

Effects of Coating Treatments on the Mechanical Behavior of Wood-Fiber-Filled Polystyrene Composites. I. Use of Polyethylene and Isocyanate as Coating Components

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Synopsis

The influence of different grades of polyethylenes and poly[methylene (polyphenyl isocyanate)] (used to precoat the fiber) on the mechanical properties of polystyrene (PS 201 and PS 525) and chemithermomechanical pulp composites have been investigated. Mechanical properties, including impact strength of PS 201 based composites, improved when polyethylene was used along with isocyanate, whereas PS 525 based composites performed less well in this respect. Polystyrene itself seems a better partner for isocyanate as a coating component.

INTRODUCTION

The compatibility, as well as dispersibility, of wood fibers with nonpolar thermoplastics, e.g., polystyrene, are serious drawbacks to achieving composite materials with improved mechanical properties. An important technique for improving compatibility and dispersibility is to develop a hydrophobic coating of a compatible polymer on the surface of the filler before being mixed with the polymer matrix.¹ When coating components comprise different polymers, it is important to select those polymers which are molten at the mixing temperatures employed and which act to coat the fillers to prevent fiber-to-fiber interaction.^{2,3} Moreover, in order to enhance some chemical affinity between the filler and thermoplastic, selection of a coupling agent, e.g., isocyanate, is sometimes beneficial.⁴⁻⁹ In fact, coupling agents improve the ultimate mechanical properties. In the present investigation, mixtures of different grades of polyethylene as well as polystyrene and poly[methylene (polyphenyl isocyanate)] have been selected as coating components for fillers in chemithermomechanical pulp-polystyrene composites. The mechanical properties of the resulting composites have been evaluated.

MATERIALS

Thermoplastics

(i) High impact polystyrene (PS 525) and (ii) high heat crystal polystyrene (PS 201) were supplied by Polysar Limited, Sarnia, Ontario, Canada. (iii)

Linear low density polyethylene (LLDPE) Novapol GF-0118-A and a high density polyethylene (HDPE) GRSN-8907 were supplied by Novacor Chemical Ltd., and (iv) medium density polyethylene (MDPE) CIL-560-B was supplied by CIL. The physical properties of these polymers as supplied by manufacturer, are summarized in Table I.

Fiber

Hardwood aspen (*Populus Tremuloides Michx*) was used in the form of chemithermomechanical pulp (CTMP). This pulp was prepared in a Sund Defibrator under the same conditions as described earlier.⁸

Coupling Agent

Poly[methylene (polyphenyl isocyanate)] (PMPPIC) was supplied by Poly Science Inc., U.S.A.

EXPERIMENTAL

CTMP aspen pulp was oven-dried by circulating air at 55°C for 48 h, and then ground to a mesh size 60 mixture: 60.5%, mesh 60; 20.2%, mesh 80; 15.5%, mesh 100; and 3.5%, mesh 200.

Coating Treatment

Fibers were coated with polymers alone or their mixtures (10 wt %) and isocyanate (8 wt %), with the help of a Laboratory Roll Mill (C. W. Brabender, Model No. 065) at 175°C.

Preparation of Composites

Usually, a 25 g mixture of polymer and coated pulps (15–35% by weight of composite) were mixed with the roll mill at 175°C. After mixing 5–10 times, the resulting mixtures were reground to mesh size 20. The mixtures were then compression-molded (24 at a time) into "shoulder-shaped" test specimens

TABLE I
Typical Physical Properties of Thermoplastics as Supplied by Manufacturers

Property	PS 201	PS 525	LLDPE GF-0118-A	MDPE CIL-560-B	HDPE GRSN-8907
Tensile strength at yield (MPa)	52.00	24.00	40.00	13.50	23.70
Yield elongation (%)	—	—	600.00	—	9.60
Elongation at failure (%)	3.00	50.00	—	260.00	—
Tensile modulus (MPa)	3170.00	2480.00	—	—	—
0.1% secant modulus (MPa)	—	—	220.00	—	976.00
1.0% secant modulus (MPa)	—	—	—	175.00	—
Melt index (g/10 min)	1.60	3.00	1.00	2.00	7.50
Density (g/cm ³)	1.05	1.04	0.918	0.923	0.954

(ASTM D638, Type V) in a Carver Laboratory press. Standard molding conditions were: temperature, 175°C; pressure during heating and cooling, 3.8 MPa; heating time, 20 min; cooling time, 15 min. Width and thickness of each specimen were measured with the help of a micrometer.

Mechanical Tests

The mechanical properties (e.g., tensile modulus, tensile strength at maximum point, and the corresponding elongation and energy) of all the samples were measured with an Instron tester (Model 4201). A standard general Tensile Test Program method, called "PLA 10" was used, and mechanical properties were automatically calculated by an HP-86B computer. The strain rate was 1.5 mm/min and tensile modulus was reported at 0.1% strain. The impact strength (Izod, unnotched) was tested with an Impact Tester (Model TMI, No 43-01), supplied by Testing Machines Inc., U.S.A. The samples were tested after conditioning at $23 \pm 0.5^\circ\text{C}$ and 50% RH for at least 18 h in a controlled atmosphere. Mechanical properties were reported after taking the statistical average of six measurements. The coefficients of variation, 2.5–8.5%, were taken into account for each set of tests.

RESULTS AND DISCUSSION

CTMP (aspen) was coated with different grades of polyethylenes, e.g., LLDPE, MDPE and HDPE (10% by weight of fiber). The mechanical properties of coated fiber-filled and uncoated fiber-filled PS 201 composites are shown in Figures 1–4. It is obvious from these figures that mechanical properties, except modulus of noncoated fiber-filled composites, deteriorate when coated fibers are used as fillers. Figures 5–8 list the influence of coating of the CTMP fibers with the same types of polyethylene (10% by weight of fiber) and PMPPIC (8% by weight of fiber) on the mechanical properties of PS 201 composites. Figure 5 reveals that the strength of the composites containing 25% of fiber coated with 10% HDPE and PMPPIC, improved compared to that of the original polymer and of noncoated fiber-filled composites. Although the strength of all the other composites is inferior to that of original polymer, the strength of the composites containing a lower level of fibers (e.g., 15%), which were coated with either MDPE or HDPE along with PMPPIC, is superior to uncoated fiber-filled composites. Once again, the standard deviations for strength of MDPE + PMPPIC and HDPE + PMPPIC coated 15% fiber-filled composites are 1.88 and 2.53, respectively. From the statistical analysis one can say that MDPE is superior as far as lower level of fiber is considered. Elongation (Fig. 6) follows nearly similar trends as that of strength as far as noncoated fiber-filled composites are concerned compared to coated fiber-filled composites. But, in this respect, fiber-filled composites are inferior to the original polymer. Figure 7 indicates that the coating compositions, e.g., MDPE + PMPPIC and HDPE + PMPPIC, showed positive effects on energy only up to the 15 and 25% levels of fiber loading, respectively. On the contrary, the standard deviations for properties of coated fiber-filled composites are much greater than those of original polymer. As a result, it can say that energy is rather inferior compared to that of original polymer. In general, modulus of fiber-filled composites increased

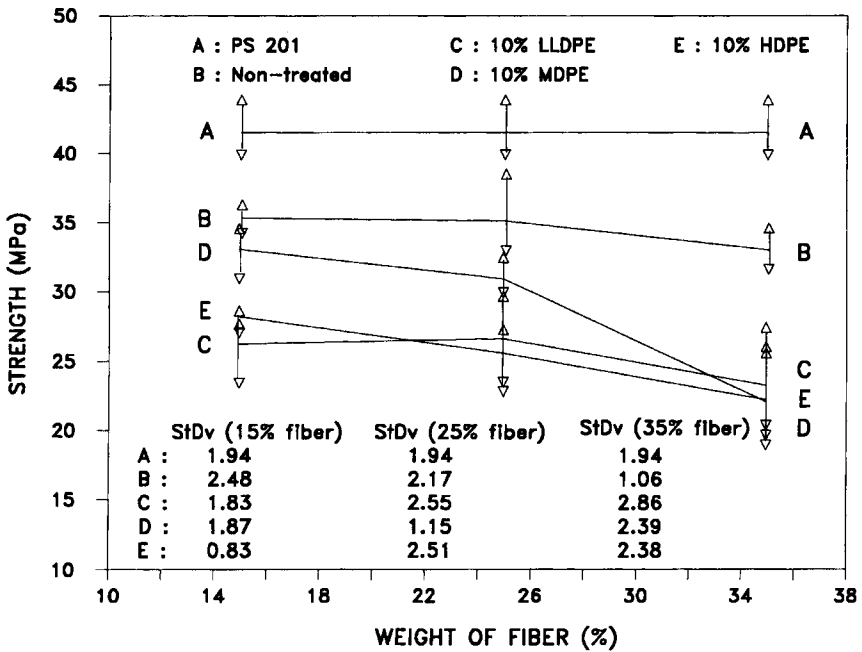


Fig. 1. Dependence of strength on the weight of CTMP (coated with polyethylene) for PS 201 composites.

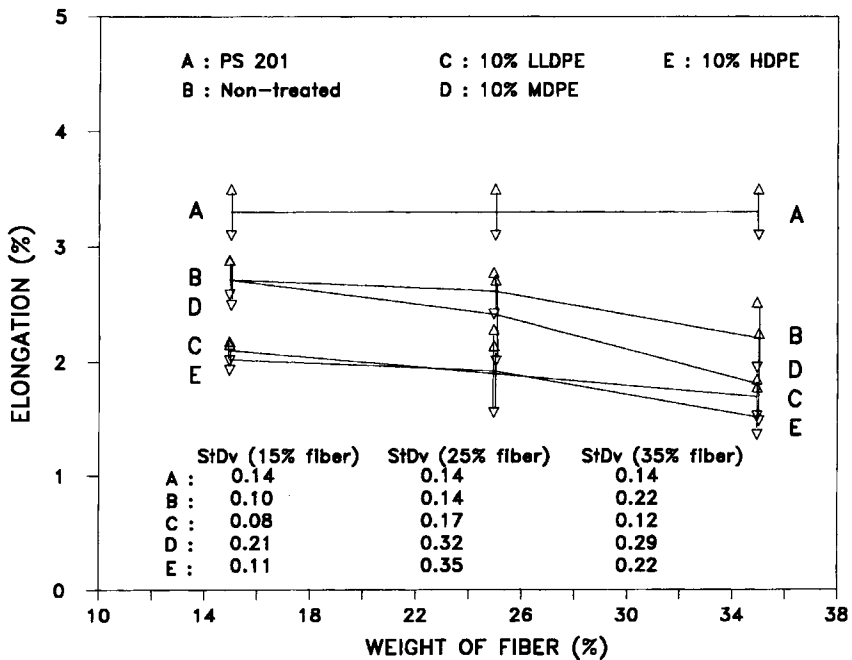


Fig. 2. Dependence of elongation on the weight of CTMP (coated with polyethylene) for PS 201 composites.

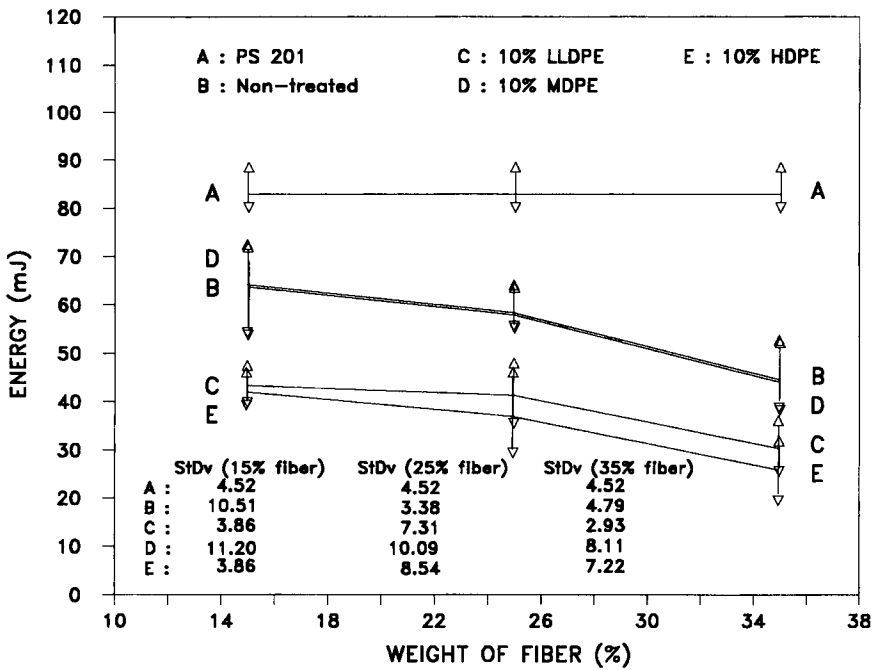


Fig. 3. Dependence of energy on the weight of CTMP (coated with polyethylene) for PS 201 composites.

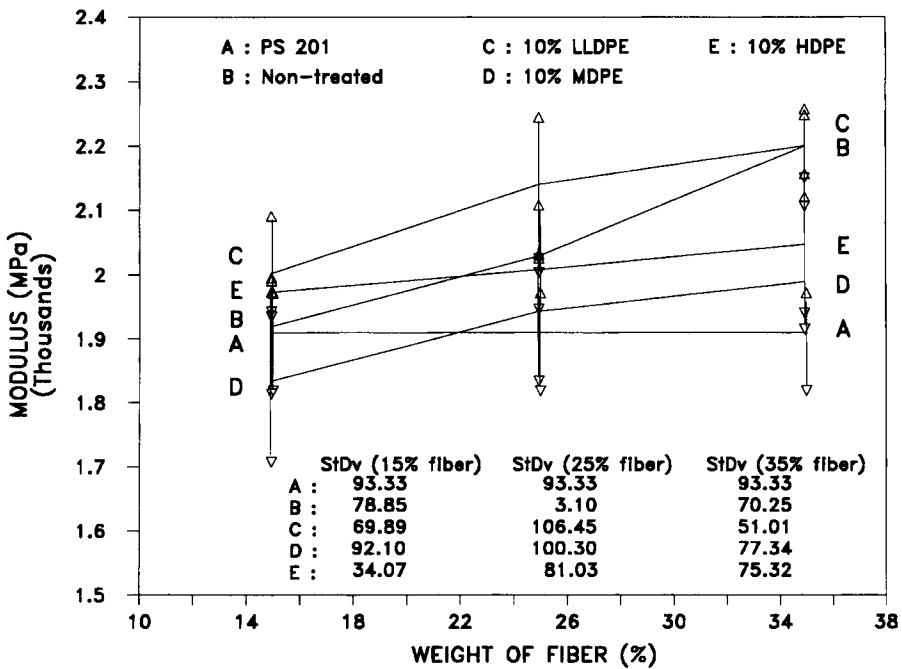


Fig. 4. Dependence of modulus on the weight of CTMP (coated with polyethylene) for PS 201 composites.

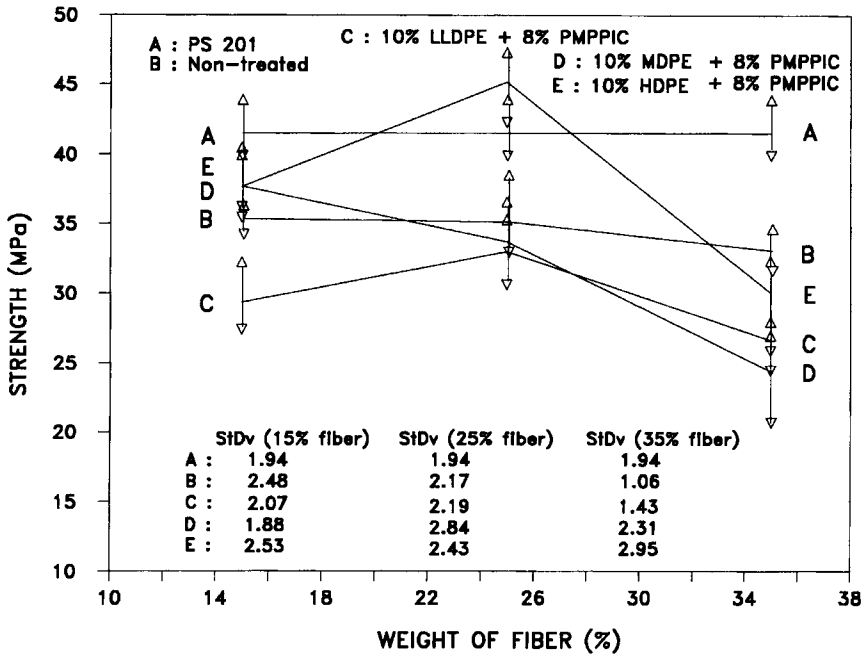


Fig. 5. Dependence of strength on the weight of CTMP (coated with polyethylene and isocyanate) for PS 201 composites.

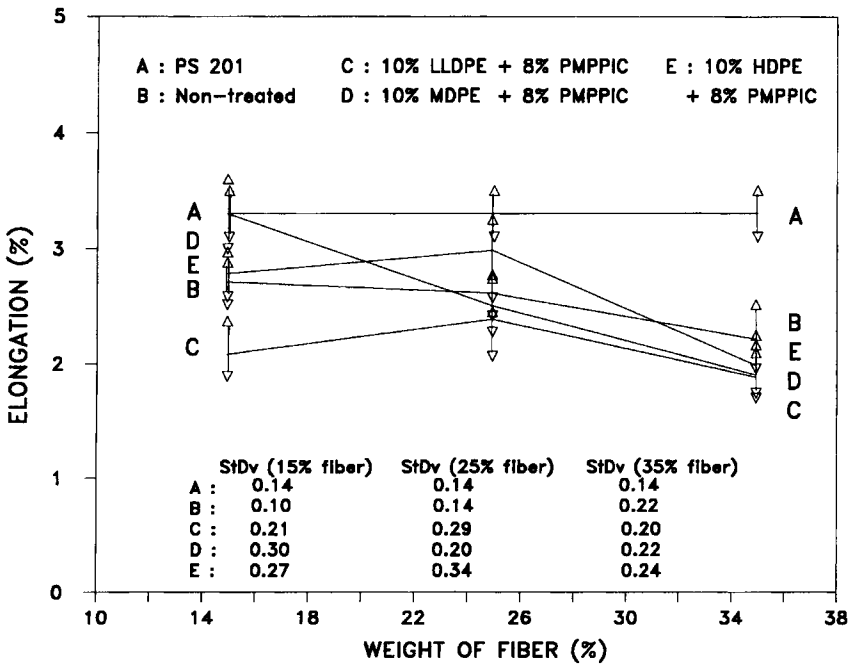


Fig. 6. Dependence of elongation on the weight of CTMP (coated with polyethylene and isocyanate) for PS 201 composites.

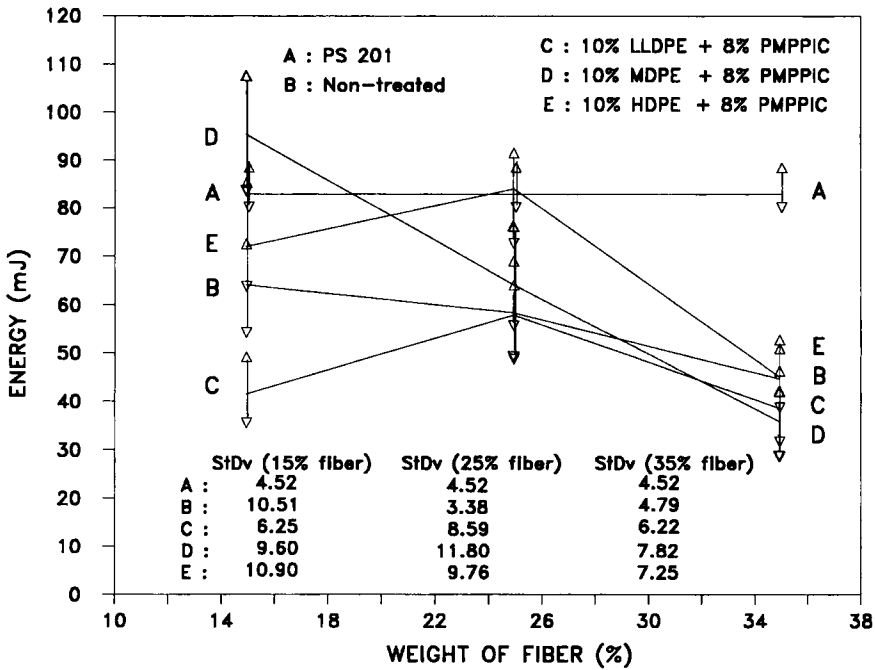


Fig. 7. Dependence of energy on the weight of CTMP (coated with polyethylene and isocyanate) for PS 201 composites.

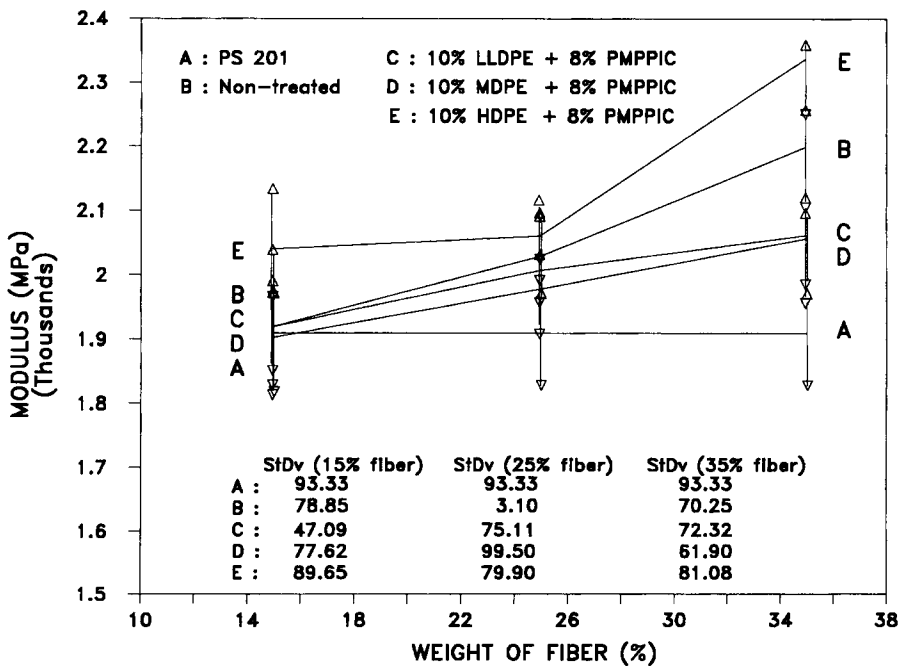


Fig. 8. Dependence of modulus on the weight of CTMP (coated with polyethylene and isocyanate) for PS 201 composites.

compared to the original polymer. HDPE + PMPPIC-coated fiber-filled composites showed the best improvements even when compared to noncoated fiber-filled composites. The performance of different polyethylenes differs widely because of the difference in their basic physical properties (see Table I).

The effect of the coating treatment on the mechanical properties of PS 525-CTMP composites is presented in Table II. CTMP fibers were also coated with mixtures of polyethylene and/or polystyrene + PMPPIC. The standard deviations for the results as presented in Table II, is shown in Table III. It is revealed from Table II that mechanical properties of the composites improve compared to those of the original polymer. Best improvement is noticed when the fibers were being coated with PS 525 and PMPPIC. Unfortunately, taking into account the standard deviations of the results the coating compositions in most cases seem inferior to even uncoated fibers.

In order to summarize the results, improvement percentages of the mechanical properties of the composite materials with respect to those of the original polymer were calculated and presented in Table IV. It is obvious from this table that polystyrene itself is a better partner for PMPPIC as a coating component for polystyrene based composites. Polyethylene along with PMPPIC showed some positive influence when PS-201-based composites are considered. But when PS-525-based composites are considered, the same coating composition produced a detrimental effect.

The Izod impact strength (unnotched) of the composites of both noncoated and coated fiber-filled PS 201 and PS 525 is shown in Table V. It is revealed from this table that the impact strength of PS-201-based composites improves when fibers are coated with PMPPIC and mixtures of polyethylene and polystyrene. Moreover, compared to noncoated fiber-filled composites, the impact strength of the same composites improves in many cases. On the other hand, the impact strength of PS-525-based composites is always lower than that of the original polymer. But in some cases, e.g., MDPE and HDPE (1 : 1 weight ratio) + PMPPIC-coated CTMP fiber-filled composites, the impact strength is superior even to noncoated fiber-filled composites.

Mechanical properties deteriorate when fibers are coated with polymer only. Cellulosic fibers and thermoplastics used in the present study are divergent in polarity. As a result, the compatibility between them could not be improved. But when PMPPIC was used, along with polymers as a coating component, the isocyanate groups chemically linked to $-OH$ groups of cellulose and, as a result, hydrophilicity of the fibers increased. The fibers with reduced hydrophilicity, in addition to the presence of hydrophobic polyethylene, promote better dispersion with hydrophobic polystyrene. But when polystyrene itself is used along with PMPPIC as a coating component, the extent of improvement in the mechanical properties (except for impact strength) is superior to that of polyethylene. Due to the presence of a benzene ring in both PMPPIC and in polystyrene, the delocalized π -electrons interact with each other, which leads to formation of a "bridge" between fiber and coated polymer.^{8,9} Since the base polymer is polystyrene, the interfacial area should be stronger.

Once again, polyethylene showed some positive effects in PS-201-based composites, but it exhibited inhibiting action when PS-525-based composites were considered. In fact, PS 525 is a copolymer of styrene and butadiene, whereas PS 201 is a pure polystyrene, and the former shows superior behavior compared

TABLE II
Influence of Various Coating Compositions on the Mechanical Properties of PS 525-CTMP Composites

Composition of coated materials ^a		Mechanical Properties												
Polymer	2 (wt % of fiber)	PMPPIC	Strength (MPa)			Elongation (%)			Energy (mJ)			Modulus (MPa)		
			15	25	35	15	25	35	15	25	35	15	25	35
— ^b			18.9	22.3	21.5	1.6	1.7	2.2	22.9	17.2	39.7	1790.0	1420.0	2320.0
— ^c			17.3	15.8	12.6	1.5	1.4	1.1	17.7	17.6	11.8	1509.3	1582.5	1606.8
LLDPE (10%)	—		17.2	15.5	14.5	1.6	1.6	1.5	18.3	17.8	17.4	1393.4	1504.8	1551.3
LLDPE (10%)	8%		15.5	14.1	11.9	1.4	1.2	1.1	15.6	12.0	10.8	1388.5	1541.0	1621.8
MDPE (10%)	—		16.4	17.1	18.5	3.0	2.1	2.0	48.2	31.0	29.4	1464.3	1522.2	1772.3
LLDPE (5%)	8%		16.9	17.8	12.9	1.8	2.0	1.2	24.6	28.0	13.0	1505.7	1554.3	1628.5
HDPE (10%)	—	MDPE (5%)	15.2	18.6	14.9	1.5	2.0	1.3	18.4	28.9	16.8	1452.2	1651.0	1750.2
HDPE (10%)	8%		16.7	17.2	14.9	2.1	1.8	1.3	29.0	25.6	15.0	1478.3	1548.8	1686.6
LLDPE (5%)	8%		16.5	18.1	15.9	1.5	2.0	1.3	18.1	28.4	14.3	1419.4	1650.3	1790.1
MDPE (5%)	8%	HDPE (5%)	17.2	16.0	14.3	1.6	1.5	1.2	20.4	19.6	13.3	1506.7	1658.6	1723.3
PS 525 (5%)	8%	LLDPE (5%)	17.7	16.8	15.9	2.2	1.6	1.2	34.0	21.0	14.9	1574.9	1692.3	1830.6
PS 525 (5%)	8%	MDPE (5%)	16.6	17.3	16.8	1.9	1.7	1.5	25.4	24.4	18.5	1527.9	1604.8	1728.6
PS 525 (5%)	8%	HDPE (5%)	16.9	18.8	16.3	1.9	1.9	1.3	27.2	26.7	16.0	1431.4	1724.1	1796.3
PS 525 (10%)	8%	—	17.9	23.3	20.0	2.9	3.7	3.5	46.9	76.8	58.7	1540.0	1740.0	1830.0

^a By weight of fiber.

^b Only PS 525.

^c Noncoated CTMP.

TABLE III
The Standard Deviations for the Mechanical Properties of Various Coated CTMP-Filled PS 525 Composites

Composition of coated materials ^a		Standard deviation												
Polymer	2 (wt % of fiber)	PMPPIC	Strength (MPa)			Elongation (%)			Energy (mJ)			Modulus (MPa)		
			15	25	35	15	25	35	15	25	35	15	25	35
— ^b			0.20			0.06			1.50			22.71		
— ^c			2.13	2.47	1.06	0.10	0.14	0.73	1.10	2.70	1.54	53.22	92.14	70.25
LLDPE (10%)		—	0.75	2.02	0.42	0.21	0.22	0.03	2.45	3.06	0.90	72.97	37.42	84.44
LLDPE (10%)		8%	0.38	0.90	1.48	0.09	0.21	0.17	2.00	3.30	1.60	92.96	79.58	79.71
MDPE (10%)		—	0.80	1.05	0.19	0.10	0.13	0.05	2.82	2.87	0.74	45.46	38.85	103.03
MDPE (10%)		8%	1.03	2.04	2.64	0.43	0.52	0.29	1.18	2.72	3.58	99.92	61.82	96.26
LLDPE (5%)		8%	1.89	2.24	1.41	0.30	0.63	0.31	2.00	3.43	1.79	109.10	67.83	73.29
HDPE (10%)		—	1.21	2.83	1.92	0.08	0.28	0.23	1.08	2.49	1.16	59.13	106.37	78.42
HDPE (10%)		8%	1.67	2.00	1.05	0.55	0.52	0.10	2.40	2.19	3.72	110.4	93.68	105.72
LLDPE (5%)		8%	0.57	1.67	0.55	0.08	0.21	0.12	2.39	2.51	2.57	46.28	92.06	83.13
MDPE (5%)		8%	1.77	0.95	0.82	0.19	0.16	0.50	3.77	2.43	1.00	111.40	109.37	77.52
PS 525 (5%)		8%	0.96	0.86	1.51	0.79	0.19	0.13	1.45	3.20	2.64	86.17	100.12	79.96
PS 525 (5%)		8%	0.43	1.46	0.64	0.31	0.32	0.18	2.53	1.69	3.66	80.69	76.33	110.96
PS 525 (5%)		8%	1.02	2.49	1.46	0.61	0.33	0.13	3.59	2.78	3.40	66.21	59.90	81.56
PS 525 (10%)		8%	0.38	2.99	1.60	0.50	3.00	0.22	1.71	2.45	1.65	88.55	91.0	46.00

^a By weight of fiber.

^b Only PS 525.

^c Noncoated CTMP.

TABLE IV
Comparison of the Improvement in Mechanical Properties of Polystyrene-CTMP Composites

Coated materials ^a		Polystyrene 201						Polystyrene 525										
1	Polymer	PMPPC	Improvement (%)			wt %	Improvement (%)			wt %	Improvement (%)							
			Pulp	Strength	Elongation		Energy	Modulus	Pulp		Strength	Elongation	Energy	Modulus				
			15 ^b	-13.3	-18.2	-20.9	+0.5	+28.0	+46.7	+130.8	35	+28.0	+46.7	+130.8	35	+28.0	+46.7	+130.8
	LLDPE (10%)	—	25	-33.5	-42.2	-48.5	+12.1	+3.0	0	+2.9	15	+3.0	0	+2.9	15	+3.0	0	+2.9
	LLDPE (10%)	8%	25	-18.6	-27.3	-27.7	+4.9	+2.4	+6.7	+6.4	15	+2.4	+6.7	+6.4	15	+2.4	+6.7	+6.4
	MDPE (10%)	—	15	-19.3	-18.2	-16.4	-3.8	-7.7	-6.7	-9.3	15	-7.7	-6.7	-9.3	15	-7.7	-6.7	-9.3
	MDPE (10%)	8%	15	-8.0	0	+18.4	-0.2	+10.1	+33.3	+70.9	35	+10.1	+33.3	+70.9	35	+10.1	+33.3	+70.9
	LLDPE (5%)	8%	15	-9.6	-9.1	+2.1	-3.4	+6.0	+33.3	+62.8	25	+6.0	+33.3	+62.8	25	+6.0	+33.3	+62.8
	HDPE (10%)	—	15	-29.6	-39.4	-48.3	+3.5	+10.7	+33.3	+68.0	25	+10.7	+33.3	+68.0	25	+10.7	+33.3	+68.0
	HDPE (10%)	8%	25	+9.0	-9.1	+4.0	+7.8	+2.4	+20.0	+48.8	25	+2.4	+20.0	+48.8	25	+2.4	+20.0	+48.8
	LLDPE (5%)	8%	15	-10.6	-21.2	-11.6	+1.6	+7.7	+33.3	+16.2	25	+7.7	+33.3	+16.2	25	+7.7	+33.3	+16.2
	MDPE (5%)	8%	15	-8.0	-21.2	-12.2	+6.1	+2.4	+6.7	+6.1	15	+2.4	+6.7	+6.1	15	+2.4	+6.7	+6.1
	PS 525 (5%)	8%	25	-23.4	-36.7	-26.5	+15.2	+5.4	+46.7	+98.3	15	+5.4	+46.7	+98.3	15	+5.4	+46.7	+98.3
	PS 525 (5%)	8%	15	-7.5	-15.2	-0.6	+2.0	+3.0	+13.3	+43.0	25	+3.0	+13.3	+43.0	25	+3.0	+13.3	+43.0
	PS 525 (5%)	8%	25	-12.5	-36.4	-39.3	+16.3	+11.9	+26.7	+55.2	25	+11.9	+26.7	+55.2	25	+11.9	+26.7	+55.2
	PS 525 (10%)	8%	25	-8.7	-27.3	-25.4	+17.3	+38.7	+146.7	+346.5	25	+38.7	+146.7	+346.5	25	+38.7	+146.7	+346.5
	PS 201 (10%)	8%	25	+17.3	+12.1	+45.8	+9.9	—	—	—	—	—	—	—	—	—	—	—

^a By weight of fiber.

^b Noncoated CTMP.

TABLE V
Influence of Various Coating Compositions on the Impact Strength
of Polystyrene-CTMP Composites

Composition of coated materials ^a			Izod impact strength (J/m)					
Polymer			Polystyrene 201			Polystyrene 525		
1	2 (wt % of fiber)	PMPPIC	15	25	35	15	25	35
— ^b				7.8			25.2	
— ^c			6.3	6.1	4.9	12.0	11.3	7.0
LLDPE (10%)		—	5.8	6.5	5.7	11.6	12.5	9.0
LLDPE (10%)		8%	7.3	6.4	6.8	11.6	8.5	8.2
MDPE (10%)		—	6.7	6.6	6.4	7.8	7.6	6.2
MDPE (10%)		8%	7.0	6.9	6.7	10.4	8.6	7.1
LLDPE (5%)	MDPE (5%)	8%	6.4	6.9	7.7	11.8	12.8	10.2
HDPE (10%)		—	7.6	6.2	5.5	9.8	10.5	10.5
HDPE (10%)		8%	7.7	8.2	6.7	9.3	8.9	6.4
LLDPE (5%)	HDPE (5%)	8%	9.3	10.1	5.2	10.7	9.8	8.4
MDPE (5%)	HDPE (5%)	8%	7.2	7.9	9.8	20.2	10.4	7.1
PS 525 (5%)	LLDPE (5%)	8%	8.5	7.0	5.6	10.7	11.3	8.0
PS 525 (5%)	MDPE (5%)	8%	7.9	7.2	6.8	11.6	10.2	7.0
PS 525 (5%)	HDPE (5%)	8%	8.6	7.3	6.3	10.7	11.5	7.4
PS 525 (10%)	—	8%	5.4	5.6	6.9	11.5	12.2	9.0
PS 201 (10%)		8%	5.8	6.3	6.6	—	—	—

^a By weight of fiber.

^b Only PS 525.

^c Noncoated CTMP.

to the latter ones. As a result, mechanical properties of rigid polystyrene PS 201 could be changed because of the presence of other flexible polymers, e.g., polyethylene, whereas high impact polystyrene PS 525 does not.

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