Influence of Coupling Agents and Treatments on the Mechanical Properties of Cellulose Fiber–Polystyrene Composites

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Synopsis

Wood fibers of aspen in the form of chemithermomechanical pulp (CTMP) and Tembec 6816 have been used as reinforcing fillers in different varieties of polystyrene. The tensile strength, elongation, and energy at maximum point, as well as tensile modulus at 0.1% strain is reported. Also revealed is the optimum condition of compression molding. The influence of different coupling agents, such as poly[methylene(polyphenyl isocyanate)], silanes (A-172, A-174, A-1100), and grating on the mechanical properties of composites is discussed. The extent of increase in mechanical properties depends on the weight percentage of fibers, the concentration of coupling agents, and the grafting level (add-on %). Coating followed by an isocyanate treatment appears to be the best treatment. In addition, the isocyanate treatment and grafting are superior to the silane treatment. Experimental results are explained on the basis of possible interactions among cellulose fiber-coupling agent–polymer in the interfacial area.

INTRODUCTION

Thermoplastics are replacing metals in many applications. They offer superior corrosion resistance, lower costs, lighter weight per item, and better flexibility in part design.[1] The ongoing trend toward grade specialty in thermoplastic materials and manufacturing techniques accelerates each year to meet the demand for increasingly widespread use of thermoplastics.[2] Unfortunately, poor performance in some mechanical properties, for example, impact toughness, stress relaxation behavior, and low modulus in many synthetic polymers sometimes limits their commercial applications. One of the most effective ways of improving the mechanical properties of polymers is judicious compounding with reinforcing fibers/particles. Originally, fillers were chosen as a means of reducing costs as well as producing new materials to meet possible future shortages of some critical materials.

During the past decade, several investigators have directed their attention for preparing and characterizing wood fiber composites comprising polyolefins[3-8] and polyvinyls.[9-12] In the literature, it is advocated that the interfacial bond between the reinforcing fiber and the matrix has a significant effect on the performance of a composite material. Due to the divergent behavior of cellulose, which is hydrophilic, and polymer, which is hydrophobic, the problems of compatibility and dispersibility are heightened with cellulose.

In this investigation, attempts have been made to standardize the method of preparing composites of different varieties of polystyrene and cellulose fiber

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(chemithermomechanical pulp of aspen), as well as to study the effect of different coupling agents (e.g., alkoxysilanes, isocyanate, and grafting) on the mechanical properties of composites. In previous work on similar systems, Kokta et al.[12] have shown improvement in the composite's mechanical properties due to the grafting of pulp with styrene. Pauls et al.[13] reported a significant improvement in the flow of birchwood sawdust-polystyrene mixture under molding or extrusion conditions due to the addition of 1–20% of plasticizer. Zoldner et al.[14] showed that the composites of birch wood sawdust and a polystyrene copolymer containing 5% of polar monomer increased the maximum composite strength. The same study showed an increase in strength attributed to the graft polymerization of 6% of the polar monomer to the wood, before mixing with polystyrene. Alkoxysilane coupling agents[8,15,16] and isocyanates[17–19] have been used to modify the interface between wood fibers and polymers.

EXPERIMENTAL

Materials

Pulp

In this study, three different pulps were evaluated as fillers in polystyrene.

The first was nonbleached chemithermomechanical pulp (CTMP) of aspen (*Populus tremuloides Michx*) prepared in a Sund Defibrator: temperature, 126°C; retention time, 5 min; pressure, 0.12 MPa; refining energy, 5.26 MJ/kg; Na_2SO_3, 5% by weight; NaOH, 5% by weight; pH, 12.9. The characteristics of such pulp are described in Table I.

The second was bleached chemithermomechanical pulp of aspen prepared under the conditions described above and bleached as described in ref. 20.

Finally, Tembec 6816, supplied by Tembec Inc., Temiscaming, Québec, Canada, pulp was prepared from a wood species mixture (75% spruce, 20% fir, and 5% aspen) using sulfite process (active agents, $HSO_3^- + H^+$; yield 45%) and bleached CEHDED to very high α-cellulose (95%). Its properties are described in Table II.

TABLE I
Physical Properties of Chemithermomechanical Aspen Pulp

Properties	
Drainage index (CSF) (mL)	119.0
Brightness, Elrepho (%)	60.9
Opacity (%)	91.4
Breaking length (km)	4.5
Elongation (%)	1.8
Tear index (mN m²/g)	7.2
Burst, index (kPa m²/g)	2.6
Yield (%)	92.0
Kappa index no.	121.7
Lignin (%)	17.9

TABLE II
Properties of Tembec 6816

Analytical data		Physical data	
Alpha cellulose (%)	93.4	Basis weight (g/m^2)	724.0
		Approx. density (g/CC)	0.79
Resin (%)	0.03	Air dry weight (%)	104.2
Ash (%)	—	Copper number	0.54
Pentosan (%)	1.3	Dirt m^2 of surface	20.0
Calcium (ppm)	91.0	Brightness, Elrepho (%)	94.2
Copper (ppm)	1.7		
Iron (ppm)	8.2		
Manganese (ppm)	0.1		

Coupling Agents

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

Vinyltri(2-Methoxyethoxy)silane (A-172) and Gamma-Methacryloxypropyltrimethoxy silane (A-1100) were supplied by Union Carbide Company, Montreal, Canada. All these coupling agents were stored in a refrigerator and used without further treatment.

Monomer

Styrene (Eastman Chemical Grade) was purified by distillation and stored in dark bottles in a refrigerator. All other chemicals in this study were of an analytical grade and used as supplied by the manufacturers.

Polymer

Four different types of polystyrene were used. General Purpose, High Heat Polystyrene (Styron 685D) and General Purpose Polystyrene (Styron 667) were supplied by Dow Chemical Company, Ontario, Canada. High Heat Crystal Polystyrene (Polysar Polystyrene 201) and High Impact Polystyrene (Polysar Polystyrene 525) were supplied by Polysar Limited, Sarnia, Ontario, Canada.

The physical properties of these four polymers are summarized in Table III.

TABLE III
Physical Properties of Polystyrenes

Property	PS685D	PS667	PS201	PS525
Tensile strength at yield (MPa)	42.7	35.8	52	24
Ultimate tensile strength (MPa)	42.7	35.8	—	—
Elongation at failure (%)	—	—	3.0	50
Yield elongation (%)	1.5	1.0	—	—
Tensile modulus (MPa)	3240	3171	3170	2480
Vicat softening point (°C)	107.7	100.6	106.0	99
Melt-flow rate (g/10 min)	1.5	8.0	1.6	3.0
Specific gravity	1.04	1.04	1.05	1.04

Procedure

Polymer and fiber were mixed with a roll mill, a C. W. Brabender Laboratory Prep. Mill, Model No. 065. Before being mixed or undergoing any other treatment, polymer and pulp were ground to mesh size 20 and 60, respectively.

Treatment with PMPPIC

Treatment of fiber and polymer with isocyanate was performed by mixing with a roll mill at different temperatures. The percentage of isocyanate in this treatment varied between 0.5% and 4% of the weight of the polymer used.

Isocyanate-Coated Fiber

Before mixing with polymer, the fiber was coated with polymer and isocyanate (PMPPIC) in different percentage levels (e.g., 10:8.5 and 8.5:4) in a roll mill at 175°C. The coated fibers were reground again to mesh size 20.

Silane-Coated Fiber

Oven-dried pulp was mixed with CCl_4 (1:12, weight ratio), dicumyl peroxide (2%), and silane (1–4%). The resulting mixture was heated under reflux at 70–75°C with constant agitation for 3 h with a magnetic stirrer. After reaction, CCl_4 was evaporated and the coated pulp dried for 24 h in a circulating air oven at 55°C.

In the case of silane A-1100, a mixture of polymer (10%), p-xylene (4.3 times the weight of fiber), dicumyl peroxide (0.5%), and maleic anhydride (1%) was agitated at room temperature with a magnetic stirrer. After 3 h of mixing, the coated oven-dried fibers (such as those made in first step) were added to the mixture. The whole content was again kept under reflux and submitted to constant stirring at 80–85°C for 2 h. After coating, the fiber was filtered in a sintered glass funnel, washed with distilled water, dried at 55°C, and reground to mesh size 60.

Grafting and Extraction

The xanthate method of grafting using a hydrogen peroxide-ferrous ion initiation system was employed to graft polystyrene on to wood fibers. The pulp-conditioning procedure and the xanthate method of graft copolymerization have been described in a previous report.[21] Using acetone, it required 15 h to remove (by Soxhlet extraction) the ungrafted homopolymer. Polymer add-on % was calculated as follows: $((A - B)/B) \times 100$ (A is the weight of the product after copolymerization and extraction and B the weight of the pulp).

Preparation of Composites

To mix the polymer and fiber, the temperature of the roll mill varied from 145°C to 225°C with the preferred temperature near 175°C. Mixtures of 20 g polymer and fiber having weight percentages of 10, 20, 30, and 40 were mixed repeatedly (5 to 6 times) on a roll mill. After cooling to room temperature, the mixtures were reground to mesh size 20.

The polymer and fiber mixture was molded into "shoulder-shaped" specimens in a Carver Laboratory press at temperatures between 150 to 190°C and pressures between 1.1 and 4.34 MPa. The heating and cooling times of the mold in the press also varied. The preferred molding conditions were as follows: temperature, 175°C for 30 min at a constant pressure of 3.8 MPa, with a cooling time of 20 min at a pressure of 1.1 MPa.

The approximate weight and dimension of each specimen were: weight, 0.9 g (0.8 g after being trimmed); width, 0.31–0.33 cm; thickness, 0.15–0.17 cm; length, 6.4 cm (1.7 cm between grips).

Mechanical Tests

Mechanical measurements were made on an Instron Tester (Model 4201) at room temperature (23°C) and 50% relative humidity. The standard General Tensile Test Program method, called "PLA," was used to evaluate the mechanical properties. The rate of elongation was 0.75 mm/min and gauge length was 1.7 cm. Dimensions of all specimens were measured with a micrometer. Mechanical properties were reported after taking the statistical average of six measurements.

The mechanical properties of the original polystyrenes as shown in Table III were reported by suppliers either at yield point or at breakpoint. In the present study, all mechanical properties were calculated at the peak point. In the case of fiber-filled composites, the yield points were not found and the difference between peak points and break points were negligible.

The tensile modulus was reported at 0.1% strain. Average coefficients of variations for mechanical properties were in the range of 2.5 to 8.5%.

Results and Discussion

Polystyrene powders were treated at different temperatures in a roll mill at temperatures similar to those used for mixing fibers and polymers. After mixing, molding was undertaken at different temperatures. The effect of mixing and molding temperatures as well as the concentration of coupling agents (e.g., PMPPIC on the mechanical properties of four different polystyrenes: PS667, PS685D, PS201, and PS525) appear in Table IV and Figures 1–4. To compare the results, polystyrene powders were also directly molded. From the table and figures mentioned above, it is obvious that polystyrene, when treated in a roll mill at different temperatures, shows a slight decrease in mechanical properties and this tendency is emphasized at temperatures above 205°C. When mixing polystyrene alone at a temperature above its melting point (as listed in Table III), slow oxidation[22,23] (in the presence of air) accompanied by degradation of the main chains, as well as cross linking may take place. As a result, mechanical properties can be affected.

Mechanical properties are also reduced with an increase in the concentration of isocyanate (as shown in Table IV). In fact, there should not be any chemical reaction between polystyrene and isocyanate even under drastic conditions. During slow oxidation of polystyrene during mixing on the roll mill, the isocyanate group(−NCO) of PMPPIC may react with the oxidized

TABLE IV
Effect of Mixing and Molding Temperatures on Polystyrene

Temperature (°C) (Polystyrene, PS)		Stress (MPa)				Elongation (%)				Energy (J) × 10³				Modulus (MPa) × 10⁻²			
Mixing	Molding	685D	667	201	525	684D	667	201	525	685D	667	201	525	685D	667	201	525
145	150	39.1	33.9			3.8	2.7			75.5	39.9			16.0	15.8		
160	160	39.5	34.1			3.6	2.6			67.4	43.1			15.1	14.8		
—	175	40.5	35.2	39.5	15.0	3.3	2.7	3.1	1.7	69.1	49.9	57.8	15.0	15.8	16.0	16.8	11.8
175[a]	175	39.1	33.5			2.8	2.5			54.4	41.5			15.8	15.8		
175[b]	175	38.4	31.1			2.3	2.3			40.9	34.1			14.3	15.4		
190	190	38.1	33.6			3.0	2.7			52.7	39.6			15.6	15.1		

[a] Treated with 0.5% PMPPIC.
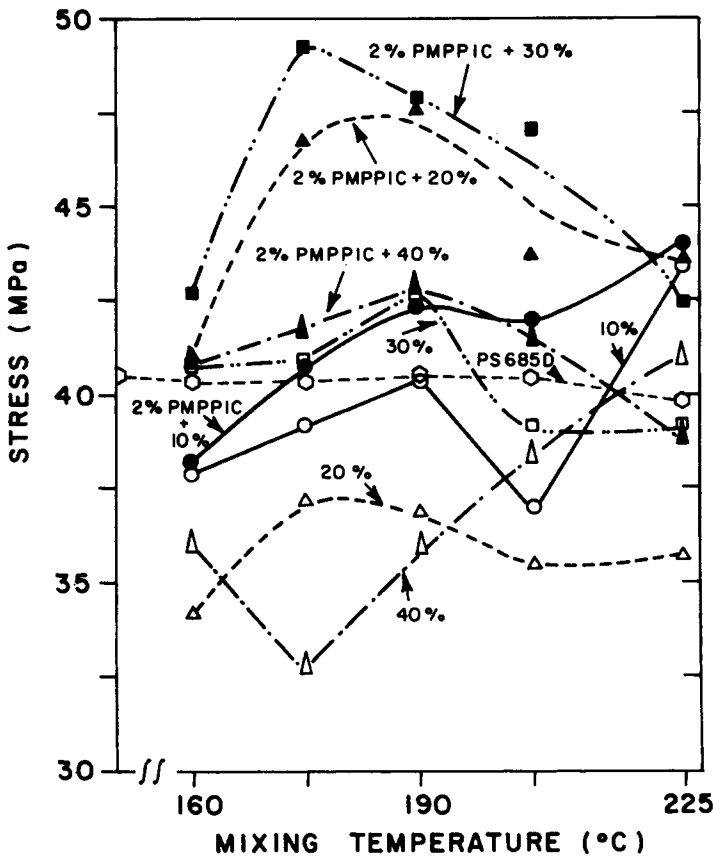[b] Treated with 2% PMPPIC.

Fig. 1. Effect of mixing temperature at a molding level of 175°C on stress of CTMP (nonbleached aspen) – PS685D composites; nontreated and treated with 2% PMPPIC. Percentages indicate the weight percentage of fibers in the composites.

products of polymer.[22, 23] As the probability of oxidation is slight, the unreacted isocyanates tend to decrease the mechanical properties of polystyrene.

Tables V and VI show the mechanical properties of untreated PS685D-CTMP (nonbleached aspen) and 2% treated PMPPIC composites, respectively, at different mixing and molding temperatures. The variation in mechanical properties accompanied by a change in the mixing temperature appears in Figures 1–4. The effect of different weight percentages of fibers in the composites has been determined and are shown in the same figures.

It is apparent that the mechanical properties reach a maximum when mixing and molding temperatures are in the temperature range 175–190°C. Above this temperature the mechanical properties start to decrease. At temperatures above 200°C, the pulp components such as lignin and hemicellulose begin to degrade.[7] Decomposition of the pulp components creates voids inside the composite, causing a reduction in the mechanical properties. Czarnecki and White[9] studied cellulose fiber damage during the processing of polystyrene and cellulose fibers at 180°C. They reported that cellulose fibers showed the least damage during processing at this temperature. In order to

Fig. 2. Effect of mixing temperature at a molding level of 175°C on elongation of CTMP (nonbleached aspen) – PS685D composites; nontreated and treated with 2% PMPPIC. Percentages indicate the weight percentage of fibers in the composites.

Fig. 3. Effect of mixing temperature at a molding level of 175°C on energy of CTMP (nonbleached aspen) – PS685D composites; nontreated and treated with 2% PMPPIC. Percentages indicate the weight percentage of fibers in the composites.
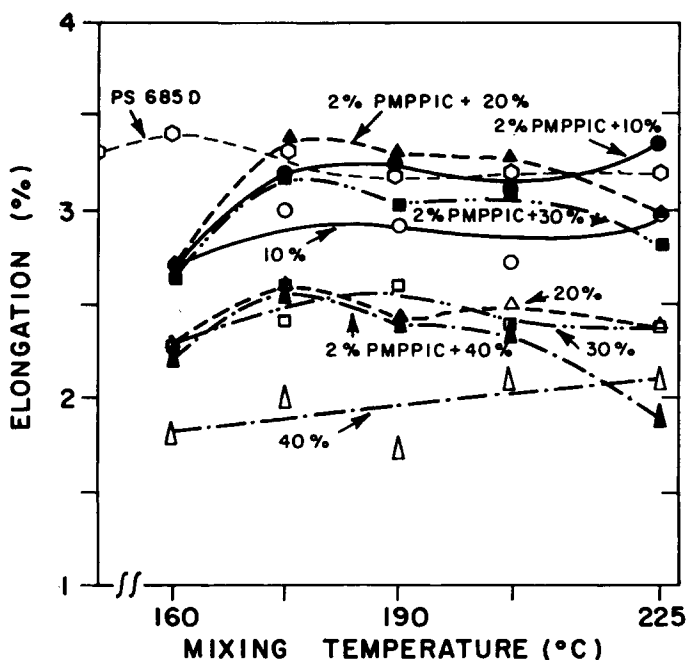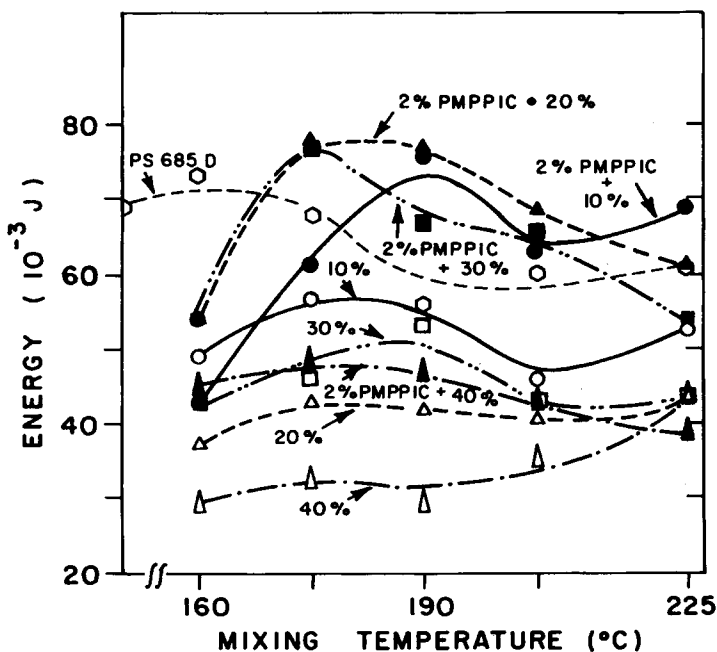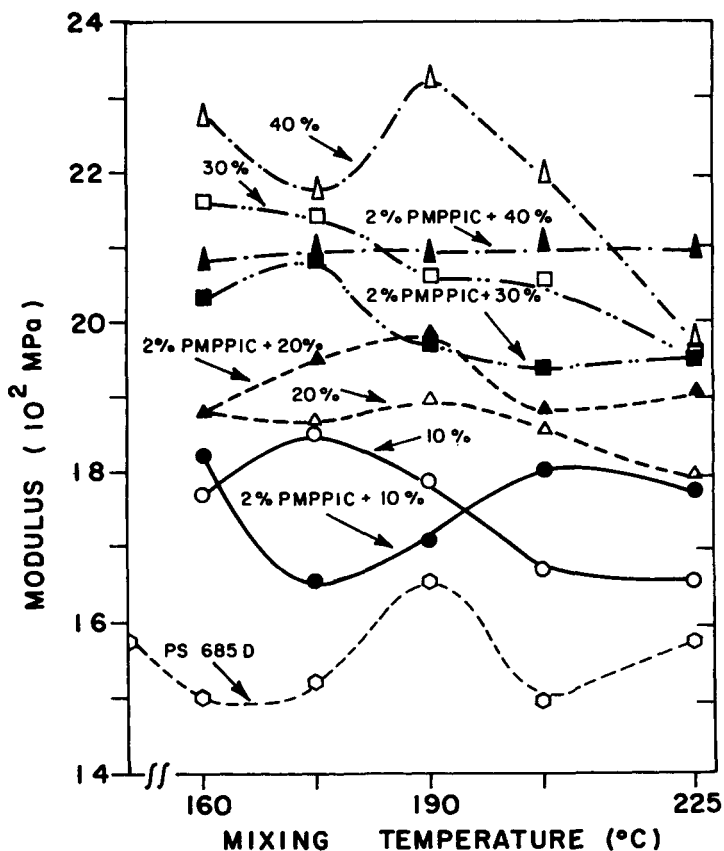
Fig. 4. Effect of mixing temperature at a molding level of 175°C on modulus of CTMP (nonbleached aspen) — PS685D composites; nontreated and treated with 2% PMPPIC. Percentages indicate the weight percentage of fibers in the composites.

maximize the mechanical properties and avoid damage to the cellulose fibers, 175°C was selected as the preferred mixing and molding temperatures.

When we consider the effect of the addition of fiber in nontreated composites, it is observed that stress increases if a 30% fiber content is added to composites. While the modulus also increases with an increase in fiber concentration, the elongation and energy usually decrease. Cellulose fibers are believed[5] to be rigid as compared to polymer. As a result, optimum stress transfer between a high modulus cellulose fiber and a low modulus polymer requires an interphase region of intermediate modulus. In the present case, poor adhesion between fiber and polymer is responsible for decreasing trends in certain mechanical properties, particularly elongation and energy.[5]

An abrupt increase in mechanical properties (as shown in Table VI and Figs. 1–4) was noticed when PMPPIC (2%) was employed as the coupling agent. Elongation increased to 20%, whereas the stress and energy increased to 20–30% of fiber level in the composites. Modulus values showed the same trend as composites without a coupling agent. The improvements in elongation and energy indicate better compatibility of fiber with polymer.[24]

TABLE V
Composites of PS685D-CTMP (Nonbleached Aspen) Fiber: Effect of Mixing and Molding Temperatures

Temperature (°C) (wt% of fiber)		Stress (MPa)				Elongation (%)				Energy (J) $\times 10^3$				Modulus (MPa) $\times 10^{-2}$			
Mixing	Molding	10	20	30	40	10	20	30	40	10	20	30	40	10	20	30	40
145	150	39.4	36.9	37.2	29.5	3.5	2.7	2.3	1.5	69.4	49.3	40.1	20.0	17.0	18.2	19.7	22.3
160	160	37.6	33.9	32.5	30.0	3.0	2.3	2.2	1.8	56.7	38.2	33.2	25.3	16.7	16.5	18.4	17.8
190	190	40.4	40.7	41.9	38.8	3.4	2.8	2.5	2.1	72.9	55.0	51.0	37.3	16.2	18.2	20.2	21.6
175	(PS667)175			40.3				3.3				67.3				15.2	

TABLE VI
Composites of 2% PMPPIC-Treated PS685D-CTMP (Nonbleached Aspen) Fiber: Effect of Mixing and Molding Temperatures

Temperature (°C) (wt% of fiber)		Stress (MPa)				Elongation (%)				Energy (J) $\times 10^3$				Modulus (MPa) $\times 10^{-2}$			
Mixing	Molding	10	20	30	40	10	20	30	40	10	20	30	40	10	20	30	40
160	160	35.5	39.8	39.7	39.4	2.6	2.7	2.5	2.3	42.8	51.1	47.1	42.7	16.9	18.5	19.2	20.9
190	190	42.3	41.9	44.2	46.0	3.5	2.8	3.0	2.6	72.7	55.3	62.9	57.9	17.4	18.2	18.1	21.1
175[a]	175[a]	39.1	37.1	40.7	32.7	3.0	2.6	2.4	2.0	56.6	42.5	45.8	32.5	18.5	18.7	21.4	21.7
"(PS685D)"				40.3				3.3				67.3				15.2	

[a] Nontreated composites.

TABLE VII
Composites of PS685D-CTMP (Bleached Aspen) Fiber: Optimum Condition of Molding

Pressure (MPa) (wt% of fiber)		Stress (MPa)				Elongation (%)				Energy (J) $\times 10^3$				Modulus (MPa) $\times 10^{-2}$			
Heating	Cooling	10	20	30	40	10	20	30	40	10	20	30	40	10	20	30	40
3.8	3.8	39.3	37.3	38.6	35.9	3.0	2.5	2.4	2.1	54.5	43.3	43.6	37.4	15.2	17.2	19.0	19.8
3.8	1.1	39.1	38.3	38.7	38.8	3.1	2.7	2.6	2.2	61.3	53.2	51.0	42.7	15.2	17.6	18.2	19.9
3.8	1.1[a]	37.2	37.1	25.4	30.5	2.8	2.6	1.8	2.0	48.9	42.1	21.5	28.0	15.2	17.2	17.0	19.0
3.8[a]	1.1[a]	39.4	38.0	41.5	33.2	3.1	2.6	2.7	2.2	50.5	40.0	45.4	31.8	16.1	17.2	19.9	19.7

[a] Applying directly to the mold.

TABLE VIII
Composites of PS685D-Nontreated Fibers

Composition (wt% of fiber)		Stress (MPa)				Elongation (%)				Energy (J) $\times 10^3$				Modulus (MPa) $\times 10^{-2}$			
Polymer	Fiber	10	20	30	40	10	20	30	40	10	20	30	40	10	20	30	40
PS685D	—			40.3				3.3				67.3				15.2	
PS685D	CTMP (nonbleached aspen)	39.1	37.1	40.7	32.7	3.0	2.6	2.4	2.0	56.6	42.5	45.8	32.5	18.5	18.7	21.4	21.7
PS685D	CTMP (bleached aspen)	39.3	37.3	38.6	35.9	3.0	2.5	2.4	2.1	54.5	43.3	43.6	37.4	15.2	17.2	19.0	19.8
PS685D	Tembec 6816	37.1	36.1	34.7	32.3	2.4	2.3	2.1	1.8	45.5	41.2	33.6	25.8	18.1	19.6	21.2	22.8

It is well known that there is a considerable difference in thermal expansion coefficients[10] between cellulose and polystyrene. Proper care should thus be taken when cooling the composite in the mold, otherwise numerous voids may develop.[7] To discover the optimum cooling conditions, different techniques including pressure variation were applied while maintaining constant pressure. Molds were covered with a copper plate through which pressure was applied in the press. In the present study, pressure was also applied directly to individual specimens by using cover pins (ASTM D638, TYPE V) during heating as well as during cooling. The mechanical properties of untreated PS685D-CTMP (bleached aspen) composites are listed in Table VII. This table reveals that higher pressure or pressure applied directly to the specimens during cooling is detrimental to mechanical properties of the composites. The optimum cooling pressure was found to be 1.1 MPa while the applied pressure during hot-pressing was 3.8 MPa.
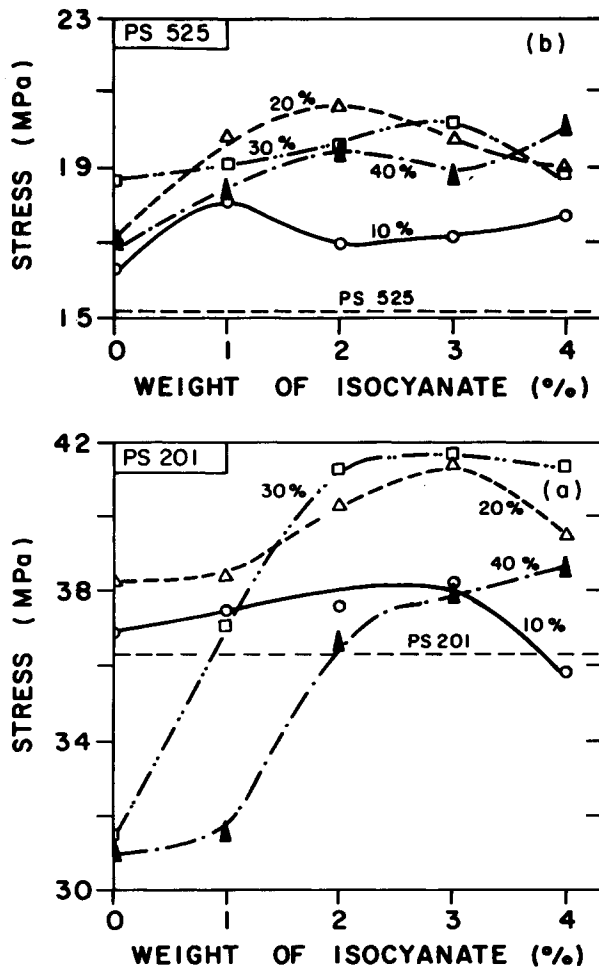

Fig. 5. Effect of concentration of isocyanate, PMPPIC (percentage weight of polymer) on stress: (a) CTMP (nonbleached aspen) − PS201 composites; (b) CTMP (nonbleached aspen) − PS525 composites. Percentages indicate the weight percentage of fibers in the composites.

Mechanical properties of composites containing PS685D and different fibers (e.g., bleached and nonbleached Aspen CTMP, Tembec 6816) are presented in Table VIII. This table shows that stress increases up to 30% of fiber content in the case of nonbleached CTMP fibers; it increases only up to 10% in other cases. In general, elongation and energy regularly decrease, while modulus increases with the addition of fibers to the composites. Unfortunately, most of the mechanical properties are inferior to those of the original polystyrene. This can be explained by the poor interface contact between nontreated wood fibers and polystyrenes.[5,10] From Table VIII, it is also obvious that the nonbleached CTMP fiber compares best insofar as the mechanical properties of the composites are concerned. This type of discrimination can be explained by the difference in the chemical composition of the fibers. The presence of
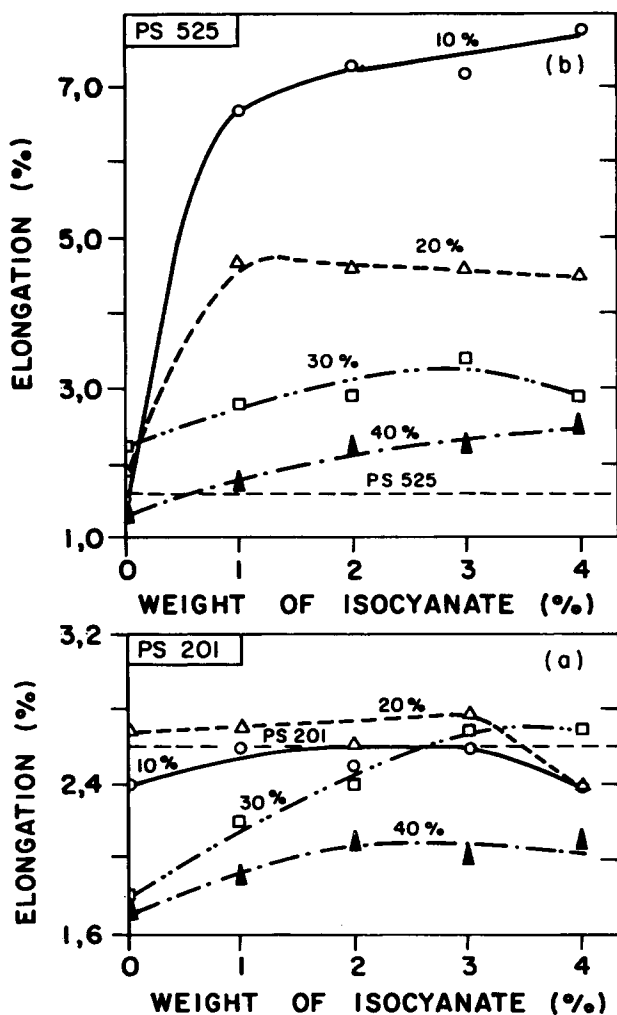

Fig. 6. Effect of concentration of isocyanate, PMPPIC (percentage weight of polymer) on elongation: (a) CTMP (nonbleached aspen) − PS201 composites; (b) CTMP (nonbleached aspen) − PS525 composites. Percentages indicate the weight percentage of fibers in the composites.
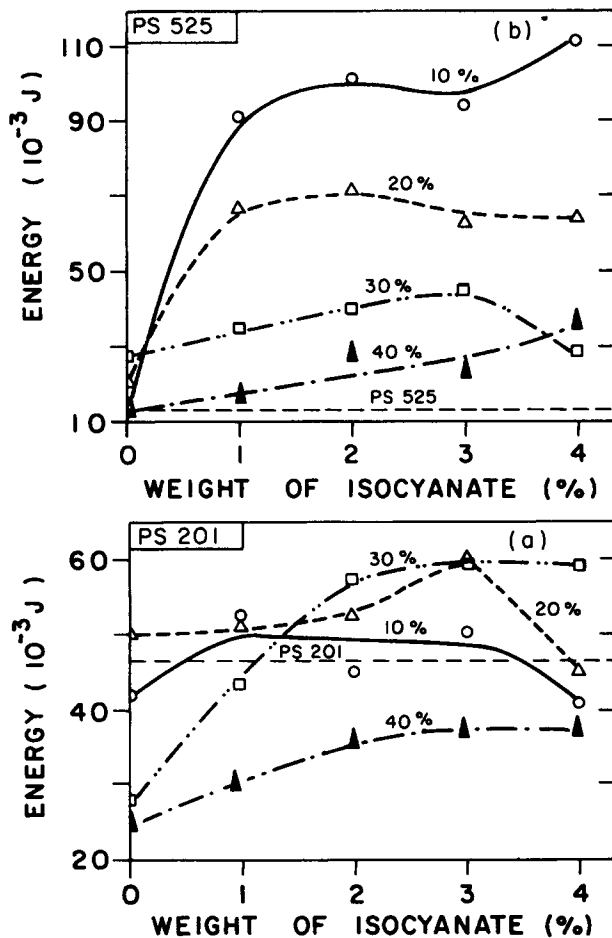
Fig. 7. Effect of concentration of isocyanate, PMPPIC (percentage weight of polymer) on energy: (a) CTMP (nonbleached aspen) – PS201 composites; (b) CTMP (nonbleached aspen) – PS525 composites. Percentages indicate the weight percentage of fibers in the composites.

lignin (~ 18%) in nonbleached CTMP fibers produces better mechanical properties as compared to lower lignin contents in bleached fibers.

The variation in mechanical properties accompanied by the change in the isocyanate concentration of composites which include CTMP (nonbleached aspen) and PS201, PS525, are shown in Figures 5–8. Results of a similar study with PS685D and PS667 are given in Table IX. From the data, it is obvious that most of the mechanical properties of both polystyrenes increase with increased isocyanate concentration in the beginning phase, and then level off within the limit of 2–3% of isocyanate. In the case of PS685D-CTMP composites (as shown in Table IX), only two concentrations (e.g., 1% and 2%) were used; still a distinct upward trend in mechanical properties was observed with an increase of isocyanate concentration.

For both PS201 and PS685D, stress and elongation improved up to 30% and 20% of fiber content, respectively. The energy of PS201 composites increased up to 30% of fiber level; for PS685D, it increased up to 20% of fiber level.
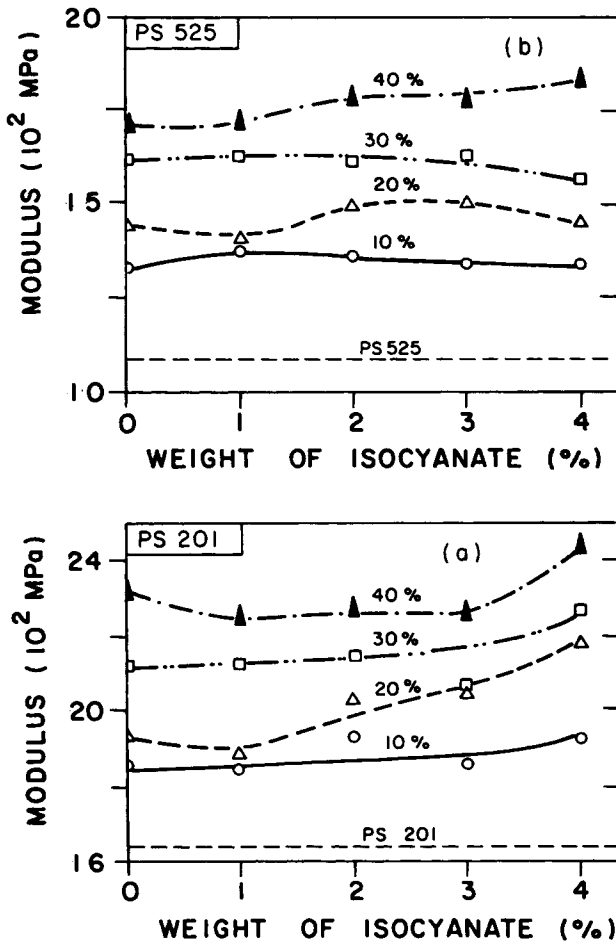
Fig. 8. Effect of concentration of isocyanate, PMPPIC (percentage weight of polymer) on modulus: (a) CTMP (nonbleached aspen) − PS201 composites; (b) CTMP (nonbleached aspen) − PS525 composites. Percentages indicate the weight percentage of fibers in the composites.

Mechanical properties relating to PS525 show maxima at different fiber levels: stress at 20%, elongation and energy both at 10%. Modulus in all cases increased with fiber content in the composites. These improvements in mechanical properties compared with original polymers and untreated composites again support the suggestion that isocyanate is a reliable coupling agent. The appearance of maxima at different fiber levels for different polystyrene composites is due to the difference in their basic physical properties (see Table III).

Mechanical properties of CTMP fibers which were coated with different compositions (expressed as weight percentage based on fiber) of polymer (PS685D, PS201, or PS525) and isocyanate are shown in Table X. Coated fibers were also treated further with 1% isocyanate. As in the case of isocyanate-treated composites, mechanical properties were improved due to the fiber coating. It is interesting that individual mechanical properties of coated fibers follow the same trend as the fibers treated with isocyanate only. Again,

TABLE IX
Composites of Isocyanate-Treated CTMP (Nonbleached Aspen) Fiber: Effect of Concentration of PMPPIC

Composition (wt% of fiber)		Stress (MPa)				Elongation (%)				Energy (J) × 10³				Modulus (MPa) × 10⁻²			
Polymer	Isocyanate[a] (wt%)	10	20	30	40	10	20	30	40	10	20	30	40	10	20	30	40
PS685D	—			40.3				3.3				67.3				15.2	
PS685D	—	39.1	37.1	40.7	32.7	3.0	2.6	2.4	2.0	56.6	42.5	45.8	32.5	18.5	18.7	21.4	21.7
PS685D	1.0	41.6	44.8	47.6	47.4	3.1	3.2	3.0	2.7	66.2	77.1	65.0	62.8	17.5	19.5	20.7	22.8
PS685D	2.0	40.7	46.8	49.3	41.7	3.2	3.4	3.2	2.6	61.2	77.7	77.1	47.8	16.5	19.5	20.9	21.0
PS667	—			34.2				2.6				42.4				15.9	
PS667	—	35.6	37.8	38.2	39.2	2.5	2.7	2.3	2.2	43.1	47.3	41.7	44.5	17.3	18.2	20.5	21.5
PS667	2.0	34.8	40.1	45.0	42.1	2.5	3.1	3.5	2.9	40.6	67.3	81.9	61.8	17.4	18.8	21.4	20.7

[a] Weight percentage of polymer used.

TABLE X
Composites of Isocyanate and Polymer-Coated CTMP (Nonbleached Aspen) Fiber

Treatment (wt% of fiber) Coating[a] / Post[b] Polymer PMPPIC	Stress (MPa)				Elongation (%)				Energy (J) × 10³				Modulus (MPa) × 10⁻²			
	10	20	30	40	10	20	30	40	10	20	30	40	10	20	30	40
PS685D			40.3				3.3				67.3				15.2	
Without coating	39.1	37.1	40.7	32.7	3.0	2.6	2.4	2.0	56.6	42.5	45.8	32.5	18.5	18.7	21.4	21.7
10 8	38.7	40.2	46.6	45.6	2.6	2.5	2.9	2.8	47.0	47.4	70.6	62.1	18.1	19.1	20.0	22.6
10 8 1%PMPPIC	42.9	43.3	47.0	44.7	3.1	2.9	3.1	2.6	64.5	57.9	72.3	56.7	18.9	19.6	20.4	21.3
PS201			36.3				2.6				46.6				16.4	
Without coating	36.9	38.3	31.5	31.0	2.4	2.7	1.8	1.7	42.1	50.0	28.2	24.5	18.5	19.3	21.2	23.2
10 8	39.8	41.1	41.9	37.8	2.9	2.9	2.5	2.0	58.5	57.1	55.8	42.6	18.9	18.9	20.5	21.1
5 8	38.4	42.9	41.4	39.3	2.8	2.9	2.3	2.0	59.2	66.8	44.8	39.0	17.6	20.0	21.4	22.9
5 4	40.3	38.0	40.8	36.7	2.8	2.5	2.2	2.1	60.2	49.0	42.7	37.7	18.2	19.6	20.9	22.5
5 4 1%PMPPIC	39.7	41.4	42.3	38.2	2.8	2.5	2.6	2.1	59.1	56.5	53.2	40.9	18.3	20.6	21.5	21.8
PS525			15.2				1.6				12.8				10.9	
Without coating	16.3	17.1	18.7	16.8	1.5	1.9	2.2	1.3	12.9	20.5	27.6	13.3	13.3	14.4	16.2	17.1
10 8	16.2	16.6	18.9	21.2	5.1	3.6	3.2	2.5	60.4	44.8	44.7	34.4	13.7	14.1	15.7	17.2
5 8	15.7	18.1	20.8	20.8	4.1	3.5	3.0	2.4	46.7	43.7	44.8	31.8	13.3	15.2	16.9	17.8
5 8 1%PMPPIC	17.0	18.8	23.5	20.9	7.9	4.4	3.3	2.2	109.8	62.7	50.2	33.8	13.3	15.1	17.4	18.3

[a] % By weight of fiber.
[b] % By weight of polymer.

TABLE XI
Net Weight Percentage of Isocyanate (PMPPIC) in Composites due to
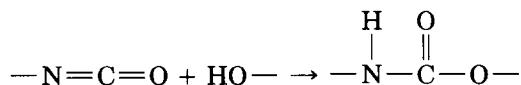Different Treatment at Best Improvement Points

Composition of composites	Net weight percentage of Isocyanate (PMPPIC) in composites
a) 30% fiber + PMPPIC, 2% (of polymer wt)	1.4
b) 30% fiber + PMPPIC, 3% (of polymer wt)	2.1
c) 30% fiber + PMPPIC, 4% (of polymer wt)	2.8
d) 30% fiber coated with (polymer (5%) + PMPPIC (4%))	1.2
e) 30% fiber coated with (polymer (5%) + PMPPIC (4%)) + PMPPIC, 1% (of polymer wt)	1.9
f) 30% fiber coated with (polymer (5 or 10%) + PMPPIC (8%))	2.4
g) 30% fiber coated with (polymer (5 or 10%) + PMPPIC (8%)) + PMPPIC, 1% (of polymer wt)	3.1

with a percentage increase of isocyanates in the coated fiber, a property improvement trend is observed. This upward trend is maintained when coated fibers are further treated with isocyanates. On the other hand, a change in polymer concentration during the coating treatment affects mechanical properties only slightly.

Mechanical property improvements of composites as a function of an isocyanate treatment are summarized in Tables XI and XII, respectively. In Table XII, one learns that improvements in mechanical properties of composites which include the polystyrene- (10%) and PMPPIC-coated (8%) fibers, are comparable to those made through a direct treatment with 3% PMPPIC. Table XI shows that the net concentration of isocyanate for the two different modes of operation does not differ much, while properties improve in a similar way. An exception is in the case of composites of PS685D, where an isocyanate treatment (2%) led to a better behavior than was the case with the coating treatment, although the latter contained less isocyanate.

When coated fibers were retreated with PMPPIC (1%), the composites showed superior mechanical properties. Tables XI and XII show that further treatment with isocyanates increases isocyanate content of the composite than when they are added during the coating treatment. When isocyanate is treated in a one-step process, the saturation of interface reaches its premature stage. The two-step process (e.g., coating followed by treatment) helps to increase the interface area,[10] and mechanical properties are improved accordingly.

The $-N=C-O$ group in isocyanate is highly reactive to the $-OH$ group of cellulose and lignin present in unbleached fiber[25]

$$-N=C=O + HO- \rightarrow -\overset{\overset{\textstyle H}{\textstyle |}}{N}-\overset{\overset{\textstyle O}{\textstyle \|}}{C}-O-$$

TABLE XII
Comparison of the Property Improvement of Composites

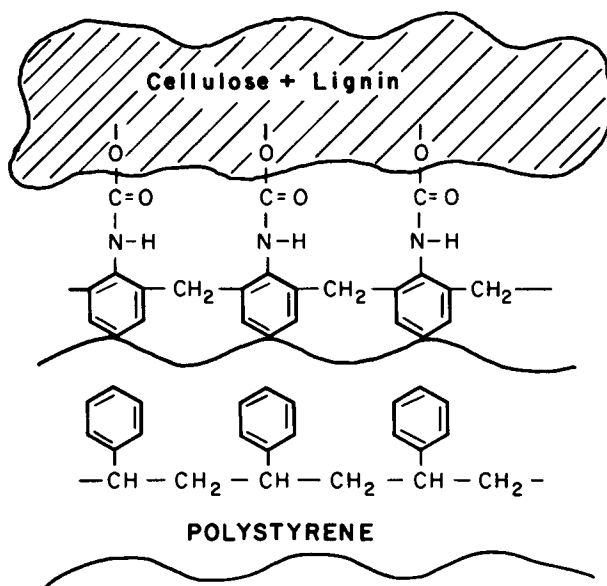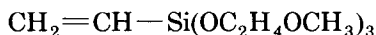| Composition (%) of composite	Improvement % of				Composition (%) of composite	Improvement % of			
	Stress	Elongation	Energy	Modulus		Stress	Elongation	Energy	Modulus
Polystyrene 667					Polystyrene 685D				
CTMP (30%)	+11.7	−11.5	−1.7	+28.9	CTMP (30%)	1.0	−27.0	−32.4	+40.8
CTMP (30%) + PMPPIC (2%)	+31.6	+34.6	+93.2	+34.6	CTMP (30%) + PMPPIC (2%)	+22.3	−3.0	+14.6	+37.5
					CTMP (30%) + Silane A-172 (4%)	+3.0	−21.2	−20.1	+44.1
					CTMP (30%) + Silane A-174 (4%)	−6.7	−36.4	−45.5	+40.8
					CTMP (30%) + Silane A-1100 (4%)	+5.7	−18.2	−19.2	+25.0
					CTMP [(coated: PS (10%) + PMPPIC (8%)) 30%] + PMPPIC (1%)	+16.6	−6.1	+7.4	+34.2
Polystyrene 201					Polystyrene 525				
CTMP (20%)	+5.5	+3.8	+7.3	+17.7	CTMP (30%)	+23.0	+37.5	+115.6	+48.6
CTMP (30%) + PMPPIC (3%)	+14.9	+3.8	+27.3	+25.6	CTMP (30%) + PMPPIC (3%)	+32.9	+112.5	+248.4	+49.5
CTMP [(coated: PS (10%) + PMPPIC (8%)) 30%]	+15.4	−3.8	+19.3	+25.0	CTMP [(coated: PS (10%) + PMPPIC (8%)) 30%]	+24.3	+100.0	+249.2	+44.0
CTMP [(coated: PS (5%) + PMPPIC (4%)) 30%] + PMPPIC (1%)	+16.5	0.0	+14.2	+31.1	CTMP [(coated: PS (5%) + PMPPIC (8%)) 30%] + PMPPIC (1%)	+54.6	+106.3	+292.2	+59.6
CTMP (20%) grafted with PS (56.2%)	+13.2	+3.8	+22.3	+20.1	CTMP (30%) grafted with PS (56.2%)	+34.2	+56.3	+200.0	+59.6

Fig. 9. Hypothetical chemical structure of cellulose–PMPPIC–polystyrene in the interfacial area.

Thus, PMPPIC is chemically linked to the cellulose matrix through strong covalent bonds. Both PMPPIC and polystyrene contain benzene rings. The delocalized π-electrons of benzene rings provide strong interactions which result in strong adhesion bonds between PMPPIC and polystyrene. Ultimately, PMPPIC completes the bridge between fillers and thermoplastics in the interface. The possible hypothetical chemical structure in the interfacial area can be depicted as in Figure 9.
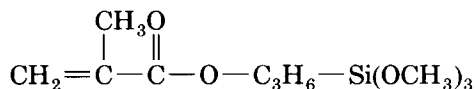
Three different kinds of fibers (e.g., bleached and nonbleached CTMP (aspen), Tembec 6816) were coated with two different concentrations (1% and 4%) of three types of silanes (e.g., silane A-172, silane A-174, and silane A-1100) (see Table XIII). In general, some improvements in mechanical properties were noticed, but only when fibers were treated with 4% of either silane A-172 or silane A-1100. Silane A-1100 was observed to obtain better results than silane A-172.

Below are chemical formulas of three kinds of silanes:

Vinyl Tri(2-Methoxyethoxy) Silane (A-172)

$$CH_2{=}CH{-}Si(OC_2H_4OCH_3)_3$$

Gamma-Methacryloxypropyltrimethoxy Silane (A-174)

$$CH_2{=}\overset{\overset{CH_3}{|}}{C}{-}\overset{\overset{O}{\|}}{C}{-}O{-}C_3H_6{-}Si(OCH_3)_3$$

Gamma-Amino Propyltriethoxy Silane (A-1100)
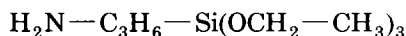
$$H_2N{-}C_3H_6{-}Si(OCH_2{-}CH_3)_3$$

TABLE XIII

Composites of PS685D-CTMP (Bleached and Nonbleached Aspen) and Tembec 6816 Fiber: Effect of Silane Treatment

Composition (wt% of fiber)	Stress (MPa)				Elongation (%)				Energy (J) × 10³				Modulus (MPa) × 10^{-2}			
	10	20	30	40	10	20	30	40	10	20	30	40	10	20	30	40
PS685D Fiber — / Silane[a]			40.3				3.3				67.3				15.2	
CTMP (nonbleached aspen) 1% Silane A-172	39.1	37.1	40.7	32.7	3.0	2.6	2.4	2.0	56.6	42.5	45.8	32.5	18.5	18.7	21.4	21.7
4% Silane A-172	37.4	38.1	37.3		2.5	2.4	2.2		44.4	45.9	37.6		17.5	18.7	19.6	
4% Silane A-172	38.2	40.7	41.5	33.4	2.7	2.8	2.6	2.0	47.9	52.5	53.8	33.4	18.7	19.8	21.9	20.2
4% Silane A-174	39.5	39.2	37.6	38.1	2.9	2.7	2.1	2.2	58.1	53.1	36.7	38.5	17.7	19.3	21.4	23.2
4% Silane A-1100	40.0	41.0	42.6	35.2	3.1	3.0	2.7	2.1	63.4	60.7	54.4	34.8	16.6	18.8	21.2	20.4
CTMP (bleached 1% aspen) — Silane	39.3	37.3	38.6	35.9	3.0	2.5	2.4	2.1	54.5	43.3	43.6	37.4	15.2	17.2	19.0	19.8
1% Silane A-172	38.3	38.9	37.4		2.6	2.5	2.2		50.0	48.7	37.9		17.7	18.6	20.0	
4% Silane A-172	37.1	36.1	34.7	32.3	2.4	2.3	2.1	1.8	45.5	41.2	33.6	25.8	18.1	19.6	21.2	22.8
4% Silane A-172	38.1	38.7	35.4		2.8	2.4	2.2		54.9	40.5	36.3		17.1	19.4	20.5	
1% Silane A-172	40.9	38.2	39.6	36.8	2.9	2.4	2.5	2.1	56.2	41.2	49.7	38.6	18.7	20.3	21.4	22.5
4% Silane A-174	36.8	32.7	34.5		2.6	2.2	2.2		46.0	34.0	38.0		17.4	17.8	18.9	
4% Silane A-174	38.3	36.6	35.9	37.8	2.8	2.4	2.1	2.2	49.8	40.6	38.2	40.0	18.0	19.4	21.9	22.2
Tembec 6816 4% Silane A-1100	41.3	40.9	41.1	40.3	3.0	2.9	2.6	2.3	58.0	56.9	53.4	46.2	18.0	19.2	20.2	21.1

[a] wt% of fiber wt.

The general formula for these silane coupling agents[26] is $YR_1Si(OR_2)_3$. The OR_2 unit in this formula is susceptible to water. Generally, wood samples contain moisture and during the coating treatment $-OR_2$ groups of silanes may hydrolyze to some extent to form silanols.[16]

$$YR_1Si(OR_2)_3 \xrightarrow{H_2O} YR_1Si(OH)_3$$
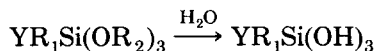
The resulting $-OH$ group or $-OR_2$ group provides a link to cellulose or lignin parts through their $-OH$ groups by the formation of hydrogen bonds.

The Y unit is a polymerizable vinyl group, as in the case of A-172 and A-174. During coating, an initiator (e.g., dicumyl peroxide) was used, which helped to polymerize vinyl groups. Individual silane coupling agent molecules which are supposed to attach to cellulose matrix formed a continuous link. The long hydrophobic polymer chain of polymerized silane can adhere to polystyrene due to a Van der Waals type of adhesive force. As a result, silane coupling agents form a bridge in the interface.[23] In silane A-174, the polar methacryloxy group forms a polymer chain more hydrophilic than that of A-172 which leads to poorer adhesion when in contact with PS.

In the case of silane A-1100, the Y unit is $-NH_2$ group which can react with $-OH$ groups of silanes or cellulose or lignin to form condensation-type polymers. Furthermore, the $-NH_2$ group can also form hydrogen bonds with another $-NH_2$ group or $-OR_2$ groups, or even $-OH$ groups. Therefore, silane A-1100 contains four reacting groups, including the $-NH_2$ group, which may link to the OH group of cellulose and lignin. As a result, a cagelike structure is formed between and polymers may be entrapped in the interphase. Moreover, during coating of silane A-1100, an extra step is undertaken;
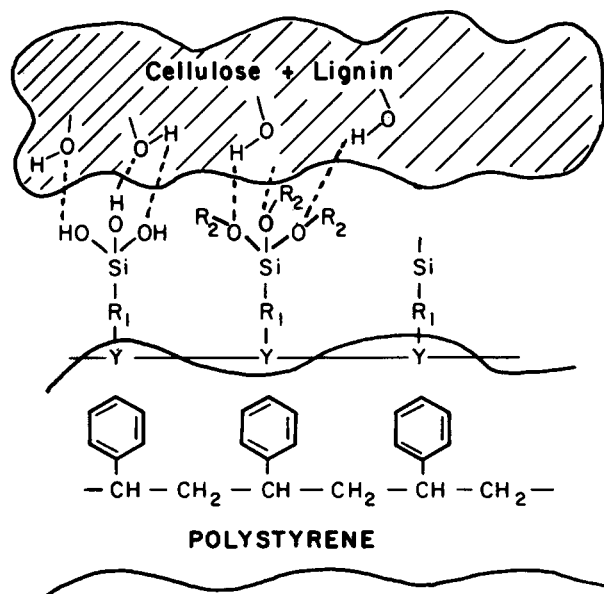

Fig. 10. Hypothetical chemical structure of cellulose–silane coupling agent–polystyrene in the interfacial area.

TABLE XIV
Composites of Grafted CTMP (Nonbleached Aspen) Fiber

Add-on % (wt% of fiber)		Stress (MPa)				Elongation (%)				Energy (J) $\times 10^3$				Modulus (MPa) $\times 10^{-2}$			
Graft	Homopolymer	10	20	30	40	10	20	30	40	10	20	30	40	10	20	30	40
PS201																	
Nongrafted			36.3				2.6				46.6				16.4		
56.2	15.4	36.9	38.3	31.5	31.0	2.4	2.7	1.8	1.7	42.1	50.0	28.2	24.5	18.5	19.3	21.2	23.2
56.2	—	39.6	37.9	38.7	33.9	2.9	2.4	2.5	2.1	60.6	46.5	44.1	32.2	17.8	18.8	19.6	20.1
5.0	8.7	40.5	41.1	39.3	37.0	2.8	2.7	2.4	2.1	57.8	57.0	45.4	36.0	18.5	19.7	20.0	21.3
5.0	—	36.6	34.7	28.1	23.7	2.5	2.2	1.5	1.4	46.4	39.3	19.6	15.8	18.1	19.8	21.2	22.1
PS525																	
Nongrafted			15.2				1.6				12.8				10.9		
56.2	15.4	16.3	17.1	18.7	16.8	1.5	1.9	2.2	1.3	12.9	20.5	27.6	13.3	13.3	14.4	16.2	17.1
56.2	—	16.0	16.8	19.7	20.6	1.5	2.0	2.4	1.9	12.6	19.7	32.0	24.7	14.0	14.6	15.9	17.7
5.0	8.7	16.5	17.6	20.4	22.0	8.5	3.3	2.5	2.2	117.5	43.0	33.1	30.0	13.6	14.6	17.4	17.6
5.0	—	15.3	15.0	15.6	12.5	1.5	1.2	1.3	1.0	11.7	9.4	11.3	6.9	13.2	15.1	16.2	16.3
5.0	—	14.9	15.6	17.2	17.5	1.6	1.5	1.5	1.4	12.6	13.4	15.5	14.8	13.3	15.2	16.4	17.3

treatment of coated fibers with polymer, initiator, and maleic anhydride (already mentioned in the procedure). This additional treatment provides some acid groups on to the polymer matrix.[27] In this way, hydrophilicity of polystyrene involved in the interface increased and, at the same time, $-NH_2$ group of silane may react with the acid group. These are the possible explanations why silane A-1100 is the better compared to the other two silanes. Incidentally, Bataille et al.[23] reported in their very recent publication that treatment of cellulose fibers with coupling agent (silanes) as well as maleic anhydride, improve significantly the interfacial adhesion, and accordingly the mechanical properties of polypropylrne composites. The scanning electron micrographs (SEM) of treated composites showed that the shear stress was sufficiently high to break and delaminate the cellulosic fibers.

Although the real structure of interface is very complex and still unresolved, a simple hypothetical chemical structure containing cellulose, silane coupling agent and polymer can be observed (Fig. 10).

Table XIV shows the mechanical properties of the composites containing polystyrene-grafted CTMP (nonbleached aspen) fibers and PS 201, PS 525. Composites were made with fibers having different amounts of grafted polymer. These fibers sometimes contained homopolymers. From this table, it is obvious that mechanical properties are improved due to grafting and increased with the add-on % of polystyrene onto CTMP fibers. Moreover, the mechanical properties of the extracted (graft only) fibers are superior to those of unextracted (graft + homopolymer) fibers. Due to grafting, even elongation of the composites increased. Actually, through grafting, polystyrenes are covalently linked to cellulose, and hydrophilicity of the fiber is reduced. As a result, the problem of compatibility between cellulose fibers and polystyrene might be overcome by attaching a polymeric segment to the wood fibers having solubility parameters[8, 28, 29] similar to the polymeric matrix used. The presence of low molecular weight homopolymer in unextracted grafted fiber neither helps to increase the hydrophobicity of fiber nor acts as a coupling agent in the interface.

CONCLUSION

The findings of this study indicate that the coupling agents (e.g., isocyanate and silanes) or some special treatments (e.g., grafting) play an important role in improving the mechanical properties of thermoplastic composites containing cellulose fibers. When comparing the effectiveness of different coupling agents and treatments, it is observed (from the Table XII) that coating followed by a isocyanate treatment is the most effective. Again, results of CTMP with a 56.2% grafting level are comparable to those of a 3% isocyanate treatment. Silane treatment is inferior to other treatments. The active participation of isocyanate in the chemical reaction with cellulose accompanied by a strong interaction of delocalized π-electrons of benzene rings, as well as the covalently linked polystyrene to cellulose in grafted fiber provide a superior interfacial area when compared to hydrogen bonds and weak Van der Waals-type forces involving cellulose–silane coupling agent–polymer composites.

High impact polystyrene (e.g., PS525) yields the best balance of mechanical properties compared to other grades of polystyrene.

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