

Effect of compatibilizing agents on rice-husk flour reinforced polypropylene composites

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Abstract

The effect of compatibilizing agents on mechanical properties and morphology of a lignocellulosic material-thermoplastic polymer composite was examined. Using rice-husk flour as the reinforcing filler and polypropylene as the thermoplastic matrix polymer, a particle-reinforced composite was prepared, and its mechanical and morphological properties examined as a function of the amount of compatibilizing agent used. In the sample preparation, four levels of filler loading (10, 20, 30 and 40 wt%) and three levels of compatibilizing agent content (1, 3 and 5 wt%) were used, and in the tensile test, six test temperatures (−30, 0, 20, 50, 80 and 110 °C) and five crosshead speeds (2, 10, 100, 500 and 1500 mm/min) were used. The tensile strengths of the composites decreased as the filler loading increased, but the tensile properties were significantly improved with the addition of the compatibilizing agent. Both the notched and unnotched Izod impact strengths were almost the same with the addition of compatibilizing agent. A morphological study revealed that the positive effect of compatibilizing agent on interfacial bonding.

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1. Introduction

The need for materials having specific characteristics for specific purposes, while at the same time being non-toxic and environmentally friendly, is increasing, due to a lack of resources and increasing environmental pollution. Studies are ongoing to find ways to use lignocellulosic materials in place of synthetic materials as reinforcing fillers. Thus, research on the development of composites prepared using various recycled materials is being actively pursued. Among the possible alterna-

tives, the development of composites using agro-wastes or lignocellulosic materials as reinforcing fillers and thermoplastic polymers as matrixes is currently at the center of attention. These composites would resolve environmental problems [4] and offer the possibility of producing products having a range of different physical properties and functions. In order to emulate the properties of various types of synthetic polymers and to improve the mechanical properties, fibrous reinforcing fillers and inorganic materials are combined with the matrix polymer. Studies are also under way on the possibility of using cellulosic or lignocellulosic materials as reinforcing fillers in place of synthetic fibers or inorganic materials. Since composites prepared using natural reinforcing fillers are inexpensive and could minimize

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environmental pollution due to their characteristic biodegradability [4], they could play a huge role in solving the environmental problems that we would otherwise have to face in the future. In this research, the thermoplastic polymer, polypropylene was used as the matrix polymer and the agro-waste, rice-husk flour was used as the reinforcing filler to prepare a particle-reinforced composite. Compared with talc, silica, glass fiber, carbon fiber and other synthetic fibers, these lignocellulosic materials could be used throughout the world and reproduced, offer superior quality with respect to their light weight [9], decreased wear in the machine used for their production, and are inexpensive. Furthermore, they are biodegradable [4] and do not leave residues or result in by-products that are toxic when combusted. Another benefit is the appropriate recycling of agro-wastes. However, the mechanical properties of these composites are somewhat lower than their synthetic counterparts due to the hydrophilic properties of lignocellulosic materials. Poor interfacial bonding between the lignocellulosic material and the hydrophobic matrix polymer causes the mechanical properties of the composites to be lowered. This problem can be alleviated by the use of compatibilizing agents (maleated polypropylene: MAPP). These compatibilizing agents become chemically linked with the hydrophilic lignocellulosic filler on one side, while facilitating the wetting of the hydrophobic polymer chain on the other side. In other words, they have dual characteristics in that they possess both the hydrophilic and hydrophobic properties needed for them to adhere well with the lignocellulosic filler and matrix polymer. The purpose of the current research was to examine the effect of the compatibilizing agent on the interfacial bonding between hydrophilic filler and hydrophobic matrix polymer. The mechanical and morphological properties of the composite were examined at different test conditions (crosshead speed, test temperature), while varying the filler loading and the amount of compatibilizing agent used.

2. Experimental

2.1. Materials

The rice-husk flour (RHF) used as reinforcing filler was supplied by Saron Filler Co., South Korea. The mean particle diameter was 209 μm . The chemical constituents of the rice-husk flour are shown in Table 1. The thermoplastic polymer polypropylene was supplied by Hanwha L&C Corp., South Korea, in the form of homopolymer pellets with a density of 0.91 g/cm^3 and a melt flow index of 12 $\text{g}/10 \text{ min}$ (230 $^\circ\text{C}/2160 \text{ g}$). The compatibilizing agents, maleated polypropylenes were obtained from Eastman Chemical Products, Inc.; Epolene E-43TM has an acid number of 45, and a molecular

Table 1

The chemical constituents of the lignocellulosic fillers

| | Holocellulose | Lignin | Ash | Others |
|------------------|---------------|--------|------|--------|
| RHF ^a | 59.9 | 20.6 | 13.2 | 6.5 |
| WF ^a | 62.5 | 26.2 | 0.4 | 10.9 |
| RHP ^b | 60 | 20 | 17 | 3 |

Values are percentages by weight.

^a Spec. from Saron Filler Co.

^b Rice-husk powder from [4].

weight (M_w) of 9100. Epolene G-3003TM has an acid number of 8, and a molecular weight of 103,500.

2.2. Sample preparation

RHF was oven-dried at 100 $^\circ\text{C}$ for 24 h to maintain less than 4 wt% moisture content and then stored over a desiccant in sealed containers. The polypropylene was blended with the RHF and the compatibilizing agent in a two-roll rheomixer. Mixing was performed at 200 $^\circ\text{C}$ for 15 min at a rotor speed of 20 rpm. A laboratory-size, single-screw extruder was employed to compound the RHF with the polypropylene, the latter being used as a matrix polymer. The extruded strand was pelletized and stored in sealed packs containing desiccant. Four levels of filler loading (10, 20, 30 and 40 wt%) and three levels of compatibilizing agent (MAPP) content (1, 3 and 5 wt%) were used in the sample preparation. Tensile and Izod impact test specimens were injection molded at 200 $^\circ\text{C}$, an injection pressure of 1200 psi, and a device pressure of 1500 psi. After molding, test specimens were conditioned at 23 ± 2 $^\circ\text{C}$, $50 \pm 5\%$ RH for at least 40 h according to ASTM D 618-99 [2].

2.3. Tensile test

Tensile tests were conducted according to ASTM D 638-99 [2] with a Universal Testing Machine (Zwick Co., NICEM at Seoul National University). The tests were performed at crosshead speeds of 2, 10, 100, 500 and 1500 mm/min, and temperatures of -30 , 0, 20, 50, 80 and 110 $^\circ\text{C}$ after 30 min in the chamber. Each value obtained represented the average of five samples.

2.4. Izod impact test

Notched and unnotched Izod impact tests were conducted according to ASTM D 256-97 [1] at room temperature. Each value obtained represented the average of five samples.

2.5. Morphology

Studies on the morphology of the tensile and Izod impact fracture surfaces of the composites were carried out

using a JSM-5410 LV scanning electron microscope (JEOL Co. Ltd., NICEM at Seoul National University).

3. Results and discussion

3.1. Effect of compatibilizing agents on tensile properties

According to the previous researches, the tensile strengths of the composites decreased with increasing filler loading [6–8,16], increased with increasing crosshead speed [15,16] and the tensile strength and modulus decreased with increasing test temperature [16]. The tensile strength decreased with increasing filler loading due to the poor interfacial bonding between hydrophilic filler and hydrophobic matrix polymer as shown in Fig. 1. This weak bonding between the hydrophilic filler and the hydrophobic matrix polymer causes decreased tensile strength. To improve the bonding strength between the filler and the matrix polymer, compatibilizing agents were used. With the addition of the compatibilizing agent, tensile strength of the composite significantly improved up to the same level of pure PP. The mechanism of compatibilizing agent is shown in Fig. 2. The compatibilizing agent chemically bonded with hydrophilic filler and blended by wetting in the polymer chain. The tensile strengths of the RHF (30 wt%)-PP composites at different compatibilizing agent (Epolene E-43™ and G-

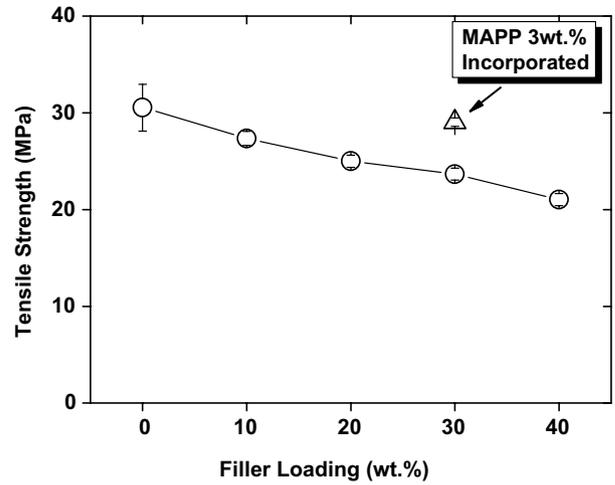


Fig. 1. The tensile strengths of the composites at various filler loadings.

3003™) contents, crosshead speeds and test temperatures are shown in Figs. 3 and 4, and the tensile strengths at different compatibilizing agents contents and temperatures are shown in Fig. 5. Each composite made with Epolene E-43™ and G-3003™ exhibited almost the same tensile properties. The tendency of the test results in relation to the crosshead speed and test temperature is the same as previous study [16]. The tensile strength improved with increasing compatibilizing agent content, which is in agreement with previous study [6]. Poor

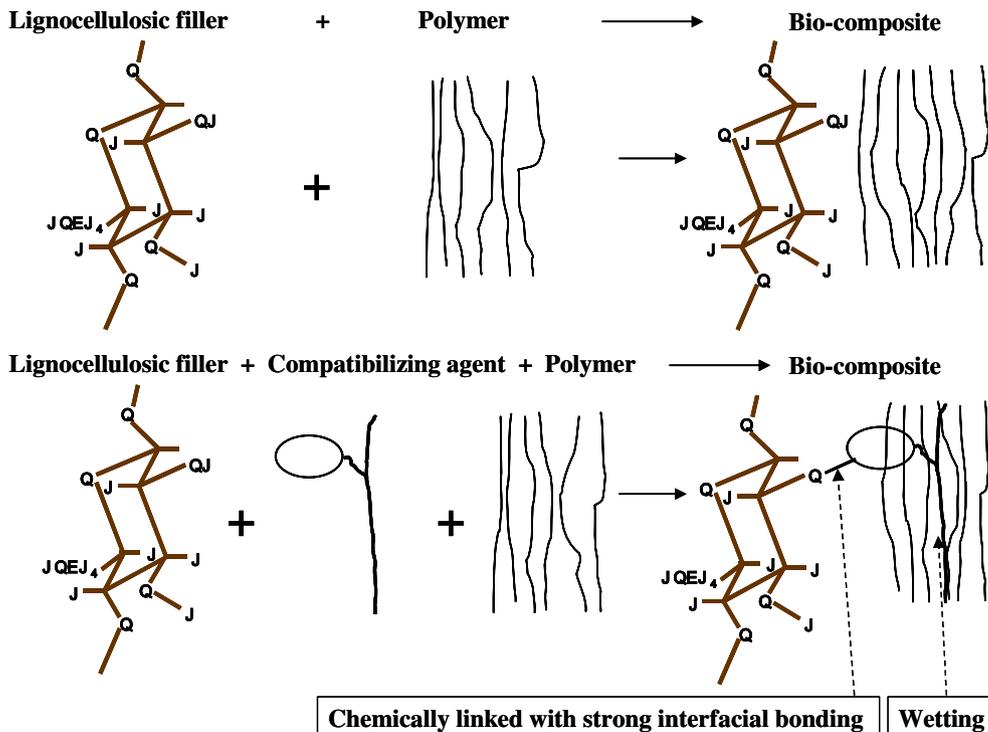


Fig. 2. Mechanism of compatibilizing agent between hydrophilic filler and hydrophobic matrix polymer.

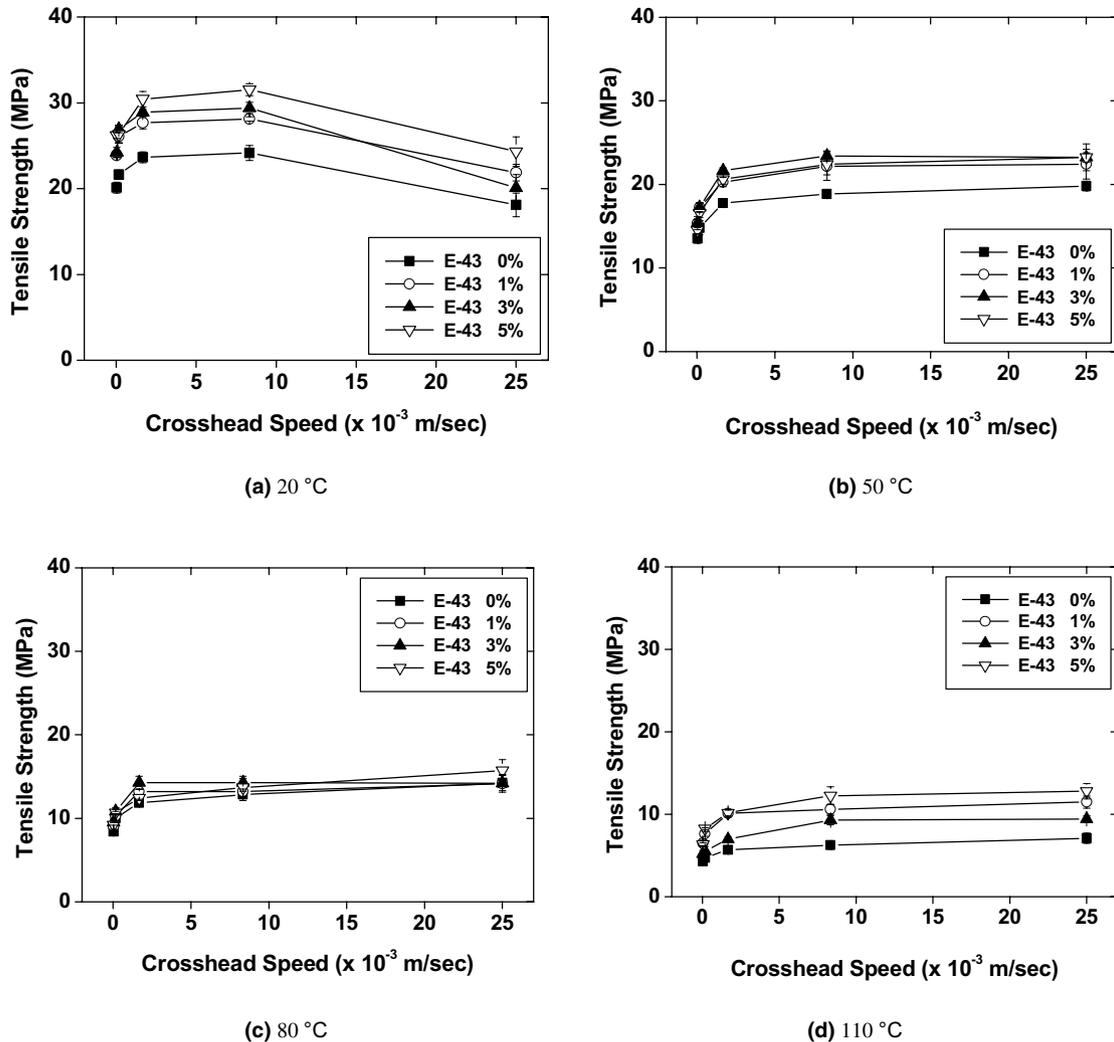


Fig. 3. The tensile strengths of the composites with compatibilizing agent (Epolene E-43TM) at various compatibilizing agent contents, crosshead speeds and test temperatures (30 wt% of filler loading).

interfacial bonding causes partially separated microspaces between the filler and the matrix polymer, which obstructs stress propagation, when tensile stress is applied, and induces decreased strength and increased brittleness but compatibilizing agent can solve this problem. Most effective content of compatibilizing agent is 3 wt% as shown in Fig. 5. At 5 wt% of compatibilizing agent content, the tensile strength is almost the same level as 3 wt%. The stress–strain curves of the composites with compatibilizing agent (Epolene E-43TM) at different compatibilizing agent contents and test temperatures are shown in Fig. 6. The tensile strength and modulus of the composite improved and the composite began to exhibit brittle fractures with increasing compatibilizing agent content at room temperature [4], due to the superior stress propagation. But this effect was lowered with increasing test temperature due to the increasing ductility of the matrix polymer, and shows plastic deformation as the test temperature increased. The improved

interfacial bonding between the filler and the matrix polymer resulted in good stress propagation and improved the tensile strength, but fractures arose at the filler, and these fractures were more brittle than those in the matrix polymer. The composite became more ductile as the test temperature increased, with this brittle property was gradually disappearing due to the composite exhibiting plastic deformation. The typical stress–strain curves of the composites according to compatibilizing agent content in the tensile test are shown in Fig. 7. As the compatibilizing agent content increased, the tensile strength and modulus both increased [7,13]. The tensile strength and modulus of the composite decreased as the test temperature increased. The tensile strengths at different test temperatures are shown in Fig. 8. The composite with 3 wt% compatibilizing agent (30 wt% filler loading) show almost the same strength level as pure PP. At the lower temperatures (–30 and 0 °C, the composites exhibited strong and brittle properties like glass,

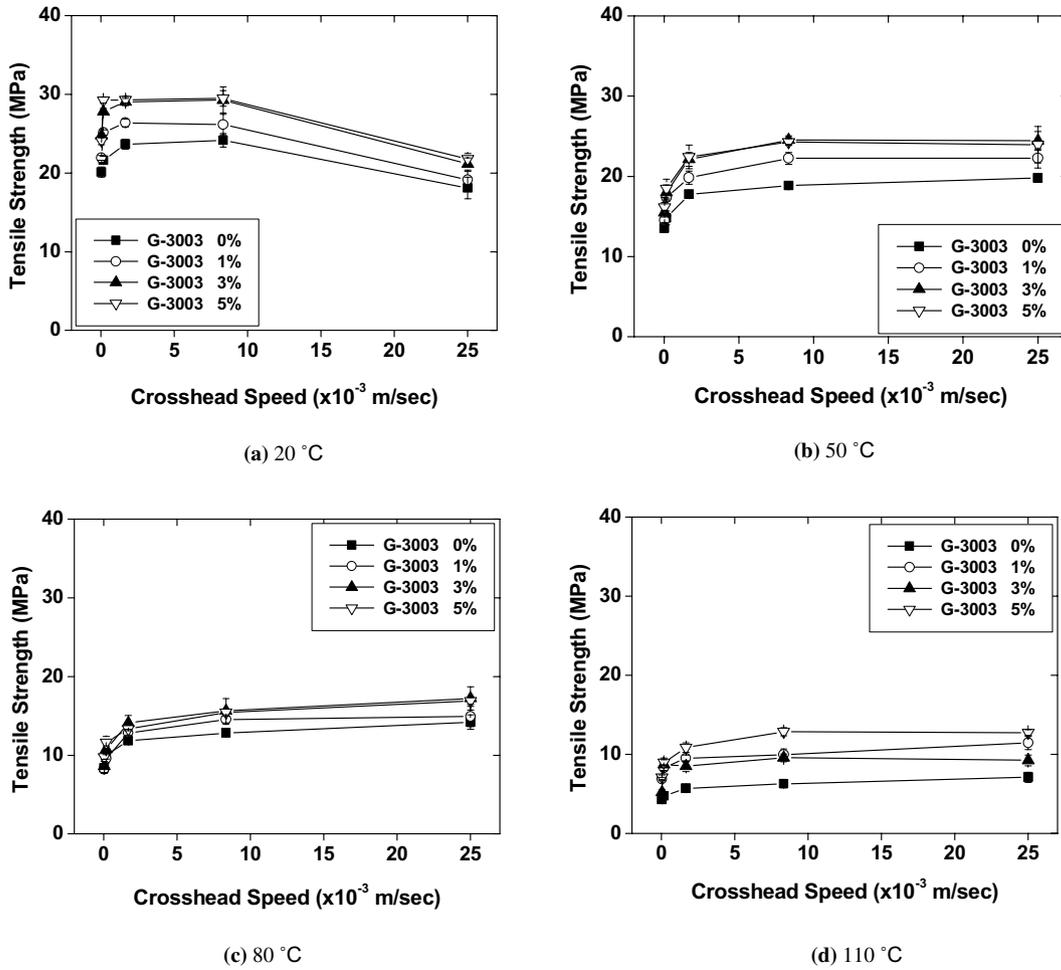


Fig. 4. The tensile strengths of the composites with compatibilizing agent (Epolene G-3003™) at various compatibilizing agent contents, crosshead speeds and test temperatures (30 wt% of filler loading).

but the tensile strength drastically decreased as the test temperature was increased from 0 to 20 °C due to the glass transition temperature of the matrix polymer (polypropylene) lying in this temperature range [10]. The matrix polymer became more ductile and softened as the test temperature increased, which is the same tendency as that seen in the composites made without any compatibilizing agent [16]. The stress–strain curves of the composites with compatibilizing agents at different test temperatures are shown in Fig. 9. As the test temperature increased, both the tensile strength and modulus decreased, with the composite gradually beginning to exhibit plastic deformation. This is the same tendency as that exhibited by the composites made without any compatibilizing agent [16].

3.2. Izod impact strength

The Izod impact tests were conducted at room temperature. The notched and unnotched specimens were tested and Fig. 10 shows the Izod impact strengths of

the composites at different compatibilizing agent contents. The Izod impact strength of the composites decreased as the filler content increased [3]. The poor interfacial bonding between the filler and the matrix polymer causes micro-cracks to occur at the point of impact, which cause the cracks to easily propagate in the composite without any compatibilizing agent [16]. These micro-cracks cause decreased impact strength of the composites. The notched specimens exhibited lower impact strength than the unnotched specimens. The notched tip is the stress concentrating point when impact occurs, and the easy propagation of the crack results in there being relatively low impact strength in the notched sample [16]. In the case of the unnotched specimen, the filler–matrix interface is the stress concentrating point and crack propagation begins at micro-cracks in the composite. The unnotched specimen made with 100 wt% of polypropylene exhibited significantly higher impact strength than the specimen made with 10 wt% of filler loading. The unnotched Izod impact energies were considerably larger than the notched Izod

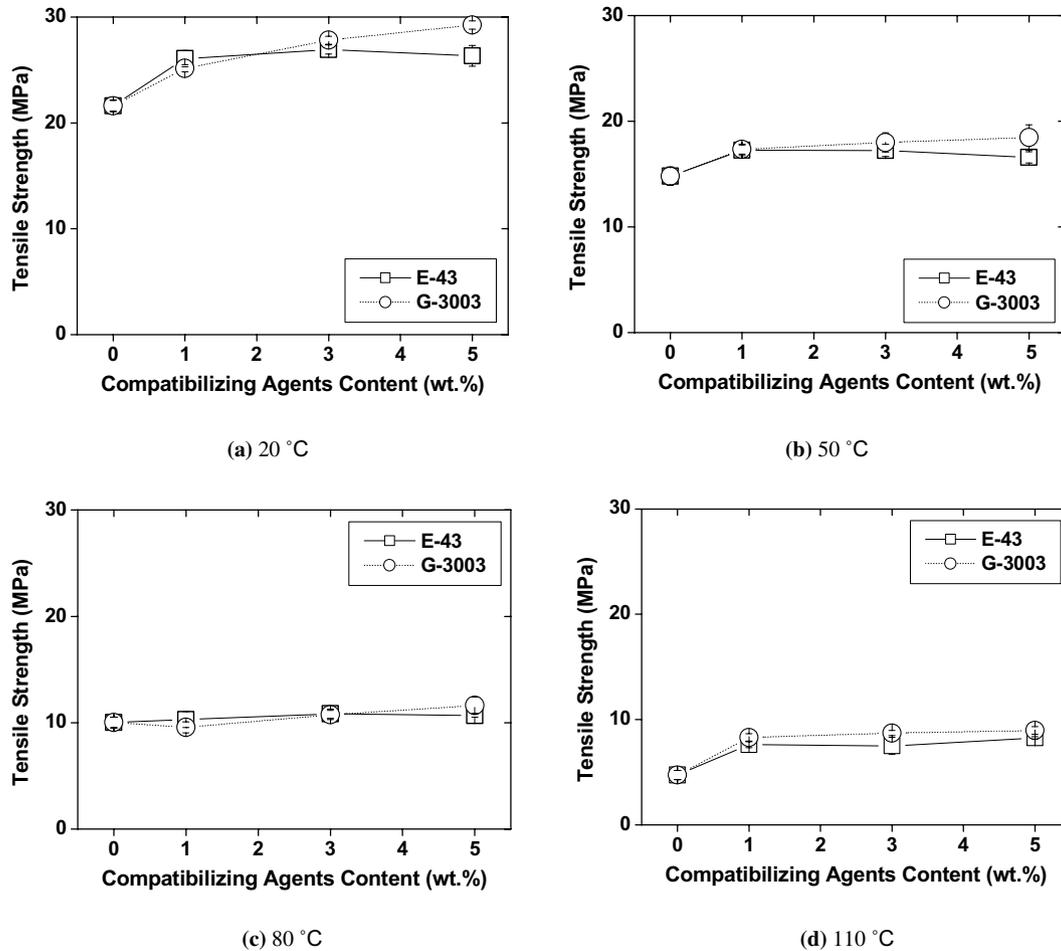


Fig. 5. The tensile strengths of the composites at various compatibilizing agent contents and test temperatures (crosshead speed: 10 mm/min).

impact energies, and this is due to the different fracture processes involved in the notched and unnotched samples. The unnotched impact behavior is controlled to a considerable extent by fracture initiation processes that, in turn, are controlled by stress concentrations at defects in the system. Notched impact behavior is controlled to a greater extent by factors affecting the propagation of fractures initiated at the predominating stress concentration at the notched tip. In other words, the unnotched Izod impact energies are not only a measure of crack propagation, but also of crack initiation [3,12]. In the case of the notched specimen made with 100 wt% of PP with the notched tip, the crack is initiated at the impact occurrence, but the unnotched specimen has no such defect and therefore shows significantly higher impact strength. The addition of the filler leads to the creation of an interface between the filler and the matrix polymer, which then constitutes the stress concentrating and crack initiating point, and this causes significantly reduced impact strength in the unnotched specimen [16].

As the compatibilizing agent content increased, the impact strength of the composite slightly decreased

[13,14] and the compatibilizing agent had no effect on the impact strength. With the addition of the compatibilizing agent, the interfacial bonding between the filler and the matrix polymer was highly improved, thus the crack was not initiated at the interface, but at the filler itself, when the impact occurred. The filler is more brittle than the matrix polymer, and this causes decreased impact strength in the composite. Traces where the filler was pulled-out in the composite without any compatibilizing agent were seen at the impact fracture surface of the specimen, and this means that the impact was absorbed by filler being pulled-out. However, there is no trace where the filler was pulled-out in the impact fracture surface of the composite with compatibilizing agent, and fractured filler can be seen in the SEM micrographs.

3.3. Morphological characteristics

The tensile fracture surfaces of the composites at different filler loadings with compatibilizing agent are shown in Fig. 11. In the case of the composite without any compatibilizing agent at 20 wt% of filler loading,

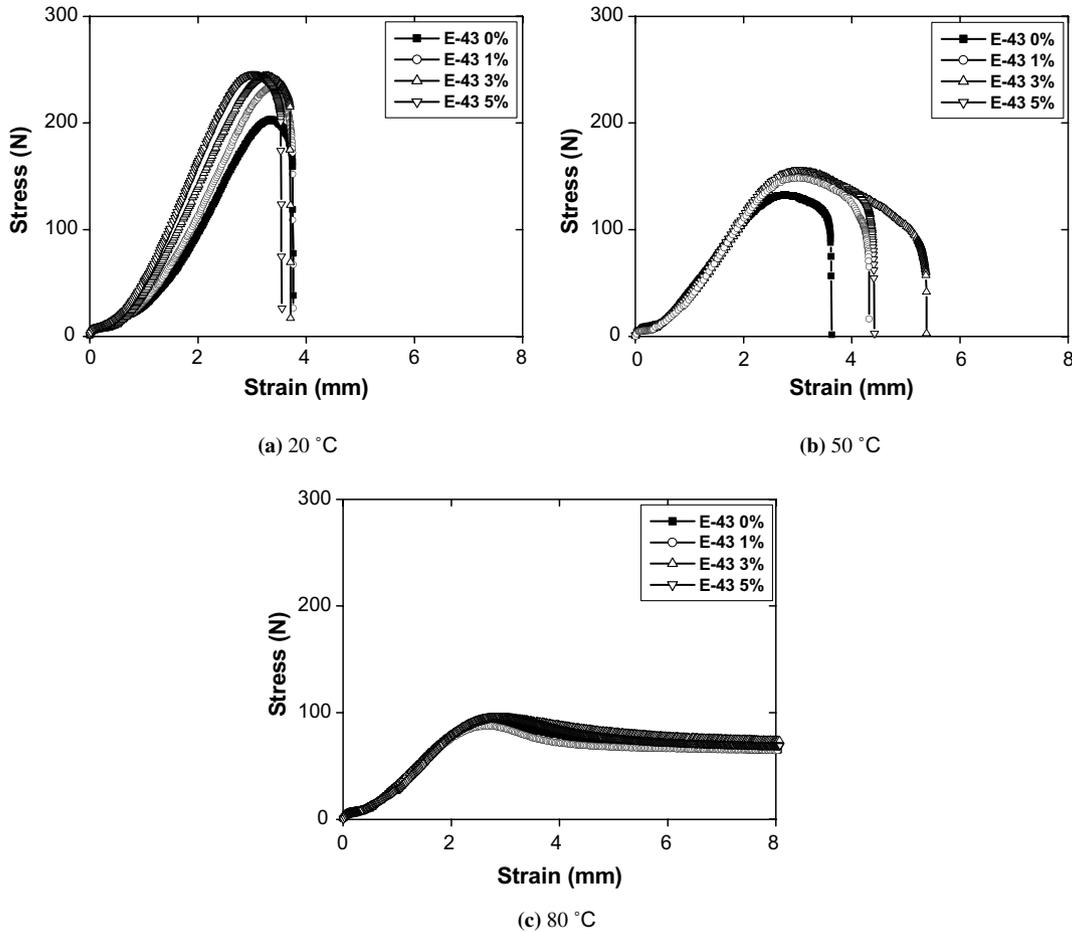


Fig. 6. The stress–strain curves of the composites with compatibilizing agent (Epolene E-43™) at various compatibilizing agent contents and test temperatures (crosshead speed: 10 mm/min and filler loading: 30 wt%).

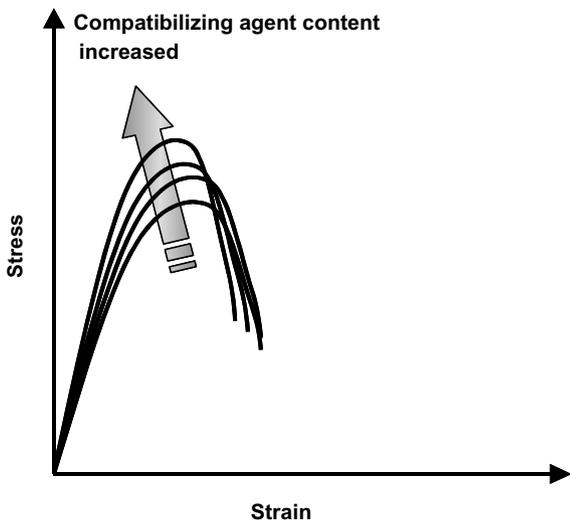


Fig. 7. The typical stress–strain curves of the composites according to compatibilizing agent contents.

few filler particles are to be seen at the tensile fracture surfaces, with the main component being matrix poly-

mer, and some cavities are to be seen where the filler has been pulled-out. The presence of these cavities means that the interfacial bonding between the filler and the matrix polymer is poor and weak. At 40 wt% of filler loading, filler particles become the main component and some traces are to be seen where the filler has been pulled-out. As the filler content increases, the poorly bonded interfaces and the brittleness of the filler affect the tensile property (decreased strength and increased modulus). The filler itself is not fractured in the micrographs of the composite made without any compatibilizing agent. In the case of the composite made with compatibilizing agent, the interfacial bonding between the filler and the matrix polymer is strong, and the fracture occurred not at the interface but at the filler itself. This characteristic of the composite with compatibilizing agent causes brittle deformation of the composite when tensile stress is applied. Improved interfacial bonding leads to improved tensile property, which is reflected in the increased strength and modulus of the composite made with compatibilizing agent. Few traces where filler particles have been pulled-out are to be seen,

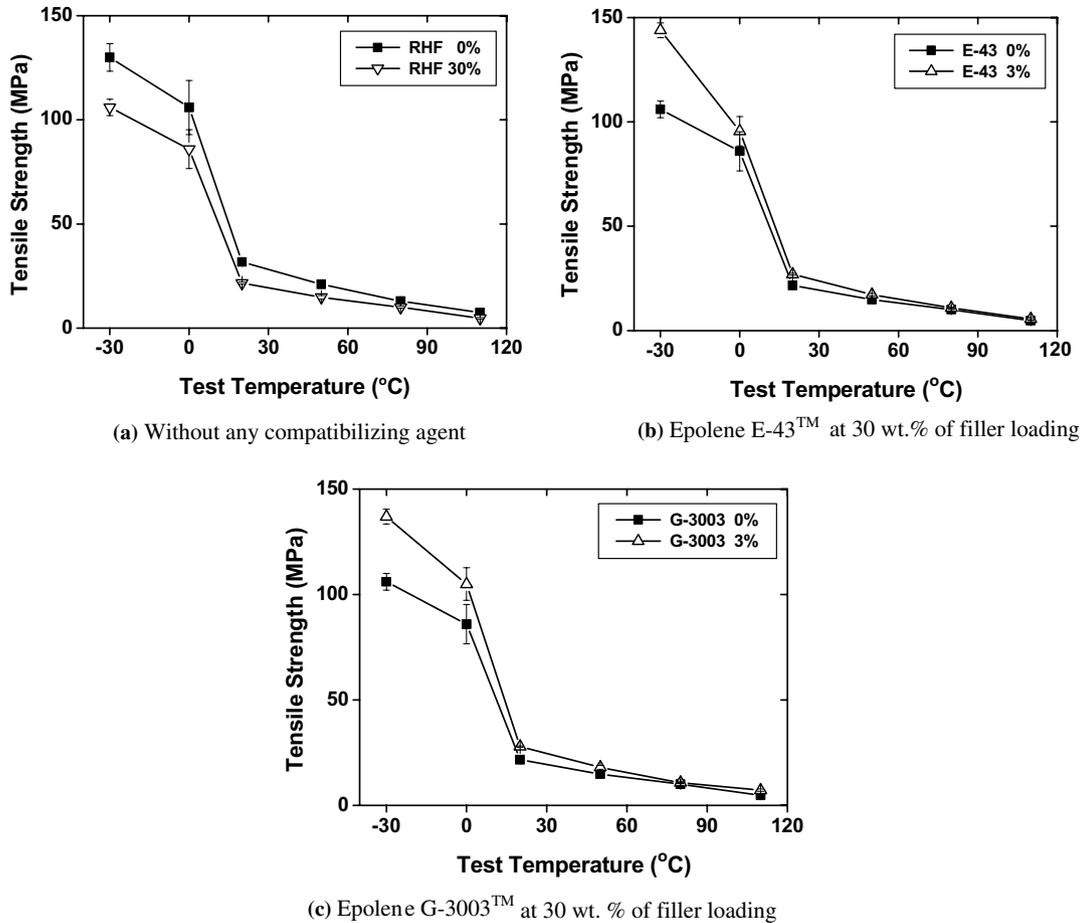


Fig. 8. The tensile strengths of the composites at various test temperatures, filler loadings and compatibilizing agent contents (crosshead speed: 10 mm/min).

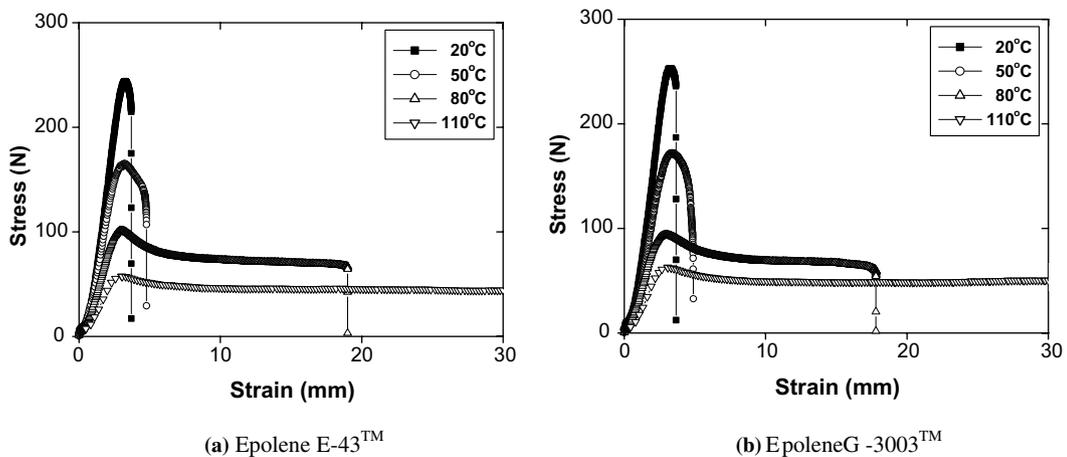


Fig. 9. The stress–strain curves of the composites with compatibilizing agent at various test temperatures (crosshead speed: 10 mm/min, filler loading: 30 wt% and compatibilizing agent content: 3 wt%).

while fractured filler particles are to be seen, in all of the micrographs of the composites containing either Epolene E-43™ or G-3003™.

Fig. 12 shows the notched and unnotched Izod impact fracture surfaces of the composites at the notched tip with 30 wt% of filler loading. The SEM micrographs

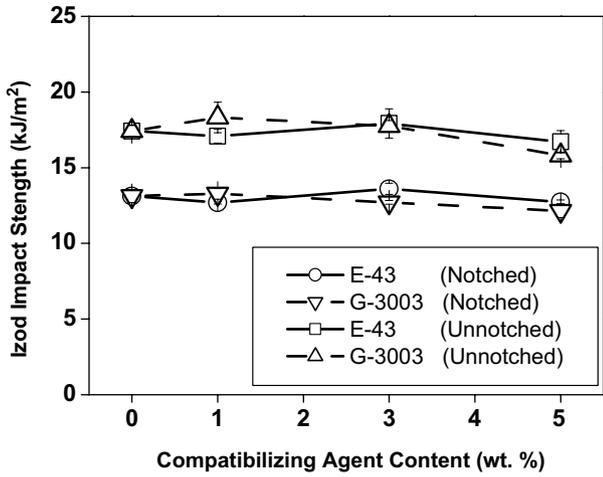


Fig. 10. Izod impact strengths of the composites at various compatibilizing agent contents (30 wt% of filler loading).

of the notched samples show clearly fractured surfaces at the notched tip which, as the stress concentrating point, causes easy propagation of the crack when impact

occurs. The unnotched sample without any compatibilizing agent shows irregularly fractured surfaces, representing the interfacial area between the filler and the matrix polymer. Pulled-out traces of filler particles are to be seen in both the notched and unnotched samples made without any compatibilizing agent, and this is due to the weak bonding between the filler and the matrix polymer. In the case of the unnotched sample with compatibilizing agent, the crack was initiated not at the filler–matrix interface, but rather involved the filler particles themselves, due to the strong bonding between the filler and the matrix polymer. Fractured filler particles are to be seen in the corresponding micrographs, demonstrating the increased brittleness of the composite, and leading to decreased impact strength. The micrograph of the notched sample also shows fractured filler particles and shows the same tendency (increased brittleness and decreased impact strength). Few pulled-out traces of filler particles are to be seen in the micrographs of the composite with compatibilizing agent, and this is due to the strong interfacial bonding between the filler and the matrix polymer.

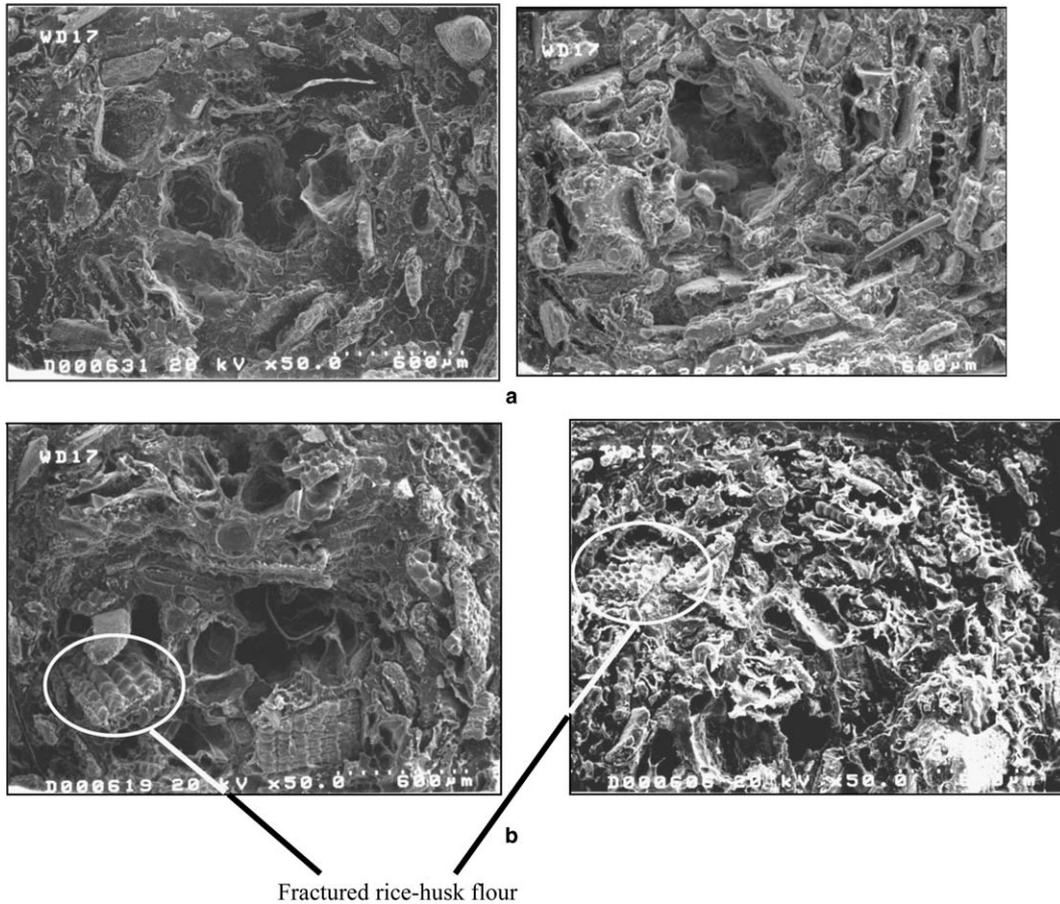


Fig. 11. SEM micrographs of the tensile fracture surfaces at various filler loadings with compatibilizing agent (magnification of $\times 50$). (a) 20 wt% (left) and 40 wt% (right) of filler loading (without compatibilizing agent); (b) 3 wt% of Epolene E-43™ (left) and G-3003™ (right) content (30 wt% of filler loading).

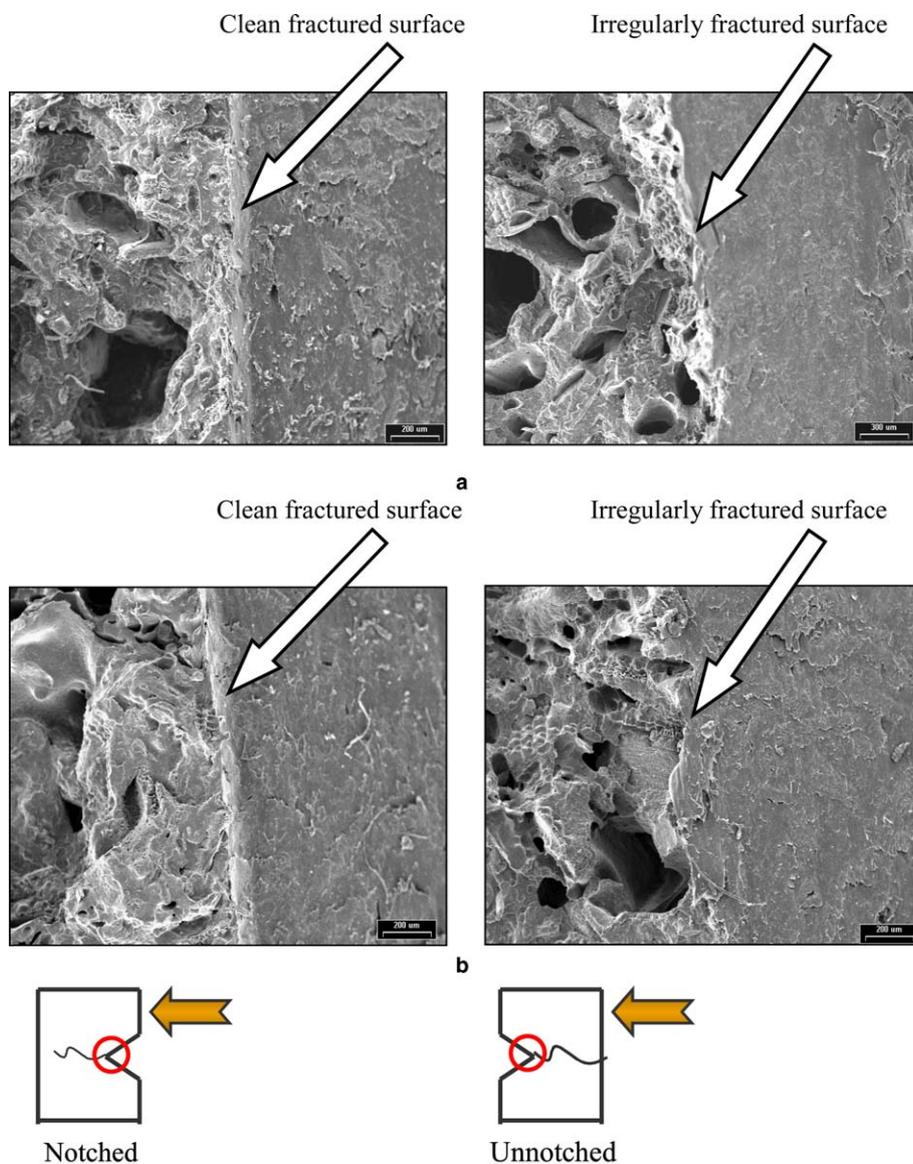


Fig. 12. SEM micrographs of the Izod impact fracture surfaces with and without compatibilizing agent at 30 wt% of filler loading. (a) Notched (left) and unnotched (right) sample without any compatibilizing agent; (b) notched (left) and unnotched (right) sample with 3 wt% of Epolene G-30003™.

4. Conclusion

As the filler loading increased, the composite made without any compatibilizing agent showed decreased tensile strength and more brittleness, but the mechanical properties greatly improved by incorporating the compatibilizing agent. The poor interfacial bonding between the filler and the matrix polymer causes the composites to have decreased tensile strengths, but the tensile strength and modulus were improved with the addition of compatibilizing agent. The compatibilizing agent had no positive effect on Izod impact strength. This is due to the strong bonding between the filler and the matrix polymer. As the test temperature increased, the thermoplastic matrix polymer was softened and the composite showed plastic matrix deformation, leading

to decreased tensile strength and modulus. As the filler loading increased, more filler particles or traces of pulled-out filler particles were to be seen, while the fractured filler particles were observed in samples with compatibilizing agents using a scanning electron microscope. Due to the strong interfacial bonding between the filler and the matrix polymer, the fracture occurred not at the interface, but at the filler particles themselves, and the composite showed more brittleness in terms of its tensile and impact properties.

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