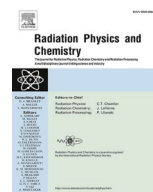


Recycling waste tire rubber through an innovative water-medium ionizing radiation treatment: Enhancing compatibility and mechanical performance

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# Recycling waste tire rubber through an innovative water-medium ionizing radiation treatment: Enhancing compatibility and mechanical performance

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## ABSTRACT

In this research, we solved the compatibility problems of rubber mixtures containing waste ground tire rubber (GTR) with an innovative and environmentally friendly, water-based ionizing radiation treatment, meaning that the GTR is under water. Our hypothesis was that the strong oxidizing agents that appear during the radiolysis of water can activate the surface of the GTR, resulting in reactive functional groups containing oxygen, which can help establish a better interaction between the matrix and the GTR. We treated the GTR using different absorbed doses and examined the changes in the GTR using Soxhlet-extraction and cross-link density measurements. The surface of GTR was characterized by Fourier-transform infrared spectroscopy. Then we prepared GTR-containing natural rubber-based mixtures in an internal mixer, using two different mixing techniques. The mixtures were vulcanized in a hydraulic press, and the mechanical and morphological properties were investigated. As a result of the radiation treatment, cross-link density decreased slightly, while sol content did not change significantly. The FTIR spectra indicated that oxygen-containing groups appeared on the surface of the treated GTR. In the case of one-step vulcanizates, tensile strength increased by 11% and tear strength by 40%, while elongation at break remained high. For the two-step mixtures, tensile strength improved by 25%, tear strength by 35%, while elongation at break was over 400%. An irradiation dose of 20 kGy produced the best result, which is sustainable in mass production.

## 1. Introduction

The rapid growth of vehicle ownership results in a large number of waste tires each year (Li et al., 2021). Nowadays, the idea of a circular economy is of paramount importance. It could be realized in tire production, but sadly, it is not. The reason for this is that end-of-life tires are still incinerated in large numbers and material recycling is neglected (Abbas-Abadi et al., 2022; Formela, 2021; Innes et al., 2022). Tires are comprised of a variety of high-quality parts, including steel wires, textile cords, and diverse rubber compounds, which makes recycling used tires exceedingly difficult (Mohajerani et al., 2020). Most of the rubber fraction consists of natural rubber (NR), which comes from a renewable resource. However, the greatest challenge in recycling used tires is the cross-linked structure of the rubber. Unlike thermoplastics, rubbers cannot be re-processed again with traditional technologies like injection molding or extrusion (Fazli and Rodrigue, 2020; Karabork, 2022; Sienkiewicz et al., 2012; Valentini and Pegoretti, 2022).

The most commonly used method for the recycling of waste tires starts with the production of ground tire rubber (GTR). The GTR is then used in different matrices that include bitumen (Agudelo et al., 2019; Li et al., 2022; Lo Presti, 2013), thermoplastic polymers (Fazli and Rodrigue, 2022; Halász et al., 2020; Liu et al., 2022; Mészáros et al., 2012), or rubbers (Mangili et al., 2015; Nicolas et al., 2022; Simon and Bárány, 2021; Simon et al., 2020a). This allows tires to be integrated into the circular economy, which reduces the amount of rubber waste in our environment (Araujo-Morera et al., 2021). Unfortunately, there is often one big problem with these mixtures containing GTR, adhesion between the phases. As a result of inadequate adhesion, the properties of the materials produced are not suitable for engineering applications. Therefore, it is necessary to develop environmentally friendly and economical technologies to improve the connection between the phases (Karger-Kocsis et al., 2013; Phiri et al., 2021).

The purpose of the most commonly used and researched technologies to improve compatibility is to improve the surface activity of the GTR

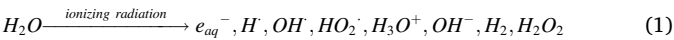
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(Phiri et al., 2021, 2022). The first methods were acid etching (Colom et al., 2007, 2009; Elenien et al., 2018), oxidation (He et al., 2016; Sonnier et al., 2007, 2008), and hydroxylation (Nuzaimah et al., 2021), which all use chemicals harmful to people and the environment. This makes it difficult to use them on an industrial scale. However, surface activation can be achieved with the use of ionizing radiation, which is a promising method in recycling polymers (Czvikovszky, 2003; Martí-nez-Barrera et al., 2020; Meszaros and Kiss, 2021; Ponomarev et al., 2022; Ratnam et al., 2013). Several reactions may occur as ionizing radiation interacts with polymers, such as cross-linking, chain scission, grafting, and oxidation. The latter is particularly important for recycling purposes (Keizo and Song, 2012).

The radiation-induced surface oxidation of polymers can significantly improve adhesion with the formation of reactive, polar functional groups. Studies have demonstrated the appearance of these groups after radiation treatment in air (Rajalingam et al., 1993; Sonnier et al., 2007). Among the groups, various peroxides are of particular importance. They can decompose during processing, forming radicals that react with the rubber system, eventually forming covalent bonds between the phases, which greatly improves compatibility. Based on our previous research (Kiss et al., 2022), the radiation treatment of GTR in air can improve the mechanical properties (tensile, tear strength) of vulcanizates containing GTR, without reducing elongation at break. The best results were obtained with an absorbed dose of 60–80 kGy. From an economical and environmental point of view, lower doses would be desirable.

In a water medium, treatment with lower doses can produce similarly good results. This is a completely new method for activating the surface of polymers (Khusyainova et al., 2022).

To understand the processes during the treatment, we need to know the radiolytic products of water produced by ionizing radiation (Eq (1)).



During the radiolysis of water, several strong oxidizing agents are produced (mainly hydroxyl radicals and hydrogen peroxide), which can form reactive functional groups on the surface of GTR with a high yield. In practice, continuous air bubbling is used during aqueous irradiation, which prevents the depletion of oxygen, thus increasing the number of strong oxidizing agents (Colliaux et al., 2015; Ferradini and Jay-Gerin, 2000; Le Caër, 2011). A major advantage of radiation treatment in water is that it can be easily integrated into the commonly used water-jet milling process, which is used to produce high-quality ground tire rubber.

In this study, we investigate the applicability of a new, water-based ionizing radiation treatment on ground tire rubber to activate its surface and thus improve its adhesion to the matrix material (natural rubber). We also to explore the effects of two different mixing techniques on these vulcanizates containing GTR. We investigated the surface characteristics of GTR using Fourier transform infrared spectroscopy (FTIR) and Soxhlet extraction with swelling tests to determine the chemical changes that took place in the GTR due to radiation. The vulcanization kinetics of the mixtures were examined and various mechanical tests were performed including tensile, tear strength and hardness tests. To explore how well the GTR was able to integrate into the matrix (morphology) we used scanning electron microscopy. With these results, it is possible to better understand the impact of ionizing radiation and mixing technology, which can help solve the problem of recycling rubber waste.

2. Experimental

2.1. Materials

The waterjet-milled ground tire rubber from the tread and sidewall of truck tires was kindly provided by Aquajet Ltd. (Budapest, Hungary).

Table 1  
The additives used to prepare the mixtures containing GTR.

Material	Manufacturer	Trade name
Stearic acid	Oleon (Ertvelde, Belgium)	Radia0444
Zinc oxide (ZnO)	Werco Metal (Zlatna, Romania)	ZnO WZ-1
Paraffin oil	Hansen und Rosenthal (Hamburg, Germany)	Tudalen 3036
N-cyclohexyl-2-benzothiazole sulfonamide (CBS)	Rhein Chemie (Mannheim, Germany)	Rhenogran® CBS-80
tetramethyl thiuram disulfide (TMTD)	Lanxess (Cologne, Germany)	Rhenogran® TMTD-70
N772 carbon black (CB)	Omsk Carbon Group (Omsk, Russia)	N-772 OMSK
Sulfur	Ningbo Actmix Polymer (Ningbo, China)	Curekind Sulfur

We used a BA 200N type sieve shaker (CISA Cedaceria Industrial, Barcelona, Spain) with 75, 125, 250, and 500 μm sieves to determine the particle size distribution of the GTR. The average particle size was 0.208 μm ± 0,04. More detailed information regarding the ground tire rubber can be found in our previous study (Kiss et al., 2022). As a result of waterjet milling, the GTR is free from textile and steel pollutants.

For the production of the vulcanizates, NR CV 60 (Sud Comoe Caoutchuc, Ivory Coast) natural rubber was used. The additives are summarized in Table 1.

2.2. Radiation treatment

The radiation treatment of the GTR was performed at the Institute of Isotopes Ltd. (Budapest, Hungary), with a panoramic SLL-01 type <sup>60</sup>Co radiation source. The dose rate was 2 kGy/h in all cases and the applied doses were the following: 20, 40, 60, 80, and 100 kGy. The ground tire rubber (100 g) was placed in closed containers and then filled with distilled water (400 ml). In order to reduce the surface tension, 2 ml of surface-active material (Triton X-100) was added to the system. Without this step, the GTR would only have floated on the surface of the water due to its hydrophobic nature, but this way, we were able to produce suspensions. Oxygen was continuously bubbled into the containers through a silicone tube, thus ensuring that the oxidizing agents produced during radiolysis (as seen in Eq (1).) were always present in sufficient quantities. After the treatment, water-based suspensions were filtered through 615 MN pleated filter paper, then air-dried at room temperature until constant weight was achieved.

2.3. Preparation of vulcanizates

We used two different mixing techniques to produce rubber mixtures containing GTR: a one-step and a two-step method. Mixtures produced in one step are based on a general tire tread recipe (Simon et al., 2020b). For mixtures produced in the two steps, the same recipe was used, but before mixing, the GTR was mixed with an additional vulcanizing system (pre-mixtures), and these were added to the model recipe, instead of

Table 2  
The general rubber mixture recipe used in the experiments.

Component	Amount (phr)
NR	100
CB	60
ZnO	10
Stearic acid	2
GTR	100
Paraffin oil	10
CBS	1.25
TMTD	0.6
Sulfur	0.6

**Table 3**

The composition of the GTR pre-mixtures.

Component	Amount (phr)
ZnO	10
Stearic acid	2
GTR	100
Paraffin oil	10
CBS	1.25
TMTD	0.6
Sulfur	0.6

the GTR.

We used two-step mixing because we had found (Kiss et al., 2022) that it results in better mechanical properties (higher tensile and tear strength, etc.) when combined with radiation treatment than one-step mixing. The GTR may have degraded to some extent during its production (Fazli and Rodrigue, 2020), and some amount of chain-scission may have occurred during the radiation treatment (in addition to surface activation) (Kiss et al., 2022), which justify the use of extra vulcanizing agent.

The composition of the compounds produced by one-step mixing is described in Table 2. The reference material contained untreated GTR and was abbreviated as NR\_GTR, while the mixtures containing radiation-treated GTR were named NR\_GTR\_IR\*, where \* stands for the absorbed dose, thus the sample containing 20 kGy absorbed GTR is denoted as NR\_GTR\_IR20. The appearance of components in Table 2 corresponds to the order of mixing.

In order to include the extra vulcanizing agent in the two-step materials, we prepared GTR pre-mixtures. These differed from the composition of the NR-based mixtures (Table 2) in that we did not use NR or CB to prepare them. We produced these pre-mixtures (Table 3) using untreated and treated GTR (for every absorbed dose).

Lastly, we performed the second step of two-step mixing. The formulation of these materials was identical to the materials produced by one-step mixing (Table 2) but instead of 100 phr GTR, they contained 100 phr of the corresponding GTR pre-mixture. The reference mixture was NR\_GTR\_A, which contained the pre-mixture with untreated GTR. The materials containing radiation-treated GTR pre-mixtures were named NR\_GTR\_IR\*\_A, where \* stands for the absorbed dose, so the sample containing a GTR pre-mixture that absorbed 20 kGy is denoted NR\_GTR\_IR20\_A.

The mixtures were prepared in a Brabender Lab-Station internal mixer (Brabender GmbH & Co. KG, Duisburg, Germany) at a temperature of 50 °C and with a rotor speed of 40 rpm. The order of appearance of the components in the tables above reflects the mixing order.

We recorded the vulcanization curves of the mixtures with a Mon-Tech D-RPA 3000 moving die rheometer (MonTech Werkstoffprüfmaschinen GmbH, Buchen, Germany) to determine the curing characteristics of the compounds. The temperature was 160 °C, amplitude was 1°, frequency was 1.67 Hz and the time was 20 min.

The compounds were vulcanized in a Teach-Line Platen Press 200E (Dr. Collin GmbH, Munich, Germany) hydraulic press at 160 °C and the pressure was 2.8 MPa. Each compound was pressed into 200 mm × 200 mm × 2 mm sheets. Curing lasted for  $t_{90}$  (vulcanization time), which is the time needed for 90% vulcanization. These times were acquired from the vulcanization curves.

#### 2.4. Characterization of ground tire rubber

In order to explore the chemical changes due to radiation in the GTR, we determined the sol fractions by Soxhlet extraction. The solvent was toluene and we ran the extractions for 16 h. Subsequently, we dried the samples until reaching a constant weight at 80 °C. The samples were weighed twice: prior to extraction and after drying. The sol fraction was calculated according to Eq. (2).

$$\text{Sol fraction (\%)} = \left(1 - \frac{m_f}{m_i}\right) \cdot 100, \quad (2)$$

where  $m_i$  and  $m_f$  are the mass of GTR before and after the extraction, respectively.

We measured the cross-link density of the ground tire rubbers using swelling tests according to the ASTM D 6814-02 standard and using the Flory-Rehner equation (Eq. 3.) (Flory and Rehner, 1943). We performed the tests in toluene for 72 h, and then dried the samples at 80 °C until their weight was constant.

$$\nu_e = \frac{-[\ln(1 - V_r) + V_r + \chi_1 \cdot V_r^2]}{[V_1 \cdot (V_r^{1/3} - V_r)] / 2}, \quad (3)$$

where  $\nu_e$  is cross-link density (mol/dm<sup>3</sup>),  $V_1$  is the molar volume of the solvent (in the case of toluene, it is 0.10613 dm<sup>3</sup>/mol),  $\chi_1$  is the rubber-solvent interaction parameter (0.39), and  $V_r$  is the volume fraction of the rubber in the swollen sample calculated with the Ellis and Welding (1964) equation (Eq. 4.).

$$V_r = \frac{\frac{m_r}{\rho_r}}{\frac{m_r}{\rho_r} + \frac{m_s}{\rho_s}}, \quad (4)$$

where  $m_r$  is the mass of the dry rubber (g),  $m_s$  is the mass of the swollen rubber (g),  $\rho_s$  is the density of the solvent (866.9 g/dm<sup>3</sup>), and  $\rho_r$  is the density of the GTR (1200 g/dm<sup>3</sup>).

We calculated the degree of devulcanization (Dev %), which is the decrease in cross-link density using Eq. (5).

$$\text{Dev (\%)} = \left(1 - \frac{\nu_f}{\nu_i}\right) \cdot 100, \quad (5)$$

where  $\nu_f$  is the cross-link density of the radiation-treated ground tire rubber and  $\nu_i$  is the cross-link density of the untreated (reference) GTR.

We examined the surface changes using a Bruker Tensor II (Bruker Corporation, Billerica, USA) Fourier transform infrared spectroscope (FTIR) in attenuated total reflection (ATR) mode. The wavelength range was 400–2000 cm<sup>−1</sup> and the resolution was 4 cm<sup>−1</sup>. During the evaluation of the spectra, we subtracted the spectrum of the untreated (reference) sample from the spectra of the radiation-treated GTR samples. This enhanced the visible differences and facilitated the assessment of surface changes.

#### 2.5. Characterization of the vulcanizates

We examined the mechanical properties of the vulcanizates using a Zwick-Z005 universal testing machine (Zwick GmbH., Ulm, Germany) at room temperature. Tensile tests were performed according to the DIN 53504 standard, with the use of type 1 specimens, with a clamping distance of 60 mm and a crosshead speed of 500 mm/min. Tear strength tests were carried out according to the ASTM D624 standard on type C specimens with a test speed of 500 mm/min and a clamping distance of 56 mm. The average and standard deviation of tensile strength, tear strength, and elongation at break was determined for each compound.

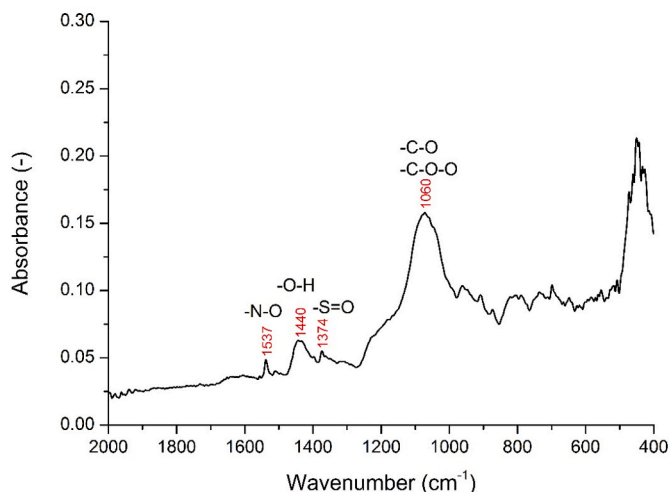
The hardness of the cured compounds was measured according to the ISO 48-4:2018 Shore A method on a Zwick H04.3150.000 hardness tester (Zwick GmbH., Ulm, Germany). For each material, ten tests were performed, and the average and standard deviation was calculated.

We studied the morphology of the fracture surfaces of the tensile specimens using scanning electron microscopy. Prior to this, the specimens were sputtered with a thin layer of gold. The SEM was a JEOL JSM 6380LA (Jeol Ltd., Tokyo, Japan) microscope.

**Table 4**

The soluble content, cross-link density and devulcanization degree of GTRs.

Dose (kGy)	Sol fraction (%)	Cross-link density ( $10^{-4}$ mol/cm <sup>3</sup> )	Devulcanization (%)
0	10.7 ± 0.5	7.9 ± 0.7	0
20	11.9 ± 0.2	7.7 ± 0.5	2.6
40	12.4 ± 0.4	7.5 ± 0.4	4.1
60	11.9 ± 0.4	7.0 ± 0.2	10.3
80	12.1 ± 0.5	7.1 ± 0.4	9.7
100	11.9 ± 0.5	7.2 ± 0.2	7.9

**Fig. 1.** The remaining FTIR spectrum of the 20 kGy sample (after the spectrum of the untreated GTR was subtracted from the measured spectrum).

### 3. Results and discussion

#### 3.1. The effect of radiation treatment on ground tire rubber

Table 4 contains the results of the Soxhlet extraction and swelling tests (soluble material content, cross-link density, and degree of devulcanization). The soluble material content of the irradiated ground tire rubbers only increased slightly (by 1–2%) compared to the untreated sample, while bulk density decreased with increasing absorbed dose. The degree of devulcanization remained at a maximum of 10% even at higher doses, which can be considered minor. At the examined doses ionizing radiation primarily cleaved the sulfur cross-links, rather than the polymer backbone, which we demonstrated in a previous study of ours using Horikx analysis (Kiss et al., 2022). This is why soluble content was low.

In FTIR spectra of the GTR treated with a dose of 20 kGy (Fig. 1), we

**Table 5**

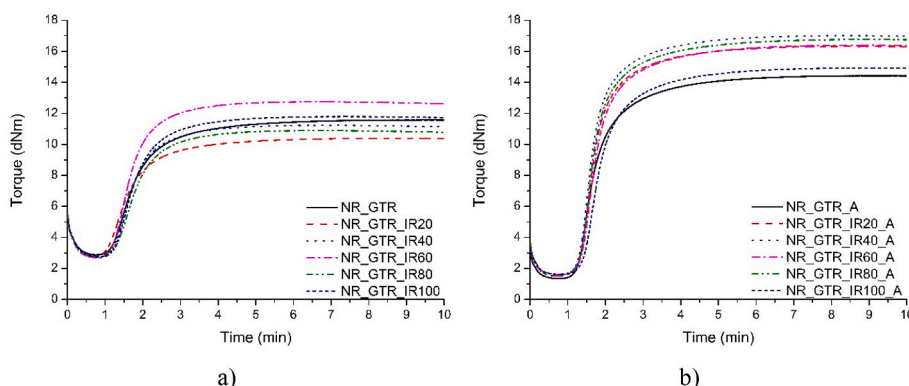
Curing parameters of mixtures containing GTR.

Sample	$S'_{min}$ (dNm)	$S'_{max}$ (dNm)	$t_{90}$ (min)	Peak rate (dNm/min)
NR_GTR	2.9	11.6	3.3	8.2
NR_GTR_IR20	2.8	10.4	3.0	7.4
NR_GTR_IR40	2.8	11.2	2.8	9.0
NR_GTR_IR60	2.7	12.7	2.7	10.2
NR_GTR_IR80	2.7	10.9	2.9	7.9
NR_GTR_IR100	2.7	11.8	3.0	9.1
NR_GTR_A	1.3	14.4	3.2	16.9
NR_GTR_IR20_A	1.5	16.3	2.9	20.4
NR_GTR_IR40_A	1.5	17.0	2.8	22.6
NR_GTR_IR60_A	1.6	16.4	3.1	19.3
NR_GTR_IR80_A	1.6	16.8	3.0	22.1
NR_GTR_IR100_A	1.6	14.9	3.3	16.9

subtracted the spectra of the untreated GTR from the treated GTR, so the changes can be observed better. Gamma radiation led to the formation of new functional groups on the surface of the GTR, as evidenced by the new peaks in the FTIR spectrum. The appearance of absorption peaks at 1535–1537  $\text{cm}^{-1}$  indicates the formation of N–O bonds, while the peaks at 1372–1374  $\text{cm}^{-1}$  indicate the development of sulfonate groups (Nandiyanto et al., 2019). Additional absorption peaks appeared in the FTIR spectrum around 1430–1440  $\text{cm}^{-1}$ , which can be attributed to the vibration of hydroxyl (O–H) groups (Nandiyanto et al., 2019). Significant absorption peaks were observed at 1050–1200  $\text{cm}^{-1}$ , indicating the stretching of C–O groups, and the presence of ozonide and peroxide absorption bands (C–O–O) as a result of irradiation (Cataldo et al., 2010). These reactive functional groups can decompose during processing due to heat and shearing, resulting in free radicals, which can attack the double bonds of the natural rubber, thus increasing the efficiency of the vulcanizing system (Cataldo et al., 2010). These radicals can also recombine, which also results in more cross-links, making the connection between the phases better.

#### 3.2. Using radiation-treated GTR in rubber mixtures

Fig. 2 shows the vulcanization curves of the compounds. For the mixtures produced in a single step (Fig. 2a), the maximum torque ( $S'_{max}$ ) increased with the absorbed doses of 60 kGy (~10%) and 100 kGy (~2%). The minimum torque ( $S'_{min}$ ) and the shape of the curves (vulcanization kinetics) were not affected by the radiation treatment. Fig. 2b shows the vulcanization curves of the mixtures produced in two steps. Compared to the reference (NR\_GTR\_A),  $S'_{max}$  increased in all cases; the best result was obtained with the sample irradiated with 40 kGy (~18%).  $S'_{max}$  was higher in all cases compared to mixtures produced in a single step. This can be attributed to the increased amount of vulcanizing agents, which formed more cross-links. The combination of radiation treatment and two-step mixing probably led to the formation

**Fig. 2.** The vulcanization curves for a) one-step and b) two-step mixtures.



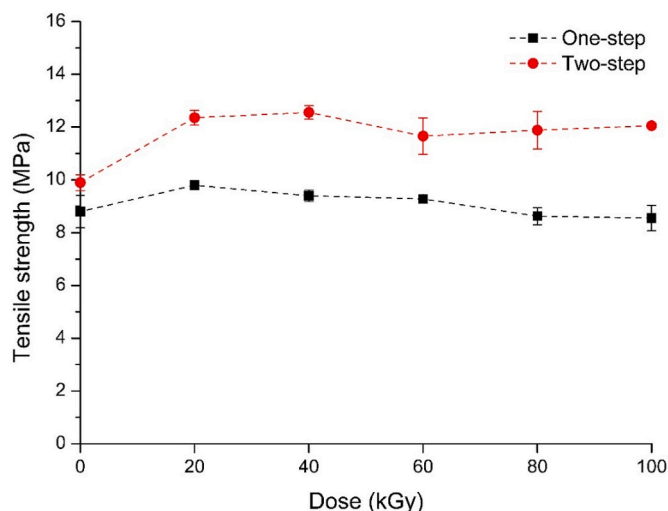


Fig. 3. Tensile strength of the vulcanizates containing GTR.

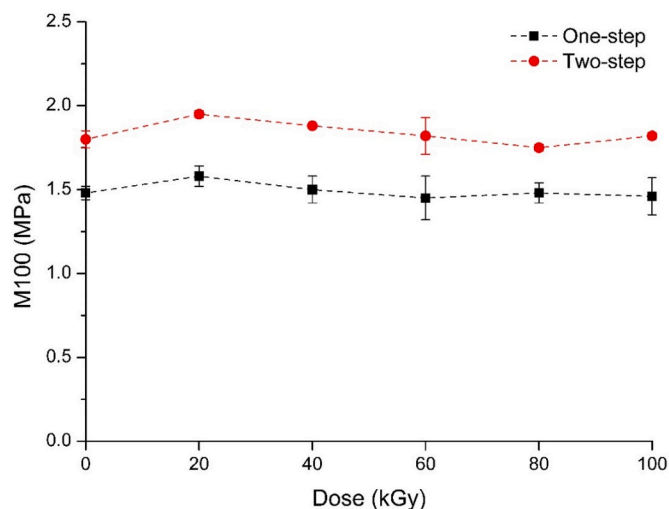


Fig. 5. Stress at 100% (M100) elongation of the investigated mixtures.

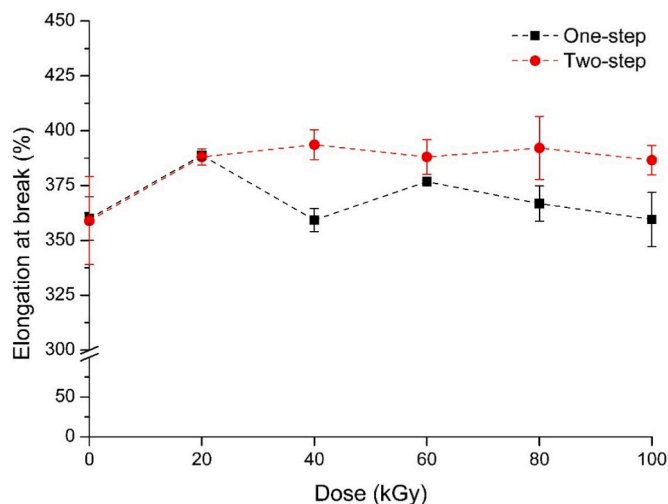


Fig. 4. Elongation at break of the examined vulcanizates.

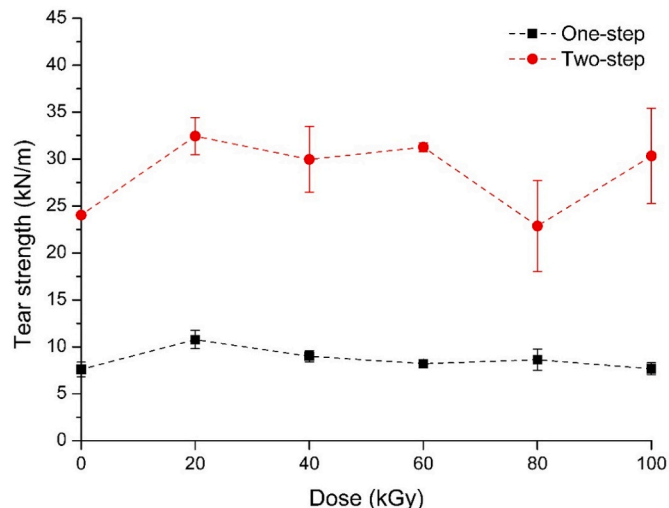


Fig. 6. Tear strength of the investigated materials.

of even more cross-links, thus the higher  $S'_{\max}$  values. In the two-step mixtures, the reactive groups (peroxides, ozonides etc.) and the additional vulcanizing system most likely reacted with each other, creating a large number of active sites on the surface of the GTR, which resulted in more cross-links in the finished materials. Table 5 shows the curing parameters for the mixtures.

The vulcanization times ( $t_{90}$ ) remained nearly the same (around 3 min) but the kinetics changed. The peak rate (Table 5.) more than doubled in most mixtures produced with two steps (steeper ramp-up section on the curves), probably because the extra vulcanizing agent and active groups resulted in a faster reaction.

From the results of the tensile tests, we determined the tensile strength of the materials (Fig. 3). As a result of the radiation treatment, the tensile strength of one-step mixtures increased (~11%); the best results were obtained with low doses. This indicates that interfacial interaction was better between the phases, due to the active functional groups (peroxides, hydroxyl, ozonides etc.) on the surface of the GTR—the products of the radiolysis functionalized the surface. These can decompose, resulting in radicals that can initiate cross-linking reactions, hence the higher strength. The extra vulcanizing agent also had a positive effect on tensile strength of references (11% increase). However, when radiation treatment was combined with two-step mixing, the tensile strength increased even more; at 20 kGy the increase is over 25%,

compared to the reference containing extra vulcanizing agent. In the first step, the peroxides probably reacted with the additional vulcanizing system, resulting in a large number of active sites (e.g.: radicals), which latter initiated a great number of cross-linking reactions, hence the significant improvement in tensile strength.

There is no notable difference in elongation at break (Fig. 4) between the two references (mixtures containing untreated GTR). However, due to the combined effect of radiation treatment and two-step mixing, elongation at break increased by 8% in the case of the sample irradiated with 20 kGy. The elongation at break of the vulcanizates made with two-step mixing and containing radiation-treated GTR was in a higher range (approx. 400%), while the vulcanizates made with treated GTR but with one-step mixing were lower, around 350%, which is still excellent. We were able to increase the tensile strength of the materials, without decreasing their elongation at break—we even improved it with two-step mixing. This means that the connection between the phases is better due to the treatments.

In the case of rubbers, the modulus can be expressed as the stress at 100% elongation (M100) (Fig. 5). The modulus of materials produced in two steps higher (similarly to tensile strength), which can be attributed to the better interfacial adhesion between the phases. We obtained the highest modulus with an absorbed dose of 20 kGy. With increasing dose, the general tendency is a slight decrease in modulus.

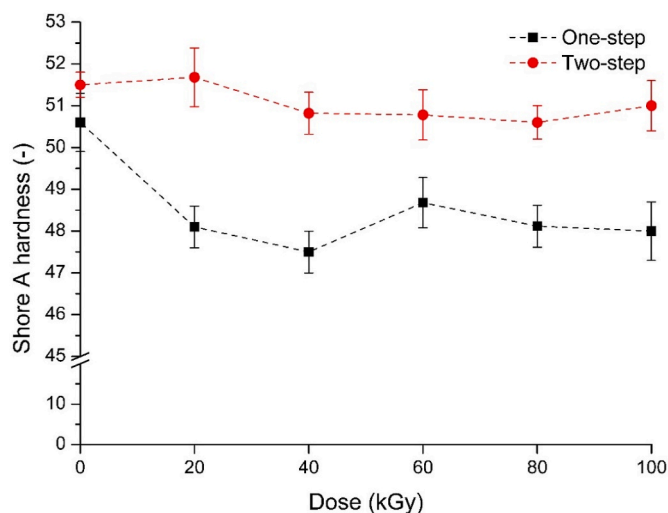


Fig. 7. Shore A hardness of the investigated materials.

Fig. 6 shows the tear strength values of the investigated vulcanizates. The tear strength of the materials produced in two steps was more than double that of mixtures produced in one step, which can be attributed to the additional vulcanizing agent. The radiation treatment successfully activated the surface of the GTR; with a dose of 20 kGy, tear strength was more than 40% higher than the reference containing untreated GTR and produced in a single step. Interfacial adhesion between the phases improved, and interfacial interaction was stronger due to the irradiation treatment. It is likely that the radicals formed from the active groups that appeared on the surface attacked the double bonds of the rubber. This made the creation of new cross-links easier. Also, these radicals probably recombined (different chains), which also increased cross-link density, improving tear strength. The combined use of radiation-treated GTR and additional vulcanizing agent resulted in a 35% increase in tear strength with an absorbed dose of 20 kGy compared to the reference mixture produced in two steps. In the first step, the active groups probably reacted with the vulcanizing system, creating highly active spots on the

surface of the materials, even radicals, which established covalent bonds with natural rubber in the second step. This ensured the proper connection between the phases, hence the improved mechanical properties. For materials produced in a single step and treated with doses above 20 kGy, tear strength decreased with increasing dose. With higher doses, it is possible that there was more degradation in the GTR, which impaired mechanical properties. The maximum of tear strength of mixtures produced with two steps was also at 20 kGy but above that dose, the tendency was not clear, probably due to the high standard deviations.

The results of the hardness test (Fig. 7) show a weak general tendency of decrease as a function of absorbed dose. This can be attributed to the small degree of chain scission during the radiation treatment of the GTR. The hardness of the vulcanizates produced with two-step mixing, changed less as the additional vulcanizing agent compensated for chain scission.

We produced SEM micrographs of the fracture surfaces of the tensile specimens (Fig. 8), in order to examine their morphology. The micrographs show that the different mixing methods had no effect on morphology. Even with untreated GTR, embedment in the matrix was considerable for both one-step (Fig. 8a) and two-step (Fig. 8b) mixtures. The radiation treatment, even at the highest dose (Fig. 8c and d) did not affect the morphology either; in all cases, the GTR integrated well into the matrix and the particles are not visible.

#### 4. Conclusion

In this study, we applied an innovative, water-based irradiation technique to activate the surface of ground tire rubber, which helps to expand its application possibilities in different matrices. As a result of the radiation treatment, cross-link density decreased slightly (no more than 10%) with increasing absorbed dose, while the soluble content remained approximately constant. New, oxygen-containing functional groups appeared (hydroxyl, peroxide, sulfonate, ozonide etc.) on the surface of the GTR, which were identified by FTIR analysis. These groups most likely decomposed during processing, resulting in active radicals, which attacked the double bonds of the rubber, making it easier for the sulfur to establish covalent bonds. These radicals probably recombined

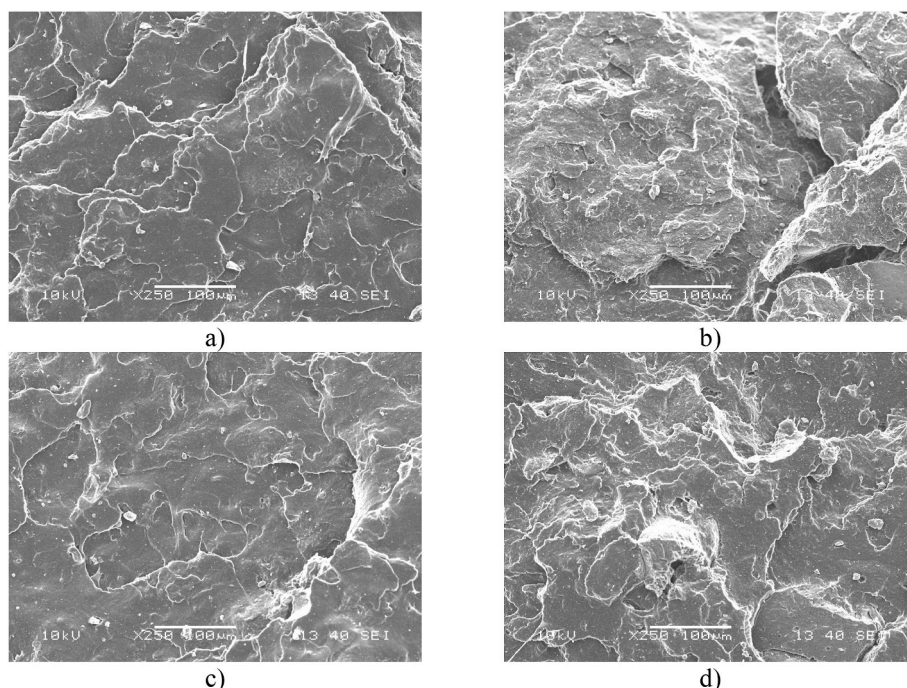


Fig. 8. SEM micrographs of the fracture surfaces of the a) NR\_GTR; b) NR\_GTR\_A; c) NR\_GTR\_IR100, and d) NR\_GTR\_IR100\_A.

with each other in polymer chains of the ground tire rubber and matrix material, thus increasing the cross-link density of the vulcanizates.

We examined the vulcanization properties of the mixtures and the vulcanization curves of the mixtures prepared in two steps shifted to a higher torque range and the peak rate doubled compared to the mixtures produced in one step. Due to the radiation treatment of the GTR, tensile strength increased by 11% (one-step) and 25% (two-step), while elongation at break stayed in a high range (~350–400%) for the vulcanizates with GTR. The tear strength of the mixtures also improved—the active groups on the surface established a better connection with the matrix, resulting in a 40% increase in tear strength for mixtures produced in one step and 35% for mixtures prepared in two steps. The Shore A hardness of the materials did not change considerably. After examining the morphology using SEM images, we concluded that the GTR integrated well into the rubber matrix.

The results indicated that surface activation was successful; the active groups (peroxides, ozonides etc.) established a better connection between the phases. In the mixtures produced in two steps, the additional vulcanizing agent probably pre-reacted with the functional groups, thus creating an even more reactive system, which resulted in better mechanical properties. Lastly, the best results were obtained with an absorbed dose of 20 kGy, which is very good for mass production.

#### Author contribution statement

Lóránt Kiss: experimental work, manuscript writing, results evaluation.

László Mészáros: experimental design, supervision, reviewing the manuscript.

#### Declaration of competing interest

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

#### Data availability

No data was used for the research described in the article.

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