Rotomolding of Thermoplastic Elastomers Based on Low-Density Polyethylene and Recycled Natural Rubber

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Abstract: In this study, regenerated and nonregenerated off-the-road (OTR) ground tire rubber (GTR) was blended with low-density polyethylene (LDPE) to produce thermoplastic elastomers (TPE) by rotational molding. In particular, blending was performed by two different methods: melt blending (extrusion) and dry blending (high shear mixer). Then, different GTR concentrations (0, 20, 35, and 50 wt %) were used to determine the effect of rubber content on the processability and properties of the rotomolded compounds. From the samples produced, a complete morphological (optical and scanning electron microscopy), physical (density and hardness), and mechanical (tension, flexion, and impact) characterization was performed. The results showed that increasing the rubber content decreased the mechanical rigidity and strength but increased the elasticity and ductility. Finally, although melt blending led to slightly better properties than dry blending, the latter is more interesting to limit possible material degradation (mechanical, thermal, and oxidative), while reducing processing cost and time.

Keywords: polyethylene; natural rubber; recycling; rotomolding; process optimization

1. Introduction

Today, plastics and rubbers are widely used in different applications, and this is why the recent decades are sometimes called the “plastic age” [1]. One of the most prominent examples of this increasing trend is the production and uses of rubbers (natural and synthetic). In 2019, the global rubber and tire market grew by 4% to reach a volume of 3 billion tires [2]. Large amounts of rubbers are used to produce tires for airplanes, cars, trucks, etc. However, after the end of their service life, only a very limited amount of rubber (1%) is lost from the original tire [3]. This indicates that a large amount of rubber can still be used for other applications.

Residual rubbers belong to the group of non-environmental resources as they are insoluble and infusible (highly cross-linked material). They also cannot return to the environment via usual biodegradation. So, the problem of waste rubber management becomes critical, and solutions must be proposed to use this material available everywhere on the planet.

The main problems associated with the recycling or recovery of scrap tire rubbers are associated to their complex structures made from cross-linked rubbers with steel and polymer fibers (cellulose, nylon, and polyester) as reinforcement. So, each component must be separated from the rubber during a mechanical recycling process. It is known that 12 components at minimum are used in a passenger vehicle tire, while a truck tire has about 20 components [4]. In general, styrenes–butadiene rubber (SBR) is used to produce passenger tires, while natural rubber (NR) is the main component for truck tires [5].

Table 1 presents the typical compositions of different tire structures.
Table 1. Composition (wt %) of different tire structures [6].

| Component          | Passenger Cars | Trucks/Buses |
|--------------------|----------------|--------------|
| Rubber/elastomer   | 41–48          | 41–45        |
| Carbon black       | 22–28          | 20–28        |
| Metal/steel        | 13–16          | 20–27        |
| Textile            | 4–6            | 0–10         |
| Additives          | 10–12          | 7–10         |

Due to increasing environmental concerns, a great deal of work has been undertaken to develop tire recycling methods (devulcanization/regeneration) and to find applications for these waste rubber products [7,8]. Hence, various techniques/methods have been proposed to reduce the high amount of waste rubbers. One of the most useful techniques, at least as a starting point, is grinding (particle size reduction) to use the resulting ground tire rubber (GTR) in polymer compounds (blends, composites) as a filler (active or not) or as an impact modifier to improve the elasticity/ductility/toughness of a neat resin (thermoplastic or thermoset). For instance, ground tire rubbers can be introduced into thermoplastic resins to produce thermoplastic elastomers (TPE) [9]. The main matrixes studied so far are polyolefins (polyethylene and polypropylene). Recently, the market for these materials has grown because TPE can be reprocessed and recycled using standard thermoplastic (melt) processes. However, several studies have reported that the addition of a rubber phase into a thermoplastic matrix results in lower overall mechanical properties (stiffness and strength) [10]. Lower mechanical properties of TPE in industrial applications such as O-rings and insulators in the oil and gas industry, or rubber gaskets for window, door, and gas seals in the automotive industry, can lead to lower safety and shorter product life. These materials have the advantages of both thermoplastics and elastomers, such as mechanical properties similar to those of elastomers and the processability of thermoplastics. However, as for most immiscible multicomponent systems, interfacial compatibility/adhesion becomes an issue; this is also reported for other composites like ceramic and metal composites [11,12].

One way to increase the compatibility between the components is GTR chemical modification by reducing the degree of cross-linking (devulcanization/regeneration), at least on the particle surfaces, because a high degree of cross-linking hinders chain mobility (molecular diffusion) and prevents molecular interaction between the matrix and GTR. Another important parameter is the particle size distribution controlling the degree of phase separation or interfacial properties modifying the interfacial contact area. There is also the possibility of mixing raw rubber with recycled, and adding compatibilizers/coupling agents such as ethylene vinyl acetate (EVA), maleic-anhydride-grafted polyethylene (MAPE), and ethylene–propylene–diene monomer (EPDM) [13,14].

Over the last few years, increasing demands for TPE have been observed in the construction, automotive, and building industries because of their easy processing and wide range of properties which can be adjusted by the relative contents of the thermoplastic and elastomer phases. Although several reports have been published on standard processes like extrusion [15] and injection [16] and compression molding [17], very few works have been published on rotomolding.

Rotational molding is a low-stress/shear process producing stress-free and seamless hollow parts such as containers, tanks, toys, medical equipment, and several similar products. Rotational molding can also produce parts over a wide range of sizes: from doll parts (less than 1 cm$^3$) up to large tanks (more than 20,000 L). Complex shapes with excellent detail reproduction can be made due to simple mold fabrication, but complex structures such as fiber-reinforced, double-skinned products and foamed materials can also be processed. Furthermore, rotational molding provides more design freedom than any other plastics-generating process [18]. Unlike other processing methods, such as injection molding or blow molding, a specific feature of rotomolding is that there is no need to apply pressure [19]. The material melts and forms in the same mold. Also, there is no need to move the material from one part to another part of the machine. This means that low shear rates are applied on the polymer [20]. Nevertheless, the thermal efficiency (heat transfer) of the process is low, leading to
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long cycles (close to 60 min). In the case of solid polymers, the size of the material has to be reduced to a powder form before processing, and the flow characteristics of these powders have to be good enough to achieve high-quality moldings. As a result, there are relatively few materials appropriate for rotational molding. Increased cost related to the grinding process is observed for most of these materials. In addition, only a few polymers can be used for rotational molding since the materials require special properties such as low viscosity and high thermal stability [21]. This is the main reason why polyethylene (PE) in its several forms is used to produce rotomolded parts. Today, low-density polyethylene (LDPE), high-density polyethylene (HDPE), linear low-density polyethylene (LLDPE), linear medium-density polyethylene (LMDPE), and medium-density polyethylene (MDPE) constitute close to 90% of all polymers which are rotationally molded [22]. The main reasons are PE’s low cost and excellent resistance to processing (time and temperature). Nevertheless, there is a need to develop other materials for different applications where a balance between strength and ductility is needed. This is where TPE are of interest with controlled rubber content in a specific matrix.

To produce rotomolded parts, an important parameter, seldom discussed in the literature, is the speed ratio, which must be carefully selected according to the mold shape. In rotational molding, the speed ratio is defined as follows [22].

\[
\text{Speed ratio} = \frac{\text{Major axis rpm}}{(\text{Minor axis rpm} - \text{Major axis rpm})}
\]  

(1)

Normally, the speed ratio for symmetric shapes like spheres or cubes is 4 to 1 (major to minor axis rpm speed) [23]. Once the rotation speed ratio is specified, the next main parameter is the mold rotational speed. This parameter is related to the material’s viscosity and melting temperature. If the viscosity of the material is low, the rotational speed must be increased, while for higher viscosity, lower speed would be best. However, for very large molds, high speeds can result in machine damage.

To produce rotomolded parts based on multiphase systems (blends, composites, and foams), two techniques can be used to mix the components. The first method is to produce a compound by melt blending (twin-screw extruder, batch mixer, etc.), then pelletize and pulverize the compounds. Good adhesion and dispersion of the particles are expected by this technique. However, mechanical, thermal, and oxidative degradation of the materials (matrix and filler) is expected in each processing step [24]. The second method is via dry blending (high-speed mixers, rotating drums, etc.) to mix all the materials in a powder form before being introduced into the mold. Speed, low cost, and limited material degradation are the benefits of this method. Nevertheless, this technique has some limitations like poor adhesion at the filler–matrix interface and absence of pressure to compact the materials, usually leading to lower mechanical properties of the final products.

In this work, the effect of oven temperature, heating time, rotational speed, and particle size/concentration for both matrix and filler was studied. Up to 50 wt % of regenerated (RR) and nonregenerated GTR (NRR) was introduced into LDPE. For comparison, two techniques were used (melt blending and dry blending) to mix the components before their introduction into the mold. Finally, a complete morphological, mechanical, and physical characterization was performed to compare the properties of the compounds produced.

2. Materials and Methods

The matrix selected was low-density polyethylene (LDPE) from Ra-Plast Inc. (Terrebonne, QC, Canada). This polymer has a density of 0.906 g/cm³, a peak melting temperature of 115 °C, and a melt flow index of 22 g/10 min (2.16 kg/190 °C). The ground tire rubber (GTR) was supplied in two forms: regenerated (RR) and nonregenerated (NRR) natural rubber from Phoenix Innovation Technologies (Montreal, QC, Canada). The nonregenerated rubber has a density of 1.169 g/cm³, while the regenerated one has a density of 1.246 g/cm³.
2.1. Material Mixing

In this study, two mixing strategies were used. Firstly, melt blending was performed in a co-rotating twin-screw extruder Leistritz ZSE-27 with an L/D ratio of 40 to produce compounds at different GTR contents (0, 20, 35, and 50 wt %). The screw speed was fixed at 100 rpm with a flat barrel temperature profile of 170 °C. A circular die (2.7 mm in diameter) at 175 °C was used to give a total flow rate of 2 kg/h. At the die exit, the compounds were cooled in a water bath and then pelletized using a model 304 pelletizer (Conair, Stanford, CT, USA). Then, the pellets were dried in a convection oven for 4 h at 75 °C before being pulverized by a model PKA18 pulverizer (Powder King, Phoenix, AZ USA) and sieved to keep an average particle size of around 500 microns (minimum size = 355 microns, maximum size = 600 microns). The second mixing method used was dry blending. In this case, all the materials (LDPE and GTR) in a powder form were dry blended using an LAR-15LMB high-speed mixer (Skyfood, New York, NY, USA) at 3320 rpm with fixed periods of 1 min of blending and 1 min of cooling, repeated 4 or 5 times.

2.2. Rotational Molding

For processing, a Rotolab model 22 laboratory-scale rotational molding machine (Medkeff Nye, Barberton, OH, USA) was used. The parts were produced using a cubic aluminum mold with 3.6 mm wall thickness and internal side length of 19 cm. A demolding agent (Trasys 420, DuPont, Midland, MI, USA) was used to coat the internal surface of the mold before material loading (650 g). To prevent powder losses, the vent (diameter of 10 mm) was filled with glass wool. After primary runs, the optimal processing conditions were a heating time of 25 min with an electrically heated oven, temperature of 185 °C, a cooling time of 30 min with forced air, and a 4:1 speed ratio. Finally, the part was demolded from the opened mold. Then, the specimens were cut from the molded parts to perform the characterizations. To compare the effects of oven temperature, heating time, speed ratio, and particle size of the matrix and rubber (controlled via mechanical sieving), different conditions were studied as shown in Table 2.

| Oven temperature (°C) | 170 | 185 | 200 |
|-----------------------|-----|-----|-----|
| Heating time (min)    | 20  | 25  | 35  |
| Rotational speed (rpm/rpm) | 4:5 | 8:10 | 12:15 |
| Matrix particle size (µm) | 600–500 | 500–355 | 355–250 |
| Rubber particle size (µm) | 600–500 | 500–355 | 355–250 |

2.3. Morphological Characterization

To perform morphology characterization of the raw materials and molded parts, the samples were cryofractured (liquid nitrogen) and the exposed surfaces were covered with gold–palladium. Afterward, an Inspect F50 scanning electron microscope (SEM) (FEI, Hillsboro, OR, USA) was used at 15 kV. A Spot Insight (Diagnostic Instrument, Sterling Heights, MI USA) high-resolution (1600 × 1200 pixels) camera coupled to an Olympus SZ6 stereomicroscope was used to take optical images at different magnifications.

2.4. Density and Hardness

Density was measured using a gas pycnometer, model Ultrapyc 1200e (Quantachrome, Boynton Beach, FL, USA). Nitrogen (N₂) was used as the gas phase, and the test was repeated three times for each sample. Hardness (Shore A and Shore D) was measured using a model 307L durometer (PTC Instruments, Boston, MA, USA). The values are the average and standard deviation of 10 repetitions.
2.5. Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) of the raw materials was done on a Q5000IR TGA analyzer (TA Instruments, New Castle, DE, USA). The measurements were made from 50 to 800 °C at a rate of 10 °C/min with a gas flow rate of 25 mL/min in both nitrogen and air atmosphere.

2.6. Mechanical Properties

The tensile properties were measured according to ASTM D638 (type V) at room temperature on an Instron (Instron, Norwood, MA, USA) model 5565 universal mechanical testing machine with a 500 N load cell at a strain rate of 10 mm/min. At least five specimens were cut in the molded parts to report the tensile modulus, strength, and elongation at break.

Flexural three-point bending tests were performed according to ASTM D790 on an Instron (Instron, Norwood, MA, USA) model 5565 at room temperature with a 500 N load cell at a crosshead speed of 2 mm/min. Five rectangular specimens with dimensions of 60 × 12.7 mm² were cut to determine the average and standard deviation of the strength and modulus values. The span was fixed at 60 mm.

Notched Charpy impact tests were performed at room temperature on a Tinius Olsen (Tinius Olsen, Horsham PA, USA) model 104 according to ASTM D256. For each composition, ten rectangular samples (60 × 12.7 mm²) were cut and V-notched 24 h before testing by an automatic sample notcher, model ASN 120m (Dynisco, Franklin, MA, USA).

3. Results

3.1. Thermogravimetric Analysis (TGA)

Figure 1 presents the TGA and derivative of thermogravimetry (DTG) curves of the raw materials used: LDPE and GTR (nonregenerated (NRR) and regenerated (RR)) in air. Figure 1a shows that the weight loss of neat LDPE begins around 300 °C, and complete degradation occurs around 500 °C. On the other hand, the weight loss of GTR (NRR and RR) begins around 200 °C, and degradation is completed around 570 °C. Figure 1b shows that for LDPE, a single peak at 450 °C is observed, which is related to the neat nature of the matrix, while the GTR presents several peaks between 250 and 530 °C related to GTR decomposition and the complex structure (a mixture of several components). As expected, the presence of oxygen in air decreases the thermal stability of all materials. The highest decomposition temperature can be associated to the oxidation of carbon residues generated at lower temperatures, leading to the formation of carbon dioxide [25]. Liang et al. [26] studied the existence of inorganic compounds like silicon, calcium, and zinc in the form of SiO₂, ZnO, and CaCO₃ in GTR, individually. Therefore, a peak at around 510 °C can be related to the oxidation of inorganic components in the GTR. Furthermore, it can be observed that GTR regeneration cannot prevent the oxidation of carbon in the GTR structure since the main effect of this process is to partially break up the sulfur bonds.

Figure 2 shows the TGA and DTG curves of the raw materials in nitrogen. The DTG curve in nitrogen shows that LDPE still has a sharp peak with a maximum at 470 °C. For GTR, two peaks between 350 °C and 430 °C can be seen. In Figure 2b, the small hump around 220 °C is related to GTR degradation. Around 8% weight loss can be reported at this point. Also, Figure 2a shows that the ultimate weight loss is less than 100%. This may be due to the presence of residues/inorganics in the GTR.
Figure 1. Thermogravimetric analysis (TGA) (a) and derivative of the thermogravimetric (DTG) curve (b) curves of low-density polyethylene (LDPE) and different ground tire rubber (GTR) in air: RR: regenerated rubber and NRR nonregenerated rubber.
3.2. Effect of Processing Conditions on Surface Quality

Figure 3 presents the rotomolded parts surfaces at different magnifications. It can be seen that the external surface quality was affected by the different processing conditions used (see Table 2). This is associated with the porosity level observed.

In this study, different heating time (HT) and oven temperature (OT) were tested to see the effect of the heating process on the part surface quality. Figure 3a,c shows that by increasing the heating time or oven temperature, the number of bubbles and defects decreased due to more being available for sintering, but this can also lead to possible degradation. Both will have an effect on the part density and physical properties. On other hand, unlike other plastic manufacturing processes, the rotational molding process relies on the coalescence of the powder particles against the mold wall. Figure 3b,d,e shows that a three-dimensional network between the particles cannot be created by reducing the heating time and/or oven temperature, and the powder is able to flow freely. This can affect the part surface by providing a suitable condition for the creation of bubbles in the absence of high pressure. As a result, the best part was produced with a 25 min oven time and with 185 °C as the oven temperature.

Also, to analyze the effect of rotational speed (RS), different speeds for the major and minor axes were applied. In comparison with Figure 3f, Figure 3g shows that high rotational speeds can change the shape of the bubbles on the part surface to make them more elongated. So, high rotational speeds can improve the molding process of low-viscosity materials like LDPE and reduce the number of bubbles. For this reason, the best part was produced at a high rotational speed ratio of 12:15.
Furthermore, different matrix and filler particle sizes were used to produce the rotomolded parts. Typical process quality guidelines suggest a particle size distribution below 35-mesh (500 microns) and a maximum of 15% below 100-mesh (150 microns) as fines [27]. Figure 3h shows that decreasing the matrix particle size can decrease the number and diameter of bubbles and affect their shape to create more elongated bubbles on the part surface. However, based on Figure 3i, reduction of the rubber particle size did not substantially modify the porosity level on the part surface.

Figure 3. Cont.
Figure 3. Pictures of the rotomolded part surface under different processing conditions: (a,a’) heating time (HT) = 35 min, (b,b’) HT = 20 min, (c,c’) oven temperature (OT) = 250 °C, (d,d’) OT = 200 °C, (e,e’) OT = 170 °C, (f,f’) rotational speed (RS) = 4:5 rpm/rpm, (g,g’) RS = 8:10 rpm/rpm, (h,h’) matrix particle size = 355–250 µm, and (i,i’) rubber particle size = 355–250 µm.

3.3. Morphological Characterization

Figure 4 presents SEM images of the NRR and RR particles at different magnifications. To determine the effect of the regeneration process on the GTR particles, the size and geometry of the GTR particles can be compared by using microscopy. Figure 4a shows that NRR particles have a more irregular surface compared to RR particles, with protuberances and cracks on their surface. On other hand, Figure 4b’ shows that RR particles have a smoother surface, but a small number of cracks and protuberances are still visible. Furthermore, the particle size can be decreased by the thermo-mechanical regeneration process due to shearing forces mechanically breaking up the particles. Smaller particle size leads to an increase in particle surface area, which can modify the material properties.
Figures 5 and 6 present typical SEM images of the rotomolded samples' cross sections containing different regenerated and nonregenerated GTR contents compared with the neat LDPE. Figures 5b,e and Figure 6b,e show that due to good process conditions, a homogeneous distribution of the GTR in the matrix was achieved at low GTR content (0–20%). Nevertheless, a higher number of bubbles and defects is observed with increasing GTR content, especially for dry-blended samples (Figure 5). This is related to the higher surface area to be wetted by the high-viscosity matrix and limited GTR–LDPE interfacial interactions since no pressure was applied during rotomolding. On the other hand, the melt-blended samples (Figure 6) have fewer defects due to better dispersion and interactions (pressure) related to the extrusion step. Nevertheless, some defects can be created during the pulverization step.

Figure 4. Scanning electron microscope (SEM) images of the (a,a’) nonregenerated and (b,b’) regenerated GTR at different magnifications.
Figure 5. SEM images of the rotomolded samples with different concentrations of nonregenerated rubber (b–d) and regenerated rubber (e–g) compared with neat LDPE (a) for dry-blended samples.

Figure 6. Cont.
3.4. Density and Hardness

Figure 7 reports on the density of the raw materials and the rotomolded samples produced by dry blending and melt blending. The GTR density (NRR = 1.169 g/cm$^3$ and RR = 1.246 g/cm$^3$) is higher than the neat LDPE density (0.910 g/cm$^3$) and superior to the other tested compounds. However, the density of the GTR/LDPE compounds decreases at first due to bubble formation, interfacial gaps, and voids created between two phases. In the period following, the value increases with increasing GTR content for both types of compounds (dry and melt blending). Nevertheless, it can be observed that the regeneration process did not affect the compound density as the values are close (within experimental uncertainty) for both LDPE/NRR and LDPE/RR compounds. Also, a similar trend for both blending methods is observed.

Hardness data for the rotomolded parts (Shore A and Shore D) are shown in Figure 8 for both the dry blending and melt blending methods. As expected, due to the elastic nature of the rubber particles, it is observed that hardness decreases with increasing GTR content in both methods [28]. Based on Figure 8, the regeneration process can decrease the rigidity of samples due to the presence of oil in the RR structure, but again, a limited difference in hardness is observed here.
Figure 7. Density as a function of GTR content. (a) dry blending and (b) melt blending.
3.5. Tensile Properties

Tensile modulus values for the dry-blended and melt-blended samples are reported in Figure 9. As expected, the values decrease with increasing GTR content due to the lower modulus of GTR (about 2 MPa) [29] compared to that of LDPE (72 MPa). There is also increasing porosity, as reported in Figures 3–6, leading to a lower amount of material able to sustain the applied stresses. Furthermore, the regeneration process can affect the tensile properties of LDPE/GTR compounds due to the lower cross-link density and possible reduction in the main backbone chains [30]. Based on Figure 9a, the tensile modulus of LDPE/RR samples is lower than that of LDPE/NRR parts produced by dry blending with up to 35% GTR, However, the value increases with increasing GTR content. Also,
Figure 9b shows that the tensile modulus of LDPE/RR compounds is higher than that of LDPE/NRR ones produced via melt blending with increasing GTR content due to the lower RR particle sizes. Similar trends are observed for the tensile strength in Figure 10b: the tensile strength of LDPE/RR compounds produced via melt blending is higher than that of LDPE/NRR. In this case, the interfacial adhesion/interaction is also important to control this parameter [31]. Finally, the strain at break also decreases with GTR content, as reported in Figure 11, due to increasing numbers of defects. However, most of the compounds (LDPE NRR samples up to 20 wt % in dry blending and up to 35 wt % in melt blending, LDPE/RR samples up to 20 wt % in melt blending) can be considered as good TPE since their elongations at break were above 100%. In this case, the regeneration process did not improve the strain at break due to the presence of the regeneration aid and a nonuniform structure in the blends leading to lower strain at break [32]. All these results are in agreement with previous studies [14,33,34].

Figure 9. Tensile modulus as a function of GTR concentration. (a) dry blending and (b) melt blending.
Figure 9. Tensile modulus as a function of GTR concentration. (a) dry blending and (b) melt blending.

Figure 10. Tensile strength as a function of GTR concentration. (a) dry blending and (b) melt blending.

Figure 11. Strain at break as a function of GTR concentration. (a) Dry blending and (b) melt blending.

3.6. Flexural Properties

Figure 12 presents the flexural modulus values of all the samples. A similar trend to that for the tensile modulus is observed. The values decrease with GTR content due to the flexible nature of GTR, as well as the presence of voids and poor interfacial adhesion. Figure 12 also shows that the LDPE/NRR values are higher than the LDPE/RR ones up to 20% GTR for both blending techniques. However, by increasing the GTR content, the regeneration process can modify this trend and make the flexural modulus of LDPE/RR compounds higher than that of LDPE/NRR ones.
3.6. Flexural Properties

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![Figure 12](image_url)

**Figure 12.** Flexural modulus as a function of GTR concentration. (a) dry blending and (b) melt blending.

3.7. Impact Strength

Impact strength results are presented in Figure 13. It is observed that the impact strength decreased in all compounds with increasing GTR content due to poor adhesion at the interface between GTR and LDPE and low pressure inside the mold leading to the creation of voids inside the parts. Furthermore, it can be observed that the impact strength of LDPE/NRR samples is higher than that of LDPE/RR ones due to the cross-linked structure of the GTR making the particles more deformable to absorb more energy before crack initiation [21]. Therefore, the regeneration process led to lower impact strength due to a lower cross-link density inside RR particles. Also, the impact strength of the melt-blended samples is higher than that of dry-blended ones due to better adhesion at the GTR and LDPE interface, i.e., fewer defects in the samples.
4. Conclusions

In this study, low-density polyethylene (LDPE)/natural rubber (NR) compounds were prepared by both melt blending and dry blending to produce parts via rotational molding. In particular, the effect of rubber regeneration, ground tire rubber (GTR) content, oven temperature, heating time, rotational speed, and particle size for both the matrix and filler was evaluated. On the samples produced, complete morphological (optical and scanning electron microscopy) and mechanical characterization (tension, flexion, and Charpy impact) was performed, with physical properties of interest (density and hardness) for thermoplastic elastomers (TPE) also evaluated.

According to the results obtained, several conclusions can be made.

Firstly, it was observed that at low GTR content (0–20 wt %), a homogeneous distribution of the rubber phase in LDPE can be achieved. However, at higher GTR content (up to 50 wt %), a higher number of bubbles and defects was generated. In our case, it was not possible to use GTR content above 50 wt %, especially for dry-blended samples.

**Figure 13.** Impact strength as a function of GTR concentration. (a) dry blending and (b) melt blending.
Secondly, the mechanical properties of rotomolded samples decreased with increasing GTR content due to poor adhesion at the interface between GTR and LDPE and the low pressure inside the mold leading to the creation of voids inside the parts. For example, the GTR content not only decreased both the flexural and tensile moduli, but also decreased the ultimate strength, strain at break, and impact strength in samples from both the dry and melt blending techniques. This is also related to the lower rigidity of GTR particles compared to the LDPE matrix.

Thirdly, the properties of dry-blended parts were usually slightly lower than those of melt-blended ones due to limited shear and high pressure in the dry blending technique leading to poor adhesion between LDPE and GTR. This also produced a higher number of bubbles and defects compared to melt-blended samples.

Finally, most of the compounds can be considered as good TPE since their elongations at break were above 100% with up to 20 wt % GTR. Nevertheless, more work should be done to improve on these results, especially by performing GTR surface treatment before its introduction into the LDPE matrix to improve interfacial interactions. This work is currently under investigation using different techniques.

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