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Effect of different compatibilizing agents on the mechanical properties of lignocellulosic material filled polyethylene bio-composites

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Abstract

The tensile and Izod impact strength properties of lignocellulosic filler reinforced polyethylene bio-composites, made using low- and high-density polyethylene as the matrix polymer, rice-husk flour and wood flour as the reinforcing filler and different compatibilizing agents, were examined by assessing their mechanical properties and the morphological characteristics of their fracture surfaces. Test samples made with two different compatibilizing agents were injection molded, in order to determine their mechanical and morphological properties. The tensile strengths of the bio-composites fabricated using maleated polyethylene as the compatibilizing agent were superior to those of the bio-composites fabricated using maleated polypropylene, due to the improved wetting of the former compatibilizing agent in the matrix polymer. Based on the results of the Izod impact strength tests, the bio-composites fabricated using maleated polyethylene as the compatibilizing agent were also toughened. The SEM micrographs revealed a certain number of pulled-out traces on the fracture surfaces of the test samples fabricated using maleated polypropylene as the compatibilizing agent, but no pulled-out traces and many broken fillers on the fracture surfaces of the test samples fabricated using maleated polyethylene as the compatibilizing agent, due to the stronger interfacial bonding.

Keywords: Mechanical properties; Morphological characteristics; Compatibilizing agents; Maleated polyethylene; Maleated polypropylene

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1. Introduction

Wood–plastic composites (WPCs) are a new type of material used for house-wares, car interior (dashboards and rigid panel components) and various construction materials. They combine the favorable performance and low cost attributes of wood and plastics. In recent years, their utilization has developed rapidly, especially in Europe, the US and Canada.

The convenience of these composites lies in the fact that one of their ingredients (i.e. wood/lignocellulosic material) can be easily obtained from natural resources and they can be made relatively easily [1]. They offer the possibility of resolving various environmental problems and fabricating products with a variety of physical properties and effective functions. The greater use of plastics and lignocellulosic materials would contribute to the conservation of the limited wood based resources. The substitution of the inorganic substances and synthetic fibers generally used as reinforcing fillers in plastics by lignocellulosic materials would be highly beneficial from the point of view of environmental protection. The benefits offered by lignocellulosic materials include making the final product lighter and decreasing the wear of the machinery used in the production process. Moreover, lignocellulosic materials have the advantages of low cost, biodegradability, and the absence of residues or toxic byproducts, whereas inorganic materials such as glass fiber, carbon fiber, talc, clay, synthetic fiber, etc. do not have these benefits [1–3]. Yet another attraction of using these materials is the fact that it would allow various agro-wastes to be appropriately

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recycled. As a result, composites using lignocellulosic materials as reinforcing fillers have come to be used extensively in the automotive industry and as interior finishing materials, such as window frames and wood decks. More recently, their utilization has been extended to such areas as flooring, instrument grips, and pallets.

However, the most important issue associated with these composites is the interfacial adhesion between the natural reinforcing fillers and matrix polymers. In order to obtain good properties by improving the compatibility between these two materials with their different properties, reinforcing fillers are used after chemical modification. In other words, chemical modification is performed to overcome the incompatibility between the hydrophilic lignocellulosic material and the hydrophobic matrix polymer. Extensive studies are currently being performed on polyolefins (polypropylene and polyethylene) and various natural reinforcing fillers, in conjunction with various chemicals that could affect the interface [4–7]. The compatibility problem may be due to the fact that the polyolefin is non-polar and hydrophobic, whereas the natural polymer, which is a lignocellulosic material, is polar, due to the –OH groups in the cellulose. This results in poor adhesion and prevents the reinforcing filler from acting effectively within the composite. In order to solve these problems, studies have been performed on surface modification or treatment using a compatibilizing agent for the purpose of making the polyolefin chain hydrophilic [6,8]. The strong interfacial bonding strength obtained by improving the compatibility between the hydrophilic filler and hydrophobic matrix polymer can improve the physical, mechanical and thermal properties of the composite system [1,3–10].

Low-density polyethylene (LDPE) and high-density polyethylene (HDPE) are important thermoplastics due to their having a good combination of properties, such as fluidity, flexibility, transparency and a glossy surface in the case of LDPE and toughness, stiffness, solvent resistance and electrical insulation in the case of HDPE, with the result that LDPE is used as a food packing material, sheet and film, while HDPE is used as an insulating material for electric wire, for producing various types of containers, etc.

Lignocellulosic filler–thermoplastic polymer composites have various benefits and good properties, but their mechanical properties decrease slightly as the filler content is increased [2,3]. The interface compatibility between lignocellulosic fillers and thermoplastic polymers in WPCs is a key problem, but it can be alleviated by the incorporation of compatibilizing agents. For example, maleic anhydride grafted co-polymers, such as maleated polypropylene has been widely used as compatibilizing agents to improve the properties of the polymer composites. Maleated polypropylene has traditionally been used as a compatibilizing agent for various polymeric composites which are filled with lignocellulosic materials, however, when polyethylene composites need to be reinforced, maleated polypropylenes are not recommended, because of the incompatibility between polyethylene and polypropylene [4]. Thus, the use of maleated polyethylene which contains ethylene blocks is a better choice [5].

In this work, we investigate the effect of two different compatibilizing agents, maleated polypropylene and maleated polyethylene, on the properties of lignocellulosic filler-polyethylene (LDPE and HDPE) composites.

2. Experimental procedure

2.1. Materials

2.1.1. Matrix polymer

The thermoplastic polymer, low-density polyethylene (LDPE), was supplied by LG Chem., Ltd., S. Korea, in the form of homopolymer pellets with a density of 0.918 g/cm^3 and a melt flow index of 24 g/10 min (230 °C/2, 160 g). The high-density polyethylene (HDPE) was also supplied by LG Chem., Ltd., in the form of homopolymer pellets with a density of 0.957 g/cm^3 and a melt flow index of 15 g/10 min (230 °C/2, 160 g).

2.1.2. Reinforcing filler

The lignocellulosic materials used as the reinforcing filler in the composite, in order to obtain the comparative data, were rice-husk flour (RHF) and wood flour (WF), with particle sizes of 80–100 mesh. The RHF and WF were both supplied by Saron Filler Co., S. Korea. The chemical constituents of the fillers are shown in Table 1.

2.1.3. Compatibilizing agents

The compatibilizing agent, maleated polypropylene (MAPP), was obtained from Eastman Chemical Products, Inc., in the form of Epolene G-3003™. The other compatibilizing agent, maleated polyethylene, (MAPE) was obtained from Uniroyal Chemical, Inc., in the form of Polybond-3009™.

2.2. Sample preparation

The reinforcing fillers, RHF and WF, were oven dried to 1–3% moisture content using an air dryer oven at 100 °C for 24 h and then stored over a desiccant in sealed containers in an environmental controller prior to compounding. The matrix polymers, LDPE and HDPE, were blended with the lignocellulosic fillers and the compatibilizing

Table 1
Chemical constituents of the lignocellulosic fillers (rice-husk flour and wood flour)

	Holocellulose	Lignin	Ash	Others
RHF[a]	59.9	20.6	13.2	6.5
WF[a]	62.5	26.2	0.4	10.9

Values are percentage by weight.
[a] Spec. from Saron Filler Co.

agents, MAPP and MAPE. A laboratory-scale twin-screw extruder was employed to compound the RHF and WF with the polyethylene, the latter being used as a matrix polymer, using three general processes; melt blending, extrusion and pelletizing. Compounding was performed at 140 °C for LDPE and 200 °C for HDPE for 3 min with a screw speed of 300 rpm. The extruded strand was quenched in a water bath and then pelletized and stored in sealed packs containing a desiccant to avoid unexpected moisture infiltration after being oven dried for 24 h at 70 °C. Five levels of filler loading (10, 20, 30, 40 and 60 wt.%) and a fixed amount (3 wt.%) of the two different types of compatibilizing agent (MAPP and MAPE) were used in the sample preparation because it was the best recommended amount in our previous research [11].

The LDPE and HDPE specimens used for the tensile and Izod Impact tests were injection molded at 140 and 200 °C, respectively, using an injection pressure of 1200 psi and a device pressure of 1500 psi. After being molded, the test specimens were conditioned before testing at 23 ± 2 °C and 50 ± 5% RH for at least 40 h according to ASTM D 618-99 [12].

2.3. Tensile test

The tensile tests were conducted according to ASTM D 638-99 [12] with a Universal Testing Machine (Instron Co.). The tests were performed at a crosshead speed of 100 mm/min and at room temperature. Each value obtained represented the average of five samples.

2.4. Izod impact test

The notched and unnotched Izod impact strength tests were conducted according to ASTM D 256-97 [13] 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 (JEOL Co. Ltd.) scanning electron microscope. All samples were sputtered with gold before the microscopic observations were obtained.

3. Results and discussion

3.1. Tensile properties with different compatibilizing agents

The tensile strengths of the composites made of lignocellulosic filler-polyethylene (LDPE and HDPE) are shown in Fig. 1(a) as a function of the filler loading and the compatibilizing agent. The tensile strengths of the composites decreased with increasing filler loading, due to the poor interfacial bonding and the presence of agglomerate fillers, which is the same tendency as that reported in a previous study [2]. The weak bonding between the hydrophilic lignocellulosic filler and the hydrophobic matrix polymer obstructs the stress propagation, and causes the tensile strength to decrease as the filler loading increases [2]. Pure LDPE is too flexible and weak, with the result that increasing brittleness and stiffness were observed with increasing lignocellulosic filler loading. To improve the interfacial bonding strength between the filler and the matrix polymer, compatibilizing agents were used, viz. maleated polypropylene (MAPP) and maleated polyethylene (MAPE). The tensile strengths of the 30-wt.% lignocellulosic filler filled polyethylene composites at a compatibilizing agent (MAPP and MAPE) content of 3 wt.% are also shown in Fig. 1(b). Each composite made with MAPP and MAPE exhibited different tensile properties. The tensile strength and modulus improved following the incorporation of the compatibilizing agents. The force-displacement curves of the rice-husk flour filled LDPE composites as a function of the filler loading and compatibilizing agent are shown in Figs. 2 and 3. The tensile modulus of the composite improved as shown in Fig. 2, and the tensile strength and modulus of the composite containing maleated polyethylene was superior to that of the composite containing maleated polypropylene, due to the better stress propagation of the former which is caused by the improved compatibility and wetting

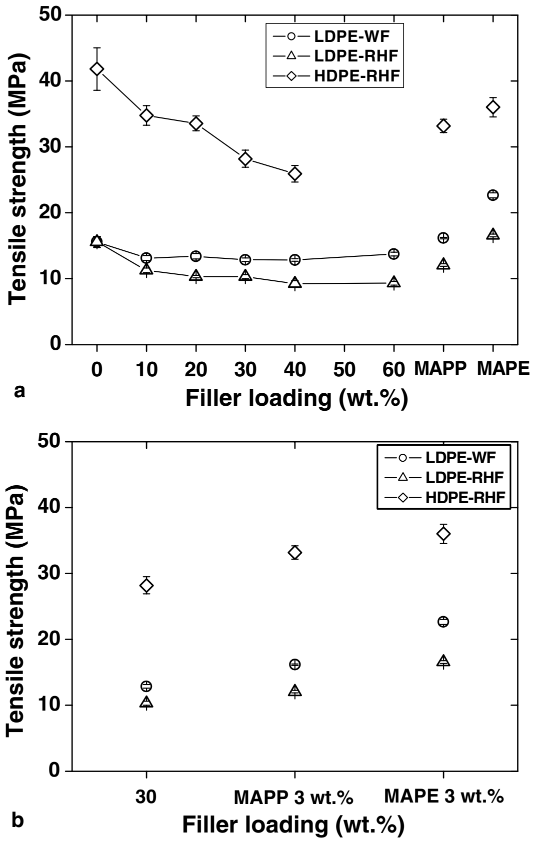

Fig. 1. Tensile strengths of the lignocellulosic filler-polyethylene composites at various filler loadings and for the two different compatibilizing agents: (a) tensile strength as a function of the filler loading; (b) tensile strength with different compatibilizing agents (30 wt.% of filler loading).

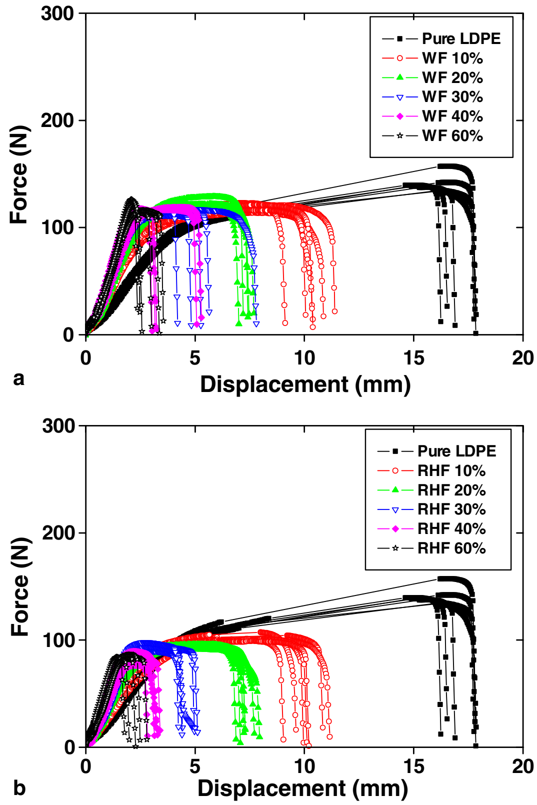

Fig. 2. Force-displacement curves of the LDPE composites at various filler loadings: (a) WF–LDPE composites; (b) RHF–LDPE composites.

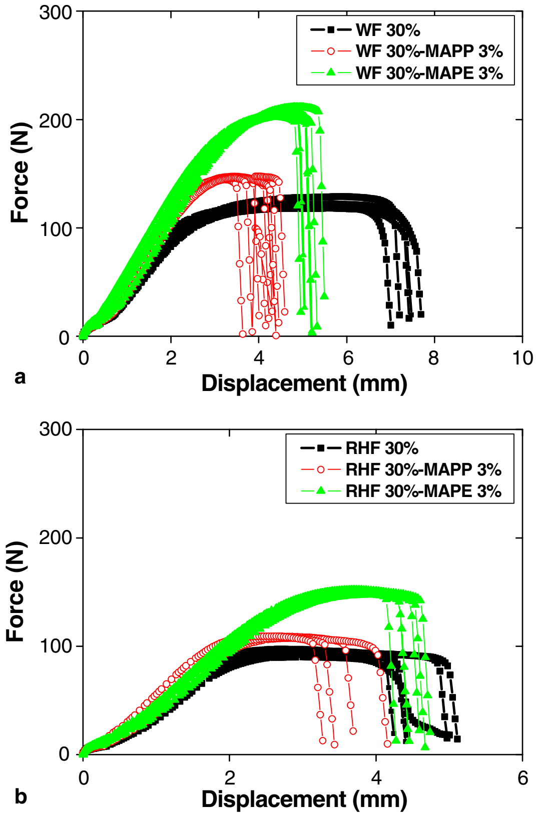

Fig. 3. Force-displacement curves of the LDPE composites with the two different compatibilizing agents: (a) WF–LDPE composite; (b) RHF–LDPE composite.

to the matrix polymer, as shown in Fig. 3. MAPP appeared less effective when the PE matrix polymer was used in the composites, because of the incompatibility between the PP backbone of MAPP and the PE matrix polymer in the composites [6] as shown in Fig. 4.

These compatibilizing agents have a positive effect on the tensile properties, because they strengthen the interfacial bonding between the filler and the matrix polymer [2,14]. In addition, the tensile strength and modulus of the MAPE incorporated composites were improved as compared with those of the MAPP incorporated composites, due to the better wetting of MAPE to the polyethylene matrix polymer [4]. This improved interfacial bonding between the filler and the matrix polymer resulted in good stress propagation and improved the tensile strength [8], but fractures arose at the filler, and these fractures were more brittle than those in the matrix polymer. The WF–LDPE composite shows a higher strength and modulus than the RHF–LDPE composite, because of the higher strength and modulus of the wood flour itself, as compared with the rice-husk flour.

3.2. Izod impact properties with different compatibilizing agents

The Izod impact tests were conducted at room temperature on both notched and unnotched specimens. Figs. 5 and 6 show the Izod impact strengths of the lignocellulosic filler-polyethylene (LDPE and HDPE) composites made with the different compatibilizing agents. The Izod impact strengths of the MAPP incorporated composites are slightly decreased following the incorporation of the compatibilizing agent at a content of 3 wt.% whereas those of the MAPE incorporated composites are almost the same or slightly increased, because the better wetting of MAPE to the polyethylene matrix polymer improved the stiffness of the composites. The notched specimens exhibited lower impact strength than the unnotched specimens, which is the same tendency as that reported in a previous study [2]. This is because the notched impact energy comprises only the crack propagation, whereas the unnotched impact energy consists of the crack initiation and crack propagation between the filler and the matrix polymer in the composite system. Overall, MAPP had no effect on the impact strength, whereas MAPE had a toughening effect [7].

3.3. Morphological characteristics

The tensile fracture surfaces of the RHF–LDPE composites at a filler loading of 30 wt.% and a compatibilizing agent (MAPP and MAPE) content of 3 wt.% are shown in Fig. 7. In the case of the composite without any compatibi-

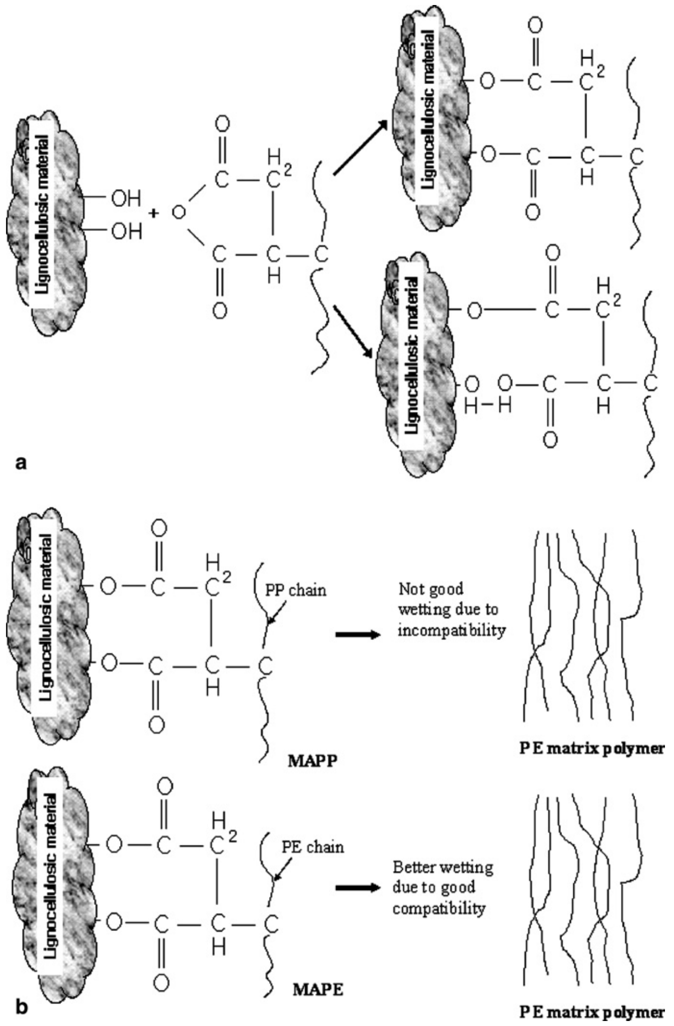

Fig. 4. Role of compatibilizing agent at the interface between natural filler and matrix polymer: (a) esterification of lignocellulosic material with compatibilizing agent; (b) wetting of compatibilizing agent treated natural filler.

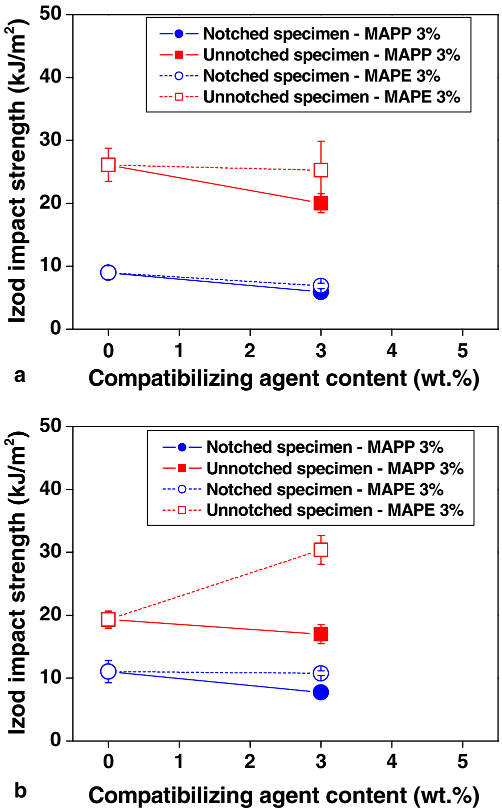

Fig. 5. Izod impact strengths of the LDPE composites with the two different compatibilizing agents as a function of the compatibilizing agent content: (a) WF–LDPE composite; (b) RHF–LDPE composite.

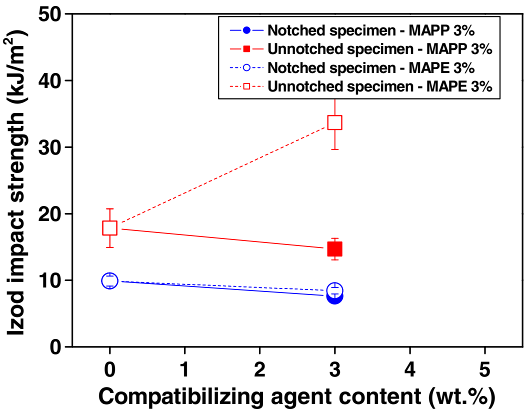

Fig. 6. Izod impact strength of the RHF–HDPE composites with the two different compatibilizing agents as a function of the compatibilizing agent content.

lizing agent at a filler loading of 30 wt.%, many 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 [2]. The fillers are not fractured in the composite made without any compatibilizing agent, but in the composite made with compatibilizing agent (MAPP and MAPE), the interfacial bonding between the filler and the matrix polymer is improved, and the fracture occurred at the filler itself. This means that the stress is well propagated between the filler and the matrix polymer in the composite incorporating the compatibilizing agent, causing it to have a higher tensile strength and modulus in response to stress. The composites made with the two different compatibilizing agents (MAPP and MAPE) show some different characteristics. The MAPP incorporated LDPE composites have inferior interfacial bonding strength as compared to the MAPE incorporated composites, while the MAPE incorporated composites exhibit superior interfacial bonding according to the tensile strength results. The results obtained from the SEM micrographs are in agreement with this. A few traces where filler particles have been pulled-out, and fractured filler particles, are to be seen in the micrographs of the MAPP incorporated composites, while no pulled-out traces and many fractured filler particles are to be seen in the micrographs of the MAPE incorporated composites. The unnotched Izod impact fracture surfaces

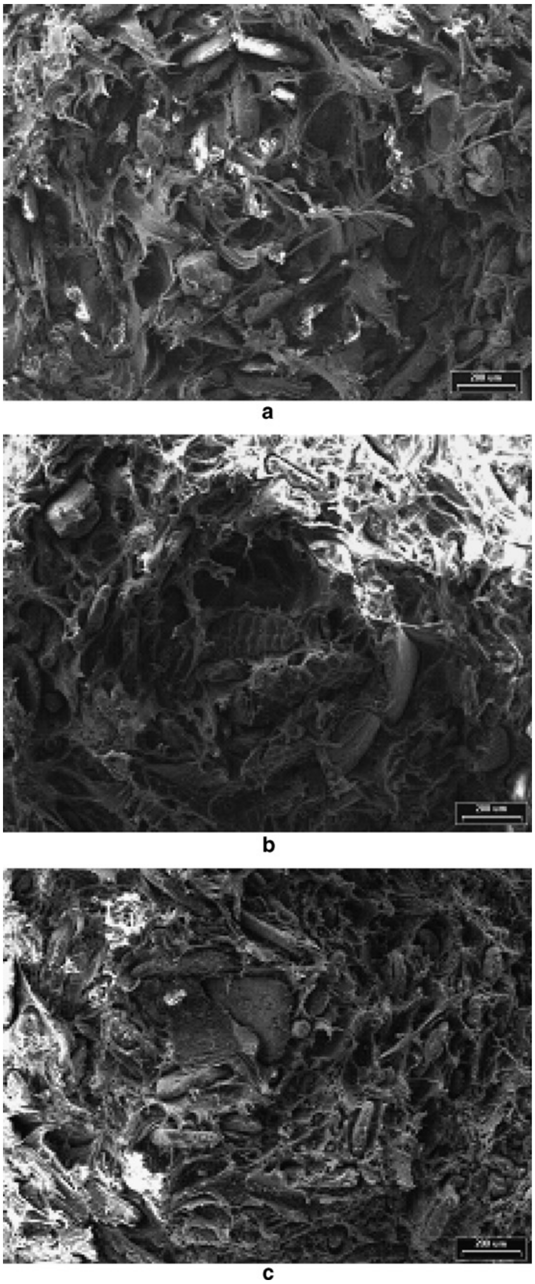

Fig. 7. Tensile fracture surfaces of the RHF–LDPE composites with the two different compatibilizing agents: (a) 30 wt.% of RHF–LDPE composite; (b) 30 wt.% of RHF–LDPE composite with 3 wt.% of MAPP; (c) 30 wt.% of RHF–LDPE composite with 3 wt.% of MAPE.

of the composites with a filler loading of 30 wt.%, and a compatibilizing agent (MAPP and MAPE) content of 3 wt.% at the notched tip are shown in Fig. 8. Many pulled-out traces of filler particles are to be seen in the samples made without any compatibilizing agent, due to the weak bonding between the filler and the matrix polymer. Some pulled-out traces and fractured filler particles are to be seen in the micrographs of the MAPP incorporated composites, while no pulled-out traces and many fractured filler particles are to be seen in the MAPE incorporated composites.

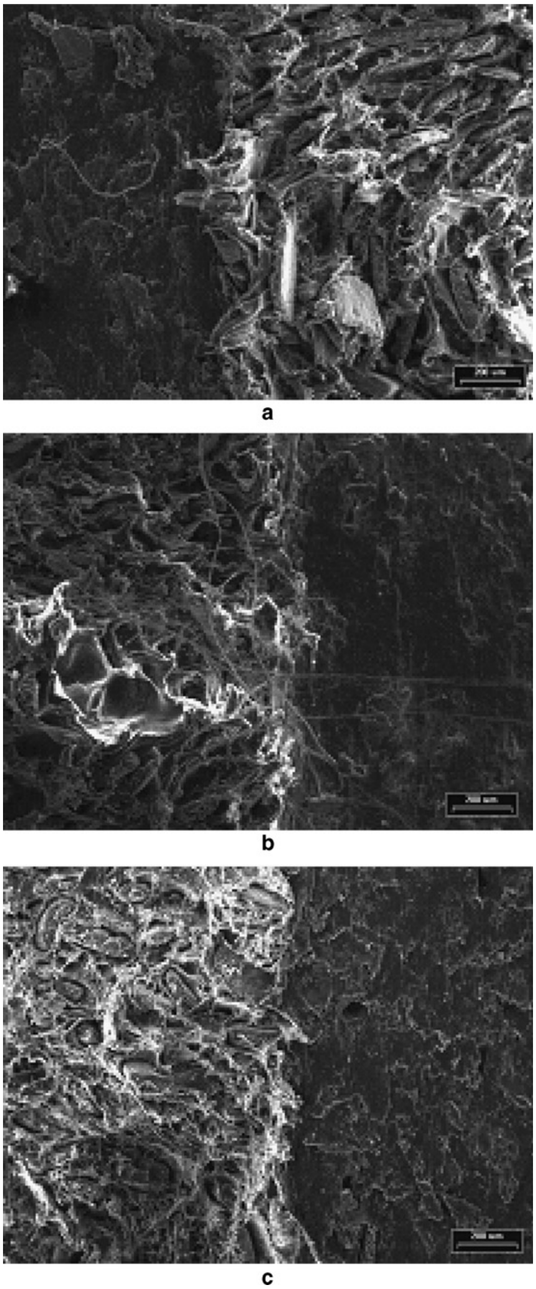

Fig. 8. Unnotched Izod impact fracture surfaces of the RHF–LDPE composites at the notched tip with the two different compatibilizing agents: (a) 30 wt.% of RHF–LDPE composite; (b) 30 wt.% of RHF–LDPE composite with 3 wt.% of MAPP; (c) 30 wt.% of RHF–LDPE composite with 3 wt.% of MAPE.

4. Conclusion

The lignocellulosic filler-polyethylene composites made with MAPP and MAPE exhibited different tensile properties. The tensile strength and modulus of the composite incorporating maleated polyethylene were significantly better than those of the composite incorporating maleated polypropylene, due to the better wetting of MAPE to the matrix polymer, which led to stronger interfacial bonding being obtained between the filler and matrix polymer, because maleic anhydride grafted polyethylene is the same kind of material as polyethylene, the matrix polymer. The Izod impact strength of the composite slightly decreased following the incorporation of MAPP, whereas it remained the same or slightly increased following the incorporation of MAPE. MAPP had no effect on the impact strength, whereas MAPE had a toughening effect.

The composites made with the two different compatibilizing agents showed different morphological characteristics. Some pulled-out traces and fractured filler particles were to be seen in the micrographs of the MAPP incorporated composites, while no pulled-out traces and many fractured filler particles were observed in the MAPE incorporated composites. In conclusion, MAPE is recommended in the polyethylene composite system, due to its better compatibility as compared with MAPP.

Acknowledgement

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