Influence of Modified Wood Fibers on the Mechanical Properties of Wood Fiber-Reinforced Polyethylene

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ABSTRACT: Wood fiber of aspen was used as a reinforced filler in linear low-density polyethylene (LLDPE). To improve the compatibility between the wood fiber and the LLDPE matrix, the wood fiber was treated with titanate coupling agents (i.e., TC-PBT and TC-POT) or grafted by acrylonitrile. Both treatments resulted in an improvement in the mechanical properties of the resultant composites compared with the composites filled with the untreated wood fiber. Moreover, the grafting method displayed a more obvious benefit than that of titanate coupling methods to the mechanical property improvement. This was attributed to the crystalline structure of the wood fiber to be destroyed by grafting acrylonitrile, and the amorphous fiber was easily deformed to enhance fiber adhesion at the LLDPE matrix. In addition, the effect of the concentration of the filled wood fiber and the amount of coupling agent or grafting ratio on the mechanical properties of composites are discussed. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **66:** 1561–1568, 1997

INTRODUCTION

Natural organic fillers such as wood fiber have traditionally composed a small percentage of the filler market for thermoplastics when compared to mineral or glass-fiber reinforcements. But the wood fiber offers many advantages such as (1) lower density, (2) high specific strength and modulus, (3) renewable nature, and (4) less breakage of the fiber during mixing compared to the commonly used inorganic reinforced fibers.[1–3] But the main problem in these wood fiber–thermoplastic composites is the poor interfacial adhesion between the hydrophobic polymer matrix and the hydrophilic wood fiber. These can be solved by chemical modification of the wood fiber surface,[4–7] e.g., grafting a short-chain molecule onto the wood fiber surface[8] as well as by using various coupling agents/adhesion-promoting agents such as stearic acid and maleated propylene wax.[9,10] In addition, the method of preparation of the composites also affects the ultimate properties of the composites. In the present study, to improve the interfacial adhesion between the wood fiber and the LLDPE matrix, wood fiber was treated with two different titanate coupling agents and grafted acrylonitrile. The effect of the wood fiber concentration and the wood fiber treatment on the mechanical properties of the composites was studied.

EXPERIMENTAL

Materials

Linear low-density polyethylene (LLDPE, melt index: 5.0 g/10 min; density: 0.930 g/cc) was supplied by Yanshan Chemical Ltd. Co. (China). Wood fiber of aspen was prepared in our lab. Wood fiber was dried at 80°C in an air-circulating oven for 24 h and then ground to mesh size 60 before it was used.

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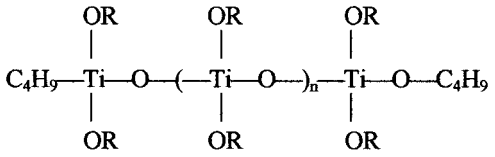
Table I Sample Number and Ratio of Grafting of Wood Fiber

	Sample No.		
	A-1	A-2	A-3
Ratio of grafting (N %)	5.34	9.70	13.74

The following titanate coupling agents were used: (a) TC-POT and (b) TC-PBT, both supplied by Shanghai Institute of Organic Chemistry, Academia Sinica. The structure was



where R is a C_8-C_{10} chain alkyl (TC-POT) or a C_4 chain alkyl (TC-PBT).

Wood Fiber Treatment

Titanates Treated

The wood fiber was soaked in a 3% titanate solution of hexane for 24 h and then the hexane was volatilized and dried at 80°C in an air-circulating oven for 24 h.

Grafting Acrylonitrile

Wood fiber grafting of acrylonitrile was carried out as described in the previous report.[11] The ratio of grafting was expressed by the nitrogen percent (N%). The resulting grafted wood fiber was ground to mesh size 60 before it was used. The sample number of grafted acrylonitrile wood fiber and the ratio of grafting are listed in Table I.

Preparation of Composites

A mixture of modified wood fiber and LLDPE was mixed at 160°C for 10 min in a two-roll mill. Then, it was cooled to room temperature and reground to mesh size 20. The wood fiber concentration varied from 0 to 40.0% by weight of the composites. The mixtures were molded into shoulder-shaped specimens in a mold which was covered by metal plates on both sides. Molding temperature of 170°C, molding pressure of 4 MPa, heating time of 10 min, and cooling time of 15 min were used.

Measurement of Mechanical Properties

Tensile properties of the composites were studied using an autograph electrontensile testing machine (XL2500, China). The properties were measured at room temperature and the strain rate was 10 mm/min. Tensile strength was measured at the peak point. The tensile modulus was calculated at 0.1% of elongation. Six samples were tested in each series. The average coefficient of variation was less than 7.0%.

Characteristic of Grafted Wood Fiber

The crystallinity of grafted wood fiber was measured by an X-ray diffractometer of D/max 1200II. CuKα radiation was used. The accelerating voltage and electric current used were 40 kV and 30 mA, respectively. The ratio of grafting of the fiber (N%) was measured by an ultimate analyzer.

RESULTS AND DISCUSSION

Effect of Titanate-Treated Wood Fiber on Mechanical Properties of Composites

The composites containing TC-POT- or TC-PBT-treated wood fibers had higher tensile strength compared to untreated fiber composites, but the improvement was not very remarkable (Fig. 1). At same time, the tensile strength of these composites increased slightly with increase in the wood fiber concentration, whereas the tensile strength of untreated wood fiber composites decreased steadily with increase in the wood fiber concentration.

Elongation decreased drastically with increase in the wood fiber concentration in the composites (Fig. 2). The TC-POT- or TC-PBT-treated fiber composites had higher elongation compared to the untreated fiber composites.

The modulus continued to increase with fiber concentration and was not much affected by the fiber treatment (Fig. 3). A higher increase in modulus was observed when the fiber concentration exceeded 10% in the composites.

From Figures 1 and 2, one can find that the mechanical properties, such as tensile strength and elongation, of TC-POT-treated fiber composites are somewhat better than those of TC-PBT-treated fiber composites. These may be attributed to the longer carbon side chains in TC-POT which are more compatible with the LLDPE matrix than those of short carbon side chains in TC-PBT. In

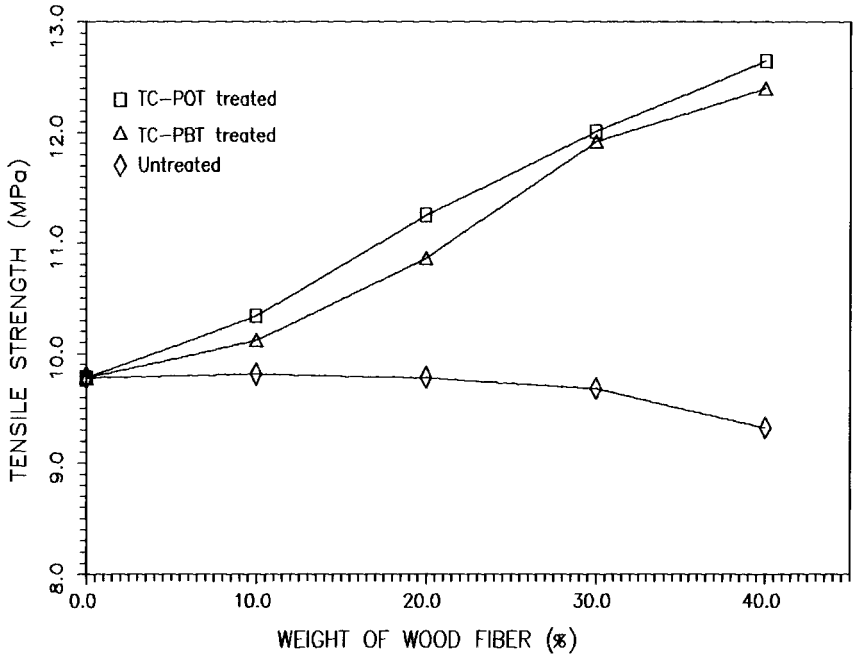


Figure 1 Effect of wood fiber treatment on tensile strength of LLDPE–wood fiber composites.

addition, the transesterification between the —OH group of fiber and the —OR group of titanate resulted in the TC-POT or TC-PBT to be an effective coupling agent in the wood fiber/LLDPE composites.

Effect of Concentration of Titanates (TC-POT, TC-PBT)

The variation in mechanical properties along with the change of the titanate (TC-POT, TC-PBT)

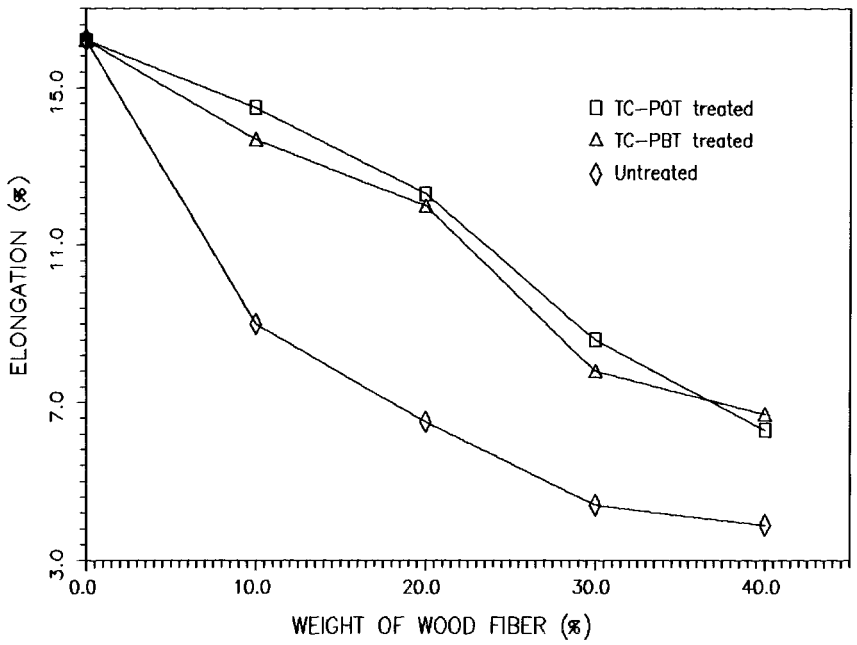


Figure 2 Effect of wood fiber treatment on elongation of LLDPE–wood fiber composites.

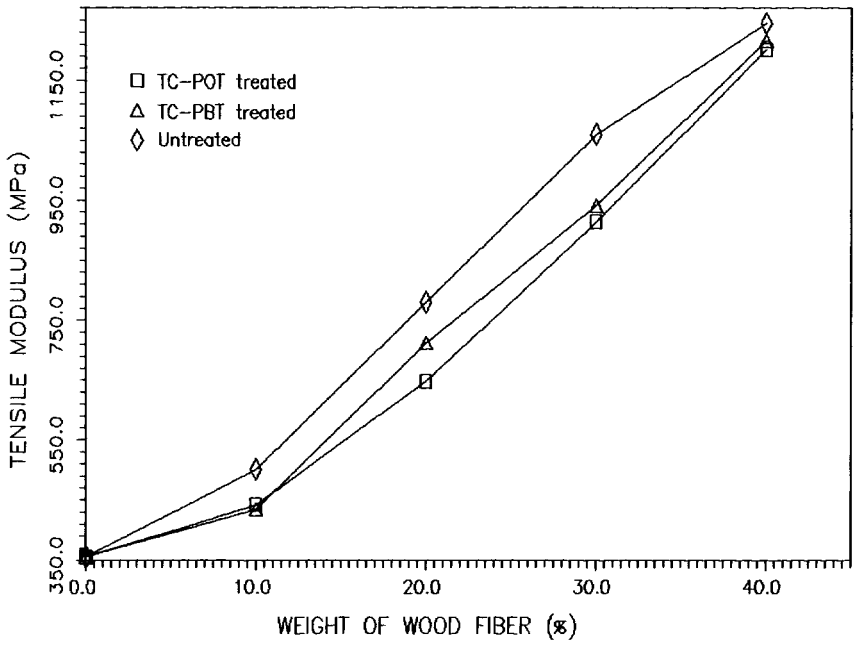


Figure 3 Effect of wood fiber treatment on tensile modulus of LLDPE–wood fiber composites.

concentration (0–1% by weight of wood fiber) in the composite of LLDPE and wood fiber (20% by weight of composite) are shown in Figures 4 and 5. The tensile strength increased with increase in the TC-POT or TC-PBT concentration from 0% (i.e., untreated wood fiber composite) to 3% and then leveled off (Fig. 4).

Elongation increased slightly with increase in

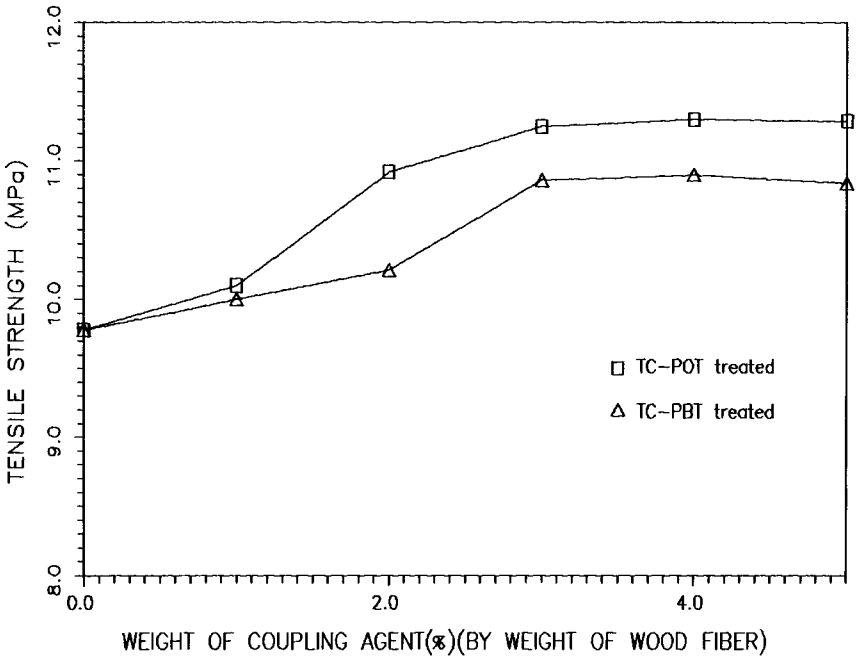


Figure 4 Effect of coupling agent concentration on tensile strength of LLDPE–wood fiber composites.

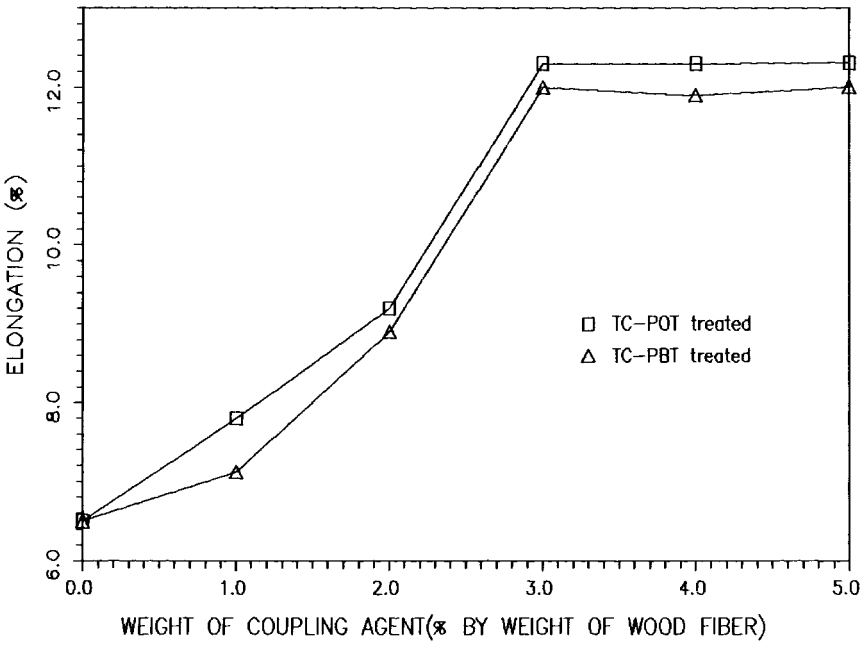


Figure 5 Effect of coupling agent concentration on elongation of LLDPE–wood fiber composites.

the TC-POT or TC-PBT concentration in the composites (Fig. 5) and was mixed when the concentration of TC-POT or TC-PBT exceeded 3% (by weight of wood fiber). These results indicated that the optimum concentration of titanate for 20% wood fiber-filled LLDPE composites is 3%.

Effect of Grafted Acrylonitrile Wood Fiber on Mechanical Properties of Composites

The tensile strength of grafted acrylonitrile wood-fiber composites increased drastically with increase in the concentration of the wood fiber and

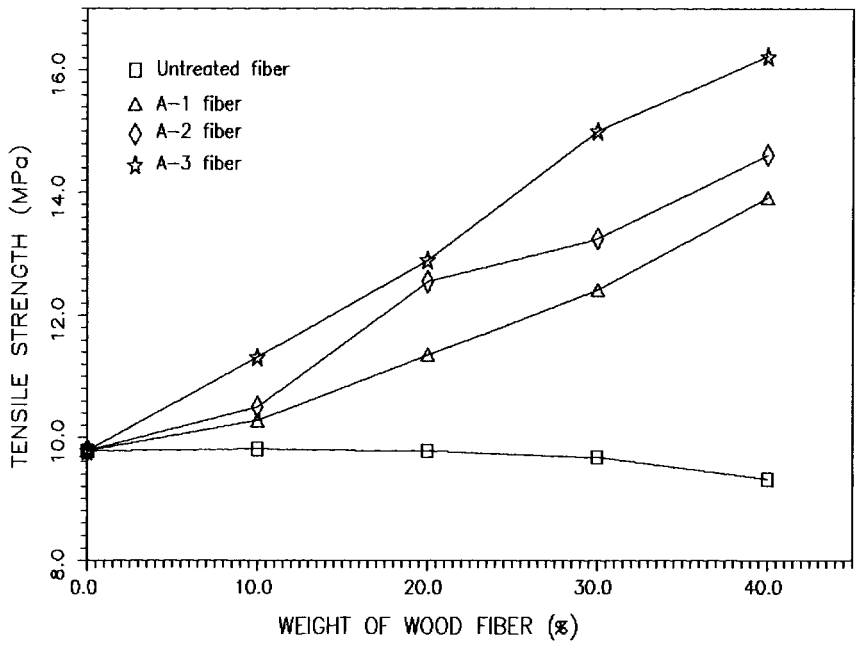


Figure 6 Effect of grafted wood fiber treatment on tensile strength of LLDPE–wood fiber composites.

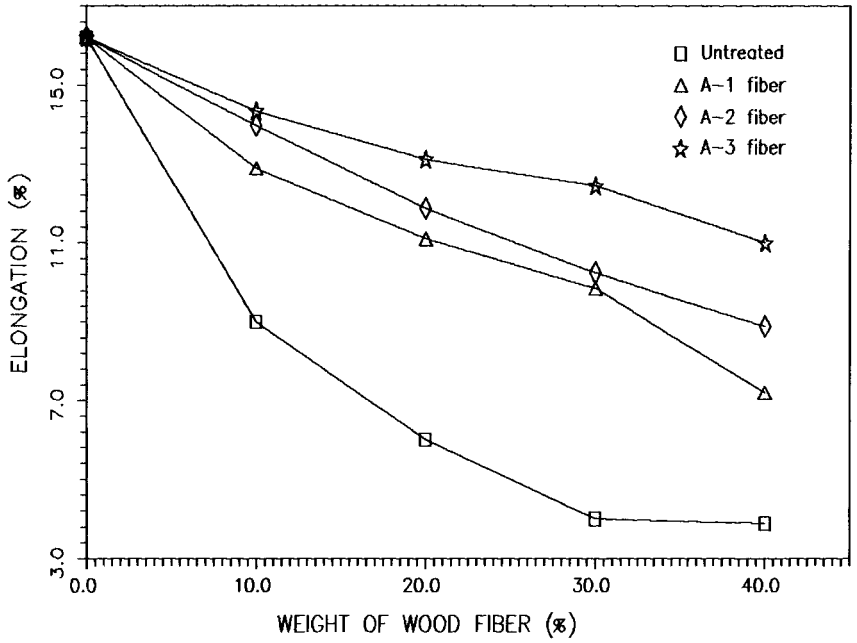


Figure 7 Effect of grafted wood fiber treatment on elongation of LLDPE–wood fiber composites.

the ratio of grafting of wood fiber compared to the untreated fiber composites (Fig. 6) and titanate-treated wood fiber composites (Fig. 1). In the composites containing wood fiber that had a higher ratio of grafting (A-3), the strength increased to 16.3 MPa at 40% wood fiber concentration compared to 9.78 MPa of untreated fiber composites and to 12.6 MPa of TC-POT-treated and 12.3 MPa of TC-PBT-treated fiber composites (Fig. 1).

The elongation decreased with increase in the

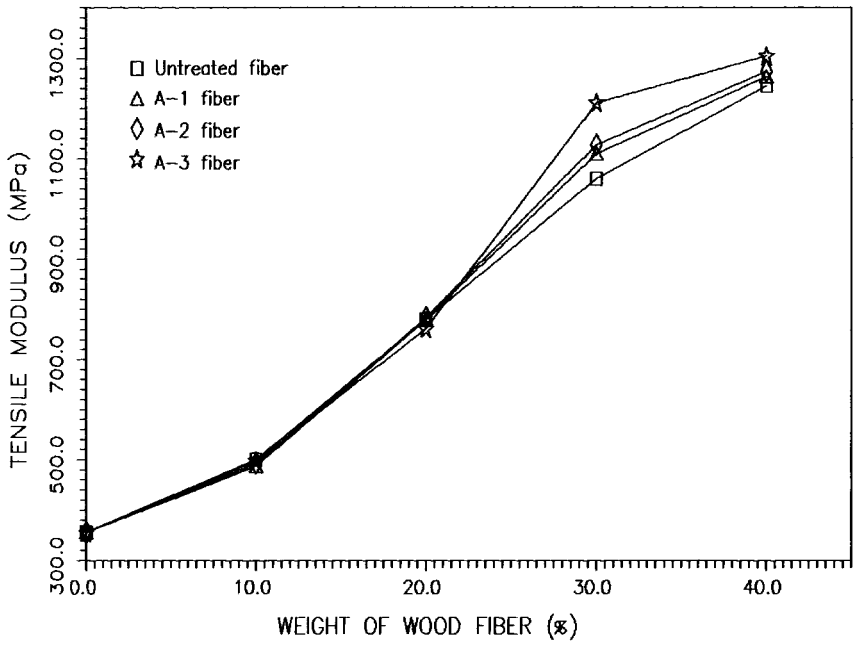


Figure 8 Effect of grafted wood fiber treatment on tensile modulus of LLDPE–wood fiber composites.

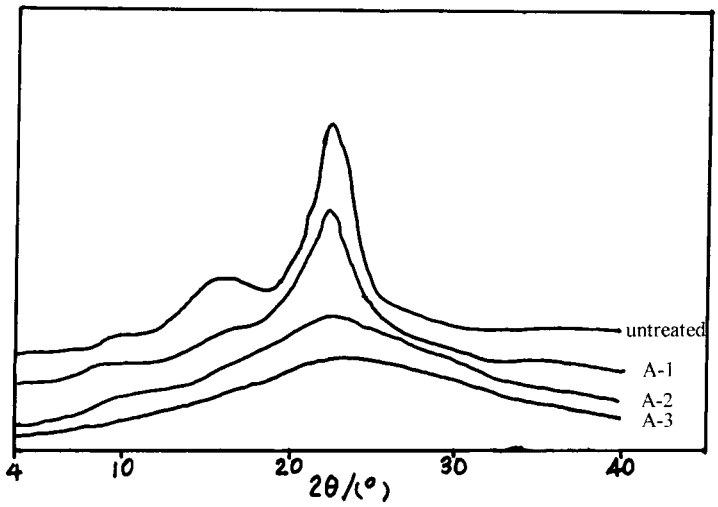


Figure 9 X-ray diffraction patterns of grafted wood fiber.

wood fiber concentration as seen from Figure 7. But the elongation increased with increase in the ratio of grafting of wood fiber and was higher than that of untreated fiber composites. The grafted acrylonitrile wood fiber also produced a higher elongation compared to TC-POT- or TC-PBT-treated fiber (Fig. 2). The tensile modulus increased with increase in the concentration and was not much affected by the fiber treatment (Fig. 8).

The acrylonitrile can react with the —OH group of the wood fiber:

$$\text{wood fiber} —OH + CH_2{=}CH—CN \rightarrow \text{wood fiber} —O—CH_2—CH_2—CN$$

substituting a hydrophilic —OH group on the surface of wood fibers with a hydrophobic —O—CH2—CH—CN group. This may explain the improved tensile properties of wood fiber/

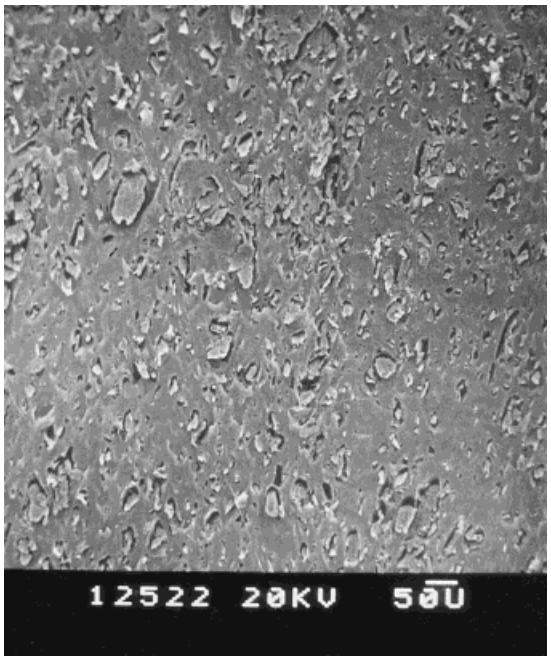


Figure 10 Fracture surface of LLDPE–untreated wood fiber (20.0% fiber weight).

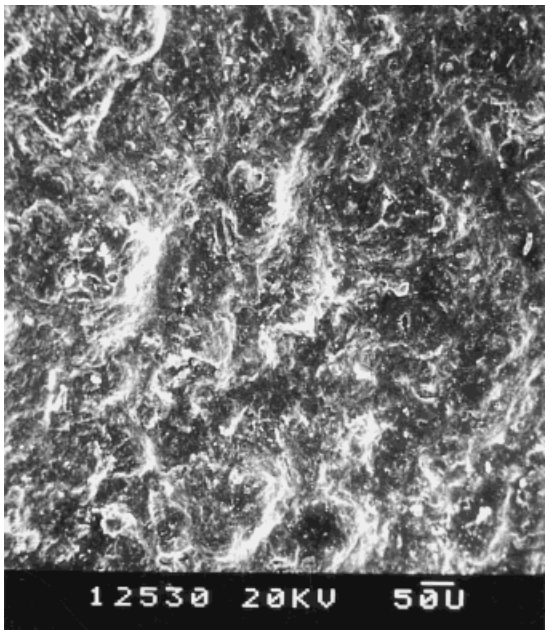


Figure 11 Fracture surface of LLDPE-grafted wood fiber (A-3) (20.0% fiber weight).

LLDPE composites. With increase in the ratio of grafting, the —OH group in the internal matrix of the wood fiber might react with acrylonitrile, which might result in a decrease in crystallinity of the grafted wood fiber.

The crystallinity of wood fiber decreased with increase in the ratio of grafting as seen in Figure 9. One can find that at the higher ratio of grafting (A-2, A-3) the wood fiber displays amorphous patterns. When mixing with LLDPE, the amorphous wood fiber easily assumed a beneficial conformation to the interfacial interaction between the wood fiber and the LLDPE matrix and this may benefit the improvement of the mechanical properties of the composites.

The SEM observations for the untreated wood fiber and the wood fiber with a higher ratio of grafting are shown in Figures 10 and 11, respectively. LLDPE filled with untreated wood fiber showed more fiber pullout from the matrix during the fracture (Fig. 10), whereas the grafting modification made the fiber easily deformable and enhanced fiber adhesion at the interface as seen in Figure 11. In this case, the failure of the material was caused by fiber fracture rather than by fiber pullout from the matrix.

CONCLUSION

LLDPE filled with grafted acrylonitrile wood fibers or filled with titanate-treated wood fibers produced an increase in tensile strength and elongation compared to untreated fiber composites. But the composites containing grafted acrylonitrile wood fibers produced a significant increase in tensile strength and elongation compared to titanate-treated wood fiber composites. The tensile strength and elongation of the composites increased with increase in the ratio of grafting of the wood fiber. The modulus was not much affected by the fiber treatment and it depended primarily on the wood fiber concentration in the material.

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