Recycling of waste tire rubber: Microwave devulcanization and incorporation in a thermoset resin

CrossMark

Karima Aoudia [a], Saïd Azem [a], Nourredine Aït Hocine [b,*], Michel Gratton [b], Valeria Pettarin [c], Saïd Seghar [d]

[a] LEC2M, Université Mouloud Mammeri de Tizi-Ouzou, B.P. 17, Hasnaoua, 15000 Tizi-Ouzou, Algeria
[b] LMR, INSA Centre Val de Loire, 3 rue de la Chocolaterie, BP 3410, 41034 Blois Cedex, France
[c] INTEMA, CONICET, University of Mar del Plata, Av. Juan B. Justo 4302, B7608FDQ Mar del Plata, Argentina
[d] PHENIX TECHNOLGIES, 29 Rue de Champfroid, 28800 Sancheville, France

ARTICLE INFO

ABSTRACT

This study focused on the possibility of recycling Waste Tire Rubber (WTR) to be used as polymer modifier. Thus, WTR was grinded into powder, at ambient temperature, with a disc mill PQ500 and microwave electromagnetic energy was used to devulcanize this powder with the final aim of producing a new composite by its incorporation in a thermoset resin. The influence of the treatment microwave energy on the devulcanization ratio was investigated. FTIR analysis revealed that rupture of Sulfur-Sulfur (S—S) and Carbon-Sulfur (C—S) bonds have occurred during the treatment. Swelling analysis showed that the microwave treatment can lead to a very significant degree of devulcanization. The Ground Tire Rubber (GTR) and the Devulcanized Ground Tire Rubber (DGTR) were then separately used to prepare epoxy based composites. It appeared that epoxy composites filled with DGTR have better mechanical properties than those filled with untreated GTR. This result agrees with scanning electron microscopy observations which highlighted a better interface coherence between DGTR and epoxy. A complementary analysis pointed out a linear relationship between the rubber modulus and the number of crosslink per chain.

1. Introduction

Storage and elimination of used tires have become an urgent word preoccupation from the environmental point of view. In fact, each year, hundreds of used tires are generated and accumulated in many countries.

Among the waste treatment procedures for used tires, grinding is the most important method for converting the waste rubber into ground material. As such, it can be used in surfaces of athletic tracks or games, or in combination with other materials such as asphalts (Kocevski et al., 2012; Vazquez et al., 2016; Zhou et al., 2015; Shafabakhsh et al., 2014; Presti et al., 2012; Juganaru et al., 2015), concrete (Afshinnia and Poursaee, 2015; Gupta et al., 2016; Thomas et al., 2015,2016), mortars (Popovici et al., 2015), rubber and thermoplastic matrices (Mathew et al., 2001; Radhesh Kumar et al., 2002; Yagneswaran et al., 2008; Zhang et al., 2010a, 2010b; Xu and Li, 2012; Sivaraosa et al., 2013; Azeez et al., 2014), and epoxy resins (Chekanov et al., 1997; He et al., 1999; Harsch et al., 2007; Yagneswaran et al., 2008, 2013; Piszczyk et al., 2015).

Epoxy resins are well known to have good physicochemical, bonding, mechanical and thermal properties (Chozhan et al., 2007). However, their mechanical characteristics are not sufficient to meet the widespread applications. Thus, modification of epoxy resins becomes essential to improve their properties. One effective approach is to fill such polymers with reinforcing particles including silica (Jia et al., 2006), minerals (Jia et al., 2006), carbon fiber (Jia et al., 2006), fiberglass (Wingard, 2000) and Ground Tire Rubber (GTR) (Chekanov et al., 1997; He et al., 1999; Harsch et al., 2007; Yagneswaran et al., 2008, 2013; Piszczyk et al., 2015).

He et al. (1999) studied the influence of the concentration of preformed rubber (acrylic) particles on epoxy fracture behavior. Fracture results showed that toughness increased to a maximum and then decreased as the concentration was increased, suggesting an optimum concentration for toughening. These results were supported by micrograph observations. Yagneswaran et al. (2008, 2013) used mechanochemical devulcanized GTR powder to prepare epoxy composites. Structural and thermal analyses were performed with different techniques (SEM-EDX, FTIR, DSC and TGA). Results mainly showed an increase in thermal stability with increasing GTR content and good dispersion and interaction of GTR in the epoxy matrix (Yagneswaran et al., 2008). A dominant catalyzing effect of GTR on the curing reaction was highlighted

since it was observed that the presence of GTR promotes the curing of epoxy resin (Yagneswaran et al., 2013). In the work reported by Piszczyk et al. (2015), flexible polyurethane foams were modified with two kinds of GTR, untreated and thermomechanically reclaimed. The impact of the rubber treatment on the mechanical and thermal properties of resulting polyurethane composites was analyzed. It appeared that the incorporation of rubber particles into polyurethane foam caused significant changes in the structure of this matrix. It particularly enhanced its cross-link density and had positive influence on its thermal stability and its compressive strength.

However, cross-linked structure of rubbers caused by the vulcanization process restricts the movement of rubber molecular chains and limits the interaction forces between GTR particles and the polymer matrix, resulting in a decrease of the composite's performance (Oliphant and Baker, 1993; Naskar et al., 2001, 2002). To obtain materials with improved properties, it seems useful to break the sulfur crosslinks formed during vulcanization. This process is named devulcanization.

Vulcanization is the thermo-chemical process mainly consisting of incorporating sulfur into a mixture of rubber to generate a 3D network, providing the elasticity and other properties desired in manufactured products. In fact, some degree of crosslinking in rubber phase is desired for its use alone or as a component in thermoplastics elastomers (Coran, 1995). In this process, sulfur atoms are chemically linked to rubber molecules to form Carbone-Sulfur-Carbon (C—S—C) and Carbone-Sulfur-Sulfur-...-Carbon (C—S_x—C) bonds. The vulcanization process is irreversible at standard atmospheric conditions of temperature and pressure.

Optimum devulcanization treatment, therefore, have to break C—S and/or S—S bonds without affecting hydrocarbon backbone chains. This operation occurs when the energy provided is higher than the link energies of C—S and S—S bonds, without reaching that of C—C bonds.

Several methods have been applied to devulcanize the Waste Tire Rubber (WTR) for reuse in rubber processing. Thermomechanical shearing devulcanization (Radhesh Kumar et al., 2002; Zhang et al., 2010a, 2010b; Sutanto et al., 2006a) is one of the most employed techniques. During this process, a strong rise in temperature occurs that can lead to the degradation of the rubber network. Most often, extruders are used to perform this procedure (Zhang et al., 2010a, 2010b; Sutanto et al., 2006a; Tao et al., 2013). Adding a chemical component defines a mechanochemical method (Yagneswaran et al., 2008; Sutanto et al., 2006a, 2006b; Dubkov et al., 2012). Various chemical compounds have been used in this method as devulcanizing agent. The main disadvantage of such compounds lies in their toxicity which pollutes the environment. Another process for rubber devulcanization is based on the use of high power ultrasound electromagnetic radiation (Li et al., 2004). Ultrasonic waves at certain level, can quickly break up the three dimensional cross-linked structure of vulcanized rubber in the presence of pressure and temperature. Ultrasonic devulcanization system is composed of an extruder and ultrasonic generator in order to combine the ultrasonic action with mechanical forces. There is also a devulcanization process based in the use of bacteria. Although vulcanized rubbers are not biodegradable, some microorganisms are able to attack the sulfur bonds of these materials, in order to remove the sulfur and oxidize it to sulfate (Li et al., 2011; Bredberg et al., 2002; Yao et al., 2013). The devulcanized powder obtained by this method could be incorporated in new rubber formulations, without significant loss in proprieties (Presti, 2013). However, the slowness of the devulcanization process, the necessity to treat the rubber in order to eliminate components that can kill bacteria and the difficulty of controlling the bacterial culture are the main factors that discourage the use of this method (Guo et al., 2010; Selbes et al., 2015).

Another method is microwave devulcanization that uses electromagnetic energy to break the cross-links of sulfur—sulfur (S—S) and carbon—sulfur (C—S) in rubbers. Microwave radiation can be absorbed by material through molecular interaction with the electromagnetic field and converted to heat. The material temperature increases quickly, reaching 260–350 °C during microwave treatment. This process promotes crosslink breaking while the chemical carbon—carbon bonds in the main chain are preserved (Rajan et al., 2006). However, several authors have found that long microwave exposure periods resulted in many structural changes and in breaking of the main polymer chain and the C═C chemical bonds, leading to lower molecular mass fractions (Garcia et al., 2015; Karger-Kocsis et al., 2013; Scuracchio et al., 2007; Isayev and Sujan, 2006). This can make the formation of new cross-links difficult in Devulcanized Ground Tire Rubber (DGTR) during their revulcanization in a following step for recycling. Among several techniques, microwave devulcanization presents some advantages that make it one of the most promising method for rubber recycling (Adhikari et al., 2000). These advantages include the ability to treat large amounts of material, the possibility of continuous processing and the easy adjustment of the process parameters, such as the power source and the time of treatment. Because microwave radiation can penetrate materials and deposit energy, heat can be generated throughout the volume of the material. The transference of energy does not rely on diffusion of heat from surfaces, and it is possible to achieve rapid and uniform heating of thick materials (Thostenson and Chou, 1999), i.e. this method enables to apply large amounts of energy rapidly and uniformly to the rubber, without using chemical reagents during the process (Isayev, 2005), which makes it an eco-friendly process (Hong et al., 2015).

In this study, microwave electromagnetic energy is used in an effort to break S—S and C—S bonds of powder rubber issued from WTR, leading to Devulcanized Ground Tire Rubber (DGTR). Crosslink densities of GTR and DGTR were estimated by swelling test in toluene. Analysis of bonds present in GTR and DGTR was performed by Fourier Transform Infrared analysis (FTIR). Then, GTR and DGTR were used to prepare epoxy based composites. Mechanical properties of these composites were evaluated by means of 3-point bending tests and fracture surfaces were observed by SEM, to correlate macroscopic properties with morphology. A complementary analysis was achieved to identify a relationship between the rubber modulus and the number of crosslink per chain.

2. Experimental procedures

2.1. Materials

GTR used in this study was kindly provided by Phenix Technologies (Sancheville 28800, France). It is mainly constituted of Styrene Butadiene Rubber (SBR) and originated from tire sidewalls. Its statistic size distribution was evaluated using an electrical sifter supplied by Retsch (France), with mesh sieves of 125 μm, 160 μm, 250 μm, 315 μm, 500 μm and 630 μm.

Composites were prepared by adding 10 wt% of GTR and DGTR powder to a mixture of a Bisphenol-A-(Epichlorhydrine) epoxy resin (molecular weight max 700) and bisphenol-F epoxy resin (molecular weight ⩽ 700/C13/C15 Alkyl glycidyl ether), by SOLO-PLAST (Germany). A hardener of composition: 3 aminomethyl-3,5 ,5-trimethyl-cycloexyl amine, Bisphenol A-epoxy resin (molecular weight < 700) and alcohol benzyl, was used.

Unfilled material has been prepared by mixing for 15 min the epoxy resin with 45 wt% of hardener, in an internal propeller mixer. GTR or DGTR powder was added during mixing operation when preparing composites. The mixture is then poured into a

glass mold for undergoing polymerization. Material plates of 4 mm thickness were finally obtained.

2.2. Devulcanization treatment of GTR

GTR devulcanization was performed in a Whirlpool domestic microwave oven, equipped with a double emission system. Samples of mass $m = 2.7$ g were exposed to electromagnetic microwave irradiations for times t equal to 15 and 60 s, and under microwave power range P from 350 to 900 W. The corresponding microwave specific energy E (J/kg) was evaluated from the following equation:

$$E = \frac{P \cdot t}{m} \tag{1}$$

Experimental treatment conditions are summarized in Table 1.

2.3. Evaluation of rubber devulcanization degree

Physical–chemical characterization of GTR and DGTR was conducted using Bruker tensor 27 Fourier Transform Infrared (FTIR) spectroscopy instrument. All spectra were measured and collected under the same conditions, in transmission mode, with wave frequencies ranging from 500 to 4000 cm^{-1}, a resolution of 4 cm^{-1} and using 32 scans.

Crosslink densities of GTR and DGTR were determined by swelling in toluene. 1 g of the powder was immersed in toluene for 72 h at room temperature, until the equilibrium swelling was reached. Then, the sample was taken out and the excess solvent on its surface was removed by blotting with filter paper and immediately weighted. The swelling test aimed to remove the non-polar components such as oil and non-crosslinked polymer residues or soluble polymer chains released from the network by the devulcanization process. Swelling values S (%) were calculated using the following equation:

$$S\ (\%) = \frac{m_f - m_i}{m_i} \cdot 100, \tag{2}$$

where m_i is initial mass of the sample and m_f is the mass of this sample after equilibrium swelling in toluene.

To further evaluate the devulcanization degree, theoretical relationship developed by Horikx (1956) was used, which correlates the rubber soluble fraction of the devulcanizates and the relative decrease in crosslink density. For pure crosslink scission, the soluble fraction is related to the relative decrease in crosslink density by (3):

$$1 - \frac{v_f}{v_i} = 1 - \left[\frac{\gamma_f (1 - \sqrt{S_f})}{\gamma_i (1 - \sqrt{S_i})} \right], \tag{3}$$

where S_i and S_f are the soluble fraction of GTR and DGTR respectively, v_i is the crosslink density of GTR and v_f is the crosslink den-

sity of DGTR, and γ_i and γ_f are the average numbers of cross linked units per chain before and after treatment respectively. These last parameters were determined from the relation between soluble fraction S (Eq. (2)) and the number of crosslinked units per chain γ, given by Charlesby (1953) as:

$$S = \frac{1}{(1 + \gamma - \gamma s)^2} \tag{4}$$

The percent devulcanization was calculated according to the standard ASTM D6814-02, using Eq. (5):

$$Dev\ (\%) = \left(1 - \frac{v_f}{v_i} \right) \cdot 100, \tag{5}$$

2.4. Mechanical characterization of composites

Mechanical properties of epoxy/GTR and epoxy/DGTR composites were determined by means of three point bending tests, using a Zwick Z20 testing machine. Parallelipipedic specimens of 80 mm × 10 mm × 4 mm were cut from the plates of material using a diamond blade. Distance between sills was fixed at 64 mm. Tests were carried out at ambient temperature and at a crosshead speed of 2 mm min^{-1}. Stress-strain curves were recorded up to total breaking of the specimens. Young modulus, strength at break and strain at break of the neat matrix and composites were deduced from these stress-strain curves.

2.5. Scanning electron microscopy

Morphological analysis of GTR was achieved by Scanning electron microscopy performed in a SEM, Philips ESEM XL30, equipped with a tungsten filament and an EDS-X (Energy Dispersive Spectrometry) system. The working accelerating voltage was 20 kV. GTR powder was also analyzed with EDX technique in order to identify its components and evaluate their proportion. Also postmortem fracture surfaces of bending samples were observed, to aid in the understanding of mechanical tests' results.

3. Results and discussion

3.1. GTR characterization

Fig. 1 shows the particle size distribution of used GTR. Main GTR particle size ranged between 250 and 500 μm. Morphology of rubber powder as observed by SEM is shown in Fig. 2. It was seen that GTR is formed of individual aggregates between ~250 and
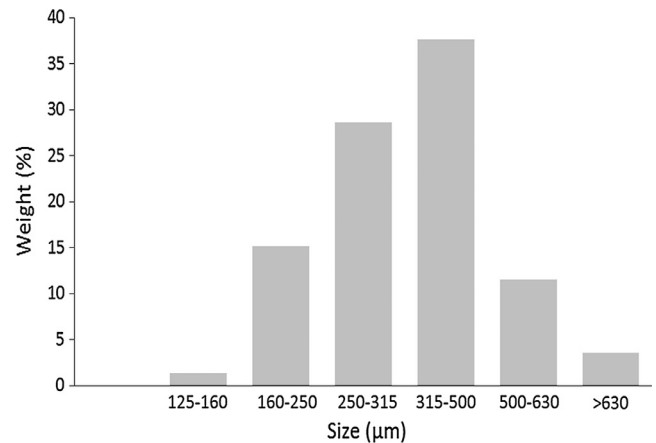
Table 1
Devulcanization parameters.

Specimen label	Weight (g)	Time of treatment t (s)	Microwave power P (W)	Energy E (J kg^{-1})
1	2.7	15	350	540
2			500	772
3			650	1003
4			750	1157
5			900	1389
6	2.7	60	350	2160
7			500	3086
8			650	4012
9			750	4630
10			900	5556

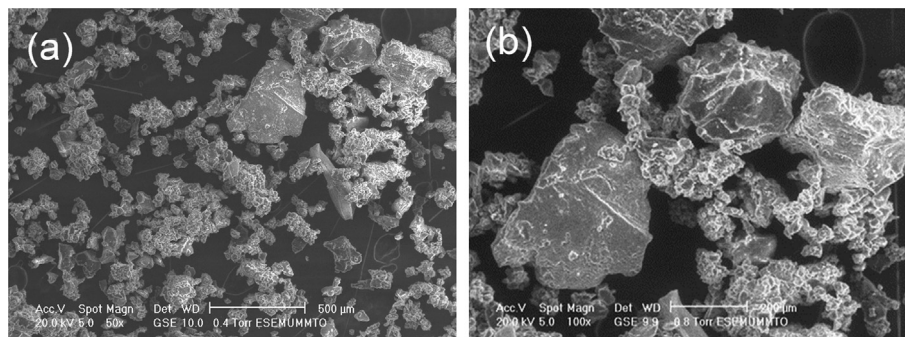**Fig. 1.** Particle size distribution of GTR.

Fig. 2. SEM micrographs of GTR: zoom (a) 50× (b) 100×.

Table 2
Chemical composition of GTR.

Elements	Weight percentages	Atomic percentages
Carbon	84.37	91.64
Aluminum	7.89	3.82
Oxygen	4.24	3.46
Sulfur	1.46	0.60
Zinc	1.24	0.25
Copper	0.49	0.10
Silicon	0.31	0.14

~500 μm, and small micrometric particles which are gathered to form agglomerates ranging from 10 to 100 μm.

Surface composition of several small and large aggregates of GTR powder was also analyzed with EDX technique and the results were quite similar. Components detected by scanning a zone of 107 μm × 74 μm of a large aggregate are reported, as an example, in Table 2. These results revealed that GTR is mainly constituted of carbon (C) and aluminum (Al). Carbon represents a principal element of rubber macromolecules and could also belong to carbon particles commonly used to reinforce rubbers. Al is probably issued from metallic cords which are used for the reinforcement of tires. Detected 1.46 wt% of sulfur (S) corresponds to the vulcanization agent. The 1.24 wt% of zinc (Zn) plays the role of the vulcanization activator. The presence of 0.31 wt% of silicon (Si) might be related to the silica ordinarily used as reinforcing particles of rubbers. In fact, it's well known that the addition of silica to a polymer gener-

ally improves its physical and mechanical properties. The small fraction of copper detected (0.49 wt%) could certainly come from copper oxide (CuO) present in tires. A part of 4.24 wt% oxygen is probably related to raw structure of some components used in the rubber formulation, as ZnO and SiO_2.

3.2. Characterization of the devulcanization treatment

Fig. 3 shows FTIR spectra of DGTR exposed to microwaves at different power values for 15 s along with untreated GTR spectrum.

Table 3
Main FTIR characteristic peaks of the GTR.

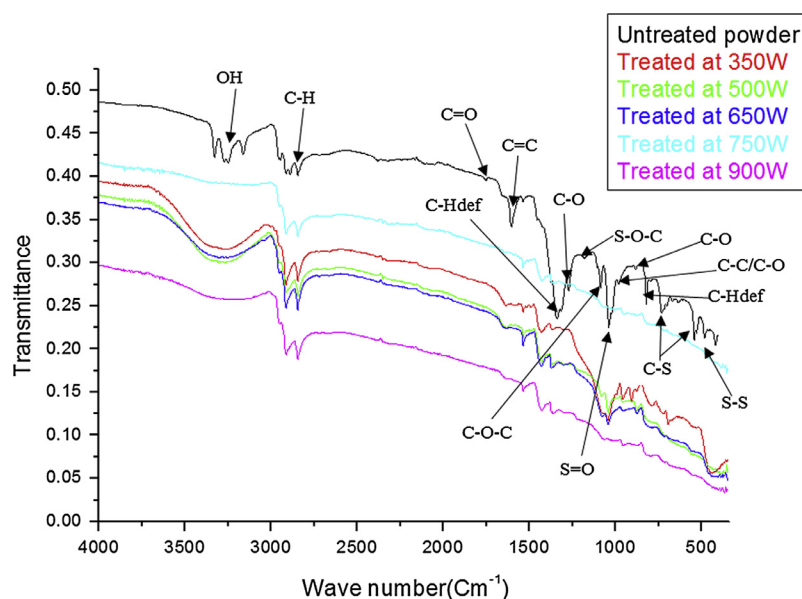| Wavenumber (cm^{-1})	Attribution
3250	O—H
3150–2850	C—H
1870–1650 (1750)	C=O
1680–1600 (1610)	C=C
1340	C—H deformation
1300–1000 (1270)	C—O
1300–1000 (1180)	S—O—C
1080	C—O—C
1280–1150 (1045)	S=O
980	C—C/C—O
880	C—O
820	C—H deformation
775–570 (730, 540, 530)	C—S
485	S—S

Fig. 3. Superposition of the FTIR spectra of GTR and DGTR treated at different powers for 15 s.

Main transmission peaks of GTR spectrum along with their attributions are listed in Table 3, in accordance with the literature (Lambert et al., 1987; Pavia et al., 1979). It can be seen from Fig. 3 that the material undergoes many structural changes during the devulcanization treatment. Indeed, the occurrence of new chemical links and the disappearance of some peaks can be observed. To better analyze these chemical links and functions, zooms in specific zones of Fig. 3 were performed and depicted in Fig. 4.

Fig. 4a shows a zoom in the range from 3750 to 3000 cm^{-1} in which the hydroxyl functionality is represented. Three small initial peaks can be clearly observed in the untreated rubber around 3250 cm^{-1}, and a wide band for the DTGR treated at 350, 500 and 650 W; corresponding to the formation of hydroperoxides (—OOH). This large band blunts for DTGR treated with a power of 750 and 900 W, confirming the well-known thermal instability of such hydroperoxides.

Peak of C—H link located in the range from 3000 to 2800 cm^{-1} (Fig. 4b) does not show differences between GTR and DGTR, suggesting that the hydrocarbon backbone of GTR was not degraded by microwave irradiation, even at high power levels.
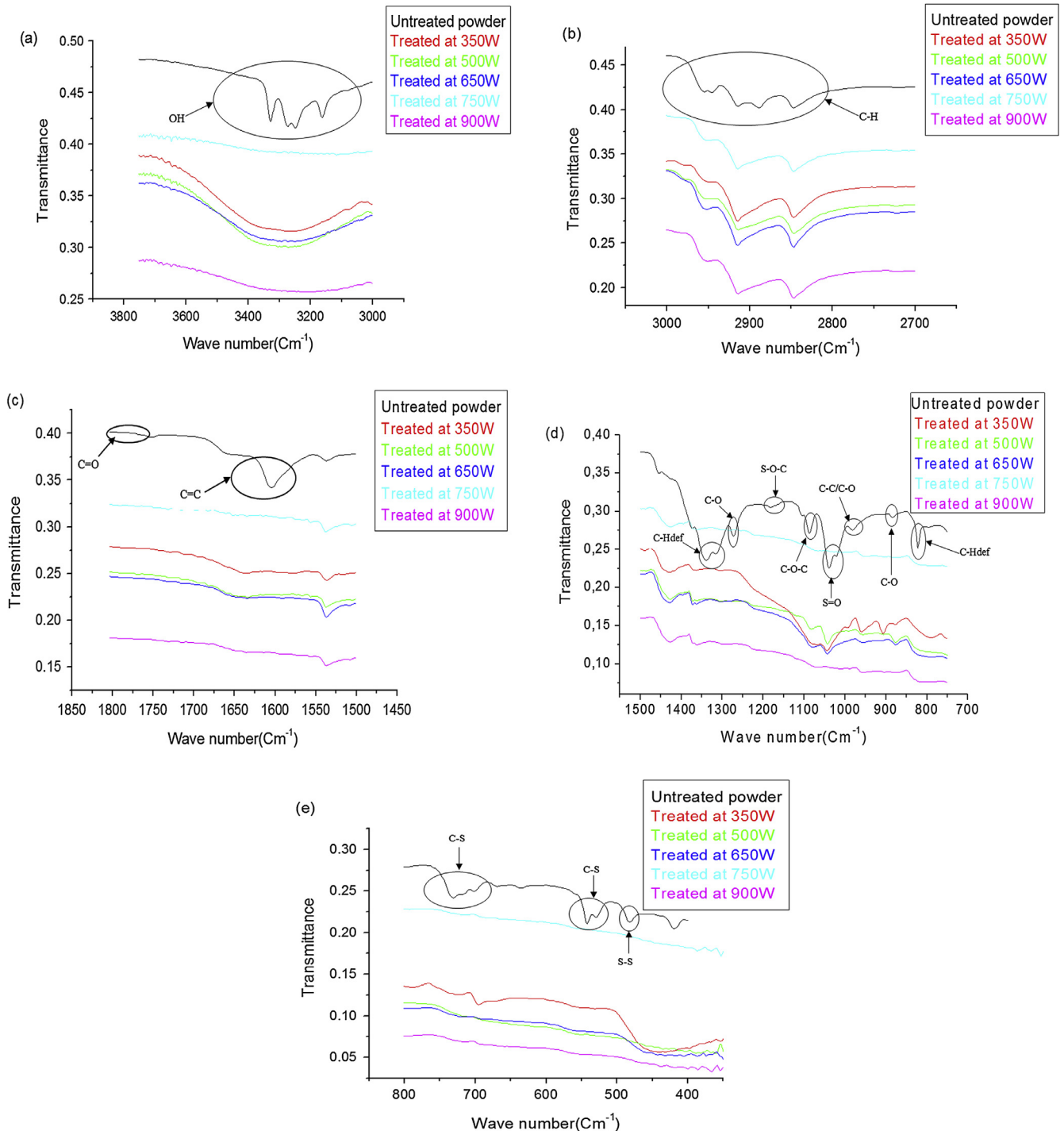

Fig. 4. Zooms of FTIR spectra of Fig. 5 in the range: (a) from 3750 to 3000 cm^{-1}; (b) from 3000 to 2700 cm^{-1}; (c) from 1800 to 1500 cm^{-1}; (d) from 1500 to 750 cm^{-1}; (e) from 800 to 350 cm^{-1}.

The region of the FTIR spectrum corresponding to the carbonyl between 1800 and 1500 cm^{-1} shows that important modifications took place during treatments, as seen in Fig. 4c. In fact, peaks corresponding to C=C and C=O links vanish in DGTR spectra, whatever the treatment microwave power. These results are in agreement with those reported in literature that conclude long microwave exposure periods result in many structural changes and in breaking of the main polymer chain (Garcia et al., 2015; Karger-Kocsis et al., 2013; Scuracchio et al., 2007; Isayev and Sujan, 2006). The rupture of C=C and C=O bonds would lead respectively to lower macromolecular mass fractions and to the formation of, among others, sulfur dioxide (SO$_2$).

Summarizing, results exhibited in Fig. 4b and c suggest that the principal macromolecular backbone of the rubber was only partially degraded by the microwave devulcanization process: C—H bonds remained intact but some C=C links were broken.

Fig. 4d shows important modifications of the FTIR spectra in the range from 1500 to 750 cm^{-1}. It is seen that the bands corresponding to C—O, S—O—C, C—O—C, S=O, C—C bonds undergo a strong decrease for the treatment power of 350, 500 and 650 W and form a single band around 1050 cm^{-1} assigned to sulfonyl groups such as sulfone —R—SO$_2$—R— and sulfoxide R—S=O (Lambert et al., 1987). These bands disappear for the treatment power of 750 and 900 W, suggesting that the elements containing these bonds reacted with oxygen and hydrogen to form gas. These results confirm that an oxidative degradation of principal chain occurred simultaneously with the rubber devulcanization during the microwave treatment. This oxidative phenomenon seems to be more significant at high microwave powers.

FTIR spectra zoomed in the range from 750 to 400 cm^{-1} revealed a strong decrease of peak heights of C—S and S—S bonds, for the treatment power of 350 W (Fig. 4e). These bands disappeared in the DGTR treated with the higher microwave powers, confirming the breaking of a large proportion of the vulcanization links i.e. the success of the material devulcanization treatment.

FTIR spectra of DGTR exposed to microwaves for 60 s, at different power values along with GTR spectrum, are shown in Fig. 5.

Fig. 6 shows enlargements and superposition of various zones to attain a better understanding. Results showed similar trends to those corresponding to 15 s treatments and discussed above. In fact, Fig. 6a shows the disappearance of the hydroxyl group for all the microwave power values applied in the devulcanization treatment. The peak of C—H stretching vibration does not show differences between the GTR and DGTR for all microwave power values of treatment, as depicted in Fig. 6b, meaning that the hydrocarbon backbone is not degraded, whatever the microwave power level applied. The disappearance of the bands assigned to the C=C and C=O vibrations is observed in the region of the carbonyl located between 1800 and 1500 cm^{-1} (Fig. 6c), whatever the microwave power value of the treatment, which argues in favor of the rubber degradation. Fig. 6d shows significant modification of the FTIR spectra in the range from 1500 to 750 cm^{-1}, mainly characterizing the C—O, S—O—C, C—C and S=O bonds. It is easily seen that these bands disappear or, at least, undergo a strong decrease. This indicates that – simultaneously with the rubber devulcanization – occur two phenomena during the treatment: degradation which is revealed by the breaking of C—C bonds and deoxidation by eliminating oxygen.

Fig. 6e shows the disappearance of FTIR C—S and S—S bonds in the range from 750 to 400 cm^{-1}, for all the applied microwave powers, suggesting the success of the devulcanization treatment.

In conclusion, FTIR analysis shows that microwave irradiations of GTR induced a double effect: devulcanization and partial degradation of the ground rubber. This phenomenon is commonly called regeneration.

Table 4 reports results of swelling tests in terms of material swelling values S as a function of treatment microwave energy.

Swelling values S are shown in Fig. 7 as a function of microwave energy. It can be clearly seen that the value of S sharply increases with increasing the treatment specific energy, reaching 63.22% for 1.389 kJ kg^{-1}. Beyond that critical energy level, it tends to stabilize i.e. specific energy should be highly increased to obtain a significant gain in the swelling value. Devulcanization degree (Eq. (5)) is also reported in Fig. 7 as a function of microwave energy. Devulcanization degree exhibits the same trend as swelling degree, confirming existence of a relationship between the two quantities (Eqs. (2) and (5)). In fact, it is found that devulcanization degree increases with energy employed in microwave treatment up to 1.389 kJ kg^{-1}. Beyond this threshold value, only a little improvement in devulcanization degree is observed, since it approaches asymptotically to 95%. These results suggest that a weak energy is enough to accomplish the devulcanization or regeneration process. Moreover, the high measured values of devulcanization
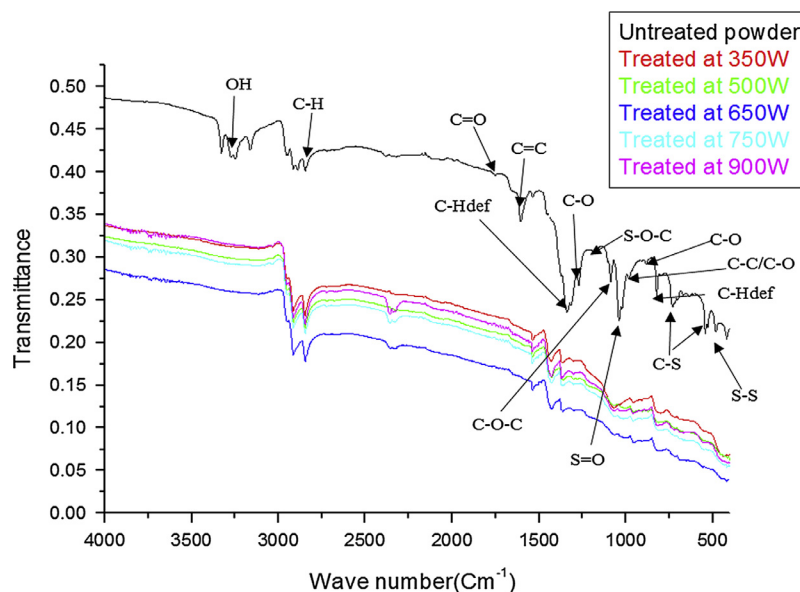

Fig. 5. Superposition of the FTIR spectra of GTR and DGTR treated at different powers for 60 s.
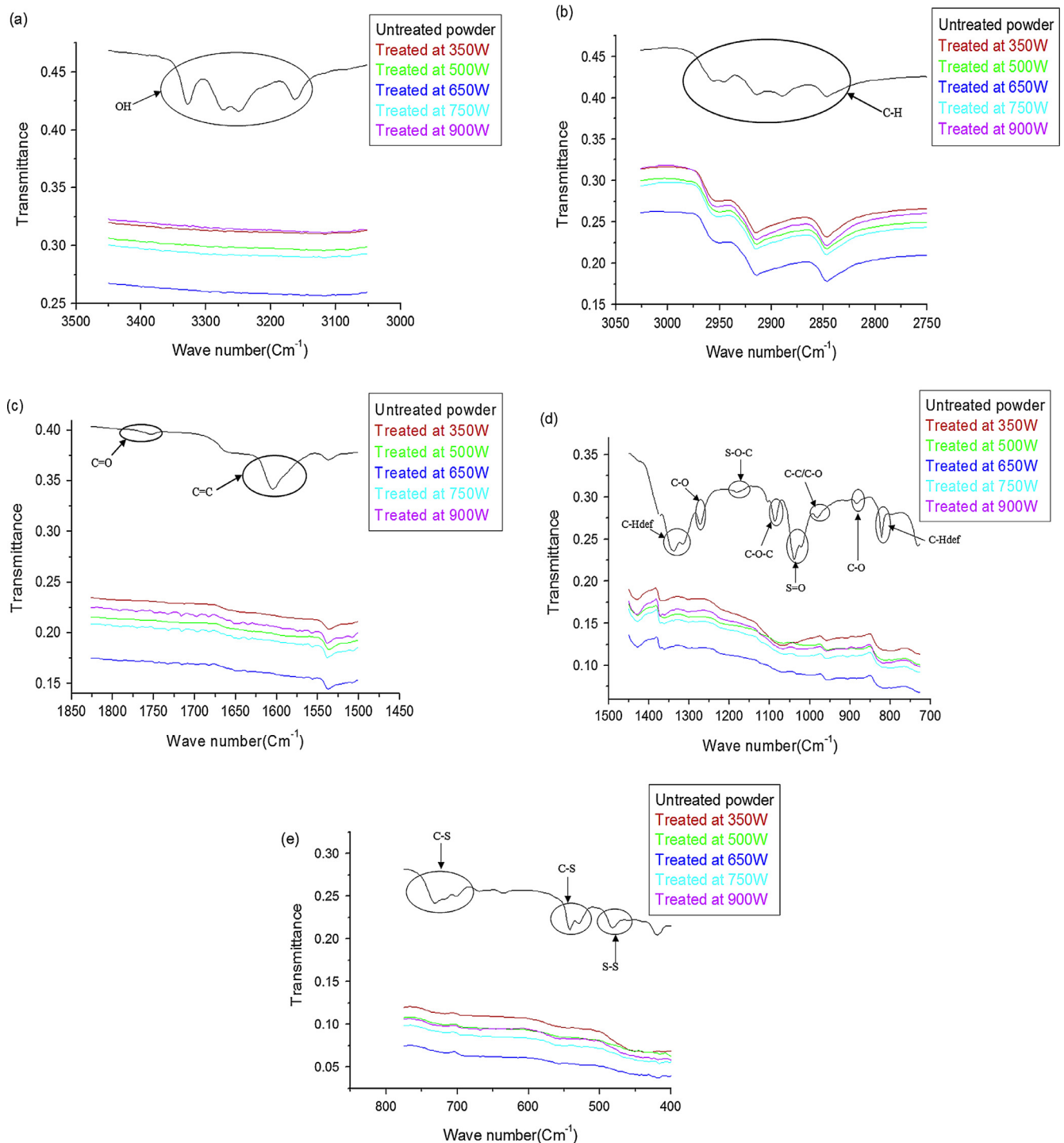
Fig. 6. Zooms of FTIR spectra of Fig. 5 in the ranges: (a) from 3450 to 3050 cm^{-1}, (b) from 3025 to 2750 cm^{-1}, (c) from 1825 to 1500 cm^{-1}, (d) from 1450 to 750 cm^{-1}, (e) from 800 to 400 cm^{-1}.

support FTIR outcomes, i.e. a decrease of rubber crosslink density or a strong regeneration of DGTR.

Based in these observations, DGTR particles treated with energy levels smaller than 2.16 kJ kg^{-1}, i.e. treated during 15 s, where chosen to be used as fillers in the epoxy matrix.

3.3. Properties of GTR and DGTR epoxy composites

Stress at break, strain at break and Young's modulus of epoxy obtained from three-point bending tests are respectively

21.35 MPa, 0.044 and 723.73 MPa. Composites' mechanical properties also obtained from these tests are reported in Figs. 8–10 as a function of the treatment microwave energy. It appears that incorporation of GTR or DGTR in the epoxy matrix resulted in a decrease of its mechanical properties. Nevertheless, despite experimental discrepancies particularly visible in the stress at break values (Fig. 8), results show that microwave treatment of GTR induced a relative improvement in the flexural stress and strain at break of the composites (Figs. 8 and 9). This suggests that DGTR particles' surfaces are more chemically reactive and have better adhesion

Table 4
Swelling values of samples.

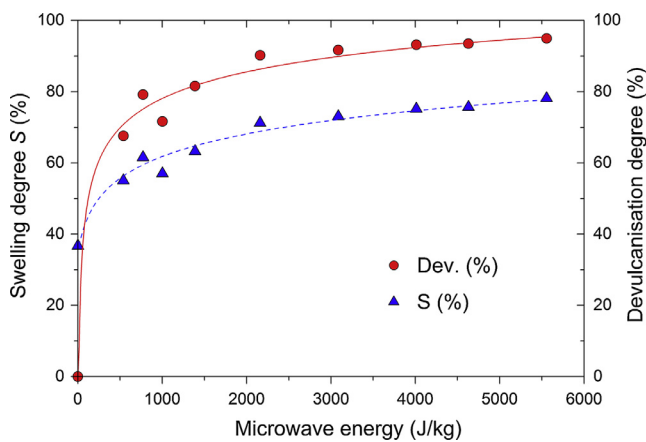| Specimen label	t (s)	P (W)	E (J kg^{-1})	M$_i$ (g)	M$_f$ (g)	S (%)
0	–	–	–	1	1.367	36.7
1	15	350	540	1	1.5499	54.99
2		500	772		1.6152	61.52
3		650	1003		1.5700	57.00
4		750	1157		1.8534	85.53
5		900	1389		1.6322	63.22
6	60	350	2160	1	1.7126	71.26
7		500	3086		1.7305	73.05
8		650	4012		1.7518	75.18
9		750	4630		1.7567	75.67
10		900	5556		1.7814	78.14

Fig. 7. Swelling degree and devulcanization degree as functions of treatment energy.
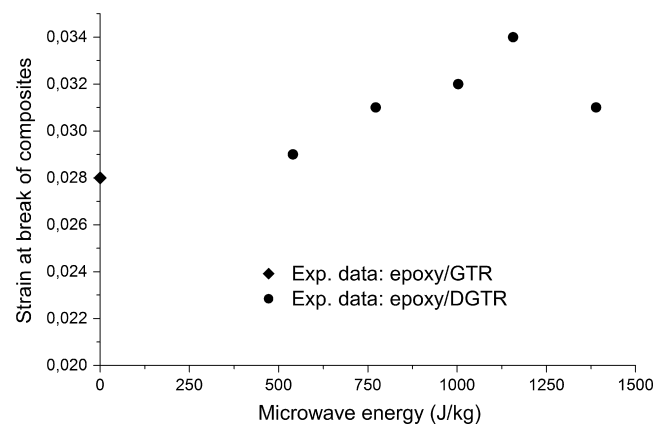

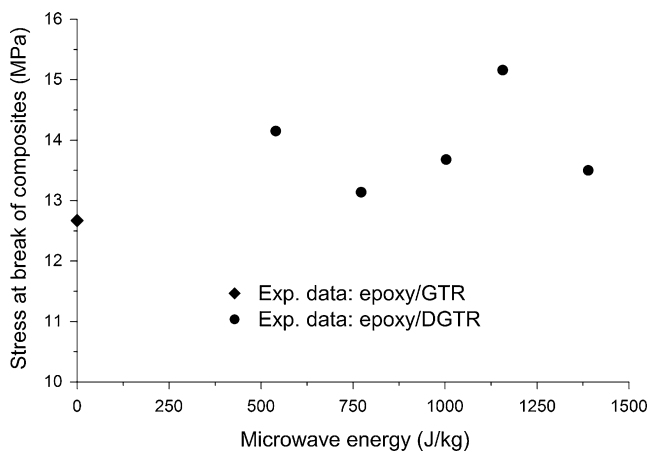**Fig. 9.** Strain at break of composites as a function of treatment energy.

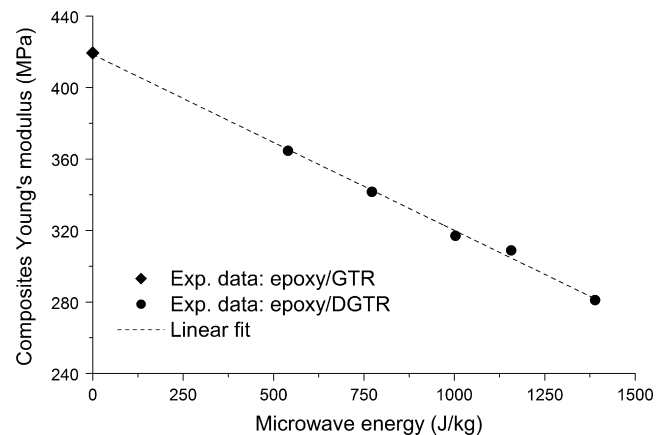**Fig. 8.** Stress at break of composites as a function of treatment energy.

Fig. 10. Composites Young's modulus as a function of treatment energy.

with epoxy matrix than GTR particles. Consequently, more chemical bonds could be formed at the epoxy/DGTR interface. This interaction seems to be higher for DGTR powder treated with 1157 J kg^{-1} i.e. at 750 W during 15 s, which leads to an increase of ~20% in flexural stress and strain at break of the epoxy/DGTR composite, compared to the epoxy/GTR composite. However, such increase is less significant for composite filled with DGTR particles treated with 1389 J kg^{-1} i.e. at 900 W during 15 s, which could be related to a partial degradation of the DGTR treated with high microwave energy value.

Generally, when a rubber modifier is added to a thermoset resin, its toughness increase is accompanied by a significant decrease in Young's modulus due to the elastomeric character of the modifier. In our case, a significant decrease in composites Young's modulus is observed with the increase of the treatment microwave energy, which may be explained by the rubber rigidity diminution with increasing devulcanization degree. This affects the composites Young's modulus more significantly as the forces at the epoxy/DGTR interface are stronger. It is also interesting to note that the decrease of the composites Young's modulus follows a linear regression as a function of the treatment microwave energy (Fig. 10).

As a complementary analysis, Young modulus of rubber, E_r, can be estimated by assuming an imperfect adhesion between matrix and rubber particles, i.e. an iso-stress model:
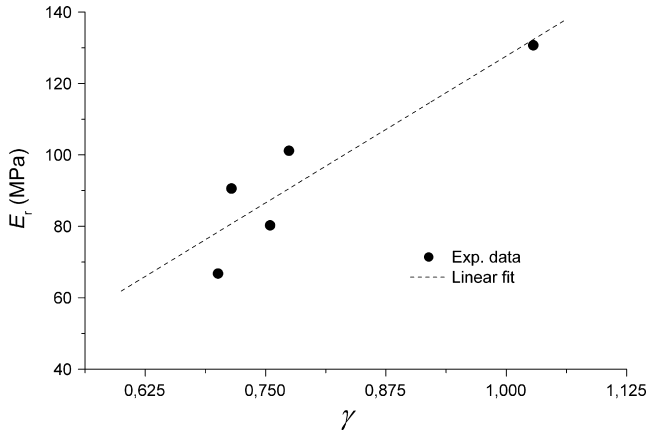
Fig. 11. Rubber modulus estimated from an iso-stress model as a function of the average number of crosslinked units per chain.

$$\frac{1}{E} = \frac{1}{E_m} V_m + \frac{1}{E_r} V_r, \tag{6}$$

in which E and E_m are the Young modulus of composite and matrix respectively, and V_m and V_r are matrix and rubber volume fractions.

It would be useful here to recall the theory of rubber elasticity (Treloar, 1975), which states that:

$$G_r = \frac{\rho R T}{M_c}, \tag{7}$$

G_r being the shear modulus related to E_r by (8):

$$G_r = \frac{E_r}{2(1 + v_r)}, \tag{8}$$

with v_r the Poisson coefficient, ρ the density of the rubber, R the gas constant, T the temperature and M_c the molecular weight of the network chain, which is inversely proportional to the average number of cross linked units per chain γ.

It is then easy to conclude that:

$$E_r \propto \frac{1}{M_c} \propto \gamma, \tag{9}$$

i.e. that a linear dependence of the rubber modulus with the average number of cross linked units per chain should be expected. Actually, this linear dependence was found for E_r values estimated assuming imperfect adhesion (Fig. 11), so inferring a bad interface between matrix and particles. The problem of compatibility with the matrix, as well as the discontinuity at the interface between the two phases, is an already known problem that should be
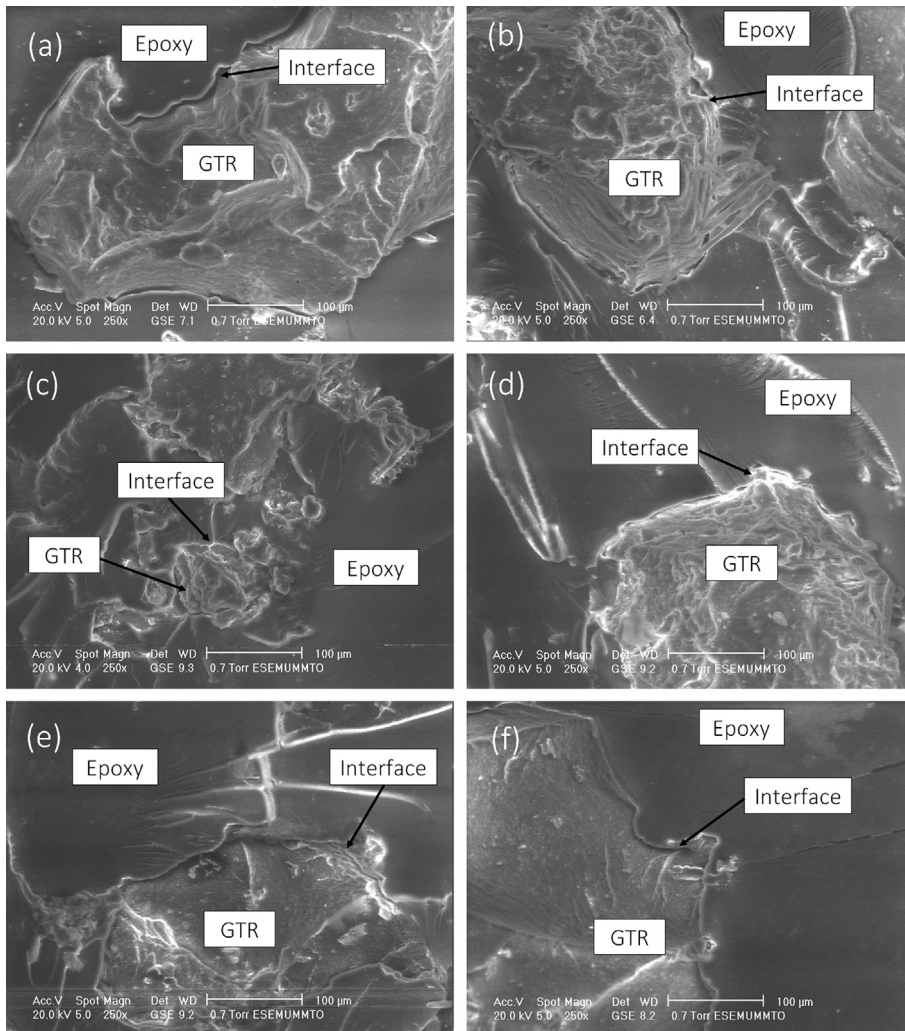

Fig. 12. SEM micrographs of failure surfaces of epoxy composites filled with: (a) GTR; (b) DGTR treated with 540 J kg^{-1}, (c) DGTR treated with 772 J kg^{-1}, (d) DGTR treated with 1003 J kg^{-1}, (e) DGTR treated with 1157 J kg^{-1}, (f) DGTR treated with 1389 J kg^{-1}.

considered. It is been stated that rubber products containing ground rubber have low tensile properties due to insufficient bonding between the ground rubber and the virgin matrix. However, this bonding can be improved in the case of the addition of devulcanized rubber (Isayev, 2013).

SEM observations of fracture surfaces were performed to analyze the effect of the microwave treatment on composites' microstructure, particularly on the epoxy/rubber interface. Micrographs are shown in Fig. 12. A noticeable gap is highlighted in Fig. 12a between the untreated GTR and the matrix, suggesting a weak adhesion of the GTR to the epoxy matrix. This led to an easy pull of the GTR from the matrix during flexural tests, in accordance with composites mechanical properties discussed above. Failure surfaces of composites with DGTR (Fig. 12b–f) show more continuous interfaces than that obtained with GTR. This effect seems to be more marked as microwave energy increases, which is probably due to good physicochemical interactions generated at the interfaces by functional groups created on DGTR surface during devulcanization treatment. Such interactions result in an increase of ultimate stress and strain of epoxy/DGTR composites, with increasing microwave energy up to 1157 J kg^{-1}. Beyond this limit, mechanical properties decrease despite the apparent better interface between epoxy and DGTR (Fig. 12f). This decrease is probably related to the pronounced degradation of DGTR which prevails over the devulcanization effect.

In conclusion, it is generally accepted that parameters affecting rubber-toughening are: matrix ductility, rubber concentration, morphology of the blend, particle cavitation, and particle to matrix adhesion (interface) (Bagheri et al., 2009). It can be claimed that modification of the particle/matrix interface in rubber-modified epoxies may affects the toughening mechanism and the magnitude of the fracture toughness. Better interfaces shown by DGTR particles result promising if enhancement of toughness is required.

4. Conclusions

In this study, microwave electromagnetic energy was used to devulcanize GTR powder.

FTIR analysis combined with swelling measurements of GTR and DGTR were performed to check the effectiveness of the devulcanization treatment. Results showed that microwave irradiations induced a so-called regeneration phenomenon i.e. the combined devulcanization and degradation of the rubber material. Swelling measurements in toluene allowed the qualitative evaluation of the regeneration level. Results revealed that GTR underwent regeneration during its irradiation with microwaves. A dependence of devulcanization degree with microwave energy was observed, concluding that the maximum energy to be used should be 1.389 kJ kg^{-1}, since higher energies did not produce major changes in the degree of devulcanization. However, it is necessary to optimize the microwave treatment i.e. to identify the adequate microwave energy, leading to devulcanization with low or without rubber degradation.

GTR and DGTR were used as reinforcement particles in an epoxy matrix and obtained composites were characterized by three-point flexural tests. As a result of microwave devulcanization, epoxy composites filled with DGTR had better mechanical properties than those filled with GTR, at the same loading.

Using a mechanical model assuming imperfect adhesion between matrix and rubber particles, a linear relationship was highlighted between the rubber modulus and the number of crosslink per chain, confirming the imperfect adhesion. However, microscopic study of failure surfaces showed that DGTR/epoxy adhesion seemed to be better than that obtained with untreated GTR, confirming the benefic role of the microwave treatment in recycling of waste tire rubbers.

References

Adhikari, B., De, D., Maiti, S., 2000. Reclamation and recycling of waste rubber. Prog. Polym. Sci. 25, 909–948.

Afshinnia, K., Poursaee, A., 2015. The influence of waste crumb rubber in reducing the alkali–silica reaction in mortar bars. J. Build. Eng. 4, 231–236.

Azeez, A.B., Mohammed, K.S., Abdullah, M.M.A.B., Zulkepli, N.N., Sandu, A.V., Hussin, K., Rahmat, A., 2014. Design of flexible green antiradiation shielding material against gamma-ray. Mater. Plast. 51, 300–308.

Bagheri, R., Marouf, B.T., Pearson, R.A., 2009. Rubber-toughened epoxies: a critical review. Polym. Rev. Part C: Polym. Rev. 3, 201–225.

Bredberg, K., Andersson, B.E., Landfors, E., Holst, O., 2002. Microbial detoxification of waste rubber material by wood-rotting fungi. Bioresour. Technol. 83, 221–224.

Charlesby, A., 1953. Solubility and molecular size distribution of crosslinked polystyrene. J. Polym. Sci. 11, 513–520.

Chekanov, Y., Arrington, D., Brust, G., Pojman, J.A., 1997. Frontal curing of epoxy resins: comparison of mechanical and thermal properties to batch-cured materials. J. Appl. Polym. Sci. 66, 1209–1216.

Chozhan, C.K., Alagar, M., Sharmila, R.J., Gnanasundaram, P., 2007. Thermo mechanical behaviour of unsaturated polyester toughened epoxy–clay hybrid nanocomposites. J. Polym. Res. 14 (4), 319–328.

Coran, A.Y., 1995. Vulcanization: conventional and dynamic. Rubber Chem. Technol. 68, 351–375.

Dubkov, K.A., Semikolenov, S.V., Ivanov, D.P., Babushkin, D.E., Panov, G.I., Parmon, V. N., 2012. Reclamation of waste tyre rubber with nitrous oxide. Polym. Degrad. Stab. 97, 1123–1130.

Garcia, P.S., de Sousa, F.D.B., de Lima, J.A., Cruz, S.A., Scuracchio, C.H., 2015. Devulcanization of ground tire rubber: physical and chemical changes after different microwave exposure times. Express Polym. Lett. 9, 1015–1026.

Guo, X., Xiang, D., Duan, G., Mou, P., 2010. A review of mechanochemistry applications in waste management. Waste Manage. 30, 4–10.

Gupta, T., Chaudhary, S., Sharma, R.K., 2016. Mechanical and durability properties of waste rubber fiber concrete with and without silica fume. J. Clean. Prod. 112, 702–711.

Harsch, M., Karger-Kocsis, J.Z., Holst, M., 2007. Influence of fillers and additives on the cure kinetics of an epoxy/anhydride resin. Eur. Polymer J. 43, 1168–1178.

He, J., Raghavan, D., Hoffman, D., Hunston, D., 1999. The influence of elastomer concentration on toughness in dispersions containing preformed acrylic elastomeric particles in an epoxy matrix. Polymer 40, 1923–1933.

Hong, Y.J., Jeong, K.M., Saha, P., Suh, J., Kim, J.K., 2015. Processing and characterization of microwave and ultrasonically treated waste-EPDM/LDPE polymer composites. Polym. Eng. Sci. 55, 533–540.

Horikx, M.M., 1956. Chain scissions in a polymer network. J. Polym. Sci. 19, 445–454.

Isayev, A.I., 2005. Recycling of rubbers. In: Mark, J.E., Erman, B., Eirich, F.R. (Eds.), Science and Technology of Rubber, vol. 3. Elsevier, New York, pp. 663–701.

Isayev, A.I., Sujan, B., 2006. Nonisothermal vulcanization of devulcanized GRT with reversion type behavior. J. Elastomers Plast. 38, 291–318.

Isayev, A.I., Recycling of Rubbers. In: Erman Burak, Mark James E., Michael Roland C. (Eds.). The Science and Technology of Rubber, 2013.

Jia, Q.M., Zheng, M., Xu, C.Z., Chen, H.X., 2006. The mechanical properties and tribological behavior of epoxy resin composites modified by different shape nanofillers. Polym. Adv. Technol. 17, 168–173.

Juganaru, T., Bombos, M., Vasilievici, G., Bombos, D., 2015. Devulcanized rubber for bitumen modification. Mater. Plast. 52, 336–339.

Karger-Kocsis, J., Mészáros, L., Bárány, T., 2013. Ground tyre rubber (GTR) in thermoplastics, thermosets, and rubbers. J. Mater. Sci. 48, 1–38.

Kocevski, S., Yagneswaran, S., Xiao, F., Punith, V.S., Smith Jr., D.W., Amirkhanian, S., 2012. Surface modified ground rubber tire by grafting acrylic acid for paving applications. Constr. Build. Mater. 34, 83–90.

Lambert, J.B., Shurvell, H.F., Cooks, R.G., 1987. Introduction to Organic Spectroscopy. Macmillan Publishers, New York.

Li, J., Liang, M., Guo, S., Lin, Y., 2004. Studies on chain scission and extension of polyamide 6 melt in the presence of ultrasonic irradiation. Polym. Degrad. Stab. 86, 323–329.

Li, Y., Zhao, S., Wang, Y., 2011. Microbial desulfurization of ground tire rubber by Thiobacillusferrooxidans. Polym. Degrad. Stab. 96, 1662–1668.

Mathew, G., Singh, R.P., Nair, N.R., Thomas, S., 2001. Recycling of natural rubber latex waste and its interaction in epoxidised natural rubber. Polymer 42, 2137–2165.

Naskar, A.K., Bhowmick, A.K., De, S.K., 2001. Thermoplastic elastomeric composition based on ground rubber tire. Polym. Eng. Sci. 41, 1087–1098.

Naskar, A.K., De, S.K., Bhowmick, A.K., 2002. Thermoplastic elastomeric composition based on maleic anhydride–grafted ground rubber tire. J. Appl. Polym. Sci. 84, 370–378.

Oliphant, K., Baker, W.E., 1993. The use of cryogenically ground rubber tires as a filler in polyolefin blends. Polym. Eng. Sci. 33, 166–174.

Pavia, D.L., Lampman, G.M., Kriz, G.S., 1979. Introduction to Spectroscopy: A Guide for Students of Organic Chemistry. W.B. Saunders Co, Philadelphia.

Piszczyk, Ł., Hejna, A., Formela, K., Danowska, M., Strankowski, M., 2015. Effect of ground tire rubber on structural, mechanical and thermal properties of flexible polyurethane foams. Iran. Polym. J. 24, 75–84.

Popovici, A., Corbu, O., Popita, G.E., Rosu, C., Proorocu, M., Sandu, A.V., Abdullah, M. M.A.B., 2015. Modern mortars with electronic waste scraps (glass and plastic). Mater. Plast. 52, 588–592.

Presti, D.L., 2013. Recycled tyre rubber modified bitumens for road asphalt mixtures: a literature review. Constr. Build. Mater. 49, 863–881.

Presti, D.L., Airey, G., Partal, P., 2012. Manufacturing terminal and field bitumen-tyre rubber blends: the importance of processing conditions. Proc. Soc. Behav. Sci. 53, 485–494.

Radhesh Kumar, C., Fuhrmann, I., Karger-Kocsis, J., 2002. LDPE-based thermoplastic elastomers containing ground tire rubber with and without dynamic curing. Polym. Degrad. Stab. 76, 137–144.

Rajan, V.V., Dierkes, W.K., Joseph, R., Noordermeer, J.W.N., 2006. Science and technology of rubber reclamation with special attention to NR-based waste latex products. Prog. Polym. Sci. 31, 811–834.

Scuracchio, C.H., Waki, D.A., da Silva, M.L.C.P., 2007. Thermal analysis of ground tire rubber devulcanized by microwaves. J. Therm. Anal. Calorim. 87, 893–897.

Selbes, M., Yilmaz, O., Khan, A.A., Karanfil, T., 2015. Leaching of DOC, DN, and inorganic constituents from scrap tires. Chemosphere 139, 617–623.

Shafabakhsh, G.H., Sadeghnejad, M., Sajed, Y., 2014. Case study of rutting performance of HMA modified with waste rubber powder. Case Stud. Constr. Mater. 1, 69–76.

Sivaraosa, Yap, T.C., Qumrul, Amran, M.A., Anand, T.J.S., Izamshah, R., Aziz, A.A., 2013. Friction performance analysis of waste tire rubber powder reinforced polypropylene using pin-on-disk tribometer. Proc. Eng. 68, 743–749.

Sutanto, P., Picchioni, F., Janssen, L.P.B.M., 2006a. Modelling a continuous devulcanization in an extruder. Chem. Eng. Sci. 61, 7077–7086.

Sutanto, P., Laksmana, F.L., Picchioni, F., Janssen, L.P.B.M., 2006b. Modeling on the kinetics of an EPDM devulcanization in an internal batch mixer using an amine as the devulcanizing agent. Chem. Eng. Sci. 61, 6442–6453.

Tao, G., He, Q., Xia, Y., Jia, G., Yang, H., Ma, W., 2013. The effect of devulcanization level on mechanical properties of reclaimed rubber by thermal-mechanical shearing devulcanization. J. Appl. Polym. Sci. 129, 2598–2605.

Thomas, B.S., Gupta, R.C., Panicker, V.J., 2015. Experimental and modelling studies on high strength concrete containing waste tire rubber. Sustain. Cities Soc. 19, 68–73.

Thomas, B.S., Gupta, R.C., Panicker, V.J., 2016. Recycling of waste tire rubber as aggregate in concrete: durability-related performance. J. Clean. Prod. 112, 504–513.

Thostenson, E.T., Chou, T.W., 1999. Microwave processing: fundamentals and applications. Compos. Part A 30 (9), 1055–1071.

Treloar, L.G.R., 1975. The Physics of Rubber Elasticity. Clarendon Press, Oxford, UK.

Vazquez, V.F., Luong, J., Bueno, M., Teran, F., Paje, S.E., 2016. Assessment of an action against environmental noise, acoustic durability of a pavement surface with crumb rubber. Sci. Total Environ. 542, 223–230.

Wingard, C.D., 2000. Characterization of prepreg and cured epoxy/fiberglass composite material for use in advanced composite piping systems. Thermochim. Acta 357–358, 293–301.

Xu, M., Li, J., 2012. Effect of adding rubber powder to poplar particles on composite properties. Bioresour. Technol. 118, 56–60.

Yagneswaran, S., Tomar, N., Smith, D.W., 2008. Thermal and morphological of mechanochemical devulcanized ground tire rubber (GTR) filed epoxy composites. Presented at the Fall 174th Technical Meeting of the Rubber Division of the American Chemical Society, Inc., Louisville, KY October 14–16, ISSN: 1547–1950.

Yagneswaran, S., Tomar, N., Smith, D.W., 2013. Non-isothermal curing kinetics of epoxy/mechanochemical devulcanized ground rubber tire (GRT) composites. Polym. Bull. 70, 1337–1351.

Yao, C., Zhao, S., Wang, Y., Wang, B., Wei, M., Hua, M., 2013. Microbial desulfurization of waste latex rubber with *Alicyclobacillus* sp. Polym. Degrad. Stab. 98, 1724–1730.

Zhang, S.L., Zhang, Z.X., Xin, Z.X., Pal, K., Kim, J.K., 2010a. Prediction of mechanical properties of polypropylene/waste ground rubber tire powder treated by bitumen composites via uniform design and artificial neural networks. Mater. Des. 31, 1900–1905.

Zhang, S.L., Zhang, Z.X., Pal, K., Xin, Z.X., Suh, J., Kim, J.K., 2010b. Prediction of mechanical properties of waste polypropylene/waste ground rubber tire powder blends using artificial neural networks. Mater. Des. 31, 3624–3629.

Zhou, X., Wang, X., Yuan, X., Kuang, M., Song, Y., Li, C., 2015. Usage of slurry oil for the preparation of crumb-rubber-modified asphalt emulsions. Constr. Build. Mater. 76, 279–285.