Influence of microwave treatment conditions of GTR on physico-mechanical and structural properties of NBR/NR/GTR composites

J. Cañavate[1*], X. Colom[1], M. R. Saeb[2], M. Przybysz[3], L. Zedler[3], K. Formela[3]
[1] Department of Chemical Engineering, Universitat Politècnica de Catalunya Barcelona Tech, Carrer de Colom, 1, 08222 Terrassa, Barcelona, Spain. [2]Department of Resin and Additives, Institute for Color Science and Technology, 16765-654 Teheran, Iran. [3] Department of Polymer Technology, Faculty of Chemistry, Gdańsk University of Technology, Gabriela Narutowicza 11/12, 80–233 Gdańsk, Poland

Influencia de las condiciones de tratamiento con microondas de caucho triturado de neumático sobre las propiedades físico-mecánicas y estructurales de composites NBR / NR / GTR

Influència de les condicions de tractament amb microones de cautxú triturat de pneumàtic sobre les propietats físico-mecàniques i estructurals de compòsits NBR/NR/GTR

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SUMMARY

The increasing amount of tires used in the industry induces the researchers to find alternatives to the recycling of the end-of-life tires. Several alternatives in order to application of ground tire rubber GTR include their incorporation as a filler in composites. The main issue in this approach is the lack of compatibility between GTR and polymer matrix. In order to solve this problem the devulcanization by microwaves has been proposed as an interesting approach in order to improve the subsequent crosslinking when the GTR is incorporated to an elastomeric matrix and subsequently co-vulcanizated. In this article a blend formed by natural rubber NR and nitrile butadiene rubber NBR has been proposed as a suitable matrix for composites including GTR. In order to improve the compatibility, the GTR was treated by microwaves prior to its application as semi-reinforcement in rubber matrix. The results indicate that the pretreatment of GTR by microwaves improves the cross-linking and co-vulcanization of used elastomers, what have a positive influence on the mechanical behaviour and microstructure of the NR/NBR/GTR composites evaluated by tensile tests, equilibrium swelling, Thermo Gravimetric Analysis (TGA), Infrared Spectroscopy (FTIR) and Scanning Electronic Microscopy (SEM).

Keywords: Recycling; Ground Tire Rubber; Microwave irradiation; Rubber Composites; Structure-property relationship

RESUMEN

La creciente cantidad de neumáticos utilizados en la industria ha inducido a los investigadores a encontrar alternativas para el reciclaje de los neumáticos al final de su vida útil. Varias alternativas propuestas para este fin incluyen la incorporacion de caucho triturado de neumático GTR como relleno en materiales compuestos. El principal inconveniente que presenta este método es la falta de compatibilidad entre el GTR y la matriz de polímero. Con el fin de resolver este problema, la desvulcanización por microondas se ha revelado un procedimiento interesante puesto que cuando el GTR tratado con microondas se incorpora a una matriz elastomérica, puede conseguirse mejorar la reticulación posterior si se realiza un vulcanizado. En este artículo, una mezcla formada por caucho natural NR y caucho de nitrilo NBR se ha propuesto como matriz para materiales compuestos

***Correponding author: francisco.javier.canavate@upc.edu**

que incluyen GTR. Para mejorar la compatibilidad, el GTR ha sido tratado con microondas antes de su aplicación como refuerzo en la matriz elastomérica. Los resultados indican que el tratamiento previo de GTR por microondas mejora la reticulación y la co-vulcanización de los elastómeros usados, lo que tiene una influencia positiva en el comportamiento mecánico y la microestructura de los materiales compuestos NR/NBR/GTR. Los materiales han sido evaluados mediante ensayos de tracción, ensayo de hinchamiento, Análisis TGA, FTIR y SEM.

Palabras clave: Reciclaje; caucho triturado de neumático de tierra; Irradiación con microondas; compuestos de caucho; relación estructura-propiedades

RESUM

La creixent quantitat de pneumàtics utilitzats en la indústria ha impulsat els investigadors a trobar alternatives per al reciclatge Existeixen diverses alternatives proposades per a aquest fi, incloent la incorporació de cautxú triturat de pneumàtic GTR com a farciment en materials compostos. El principal inconvenient que presenta aquest mètode és la manca de compatibilitat entre el GTR i la matriu de polímer. Per tal de resoldre aquest problema, la desvulcanització per microones sembla un procediment interessant, ja que quan el GTR tractat amb microones s'incorpora a una matriu elastomèrica, es pot aconseguir una major reticulació posterior si a continuació es realitza un vulcanitzat. En aquest article, una barreja formada per cautxú natural NR i cautxú de nitril NBR s'ha proposat com a matriu per a materials compostos que inclouen GTR. Per millorar la compatibilitat, el GTR ha estat tractat amb microones abans de la seva aplicació com a reforç a la matriu elastomèrica. Els resultats indiquen que el tractament previ de GTR per microones millora la reticulació i la co-vulcanització dels elastòmers usats i té una influència positiva en el comportament mecànic i la microestructura dels materials compostos NR/NBR/GTR. Els materials han estat avaluats mitjançant assajos de tracció, assaig d'inflament, anàlisi TGA, FTIR i SEM.

Paraules clau: Reciclatge; cautxú triturat de pneumàtic; Irradiació amb microones; composites de cautxú; relació estructura-propietats

INTRODUCTION

According to estimated data, the number of discarded waste tires in 2030, can reach 1200 million annually[1]. Only in Europe, 289 million of passenger car tyres and light trucks were sold in 2017[2] . In tonnes, it is estimated that every year, about 3.2 million tonnes of used tires are generated in Europe. The amount of tyres recycled or recovered ascends to 2.5 million tonnes, approximately 250 million units.

The numbers cited speak by themselves. Under a circular economy approach, the end of life tyres ELT should be considered as an important product, a source of energy and materials, with consequent environmental and also economic benefits.

Several research groups have proposed blends using Ground Tyre Rubber GTR, an available product supplied by recycling companies, as a component in blends with thermoplastics. The aim is producing useful composites industrially viable and competitive. These materials present the problem of the lack of compatibility between the GTR and the matrix. Different attempts to improve the interaction GTR-matrix were investigated, including pretreatments[3,4], additives[5]or surface modification[6].

A complementary approach to overcome the incompatibility in blends has been founded on the devulcanization. Ideally, through this process the scrap tyre would be transformed in a product suitable of re-vulcanization and reuse in similar conditions to the original rubber. In order to achieve this goal, the devulcanization of the cross-linked structure of the GTR would imply the scission of the sulfide bonds present in the rubber. The breaking of the bonds that form the polymeric network can be performed by: supercritical CO_2[7], ultrasonic treatment[8], mechano-chemical[9,10] or microbial methods[11].

Some research groups have opted for the use of microwaves as energy source to devulcanize GTR and elastomeric samples. The advantages of microwaves include a faster, more precise and homogeneus, increase of the temperature of the sample, which allows a more selective breaking of the sulfide bridges, leaving the C-C bonds relatively unaffected. The effects of this pre-treatment have been studied on several vulcanizates NR, SBR, EPDM[12] and on GTR[13].

Considering the microwave irradiation a promising technique to improve the properties of the elastomeric samples including GTR, our research group has studied the effects of the microwaves on the GTR[14] and the structure of different types of GTR and its influence on the devulcanization process[15]. In order to explore the possibilities of producing useful composites by using formulations including other components that improve the properties, we have studied blends including GTR and natural rubber with interesting results[16].

In this work we study a different blend, composed by nitrile butadiene rubber, natural rubber and GTR irradiated with microwaves at different exposure times. The aim is to optimize the irradiation time and the formulation in order to increase the amount of GTR present in the blend preserving applicability. We have tested the mechanical properties in order to determine the real possibilities of application and studied the microstructure to provide a better understanding of macroscopic behaviour of the materials.

EXPERIMENTAL

Materials

Natural rubber NR grade SVR 3L Vietnam Natural Rubber with ash content: 0.5 %wt., volatile matter content: 0.8 %wt. and density: 0.92 g/cm^3 and nitrile butadiene rubber type 1502, density 0.907 g/cm^3 were supplied by Hexpol Rubi Spain. Ground tire rubber GTR was supplied by GMN Maials Spain. The particle size distribution of the used GTR has been published elsewhere[16]. The particle size distribution had an average value of 390 μm.

Carbon black N-330, vulcanization accelerators TBBS- N-tert-butyl-2-benzothiazole sulfonamide, TMTD - tetramethylthiuram disulfide, stearic acid, zinc oxide and sulfur with technical purity were supplied by Vigar Vilafranca del Penadès Spain.

Microwave devulcanization of GTR

GTR was devulcanized in a special prototype microwave reactor constructed in our lab. The system is based in a conventional microwave oven provided with a sample container adapted with a motorized stirring system designed in PTFE. The design of the container and the stirrer favours an homogeneous irradiation of the sample. Power and time of irradiation can be controlled independently. Samples of 60 g GTR were used. Devulcanization process was performed setting the magnetron power to 700W, 80 rpm and exposure times of 3, 5 and 10 min. This methodology is based on preliminary studies previously published in works[16,17]. After some previous tests, in order to avoid GTR degradation, treatment time was limited to 10 min.

Samples preparation

NBR/NR/GTR composites were prepared at 70 °C using a Brabender plastograph batch mixer. The rotational speed of the rotors was 100 rpm. The blend of nitrile butadiene-natural rubber was previously masticated for 2 minutes, then mixed with carbon black, GTR and devulcanizated GTR dGTR for 4 minutes, followed by 2 minutes of mixing with the cure agents. Total mixing time was 8 minutes.

GTR content in the samples was 0, 10, 30 and 50 parts per hundred of rubber (phr). The curing system was constituted by zinc oxide 5.0 phr, stearic acid 3.0 phr, TBBS 1.0 phr TMTD 0.25 phr and sulphur 2.0 phr.

The NBR/NR/GTR compounds were compression moulded into 3 mm thick samples using a laboratory plate press type P 200E from Dr. Collin GmbH Germany. The settings were 160 °C and 4.9 MPa. Optimal vulcanization time under pressure was determined at 12 min[16]. Unfilled elastomeric compositions NBR/NR were also processed and tested to use them as reference sample.

Testing and measurements

Chemical structure and properties of NR/NBR/GTR composites were studied by means of several techniques.

Samples were analysed by Fourier transform infrared spectroscopy FTIR using a Nicolet iS10 spectrometer from Thermo Scientific USA provided with an ATR attachment with a germanium crystal. Spectra were registered at 4 cm^{-1} resolution and 64 scans in the range of 4000-550 cm^{-1}. This range includes the typical bands present in natural rubber that are related to CH_2 deformation 1450 cm^{-1}, CH_3 asymmetric deformation 1375 cm^{-1} and =CH out-of-plane bending 831 cm^{-1}[15]. NBR presents similar bands with slight displacements in the wave number plus the bands corresponding to the stretching of -CN 2233 cm^{-1}[18].

Tensile strength and elongation at break were tested according to the standard ISO 37 using a Instron 3366 testing machine USA with cell load capacity of 20 kN. Cross-head speed was 500 mm/min at RH of 50±5% and temperature 23±2°C. Measurements of extension were conducted directly, using an extensometer with sensor arms. Hardness was determined according to ISO 7619-1 using a Zwick 3130 durometer Shore A Germany. Presented results of tensile and hardness tests are the average of 5 values of measurements per sample.

Swelling degree of rubber composites was determined on 0.2 g of sample by equilibrium swelling in toluene at room temperature. The samples were immersed for 72 h. In previous studies[16,17] we have found that after 72 h the swelling has achieved equilibrium state. Swelling degree was calculated with the formula 1:

$$Q = \frac{m_t - m_o}{m_o} \times 100\% \qquad (1)$$

where: Q – swelling degree; m_t – mass of the sample swollen g; m_o – initial mass of sample g.

Thermogravimetric analysis TGA was performed on a Mettler Toledo TGA/SDTA 851 apparatus USA. NR/NBR/GTR composites weighing approx. 10-mg were placed in a corundum dish. The measurement was conducted in the temperature range of 40-600 °C and under nitrogen atmosphere 30 ml/min, at a heating rate of 20 °C/min. Presented results are the average of 3 measurements per sample.

The morphology of NR/NBR/GTR fracture surfaces obtained after the tensile test performed on the samples was observed with a JEOL 5610 scanning electron microscope Japan. In order to increase the conductivity, before observation the samples were covered with a fine gold-palladium layer in a vacuum chamber.

RESULTS AND DISCUSSION

Mechanical properties

Tables 1-3 show mechanical properties of the different NR/NBR/GTR composites as a function of the GTR content and the microwave irradiation time used in the devulcanization process. The values show some trends in the mechanical behaviour of the samples.

Table 1. *Young modulus at 300% MPa of the NR/NBR/GTR blends as a function of the microwave treatment (MW) and the composition of the composites*

Sample code	0 phr GTR	50 phr GTR			
		0 min MW	3 min MW	5 min MW	10 min MW
NR25NBR75	1.6±0.05	1.6±0.07	1.6±0.02	1.7±0.06	1.5±0.09
NR50NBR50	2.1±0.03	1.8±0.04	1.8±0.05	2.1±0.19	2.1±0.09
NR75NBR25	2.4±0.09	1.8±0.07	1.8±0.04	2.0±0.12	1.9±0.09
NR100	2.2±0.1	2.1±0.1	2.1±0.1	2.2±0.3	2.2±0.1

Observing the values of Young modulus, the proportion of NR/NBR, as expected, has influence in their behaviour. An increase of the amount of NR in the blend increase the young modulus up to a 43.7%. These values are coherent because of the higher modulus of the NR 2.2 MPa[17] compared with the NBR 1.5 MPa used in the preparation of the samples.

Adding 50 phr of GTR to the NR/NBR always decrease the values of young modulus and mechanical properties in general. This behaviour has been reported previously in other research work[15]. The lack of compatibility between the GTR and the difficulties achieving a homogeneous cross-linked network are responsible for that decrease. However, when the GTR has been previously treated with microwaves, there is an increase of the modulus of the samples. The increase can be as high as 19% in case of NR50NBR50 with 5 min MW. Microwaves enhance devulcanization that increases the possibilities of blending regularly with the NR/NBR matrix. The cross-linking provides a structure where the GTR becomes integrated to the matrix by the S-S bonds formed during the vulcanization achieving an improvement of the mechanical properties, in this case, of the Young modulus.

The values of Young modulus tend to increase with the microwave treatment time, being higher at 5 min than at 3 min but at 10 min, a decrease can be observed. That implies that, after 10 min, there is a reclaiming of the rubber, the amount of energy provided by the microwaves is too high and there is a breaking of the C-C bonds that are not revulcanizable relinked again, producing a less cross-linked structure and lower values of Young modulus.

Table 2.- *Tensile strength MPa of the NR/NBR/GTR blends as a function of the microwave treatment and the composition of the elastomeric samples*

Sample code	0 phr GTR	50 phr GTR			
		0 min MW	3 min MW	5 min MW	10 min MW
NR25NBR75	17.3±1.5	12.0±0.05	12.6±0,9	12.8±0.2	11.7±1.1
NR50NBR50	18.0±0.4	13.2±0.6	13.3±0.8	14.7±1,0	14.6±0.7
NR75NBR25	22.5±0.7	14.7±0.3	15.7±0.6	16.2±0.4	15.6±0.8
NR100*	26.1±1.9	15.5±1.0	16.4±1.3	15.8±1.4	16.0±0.9

*from reference 16

Tensile strength shows a similar pattern in all aforementioned aspects. Again, at NR50NBR50 with 5 min MW the highest value is obtained, with an increase of about a 11% comparing to the sample not treated.

Table 3. *Elongation at break % of the NR/NBR/GTR blends as a function of the microwave treatment and the composition of the composites*

Sample code	0 phr GTR	50 phr GTR			
		0 min MW	3 min MW	5 min MW	10 min MW
NR25NBR75	678±39	570±20	590±29	570±8	580±25
NR50NBR50	698±13	620±26	625±26	602±19	623±13
NR75NBR25	735±21	671±11	687±22	683±13	683±10
NR100*	854±68	695±81	705±78	671±94	728±60

*from reference 16

Elongation at break constitutes a slightly different case. GTR, even when is formed basically for NR, has less elongation that the initial NR/NBR blend. Then, two effects are combined. First the interaction of the GTR and the NR/NBR blend, if there is a lack of adhesion of the particles of GTR to the matrix the elongation at break as the other properties will be decreased. Second, the lower elongation of the GTR and the increase of cross-linking caused by the microwave treatment causes that, even with an improvement of the compatibility with the GTR particles caused by microwaves, the increase in elongation at break of the whole system is uncertain and depends the relative effect of these combined factors. Anyway, the system is complex and a possible migration of the sulphur or the carbon black could also have influence.

From the analysis of the mechanical properties we can conclude that the vulcanization of different elastomeric samples create a linkages of the GTR to the NR/NBR matrix by the co-vulcanization process, which links the GTR particles through covalent bonds. The results obtained by the other techniques applied to the samples corroborate this.

Thermogravimetric analysis

The thermogravimetric analysis (TGA) and derivative thermogravimetric analysis (DTG) to the samples provides information about the thermal stability of the samples. In this sense, a sample with more degree of cross-linking will be more stable and decompose to higher temperatures. However, the analysis of this system is more complex, because it includes different microphases that evolve separately.

Temperatures of peak obtained by DTG are included in table 4.

Table 4. *Temperatures of decomposition of the NR/NBR/GTR blends as a function of the microwave treatment and the composition of the composites*

Sample code	0 phr GTR	50 phr GTR			
		0 min MW	3 min MW	5 min MW	10 min MW
	Tp °C	Tp °C	Tp °C	Tp °C	Tp °C
NBR100	485	430/483	432/481	432/484	432/484
NR25NBR75	406/485	402/486	402/486	406/486	407/487
NR50NBR50	402/483	402/478	401/473	403/480	401/479
NR75NBR25	402/466	400/431	400/460	403/480	396/477
NR100*	401	401/443	401/443	401/445	401/446

*from reference 16

Natural rubber, in the conditions of the samples of this study presents a decomposition temperature T_p of 401°C, while NBR has a T_p of 485°C. When these polymers are blended and revulcanized, the DTG shows the two peaks corresponding to each polymer. The NR and NBR are not compatible and therefore, there are domains of both polymers present in the blend. Nevertheless, there is a partial miscibility of the NR and NBR where the polymeric chains interact and possibly crosslink together, causing a displacement of the T_p. Then, the blends show a displacement of their T_p according to the composition that tends to bring closer the two initial peaks. This is more evident in the case of the peak corresponding to the NBR, the T_p evolves from the initial 485°C when there is no NR to a 466°C when the proportion is NR75NBR25. NR shows also a displacement in its T_p, evolving from 401°C when there is no NBR present to a 406°C in the NR25NBR75 sample.

The TGA of the GTR is also basically represented by two peaks. One of them is situated at 402°C and it is related to the NR present in the tyre. The second is a big peak at 467°C, which is originated by the decomposition of the SBR. The TGA shows also other small peaks or shoulders close to the main peaks that are representative of other additives or interactions of the main polymers between them or with some other components of the tyre.

Figure 1 shows the TGA and the derivative graph obtained when adding GTR to the 25NR/75NBR elastomeric sample producing a displacement of the decomposition temperature T_p. The T_p of the different blends show a displacement between the two temperatures 485°C of NBR and 401°C of NR related to the proportions of the initial blend and the contribution of different elastomers NR, SBR, BR, NBR included in the GTR. This displacement is produced by the interactions between the two types of NR the one present in the GTR and the other present in the elastomeric sample.

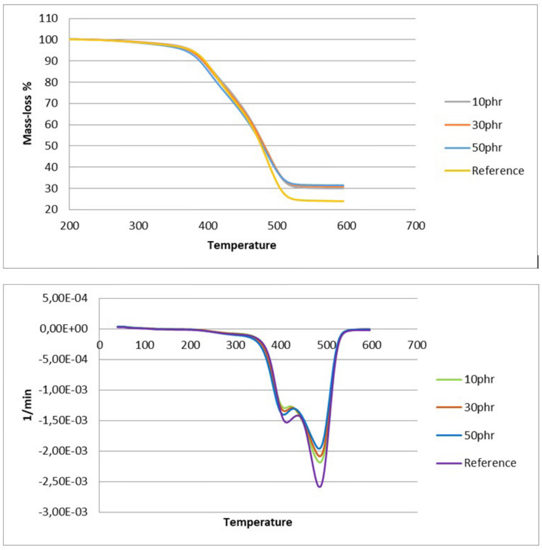

Figure 1.- *TGA of samples 25NBR/75NR containing untreated GTR in several proportions.*

Nevertheless of the samples, the microwaves treatment tends to slightly increase the T_p of the elastomeric samples, because of an increase in the thermal stability of the samples produced by the devulcanization that results in a posterior improvement of the cross-linking. The higher values are obtained at 5 and 10 minutes of treatment. In some cases, as described in the discussion of the mechanical properties, 10 minutes seem to provide less stability than 5 because of the reclaiming of the samples produced by an excessive treatment time, that provokes not only devulcanization if not breaking in the main chain.

The T_p of the NR tends also to increase with the microwave treatment of GTR, being the increase slightly bigger than NBR. The devulcanization acts preferently on disulfide present in the NR phase of the GTR, producing posteriorly, after revulcanization a more compact phase that has improved thermal stability.

SWELLING DEGREE

The swelling test was performed to evaluate the cross-link density of the samples, in order to confirm the TGA data discussed above. It was found that after 72 hours the samples had achieved a maximum stabilized value and the swelling reached an equilibrium. The swelling values obtained are shown in table 5

Table 5.- *Swelling degree % as a function of the microwave treatment and the composition of the composites*

Sample code	0 phr GTR	50 phr GTR			
		0 min MW	3 min MW	5 min MW	10 min MW
NR25NBR75	158.2	169.5	163.9	168.1	163.5
NR50NBR50	177.7	186.2	186.3	173.6	180.4
NR75NBR25	179.5	189.4	194.5	173.6	195.5
NR100	219.3	245.1	243.0	230.5	229.3

Differences in swelling related to NR/NBR ratio without GTR addition can be observed. The samples containing higher proportion of NR present higher values of swelling[17]. While the sample NR25NBR75 shows a 159% of swelling, the sample containing NR75NBR25 swells up to 179.5% and the sample NR100 increases until 219%, which constitutes more than a 12% and 38% respectively of increase. The difference is attributed to the superior resistance to non-polar solvents of polar nitril butadiene rubber which prevents from swelling. However the effects of toluene in NBR are slightly different than those produced by other solvents i.e. heptane having further incidence in the structural destabilization of the rubber, as reported by other authors[19,20].

Adding GTR to the blend in general increase the swelling. Samples containing NR25NBR75 increase their swelling from 158.9% to a 169.5% a 6.7% when adding 50 phr GTR. GTR includes both NR and, in smaller amount NBR, then increasing the total amount of NR produces an increase in swelling. Also the existence of fillers and other products non crosslinkable in GTR justify this increase. The effect of including 30 phr of GTR is similar but less marked because of the lower amount of GTR included in the blend. The variation in this case from 150% to 162,8%.

The samples including NR50NBR50 also increase their swelling when adding GTR, 50 phr GTR produce an increase from 177.7 to a 186.2% equalling to about a 5%. The relative increase in these samples is lower than in the NR25NBR75 because the amount of NR provided by the 50 phr of GTR is relatively lower compared to the included in the original compound NR50NBR50.

The samples NR75NBR25 also increase moderately their swelling with the addition of GTR. In this case, the maximum increment with 50 phr is from 179.5% to 189.4% 5.5 %. The addition of more GTR to a sample that is already very rich in natural rubber does not provide a relatively high increase of the content on natural rubber of the composition.

These results imply that the inclusion of GTR decreases the possibility of crosslinking in the samples. This effect is related to the lower cross-linking of the natural rubber compared to the NBR and also to the inclusion in the samples of fillers like silica or carbon black which do not contribute to the cross-linking. Samples containing GTR tend, because of these considerations to swell more. This is also in concordance with the decrease of mechanical properties experimented by including GTR in samples and the TGA results, where the inclusion of GTR produces a decrease of the thermal stability.

The microwave treatment of GTR tends to reduce the swelling in studied NR/NBR/GTR composites. The effect is not very evident and presents variability in the studied samples but in general microwaves improve compatibility as shown in mechanical properties and TGA studies and this is reflected in less swelling. It must be taken into account that the addition of GTR to the NR/NBR samples involves several phenomena together that include the variation in the amount of NR present in the whole sample, but also the presence of fillers as silica or carbon black.

FTIR analysis

The study of the samples by FTIR spectroscopy shows that the presence of zinc stearate ZnSt on the surface of the samples is affected by the presence of GTR. ZnSt is related to the band of 1540 cm^{-1} and previous studies have demonstrated that there is a migration of this compound to the surface during the processing of rubber samples[21,22].

A spectrum of the 25NR/75NBR blend containing GTR in different proportions and at the three times of irradiation is shown at Figure 2.

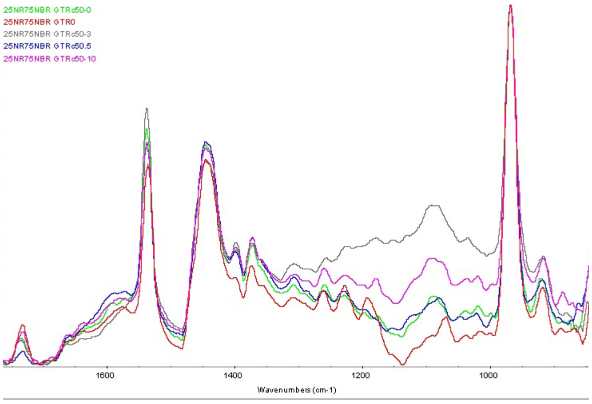

Figure 2.- *Spectrum of the 25NR/75NBR blend containing different amounts of GTR irradiated 0, 3, 5 and 10 min.*

In the spectrum an increase in the band of 1540 cm^{-1} is observed. The lowest values corresponds to the sample without GTR. All the other samples containing 50 phr GTR present higher contents of ZnSt.

This indicates that the migration of the ZnSt changes according to the samples degree of cross-linking. The crosslinked chains affect to the possibility of the diffusion of the ZnSt, a network structure slows the molecules ability to reach the surface.

This observation also agrees with the results of the swelling degree, and the mechanical properties. The sample without GTR swells less, has longer elongation and has higher strength, which is coherent with a higher degree of cross-linking. Another possibility, also coherent with the mechanical and swelling results is that the increase of the mobility of the molecules of ZnSt observed when adding GTR is caused by the creation of pores and microvoids which have been observed by SEM and disscused later in this article. The formation of aforementioned viod structures favors the migration of the ZnSt to the surface. Figure 2 also shows the effect of the irradiation time on the migration of the ZnSt. Samples with 0 and 3 min irradiation presents higher amount of ZnSt in their surface, while in samples that have been submitted to 5 and 10 min of microwave treatment, the band is lower. This is related to the effect of the microwave treatment on the cross-linking of the samples. As previous results have shown, the treatment with microwaves favours the crosslinking contributing to making the diffusion of the ZnSt more difficult and slowing the migration.

SEM analysis

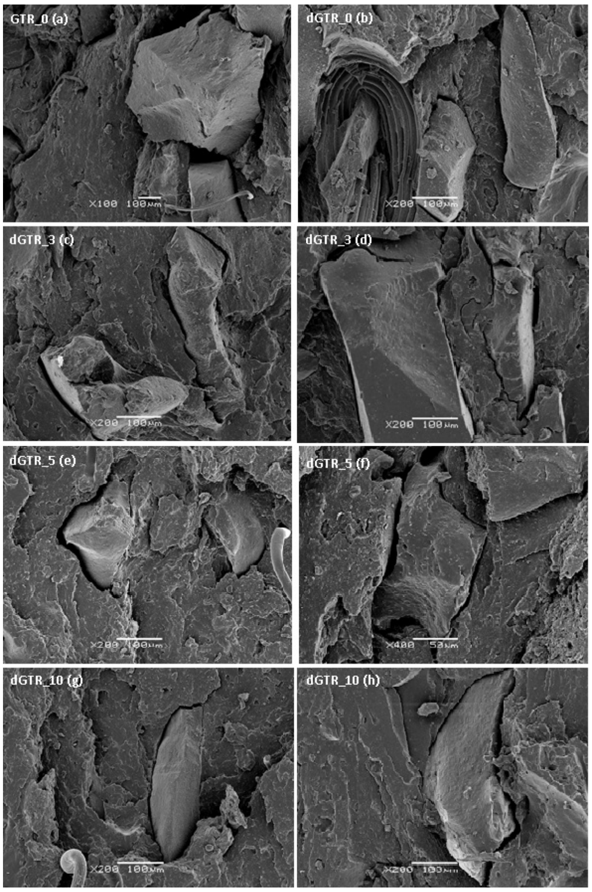

Figure 3.- *Fracture surfaces of the samples 25NR75NBR containing 50phr. of GTR at different times of microwave treatment a, b: 0 min c,d :3 min, e, f: 5min g, h: 10 min*

The morphology of the fracture surfaces of the samples used for the mechanical testing was observed by SEM. The fracture surfaces of the samples 25NR75NBR containing 50 phr of GTR at different times of microwave treatment are presented in Figure 3. A GTR particle is visible in every image. These pictures could give an indication on the degree of interaction between the matrix and the particles. Poor adhesion should show as voids or cracks in the interface area. The fracture shows propagation interfacial on at the surface of the GTR particles, this is consistent with the mechanical results that shows a decrease of mechanical properties as elongation at break or tensile strength.

There are visible voids or cracks between the particles and the matrix in nearly all samples, especially prominent in the samples containing GTR without microwave irradiation a and b. In picture a, the particle appears to be completely separated from the matrix, indicating a lack of interaction between matrix and GTR. There is a tendency towards an improved adhesion caused by the microwave exposure. In pictures g and h, containing GTR irradiated 10 min by microwaves, the particles are more linked to the matrix. These results are also in consonance with the mechanical testing and the migration of ZnSt. The treatment of GTR with microwaves improves the properties of NR/NBR/GTR composites because of the improved adhesion between GTR and NR/NBR matrix was achieved.

Not only the microwave treatment but also the amount of natural rubber present in the samples affects to the interfacial adhesion. An example is shown in figure 4.

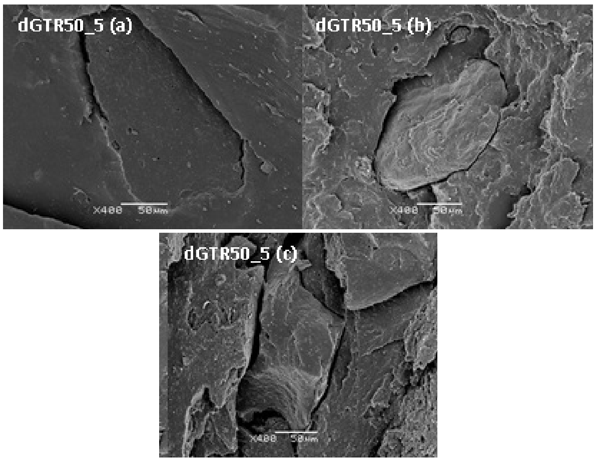

Figure 4.- *SEM microphotographies of samples containing 50 phr GTR devulcanized 5 min. a: 75%NR/25%NBR, b: 50NR/5NBR, c: 25%NR/75%NBR*

In the pictures showed in figure 4, the presence of voids along the surface of the particles, can be observed. On the other hand, NBR presents low compatibility with the GTR, the samples containing higher amount of NR present a better interfacial adhesion and the particles are more connected to the matrix. The particles appear surrounded by the matrix with less voids and cracks in the interface.

CONCLUSIONS

The study of the NR/NBR/GTR composites shows important microstructural effects that improve the understanding of the mechanisms of crosslinking and its effects on the final properties of the composites.

As found in previous studies the addition of unmodified GTR to an elastomeric blend produces a decrease of the mechanical properties because of the lack of interaction between the particles of the GTR and the matrix.

The treatment of GTR by microwaves improves slightly these properties. The devulcanizing effect produces an increase of cross-linking that has resulted in an improvement of the mechanical properties, improving the possibilities of use and application.

The improvement of the cross-linking causing the increase of the mechanical properties is observed in the TGA and swelling studies. The FTIR also corroborates these data and provides information about the migration of the ZnSt to the surface of the samples, which is lower in samples treated by microwaves because of the higher crosslinking of the samples.

The fracture surfaces observed by SEM show a better interaction between the particles and the matrix in the samples treated by microwaves. The inclusion of natural rubber in the matrix favours also the integration of the particles in the matrix and can be responsible for an improvement of the mechanical properties.

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