Design of a new generation of sustainable SBR compounds with good trade-off between mechanical properties and self-healing ability

Marianella Hernández Santana*, María Huete, Patricia Lamedá, Javier Araujo, Raquel Verdejo and Miguel A. López-Manchado

Institute of Polymer Science and Technology (ICTP-CSIC), Juan de la Cierva 3, Madrid 28006, Spain

*corresponding author: marherna@ictp.csic.es

ABSTRACT

Self-healing polymers typically face an enforced trade-off between repairability and mechanical properties, with a high degree of self-healing being achieved mainly by materials having low mechanical strength and stiffness. This study focuses on the development of SBR compounds that can combine together self-healing properties with the use of ground tire rubber (GTR) as alternative sustainable filler. The self-healing efficiency of GTR filled SBR compounds is compared to conventional carbon black filled compounds. The influence of the vulcanization system and the addition of silane-based coupling agents are also assessed. Results show that SBR compounds vulcanized by means of a semi-efficient sulfur based system recover around 50% of their mechanical strength, being the self-healing response related to the presence of disulfide bonds. Contrary to carbon black compounds, GTR samples present similar healing efficiency to the unfilled SBR samples, improving mechanical properties in 50%. Moreover, the coupling agent enhances even more (up to 80%) the mechanical strength of the SBR-GTR compounds without adversely affecting the healing efficiency. These results can thus be seen as a starting model material for developing new sustainable applications economically and environmentally convenient with good mechanical properties as well as healing ability.

KEYWORDS: styrene-butadiene rubber (SBR), self-healing, ground tire rubber (GTR), mechanical properties, silane, sustainable

INTRODUCTION

Elastomers are a special class of polymeric materials with a wide range of application. Apart from their common use in our daily life as tires or shoes they are also extensively used in other industrial sectors like the aerospace or the biomedical industry. Such a widespread usage is due to the unique properties these materials display, namely their large elastic deformation and their excellent noise and vibration damping capabilities. While these materials can sustain large deflections with little or no permanent deformation, elastomers can also fail through fracture and fatigue processes. This inherent weakness makes the prospect of self-healing materials more than ever attractive. Intrinsic self-healing polymers make use of reversible moieties to obtain on-demand or autonomous repair of macroscopic, microscopic or even molecular damages leading to the loss of certain functionality.[1]

Developments of self-healing rubbers started with the pioneering work of Cordier et al. in 2008.[2] They reported the synthesis of an autonomous healing rubber based on supramolecular assembly. Since then, many different healing routes have been developed and new families of

self-healing rubbery-like materials and crosslinked elastomers have evolved.[3-19] All self-healing methods have the aim to generate crosslinks in networks, either by physical interactions (molecular interdiffusion/rearrangements), and/or by chemical reactions of various kinds of functional groups (dynamic bonds). In general terms, the first steps of healing involve physical interactions, while at later stages, the chemical reactions occur. Over time the rearrangement of the chains on the damaged surface progresses into diffusion on a low level, and then further into a seemingly random and complete diffusion of the chains, making the material appear as one again.[20] As an example, Yamaguchi et al. designed polyurethanes (PU) in which the chemically controlled chain ends facilitated the autonomous healing of a fully cut polymer at $T > T_g$ in about 10min.[3] It was hypothesized that the relatively long distance between the free end of the molecule and its first physical crosslink point ("the dangling length") facilitate the observed crack disappearance. In a later review paper, the healing efficiency of similar PU was presented and defined as the tear strength of the healed material over the virgin material.[18] The phenomenon of healing facilitated by dangling chains has also been investigated leading to high healing degrees at room temperature in a mechanically interesting thermoplastic elastomer.[15] In their work the authors used a biobased aliphatic dimer diamine (DD1). The synthesis of DD1 with a dianhydride (DA) led to a densely branched polyetherimide where 9-C aliphatic chains act as the dangling brushes. By varying the ratio of the DD1/DA and using multiple techniques the authors unveiled the healing mechanism and showed the multiple healing steps leading to a full interfacial recovery.

Despite all the research taking place and positive proof-of-concept, results are still far from satisfactory when thinking about extrapolating them to real life applications. Healing requires chain mobility and, therefore, seems to be in direct contradiction with the fixation needed to form a permanent network in a fully crosslinked elastomer. Therefore, the challenge of obtaining a crosslinked network with weaker covalent bonds that can infer healing capabilities to the rubber as well as good mechanical properties still remains. The inclusion of fillers can then be considered as a good approach for improving the overall mechanical performance of self-healing rubbers.

Nanofillers of different nature have been added to various self-healing rubbers. Li et al.[21] prepared a covalently bonded graphene oxide/polyurethane (GO/PU) composite with significant reinforcement and thermally healable properties. The use of attapulgite (AT) as nanofiller in PU systems has also caught attention and can be seen as a promising low cost replacement for carbon nanotubes (CNTs) and graphene which are far more costly. A series of PU/AT nanocomposites were prepared by solution blending by Xu and Chen.[22] They added 1 to 5% of AT to a self-healing PU based on disulfide bonds and shape memory effect. After a healing process of 4h at 80°C, all samples regained different levels of their original tensile strength. Another example of enhancement of mechanical properties without detriment of healing capability was reported by Kuang et al.[23] adding MWCNTs to SBR on the basis of Diels-Alder bonding. The nanotubes played dual roles of reinforcing and healing agent. Nanofillers can also be used for restoring other functionalities, i.e. non-mechanical properties such as thermal conduction, electrical conduction and magnetic shielding, among others. Hernández et al.[24] aimed at restoring more than one functionality after healing a macroscopic damage in NR/graphene composites. They evaluated the restoration of electrical and thermal conductivity in a mechanically damaged sample. They found that the dependence of the various healing efficiencies with graphene content is due to a combination of the graphene induced lower cross-linking density, as well as the presence of strong polymer-graphene interactions at the healed

interphase. Fu et al.[25] developed a new kind of thermally reversible self-healing PU that simultaneously had good processing properties, high thermal stability and improved electrostatic dissipation capacity. With small loadings of CNTs (1-2wt.%), they achieved a healing efficiency as high as 93%.

Ground tire rubber (GTR) and reclaimed rubber are also used in the rubber industry as cheap substitutes for fillers and elastomers in rubber compounds and even in asphalt mixtures for road construction or in cement-based materials, amongst others. Several reviews have recently been published giving a thorough assessment on processing GTR into polymeric systems.[26-28] The size reduction method in the form of grinding is among the most commonly applied end-of-life recycling technique for waste tires. It appears to be more “green” than the devulcanization process, relying on mechanical shear stress to break the crosslinking bonds, although some researchers have recently proposed alternative green devulcanization processes for the recycling of rubber vulcanizates.[29-30] Mechanical disintegration of the waste tire rubber is conducted at room temperature or under cryogenic conditions until the required particle size is reached. Grinding conditions are of great practical relevance because the properties of compounds are mostly controlled by particle size distribution and mean particle size and thus, by interphase interactions between matrix and waste rubber.

This work is part of an ongoing study that aims to develop elastomeric systems that can combine together self-healing properties with the use of waste rubber. With no doubt, this research appears as an innovative route and key challenge for developing new sustainable applications economically, energetically and environmentally convenient. Thus, the purpose of the present work is to develop eco-friendly self-healing SBR compounds. Hence, the use of ground tire rubber (GTR) as alternative filler will be assessed and compared to traditional fillers, like carbon black. The presence of coupling agents will be considered as well.

EXPERIMENTAL

Materials and compounding

Styrene-butadiene rubber (E-SBR Europrene 1502), commercial grade vulcanizing additives and carbon black filler (N-330) supplied by Cabot were used as-received. Ground tire rubber (GTR) obtained by ambient grinding of used tires (combination of passenger car and truck tires of unknown composition) was supplied by *Signus*. A coupling agent bis[3-(triethoxysilyl)propyl]tetrasulfide (*Sigma Aldrich*) from hereon called TESPT was also incorporated in selected recipes. Rubber compounds were prepared according to the compositions shown in Table 1 and Table 2, varying the accelerant/sulfur ratio (A/S), the filler content and type (N-330 and GTR) and the coupling agent content. The amount of sulfur was kept constant in all compositions.

Table 1. SBR compound recipes in phr (parts per hundred parts of rubber), varying A/S ratio and carbon black (CB) content.

Ingredients (phr)	Compound					
	C1 A/S=0.2	C2 A/S=1	C3 A/S=4	C2-10CB A/S=1	C2-20CB A/S=1	C2-30CB A/S=1
SBR	100	100	100	100	100	100
ZnO	5	5	5	5	5	5

SA	1	1	1	1	1	1
CBS	0.14	0.70	2.80	0.70	0.70	0.70
S	0.70	0.70	0.70	0.70	0.70	0.70
N-330	0	0	0	10	20	30

Table 2. SBR compound recipes in phr (parts per hundred parts of rubber), varying TESPT content and with GTR as filler.

Ingredients (phr)	Compound				
	C2-2.5 A/S=1	C2-5 A/S=1	C2-10 A/S=1	C2-GTR1 A/S=1	C2-5-GTR1 A/S=1
SBR	100	100	100	100	100
ZnO	5	5	5	5	5
SA	1	1	1	1	1
CBS	0.70	0.70	2.80	0.70	0.70
S	0.70	0.70	0.70	0.70	0.70
TESPT	2.5	5	10		5
GTR1	0	0	0	10	10

Mixing was performed in an open two-roll mill (*Comerio Ercole* MGN-300S) at room temperature. The rotors operated at a speed ratio of 1:1.2. First, rubber was passed through the rolls until a band was formed. The activating complex (zinc oxide (ZnO), stearic acid (SA)), TESPT and filler (N-330 or GTR) were then progressively added to the rubber and, finally, the curatives (N-cyclohexylbenzothiazole-2-sulphenamide (CBS) and sulfur (S)) were added.

The crosslinking process was followed using a Rubber Process Analyzer (*Alpha Technologies* RPA2000) at curing temperature $T_c=160^\circ\text{C}$, frequency 0.833Hz and 2.79% strain for 60min, monitoring the torque variation as function of time. The compounds were then vulcanized in an electrically heated hydraulic press (*Gumix*) at 160°C and 200MPa according to their t_{90} as derived from the corresponding curing curves. Samples were cut out from press-cured sheets to perform damage and healing tests. As-produced samples were optically homogeneous and free of bubbles or other defects.

Material characterization

Crosslinking density. The average mass of network chains between crosslinks (crosslinking density, ν) was determined on the basis of solvent-swelling measurements in toluene by application of the Flory–Rehner[31] equation and assuming the formation of tetra-functional crosslinks during the vulcanization reaction.

Differential scanning calorimetry (DSC). Differential scanning calorimetry (*Mettler Toledo* DSC 822 $^\circ$ /500) was performed at a scan rate of $10^\circ\text{C}/\text{min}$ in the temperature range from -90 to 25°C , following a heating/cooling/heating cycle in nitrogen atmosphere. The mid-point of the transition was taken as the value of T_g . The accuracy of the determination was $\pm 1^\circ\text{C}$ in each case.

Thermogravimetric analysis (TGA). Thermogravimetric curves were obtained using a thermal analyzer (*Mettler-Toledo* TA851 $^\circ$). Samples of $\sim 5\text{mg}$ were heated from 25 to 630°C under

nitrogen atmosphere and in air from 630 to 1000°C at a heating rate of 30°C/min. Degradation temperature was taken as the inflection point.

Fourier transform infrared spectroscopy (FT-IR). FT-IR spectra (*Perkin Elmer Spectrum one*) of GTR and rubber compounds were recorded in ATR mode, in a wavenumber range from 4000 to 400cm⁻¹. Data were collected at 4 cm⁻¹ resolution co-adding 4 scans per spectrum.

Scanning electron microscopy (SEM). Morphological analysis of SBR compounds and GTR was achieved by scanning electron microscopy performed in a SEM (*Philips ESEM XL30*) equipped with a tungsten filament. Samples were sputter-coated with gold-palladium prior to observation.

Grinding. Selected GTR was further pulverized under cryogenic conditions using a Cryomill (*Retsch*). A milling protocol consisting of 18 cycles (2min grinding, 1min intermediate cooling) was tested. Other milling protocols are being discussed in an upcoming paper.

Particle size distribution. GTR powder (~0.05g) was previously dispersed in 20ml of a water/ethanol 70/30 solution with 0.2 ml of surfactant Triton X-100. The suspension was sonicated for about 2h. The particle size distribution was obtained by means of a laser scattering particle size distribution analyzer (*Coulter LS 200*). A volume standard cumulative distribution was measured under stabilized conditions. Each sample was subjected to a 60s optical measurement.

Density. The density of GTR samples was determined by hydrostatic weighing method in accordance with the standard ISO 2781.

Tensile testing. Dog-bone shape samples were used for uniaxial tensile testing. Tests were done on a universal mechanical testing machine (*Instron 3366*) equipped with a 1kN load cell. Samples were stretched until failure at a constant crosshead speed of 500mm/min at room temperature. Stress at break (ultimate stress) and strain at break (ultimate strain) were determined in order to mechanically characterize the SBR compounds and to evaluate their healing efficiency.[32] Data reported represent the average value from at least five samples.

Mechanical healing. In order to mechanically quantify the healing efficiency, the two separated parts of the tensile tested samples were carefully repositioned together by hand and allowed to equilibrate at room temperature for 24h. Afterwards, they were healed in a hydraulic press at 70°C and 10bar for 7h.[11, 33-35] Healed samples were retested according to the same tensile test conditions, as represented in Figure 1.

Figure 1. Schematic representation of healing protocol.

The healing efficiency (η) was calculated as the ratio between the tensile strength (σ_b) of healed and pristine specimens according to equation (1):

$$\eta[\%] = \frac{\sigma_b^{\text{healed}}}{\sigma_b^{\text{pristine}}} \times 100 \quad (1)$$

RESULTS AND DISCUSSION

Self-healing SBR compounds

Chemical and mechanical characterization

Effect of A/S ratio and carbon black content. Three different curing systems were evaluated, varying the accelerant/sulfur ratio (A/S) in the order: C1 (A/S= 0.2) < C2 (A/S= 1) < C3 (A/S= 4). The most relevant parameters obtained from the curing curves, such as optimum cure time (t_{90}), minimum torque (M_L), maximum torque (M_H), extent of cure ($M_H - M_L$) among others, are summarized in Table 3 and show the well-known fact that an increase of the A/S ratio reduces the length of the sulfur bridges and increases the number of crosslinks.[36-37] Table 3 also compiles the calculated values of crosslinking density based on swelling tests and mechanical properties for the different compounds, showing good agreement with the curing parameters trends. The notorious increase in crosslinking density for C3 can be ascribed to the highest amount of accelerant. Sulphenamide-type accelerants, due to the homolytic splitting at early stages of vulcanization, are able to form two free rubber radicals which can react with sulfur, thus forming crosslinks. In this way such system, once it has split up, has a self-accelerating or auto-catalytic effect.[37] C2 compounds were further selected due to their higher healing efficiency (as will be discussed in the next section) and 10, 20 and 30phr of carbon black N-330 were added. The accelerating effect of the filler is observed, by decreasing t_{10} , t_{50} and t_{90} . [38] The reinforcing effect is as expected, evidenced by the increase in M_H , tensile stress at various

deformations, tensile strength and crosslinking density, as filler content increases. Tensile curves are provided as Supplementary Information.

Table 3. Curing parameters, crosslinking density, and mechanical properties of SBR compounds.

	Compound					
	C1	C2	C3	C2-10CB	C2-20CB	C2-30CB
Curing parameters						
Minimum torque, M_L (dN.m)	0.70	0.68	0.65	0.80	0.89	1.36
Maximum torque, M_H (dN.m)	2.69	3.84	6.96	5.07	5.82	7.21
Extent of cure, $M_H - M_L$ (dN.m)	2.62	3.16	6.31	4.27	4.93	5.85
t_{10} (min)	11.2	13.0	11.6	6.5	5.1	4.4
t_{50} (min)	42.9	20.6	13.6	12.9	11.6	10.8
Optimum cure time, t_{90} (min)	109.1	35.8	18.9	26.4	25.9	23.7
Mechanical properties						
Tensile stress at 100% strain, σ_{100} (MPa)	0.52±0.01	0.54±0.03	0.81±0.01	0.64±0.04	0.82±0.02	1.12±0.01
Tensile stress at 300% strain, σ_{300} (MPa)	0.55±0.01	0.66±0.01	1.32±0.02	0.98±0.03	1.44±0.02	2.49±0.09
Tensile stress at 500% strain, σ_{500} (MPa)	0.62±0.01	0.80±0.02	1.99±0.02	1.59±0.03	2.45±0.03	4.47±0.18
Tensile strength, σ_b (MPa)	1.48±0.11	1.34±0.15	2.29±0.26	7.83±0.36	12.60±0.92	19.10±0.29
Elongation at break, ϵ_b (%)	1426±94	924±70	561±53	1457±37	1477±30	1375±13
Crosslinking density, $\nu \times 10^{-4}$ (mol/g)	1.92±0.39	7.58±0.72	33.94±0.32	10.20±0.26	10.32±0.14	14.23±0.18

Effect of TESPT content. Selected C2 compounds were chemically modified by silane coupling agent TESPT (2.5, 5 and 10 phr). As shown in Table 4, TESPT has a plasticizing effect at the early stages of the vulcanization reducing the viscosity of the compound, expressed as a decrease in M_L . An increase in M_H and in the extent of cure ($M_H - M_L$) is also observed, indicating relatively more restrained matrix resulting from improved interaction between the blend components. The improved interaction between the blend components is also indicated by the increase in the crosslinking density of the matrix. This is attributed to the fact that TESPT

contains 4 sulfur atoms on its molecule acting as accelerator and sulfur donor to the rubber compound.[39] Silane coupling agent is a bifunctional compound composed of two functionally active end groups, i.e., the readily hydrolysable alkoxy group and the organo-functional group. The latter, which is relatively non-polar, is more compatible with rubbers and also can participate in the sulfur vulcanization to form chemical linkages with the rubber matrix. The homolytic cleavage of S-S bonds of TESPT takes place forming free radicals at the curing temperature. These radicals may then combine with rubber chains and free sulfur (See Supplementary Information). Adding TESPT also reduces t_{10} , demonstrating the accelerating effect of the coupling agent on the onset of vulcanization. Nonetheless, it has a decelerating effect further in the vulcanization process, resulting in longer curing times (t_{90}) as silane content increases.[40-42] With regard to mechanical properties, C2-TESPT compounds yield a decrease in elongation at break, and an increase in tensile stress at all strains and at break compared to the control (C2), in accordance with curing characteristics.

Table 4. Curing parameters, crosslinking density, and mechanical properties of SBR-TESPT compounds.

	Compound			
	C2	C2-2.5	C2-5	C2-10
Curing parameters				
Minimum torque, M_L (dN.m)	0.68	0.61	0.54	0.51
Maximum torque, M_H (dN.m)	3.84	4.82	5.91	6.33
Extent of cure, $M_H - M_L$ (dN.m)	3.16	4.21	5.37	5.82
t_{10} (min)	13.0	8.6	7.7	6.9
t_{50} (min)	20.6	14.2	13.6	13.4
Optimum cure time, t_{90} (min)	35.8	27.3	31.3	34.6
Mechanical properties				
Tensile stress at 100% strain, σ_{100} (MPa)	0.54±0.03	0.72±0.02	0.78±0.04	0.83±0.02
Tensile stress at 300% strain, σ_{300} (MPa)	0.66±0.01	1.06±0.02	1.25±0.04	1.39±0.01
Tensile stress at 500% strain, σ_{500} (MPa)	0.80±0.02	1.45±0.02	1.84±0.01	---
Tensile strength, σ_b (MPa)	1.34±0.15	1.58±0.37	1.69±0.27	1.81±0.24
Elongation at break, ϵ_b (%)	924±70	552±87	451±61	417±60
Crosslinking density, $\nu \times 10^{-4}$ (mol/g)	7.58±0.72	14.27±0.02	20.51±0.04	24.63±0.04

The improved rubber-TESPT network can also be corroborated by the smooth and uniform appearance of the rubber matrix (see Figure 2a and b) and by the appearance of characteristic absorption bands in the FTIR spectra, as shown in Figure 3: the Si-O-Si stretching observed at 1169cm^{-1} , which is accompanied by the absorbencies at $1650\text{--}1550$ and 3500cm^{-1} assigned to Si-OH. Stretching of -S-C- bonds can be followed at wavenumbers around $1160\text{--}990\text{cm}^{-1}$, but it partially overlaps with siloxane peaks.

Figure 2. SEM images of: a) C2, b) C2-5 and c) C2-5-GTR1 compounds.

Figure 3. FT-IR spectra of SBR compounds with different content of TESPT.

Mechanical healing

Effect of A/S ratio and carbon black content. Figure 4a) shows tensile strength values of pristine and healed SBR compounds with different A/S ratio. Healed samples are considered specimens in which the restoration of the damaged interface and, thus, mechanical integrity is partially achieved. The quantification of the mechanical healing efficiency is shown in Figure 4b). Interestingly, there seems to be a correlation between both plots: lower mechanical performance rubber systems show higher healing capability, putting in evidence the compromise between mechanical properties and healing.[10] The healing efficiency increases in the order: C3 (A/S=4) < C1 (A/S=0.2) < C2 (A/S=1). C3 is a very stable and highly sulfur crosslinked network, making the restoration of the interface less possible under the studied healing conditions; while the less crosslinked networks resulting from C1 and C2 compounds allow for a substantially higher mobility, which favors rubber chain interdiffusion and the rearrangement of broken reversible bonds at the healed interface. T_g values reported as Supplementary Information also support this behavior. Short-range interactions due to entanglements between dangling chains are considered to take place during the initial stage of healing.[18] Followed by the temperature-triggered opening of di- and poly-sulfide bonds (present in the chemical structure of sulfur-cured networks, see Supplementary Information), which provides higher chain mobility for the system and allows the macroscopic flow required to close the cut.[35] The disulfide (and polysulfide) exchange reactions are thus regarded as the main contributor to

the restoration of the mechanical strength; it is presumed that the underlying healing mechanism is determined by the temperature-driven formation of sulfur radicals that bond to each other once the energetic stimulus is removed to form a new disulfide bridge across the damaged interface.[7, 10, 43-45] It has also been reported that higher healing can be achieved by replacing disulfide bonds with tetrasulfides, as the stability of the S-S bridges decreases by increasing the number of sulfur atoms beyond two.[35, 46] It would therefore be expected that the lower A/S ratio compounds (C1 and C2) with longer length sulfur bridges lead to higher healing. Thus, a combination between lower crosslinking density and lower A/S ratio seems to be the reason for the highest healing achieved by C1 and C2.

Figure 4. a) Tensile strength of pristine and healed samples and b) Healing efficiency and crosslinking density, as function of A/S ratio.

The same opposing correlation between mechanical performance and healing efficiency is seen when carbon black (CB) content varies. The presence of this reinforcing filler severely affects healing; no recovery is achieved with filler content as low as 10phr, as seen in Figure 5. All facts suggest that higher mobility restrictions, due to the presence of carbon black and increase in crosslinking density, come into play during the thermal healing treatment. This result also puts in evidence the trade-off between reparability and mechanical properties and the need of alternative fillers that can improve healing capability without detriment of the structural integrity or vice-versa.

Figure 5. Healing efficiency and crosslinking density of SBR compounds, as function of carbon black content.

Effect of TESPT content. The effect of TESPT on the healing capability of C2 compounds was also evaluated. The intention of adding TESPT was to improve the mechanical performance, as well as to increase repairability. Silane based coupling agents have been used in different networks as crosslinking agents favoring healing due to disulfide exchange reactions thanks to the presence of a tetrasulfide bond in their structure.[35, 47] The results plotted in Figure 6 show that, as previously mentioned, mechanical strength improves in presence of TESPT. Interestingly, healing efficiency is not significantly affected by the inclusion of TESPT; it remains close to that of the C2 control compound (with no TESPT) since all values are in the range of 40 to 50% of recovery. Therefore, a positive trade-off between mechanical and healing performance is achieved, contrary to the above mentioned results for highly crosslinked systems (C3) or for CB filled compounds. It can then be presumed that the tetrasulfides present in the structure of TESPT participate in the temperature triggered healing mechanism, combining with broken rubber chain radicals as well as acting as crosslinking points. SBR compounds present a wide set of mechanical properties according to the curing system (amount of sulfur, type of accelerant, accelerant/sulfur ratio), curing temperature, and presence of fillers, among others. For instance, SBR tensile strength has been reported to vary from 2 MPa [48-49], to 13MPa [50]. Hence, our self-healable SBR compounds, which show tensile strength values of 1.4 – 2.3 MPa, are similar to those reported in the literature, without adding any filler and with a lower amount of sulfur than what is normally used.

Figure 6. a) Tensile strength of pristine and healed samples and b) Healing efficiency, as function of TESPT content.

Using GTR as alternative filler in self-healing SBR compounds

Characterization of GTR

4 different batches of ground tire rubber (GTR) obtained by ambient grinding of used tires (combination of passenger car and truck tires of unknown composition) with different particle size were supplied by *Signus*, as shown in Figure 7.

Figure 7. Photographs of as-received GTR batches with different particle size.

The final properties of rubber composites, using GTR as filler, depend on both the type of rubber matrix incorporated with GTR and the adhesion between GTR and the matrix.[27] Thus, understanding of the chemical nature of GTR prior to its incorporation in a polymeric matrix is required. As can be seen in Table 5, all batches have very similar density values and glass transition temperature (T_g), as calculated by DSC, regardless their composition.

Table 5. Physical properties of as-received GTR batches.

GTR	Average particle size (mm) ¹	Density (g/cm ³)	T_g (°C)
GTR0	< 0.8	1.12 ± 0.01	-57
GTR1	0.8 - 2	1.12 ± 0.01	-56
GTR2	2 - 4	1.11 ± 0.03	-57
GTR3	4 - 8	1.12 ± 0.02	-58

¹Value reported by the supplier

TGA analysis was done to quantify the relative ratios of rubbers, carbon black and ash present in GTR. One can assume that GTR batches were composed of various blends of NR, SBR and BR as the major polymeric components. Other additives expected to be present (e.g. zinc oxide, stearic acid, accelerator and sulfur), typically included in a tire compound, were not considered in this research. Weight losses at the temperatures of degradation of the rubbers, carbon black and char residue are listed in Table 6 and a representative TGA/dTGA curve is shown in Figure 8.

Table 6. % weight loss and degradation temperature (T_d) of as-received GTR batches.

GTR	Initial loss	NR		SBR/BR		CB		Char residue
	%	%	T_d (°C)	%	T_d (°C)	%	T_d (°C)	%
GTR0	5.38	34.40	402.8	24.98	417.7	30.39	658.5	4.57
GTR1	4.71	34.99	403.3	24.31	420.9	30.29	661.9	5.66
GTR2	4.89	35.46	402.7	23.93	424.4	30.92	662.5	4.73
GTR3	5.14	32.19	402.9	29.19	415.5	30.68	658.9	5.09

Figure 8. TGA/dTGA curves of GTR1.

Major areas of weight loss are observed between 300 and 500°C in all the samples. These losses took place in an inert atmosphere, producing two peaks in each curve. The first peak starting at around 330°C is indicative of a particular rubber, while the second peak observed at higher temperature, starting around 420°C, is strongly indicative of another rubber. The third weight loss above 620°C in presence of oxygen is due to carbon black. The degradation temperatures were strongly directive towards assuming the lower temperature for NR and the higher temperature for SBR or BR or a mixture of the two;[51-52] SBR and BR have overlapping degradation temperature. The weight percentages of the rubbers were converted into phr (parts per hundred parts of rubber) as usually expressed in the rubber industry (see Table 7). The composition of all the samples studied here seems very similar independently of the batch: 55 phr NR, 45 phr SBR/BR and 50 phr CB, in average.

Table 7. TGA results showing rubber compound composition expressed in phr.

GTR	NR	SBR/BR	CB
GTR0	57.9	42.1	51.2
GTR1	59.0	41.0	51.1
GTR2	59.7	40.3	52.1
GTR3	52.4	47.6	50.0

ATR FT-IR studies were also done as shown in Figure 9. As expected, all four spectra look very similar. A slight difference could be seen in the spectrum of GTR1, since two characteristics peaks of SBR appear (the C-CH₂ stretching from trans-butadiene comonomer at 969 cm⁻¹ and the aromatic C-H stretching from styrene comonomer at 3045 cm⁻¹). The fact that all 4 batches of GTR (coming from 4 different random sources) have similar properties is a promising result for the recycling and reuse of discarded tires. More than the chemical nature of GTR what seems to govern the final properties, as will be discussed next, is the good interaction and compatibility between the rubber powder and a selected matrix. From the 4 batches analyzed, GTR1 was selected as the GTR to be included as alternative filler in the SBR compound.

Figure 9. ATR FT-IR spectra of different GTR batches.

GTR1 was further cryogenically grounded according to a grinding protocol previously evaluated. Further details on various grinding protocols will be given in an upcoming paper. Figure 10 shows the particle size distribution of GTR1. Average particle size of cryo-grounded rubber (cryo-GTR1) is of 157 μm , corroborating the size reduction with respect to the as-received batch (1519 μm). The improvement in mechanical properties derived from particle size reduction can be seen in the stress-strain curves supplied as Supplementary Information. Morphology of rubber powder as observed by SEM is shown in Figure 11. The presence of aggregates formed by smooth-grained individual particles of $\sim 5\mu\text{m}$ is observable. The cryo-grounded rubber cryo-GTR1 from now on named simply GTR1 was added to the SBR compounds.

Figure 10. Particle size distribution of as-received and cryo-grounded GTR1.

Figure 11. SEM micrographs of cryo-GTR1 at different magnifications: a) 500x, b) 2000x showing individual particle size.

Effect of GTR on mechanical properties and healing

Self-healing C2-GTR1 compounds were prepared with and without TESPT (see Table 2). Fixed contents of GTR1 (10phr) and TESPT (5phr) were selected. Lamminmaki et al.[53] in their work found that the incorporation of GTR as filler in rubber blends would be limited to 15wt.% to have balanced properties. The extent of cure decreases when GTR1 is present (see Table 8). This is attributed to the fact that GTR1 is already partially crosslinked and, hence, there are relatively less reaction sites available for further crosslinking.[42] However, the improved GTR1-matrix interactions when a silane coupling agent is present compensate this, increasing the extent of cure and the crosslinking density. From the data shown in Table 8 and in Figure 12, it is also clear that GTR1 acts as reinforcing filler increasing by 50% the tensile strength, but not as efficient as the rise obtained (466%) with equal amount of carbon black (C2-10CB). Some authors claim improvement in mechanical properties when GTR is incorporated into SBR, thanks to the presence of carbon black in the GTR.[54] Contradictory, other studies reported elsewhere[55-57] claim that migration of sulfur from the rubber matrix to the molecules of the GTR and migration of accelerants from the GTR to the rubber take place, deteriorating mechanical performance due to a decrease in crosslinking density. In this research, although crosslinking density drops from $7.58 \pm 0.72 \times 10^{-4} \text{ mol/g}$ for C2 to $4.58 \pm 0.12 \times 10^{-4} \text{ mol/g}$ for C2-GTR1, the prevailing factor for achieving better mechanical properties seems to be the carbon black incorporated in the GTR, which lies around 30% as previously determined.

Table 8. Curing parameters, crosslinking density, and mechanical properties of C2-GTR1 compounds.

	Compound		
	C2	C2-GTR1	C2-5-GTR1
Curing parameters			
Minimum torque, M_L (dN.m)	0.68	0.64	0.54
Maximum torque, M_H (dN.m)	3.84	3.24	5.91
Extent of cure, $M_H - M_L$ (dN.m)	3.16	2.60	5.37
t_{10} (min)	13.0	7.5	7.7
t_{50} (min)	20.6	13.9	13.6
Optimum cure time, t_{90} (min)	35.8	28.7	31.3

Mechanical properties

Tensile stress at 100% strain, σ_{100} (MPa)	0.54±0.03	0.58±0.01	0.79±0.01
Tensile stress at 300% strain, σ_{300} (MPa)	0.66±0.01	0.69±0.01	1.26±0.02
Tensile stress at 500% strain, σ_{500} (MPa)	0.80±0.02	0.89±0.01	1.98±0.01
Tensile strength, σ_b (MPa)	1.34±0.15	2.10±0.13	2.51±0.06
Elongation at break, ε_b (%)	924±70	1172±82	617±11
Crosslinking density, $\nu \times 10^{-4}$ (mol/g)	7.58±0.72	4.58±0.12	20.02±0.03

Figure 12. a) Increment in tensile strength with respect to C2 and b) healing efficiency, of SBR compounds.

When TESPT is added (C2-5-GTR1 compound), the tensile strength improves significantly up to 80%. This superior reinforcement capacity could be due to the rigid covalent bonding of the tetra-functional silane between GTR1 and SBR matrix which results in a stiff interphase transferring stress to GTR1, and to the ability of active crosslinking sites in GTR1 and elemental sulfur in TESPT participating in the crosslinking process.[58] This shows the importance of an effective covalent bonding between active sites in GTR and matrix in controlling mechanical properties as well as stabilizing the rubber network. These chemical bonds will also result in enhanced interfacial adhesion between the GTR and the rubber matrix. SEM images of the C2-5-GTR1 compound can be seen in Figure 2c) showing a smooth surface and uniform and homogeneous dispersion of the TESPT-GTR1 in the SBR matrix.

Figure 12 also shows the healing efficiency of SBR-GTR1 compounds with and without TESPT. The material self-healing response is related to the presence of disulfide bonds as schematically shown in Figure 13. Thanks to the mechanical shearing forces during the cryo-grinding process of GTR1, scission of S-S crosslink bonds can occur forming disulfide radicals.[59] The homolytic cleavage of S-S bonds of TESPT can also take place during the occurrence of the mechanical damage. At the healing temperature these radicals, both from GTR1 and TESPT, combine with broken polymer chain radicals as well as recombine with other disulfide radicals. The chain interdiffusion facilitated by the increased dynamics (open-close) of the disulfide bridges at the healing temperature allows re-establishing the chemical bonding across the damaged surface and thus leads to the partial recovery of the mechanical properties.[10] Very small variations on healing efficiency are seen with regard to C2 control compound, thus it is not possible to differentiate the individual contribution from the GTR and from TESPT. Nonetheless, the improved mechanical properties of the C2-5-GTR1 compound

without detriment on the healing capability allows us to conclude that the addition of GTR as filler in presence of a silane coupling agent defeats the challenge of obtaining a crosslinked network with reversible covalent bonds that can infer healing capabilities to the rubber as well as good mechanical properties.

Figure 13. Schematic representation of healing mechanism in SBR-GTR compounds.

CONCLUSIONS

The aim of the present work was to design SBR compounds with sustainable characteristics. This sustainability was to be achieved by the inclusion of ground tire rubber (GTR) as alternative filler and by the ability to repair damage (i.e. self-healing) and thus extend the service lifetime of the rubber.

Different vulcanization recipes were evaluated, as well as the presence of a silane-based coupling agent. It was found that the semi-efficient vulcanization system gives the best balance between tensile strength and healing and that a coupling agent improves even more the mechanical performance with no detriment on healing.

A comparison to carbon black filled SBR compounds was also made, resulting in an expected divergent correlation between mechanical performance and healing efficiency. An increase in reinforcing filler content, and thus in crosslinking density, severely affected healing; no recovery was achieved with carbon black content as low as 10phr. Equivalent amount of GTR was assessed for the first time as potential filler in self-healing SBR compounds. The lower improvement in mechanical properties did not allow considering it as comparable reinforcing filler. However, when a silane coupling agent was added to the SBR-GTR compounds, tensile strength increased up to 80%. This increase was obtained with no detriment in healing efficiency, which was maintained around 50%. In conclusion, SBR compounds filled with ground tire rubber and in presence of a coupling agent offer a potential versatility to self-healing applications, defeating the challenge of reaching simultaneously good repairability and good mechanical performance. Future work will continue with the aim of enhancing healing behavior.

SUPPLEMENTARY INFORMATION

S1. Tensile curves of SBR compounds; S2. Schematic reaction of TESPT with SBR; S3. Tg values obtained by DSC; S4. Characteristic Raman and NMR spectrum of sulfur-cured SBR compounds.

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SUPPLEMENTARY INFORMATION

Design of a new generation of sustainable SBR compounds with good trade-off between mechanical properties and self-healing ability

Marianella Hernández Santana*, María Huete, Patricia Lamedá, Javier Araujo, Raquel Verdejo and Miguel A. López-Manchado

Institute of Polymer Science and Technology (ICTP-CSIC), Juan de la Cierva 3, Madrid 28006, Spain

*corresponding author: marherna@ictp.csic.es

S1. Tensile curves of SBR compounds

Figure 1S. Stress-strain curves of pristine and healed SBR compounds: a) effect of A/S ratio; b) effect of CB content; c) effect of TESPT content; d) effect of GTR type. In all curves “p” stands for pristine and “h” for healed compounds.

S2. Schematic reaction of TESPT with SBR

S3. Tg values obtained by DSC

Compound	Tg (°C)
C1	-50
C2	-49
C3	-45
C2-10CB	-47
C2-20CB	-47
C2-30CB	-47

S4. Characteristic Raman and NMR spectrum of sulfur-cured SBR compounds

Figure 2S. Raman spectrum of sulfur-cured SBR.

Figure 3S. ¹³C NMR spectrum of sulfur-cured SBR.