

**Araştırma Makalesi / Research Article**

**Investigation of Mechanical and Microstructural Properties of Polyolefin Rubber and Glass Beads Filled Polypropylene Composites**

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**Geliş/ Received:** 24.03.2022;

**Kabul / Accepted:** 09.05.2022

**ABSTRACT:** In the automotive industry and many industries, parts are expected to meet certain requirements with regards to their tensile strength, stiffness, and high impact strength. For this reason, polypropylene homopolymer, which is a fragile polymer widely used in the automotive industry, is combined with additives to reduce its fragility. In this study, the mechanical and microstructural properties of polyolefin rubber and glass bead filled polypropylene composites have been investigated. Polypropylene (PP) was combined with polyolefin rubber (POE) and glass beads (GB) at different weight rates to create the composites and pure polypropylene was compared to the three prepared PP composites; 8% polyolefin rubber by weight, 8% glass bead by weight, and 8% polyolefin rubber and 8% glass bead by weight. The fracture surface examinations of the pure polypropylene (PP), and the polyolefin rubber added PP, glass bead added PP, and polyolefin rubber and glass bead added PP composites were carried out using Scanning Electron Microscopy (SEM). In addition, Energy Dispersive Spectroscopy (EDS) analysis was also performed for the characterization. It was observed that the tensile strength values of the PP composites (PP-8%POE, PP-8%GB, and PP-8%POE-8%GB) showed a slight decrease relative to the pure PP. When rigid glass beads were added to the pure PP polymer main matrix (8% by weight), the stiffness of the composite increased and the modulus of elasticity increased by approximately 8% relative to pure PP. In addition, it was observed that the % elongation at break values of the PP composites (PP-8%POE, PP-8%GB, and PP-8%POE-8%GB) increased significantly relative to the values for pure PP.

**Keywords:** Polypropylene, Polyolefin rubber, Glass beads, Mechanical properties.

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Ünal, H., Ermiş, K., Demirtaş, Ş. (2022). Investigation of Mechanical and Microstructural Properties of Polyolefin Rubber and Glass Beads Filled Polypropylene Composites. Journal of Materials and Mechatronics: A (JournalMM), 3(1), 91-105.

## 1. INTRODUCTION

The tribological performances of polymer composites vary depending on the additives and fillers used and they are added at certain rates. Stiffness is the primary property improved by particulate reinforcing fillers. Hardness can also be improved, as can thermal expansion, mold shrinkage, extensibility, and creep. Yield strength and impact strength typically show a reduction but can show a slight increase in some cases. In other words, it may vary depending on the filler type, filler particle size, and filler additive ratio (Yang et al., 2004; Liang, 2005; Liang and Wu, 2012). Polypropylene (PP) is a thermoplastic widely used in packaging and the textile and automobile industries because of its good processability (Liang and Li, 2000). Because polypropylene (PP) is inexpensive and has a low density, PP based thermoplastic elastomer blends are commercially very important. PP is resistant to oil, solvents, and high temperatures due to its crystalline structure and relatively high crystal-line melting point (145-165 °C) (Drobny, 2007)

POEs (Polyolefin rubbers) are a relatively new class of polymers that have emerged as a result of recent advances in metallocene polymerization catalysts, and they are one of the fastest-growing synthetic polymers. Polyolefins are the most common type of thermoplastic and a vital class of commercial polymers used in a wide range of applications. Polyolefin thermoplastic elastomers are defined as materials that are a combination of polyolefin semi-crystalline thermoplastic and amorphous elastomeric components (Coran and Patel, 1995). The high recoverable elasticity of thermoplastic polyolefin rubbers is difficult to explain in terms of flexible polymer chains cross-linked into an open network structure. It's probably better to think about deformation behavior at a macro scale rather than a molecular scale. A model can be imagined with a three-dimensional polypropylene mesh embedded with elastomeric domains. When stress is applied, both the open network of the rigid phase and the elastomeric domains can deform. When the tension is released, the cross-linked rubbery areas will attempt to regain their original shape, resulting in the object's recovery from deformation (Brillinger and Banks, 1976). The utilization of these rubbers is especially appealing due to their reasonable price structure, good weathering properties, seemingly negligible toxicity hazards, and ease of processability and re-processability. They have quickly gained popularity in automotive industry applications (e.g., bumper covers, door gaskets, and other car parts, cable insulation), blow molding applications (e.g., liquid containers, bleach bottles), injection molding (e.g., toys, screw caps), etc. (Whiteley et al., 2000; Liu and Qiu, 2013). They stated that POE rubber is an effective toughening agent that makes the brittle PP polymer more ductile and tough (Lim et al., 2006; Lendvai, 2021). The rubber particles, in addition to promoting crazing (Farhang and Bagheri, 2014) and shear yielding, can also improve the fracture resistance of PP by varying its crystalline structure (Jang et al., 1985; Fan et al., 2020).

Several studies have investigated the toughening process of rubber filled PP and they have found that rubber particle cavitation, crazing, and shear yielding are among the major toughening mechanisms found in rubber-added PP (Jang et al., 1985; Liang and Li, 2000; Lotti et al., 2000; Li et al., 2002; Lim et al., 2006; Lim et al., 2008; Wahit et al., 2009; Liu and Qiu, 2013; Wu et al., 2015; Shi and Xiao 2017; Cai et al., 2017; Li et al., 2019; Hu et al., 2019; Wang et al., 2019; Mao et al., 2020; Kim et al., 2020). Rubber particles can act as stress concentrators to initiate and terminate cracks (Fasihi and Mansouri, 2016). Also, the crystallinity of PP can be increased with the addition of rubber and clay particles (Li et al., 2002).

Several studies have been published on the mechanical and microstructural properties of glass bead filled PP (Liang and Li, 1998; Tang et al., 1998; Tjong and Xu, 2001; Kwok et al., 2003; Yang

et al., 2004; Unal, 2004; Liang, 2005; Liang, 2007a; Liang, 2007b; Müller, 2017; Cunha et al., 2018; Carvalho et al., 2020).

In plastics industry, the use of glass beads as an inorganic powder filler is a recent development, and glass beads have high filling capacity, excellent rheological properties and mechanical properties. Glass beads have sufficient corrosion resistance, heat resistance, compressive strength and excellent electrical insulating properties. In addition, they (GBs) have advantages such as smooth spherical surface, strong filler ability, small and well-distributed internal stress. The power consumption due to the processing and wearing of equipment can be reduced (Yang et al., 2004) because of the good flow properties of glass filled composites. The tensile modulus, and impact strength (Liang and Li, 1998) increase with the increment of the glass bead concentration, which can result in a decrease in the resistance to fracture work, while the increasing glass bead concentration causes a decrease in the tensile strength (Tang et al., 1998). Müller (2017) showed that adding a particle filler in the form of spherical glass beads B159 increased adhesive bonding strength by 14%. However, the results also showed that adding the filler into the resin led to the elimination of the influence of various loading speeds. Experimental results by Müller (2017) also showed that the tensile strength decreased with the addition of glass beads for both filler B159 and B112. This mechanism explains the common generalization on the effect of natural matrix toughness, that is, the toughening effect of incorporating inorganic particles into polymers decreases as the natural matrix toughness increases. Liang (2005) used hollow glass beads with three diameters, 11, 35, and 70  $\mu\text{m}$ , to make glass bead filled PP composites and found that the yield stress decreased gently for the 70  $\mu\text{m}$  glass bead filled PP composite, whereas it decreased relatively obviously for the 35  $\mu\text{m}$  glass bead PP composite with increasing the volume fraction of the fillers. Liang (2007a) showed that the notched Izod impact strength of glass bead filled PP filled increased gently with the increase in the volume fraction of the fillers when the volume fraction was less than 15%, and then it decreased. Also, Kwok et al. (2003) showed that the impact strength of the PP/glass bead ( $d = 2.7 \mu\text{m}$  and  $\sigma = 1.85$ ) composite increases about 4.5 times as volume fraction increases from 0 to 0.25, while the tensile modulus remains roughly unchanged.

In this study, the mechanical and microstructural properties of polyolefin rubber or/ and glass bead filled polypropylene composites were investigated. The experimental results for the pure polypropylene were compared to the results for the three PP composites, 8% polyolefin rubber by weight, 8% glass beads by weight, and 8% polyolefin rubber and 8% glass beads by weight. The images of the fracture surfaces obtained by tensile tests on the samples of pure polypropylene (PP), and polyolefin rubber filled PP, glass bead filled PP, and polyolefin rubber and glass bead filled PP composites were taken using Scanning Electron Microscopy (SEM) and analyzed by Energy Dispersive Spectroscopy (EDS) for microstructure investigations. The aim of this investigation was to get the high impact resistant polymer composites with low rigidity loss by obtaining the modulus of the core should be as higher and the modulus of the shell should be as lower as they can.

## 2. MATERIALS AND METHODS

### 2.1 Materials

In the automotive industry and many application industries, parts are expected to meet certain requirements with regards to their tensile strength, stiffness, and high impact strength. For this purpose, polypropylene homopolymer, which is widely used in the automotive industry but is fragile, was used as a matrix material. The polypropylene homopolymer main matrix material used in the

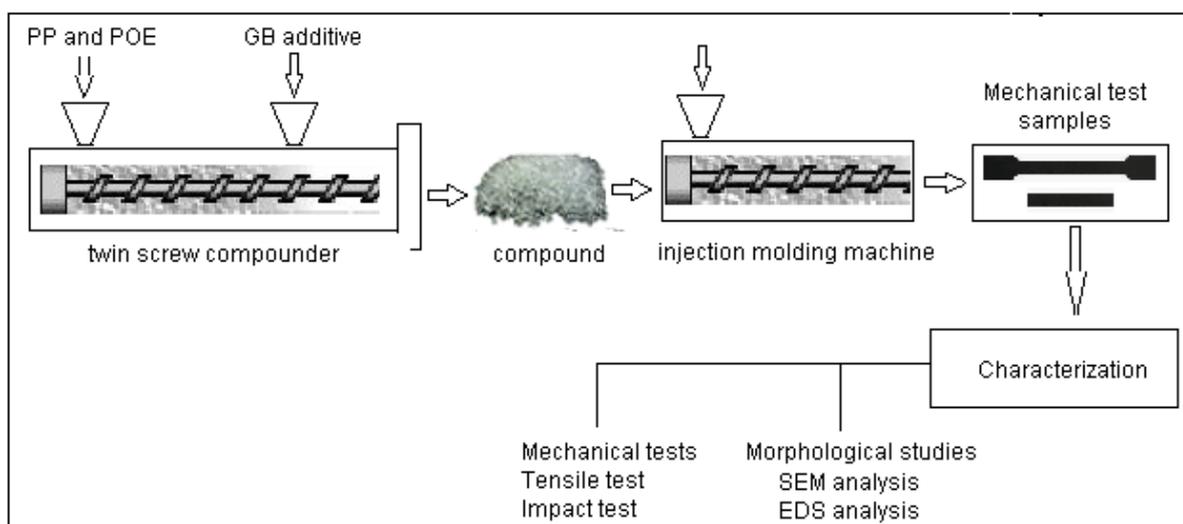
experiments was suitable for injection molding and had a density of  $0.90 \text{ g/cm}^3$ . PP was in granule form, had a natural color, and was purchased from Borealis-Australia with the commercial code BUPLEN 6531. The glass bead additive was obtained from Potters Industries and had the CP-3 surface modification code and an average particle size of  $10 \text{ }\mu\text{m}$ . The polyolefin rubber was polypropylene compatible and was obtained from “DuPont” under the trade name “Engage”. While producing granules with the compound production method, additives, such as a certain amount of lubricant, that facilitates processing and heat stabilizers were added to the polypropylene-based recipe. The compositions and process conditions of the glass bead and POE rubber added PP-based hybrid composites used in the experiments are given in Table 1.

**Table 1.** Compositions and process conditions of PP based hybrid composites with glass bead and POE rubber additives

Sequence No.	PP polymer additive ratio (by weight)	POE rubber additive ratio (by weight)	Glass bead contribution ratio (by weight)
1	100	-	-
2	92	8	-
3	92	-	8
4	84	8	8

## 2.2 Method

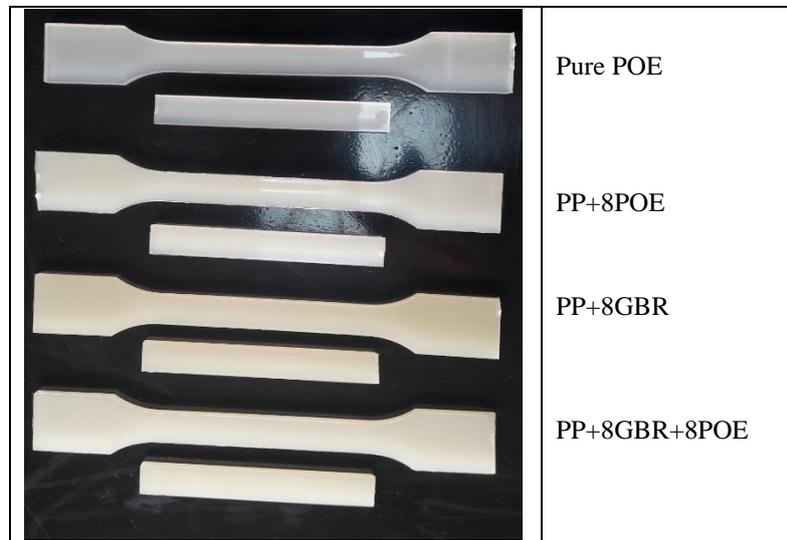
The polypropylene main matrix material and the polyolefin rubber materials used in the experiments were in the form of granules and were fed from the same feeding unit after being mechanically mixed into a twin-screw compounding machine. Glass bead additive was fed to the machine from another feeding zone. After achieving a homogeneous mixture with the help of twin screws, thin long spaghetti-like sticks were produced in the mold part of the machine and cooled in the cooling pool. Then, a PP polymer mixture in the form of granules and composite semi-finished products were produced by cutting with the help of a granulator. The heater temperatures of the compounding machine used in the production of granules were adjusted to  $180\text{-}230 \text{ }^\circ\text{C}$ . A conventional injection-molding machine was used for the preparation of tensile and impact test samples. The injection pressure was set at 400 bar and injection temperatures were set between  $180\text{-}230 \text{ }^\circ\text{C}$ . The schematic work plan for the production of polymer blend and composites are given in Figure 1.



**Figure 1.** Schematic illustration of the work flow for PP-POE blend, PP-GB and PP-POE-GB composites

## 2.2 Experimental Devices and Tests

The tensile test samples, see figure 2, used in this experimental study were produced using the injection molding technique according to the ASTM D638 standard. Tensile tests were carried out using the Zwick brand Z020 model 2-ton capacity tensile device at 10mm/min tensile speed, 50% humidity conditions, and room temperature. In the tensile tests, tensile strength, modulus of elasticity and % elongation at break values were determined. The tensile modulus of the slope of the curve in the elastic region of the stress-strain graph of the sample. Tangent  $\theta = E = \sigma/e$  E denotes tensile modulus,  $\sigma$  tensile strength and  $e$  strain in the formula. Izod notched impact tests of the samples, which were prepared to have dimensions of  $80 \times 10 \times 4$  mm<sup>3</sup>, see figure 2, and prepared according to the ASTM D256 standard, were carried out in a Zwick brand impact tester. In the impact tests, impact strength was determined. The fracture surface microstructure examinations of the tensile test samples were carried out using a JEOL JSM-6060LV brand electron microscope. In the experiments, mechanical properties such as tensile strength, modulus of elasticity, % elongation at break, and impact strength were determined. All experiments were repeated at least three times and generally, the average arithmetic values were used.

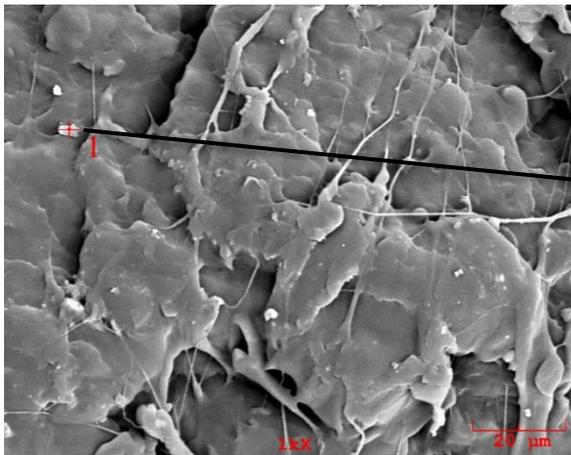


**Figure 2.** Pictures of tensile and impact test specimens used in experiments

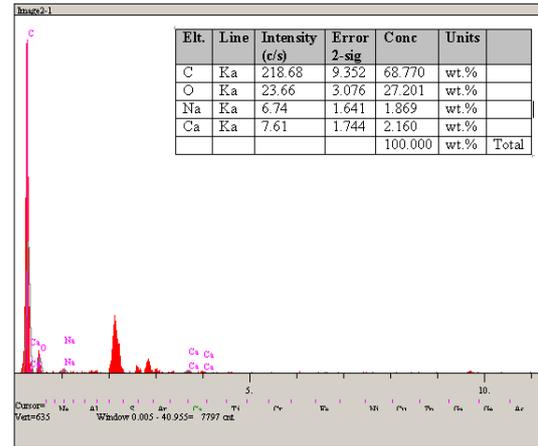
## 3. RESULTS AND DISCUSSION

SEM images for the microstructure investigations of the fracture surfaces obtained after the tensile test for the Pure PP polymer and the 8% POE rubber filled, 8% glass bead filled, 8% glass bead, and 8% POE rubber filled PP composites used in the experiments were taken using an electron microscope. SEM images and EDS analyses of the test samples are given in Figure 3 (a-d). In Figure 3a, the SEM image of the pure polypropylene polymer is given on the left, and the EDS analysis is given on the right. EDS analysis was performed from a different-looking point (point 1) on the surface and it was observed that there was a C peak. This indicates that the matrix is pure PP. The SEM image of the PP+8POE composite is given in Figure 3b. Next to the figure, the result of the EDS analysis is given. Since the POE rubber added to the polypropylene polymer is organic, it was determined to be C present in the EDS analysis. In Figure 3c, the SEM image of the glass bead added PP polymer composite is given on the left, and the EDS analysis is given on the right. In the EDS analysis taken from the point marked with a number 1 on the SEM image, it was determined that the Silica was present. As is known, glass beads contain silica, aluminum oxide, calcium oxide, magnesium oxide,

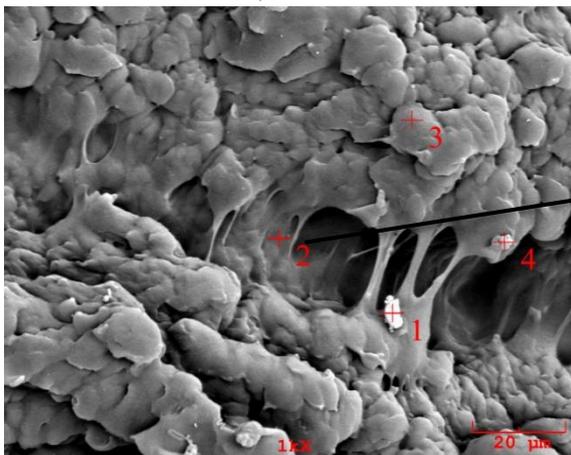
sodium oxide, and iron oxide (Purowski et al., 2012). The EDS analysis tables show the elements in the composition of the glass beads. The EDS analysis was performed from a different-looking point (point 1) on the surface and it was observed that there was a C peak. This indicates that the matrix is pure PP. In Figure 3d, the SEM image of the PP+8POE+8GB polymer composite is given on the left and the result of EDS analyses is given on the right. In the EDS analysis taken from points 2 and 5 on the image, it can be said that Si is abundant at point 2, which is due to the presence of the glass beads, and C is abundant at point 5, which is due to the presence of the polymer matrix or the POE rubber.



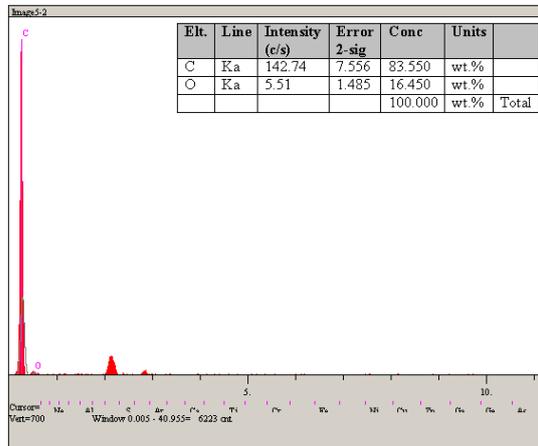
a) Pure PP



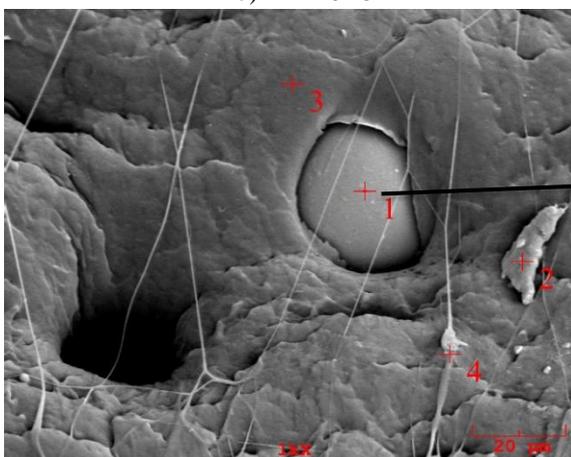
Pure PP EDS analysis



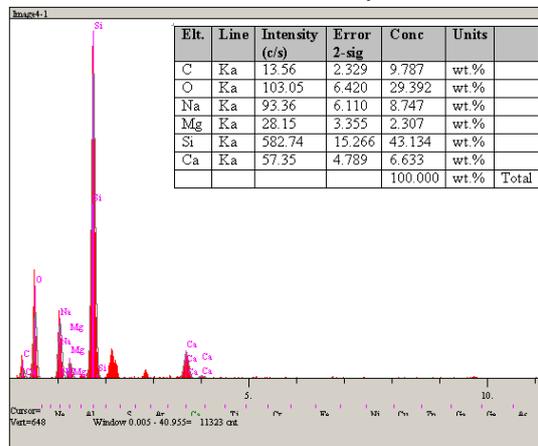
b) PP+8POE



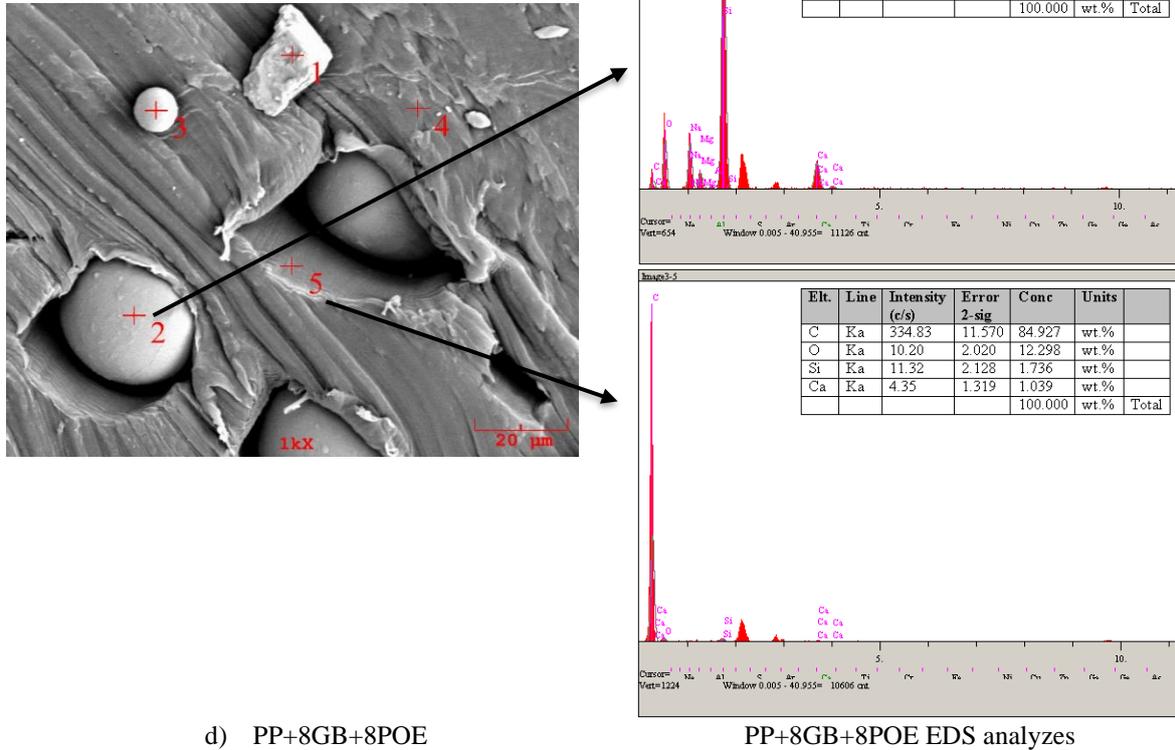
PP+8POE EDS analysis



c) PP+8GB

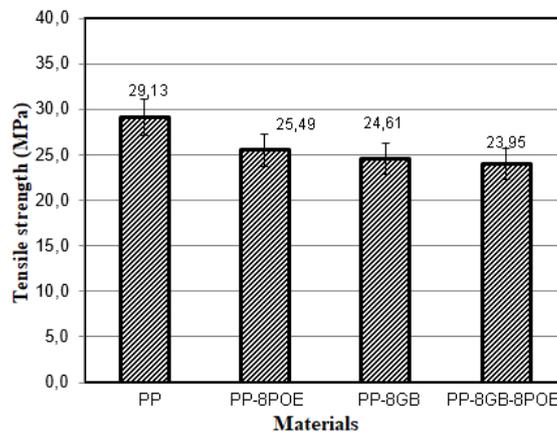


PP+8GB EDS analysis



**Figure 3.** Scanning electron microscopy images and EDS analyses of a) Pure PP, b) 8% POE rubber added PP composite, c) 8% glass bead added PP composite, and d) 8% glass bead and 8% POE rubber added PP composite

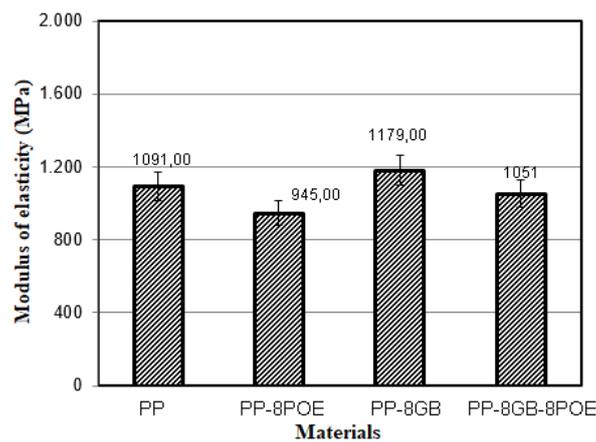
In Figure 4, the tensile strength changes of the pure PP, and the 8% glass bead filled PP, 8% rubber filled PP, and 8% glass bead and 8% rubber filled PP composites used in the experiments are given. As seen in the figure, the tensile strength values of the pure PP polymer, and the PP-8POE, PP-8GB, and PP-8GB-8POE composites were obtained as 29.13 MPa, 25.49 MPa, 24.61 MPa, and 23.95 MPa, respectively. When glass beads were added to pure PP at a ratio of 8% by weight, the tensile strength of the composite decreased by 15.5% relative to the pure PP. The reason for the decrease in tensile strength can be explained by the lack of a good interfacial bond between the glass bead and the PP polymer matrix (See Figure 8c).



**Figure 4.** Tensile strength values of pure PP and glass bead and POE rubber added PP composites

However, in a previous study by Yang et al., 2004, it was stated that the tensile strength of linear low-density polyethylene (LDPE) composites with glass bead additives increased by approximately 33% with the increase of glass beads ratio (0-10% by weight). Unal (2004) found that the tensile strength of the composite increased by approximately 12% when the glass beads were added at a rate of 10% by weight to the polyamide 6 polymer. When rubber was added to the pure PP polymer at a rate of 10% by weight, a 12.4% decrease was observed in the tensile strength relative to the pure PP polymer. Similar results were found in other studies (Liu and Qiu, 2013; Wang et al., 2019; Yu et al., 2019; Kim et al., 2020). When 8 wt.% POE was added to the PP polymer, the tensile strength of the blend was obtained as 25.49 MPa. A 12.49% reduction was observed when compared with the tensile strength of the pure PP polymer. This is because POE is softer and more elastic than pure PP polymer. The tensile strength of the PP composite that is 8% glass bead and 8% polyolefin rubber by weight also decreased by 17.7% relative to pure PP. The reason for the decrease in the tensile strength of the PP-8GB-8POE composite can be explained by the poor interfacial bond between the glass beads and polymer matrix and the presence of soft and flexible POE rubber.

The change in the modulus of elasticity of the pure PP polymer and the PP composites with 8% polyolefin rubber, 8% glass bead, 8% glass bead and 8% polyolefin rubber by weight are given in Figure 5.

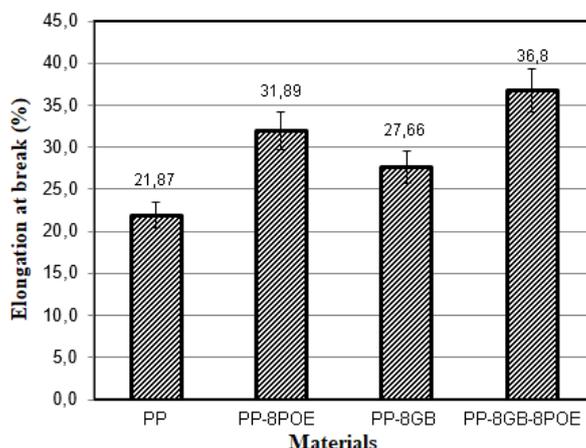


**Figure 5.** Modulus of elasticity values of pure PP and glass bead and polyolefin rubber added PP composites

The modulus of elasticity of the pure PP polymer, and the PP-8POE, PP-8GB and PP-8GB-8POE polymer composites were obtained as 1091 MPa, 945 MPa, 1179 MPa, and 1051 MPa, respectively. When rigid glass beads were added to the pure PP polymer main matrix at a rate of 8% by weight, the stiffness of the composite increased and the modulus of elasticity increased by approximately 8%. An increase in elastic modulus and a decrease in yield strength were observed with the increase of the glass bead ratio in the polypropylene main matrix (Kwok et al., 2003). The reason for this increase in stiffness is explained by the good interfacial bond between the polymer matrix and the glass bead additive. Similar results were observed in another study (Li et al., 2002) regarding the increase in the glass bead ratio and the increase in the elastic modulus of the composite. It was determined that the modulus of elasticity of the LLDPE composite increased by approximately 10% with the addition of glass fiber at a rate of 10% by weight. For a glass bead added PA6 polymer composite, the elastic modulus of the composite increased by approximately 13.6% with the addition of glass beads at a rate of 10% by weight (Unal, 2004). These results in the literature are similar to the results for the modulus of elasticity obtained from the experiments in this study and therefore

support this study. In fact, the increase in the modulus of elasticity has also been reported by other researchers (He and Jiang, 1993). The increase in the modulus of elasticity is due to stress concentrations occur around the additives in the form of particles added to the polymer main matrix. As the additive ratio in the matrix increases, these stress concentration regions coalesce and cause an increase in the modulus of elasticity. On the other hand, when softer polyolefin rubber was added to the pure PP polymer main matrix at a rate of 8% by weight, it was observed that the modulus of elasticity decreased relative to the pure PP. The reduction in modulus of elasticity was approximately 13.3%. Similar results are also found in previous studies (Wang et al., 2019; Yu et al., 2019; Kim et al., 2020). The elasticity modulus for the PP composite with 8% glass bead and 8% polyolefin rubber showed a decrease of 3.6% relative to pure PP. The modulus of elasticity of PP-8POE blend and PP-8GB composites were obtained as 945 MPa and 1179 MPa, respectively. The modulus of the elasticity of the PP-8POE-8GB composite was determined to be 1051 MPa. As expected, the obtained modulus of elasticity value was between the modulus of elasticity of PP-8POE blend and PP-8GB composites.

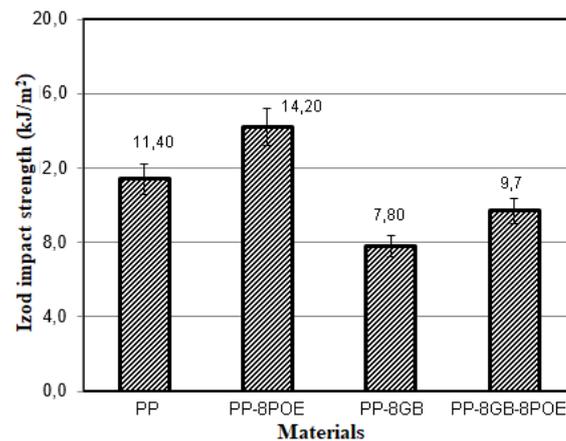
In Figure 6, the % elongation at break for the pure polypropylene, and the 8% glass bead added, 8% rubber added, and 8% glass bead and 8% polyolefin rubber added PP composites used in the experiments is given.



**Figure 6.** % elongation at break values of pure PP and glass bead and polyolefin rubber added PP composites

As seen in the figure, the % elongation at break of the pure PP polymer was determined to be 21.87%, while the % elongation at break of the PP-8POE polymer mixture was determined to be 31.89%. When polyolefin rubber was added to the polypropylene main matrix, the increase in elongation value was approximately 45.8% relative to pure PP. When glass beads were added to PP at a rate of 8% by weight, the % elongation at break increased by approximately 26.4% relative to pure PP. Similar results were found in the study by Wang et al. (2019). With the addition of POE to the PP polymer at a rate of 10% by weight, the elongation at the break of the mixture increased by 74%. The increase in % elongation at break obtained in the experiments was also observed in a previous study on linear low-density polyethylene and glass bead composites (Yang et al., 2004) and the elongation was classified as “not much change”. The % elongation at break of the PP-8GB-8POE polymer composite was determined to be 36.8%. Compared to the elongation value of the pure PP polymer, it showed a relative increase of about 68.2%.

The variation in the Izod impact strength values of the pure polypropylene polymer and the 8% glass bead added, 8% polyolefin rubber added, and 8% glass bead and 8% polyolefin rubber added PP composites are given in Figure 7.

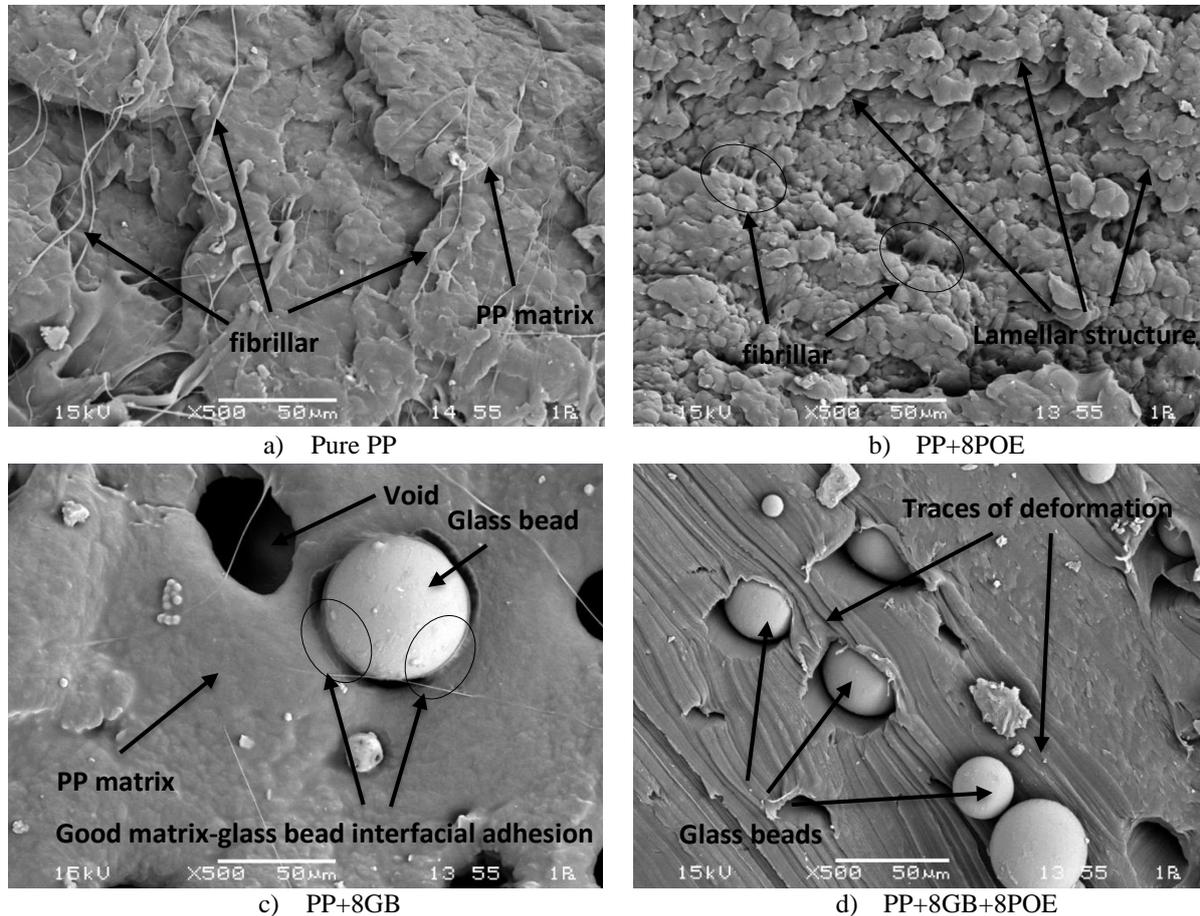


**Figure 7.** Izod impact strength values of pure PP and glass bead and polyolefin rubber added PP composites

As can be seen in the figure, the Izod impact strength of the pure PP polymer was 11.4 kJ/m<sup>2</sup>, while the toughness of the polymer mixture increased when polyolefin rubber was added to the pure PP at a rate of 8% by weight, with the impact strength of the rubber filled PP composite being 14.2 kJ/m<sup>2</sup>. In other words, relative to the impact strength of pure PP, the impact strength of the PP-8POE mixture showed an increase of about 24.5%. Similar results were obtained in previous studies in the literature (Wahit et al., 2009; Liu and Qiu, 2013; Wang et al., 2019; Mao et al., 2020; Kim et al., 2020). With the addition of the glass bead additive to the pure PP polymer, the stiffness of the composite increased relative to pure PP, and the impact strength decreased by about 31.5%. The results obtained in the experiments are in agreement with previous studies (Kwok et al., 2003; Liang, 2007a). Kwok et al. (2003) observed that the impact strength increased with the increase in the ratio of glass beads added to the polypropylene polymer and explained that the reason for this is because the interfacial bond between the polymer matrix and the glass bead additive is very strong. In other words, with the increase of the glass bead ratio, the toughness of the PP composite decreased, its stiffness increased and the impact resistance decreased. However, in a previous study by Liang et al. (2002) on linear low-density polyethylene and glass bead composites, a significant increase in impact strength was observed with increasing glass bead ratio. The glass bead added to the LLDPE structure at the rate of 5% by weight increased the impact strength of the composite by approximately 27%. He attributed this to the fact that the glass bead particle size plays an important role in the mechanical properties of the composite. Similar results were expressed in the previous study of glass bead added polypropylene composite material by Liang (2007). In fact, it was observed that the impact strength of the composite did not change much with the addition of 11 µm diameter glass beads at the rate of 5% by volume, while the impact strength of the composite decreased when larger diameter (70µm) glass beads were added. When glass beads were added at a rate of 10% by weight, it was determined that there was a slight increase in impact strength with the addition of glass beads of both diameters. Unal (2004) also stated that there was a decrease in the impact strength of the polyamide-6 polymer/glass bead composite relative to the pure polymer. It has been observed that the addition of glass beads at a rate of 10% by weight to the polyamide-6 main matrix reduces the impact strength of the composite by approximately 21%. The author claimed that additives added to the polymer main matrix make the movement of the polymer chains difficult, and this leads to bulk embrittlement. Wang et al. (2009) also found an 80% increase in impact strength with the addition of POE at a rate of 10% to the PP polymer. When polyolefin rubber was added to the PP-8GB composite at a rate of

8%, it was observed that the impact strength of the PP-8GB-8POE polymer composite increased by approximately 14.9%.

In Figure 8 (a-d) the microstructure images of the fractured surfaces of the pure PP polymer, and the 8% polyolefin rubber-added PP, 8% glass-bead-added PP and 8% glass-bead and 8% polyolefin rubber-added PP composites taken by the scanning electron microscope as a result of the tensile test are given.



**Figure 8.** Fracture surface images of a) Pure PP, b) PP+8 POE composite, c) PP+8GB composite, and d) PP+8POE+8GB composite obtained after the tensile test taken with a scanning electron microscope

In Figure 8a, the broken surface image of the pure PP polymer is given and finely deformed fibers can be seen on the surface. In Figure 8b, the fracture surface image of the PP+8POE polymer composite is given. The figure shows a lamellar and layered structure. This can be explained by strong interfacial adhesion and good compatibility between PP and POE during the deformation of the PP polymer. The POE elastomer added to the PP structure initiates the movement of the slip bands in the mixture, which acts as a stress concentration factor. There will be stress concentrations around the cracks that will likely occur as a result of slipping. However, the POE elastomer plays a role in reducing stress concentrations at the crack tips and increases the toughness of the mixture (see Figure 7). In Figure 8c, the fracture surface image of the PP+8GB polymer composite after the tensile test is given. As can be seen in Figure 8c, the glass bead is partially bonded to the composite. It can be observed that there is a gap around the glass bead, and at the same time, the polymer matrix and the glass bead appear to be well bonded. The fracture surface image of the PP+8POE+8GB polymer composite is given in Figure 8d. In Figure 8d, it can be observed that the glass beads in the composite

are not bonded to the matrix very well, and the traces formed can be explained by the fact that the POE rubber softens the matrix material and increases the deformation.

#### 4. CONCLUSION

The following results were obtained as a result of the mechanical and microstructural investigations of the pure PP polymer, and the PP+8POE, PP+8GB, and PP+8POE+8GB composites used in the experiments.

1. The glass bead additive added to the PP polymer decreased the tensile strength and impact strength of the composite while increasing the modulus of elasticity and % elongation. Compared to the pure PP polymer, the decrease in tensile strength was 15.5%, and the decrease in impact strength was 31.5%. On the other hand, the increase in the modulus of elasticity was 8% and the increase in the % elongation was 26% relative to the pure PP.
2. The addition of the POE rubber to the PP main matrix polymer leads to a decrease in the tensile strength and modulus of elasticity of the polymer and an increase in the impact strength and % elongation values. Compared to the pure PP polymer, the decrease in tensile strength and modulus of elasticity was 12.5% and 13.3%, respectively, while the increase in impact strength and elongation at break was 24.5% and 45.8%, respectively.
3. When both the POE rubber and glass bead additive were added to the main matrix, PP polymer, it was determined that the tensile strength, elastic modulus, and impact strength values decreased, while the % elongation at break values increased relative to the pure PP polymer. The decrease in tensile strength, modulus of elasticity, and impact strength were around 17%, 3.6%, and 14.9%, respectively, while the increase in the elongation at break was 68.2%. When the values obtained are compared with the values of the glass bead added PP composite, the tensile strength and modulus of elasticity of the PP+8POE+8GB composite showed a decrease of 2.68% and 10.8%, respectively, while the elongation at break and impact strength values showed an increase of 33% and 2.3%, respectively. When the values obtained are compared with the values of the POE elastomer added PP polymer, the tensile strength and impact strength of the PP-8POE-8GB composite showed a decrease of 6.0% and 31.6%, respectively, while the modulus of elasticity and the elongation at break values showed an increase of 11% and 15.3%, respectively.
4. In the microstructure images taken by scanning electron microscope, it was determined that the interfacial bond between the PP polymer matrix and the glass beads was not very strong, but the POE rubber and the PP matrix bonded well.

#### 5. CONFLICT OF INTEREST

Authors approve that to the best of their knowledge, there is not any conflict of interest or common interest with an institution/organization or a person that may affect the review process of the paper.

#### 6. AUTHOR CONTRIBUTION

Hüseyin ÜNAL conceptualization and original draft (lead); formal analysis of the research and Supervision, Şahan DEMİRTAŞ experiments, data collection and analysis, Kemal ERMİŞ Writing – Review & Editing, Investigation and interpretation of results.

## 7. REFERENCES

- Brillinger J. H., Banks S. A., Thermoplastic Elastomers for Flexible Body Components. SAE Transactions 85(4), 2340-2349, 1976.
- Cai J., Luo R., Lv R., He Y., Zhou D., H, W., Crystallization Kinetics of Ethylene-Co-Propylene Rubber/Isotactic Polypropylene Blend Investigated via Chip-Calorimeter Measurement. European Polymer Journal 96, 79-86, 2017.
- Carvalho G. B., Canevarolo S., Sousa J. A., Influence of Interfacial Interactions on The Mechanical Behavior of Hybrid Composites of Polypropylene / Short Glass Fibers / Hollow Glass Beads. Polymer Testing 85, 106418, 2020.
- Coran A.Y., Patel R.P., Thermoplastic Elastomers by Blending and Dynamic Vulcanization. In: Karger-Kocsis, J. (eds) Polypropylene Structure, blends and composites. Springer, Dordrecht.162-201, 1995.
- Cunha M. P., Grisa A. M. C., Klein J., Poletto M., Brandalise R. N., Preparation and Characterization of Hollow Glass Microspheres-Reinforced Poly (Acrylonitrile-Co-Butadiene-Co-Styrene) Composites. Materials Research 21(6), e20180201, 2018.
- Drobny J. G., Handbook of Thermoplastic Elastomers, William Andrew Inc., First Edition, pp.191-99, 2007.
- Fan Q., Zhang J., Wu Z., Yang S., Chen Y., Ying Lu, Zhang Q., Great Improvement of Low-Temperature Impact Resistance of Isotactic Polypropylene/Ethylene Propylene Diene Monomer Rubber Blends by Traces of Carbon Nanotubes and  $\beta$ -Nucleating Agents. Polymers for Advanced Technologies 31(3), 508-519, 2020.
- Farhang L., Bagheri R., Investigation of Toughening Micro-Mechanisms in Polypropylene/ Ethylene-Propylene-Diene Rubber Blends at Crack and Notch Tips. Materials Performance and Characterization 3(3), 469-488, 2014.
- Fasihi, M., Mansouri H., Effect of Rubber Interparticle Distance Distribution on Toughening Behavior of Thermoplastic Polyolefin Elastomer Toughened Polypropylene. Journal of Applied Polymer Science 133(40), 44068, 2016.
- He D., Jiang B. The Elastic Modulus of Filled Polymer Composites. Journal of Applied Polymer Science 49(4), 617-621, 1993.
- Hu S., Hou Y., Wang X., Zhang L., Zhu Y., Research Progress of Rubber and Elastomer Toughening Modified PP. Hecheng Shuzhi Ji Suliao/China Synthetic Resin and Plastics 36(5),104-109, 2019.
- Jang B. Z., Uhlmann D. R., Vander Sande J. B., Rubber-toughening in Polypropylene. Journal of Applied Polymer Science 30(6), 2485-2504, 1985.
- Kim S. Y., Ha J. U., Shin D., Jung W., Lee P. C., Mechanical Properties and Morphology of Polyamide/Polypropylene Blends. Elastomers and Composites 55(1), 1-5, 2020.
- Kwok K. W., Gao Z. M., Choy C. L., Zhu X. G., Stiffness and toughness of Polypropylene/Glass Bead Composites. Polymer Composites 24(1), 53-59, 2003.
- Lendvai L., A Novel Preparation Method of Polypropylene/Natural Rubber Blends with Improved Toughness. Polymer International 70(3), 298-307, 2021.
- Li Y., Wei G. X., Sue H. J., Morphology and toughening mechanisms in clay-modified styrene-butadiene-styrene rubber-toughened polypropylene. Journal of Materials Science 37(12), 2447-2459, 2002.

- Li F., Gao Y., Zhang Y., Jiang W., Design of High Impact Thermal Plastic Polymer Composites with Balanced Toughness and Rigidity: Toughening with One Phase Modifier. *Polymer* 191, 122237, 2020.
- Liang J. Z., Impact Fracture Toughness of Hollow Glass Bead-Filled Polypropylene Composites. *Journal of Materials Science* 42(3), 841-846, 2007a.
- Liang J. Z., Li R. K. Y., Mechanical Properties and Morphology of Glass Bead-Filled Polypropylene Composites. *Polymer Composites* 19(6), 698-703, 1998.
- Liang J. Z., Li R. K. Y., Rubber Toughening in Polypropylene: A Review. *Journal of Applied Polymer Science* 77(2), 409-417, 2000.
- Liang J. Z., Tensile and Flexural Properties of Hollow Glass Bead-Filled ABS Composites. *Journal of Elastomers and Plastics* 37(4), 361-370, 2005.
- Liang J. Z., Tensile Properties of Hollow Glass Bead-Filled Polypropylene Composites. *Journal of Applied Polymer Science* 104(3), 1697-1701, 2007b.
- Liang J. Z., Wu C. B., Effects of the Glass Bead Content and the surface treatment on the Mechanical Properties of Polypropylene Composites. *Journal of Applied Polymer Science* 123(5), 3054-3063, 2012.
- Lim J. W., Hassan A., Rahmat A. R., Wahit M. U., Phase Morphology and Mechanical Properties of Rubber-Toughened Polypropylene Nanocomposites: Effect of Elastomer Polarity. *Polymer - Plastics Technology and Engineering* 47(4), 411-419, 2008.
- Lim J. W., Hassan A., Rahmat A. R., Wahit M. U., Rubber-Toughened Polypropylene Nanocomposite: Effect of Polyethylene Octene Copolymer on Mechanical Properties and Phase Morphology. *Journal of Applied Polymer Science* 99(6), 3441-3450, 2006.
- Liu G., Qiu G., Study on the Mechanical and Morphological Properties of Toughened Polypropylene Blends for Automobile Bumpers. *Polymer Bulletin* 70(3), 849-857, 2013.
- Lotti C., Correa C. A., Canevarolo S. V., Mechanical and Morphological Characterization of Polypropylene Toughened with Olefinic Elastomer. *Materials Research* 3(2), 37-44, 2000.
- Mao H., Cheng Y., Guo W., Meng Z., Wei W., Hua L., Yang Q., Effect of POE on Mechanical Properties and Cellular Structure of PP/Nano-CaCO<sub>3</sub>composites in IMD/MIM Process. *Materials Research Express* 7(9), 095308, 2020.
- Müller M., Mechanical Properties of Resin Reinforced with Glass Beads. *Agronomy Research* 15(S1), 1107-1118, 2017.
- Purowski T., Dzierzanowski P., Bulska E., Wagner B., Nowak A., A study of glass beads from the Hallstatt C–D from southwestern Poland: implications for glass technology and provenance. *Archaeometry* 54(1), 44-166, 2012.
- Shi L., Xiao J. M. The Toughening Mechanism of Rubber Particles in Polypropylene Composite. *IOP Conference Series: Materials Science and Engineering* 164, 012027, 2017.
- Tang C. Y., Liang J. Z., Yung K. C., Li R. K. Y., Tjong S. C., Mechanical Properties of Glass Beads Filled Polypropylene Composites. *Key Engineering Materials* 149, 823-828, 1998.
- Tjong S. C., Xu S. A., Ternary Polymer Composites: PA6,6/maleated SEBS/Glass Beads. *Journal of Applied Polymer Science* 81(13), 3231-3237, 2001.
- Unal H., Morphology and Mechanical Properties of Composites based on Polyamide 6 and Mineral Additives. *Materials & Design* 25(6), 483-487, 2004.
- Wahit M. U., Hassan A., Mohd Ishak Z. A., Czigany T., Ethylene-Octene Copolymer (POE) Toughened Polyamide 6/Polypropylene Nanocomposites: Effect of POE Maleation. *Express Polymer Letters* 3(5), 309-319, 2009.

- Wang X., Hu S., Guo Y., Li G., Xu R. Toughened High-Flow Polypropylene with Polyolefin-Based Elastomers. *Polymers* 11(12), 1-16, 2019.
- Whiteley K. S., Heggs T. G., Koch H., Mawer R. L., Immel W., Polyolefins. *Ullmann's Encyclopedia of Industrial Chemistry*. A21\_487, 2000.
- Wu J. H., Chen C. W., Wu Y. T., Wu G. T., Kuo M. C., Tsai Y., Mechanical Properties, Morphology, and Crystallization Behavior of Polypropylene/Elastomer/Talc Composites. *Polymer Composites* 36(1), 69-77, 2015.
- Yang W., Shi W., Li Z. M., Xie B. H., Feng J. M., Yang M. B., Mechanical Properties of Glass Bead-filled Linear Low-Density Polyethylene. *Journal of Elastomers and Plastics* 36(3), 251-265, 2004.