless, incorporation of WTR, even modified one, resulted in the deterioration of the dynamic mechanical performance of the polyester resin. With the incorporation of WTR, the dynamic modulus was decreased, and glass transition temperature, determined as the position of a peak on the $\tan \delta$ curve was shifted towards lower temperatures, which indicated more ductile behavior of the material.

Abu-Jdayil et al. (2016a, 2016b) investigated the impact of particle size and content of WTR on structure, mechanical and thermal properties of polyester/WTR composites. The increase of WTR particle size resulted in a higher content of air inclusions in samples, which increased their porosity. Such effect may also be associated with a lower specific surface area of bigger particles and hence

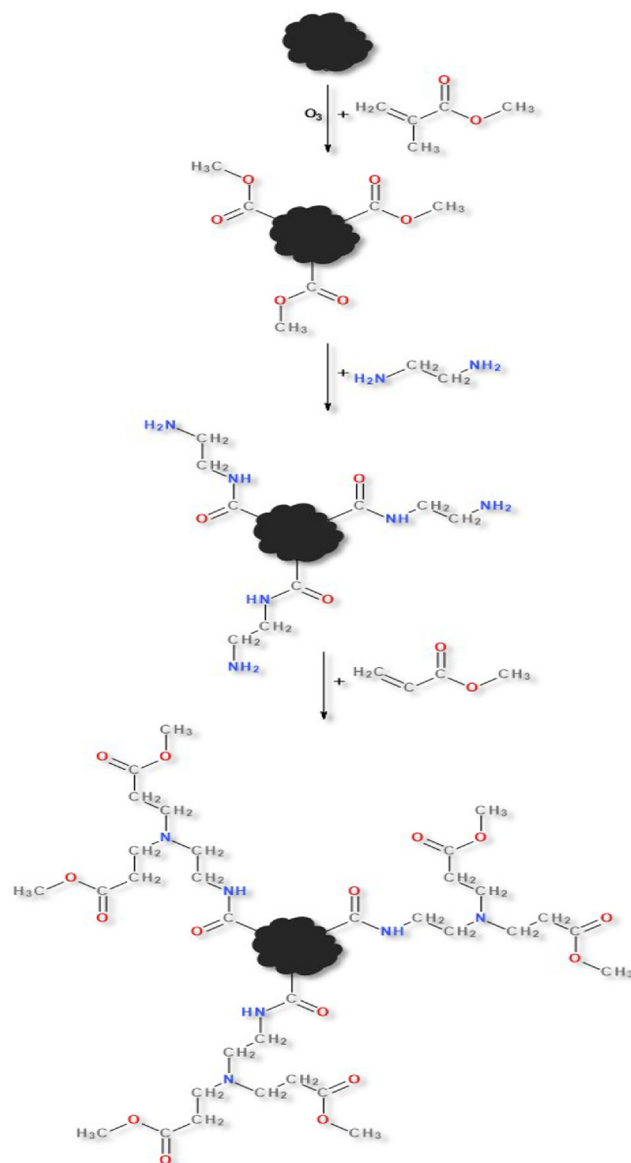


Fig. 10. Scheme of poly(amidoamine) grafting on the surface of WTR particles applied in work (Based on (Fan and Lu, 2011a)).

weaker interfacial adhesion of polyester matrix to WTR particles. Changes in materials' microstructure affected their mechanical performance. Compressive strength was lower for composites filled by WTR with larger particle size. A similar effect was observed for tensile strength. Incorporation of WTR was also associated with lowering of composites' modulus, which was caused by

Table 4
Comparison of performance properties of thermosets/WTR composites as function of used matrix.

Matrix	WTR		Performance properties				Reference
	particles size (mm)	content	Density (kg/m ³)	Tensile strength (MPa)	Elongation at break (%)	Compression strength	
Solid polyurethane	0.8–3.0	60–90 wt%	–	~0.35–1.2*	~2–70*	~0.5–9.5* MPa at yield	Strakšys et al. (2018)
Foamed polyurethane	<1	10–30 pbw	299–316	–	–	13.0–22.5 kPa at 30% deformation	Piszczczyk et al. (2015b)
Epoxy	0.355–0.500	5–10% vol.	–	18–49	0.07–0.21	–	Sipahi-Saglam et al. (2001)
Unsaturated polyester	0.8–2.0	5–40% vol.	922–1180*	1.25–22.80	–	8.42–79.20 MPa at yield	Abu-Jdayil et al. (2016a, 2016b)

* Values estimated from curves presented in the cited paper.

significantly lower stiffness of rubber compared to polyester matrix. The addition of WTR also resulted in the 25% enhancement of thermal insulation properties of the material, which was directly associated with lower thermal conductivity of rubber (0.082 W/m·K), comparing to unmodified polyester resin (0.150 W/m·K). Also increase of WTR particle size resulted in the enhancement of thermal insulation properties, which was related to the above mentioned higher porosity of the material, because air inclusions are beneficial for lowering of materials' thermal conductivity coefficient.

Ong et al. (2015) incorporated WTR into melamine-urea-formaldehyde (MUF) plywood. In order to enhance the interactions between WTR particles and plywood (MUF resin + wood flour), they were treated with 20% nitric acid, 30% hydrogen peroxide, and acetone. Based on FTIR analysis, WTR particles modified with nitric acid were selected as the most promising, due to the chemical interactions between carbonyl groups present on the surface of WTR and amine groups of MUF. Moreover, HNO₃ treatment resulted in almost complete removal of inorganic content in WTR, such as CaO, ZnO, or Ca₂SiO₄·3H₂O. Only residual magnesium oxide was observed in modified rubber particles. Moreover, to prove the assumptions based on the FTIR analysis examined shear strength and formaldehyde emission of plywood containing different modified rubber particles. Plywood containing HNO₃ modified WTR showed shear strength around 1.40 MPa, while treatment with H₂O₂ and acetone resulted in the values around 1.15 and 1.06 MPa. Moreover, the nitric acid treatment led to ~8% lower formaldehyde emission comparing to other applied modifications. Further, the Authors determined 13 wt% as the optimal concentration of filler, which provided the best balance between mechanical performance and formaldehyde emission. For higher concentrations, aggregation of solid particles occurred, which inhibited the penetration of pores with resin and limited the chemical interactions between WTR and MUF matrix. As a result, shear strength was decreased due to lower compatibility, and unbonded MUF caused higher emission of formaldehyde. Based on the presented results, the Authors stated that suitably modified WTR particles could be successfully incorporated into the manufacturing of MUF-based plywood.

4. Advances and limitations in the development of thermosets/WTR systems

As presented above, currently performed research works considered using various matrices in thermosets/WTR composites, which performance properties are compared in Table 4.

This approach allows the preparation of materials with a wide range of applications. The main advance of thermosets modified with low-cost is related to the liquid state of matrix components, therefore mixing of matrix and WTR can be easily performed at

ambient temperature without using special and usually expensive equipment. Moreover, it is worth mentioning that processing of WTR at a lower temperature significantly reduce the emission of volatile organic compounds (Gągol et al., 2015).

Thermosets chemistry allows the interfacial bonding of WTR filler during curing of matrix, which results in the improvement of thermoset/WTR system compatibility. Matrix-filler interactions can be also tailored by: i) modification of thermoset composition (e.g. using a wide range of commercially available systems or additives) or ii) suitable modification/functionalization of WTR.

Among limitations of thermosets/WTR systems development technological problems with increasing viscosity of liquid components used during thermosets preparation should be mentioned. Moreover, issues related to the stability of liquid components/WTR systems or change of humidity of WTR/modified WTR during storage are also poorly described in the literature, while these factors will affect cross-linking efficiency and consequently the possibility of application in industrial scale.

5. Conclusions and future trends

The application of WTR in polymer composites is usually very limited due to weak adhesion between the cross-linked rubber and the surface of the polymer matrix. Therefore, promoting interfacial interaction between WTR and polymer matrix is necessary in order to improve the performance properties of polymer/WTR composites. One solution to this issue is *in-situ* reactions between matrix and WTR filler during the formulation of construction and engineering materials.

It seems that ongoing investigations in this field should be focused on three main directions. The first one is modification and functionalization of WTR particles, which is very important for providing the desired level of chemical reactions and physical interactions between WTR particles and polymer matrix or *in-situ* formed polymer matrix. Additionally, modification/functionalization levels strongly affect the migration of components between WTR and matrix. This phenomenon is poorly described in the literature, while it has a significant impact on the final properties of polymer/WTR composites. Another issue that should be considered during future research is the repeatability of the functionalization/modification process and storage stability of obtained products. In order to achieve this goal and to make implementation of laboratory results in industrial scale possible, a continuous method of WTR modification/functionalization (e.g., reactive extrusion) should develop in the near future.

A second promising approach for research in the up-cycling of rubber recycling is hybrid fillers, which could be prepared during WTR modification/functionalization and used as low-cost, flexible magnetic materials or reinforcing (or semi-reinforcing) fillers in polymer composites, bitumens, and concrete.

The third direction should be related to study chemical reactions between WTR and in-situ formed polymer matrix and improvement of selected properties of obtained composites (e.g. mechanical properties, flame retardancy, biodegradability, etc.). This approach allows the preparation of novel polymeric materials with unique performance properties, which could find application in many branches of industry, e.g., 3D printing technologies (Alkadi et al., 2019).

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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