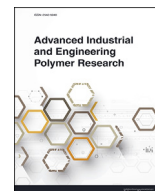Ground tire rubber filled low-density polyethylene: The effect of particle size
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# Advanced Industrial and Engineering Polymer Research

# Ground tire rubber filled low-density polyethylene: The effect of particle size

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## ARTICLE INFO

## ABSTRACT

In the present study, we investigated the possibility of value-added recycling of ultrafine ground tire rubber (uGTR) produced from water jet milling, with an average particle size of a few tens of microns. Our goal was to compare the properties of blends with different uGTR and conventional fine ground tire rubber (fGTR) contents prepared by blending with low-density polyethylene (LDPE). We also aimed to explore the property changes caused by the larger specific surface area due to the size effect. Samples were prepared with a hydraulic press after internal mixing. In the case of ground tire rubber (GTR) filled mixtures, the tensile properties showed rubber-like characteristics: with a significant decrease in modulus, elongation at break remained high, and tensile strength slightly decreased. The fracture surfaces of the samples were analyzed by scanning electron microscopy (SEM), wherein the case of materials made with uGTR showed better adhesion between the phases. In order to investigate the interfacial adhesion between the GTR and LDPE, we performed dynamic mechanical thermal analysis (DMTA). The glass transition peak of the uGTR shifted to a higher temperature and the storage modulus was higher than in the case of samples containing fGTR. Finally, we determined the Shore D hardness of the materials, which decreased with increasing GTR content, but hardness was greater in the case of uGTR samples. The better mechanical properties of blends containing uGTR were explained by better interfacial adhesion between the two phases due to the significantly higher specific surface area compared to fGTR.

## 1. Introduction

One billion scrap tires are generated every year all around the world due to the increased number of cars on the roads [1]. However, the recycling of these materials is difficult due to their chemically cross-linked three-dimensional structure [2–4]. Thus, they cannot be re-melted; therefore, it is impossible to reprocess them with conventional technologies (injection molding, extrusion, etc.). Nowadays, one of the most evolving and widespread recycling trends in rubber waste management is to grind end-of-life tires [5,6] and then create blends with thermoplastic polymers, thus reusing waste tires [7]. For this, the most commonly used matrices are polyolefins [8–12]. The advantage of this technology is that it is possible to manufacture products from relatively cheap raw materials with the use of methods suitable for mass production. These mixtures are often classified as thermoplastic elastomers (TPEs) because they can be processed by thermoplastic technologies and have rubber-like properties, i.e. at least 100% elongation at break, with tensile characteristics similar to rubbers. This method of value-added recycling of rubber waste is attractive for the industry, as it is possible to manufacture rubber products (bumpers, bucks, noise-canceling elements, tiles, etc.) in a cost-effective way [13–16].

Ground tire rubber can be produced at ambient temperature (e.g. with a two-roll cracker-type mill or water-jet), but cryogenic milling can also be used. The quality of the obtained GTR is determined by the average particle size, particle size distribution, specific surface area, and the type of contaminants. The use of water-jet milling is advantageous because it produces relatively small

particles, and the GTR produced this way typically has a complex morphology, which results in a larger specific surface area overall. This means that better interfacial adhesion can be formed, i.e. the compatibility between the phases is better than, for example, for mixtures that contain GTR produced under cryogenic conditions. The GTRs are also classified according to their average particle size, but this classification is not uniform in the literature. In this study, we categorized particle size according to Table 1 [13,14,17–19].

As several studies have pointed out [1,20–25], the average particle size used can have a significant effect on the mechanical properties of GTR containing mixtures. This is because, under mechanical stress, larger particles are more likely to cause cracks, leading to failure, while smaller particles cause micro-cracks in many places, but more energy is required for them to combine and thus cause failure. If the amount of filler material (GTR) is high, these micro-cracks can come into contact easily; therefore failure occurs quickly. Above a certain filler content (40–50 wt%), the size effect does not apply [13,14,21–28].

Our research focused on the effects of particle size and content of GTR in thermoplastic blends. We obtained GTR with an average particle size of less than 30 μm, and in a comprehensive review of the literature, we have not found any studies that used GTR this size. Thus, our goal is to make use of this ultrafine GTR by developing new materials using a thermoplastic polymer as the matrix, thus upcycling end-of-life tires. Based on our previous experiments [10,29,30] and the literature [21,31–33], we opted for a low-density polyethylene (LDPE) matrix. We also examined blends containing conventional (fine) GTR, with a particle size of less than 400 μm. The samples were subjected to mechanical, thermomechanical and morphological tests.

## 2. Materials and methods

### 2.1. Experimental materials

As matrix material, we used Tipolen FA 244–51 type LDPE (MOL Petrochemicals, Tiszaújváros, Hungary) containing 1 wt% normal butyl acrylate with $MFI_{190°C/2.16 kg} = 0.30$ g/10 min. The ground tire rubber was produced by water-jet milling, with a particle size of less than 30 μm (uGTR – Fig. 1a) and with a particle size of less than 400 μm (fGTR – Fig. 1b). The GTRs were kindly provided by AquaJet Ltd (Budapest, Hungary).

### 2.2. Preparation of blends

Blends containing LDPE/GTR were prepared in a 300 cm$^3$ Brabender Plastograph internal mixer chamber at 190 °C and 60 rpm; mixing time was 10 min. First, the LDPE, then the GTR were fed to the chamber. Materials containing 10, 20 and 30 wt% fGTR and uGTR were prepared, as well as a pure LDPE sample for reference (Table 2). Sheets of 1 mm and 2 mm thickness were pressed from the blends with a Teach-Line Platen Press 200E (Dr. Collin GmbH, Munich, Germany) hydraulic press. The sheets were formed at 180 °C for 5 min with a pressure of 2.1 MPa, and they were cooled to 40 °C before removal. The specimens for the various tests were cut from the sheets.

**Table 1**
Classification of GTR according to average particle size, based on [17].

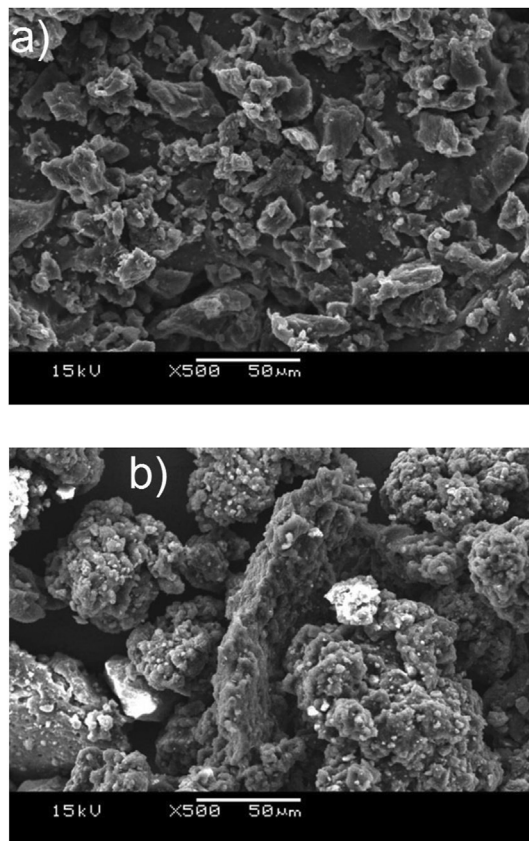| Group | Large or coarse | Mid-range | Fine | Superfine | Ultrafine |
|---|---|---|---|---|---|
| Size range (μm) | >2000 | 600–2000 | 180–425 | 75–150 | <75 |



**Fig. 1.** Scanning electron micrographs of the ground tire rubber used a) particle size below 30 μm, and b) particle size below 400 μm.

**Table 2**
Abbreviations and recipes of the tested materials.

| Abbreviation | LDPE (wt%) | fGTR (wt%) | uGTR (wt%) |
|---|---|---|---|
| 100LDPE | 100 | 0 | 0 |
| 90LDPE10fGTR | 90 | 10 | 0 |
| 80LDPE20fGTR | 80 | 20 | 0 |
| 70LDPE30fGTR | 70 | 30 | 0 |
| 90LDPE10uGTR | 90 | 0 | 10 |
| 80LDPE20uGTR | 80 | 0 | 20 |
| 70LDPE30uGTR | 70 | 0 | 30 |

### 2.3. Testing methods

#### 2.3.1. Tensile test

The tensile tests were performed with a Zwick-Z005 universal testing machine (Zwick GmbH., Ulm, Germany) at room temperature and a crosshead speed of 50 mm/min. The clamping distance was 110 mm, and the cross-section of the specimens was 2 mm × 10 mm. For each sample, at least five specimens were tested.

#### 2.3.2. Hardness testing

The hardness of the blends was measured according to the ISO 868 Shore D method on a Zwick H04.3150.000 hardness tester (Zwick GmbH., Ulm, Germany) at room temperature and with at least 40 measurement points on each sample. According to the standard, the evaluation of the hardness should be carried out on 4 mm thick sheets, which was achieved by placing two 2 mm sheets on top of each other.

### 2.3.3. Morphology characterization

The fracture surfaces of the tensile specimens and the morphology and particle size of uGTR and fGTR were analyzed with a Jeol JSM 6380 LA (Jeol Ltd., Japan, Tokyo) scanning electron microscope. The samples were coated with a thin gold layer before the examination.

### 2.3.4. Dynamic mechanical thermal analysis

The dynamic mechanical thermal analysis of the blends containing GTR was determined with a Q800 (TA Instruments) DMTA instrument. The samples were cut from the sheets and had a cross-section of 2.5 mm × 1.0 mm. During the DMTA tests of the specimens, the clamping distance was 10.0 mm. The materials were tested in tensile mode, between −80.0 °C and +90.0 °C, at a heating rate of 3 °C/min and with a constant frequency of 1 Hz. Elongation was 0.01%.

## 3. Results and discussion

The typical stress-strain curves of pure LDPE, fGTR and uGTR containing materials are represented in Fig. 2.

Fig. 3 shows the tensile strength of the investigated materials. The tensile strength of the samples containing fGTR and uGTR decreased with increasing GTR content. Blends with uGTR outperformed blends with fGTR—the larger average particle size results in a smaller specific surface area and weaker interfacial adhesion. At a GTR content of 10 wt%, samples with uGTR had a tensile strength almost 30% higher than samples with fGTR. The difference decreased with increasing GTR content; the size effect only slightly compensated for the strength-reducing effect of GTR.

The elongation at break values of the LDPE/GTR blends are represented in Fig. 4. The materials behaved like elastomers as a result of GTR; pure LDPE deformed with significant neck formation, whereas no necking took place when GTR was added. The elongation at break of materials containing uGTR increased slightly at 10 wt% filler content but decreased with higher GTR content. In the case of fGTR samples, elongation at break decreased rapidly, suggesting poor adhesion between the LDPE and GTR, although the larger specific surface area of the uGTR slightly compensated for that, giving better results.

Fig. 5 shows the Young's modulus of the investigated materials. The decreasing trend supports the fact that the GTR reduces the stiffness of the matrix material. Modulus is in the range of
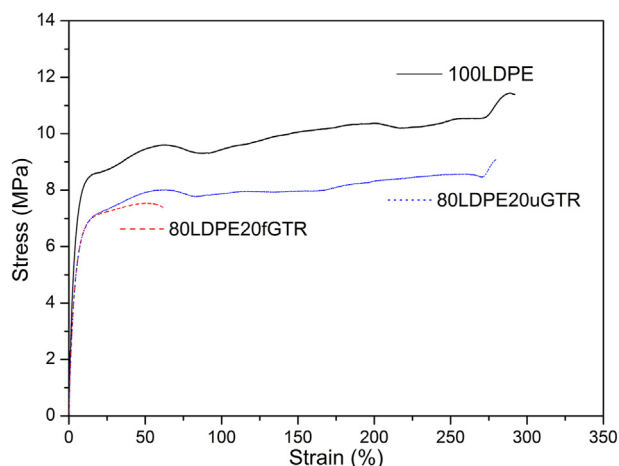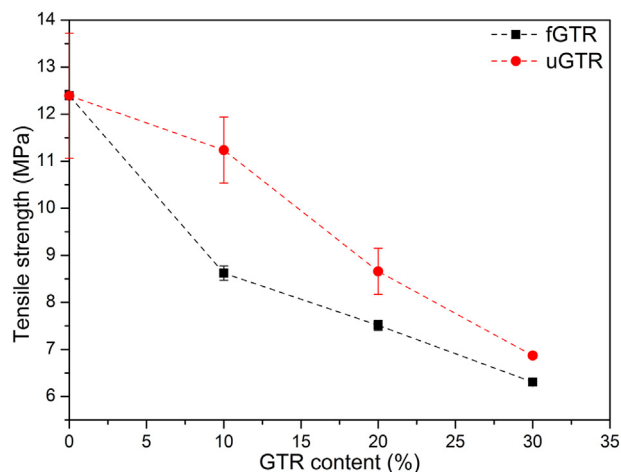


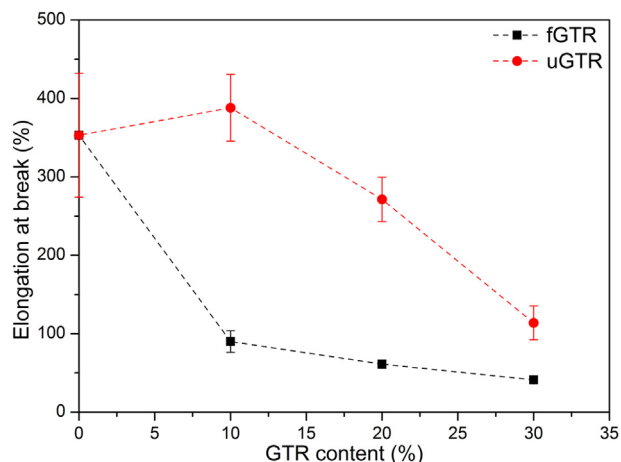**Fig. 3.** Tensile strength of the investigated materials as a function of GTR content.



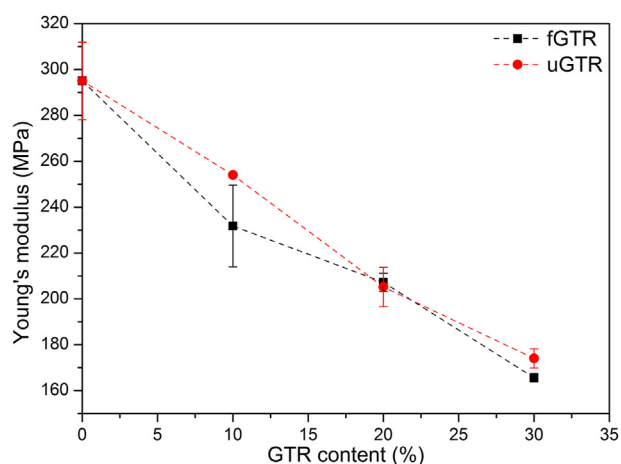**Fig. 4.** Elongation at break of the investigated materials as a function of GTR content.



**Fig. 5.** Young's modulus of the investigated materials as a function of GTR content.

elastomers, and there is no significant difference between the two samples containing GTR.

The Shore D hardness of the investigated materials is represented in Fig. 6. It shows that both the fine and the ultrafine GTR effectively decreased the hardness of the LDPE, resulting in an
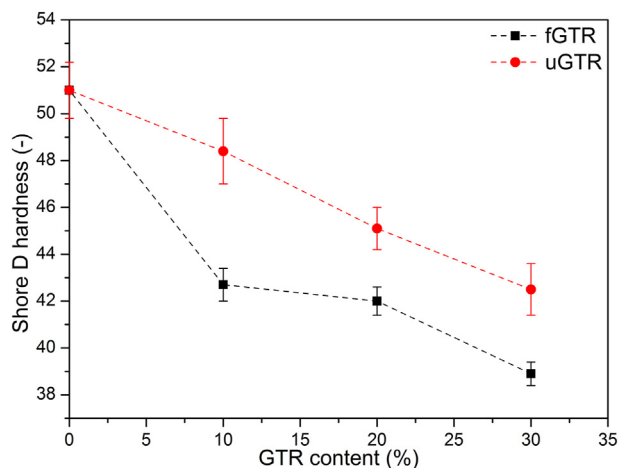


**Fig. 2.** Typical stress-strain curves of the investigated materials.

**Fig. 6.** Shore D hardness of the investigated materials as a function of GTR content.
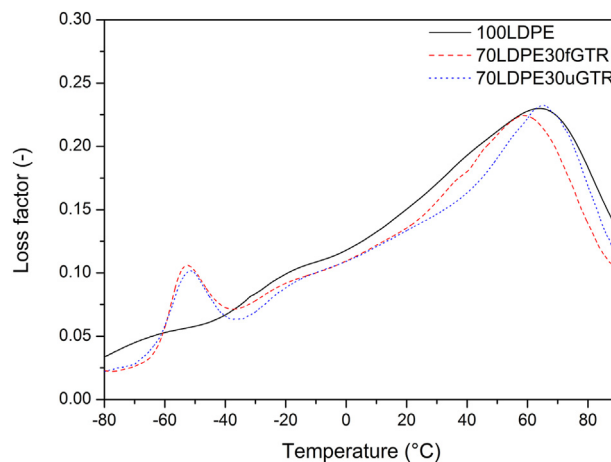


**Fig. 8.** The loss factor of the investigated materials.

elastomer-like behavior. Similar to Young's modulus, the ultrafine GTR resulted in greater hardness, which may be a result of the large interfacial area and better adhesion between the components.

We investigated the interfacial adhesion between the LDPE and the GTR with DMTA tests carried out on pure LDPE, and on the blends containing 30 wt% uGTR and 30 wt% fGTR. The storage modulus (Fig. 7) of both the 70LDPE30fGTR and the 70LDPE30uGTR blend above the glass transition temperature of the GTR is lower compared to the pure LDPE, which shows the softening effect of the elastomer component. The storage modulus of the 70LDPE30uGTR blend is higher than that of the 70LDPE30fGTR blend, as their tensile modulus shows, which indicates better adhesion between the components.

On the loss factor (tan δ) curves (Fig. 8), the peak at −52 °C is related to the glass transition of the fGTR and uGTR. In the case of the uGTR, this peak is slightly smaller and shifted to a higher temperature (from −53,8 °C to −52,0 °C), which indicates stronger interactions between the LDPE and the smaller particle size GTR. In the LDPE-uGTR blend, the interfacial area is significantly larger because of the smaller particle size, so even in the case of weak adhesion, the good connection between the two phases is maintained even at greater mechanical loads.

The morphology of the blends containing fine GTR can be seen in Fig. 9a. The SEM micrographs also show the previously
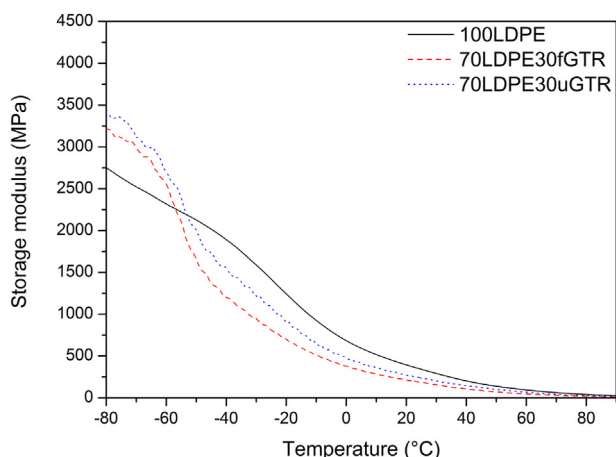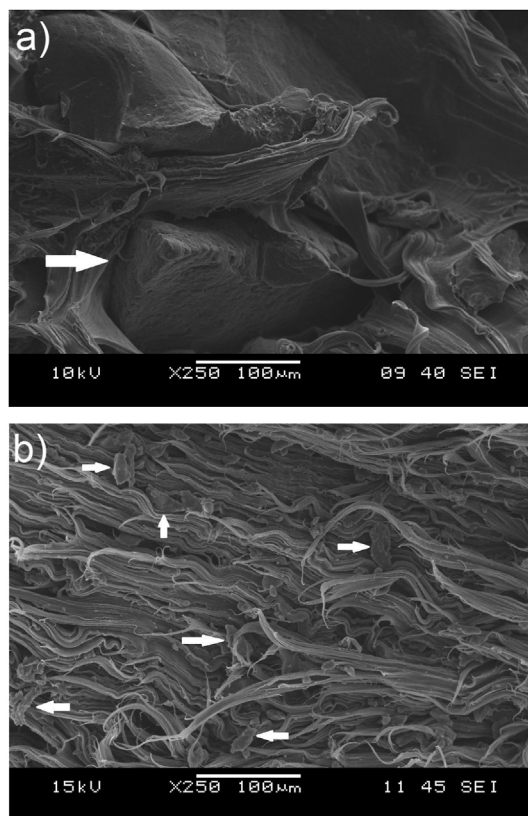


**Fig. 9.** SEM micrographs of the fracture surfaces of **a)** 70LDPE30fGTR **b)** 70LDPE30uGTR (the white arrows indicate the GTR particles).

experienced poor mechanical properties. The large particle size and small specific surface area of the GTR, as well as the complete lack of adhesion between the phases, are immediately apparent. Based on the micrographs, the GTR particles almost "separate" from the LDPE matrix, thus preventing load transfer; therefore fracture occurs in a short time. On the other hand, Fig. 9b shows a "fibrillary" fracture surface of the samples containing uGTR, indicating a good relationship between the phases. The dispersed GTR particles are barely visible, which is the reason for the excellent elongation at break; the matrix and the GTR worked well together.



**Fig. 7.** The storage modulus of the investigated materials.

**Table 3**
Mechanical properties of the obtained materials and some examples from the literature.

| Abbreviation | GTR particle size (μm) | Tensile strength (MPa) | Elongation at break (%) | Young's modulus (MPa) |
|---|---|---|---|---|
| 100LDPE | – | 12.4 ± 1.3 | 353 ± 79 | 295 ± 17 |
| 90LDPE10fGTR | <400 | 8.6 ± 0.2 | 90 ± 14 | 232 ± 18 |
| 80LDPE20fGTR | <400 | 7.5 ± 0.1 | 61 ± 5 | 207 ± 4 |
| 70LDPE30fGTR | <400 | 6.3 ± 0.1 | 41 ± 4 | 166 ± 2 |
| 90LDPE10uGTR | <30 | 11.2 ± 0.7 | 388 ± 43 | 254 ± 1 |
| 80LDPE20uGTR | <30 | 8.7 ± 0.5 | 271 ± 28 | 205 ± 9 |
| 70LDPE30uGTR | <30 | 6.9 ± 0.1 | 114 ± 22 | 174 ± 4 |
| 70LDPE30cGTR [21] | 600–700 | 11.0 ± 0.2 | 62 ± 5 | 226 ± 6 |
| 70LDPE30aGTR [21] | 600–700 | 11.2 ± 0.2 | 63 ± 4 | 255 ± 9 |
| 50LDPE50GTR [32] | <400 | 4.2 ± 0.1 | 58 ± 5 | n/a |
| 50LDPE25GTR25SBS_1 [32] | <400 | 4.32 ± 0.1 | 78 ± 4 | n/a |
| 50LDPE25GTR25SBS_2 [32] | <400 | 4.52 ± 0.1 | 125 ± 5 | n/a |

The particle size and specific surface area of the GTR are crucial in the compatibility between the phases and thus the mechanical properties of the materials.

The mechanical properties of the obtained materials, as well as the examples found in the literature, are summarized and compared in Table 3. Sonnier et al. [21] studied the effect of different grinding methods of GTR used in an LDPE matrix. The abbreviation aGTR stands for ambient and cGTR stands for cryogenic milling. It can be seen that they were able to obtain higher tensile strength and modulus values, similar to the 10 wt% uGTR containing samples, but we were able to achieve a much higher elongation at break, the same when we compared the fGTR and uGTR containing samples. It can be concluded, that the smaller particle size primarily improves this property of the materials mostly and this can be seen not only in our own results but also if we compare it to other values found in the literature.

Formela et al. [32] studied the compatibilization effect of non-polar elastomers in the case of LDPE/GTR blends. They used styrene-butadiene-styrene (SBS) block copolymers to improve the adhesion between the phases. They were able to achieve better results than the reference (50LDPE50GTR), however, it can be seen that their sample containing 25 wt% compatibilizer and GTR produced similar elongation at break as 70LDPE30uGTR, but a lower tensile strength. Based on these, it can be said that the ultrafine particle-sized GTR was able to interact with the matrix much better, than the mixture containing larger GTR particles and SBS as compatibilizer.

## 4. Conclusions

The particle size and content of the GTR had a significant effect on the properties of the investigated materials. The results of the tensile tests showed that the application of uGTR is advantageous. We obtained higher tensile strength, modulus, and elongation at break than with the use of fGTR. However, with increasing GTR content, all three parameters decreased. In the case of the DMTA tests, the glass transition temperature shifted to a higher temperature, and the storage modulus of blends containing uGTR is higher than that of fGTR blends, which indicates better adhesion between the phases. Based on the SEM micrographs, the fGTR particles almost separated from the LDPE, whereas the uGTR blends have a fibrillary fracture surface, which indicates a good relationship between the phases.

The better mechanical properties can be explained by the significantly smaller particle size of uGTR, which has a higher specific surface area. Therefore, the matrix and the GTR were able to bond on a larger surface, improving interfacial adhesion. However, the deterioration of the investigated properties at high GTR content

was not compensated by the size effect—the elastomeric effect of the GTR prevailed.

## Declaration of competing interest

The author declare no conflict of interest.

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