



Structure and properties of blends based on vulcanized rubber waste and styrene–butadiene–styrene thermoplastic elastomer

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Abstract

The paper presents the characterization and processing of a post-consumer vulcanized rubber waste for use as a filler to obtain polymer composites with thermoplastic matrix based on styrene–butadiene–styrene block copolymer (SBS). The influence of methods to improve compatibility, such as physical modification of rubber waste or dynamic crosslinking and grafting, on the characteristics of the polymer composites obtained was analyzed. To determine the composition of the rubber waste, the acetic extract and the amount of ash were determined, and a Burchfield test as well as an FTIR analysis were performed to identify the type of rubber. Based on the analyses performed, it was observed that the base elastomer in the rubber waste is styrene butadiene rubber (SBR). It was filled with silicon dioxide (SiO₂) and vulcanized with sulfur (S). The rubber waste was cryogenically milled. Mixtures based on thermoplastic elastomers such as styrene–butadiene–styrene block copolymers and milled vulcanized rubber waste (powder) were obtained using a Plasti-Corder Brabender internal mixer. Crosslinking and grafting were performed by a radical reaction mechanism, in dynamic regime, at temperatures of 135–165 °C and rotational speeds of 80 rpm, using di-2-tert-butylisopropyl benzene as crosslinking agent and trimethylolpropane trimethacrylate as crosslinking coagent. The specimens for characterizing the mixtures were made by compression on a laboratory electrical press. The samples were characterized from a structural point of view and the physical–mechanical properties were determined, in the normal state and after accelerated aging for 168 h at 70 °C. The obtained results indicate that the vulcanized rubber powder acted as an elastic filler, leading to an increase in the hardness and elasticity of the samples. Grafting and crosslinking in a dynamic mode shows a significant improvement in hardness, elasticity and tensile strength. The samples show good stability at accelerated aging.

Keywords Polymeric composites · Rubber waste · SBS · FTIR · Physical–mechanical properties

Introduction

After the discovery of the vulcanization process in 1839, by Charles Goodyear [1, 2], natural rubber began to be widely used, due to its special properties such as elasticity, tensile strength and resistance to abrasion, and good electrical insulation. Nowadays, it is also used as raw material for the synthesis of new biobased products, synthesis of diols, macrodols and esters from natural rubber [3, 4].

In the twentieth century, several types of synthetic rubbers were obtained, some of them with superior properties to natural rubber, or with special uses. These include ordinary synthetic rubbers (namely: polybutadiene, polyisoprene, styrene–butadiene copolymer), and special rubbers, such as ethylene–propylene copolymers, polychloroprene, acrylonitrile–butadiene copolymers, and polyurethanes [5, 6]. A variety of rubber products have appeared on the market, such as conveyor belts, electrical insulation, gaskets, rubber shoes and soles, baby bottles, medical devices, anti-corrosion coatings, adhesives, and car tires. The rubber processing industry has developed significantly and is still in a continuous development, the most accelerated being the production of car tires [7, 8].

When obtaining rubber articles by vulcanization method, along with vulcanization accelerators, other ingredients are

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added, such as fillers, plasticizers, antioxidants, dyes, and flame retardants, which aim to improve certain properties or reduce the production cost. Due to the synthetic rubbers, the vulcanizing agents and the ingredients that are added to the rubber materials, they are very resistant to biodegradation, photochemical decomposition or high temperatures. For these reasons, the management of post-consumer waste (generally obtained as burrs from the vulcanization operation) or the waste obtained from the decommissioning of rubber articles, and especially of car tires, has become a very serious technological, economic and ecological challenge. Thus, several regulations have been adopted and several methods of recovery, reduction, reuse and recycling of these wastes have been developed [8–10]. Progress in recent years in the management of polymer waste has led to these types of waste being perceived as a potential source of energy or new raw materials [8, 10].

The main methods of recovery of used products and rubber waste, grouped in descending order of technical efficiency of the process are [7, 8, 11]: (1) reprocessing for reuse; (2) material recycling—by grinding or grinding and devulcanization, when rubber powder is obtained which can be used both as a filler in elastomeric compositions or thermoplastic materials, as well as to obtain regenerated rubber by devulcanization (which can replace rubber); (3) pyrolysis—when carbon black or oils can be obtained; (4) energy recovery—the use as fuel for obtaining thermal energy; (5) reuse as modifying agents for various materials, used especially in the field of road construction, etc.

In this paper, we present the recycling of post-consumer non-black waste by cryogenic grinding and the use of rubber powder obtained as a filler for the production of polymer composites, in which the matrix consists of a thermoplastic elastomer referred to styrene–butadiene–styrene block copolymers (SBS). Cryogenic grinding, compared to other grinding methods such as grinding at ambient temperature, or wet grinding, has the following technical advantages: (a) advanced grinding in a small number of grinding steps, reducing the proportion of recycled material; (b) obtaining smaller particles with more uniform dimensional distributions; (c) eliminating the possibility of thermal degradation of the material; (d) grinding materials which cannot be effectively ground by conventional methods, etc. With this technology, it is possible to make rubber particles with the required parameters and smooth surface, which considerably improve the physico-chemical properties and allow their use in making tires, polymer composites, composition of asphalt mixtures, etc. The disadvantages of this method are generally due to the costs of the coolant used, or those of the drying operation [12–14].

Several studies have been carried out on the use of ground rubber waste, in the form of rubber powder, in the production

of polymer composites with a thermoplastic matrix, in which the thermoplastic materials used are mainly: polyethylene (PE) [15–18], polypropylene (PP) [19–22] polystyrene (PSt) [23], polyvinyl chloride (PVC) [24, 25], ethylene–vinyl acetate copolymer (EVA) [26, 27], polyurethane (PU) [28] etc. According to these studies, it has been observed that the mechanical properties of these polymer composites depend on the type of thermoplastic matrix used, the amount of rubber powder and its degree of dispersion in the matrix, and the nature of interactions between composite components [18, 29]. The composites obtained are generally characterized by a low adhesion between the thermoplastic matrix and the rubber powder [23, 30], and the mechanical properties decrease with the increasing amount of rubber particles introduced [31]. In order to improve the properties of these composites, the use of maleic anhydride, dicumyl peroxide [32] or bis-maleimide [33], which acts as a compatibility system, was analyzed.

In our study, the rubber waste was physically modified by cryogenic grinding, and then mixed with linear liquid polydimethylsiloxane (PDMS) to improve dispersion in the polymer matrix. The thermoplastic matrix was an SBS-type thermoplastic elastomer, which has a basic composition similar to that of the rubber identified in the rubber powder, so that the interactions between the thermoplastic matrix and the reinforcing filler (rubber powder) would be good. At the same time, for an improvement of the characteristics, a crosslinking and grafting in dynamic regime was performed. The work can contribute to the development of new methods and technologies for the superior recovery of rubber waste, which will contribute to a reduction of environmental pollution.

Experimental

Materials

The following raw materials were used for the experiments: (1) thermoplastic elastomer granules (TR) styrene–butadiene–styrene block copolymers (SBS) K03/65/9000, manufactured by KIK Compounds, Targoviste, Romania, were used as polymer matrix. These, in addition to the basic SBS elastomer, may contain filler, plasticizer, antioxidant, dyes and other ingredients; (2) a rubber powder obtained by cryogenically grinding a compact white rubber waste (from footwear) was used as a reinforcing filler, obtaining 45-mesh rubber powder size; (3) liquid linear polydimethylsiloxane (PDMS), from Sigma-Aldrich, Inc., USA, was used as plasticizer and to improve the dispersion of rubber powder in the polymer matrix; (4) Luperox F40 di-2-tert-butylisopropyl benzene (40% active substance

content) from Alkema and a crosslinking coagent, trimethylolpropane trimethacrylate (TMPTMA) monomer Alcanpoudre TMPT MA 70 (70% active substance and 30% precipitated silica) from Safic Alcan were used for the crosslinking and dynamic grafting of the polymer composite in order to improve its characteristics.

Modification of the rubber waste

The post-consumer rubber waste was physically modified by grinding using a Retsch ZM200 cyclone cryogenic mill (manufactured by Retsch GmbH in Haan, Germany) initially using a 30-mesh and then a 45-mesh sieve. Carbonic ice was used as the refrigerant. In order to improve the dispersion of the rubber powder in the polymer matrix, linear polydimethylsiloxane (PDMS) was used, which also has a plasticizer role. The obtaining method was: 5 g of PDMS were added to 95 g of rubber powder under continuous mixing (60 rpm), and the obtained mixture was kept for 6 h at 60 °C homogenizing the sample every 30 min.

Obtaining compounds and testing specimens

The blends were obtained using a Plasti-Corder Bra-bender internal mixer, at 150–170 °C for 7 min. The rotor speed was 30 rpm in the first 2 min and increased to 80 rpm for the next 5 min. The composition of the mixtures made, expressed in parts per 100 parts of rubber (phr), is presented in Table 1. Test specimens for the determination of the characteristics were obtained by the compression method, using the laboratory electrical press Fortune Presses TP 600 manufactured by Fontijne Grotnes, Vlaardingen, The Netherlands. The processing parameters were: temperature of 170 °C, pressing force 300 kN and molding time 6 min, followed by the cooling stage down to 45 °C, at 300 kN pressing force, for 10 min.

Table 1 Composition of blends

Ingredients	Sample code			
	M	A20	A20+5P	PT/A20+5P
TR K03/65/9000, g	100	100	100	100
White rubber waste powder, g	–	25	–	–
White rubber waste powder with 5% PDMS, g	–	–	25	25
Luperox F40P, g	–	–	–	1.25
Alcanpoudre TMPTMA 70, g	–	–	–	1.25

Laboratory tests

Methods of analysis of post-consumer rubber waste

In order to analyze the composition of the post-consumer rubber waste, the acetonic extract and the amount of *ash* were determined.

The determination of the acetonic extract was performed according to ISO 1407 Method B. The method is based on the property that resins have to dissolve in certain organic solvents [34, 35]. A crushed sample quantity was weighed (5.0237 g with an accuracy of ± 0.0001 g) and a medium porosity filter paper cartridge was formed. The sample cartridge was inserted into the Soxhlet apparatus (mounted on a water bath) and attached to the extraction flask previously brought to constant weight (by heating to 105 °C). The required amount of acetone was added and extracted until the liquid was observed in the level tube (18 h). After extraction, the cartridge was removed, the acetone was removed by distillation, and the flask was dried and brought to a constant mass (in an oven at 105 °C for 3 h). The acetonic extract content was calculated from the relation (1):

$$\text{acetone extraction}(\%) = \frac{m_1 - m_2}{m} \times 100 \quad (1)$$

where m_1 is the mass of the flask with residue, in g; m_2 is the mass of the empty flask, in g; m is the mass of the rubber waste test sample, in g.

The determination of the ash content (mineral substance content) was carried out in accordance with ISO 247. For the determination, a quantity of 5.2813 g of the ground rubber waste sample was weighed to the nearest ± 0.0002 g and placed in a porcelain crucible previously brought to constant weight. The crucible with material was burned with the help of a gas bulb, in the niche, until the organic material was exhausted, after which it was placed in a calcination furnace at high temperature (800 °C) until reaching constant mass. Ash content was calculated using relation (2):

$$\text{ash content}(\%) = \frac{m_i}{m_f} \times 100 \quad (2)$$

in which m_i is the mass of the material weighed initially, in g; m_f is the mass of the residue after calcination, in g.

The identification of the rubber type: present in the post-consumer rubber waste was performed by a Burchfield test, using Burchfield reagent 1 [36, 37] and by FTIR spectroscopy.

Reagent 1 was used for the Burchfield test, which consists of: 1 g of paradimethylaminobenzaldehyde, 0.01 g hydroquinone, and 100 ml of absolute methyl alcohol, to which 5 ml of concentrated hydrochloric acid, were added. Two test tubes, specimen and condensing, were used for identifying

the type of rubber. About 0.5 g of ground rubber waste were placed in the first test tube, and 2 ml of Burchfield reagent 1 was added to the second test tube. The test tube with rubber was heated by flame. The decomposition vapors reached the second test tube containing the Burchfield reagent 1, through the condensation tube. An initial color modification was observed, afterwards a double amount of methyl alcohol was introduced into the test tube and heated at 100 °C for 3 min, when the final color was set in. The obtained result was verified by FTIR spectroscopy.

Characterization of samples

The samples based on thermoplastic rubber and rubber waste in powder form were characterized in terms of structural (FTIR analysis) and physical–mechanical properties, as well as in terms of behavior after accelerated aging.

Fourier Transform Infrared Spectroscopy (FTIR) spectra of samples were obtained using Nicolet iS50 FTIR spectrophotometer in the wave number ranging from 400 to 4000 cm^{-1} , using attenuated total reflection (ATR).

Tensile strength, modulus 100% (the stress under 100% elongation), breaking elongation and residual elongation tests were carried out according to the conditions described in ISO 37, on dumb-bell shaped specimens of type 2. Tearing strength tests were carried out using angle test pieces (type II) according to ISO 34–1. Tests were carried out with a Schopper1445 strength tester and the value of deformation rate for testing pieces has a magnitude of 500 mm/min. The precision and the uncertainties of the test are ± 0.64 for tensile strength and ± 2.95 for elongation at break.

Hardness was measured in °Shore A using 6-mm-thick samples, according to ISO 48–4 (the precision and the uncertainties of the test are ± 0.05).

Resilience was determined according to ISO 4662 with a Schob test machine using 6-mm thick samples.

Abrasion resistance was determined according to ISO 4649 by the cylinder method, using a force of 10 N. The samples used were obtained from rolled and pressed mixtures, by cutting with a rotating die, and have cylindrical shape, with a diameter of 16 mm and height of min. 6 mm. Abrasion resistance was expressed by relative volume loss in relation to calibrated abrasive paper:

$$\Delta V [\text{mm}^3] = \frac{V_i \times 200}{m_g} \quad (3)$$

where V_i is volume loss of testing sample in mm^3 and m_g is weight loss of standard rubber in mg.

The densities of samples were measured according to ISO 2781 (the precision and the uncertainties of the test are ± 0.09).

Accelerated aging trial was carried out according to ISO188 using the hot air circulation oven method. Test duration was of 168 h and temperature of 70 ± 1 °C. The results were compared with those from samples not subjected to aging.

Melt flow index (MFI) of the samples was measured by means of an extrusion through a 2 mm die (capillary rheometer—Melt Flow Index—Haake) at 180 °C, and a 5 kg force was used, according to ISO 1133.

All measurements were repeated for minimum three times.

Results and discussion

Characterization of rubber waste and modified powder

Post-consumer vulcanized rubber waste has been cryogenically ground and chemically modified as described in “[Modification of the rubber waste](#)”. Ground cryogenic powder, whether or not chemically modified, was used as a reinforcing filler to obtain the samples under study. For these reasons, in order to be able to determine the way in which it influences the physical and mechanical properties of the obtained mixtures, it is necessary to know their composition and to identify the elastomer in the waste. After performing the methods of analysis described in “[Methods of analysis of post-consumer rubber waste](#)”, the analyzed rubber waste indicated an acetonic extract value of 13.45%, the amount of ash was 30.4% and the elastomer identified by the Burchfield test was styrene–butadiene rubber (SBR).

The value obtained from the acetonic extract was 13.45% and according to the data from the literature [34], this represented: the content of free sulfur, resins, processing rubber additives, mineral oil, fatty acids, antioxidants, waxes, lubricants existing in the powder, organic accelerators and their reactive product, etc.

The amount of ash obtained from the rubber waste was 30.4%, representing, according to the specifications of the standard method, the percentage of inorganic compounds in the powder such as metal oxides (zinc oxide, magnesium oxide, titanium dioxide), inorganic dyes or inorganic fillers (such as silicon dioxide) and other auxiliary additives. The ash obtained is white with a few yellow particles and was analyzed by FTIR spectroscopy (Fig. 1). The FTIR spectrum shows an absorption band at 1070 cm^{-1} specific to –Si–O–Si stretching and the bands from 457 to 784 cm^{-1} attributed to –Si–O bending. It can be concluded that the ash consists mainly of silicon dioxide, i.e., an active filler widely used in the rubber industry. The 457–784 cm^{-1} bands may overlap with specific bands of polysulphides (S–S stretch), aryl disulphides (S–S stretch) or disulphides (S–S stretch),

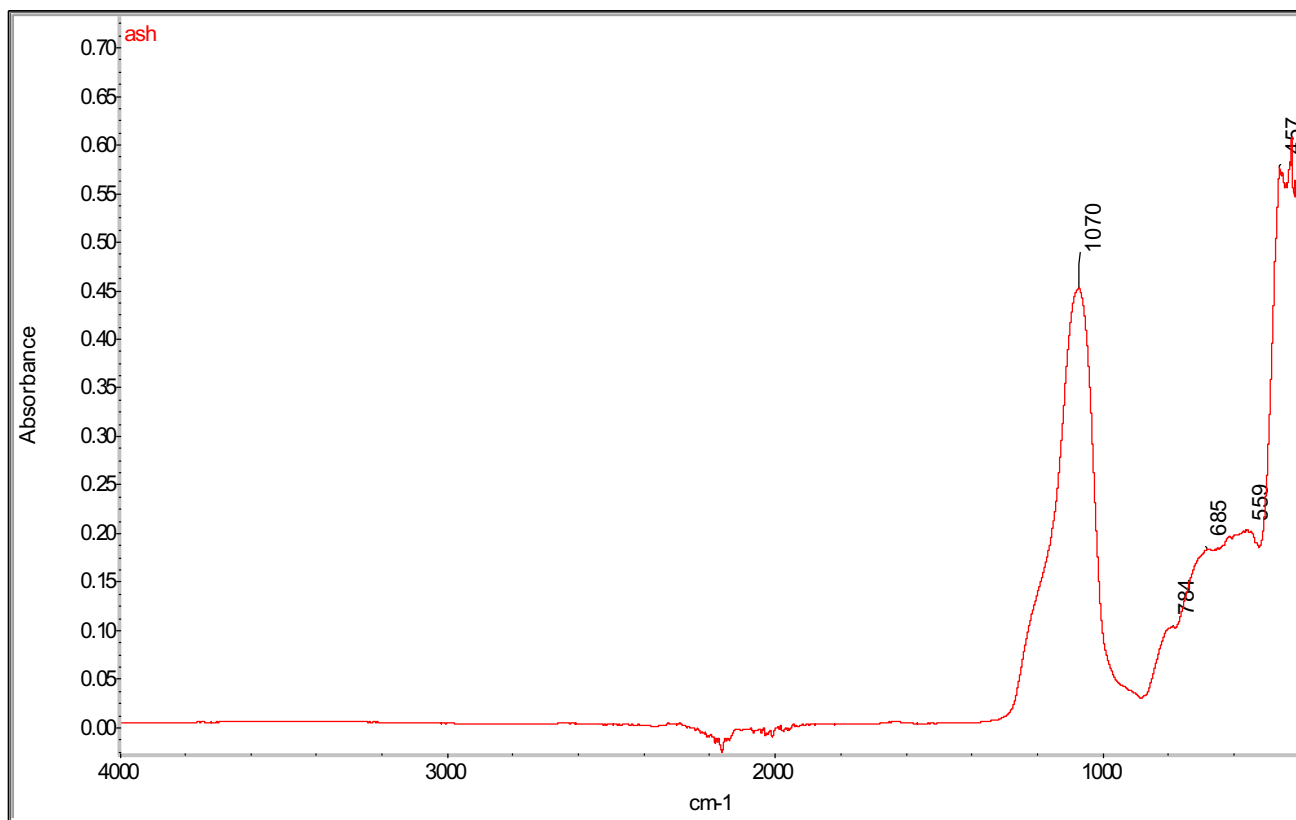


Fig. 1 FTIR spectrum for inorganic filler from rubber waste (ash analysis)

which may indicate that for the rubber mixture in the waste, vulcanization was performed with sulfur and vulcanization accelerators [38].

The Burchfield test 1 was used to identify the elastomer in the rubber waste, in which the initial color obtained was light green-yellow and the final color was dark green. According to the specifications in the literature [36, 37], the elastomer identified in the waste was styrene–butadiene rubber (SBR).

FTIR spectroscopy was used to verify the type of rubber obtained by the Burchfield test. Figure 2 shows the FTIR spectrum of rubber powder without/with 5% PDMS, respectively. Analyzing the resulting FTIR spectra, the existence of the bands corresponding to polybutadiene and polystyrene in the SBR rubber is observed, namely: (1) styrene-specific bands such as the absorption band specific to monosubstituted benzene group–deformation vibration of (C–H) from the benzene nucleus, C=C of the benzene ring or C–H of the methyl or methylene group, from 699, 1539 cm^{-1} and 1451 cm^{-1} , (2) butadiene-specific absorption bands such as those from 910, 964 cm^{-1} , due to 1.4 trans C–H, or those from the 2917 and 2848 cm^{-1} peaks are attributed to $-\text{CH}_2-$ methylene asymmetric stretching and symmetric stretching, respectively; (3) the bands specific to the sulfur bridges due to rubber vulcanization, or due to the precipitated silica filler, but there is a shift of the absorption bands

observed for the ash from the rubber waste shown in Fig. 1, these indicating the appearance of Si–C, Si–O–C, C=S bonds between the active filler, the vulcanizing agent and the SBR elastomer, respectively [38, 39]. For white rubber powder treated with 5% PDMS, the following can be observed: (a) the appearance of a band at 1260 cm^{-1} corresponding to the deformation vibration of the C–H bond in $\text{Si}(\text{CH}_3)_2$, (b) the appearance of the 800 cm^{-1} band specific to the Si–C and C–H bond, and (c) modification of the 1085 cm^{-1} band corresponding to the Si–O–C bond [40, 41].

Characteristics of plastograms

The samples were obtained on Plasti-Corder Brabender internal mixer, which records the variation of torque and temperature versus time.

The variation of the torque over time when making the mixtures (Fig. 3) indicates that for all the mixtures made there is an increase of the torque when increasing the rotational speed from 30 to 80 rpm, after which the torque decreases. The temperature during the process of obtaining the mixtures (Fig. 4) decreases initially as a result of introducing the ingredients in the mixer at room temperature, after which it increases due to the existing temperature in

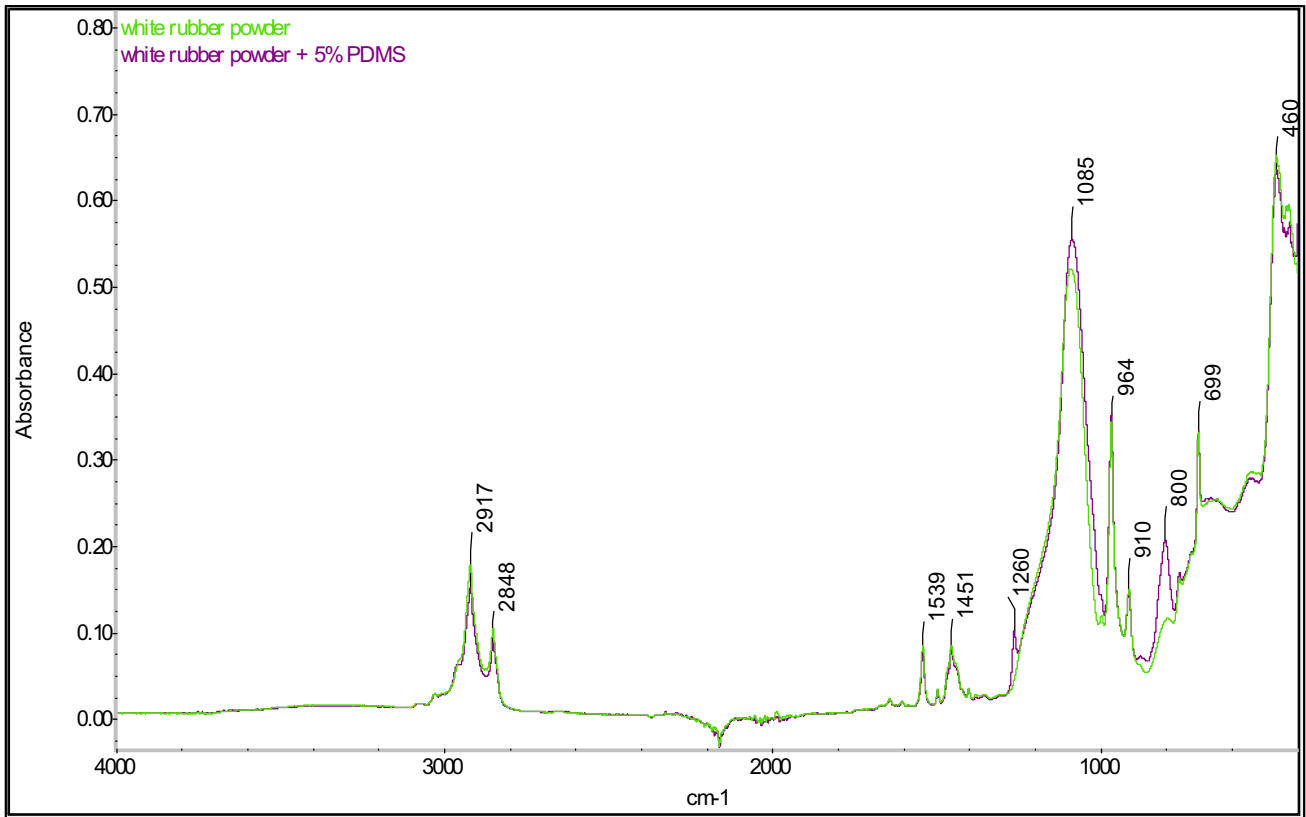


Fig. 2 FTIR spectra of vulcanized rubber powder with and without PDMS, respectively

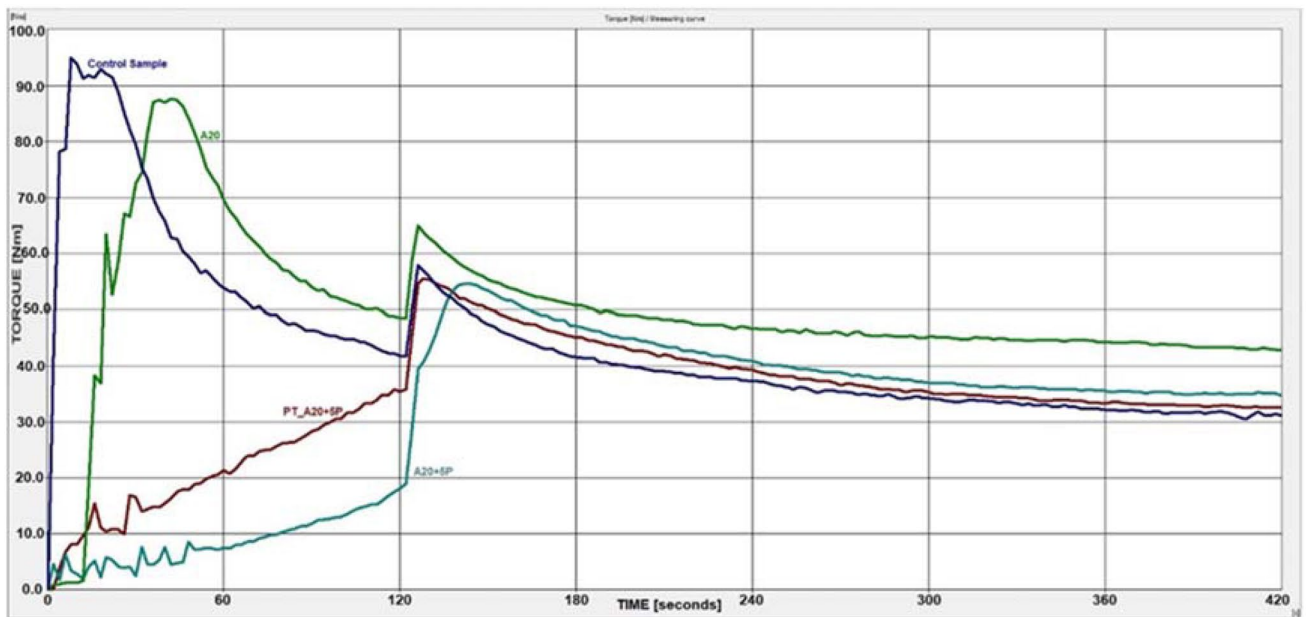


Fig. 3 Variation of torque versus time when obtaining the mixtures

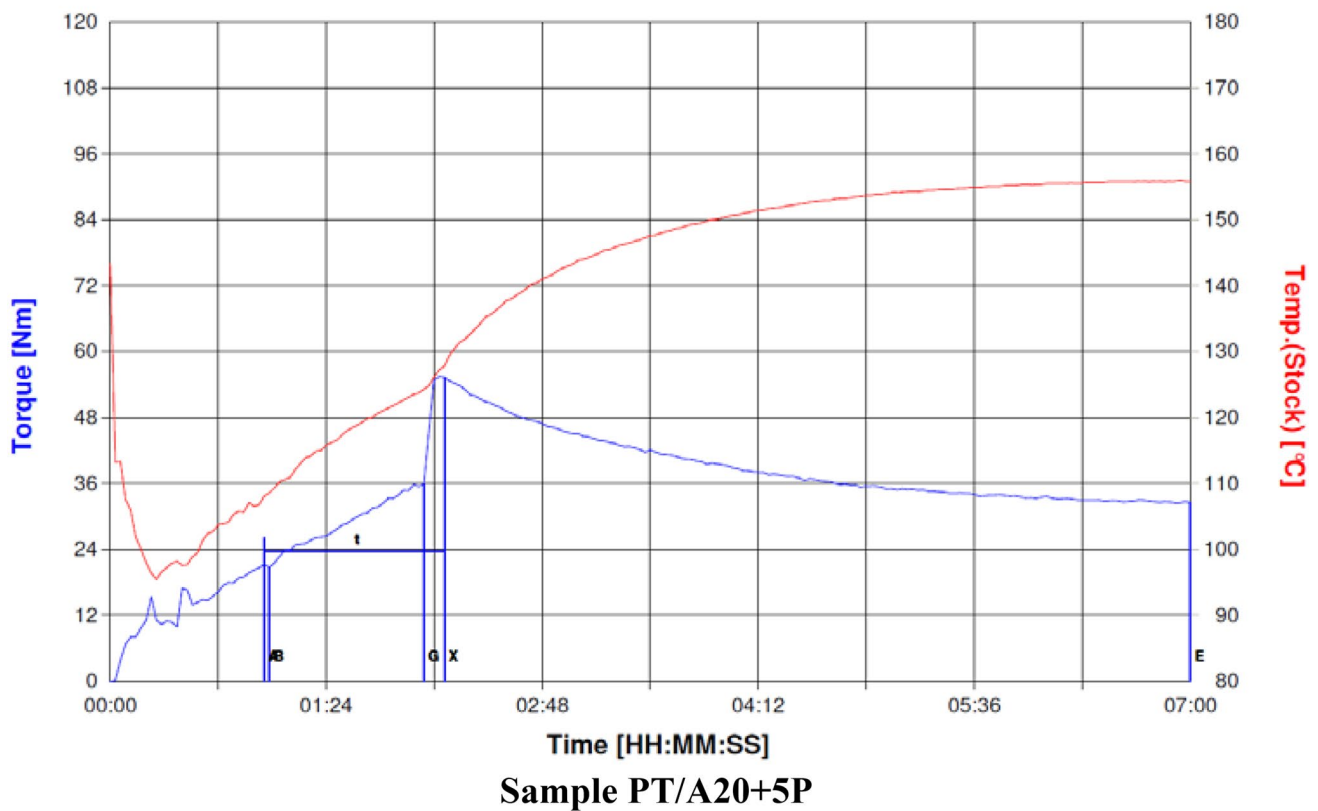
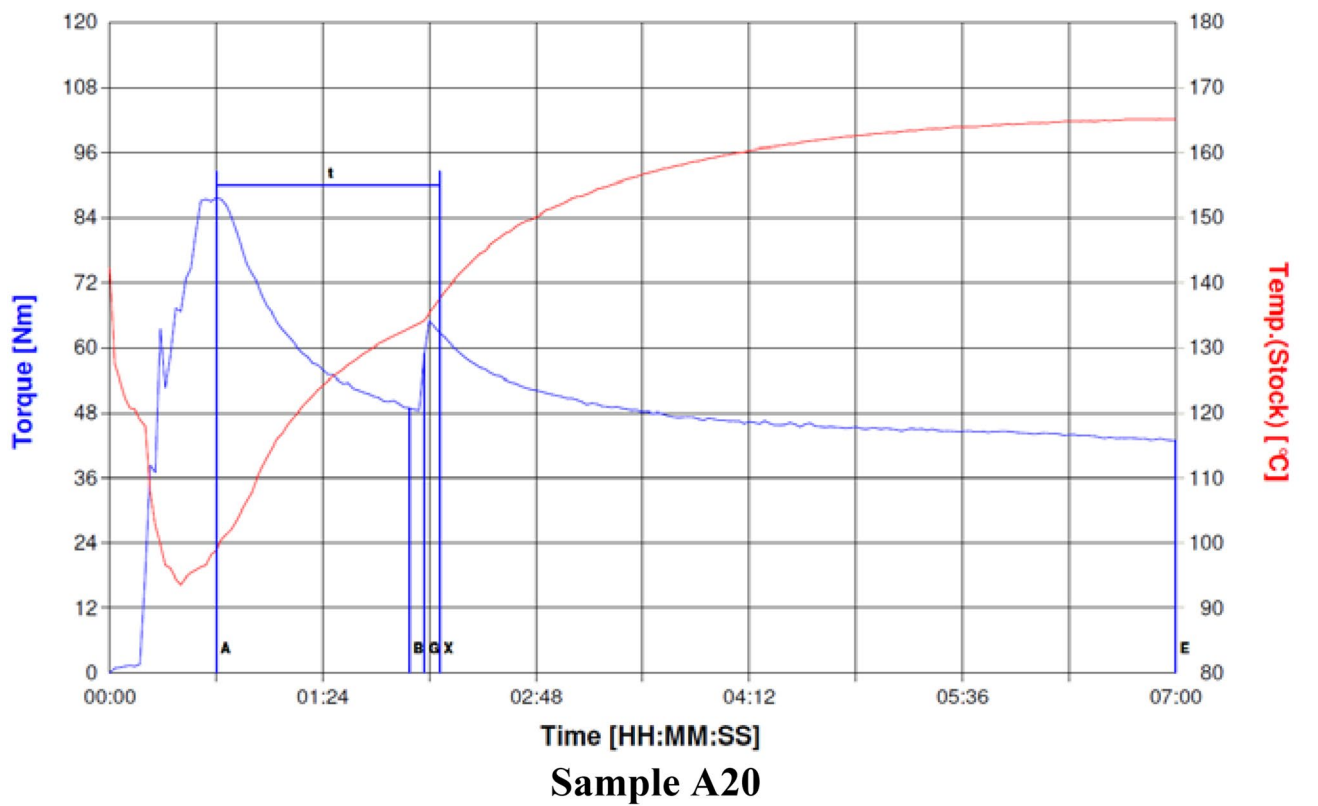


Fig. 4 Diagrams showing the variation of the torque and the temperature, when obtaining the mixtures on Plasti-Corder Brabender

Table 2 The characteristics recorded on Plasti-Corder Brabender during the mixing

Sample code	Specific energy, [kJNm/g]	Fusion time, [seconds]	Gelling rate, [Nm/min.]	Torque variation range, [Nm]	Temperature variation range, [°C]
Control (M)	0.3	122	243.1	31.1–95.1	97–163
A20	0.4	88	310.8	42.8–87.7	99–165
A20+5P	0.3	94	307.7	8.6–54.6	103–156
PT/A20+5P	0.3	70	58.2	20.7–55.3	108–156

the mixing chamber (150 °C) and due to the increase of the shear moment inside the mixing chamber.

Table 2 shows the parameters recorded during the process of obtaining the mixture. A decrease in maximum torque can be observed for samples containing PDMS-treated rubber powder with 5% PDMS, which indicates that PDMS acted as a plasticizer. Melting time and gelling rate were lower in the PT/A20+5P mixture due to crosslinking and grafting reactions occurring in the presence of peroxide and crosslinking coagent.

FTIR spectra of samples

Figure 5 shows the FTIR spectra of the control sample (M) compared to sample A20 (which has an additional 20%

white powder). According to the spectrum, it is observed that in the A20 sample there are additional bands specific to the precipitated silica-type filler or to the sulfur bonds existing in the powder. The absorption bands at 965 cm^{-1} indicating 1,4 trans polybutadiene and those at 697 cm^{-1} indicating polystyrene (CH in the benzene nucleus) overlap, which could indicate similar compositions in terms of the proportion of polybutadiene and the polystyrene, respectively, in the two types of samples, the control (which contains a thermoplastic SBS elastomer) and the A20 sample, which together with the thermoplastic SBS elastomer matrix has a quantity of 20% of SBR rubber powder vulcanized with sulfur and reinforced with precipitated silica [38, 41].

Figure 6 shows the corresponding bands of the FTIR spectra of sample A20+5P and sample PT/20+5P. A

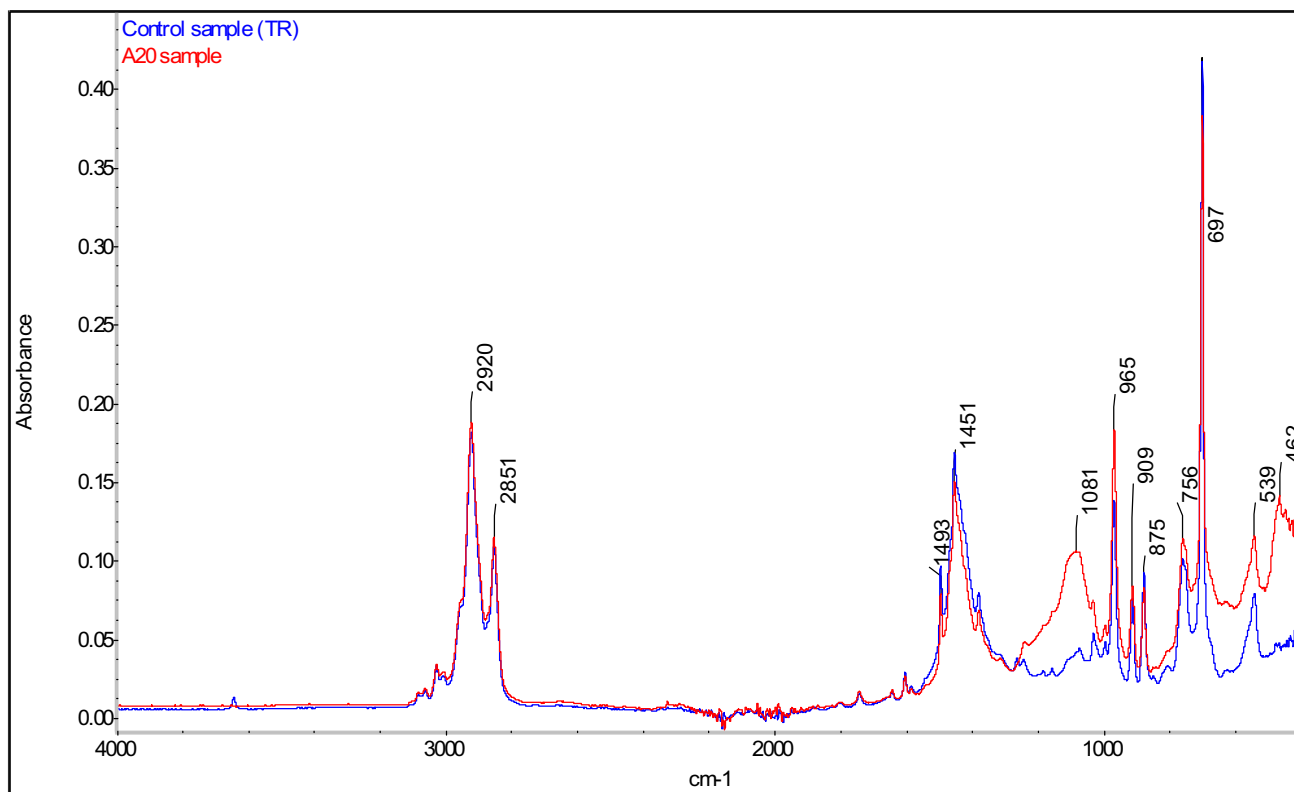


Fig. 5 Spectra of control sample and sample A20

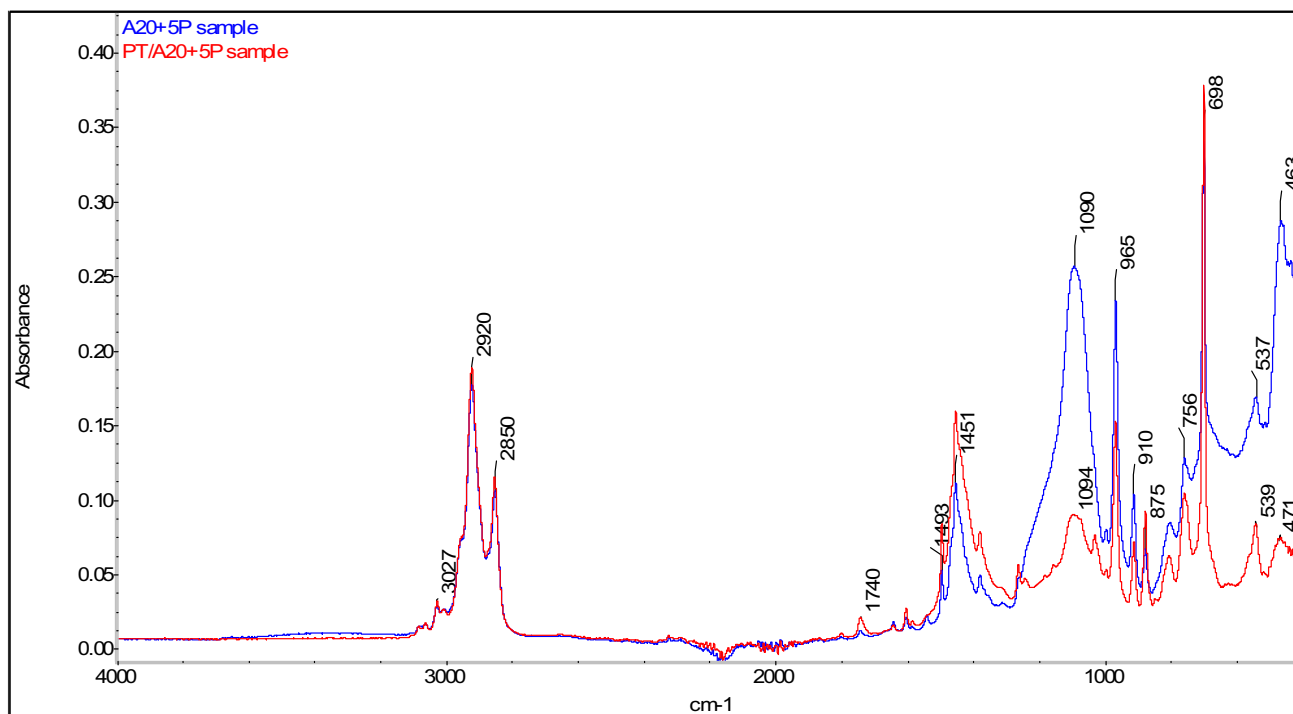


Fig. 6 FTIR spectra of sample A20 + 5P and sample PT/20 + 5P

change in the FTIR spectrum can be seen in the sample in which the grafting and crosslinking with peroxide was performed in the presence of the crosslinking coagent in the section $900\text{--}1493\text{ cm}^{-1}$, that corresponds to both double bonds in the benzene ring (1493 and 1451 cm^{-1}) as well as the double bonds corresponding to polybutadiene, namely at 910 cm^{-1} and 965 cm^{-1} , indicating that the crosslinking and grafting take place by breaking some double bonds [38–42].

Physical–mechanical characteristics

The physical–mechanical characteristics of the mixtures in normal state and after accelerated aging are presented in Fig. 7a–f.

Hardness (Fig. 7a): the analysis of the samples shows increases from 64° Shore A (sample M) to $67\text{--}68^\circ$ Shore A (samples A20 and A20 + 5P) by introducing into the mixture the rubber powder. This increase can indicate its reinforcing action, which can be determined by the amount of active filler it contains [43, 44]. An increase of 75° Shore A is observed for the sample which was grafted and crosslinked with peroxide as a result of the increase in crosslinking density [45, 46]. After accelerated aging for 168 h at 70°C , the hardness increases by $2\text{--}4^\circ$ Shore A, a variation that falls within most product standards, and which shows the stability of the sample under accelerated aging conditions.

Elasticity (Fig. 7b) increases from 12 to 14% by adding vulcanized rubber powder (indicating that the powder plays

the role of an elastic filler), and by crosslinking and grafting a significant increase in elasticity is observed (at 26%) as a result of the formation of a three-dimensional network and the formation of C–C type bonds both between the chains of the TR thermoplastic elastomer and between the latter and the vulcanized rubber powder [46]. After accelerated aging, a 15% decrease in elasticity is observed only for the PT/A20 + 5P sample, which may indicate a slight degradation.

Modulus 100% (Fig. 7c) and tensile strength (Fig. 7d) increase by adding rubber powder as a result of reinforcing mixtures, but the increase in these values is much higher (increase of 206% for modulus 100 and 22% for tensile strength) for the crosslinked and peroxide-grafted sample, due to improved adhesion between the two phases and the formation of crosslinking and grafting bonds [38]. The modulus 100% shows an increase of 2.94–18.5% and the tensile strength a variation between -13.78 and $+12.55\%$ after testing the accelerated aging samples, which may indicate an increase in the crosslinking density of the composite by maintaining a temperature of 70°C for a long time.

Elongation at break (Fig. 7e) shows a decrease of 21% by the introduction of treated/untreated rubber powder, respectively, and decreases significantly (from 580 to 180%) due to crosslinking and grafting (see sample PT/A20 + 5P) indicating a movement restriction of the polymer chains when applying a force by loading, and by grafting and crosslinking, respectively [46–48]. There is a decrease in elongation at break of 8.7–26% for the M, A20 and A20 + 5P samples

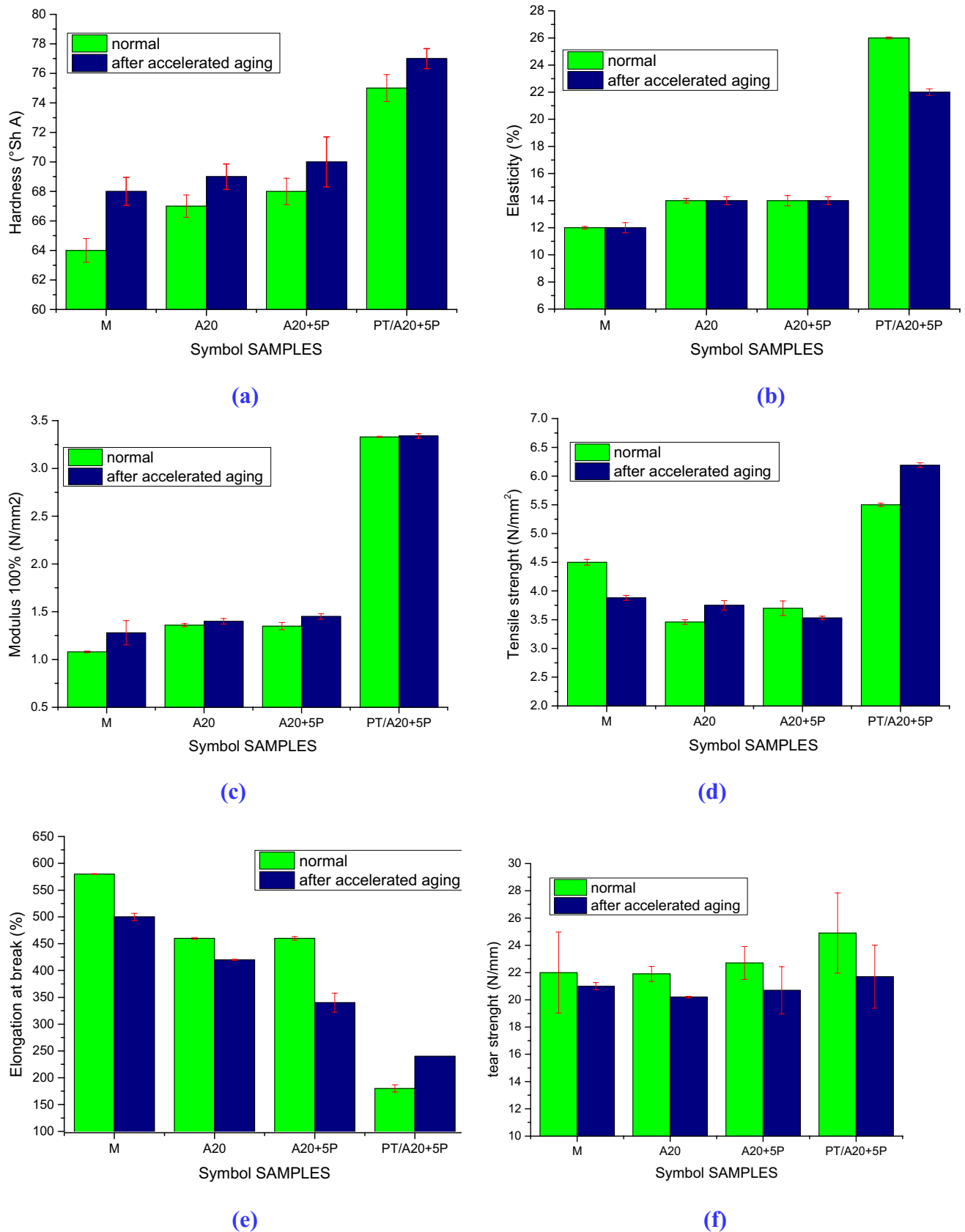


Fig. 7 Physico-mechanical characteristics of the samples: **a** hardness; **b** elasticity; **c** modulus 100%; **d** tensile strength; **e** elongation at break; **f** tear strength

and an increase of 33% for the crosslinked and grafted sample in dynamic regime, after the accelerated aging test.

Tear strength has values of 21.9–24.9 N/mm, varies with (–) 0.45 – (+) 3.18% by adding rubber powder, and increases by 13.18% for the crosslinked and grafted mixture. After accelerated aging testing, the values of tear strength show a decrease between 4.55 and 12.96%. The reductions on elongation at break and tear strength may be caused by further crosslinking of the samples after they were exposed to the heat aging [45, 49].

With the exception of elongation at break, the variation of the physical–mechanical characteristics of the samples tested at accelerated aging is below $\pm 25\%$, indicating the stability of the samples to aging.

The density of the samples (Table 3) is increased by the addition of rubber powder which has a higher density than the control sample. The sample, which contains functionalized powder and is crosslinked, is noted to have highest density.

Abrasion resistance (Table 3) has very good values, below 215 mm³, but the best value was obtained for the unloaded sample (control). It is observed that by filling, this property worsens, which may be due to both the dispersion

and the size of the rubber powder particles, as well as the rigidity of the material [49–51].

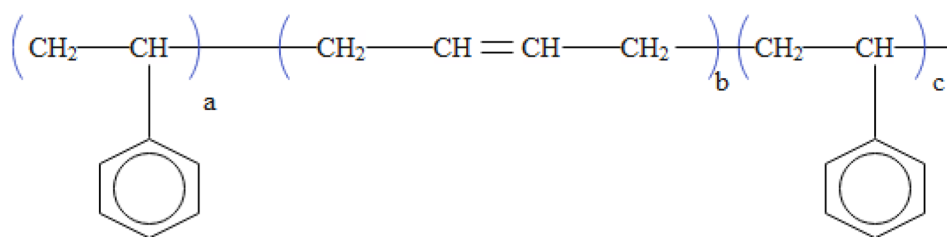
The melt flow index at 180 °C with a weight of 5 kg (Table 3) decreases from 56.6 g/10' for the control sample, to 31.2 g/10 min. for the sample with 20% rubber powder (A20 sample), and to 39.7 g/10 min for the A20+5P sample (sample containing powder with 5% PDMS), respectively. The crosslinked and peroxide-grafted sample did not flow under the conditions presented due to the three-dimensional network formed, but the plates or finished products can be processed by modeling at high temperature according to the procedure presented to obtain the specimens, thus eliminating the vulcanization operation specific to elastomers, during which many toxic gases are released [52].

Improving the physical–mechanical properties by adding vulcanized rubber powder indicates a good compatibility between the two polymer phases. This may be due to the fact that the base elastomer in the polymer matrix (SBS) has a similar structure to that of the elastomer identified in rubber powder (SBR), as can be seen in Fig. 8. The disperse phase in the polymer matrix contains a large amount of active filler such as precipitated silica (ca. 30%), which contributes, along with the vulcanized SBR elastomer, to

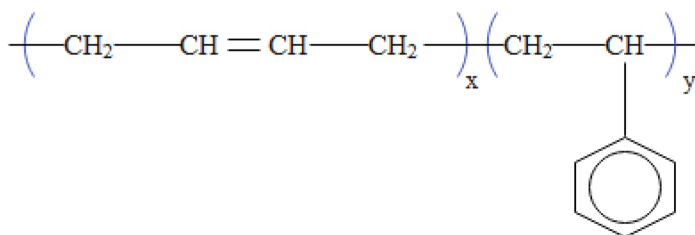
Table 3 Values of density, resistance to abrasion and melt flow index for tested samples

Characteristics	Sample code			
	M	A20	A20+5P	PT/A20+5P
Density, g/cm ³	1.03 ± 0.11	1.06 ± 0.09	1.05 ± 0.07	1.07 ± 0.05
Resistance to abrasion, mm ³	192.17 ± 0.8	203.77 ± 1.1	213.14 ± 0.9	209.18 ± 0.5
MFI, g/10 min. at 180 °C with 5 kg weight	56.6 ± 1.1	31.2 ± 0.9	39.7 ± 0.8	–

Fig. 8 Structural forms of SBS **a** and SBR **b** elastomers



a. SBS



b. SBR

reinforcing the mixture and therefore, to improving physical–mechanical characteristics.

Conclusions

For the superior recovery of post-consumer rubber waste, the waste was processed and analyzed in order to determine its composition. From the FTIR spectroscopy analysis, but also from the Burchfield test, it was observed that the rubber powder is based on SBR rubber. It is filled with silicon dioxide according to the ash analysis and FTIR characterization, and is crosslinked with sulfur. The waste was cryogenically ground to a 45-mesh size, for use as a filler in a thermoplastic matrix. In order to obtain composites with appropriate characteristics, with a good adhesion between the thermoplastic matrix and the rubber powder filler, a TR thermoplastic elastomer (based on SBS) was selected as the thermoplastic matrix. In addition, the rubber powder was plasticized with PDMS in order to improve the dispersion of the rubber powder in the polymer matrix. The samples were tested using an internal mixer at temperatures of 135–165 °C and rotational speeds of 30–80 rpm. They were characterized from a structural and physical–mechanical point of view, according to the standards in force. The analyses highlighted the formation of Si–O–C bonds, or the detachment of some double bonds, indicating the formation of some bonds between the powder filler and the elastomer, and the formation of a crosslinked network, respectively. At the same time, by adding SBR rubber powder to the TR thermoplastic matrix, the hardness and elasticity were improved. By crosslinking and grafting in a dynamic mode, a significant improvement of hardness, elasticity, but also of tensile strength is observed. From the variation of the physical–mechanical characteristics of the tested samples at accelerated aging it was observed that the samples show a good stability to aging. The samples obtained have a very good abrasion resistance (below 215 mm³).

The resulting polymer composites can be processed by methods specific to plastics, post-consumer waste can be reintroduced into the technological flow, and the physical–mechanical properties make them suitable for making consumer goods for various applications.

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Declarations

Conflict of interest The authors declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

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