

Preparation and Characterization of LDPE and PP—Wood Fiber Composites

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ABSTRACT: Natural fiber reinforced composites is an emerging area in polymer science. These natural fibers are low cost fibers with low density and high specific properties. These are biodegradable and nonabrasive. The natural fiber composites offer specific properties comparable to those of conventional fiber composites. However, in development of these composites, the incompatibility of the fibers and poor resistance to moisture often reduce the potential of natural fibers, and these drawbacks become critical issue. Wood-plastic composites (WPC) are a relatively new class of materials and one of the fastest growing sectors in the wood composites industry. Composites of wood in a thermoplastic matrix (wood-plastic composites) are considered a low maintenance solution to using wood in outdoor applications. WPCs are normally made from a mixture of wood fiber, thermoplastic, and small

amounts of process and property modifiers through an extrusion process. In this study, Wood-plastic composites (WPC) are produced by adding a maleic anhydride modified low density polyethylene coupling agent to improve interfacial adhesion between the wood fiber and the plastic. Mixing is done with twin screw extruder. Subsequently, tensile strength, the modulus of elasticity, % elongation, hardness, Izod impact strength, melt flow index (MFI), and heat deflection temperature (HDT) are determined. Thermal transition temperatures and microstructure are determined with DSC and SEM, respectively. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 3095–3102, 2009

Key words: wood fiber; polyethylene; polypropylene; composite; mechanical properties

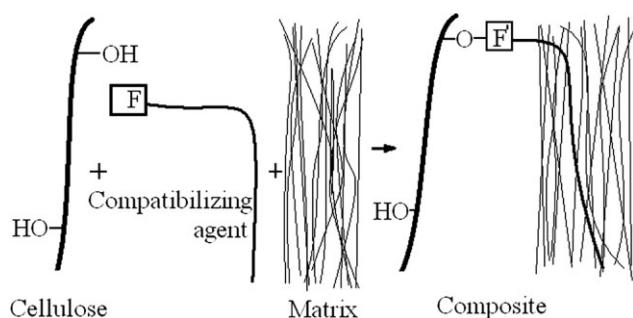
INTRODUCTION

Over the past 50 years, plastics have become a regular part of our daily lives. From containers to car parts, plastics can be shaped and made into almost anything. Fillers are often added to the plastic as a means of lowering costs and increasing the strength and stiffness of the resulting material.^{1–3} Wood-derived fillers have recently made significant inroads into the thermoplastic industry, primarily as a result of the emergence of wood-plastic composites in the construction industry. Exterior nonstructural or semi-structural building products, such as decking, fencing, siding, window framing, and roof tiles, are being introduced into the marketplace. For building products alone, ~ 500,000 tons of wood-plastic composites are predicted to be used in North America in 2006. Construction, transportation, industrial, and consumer applications are also on the rise. Currently, nearly 70% of wood-plastic composites are polyethylene matrix composites. Polypropylene and

polyvinyl chloride are also common matrix materials used by the wood-plastic composites industry.^{4,5} Wood has been used by the plastics industry as inexpensive filler for thermoplastics. These wood-filled thermoplastics, commonly called wood-plastic composites (WPCs), have many property advantages over those of composites with wood or plastics alone.²

However, WPCs also have some disadvantages compared to pure plastics, including water absorption and thickness swell.^{1,2} The bond between the wood filler and the thermoplastic matrix is very limited, allowing wood fibers to slip and pull out from the thermoplastic when stressed. The inability of wood fibers to produce effective bonds with thermoplastics is a major impediment to the continued development of WPCs. Wood fibers and particles are not compatible with hydrophilic thermoplastics because wood is hydrophilic. One approach to overcome this problem is to add a coupling agent (commonly called a compatibilizer) to improve the interfacial adhesion between the wood fibers and the plastic, thereby increasing the strength properties of the resulting WPC.^{3,6}

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Scheme 1 Chemical modifications of cellulose for compatibilization with the matrix.

In the literature, there are many studies on wood-plastic composites. Among them, Coutinho et al.⁷ investigated the effects of the treatment and mixing conditions on the mechanical properties of wood-fiber/polypropylene composites with silane coupling agents. They reported that the optimal mixing conditions for wood-fiber/polypropylene composites were a mixture temperature of 180°C and a mixing time of 10 min at a rotation speed of 60 rpm. Raj and Kokta⁸ examined the effects of coupling agents on the tensile properties of high-density polyethylene HDPE/Wood composites. Oksman et al.^{9–11} also investigated the mechanical properties and morphology of PE/WF composites modified with a styrene-ethylene/butylene-styrene triblock copolymer grafted with maleic anhydride (SEBS-g-MA). According to Raj et al.,¹² small particles are not as easily dispersed as large particles because of a higher specific surface area that exposes more hydroxyl groups. Particles agglomerate by hydrogen bonding with residual water molecules. Coupling agents increase the contact area between wood particles and PP matrix, enhance dispersion, and improve adhesion of the two components.¹³ Raj and Kokta¹⁴ also showed that composites made with fibers treated with maleated PP (MAPP) had reduced water absorption compared to composites made without coupling agent. Thorough dispersion and adhesion promote encapsulation of the wood particles with plastic matrix, which reduces moisture uptake. In the general preparation of plastic/wood composites, wood as fiber or flour is blended with thermoplastic polymers, and the resulting mixture is molded directly from the mixture or after being pelleted. When cellulosic fibers are included in polar matrices such as polyamide PA-6,6 hydrogen bonding favors interaction between the two polymers and therefore wettability and mechanical adherence. In the same manner, mechanical adherence may be sufficient with rough surfaces: thus, the surface of regenerated cellulose can be fibrillated and mechanical anchoring with a PE matrix depends on the degree of fibrillation.

TABLE I
Chemical Composition of the Polyolefin/Wood Fiber Composites and the Sample ID

Type of plastic used	Component of wood composites	Sample ID
LDPE	Pure LDPE	LDPE
	LDPE/wood fiber (90/8) +2% maleic anhydride	LDPE8M
	LDPE/wood fiber (80/18) +2% maleic anhydride	LDPE18M
	LDPE/wood fiber (70/28) +2% maleic anhydride	LDPE28M
	LDPE/wood fiber (60/38) +2% maleic anhydride	LDPE38M
	Pure PP	PP
PP	PP/wood fiber (90/8) +2% maleic anhydride	PP8M
	PP/wood fiber (80/18) +2% maleic anhydride	PP18M
	PP/wood fiber (70/28) +2% maleic anhydride	PP28M
	PP/wood fiber (60/38) +2% maleic anhydride	PP38M

However, because of its hydrophilicity, the naked cellulosic fiber must overcome some difficulties to establish a good contact with hydrophobic matrices such as PE and PP. For special applications, hydrophilization of PE or PP is possible, but most often, treatments are performed on the cellulosic fibers. Cellulosic surfaces with high energy have to be treated to lower their energies at a level compatible with PP. Many ways are possible: plasma or corona treatments can be used, but more often chemical treatment such as oxidation grafting or functionalization. The so-called compatibilizing agents possess at one end a function *F* able to react with hydroxyl groups and at the other end an alkyl chain of varying length, or at the limit a polymeric chain with a structure similar to that of the matrix (Scheme 1). Such agents are small molecules possessing two

TABLE II
Extrusion Conditions of the PE/Wood Fiber and PP/Wood Fiber Polymer Composite

Sample ID	Extrusion temperature (°C)	Extrusion screw speed (rpm)	Extrusion pressure (bar)
LDPE	90–160	150	12
LDPE8M			
LDPE18M			
LDPE28M			
LDPE38M			
PP	150–210	150	12
PP8M			
PP18M			
PP28M			
PP38M			

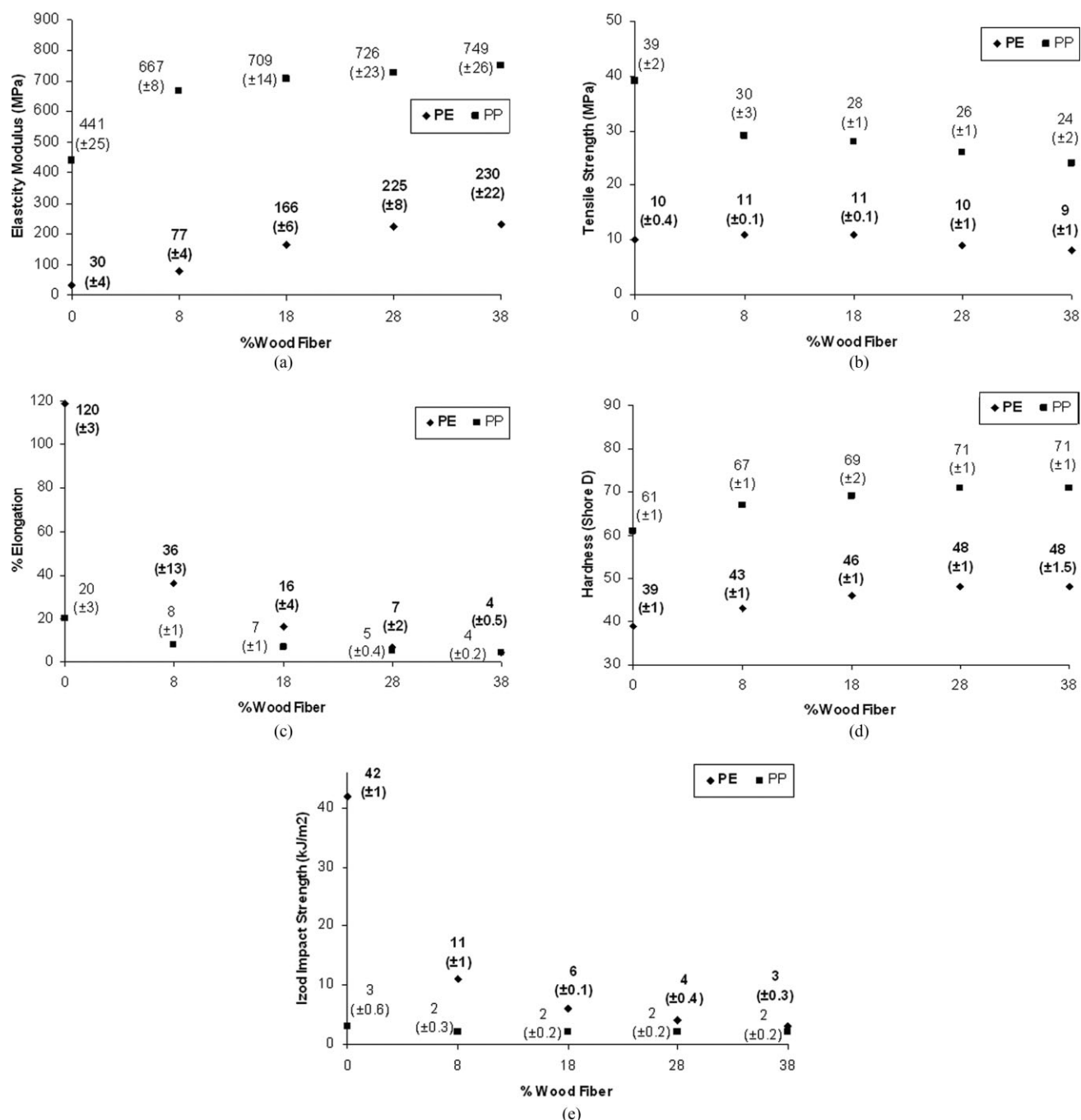


Figure 1 Mechanical properties of the LDPE-PP/wood fiber polymer composite.

different functions F and G . The first is able to react with OH groups of cellulose. The second is generally a double bond that can react with a tertiary carbon of PP or PE, for instance, by a radical reaction after elimination of a hydrogen atom. Such agents are “genuine” coupling structures that link the cellulose fiber directly to the PP or PE matrix.⁶

This study provides a better understanding of the effect of wood fiber ratio in the formation process and property variations of wood-plastic composite.

LDPE and PP were used as a matrix polymer and wood fiber was used as a filler material. Maleic anhydride (MA) was also used for improving the interfacial adhesion between the wood fiber and the LDPE and PP polymers. In addition to the surface treatment of fibers, use of a coupling agent for effective stress transfer across the interface can also be explored. Subsequently, mechanical, thermal, and morphological properties of LDPE/wood fiber and PP/wood fiber composites were investigated.

EXPERIMENTAL

Compositions and materials

Compositions of LDPE/wood fiber and PP/wood fiber composites that were formed are given in Table I.

LDPE (1922T) was supplied by Sabic (Sabic Europe, Sittard, The Netherlands). Its density is 0.919 g/cm^3 , MFI value is 22 g/10 min (190°C , $2,16 \text{ Kg}$), Vicat softening point is 152°C (10N), and melting temperature is 105°C . PP (579S) also supplied by Sabic. Its density is 0.905 g/cm^3 , MFI value is 47 g/10 min (230°C , $2,16 \text{ Kg}$) and its Vicat softening point is 152°C (10N). Maleic anhydride grafted low density polyethylene (MA-Yparex 8125) was supplied by DSM Eng Plastics (Sittard, Netherlands). Its MFI value is 24 g/10 min (190°C , $2,16 \text{ Kg}$). Vicat softening point is 103°C (10N), and its melting temperature is 124°C . Wood fiber (blend of spruce, maple, pine and oak) was supplied by Tever Sunta Co. (Ümra-riye-Turkey). Its particle dimension is 3–5 mm, and moisture content is 5–10%.

METHODS

Fiber preparation

Cellulosic fibers are hydrophilic and absorb moisture. The moisture content of the fibers can vary between 5 and 10%. This can lead to dimensional variations in composites and also affects the mechanical properties of the composites. Therefore, the wood fiber was dried in an oven at 105°C for 24 h to a moisture content of less than 1% before being blended with LDPE and PP.

Composites preparation

LDPE, PP, wood fiber, and Maleic anhydride grafted low density polyethylene (MA-Yparex 8125) were weighed and bagged according to the various fiber contents indicated in Table I. Lubricant (0.02%) was also added only used as a processing aid. They were then mixed using a Dersan (Istanbul-Turkey) brand batch blender at a rotational speed 700 rpm for 15 min. The compounded materials were then ground to prepare the granules using a Coperion Werner & Pfleiderer ZE-40 (Stuttgart-German) corotating twin-screw extruder (L/D: 40). The mixed blends were then dried at 105°C for 24 h. Test specimens were injection molded at $140\text{--}160^\circ\text{C}$ for LDPE and $190\text{--}210^\circ\text{C}$ for PP and injection pressure of $1400\text{--}1500 \text{ bar}$ with using Arburg Injection Machine (Arburg GmbH Co., Lossburg-Germany). Extrusion blending conditions are given in Table II.

Test procedure

Composite specimens were conditioned at 23°C and 50% humidity for 24 h before testing (ASTM D618). Tensile tests were performed according to ASTM D638 specification. They were carried out using a Zwick Z010 (Zwick GmbH, Ulm-Germany) testing machine with a load cell capacity of 10 kN at a cross-head speed of 50 mm/min. The tensile strength and modulus were determined from the stress–strain curves. To investigate fracture behavior, Izod impact test was done at room temperature according to ASTM D256 standard with ZWICK B5113 impact test device (Zwick GmbH & Co. KG Ulm, Germany). Flow test of all the mixtures was done according to ISO 1133 standard with ZWICK 4100 mFI equipment. Hardness test were done according to ASTM D2240 standard with Zwick hardness measurement equipment. Thermal transition temperatures were determined by TA Instruments DSC 2920 (TA Instruments, West Sussex, England) test equipment in a nitrogen atmosphere. Starting point: 24°C , ending point: 195°C , and test

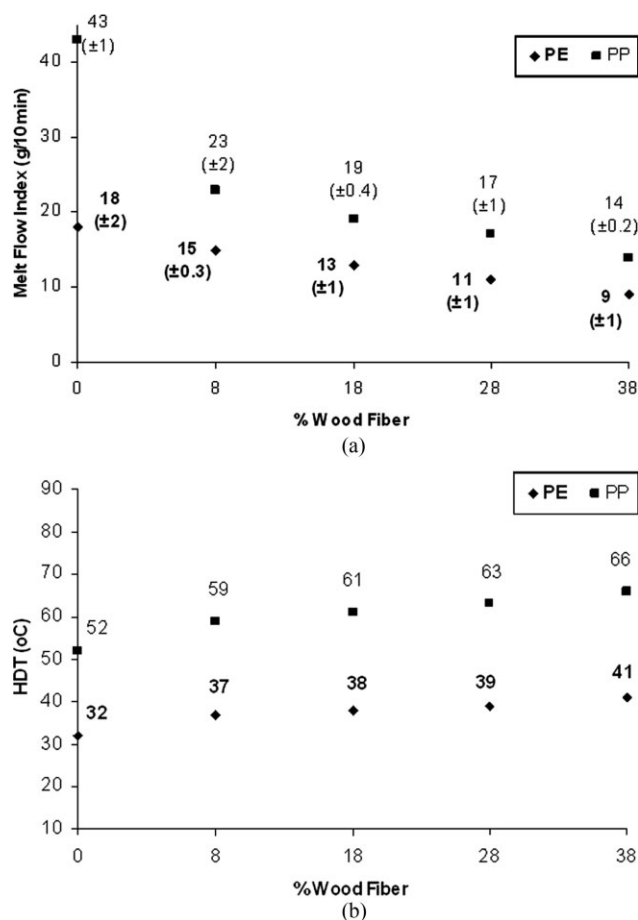


Figure 2 Mechanical properties of the LDPE-PP/wood fiber polymer composite Figure 2 MFI and HDT properties of the LDPE&PP/wood fiber polymer composites.

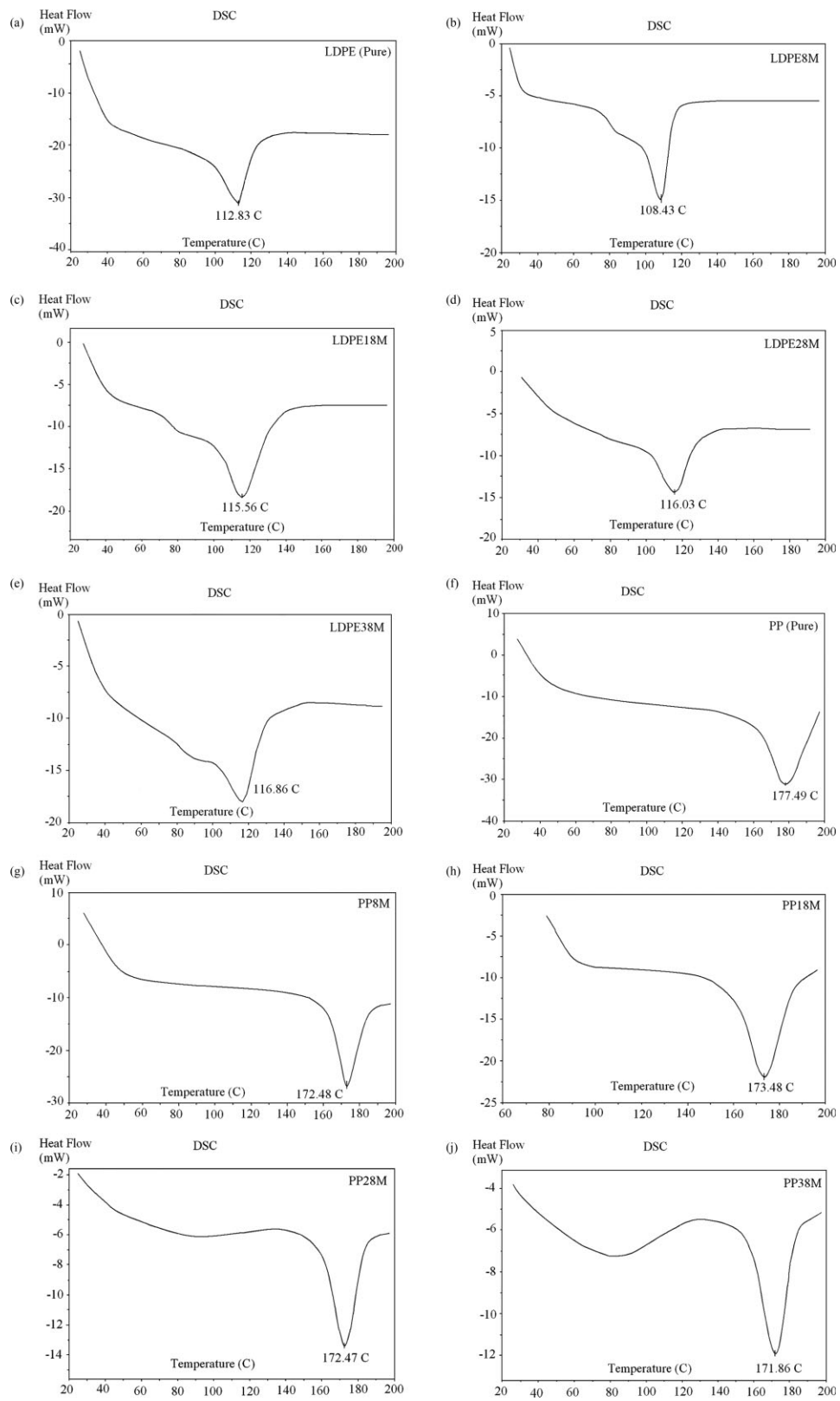


Figure 3 DSC curves of the LDPE-PP/wood fiber composites.

rate: 10°C/min. The fractured surfaces of the composites were coated about 40 Å in thickness with gold to prevent electrical charging by POLARON SC 7640

(Gala Instrumente GmbH, Bad Schwalbach-Germany). The surfaces of the prepared samples were observed by the FEI Srios (FEI Company,

Eindhoven-Nederland) scanning electron microscopy (SEM) at an acceleration voltage of 2–5 kV. HDT test were done according to ISO 307 standard with determined by CEAST 6521 (Ceast SpA Pianezza, Italy) HDT test equipment. Five samples were tested in each set and the average value was reported.

RESULTS AND DISCUSSION

The results indicated an increase in Elastic modulus and hardness of the composite with increase in the fiber content. However, the elongation at break and tensile strength decreased with increase in wood fiber content. This is due to the lower elongation at break and tensile strength values of wood fiber. The toughness of the composites decreased with an increase in the wood fiber concentration because rigid filler has been added to a tough matrix. Elastic modulus, % elongation, tensile strength, hardness, and Izod impact strength of PE/wood and PP/wood polymer composites are given in Figure 1.

MFI and HDT results are given in Figure 2. For both LDPE/wood and PP/wood polymer composites, Figure 2(A) shows that the MFI decreased with an increase in wood flour concentration. However, as seen in Figure 2(B), HDT was improved with an increase in wood flour concentration.

LDPE and PP generally has a T_m around 105–110°C and 170–175°C, respectively. The T_g of the cellulose is between 230 and 250°C, whereas lignin* has a T_g of 130–190°C at dry state.¹⁵ Figure 3 shows the DSC temperature scan diagrams of pure LDPE and PP and composites samples LDPE8M, LDPE18M, LDPE28M, LDPE38M, PP8M, PP18M, PP28M, and PP38M. The melting temperature of LDPE and PP were evident in the DSC curves, and its T_m is 112.8 and 177.4°C, respectively. Within 24–195°C temperature scan range, glass transition of lignin was not observed. The effect of wood fiber content on the melting temperature of LDPE and PP were not considerable in DSC analysis. T_m values of polyolefin/wood polymer composites are given Table III.

SEM patterns of the fractured surfaces of the composites can provide information about the interfacial compatibility between the wood fiber and LDPE and PP matrix. The image also shows the random distribution of fibers in the matrix. Adhesion between wood fiber and LDPE and PP were obtained. This

*Lignin is a complex chemical compound most commonly derived from wood and an integral part of the cell walls of plants.¹⁶

TABLE III
Melting Temperatures (T_m) of the Polyolefin/Wood Fiber Polymer Composites

Sample ID	Melting temperature T_m (°C) (starting point: 24°C ending point: 195°C, test rate: 10°C/min)
LDPE	112.8
LDPE8M	108.4
LDPE18M	115.5
LDPE28M	116.0
LDPE38M	116.8
PP	177.4
PP8M	172.4
PP18M	173.4
PP28M	172.4
PP38M	171.8

result produces a positive effect on the elastic modulus and hardness. SEM patterns of the fractured surfaces of the composites are represented in Figure 4.

CONCLUSIONS

Results show improvements in elastic modulus and hardness when wood was incorporated into the polymer matrix; however, there was also a deterioration of the toughness of the composites. The incorporation of maleic anhydride grafted low density polyethylene (MA-Yparex 8125) had beneficial effect with both LDPE and PP-based composites. This is not surprising because of the effect of compatibilizing additives used in composites, wherein hydrogen abstraction at the branched carbons along the backbone can occur by viscous heating. This is followed by the incorporation of maleic anhydride grafted low density polyethylene from the radical carbon, resulting in a polymer that has more compatibility to wood surfaces.

In conclusion, materials selection and processing conditions of LDPE/wood fiber and PP/wood fiber composites can result in improvements in some of the mechanical properties of the composites (such as modulus, hardness, and HDT), without severely affecting other properties (such as tensile strength, elongation-at-break, and toughness). Specifically, a reactive compatibilizer system, such as MA, and high MFI LDP&PP can be advantageously used to formulate acceptable composites.

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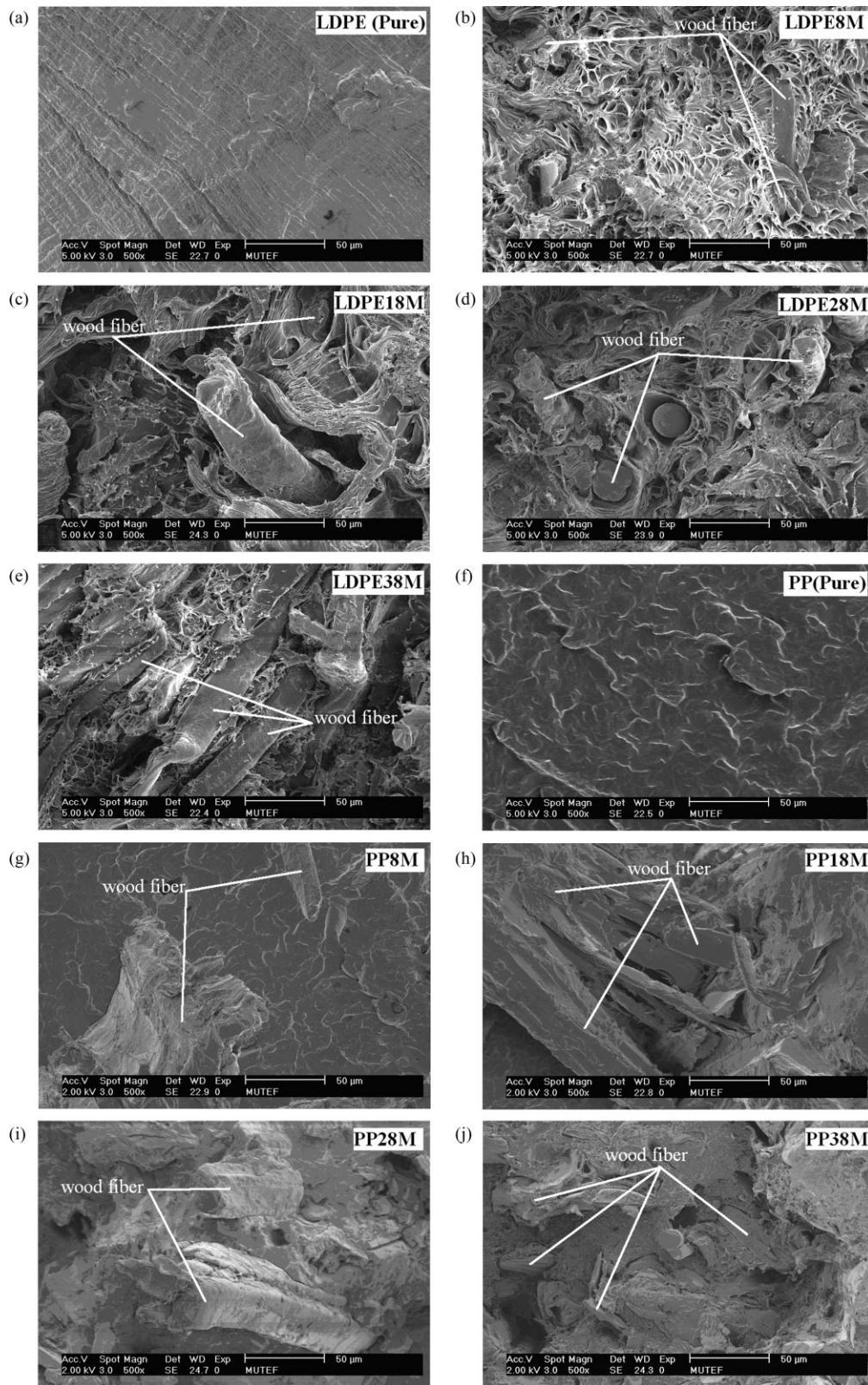


Figure 4 SEM micrographs of the fractured surfaces of the LDPE-PP/wood fiber polymer composite.

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