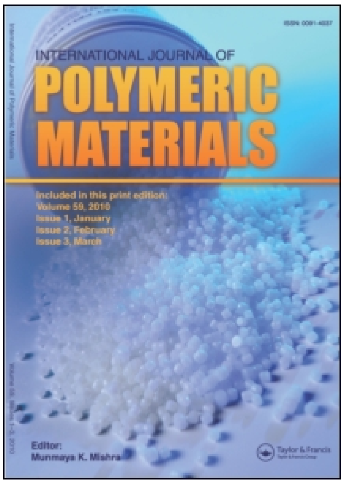

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The use of Isocyanate as a Bonding Agent to Improve the Mechanical Properties of Polyethylene-Wood Fiber Composites

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Chemithermomechanical pulp (CTMP) of aspen was used as a filler in high density (HDPE) and linear low density (LLDPE) polyethylenes. To improve the bonding between the fiber and polymer, different chemical treatments of the fiber a) treatment with different isocyanates b) coating with maleic anhydride was carried out. Composites with isocyanate treated wood fibers produced higher tensile strength compared to untreated fiber composites. But when compared to diisocyanate, the polyisocyanate treated fibers produced higher gain in strength. HDPE or LLDPE filled with maleic anhydride coated CTMP aspen fibers showed a slight decrease in strength with the increase in filler concentration. Tensile modulus generally increased with filler loading and was not much affected by fiber treatment.

1. INTRODUCTION

Cellulosic fibers have a very limited use a filler in thermoplastics compared to other commonly used inorganic fillers such as talc, mica and glass fiber. The cellulosic fillers offer many advantages such as i) lower density, ii) high specific strength and modulus, iii) renewable nature, iv) less breakage of the fiber during mixing and v) cost less compared to the commonly used inorganic fillers.[1,2] When these fibers are compounded with thermoplastic polymers, the main problem usually encountered is the poor interfacial adhesion between the hydrophobic polymer and hydrophilic filler.

The problem of compatibility of wood fibers with the thermoplastic polymer matrix can be overcome by chemical modification of wood fiber surface.[3–6] The other possibility is the treatment of the filler with adhesion promoting agents/coupling agents such as stearic acid and maleated propylene wax etc., to improve the bonding at the fiber-matrix interface.[7,8]Among the various methods to improve the bonding between the filler and matrix include wood fibers impregnated with a suitable monomer and subsequent polymerization,[9] polymer impregnation on the surface of wood fiber[10] and the most common method of all is the grafting of short chain molecules on wood fiber surface.[11]

In the present study, chemithermomechanical pulp of aspen was used as a filler/reinforcing agent in high density and linear low density polyethylenes. In order to improve the bonding at the fiber-matrix interface, the wood fibers were treated with different adhesion promoting agents such as isocyanate and maleic anhydride. The effect of filler concentration and fiber treatment on mechanical properties of the composites were examined.

2. EXPERIMENTAL

2.1. Materials

High density polyethylene (HDPE GRSN 8907, melt index: 7.5 g/10 min; density: 0.954 g/cc) and linear low density polyethylene (LLGR-0534-A, melt index: 5.0 g/10 min; density: 0.934 g/cc) was supplied by Novacor Chemicals Ltd. CTMP aspen pulp (Populus Tremuloides Michx) was prepared in a Sund defiberator.[3] The mechanical pulp was chosen because of its higher defibrillation, which can aid in the dispersion of fiber in the polymer matrix, and high yield (>85.0%) compared to the (<50.0%) chemical pulp.

The following isocyanates (Polysciences Inc.) were used:

a) Polymethylenepolyphenyl isocyanate (PMPPIC)
b) Toulene-2-4-diisocyanate (TDIC)
c) 1–6 hexamethylene diisocyanate (HMDIC)

2.2. Fiber treatment

CTMP aspen fiber was dried at 60°C in an air circulating oven for 24 hours (moisture content was less than 1.6%) and then ground to mesh size 60 before it was mixed with the polymer. The composition of the mesh 60 mixture is presented in Table I. The average fiber aspect ratio (L/D) was 17.1.

TABLE I

CTMP aspen fiber composition (mesh size 60)

Fiber fraction	av. length (L) (mm)	av. diameter (D) (mm)	Aspect ratio (L/D)
20	1.10	0.024	46.0
40	0.46	0.024	19.1
60	0.30	0.022	13.9
80	0.22	0.021	10.1
100	0.18	0.020	9.1
200	0.09	0.020	4.5

2.3. Isocyanate treated

The wood fiber was coated with different chemical agents in a roll mill (C. W. Barbender Laboratory prep. mill No. 065). A typical coating mixture consists of CTMP aspen fibers (30.0 g), isocyanate (3.0% by weight of the fiber) and polymer (HDPE or LLDPE, 5.0%) added gradually to a pre-heated roll mill at 160°C. The mixing was carried out for 10–15 minutes with frequent remixing to achieve better dispersion of isocyanate on the fiber surface.

2.4. Coated fiber 1

Wood fibers were coated with maleic anhydride (5.0% by weight of the fiber), polymer (HDPE or LLDPE, 5.0%) and an initiator (di-*t*-butyl peroxide, 1.0% by weight of the fiber) in a roll mill at 160°C.

2.5. Coated fiber 2

In this case, the amount of maleic anydride (10.0% by weight of the fiber) and the concentration of initiator (2.0% by weight of the fiber) was increased.

2.6. Preparation of composites

Compounding of polymer and wood fiber was carried out at 160°C in an extruder (CSE Max mixing extruder model CS194). The fiber concentration varied from 0 to 40.0% by weight of the fiber. The extruded samples were ground to mesh size 20 and compression molded into dog-bone shaped tensile specimens. The molding conditions were: temperature 165°C; pressure 3.8 MPa; time 15 minutes. The samples were cooled to room temperature with the pressure maintained during the process.

2.7. Mechanical tests

Tensile properties of the composites were studied using Instron 4201. The properties were measured at room temperature and at 50.0% relative humidity. The strain rate was 10 mm/min. The reported properties were measured at peak load. Tensile modulus was calculated at 0.1% of elongation. A minimum of six samples were tested in each series and the test results were automatically calculated by a HP86B computing system using Instron 2412005 General Tensile Test program. The average coefficient of variation was less than 7.0%.

3. RESULTS AND DISCUSSION

3.1. Effect of fiber treatment

Tensile properties of HDPE filled with treated CTMP aspen fibers are presented in Figures 1–3. Tensile strength increased significantly in the samples containing

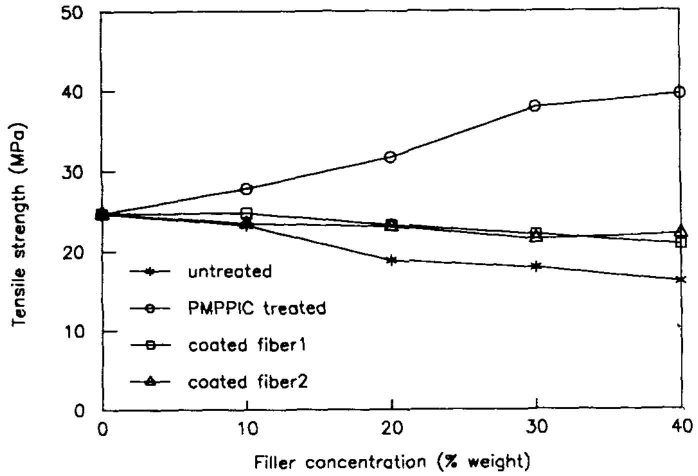

FIGURE 1 Effect of fiber treatment on tensile strength of HDPE–CTMP aspen composites.

PMPPIC treated fiber composites (Figure 1). Samples with maleic anhydride coated fibers did not produce any substantial gain in strength when compared to PMPPIC treated fiber composites. While at the same time these samples did not lose their strength as the concentration of filler increased. Whereas in HDPE filled with untreated CTMP aspen, the tensile strength decreased steadily with the rise in filler concentration.

The better performance of isocyanate treated fiber composites may be attributed to the higher reactivity of the isocyanate groups with OH group of cellulose to form a urethane structure.[8] This activated fiber surface facilitates the bonding at the interface. Increase in tensile strength after isocyanate treatment

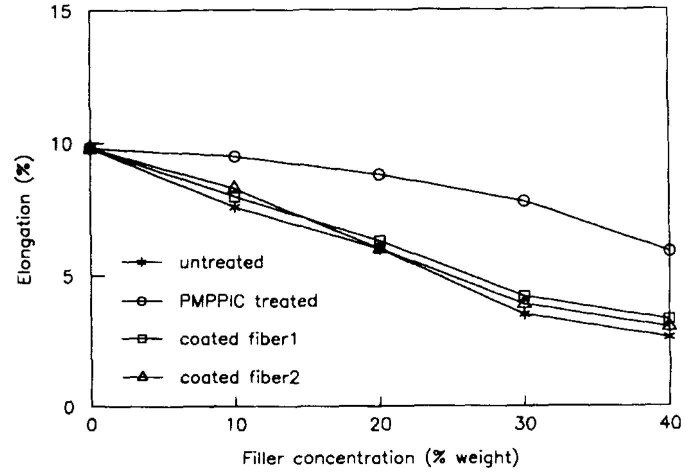

FIGURE 2 Effect of fiber treatment on elongation of HDPE–CTMP aspen composites.

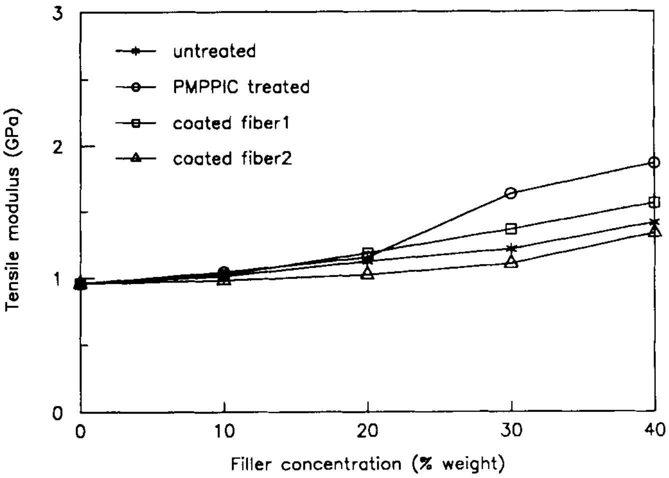

FIGURE 3 Effect of fiber treatment on tensile modulus of HDPE–CTMP aspen composites.

was also observed by Coran and Patel in the case of cellulose fibers and grafted olefin polymers.[12]

Elongation generally decreased with the increase in filler concentration in the composites (Figure 2). Compared to untreated and maleic anhydride coated fiber composites, HDPE filled with PMPPIC treated fibers performed better at filler concentrations greater than 10.0%. The modulus continued to increase with the filler concentration and was not much affected by fiber treatment (Figure 3). Higher increase in modulus was observed after 30.0% filler concentration in the samples.

Figures 4–6 show the effect of different fiber treatments on tensile properties of

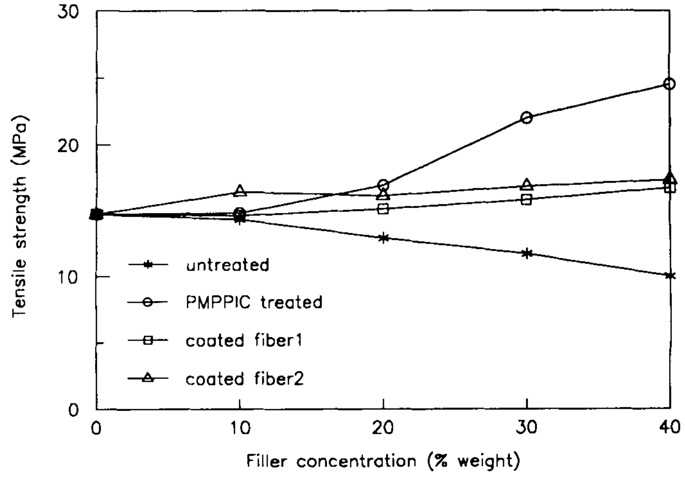

FIGURE 4 Effect of fiber treatment on tensile strength of LLDPE–CTMP aspen composites.

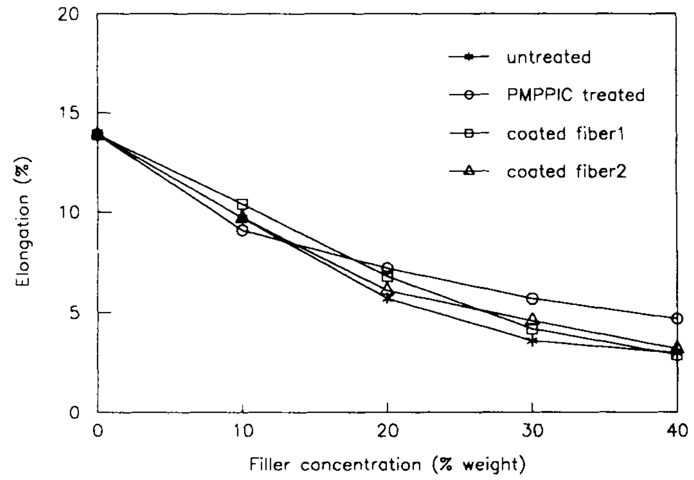

FIGURE 5 Effect of fiber treatment on elongation of LLDPE–CTMP aspen composites.

LLDPE–CTMP aspen fiber composites. There is not much improvement in tensile strength below 20.0% filler level in treated and untreated fiber composites (Figure 4). In the samples containing PMPPIC treated fibers, the strength increased to 24.5 MPa at 40.0% filler concentration compared to 11.2 MPa of untreated fiber composites. LLDPE filled with maleic anhydride coated fibers did not produce any increase in strength. In this case the strength remained constant as the concentration of the fiber increased. This behavior is similar to that observed in HDPE-maleic anhydride coated CTMP aspen fiber composites.

The elongation dropped drastically with the increase in filler concentration as seen from Figure 5. The elongation decreased more than 60.0% at 40.0% filler

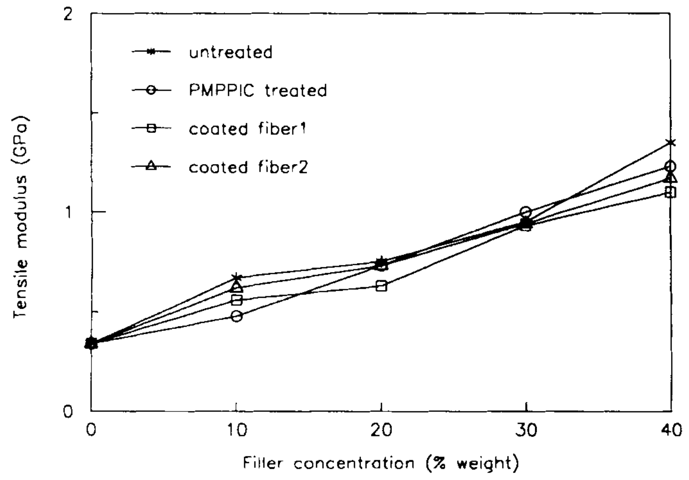

FIGURE 6 Effect of fiber treatment on tensile modulus of LLDPE–CTMP aspen composites.

level in untreated and coated fiber 2 composites. The decrease in elongation is mainly due to an increase in the stiffness of the material. The addition of filler had a positive effect on modulus of the composites (Figure 6). The modulus increased steadily with the addition of filler in the polymer matrix and was not much influenced by fiber treatment. This behavior is consistent with the earlier studies on PP-wood flour composites.[13]

3.2. Fracture surface

Figures 7 and 8 show the fiber dispersion in HDPE-untreated and PMPPIC treated CTMP aspen composites. In the case of untreated fiber composite a higher number of fiber aggregates were observed (Figure 7). Due to hydrogen bonding among the fibers there is a tendency to form aggregates. But the pre-treatment of fibers, before mixing with the polymer, greatly reduces the number of aggregates to achieve a better dispersion of fiber in the matrix (Figure 8). SEM studies of HDPE filled with untreated CTMP aspen shows more fiber pull out from the matrix (Figure 9). Whereas the PMPPIC treatment enhances the fiber adhesion at the interface as seen from Figure 10. In this case the failure of the material is caused by fiber fracture rather than fiber pull out from the matrix.

3.3. Effect of different isocyanate treatments

Since PMPPIC treated wood fibers produced higher tensile strength, further studies were made to examine the effect of different isocyanate treatment on tensile properties of the composites. Tables II and III show the effect of different isocyanates on tensile properties of HDPE–CTMP aspen and LLDPE–CTMP aspen fiber composites. HDPE filled with PMPPIC treated fibers produced a

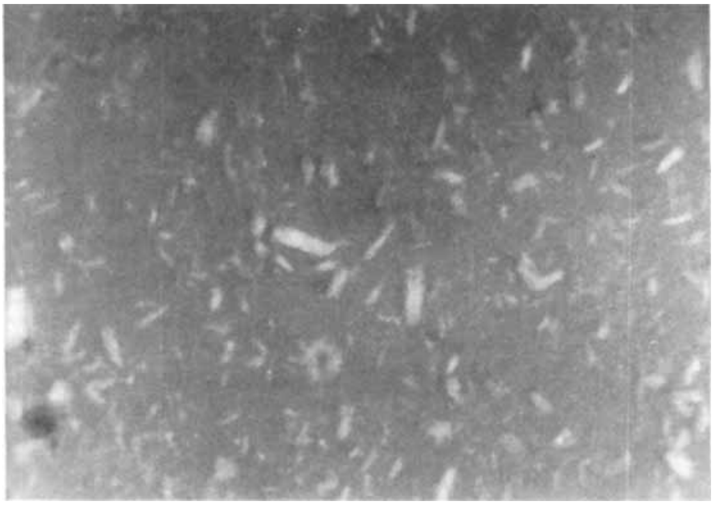

FIGURE 7 Optical micrograph of HDPE-untreated CTMP aspen composite (20.0% fiber weight) Magnification 120×.

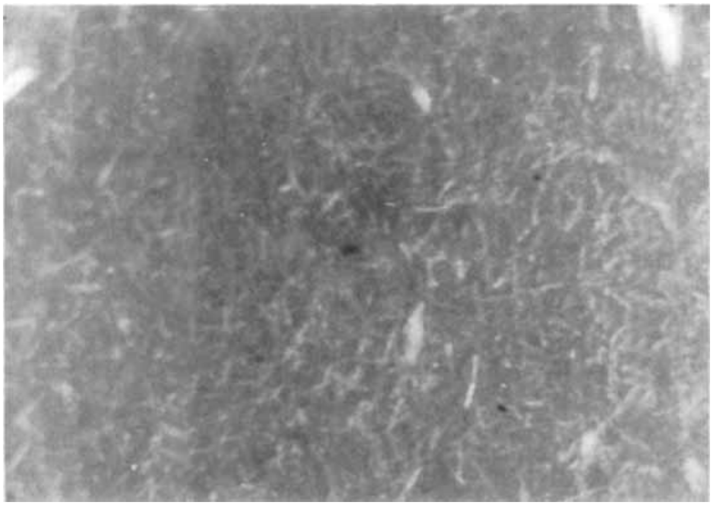

FIGURE 8 Optical micrograph of HDPE–PMPPIC treated (3.0%) CTMP aspen composite (20.0% fiber weight) Magnification 120×.

higher increase in strength, 24.7 MPa (unfilled polymer) to 39.5 MPa at 40.0% filler concentration (Table II). The gain in strength was nearly twice that of unfilled polymer, at 40.0% filler level, in LLDPE–PMPPIC treated CTMP aspen fiber composites.

It can also be seen that CTMP aspen fibers treated with toulene diisocyanate and hexamethylene diisocyanate produced higher tensile strength as the concentration of the fiber increased. But, the overall gain in strength was much less when compared to PMPPIC treated fiber composites. The better performance of PMPPIC is due to the higher surface area coverage of the wood fiber surface by

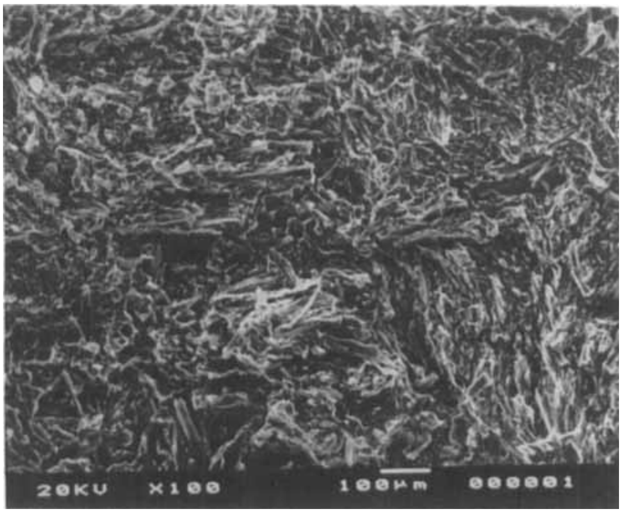

FIGURE 9 Fracture surface of HDPE-untreated CTMP aspen (30.0% fiber weight).

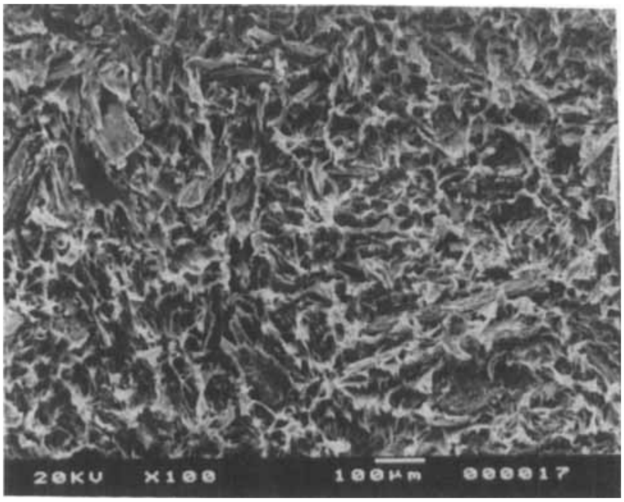

FIGURE 10 Fracture surface of HDPE–PMPPIC treated (3.0%) CTMP aspen (30.0% fiber weight).

TABLE II

Effect of different isocyanate treatments on tensile properties of HDPE–CTMP aspen and LLDPE–CTMP aspen composites

Fiber treatment	Tensile strength (MPa)				Elongation (%)			
Fiber weight (%)	10.0	20.0	30.0	40.0	10.0	20.0	30.0	40.0
HDPE (unfilled)	24.7				9.8			
PMPPIC treated	27.8	31.7	37.9	39.5	9.5	8.8	7.8	5.9
TDIC treated	25.8	28.9	30.7	31.1	7.4	7.2	6.0	4.0
HMDIC treated	26.9	29.0	30.4	28.4	7.5	5.8	5.3	3.2
LLDPE (unfilled)	14.7				13.9			
PMPPIC treated	14.8	17.0	22.1	24.5	9.2	7.3	5.8	4.9
TDIC treated	15.7	16.4	16.9	18.7	9.1	5.7	4.4	3.2
HMDIC treated	16.7	17.2	20.9	21.3	8.3	5.6	5.2	4.8

TABLE III

Effect of different isocyanate treatments on tensile properties of HDPE–CTMP aspen and LLDPE–CTMP aspen composites

Fiber treatment	Fracture energy (KJ $\times 10^{-5}$)				Tensile modulus (MPa)			
Fiber weight (%)	10.0	20.0	30.0	40.0	10.0	20.0	30.0	40.0
HDPE (unfilled)	14.6				966			
PMPPIC treated	16.7	17.1	17.7	14.4	1013	1143	1634	1862
TDIC treated	10.9	12.6	10.2	6.7	1012	1209	1501	1943
HMDIC treated	11.5	9.4	10.8	5.4	1076	1333	1542	1950
LLDPE (unfilled)	12.9				347			
PMPPIC treated	8.6	7.0	6.7	6.6	489	739	1004	1235
TDIC treated	8.2	5.4	4.7	3.4	547	646	912	1200
HMDIC treated	8.1	5.8	5.5	5.0	651	708	941	1018

the isocyanate groups which enhances the adhesion at the interface. Further studies are underway to determine the amount of isocyanate which is chemically bonded to the wood fiber surface.

The elongation decreased with the increase in filler concentration. The decrease in elongation was higher in LLDPE–CTMP aspen fiber composites. Slight improvement in fracture energy was observed when PMPPIC treated fibers were used in HDPE (Table III). In the samples containing TDIC and HMDIC treated fibers, the fracture energy decreased as the filler concentration increased. The modulus increased with the increase in filler concentration and was not much affected by isocyanate treatment. HDPE filled with HMDIC treated fiber composites produced a modulus value of 1950 MPa, at 40.0% filler content, compared to 966 MPa of unfilled polymer. Significant increase in modulus was also observed in LLDPE–CTMP aspen fiber composites. Since wood fibers have higher modulus than the polymer matrix, the increase in fiber loading increases the stiffness of the material.

3.4. Effect of isocyanate concentration

Tables IV and V show the effect of PMPPIC concentration on tensile properties of HDPE–CTMP aspen fiber composites. At 40.0% filler level, the samples with 1.0% isocyanate treated fibers showed an increase in strength of nearly twice the untreated fiber composites (Table IV). When PMPPIC concentration was increased to 3.0%, a significant increase in strength was observed. However, a further increase in PMPPIC concentration (5.0%) did not produce any substantial gain in strength. One of the possible reasons could be that at higher concentration of PMPPIC, the unreacted isocyanate may act as a plasticizer there by reducing the strength of the composite.

The elongation decreased with the increase in fiber concentration. But, the rate of decrease in elongation was lower at higher isocyanate concentration. The fracture energy increased, with the filler addition, at higher isocyanate concentration (Table V). The modulus was not much affected by the variation in PMPPIC concentration. However, it is rather difficult to explain the lower modulus values obtained in the samples containing untreated fibers at higher filler concentration.

TABLE IV

Effect of PMPPIC concentration on tensile properties of HDPE–CTMP aspen composites

PMPPIC (%)	Tensile strength (MPa)				Elongation (%)			
Fiber weight (%)	10.0	20.0	30.0	40.0	10.0	20.0	30.0	40.0
0.0	23.3	18.8	17.9	16.1	7.6	6.0	3.5	2.6
1.0	28.8	31.0	33.8	32.8	9.2	8.7	6.0	3.7
3.0	27.8	31.7	37.9	39.5	9.5	8.8	7.8	5.9
5.0	28.9	32.2	37.6	39.6	9.1	8.3	7.9	6.4

TABLE V

Effect of PMPPIC concentration on tensile properties of HDPE–CTMP aspen composites

PPMPIC (%)	Fracture energy (KJ × 10^{-5})				Tensile modulus (MPa)			
Fiber weight (%)	10.0	20.0	30.0	40.0	10.0	20.0	30.0	40.0
0.0	10.6	6.6	3.8	2.4	1002	1116	1207	1412
1.0	16.3	16.9	11.0	6.4	1091	1332	1471	1979
3.0	16.7	17.1	17.7	14.4	1013	1143	1634	1862
5.0	15.4	16.3	18.7	15.5	1142	1428	1635	1900

3.5. Comparison of different fiber treatments

A comparison of tensile properties of HDPE and LLDPE filled with untreated and treated CTMP aspen composites are presented in Tables VI and VII. The influence of fiber treatment is evident from the significant increase in tensile strength in PMPPIC treated fiber composites (Table VI). The strength increased more than 50.0% at 30.0 and 40.0% filler concentrations in HDPE and LLDPE–CTMP aspen fiber composites. A higher loss in elongation was observed in LLDPE–CTMP aspen composites. This is mainly due to an increase in the stiffness of the matrix which is reflected in the higher modulus values of the samples.

The fracture energy increased by 21.2%, at 30.0% filler level, in HDPE filled with PMPPIC treated fibers (Table VII). But in LLDPE–CTMP aspen composites the fracture energy decreased steadily as the filler concentration increased. A significant gain in modulus was achieved in the case of LLDPE–CTMP aspen composites. The increase in modulus was not affected by fiber treatment and it depends primarily on filler concentration. Earlier studies have also shown that modulus was not much influenced by fiber treatment.[8]

TABLE VI

Comparison of tensile properties of HDPE and LLDPE filled with untreated and treated CTMP aspen fibers

Fiber treatment	Tensile strength (MPa)				Elongation (%)			
Fiber weight (%)	10.0	20.0	30.0	40.0	10.0	20.0	30.0	40.0
	Increase/Decrease (%)				Increase/Decrease (%)			
HDPE (unfilled)	24.7				9.8			
Untreated	−5.7	−23.9	−27.5	−34.8	−22.4	−38.8	−61.2	−75.5
PMPPIC treated	+12.6	+28.3	+53.4	+59.9	−3.1	−10.2	−20.4	−39.8
Coated fiber 2	−4.5	−6.4	−12.9	−10.5	−15.3	−37.8	−59.2	−68.4
LLDPE (unfilled)	14.7				13.9			
Untreated	−2.7	−12.2	−20.4	−31.3	−30.2	−58.9	−73.4	−77.6
PMPPIC treated	+0.7	+15.6	+50.3	+66.7	−34.5	−47.5	−58.3	−65.5
Coated fiber 2	+12.2	+10.2	+14.3	+17.7	−29.5	−55.4	−66.9	−76.9

TABLE VII

Comparison of tensile properties of HDPE and LLDPE filled with untreated and treated CTMP aspen fibers

	Fracture energy (kJ × 10^{-5})				Tensile modulus (MPa)			
Fiber treatment	10.0	20.0	30.0	40.0	10.0	20.0	30.0	40.0
Fiber weight (%)	Increase/Decrease (%)				Increase/Decrease (%)			
HDPE (unfilled)	14.6				966			
Untreated	−27.4	−54.8	−73.9	−80.8	+1.2	+5.2	+13.4	+37.4
PMPPIC treated	+14.4	+17.1	+21.2	−1.4	+4.9	+18.3	+69.2	+92.8
Coated fiber 2	−21.9	−44.5	−67.1	−75.3	+2.8	+6.8	+36.7	+65.1
LLDPE (unfilled)	12.9				347			
Untreated	−28.7	−60.5	−76.7	−83.7	+93.1	+118.7	+176.1	+289.9
PMPPIC treated	−33.3	−45.7	−48.1	−48.8	+40.9	+112.9	+189.3	+255.9
Coated fiber 2	−27.9	−55.0	−65.9	−76.6	+80.1	+110.7	+172.9	+237.8

CONCLUSION

HDPE and LLDPE filled with isocyanate treated CTMP aspen fibers produced a significant increase in tensile strength compared to untreated fiber composites. The modulus was not much influenced by fiber treatment and it depends primarily on filler concentration in the material. PMPPIC treatment was more effective when compared to CTMP aspen coated with maleic anhydride. This study also shows that polymeric isocyanate performs better as a coupling agent than diisocyanate. Also, there exists an optimum level of PMPPIC after that the increase in isocyanate concentration did not produce any significant gain in tensile strength of the composites.

References

1. G. R. Lightsey, *Polym. Sci. and Technol.*, **17**, 193 (1981).
2. J. E. Theberge and E. Hohn, *Polym. Plast. Technol. Engg.*, **16**, 41 (1981).
3. A. D. Beshay, B. V. Kokta and C. Daneault, *Polymer Composites*, **6**, 4, 261 (1985).
4. T. Avella and B. deLhomeux, *J. Appl. Polym. Sci.*, (Polymer Symp.) **40**, 203 (1984).
5. M. H. Schneider and K. I. Brebner, *Wood Sci. Technol.*, **19**, 1, 67 (1985).
6. E. Zavin, *Adv. in Chem. Ser.* (ACS) No. 207, *Chemistry of solid wood*, 349 (1984).
7. R. T. Woodhams, G. Thomas and D. K. Rodgers, *Polym. Engg. Sci.*, **24**, 15, 1166 (1984).
8. R. G. Raj, B. V. Kokta, D. Maldas and C. Daneault, *J. Appl. Polym. Sci.*, **35**, 878 (1988).
9. A. B. Mustafa, B. M. Abd El-hady and N. A. Ghanem, *Angew. Makromol. Chem.*, **85**, 91 (1980).
10. R. G. Raj, B. V. Kokta and C. Daneault, *Die Angew. Makromol. Chem.*, **173**, 101 (189).
11. B. V. Kokta, L. Araneda and C. Daneault, *Polym. Engg. Sci.*, **24**, 950 (1984).
12. A. Y. Coran and R. Patel, U.S. Patent 4,323,625 (1982).
13. R. G. Raj, B. V. Kokta and C. Daneault, *Makromol. Chem., Macromol. Symp.* **28**, 187 (1989).