Improvement of the mechanical properties of sawdust wood fibre–polystyrene composites by chemical treatment

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(Received 21 September 1987; accepted 18 December 1987)

The mechanical properties of compression-moulded polystyrenes filled with sawdust wood residue of softwood and hardwood species have been investigated. The tensile modulus at 0.1% strain and the tensile strength, elongation and energy at the yield point are reported. The suitability of sawdust wood residue as a filler for thermoplastics has been tested using two different mesh sizes (20 and 60), as well as by varying the weight percentage of fibres from 10% to 40%. Moreover, to improve the compatibility of the wood fibres with the polymer matrices, different treatments (e.g. graft copolymerization) and coupling agents (e.g. silanes and isocyanates at various concentrations) have also been used. The extent of the improvement in mechanical properties depends on the fibre loading, on the particle size of the fibre, on the concentration and chemical structure of the coupling agents, and on whether special treatments (e.g. coating or grafting of the fibre) are used. The mechanical properties of the composites are improved up to 30% in the case of fibres having a mesh size 60 and when up to 3% of isocyanates was used.

(Keywords: thermoplastic composites; polystyrene; coupling agent; graft copolymerization; mechanical properties)

INTRODUCTION

Thermoplastic materials are being used increasingly for various applications[1]. In recent years, the addition of agro-wastes and agro-forest materials (e.g. sawdust, pulp-mill wood residue, bark, nutshells, bagasse, straw, corncobs, bamboo, etc.) to plastics for the production of new materials has been undertaken[2–5]. Thermoplastic composites are more economical to produce than the original thermoplastics and, as a result, it may be possible to meet any future shortages of thermoplastics. Also, the use of cellulosic materials in thermoplastic composites is highly beneficial, because the strength and toughness of the plastics can be improved. Moreover, cellulosic raw materials are very cheap, highly available and renewable.

The majority of cellulosic raw materials are lignocellulosic materials of different polarity to thermoplastics. As a result of this divergent behaviour, the adhesion between cellulose and polymer is very poor. But the bond between reinforcing material and thermoplastic plays an important role in the mechanical properties of a composite material. The degree of adhesion/interfacial bonding depends on a number of factors, such as the nature of the cellulosic and thermoplastic as well as their compositions, the aspect ratio of the fibre, the method of incorporating the cellulosic into the resin, the processing conditions, and on treatment of the polymer or fibre with various chemicals, plasticizers, coupling agents, etc.

The injection-moulding technique for such thermoplastics (e.g. polyethylene, polystyrene and polypropylene filled with various woodflours) has been thoroughly studied by Berggren *et al.*[6], who mentioned the suitability of such thermoplastic composites for electroplating. On adding 1–20% of different plasticizers to the composite of birchwood sawdust and polystyrene, Pauls *et al.*[7] noticed superior moulding behaviour.

With an increase of polarity in thermoplastics, the adhesion between polymer and wood particles increases. The polarity of the matrix can be increased either by using a copolymer (e.g. poly(butadiene–styrene–acrylonitrile)) to replace polystyrene[8] or by adding or grafting a polar monomer, e.g. acrylic acid or acrylonitrile, to polystyrene-type[9] non-polar polymer. The resulting product possesses higher bending strength, impact resistance and abrasion resistance.

Varteressian[10] made a composite via a different technique: mixing sawdust or woodchips with polystyrene in trichloroethylene as solvent. The resulting composite is good for construction materials. Koran and Patel[11] adapted the moulding technique for the preparation of composites of polypropylene grafted with a methylol phenolic group and various cellulosic fibres along with a bonding agent, e.g. polyisocyanate.

Woodflour having a 200 mesh and sawdust with a 3.5–28 mesh increased the modulus of elasticity on blending, the creep resistance and the defection temperature of resins, e.g. polyethylene, polypropylene and polystyrene[12]. Woodhams *et al.*[13] reported that fibres with an aspect ratio of nearly 100 are readily dispersed into high-density polyethylene or isotactic polypropylene along with some carboxylic dispersing agent. They compared the strength and modulus properties with those of glass-fibre-filled composites.

Fujimura and Suto[14] showed an improvement in the mechanical properties of composites containing polyethylene and acetylated straw. An alkoxysilane coupling agent can be used to improve the interface between vinyl polymers and various wood fibres, e.g.

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0032-3861/88/071255-11$03.00

aspen and white birch[15]. The use of isocyanate as a bonding agent for the preparation of composites comprising vinyl chloride and hardwood kraft pulp was reported by Goettler[16]. Kokta *et al.* reported the improvement in mechanical properties of composites prepared from polymers such as polystyrene[17,18], polyethylene[19] and poly(methyl methacrylate)[20], as well as grafted aspen, birch and spruce chemithermomechanical pulp. They also studied the effect of fibre length, coupling agent and extreme conditions on the mechanical properties of the composites.

In the present investigation, four different varieties of polystyrene and three different types of sawdust (e.g. spruce, aspen and birch) were used to prepare thermoplastic composites. The effects of various parameters, e.g. mesh size, nature and concentration of coupling agents (isocyanates and alkoxysilanes), coating and grafting of sawdust, on the mechanical properties of composites have been studied.

EXPERIMENTAL MATERIALS

Filler

In the present study, three different varieties of sawdust, i.e. two hardwood species (white birch = *Betula papyrifera* Marsh and aspen = *Populus tremuloides* Michx) and a softwood species mixture (75% black spruce, 20% balsam, 5% aspen), were used in the form of woodflour prepared on a laboratory (Athur) grinder. The mesh sizes of the woodflour were 20 and 60.

Thermoplastic

Four different varieties of polystyrene were used in these experiments, as follows: (i) general-purpose, high-heat polystyrene (Styron 685D) and (ii) general-purpose polystyrene (Styron 667)—supplied by Dow Chemical Co., Ontario, Canada; and (iii) high-heat crystal polystyrene (Polysar Polystyrene 201) and (iv) high-impact polystyrene (Polysar Polystyrene 525)—supplied by Polysar Ltd, Ontario, Canada. The essential physical properties of these polystyrenes as supplied by the manufacturers have been listed in *Table 1*. The polymers were ground to 20 mesh size before mixing with fibres.

Coupling agents

To discover the influence of different types of coupling agent, two main types were used in this study: isocyanates and alkoxysilanes. All of these coupling agents were stored in a refrigerator and used as supplied by the manufacturers.

Isocyanates. (i) Poly[methylene(poly(phenyl isocyanate))] (PMPPIC), (ii) toluene 2,4-diisocyanate (TDIC) and (iii) hexamethylene diisocyanate (HMDIC)—supplied by Poly Science Inc., USA.

Alkoxysilanes. (i) Vinyltri(2-methoxyethoxy)silane (A-172), (ii) γ-methacryloxypropyltrimethoxysilane (A-174) and (iii) γ-aminopropyltriethoxysilane (A-1100)—supplied by Union Carbide Co., Montréal, Canada.

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 analytical grade and used as supplied by the manufacturers.

EXPERIMENTAL PROCEDURE

Two different fibre treatments preceded compounding of the composite.

Coating of fibres with coupling agents

Isocyanate coating. Polymer and isocyanate (PMPPIC) were mixed with fibres in different percentage compositions (10%:8%, 5%:8%, 5%:4%) with the help of a roll mill (C. W. Brabender Laboratory Prep. Mill, no. 065) at 175°C. The mixtures were collected and mixed repeatedly 8–10 times for homogeneous coating. Finally, the coated fibres were ground to mesh size 20.

Silane coating. A mixture of oven-dried pulp, CCl_4 (1:12 with respect to the weight of pulp), dicumyl peroxide (2%) and silane (4%) was heated under reflux at 70–75°C for 3 h under constant stirring with a magnetic stirrer. The mixture was allowed to cool to room temperature and, when the CCl_4 had evaporated, it was dried at 55°C for 24 h.

For silane A-1100, the following additional steps were taken. Polymer (10%), *p*-xylene (4.3 times the weight of fibre), dicumyl peroxide (0.5%) and maleic anhydride (1%) were mixed thoroughly by agitating the mixture with a magnetic stirrer at room temperature for 3 h. Then the oven-dried A-1100 coated fibre was poured onto it. The whole mixture was heated under reflux at 80–85°C for 2 h under constant agitation. The mixture was allowed to cool to room temperature and filtered in a glass funnel followed by washing with distilled water. The mixture was then dried by prolonged heating at 55°C and ground to mesh size 60.

Graft copolymerization

The xanthate method of grafting was used to graft styrene onto sawdust wood pulp. The xanthate method of grafting using a peroxide–ferrous ion initiation system has been applied to graft polystyrene onto wood fibres. The procedure for pulp conditioning and the xanthate method of graft copolymerization have been described in a previous paper[21]. The true percentages of grafting were determined after Soxhlet extraction for 15 h with acetone. Polymer loading was calculated as $[(A-B)/B]\times 100$, where A is the weight of the product after copolymerization and extraction and B is the weight of the pulp.

Preparation of composites

Usually, 20 g mixtures of polymer and pulp/coated pulp were used in a roll mill at 175°C. For better results, the resulting mixtures were mixed repeatedly 5–6 times. Isocyanate coupling agents were added directly to

Table 1 The essential physical properties of the polystyrenes as supplied by the manufacturers

Property	PS685D	PS667	PS201	PS525
Tensile strength at yield point (MPa)	42.7	35.8	52.0	24.0
Ultimate tensile strength (MPa)	42.7	35.8	–	–
Elongation at failure (%)	–	–	3.0	50.0
Yield elongation (%)	1.5	1.0	–	–
Tensile modulus (MPa)	3240.0	3171.0	3170.0	2480.0
Vicat softening point (°C)	107.7	100.6	106.0	99.0
Melt flow rate (g/10 min)	1.5	8.0	1.6	3.0
Specific gravity	1.04	1.04	1.05	1.04

the mixtures of pulp and polymer, and mixed mechanically before going into the roll mill. The percentage of isocyanates in the composites ranged from 0.5% to 4%, but that of wood fibres was 10–40%. After mixing, the mixtures were allowed to cool to room temperature and then ground to mesh size 20.

The polymer–fibre mixtures were put into a mould covered by metal plates on both sides. The mould was heated at 175°C in a Carver laboratory press under a pressure of 3.8 MPa for 30 min, followed by cooling under a pressure of 1.1 MPa for 20 min.

The moulded specimens were shoulder-shaped, each with a weight of ~0.8 g, a length of ~6.4 cm (1.7 cm in between grips), a width of 0.31–0.33 cm and a thickness of 0.15–0.17 cm.

Mechanical tests

Test specimens were kept for at least 3–4 h in the testing room, which was maintained at 23°C and 50% relative humidity. The dimensions of all samples were measured with a micrometer. Mechanical measurements were made on an Instron tester (model 4201). Their properties were automatically determined by an HP86B calculator using the Instron 2412005 General Tensile Test Program (under the name 'PLA').

The mechanical properties of the polystyrenes as listed in *Table 1* were measured either at the yield point or at the break point. When wood pulp was mixed with the polymer, yield points were not available. Moreover, the differences between the mechanical properties at the yield point and at the break point were rather small. As a result, the mechanical properties reported in this work are those measured at the yield point.

The tensile modulus was reported at 0.1% strain. Statistical averages of all six measurements were taken. Average coefficients of variation were taken into account for each set of tests. They were in the range 2.5–8.5%.

RESULTS AND DISCUSSION

Composites of polystyrene and untreated sawdust fibres

The variations in mechanical properties due to the addition of different sawdust wood fibres, i.e. spruce, aspen and birch, to thermoplastic composites of polystyrene (PS667, PS685D, PS201 and PS525) are summarized in *Table 2*, which reveals that, except for modulus, there is no significant improvement in mechanical properties. In general, the other mechanical properties are inferior compared to those of the respective polystyrene. Moreover, elongation and energy decrease successively with addition of more fibre to the polymer. This can be explained by the poor adhesion between untreated wood fibres and the polymers. Incidentally, Lightsey and coworkers[5] also showed poor bonding between polystyrene plastic and wood fibre using scanning electron microscopy of the broken surface of test samples.

Effect of the concentration of PMPPIC

Figures 1–4 compare the variations of mechanical properties with the concentration of isocyanate (PMPPIC) in composites of PS685D. The variations of fibre content (10–40%), particle size of fibre (mesh size 20 and 60) and wood species (spruce and aspen) were also taken into account simultaneously. It is obvious from *Figures 1–4* that the mechanical properties of the composites improve with increase in the concentration of PMPPIC; this is true irrespective of other variables, e.g. fibre content, particle size and wood species. *Figure 1* shows that the maximum improvement in stress occurs between 20% and 30% fibre content, but in some cases it occurs at or beyond 30%. In a few cases, elongation and energy (*Figures 2* and *3*) are marginally improved compared to the original polymer. However, modulus (*Figure 4*) increases continuously with the addition of more and more fibres to the composites.

To verify the effect of increasing amounts of isocyanate (PMPPIC), the concentration of isocyanate in composites comprising aspen sawdust (mesh size 60) and two other polystyrenes, PS201 and PS525, have been varied in the range 1–4%. The results appear in *Figures 5–8*. Similar to polystyrene PS685D, the mechanical properties in these cases also increased with increase in isocyanate concentration in the composites. But the upward trend generally levels off at roughly 3% isocyanate. The best improvement in stress (*Figure 5*) for PS201 composites is found at 20% fibre content, while for PS525 it is found at 40% fibre content. Again, for PS201 composites, the elongation (*Figure 6*) only increases up to 10% fibre content, but energy (*Figure 7*) increases up to 20% fibre content. However, in the case of PS525, both elongation and energy values always exceed their original values and

Table 2 Composites of non-treated sawdust fibre[a]

Nature of		Stress (MPa)				Elongation (%)				Energy (J) × 10^3				Modulus (MPa) × 10^{-2}			
Polymer	Fibre[b]	10	20	30	40	10	20	30	40	10	20	30	40	10	20	30	40
PS667	None	34.2				2.6				42.4				15.9			
	Spruce	34.4	37.3	34.8	32.8	2.3	2.5	2.1	1.8	39.4	44.2	34.4	29.7	17.2	18.1	19.2	20.1
	Aspen	34.8	31.2	32.8	28.7	2.7	2.1	1.9	1.7	38.9	31.4	29.5	23.8	18.0	18.5	21.3	20.8
PS685D	None	40.3				3.3				67.3				15.2			
	Spruce	39.4	39.1	38.2	33.5	3.0	2.5	2.3	1.8	61.0	50.0	39.7	27.6	16.2	18.2	19.9	21.2
	Aspen	35.7	36.4	34.3	29.9	2.5	2.4	2.1	1.7	40.9	40.5	36.2	24.8	17.7	18.5	18.8	20.0
	Birch	38.7	38.3	35.2	36.2	2.7	2.6	2.1	2.0	51.1	48.7	34.6	32.3	18.3	17.7	20.7	22.0
PS201	None	36.3				2.6				46.6				16.4			
	Aspen	35.6	33.3	28.8	24.3	2.4	2.1	1.8	1.3	41.2	32.2	24.2	14.7	19.5	20.5	20.7	23.4
PS525	None	15.2				1.6				12.8				10.9			
	Aspen	16.3	16.3	15.8	16.5	1.4	1.9	1.4	1.3	11.3	18.9	12.1	12.1	14.2	15.6	16.8	17.9

[a] The columns 10, 20, 30 and 40 refer to weight percentage of fibre in composite

[b] Mesh size 60

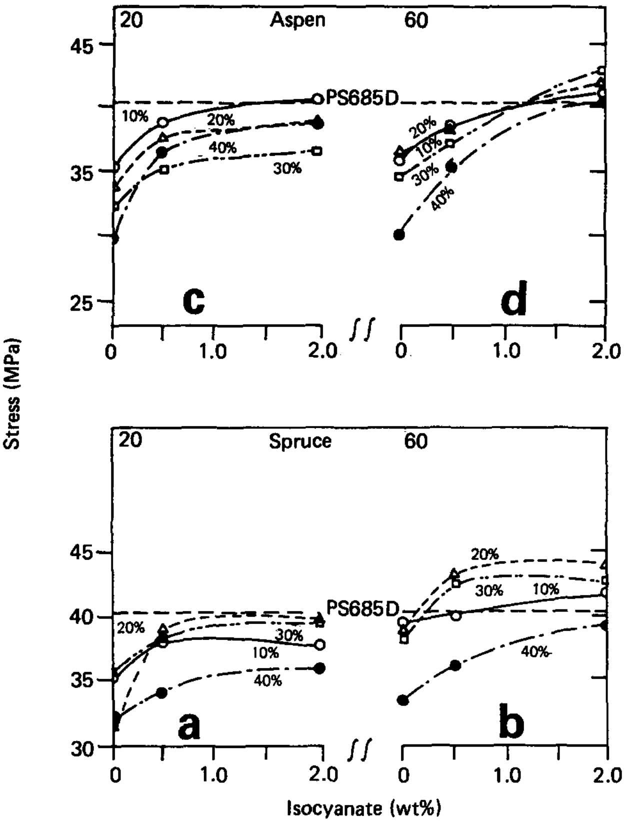


Figure 1 Effect of concentration of isocyanate, PMPPIC (weight percentage of polymer), on stress of sawdust wood fibre–PS685D composites: (a) spruce fibres of mesh size 20; (b) spruce fibres of mesh size 60; (c) aspen fibres of mesh size 20; (d) aspen fibres of mesh size 60. Percentages indicate the weight percentage of fibres in the composites

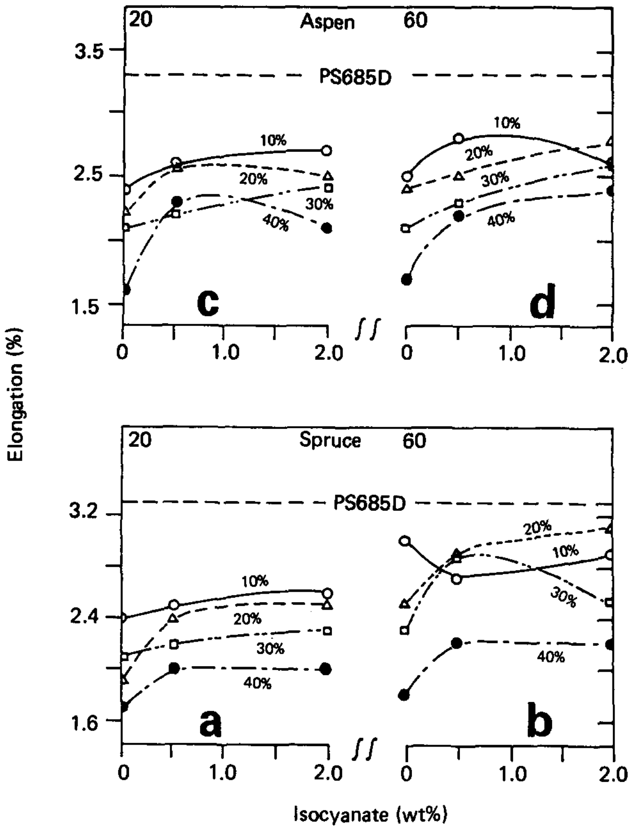
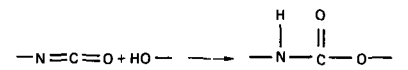


Figure 2 Effect of concentration of isocyanate, PMPPIC (weight percentage of polymer), on elongation of sawdust wood fibres–PS685D composites: (a) spruce fibres of mesh size 20; (b) spruce fibres of mesh size 60; (c) aspen fibres of mesh size 20; (d) aspen fibres of mesh size 60. Percentages indicate the weight percentage of fibres in the composites

improve even at 40% fibre content. Modulus (*Figure 8*) follows the same trend as discussed in the other cases.

The overall improvements in mechanical properties due to the addition of isocyanates to composites indicate that PMPPIC acts as a good reinforcing agent and improves the interfacial contact between fibre and polymer. The role of PMPPIC as a coupling agent can be explained in the following way. The functional group –N=C=O in isocyanate reacts chemically with the –OH group of cellulose as well as lignin to form urethane bonds[22]:



$$-N{=}C{=}O + HO- \longrightarrow -\overset{H}{\underset{}{N}}-\overset{O}{\overset{\|}{C}}-O-$$

As a result, the isocyanate parts are linked to the cellulose matrix by a chain of covalent chemical bonds. The delocalized π–electrons of the benzene rings of both polystyrene and PMPPIC provide a strong interaction. In this way, PMPPIC develops an overlapping interphase area between fibre and polymer, or, in other words, it forms a bridge between filler and polymer in the interphase. Now, stress transfer between cellulose fibre and polymer can easily take place.

Effect of nature of isocyanate

To verify the role of isocyanate as a coupling agent, two other isocyanates (TDIC and HMDIC) with completely different chemical structures from PMPPIC were studied. To compare the results, only one concentration of isocyanate (2%) and a single variety of sawdust fibres

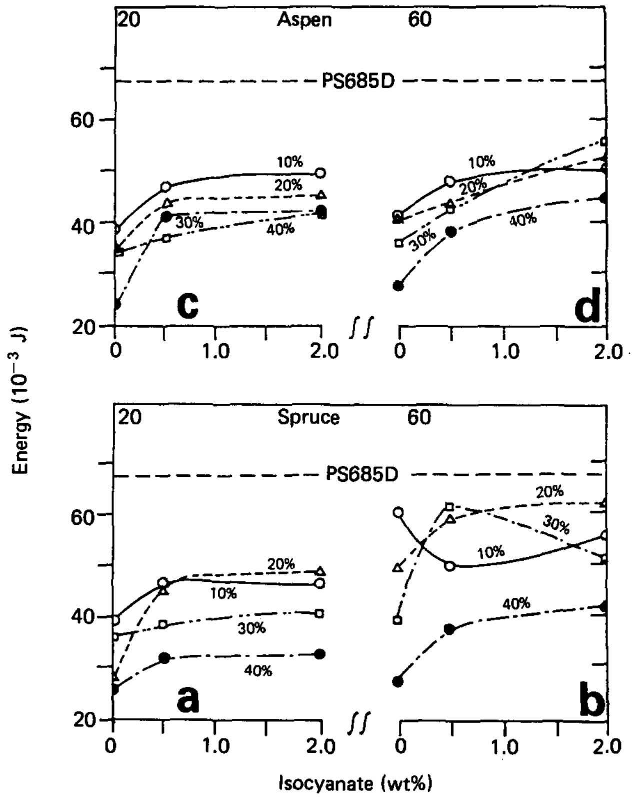


Figure 3 Effect of concentration of isocyanate, PMPPIC (weight percentage of polymer), on energy of sawdust wood fibre–PS685D composites: (a) spruce fibres of mesh size 20; (b) spruce fibres of mesh size 60; (c) aspen fibres of mesh size 20; (d) aspen fibres of mesh size 60. Percentages indicate the weight percentage of fibres in the composites

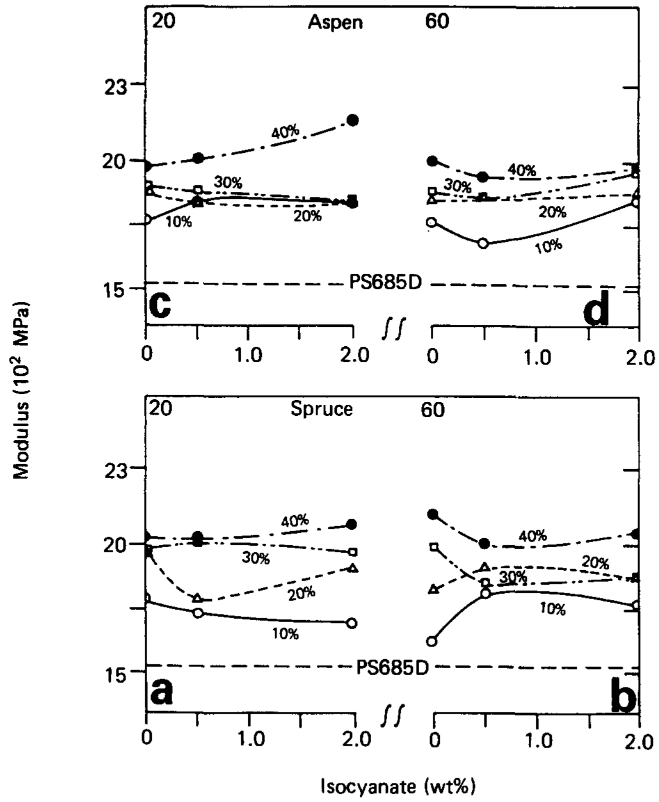


Figure 4 Effect of concentration of isocyanate, PMPPIC (weight percentage of polymer), on modulus of sawdust wood fibre–PS685D composites: (a) spruce fibres of mesh size 20; (b) spruce fibres of mesh size 60; (c) aspen fibres of mesh size 20; (d) aspen fibres of mesh size 60. Percentages indicate the weight percentage of fibres in the composites

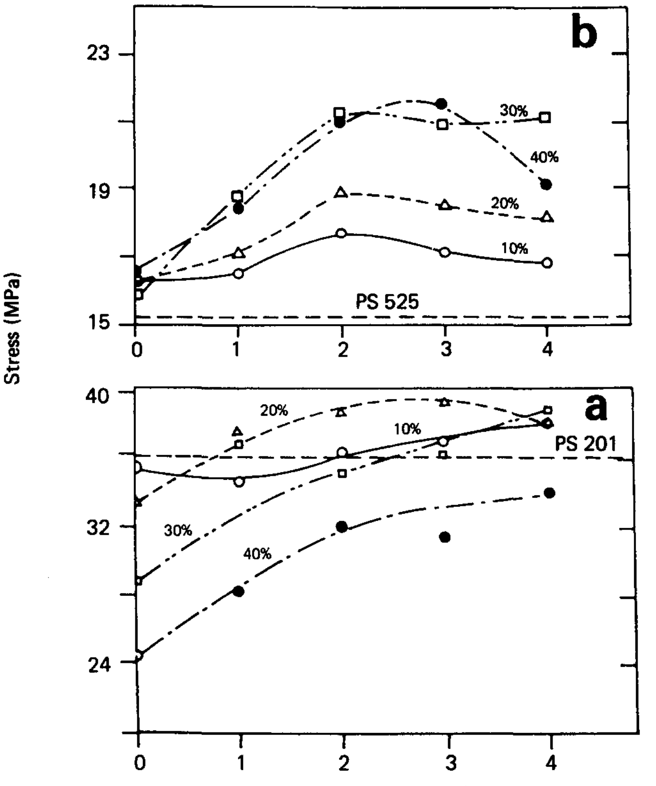
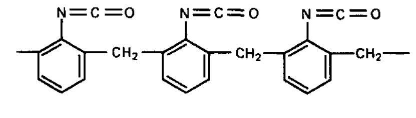


Figure 5 Effect of concentration of isocyanate, PMPPIC (weight percentage of polymer), on stress: (a) sawdust (aspen fibres of mesh size 60)–PS201 composites; (b) sawdust (aspen fibres of mesh size 60)–PS525 composites. Percentages indicate the weight percentage of fibres in the composites

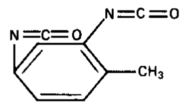
(spruce), of mesh size 20 and 60, were used. The mechanical properties of PS685D are presented in *Table 3*, which shows that for PMPPIC or TDIC, stress increased up to 30% fibre content, but it increased only up to 10% fibre content when HMDIC was used. It is also obvious from this table that there is no significant improvement in either elongation or energy, while modulus increases continuously with the fibre content in the composite.

Again, comparing the results for the three isocyanates, it can be observed that the extent of improvement decreases in the following order: PMPPIC, TDIC and HMDIC. To explain the results, we need to consider the chemical formulae of these isocyanates:

Poly[methylene(poly(phenyl isocyanate))] (PMPPIC)



Toluene 2,4-diisocyanate (TDIC)



Hexamethylene diisocyanate (HMDIC)

$O{=}C{=}N{-}H_2C{-}(CH_2)_4{-}CH_2{-}N{=}C{=}O$

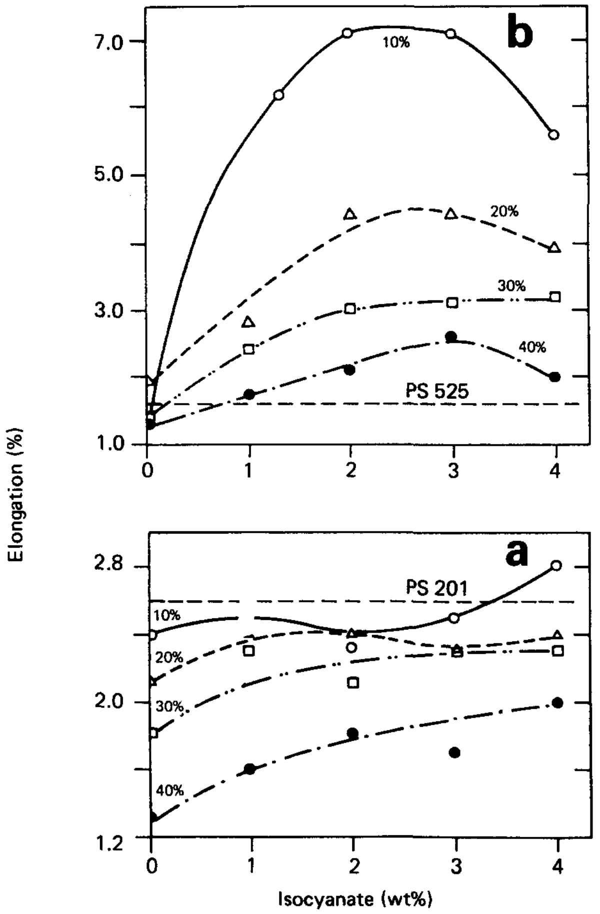
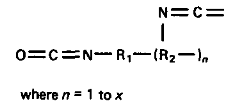


Figure 6 Effect of concentration of isocyanate, PMPPIC (weight percentage of polymer), on elongation: (a) sawdust (aspen fibres of mesh size 60)–PS201 composites; (b) sawdust (aspen fibres of mesh size 60)–PS525 composites. Percentages indicate the weight percentage of fibres in the composites

As we have already discussed, the linking of isocyanate with fibre matrix by the formation of a chain of covalent chemical bonds applies to all three isocyanates. However, the π-electrons of the benzene rings in PMPPIC and TDIC contribute to the much stronger interaction with polystyrene (which also has benzene rings) compared to HMDIC without π-electrons. Furthermore, owing to the polymeric nature of PMPPIC, the cellulose phase and the polymer phase (polystyrene) are continuously linked by it in the interface, while the discrete nature of TDIC and HMDIC make them inferior in this respect. As a result, PMPPIC is the best coupling agent when compared to the other two, while TDIC maintains a position between PMPPIC and HMDIC.

From the above chemical formulae of the isocyanates, the general chemical formula can be written as:



$$O{=}C{=}N{-}\overset{\overset{\displaystyle N{=}C{=}O}{|}}{R_1}{-}(R_2{-})_n$$

where $n = 1$ to x

Again, with the help of this general formula, the hypothetical chemical structure of the interfacial area of

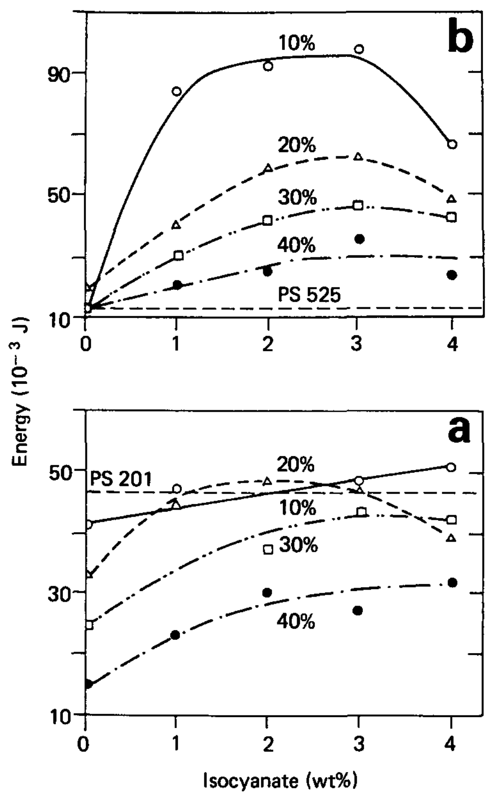


Figure 7 Effect of concentration of isocyanate, PMPPIC (weight percentage of polymer), on energy: (a) sawdust (aspen fibres of mesh size 60)–PS201 composites; (b) sawdust (aspen fibres of mesh size 60)–PS525 composites. Percentages indicate the weight percentage of fibres in the composites

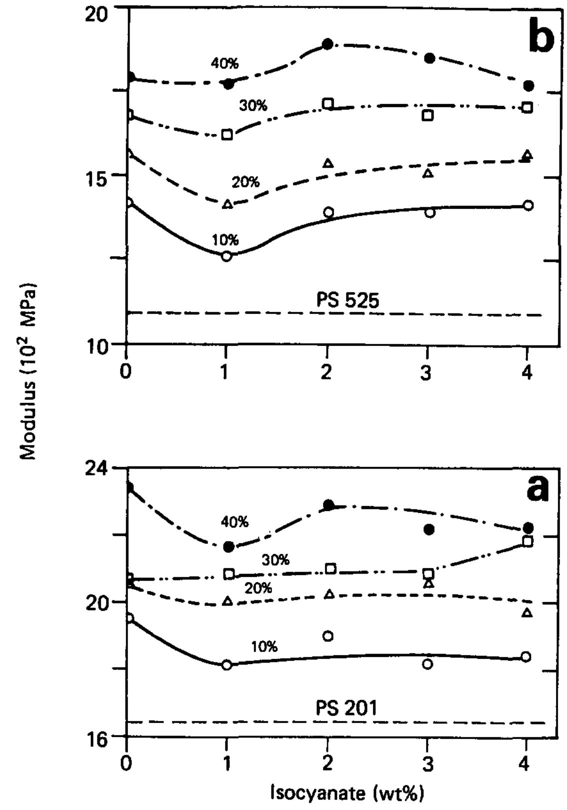


Figure 8 Effect of concentration of isocyanate, PMPPIC (weight percentage of polymer), on modulus: (a) sawdust (aspen fibres of mesh size 60)–PS201 composites; (b) sawdust (aspen fibres of mesh size 60)–PS525 composites. Percentages indicate the weight percentage of fibres in the composites

Table 3 Composites of isocyanate-treated PS685D sawdust (spruce) fibre. Effect of the nature of isocyanate

Isocyanate (wt% of polymer wt)	Fibre (mesh size)	Stress (MPa)				Elongation (%)				Energy (J) × 10^3				Modulus (MPa) × 10^{-2}			
		10	20	30	40	10	20	30	40	10	20	30	40	10	20	30	40
2% PMPPIC	None	38.4				2.3				40.9				14.3			
	20	37.7	39.7	39.5	35.9	2.6	2.5	2.3	2.0	46.8	48.4	40.8	32.3	16.9	19.1	19.7	20.8
	60	42.1	44.0	42.7	39.5	2.9	3.1	2.5	2.2	56.7	62.4	51.9	42.5	17.6	18.6	18.8	20.4
2% TDIC	None	37.3				2.8				50.8				15.2			
	20	41.3	38.5	37.0	33.4	2.8	2.6	2.3	1.9	59.5	50.1	39.4	30.0	17.1	17.0	19.1	20.2
	60	41.8	41.9	41.8	38.7	3.2	2.8	2.6	2.2	67.7	58.1	51.4	38.8	16.9	18.0	20.0	20.9
2% HMDIC	None	34.5				2.5				44.0				15.3			
	20	35.4	39.3	33.2	33.0	2.5	2.6	2.1	1.9	40.5	45.0	33.9	31.7	17.6	19.0	18.7	19.8
	60	40.5	38.7	39.8	37.0	2.8	2.6	2.5	2.3	54.7	48.5	45.1	38.0	17.1	17.5	19.5	20.3
0	20	35.3	31.4	35.6	32.0	2.4	1.9	2.1	1.7	39.2	27.9	35.9	25.3	17.9	19.7	19.8	20.3
0	60	39.4	39.1	38.2	33.5	3.0	2.5	2.3	1.8	61.0	50.0	39.7	27.6	16.2	18.2	19.9	21.2
PS685D		40.3				3.3				67.3				15.2			

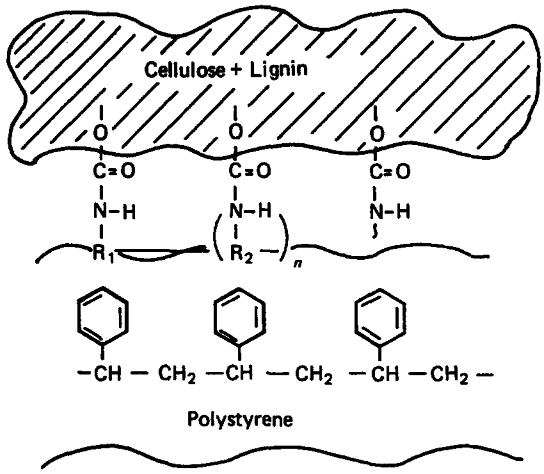


Figure 9 Hypothetical chemical structure of interfacial area of cellulose–isocyanate–polystyrene

cellulose–isocyanate–polystyrene can be developed as in *Figure 9*.

Effect of fibre size

It is well known that the size of wood fibres plays a significant role in modifying the mechanical properties of wood fibre filled thermoplastic composites. For this reason, the present study was directed towards two different sizes of wood particles, mesh size 20 and 60 with an aspect ratio (ratio of the particle length to its diameter) of 46 and 11.9 respectively[19]. The effects of mesh size have also been studied by changing other parameters, e.g. wood species (spruce and aspen), concentration of PMPPIC (0.5% and 2%) and kind of isocyanate (PMPPIC, TDIC, HMDIC). The results of these studies are shown in *Table 3* and *Figures 1–4*. It is obvious from these tables and figures that smaller particles, e.g. mesh 60, improve the mechanical properties more than larger ones. The contrary was true for the modulus values of the composites containing 40% fibre and 2% PMPPIC: it could be observed that mesh 20 fibres possess higher modulus compared to those of mesh 60. Furthermore, composites having mesh 60 fibres show the maximum improvements with regard to higher fibre content as compared to those of mesh 20 fibres.

Our present observation is in agreement with the literature[5,13,17–19]. Now, it can be speculated that wood fibres with a smaller particle size are more compatible with a polymer than are larger ones. In other words, finer particles share a greater interaction with the polymer matrix. This can be explained by the fact that short fibres offer a larger specific surface area in composites than the same weight fraction of longer ones. Moreover, the distribution of so-called short fibres is rather homogeneous compared to that of the longer ones. In this context, it is worth while to recall briefly some ideas put forward over a decade ago to give a realistic mechanism of interaction between the reinforcing fibre and the polymer matrix. Yim and coworkers[23] claimed the presence of adsorption phenomena in the interphase, while Lipatov *et al.*[24] reported that in the interphase the adhesive interaction originates by interdiffusion of the segments followed by the formation of a quasi-homogeneous blend. Ruvo and Alfthan[25] suggested from the shifting of the glass transition temperature of polystyrene and poly(vinyl acetate) filled with microcrystalline cellulose that the intensity of the interaction is a function of contact area.

Effect of wood species

Along with other variables discussed earlier, *Table 2* and *Figures 1–4* also show a comparative study of three different types of wood species, spruce, aspen and birch. Unfortunately, the birch variety of sawdust wood fibres has not been studied as thoroughly as the other two. As a result, comparing the performance of only spruce and aspen as thermoplastic composites, one can say that spruce is slightly better. This small difference can be attributed to either morphological differences between the more flexible softwood species (spruce) and stiffer hardwood (aspen) or to the slightly higher fibre aspect ratio of spruce.

Effect of coating with PMPPIC

The sawdust (aspen) fibres were coated with different compositions (weight percentage of fibre) of polymer (PS685D, PS201 and PS525) and PMPPIC. After the coating treatment, the fibres were also post-treated with 1% PMPPIC. The mechanical properties of the composites having these coated fibres are presented in *Table 4*. To compare the results, the mechanical properties of untreated and 4% isocyanate- (PMPPIC) treated composites are also listed in the same table. It goes without saying that according to this table the mechanical properties are improved due to the coating treatment. Again, the improvement trend continues with increase in the isocyanate content of the composites, either by using more isocyanate during coating or by post-treatment with isocyanate after coating. In general, stress improves up to 30–40% fibre content. In most cases, the elongation and energy of PS201 composites increase up to 10% fibre content, but in some cases these increase up to 30% fibre content. The elongation and energy of PS525 composites increase up to 40% fibre content. However, in all cases, modulus increases with increase in the fibre content of the composites. From the table, it is also obvious that, during the coating treatment, fibres treated with a lower percentage of polymer show better results than those treated with higher percentages.

To correlate the results on the basis of total isocyanate content in the composites due to different modes of operation, the net weight percentage of isocyanate (PMPPIC) in the composites at best improvement points are calculated and summarized in *Table 5*.

With the help of *Tables 4* and *5*, it is interesting to note that post-treatment of coated fibres gives superior properties as far as net isocyanate content in the composites is concerned. For example, aspen fibres coated with 5% polymer plus 4% PMPPIC followed by a 1% PMPPIC treatment contain only 1.9% isocyanate compared to 2.8% and 2.4% isocyanate after direct treatment with 4% PMPPIC and after coating with 5% polymer plus 8% PMPPIC, respectively. But the former composites gave the best results when compared with the latter ones. Moreover, modulus values of the composites with coated fibres followed by post-treatment with isocyanate (1%) are inferior to those of fibres that are only coated. This fact also supports the idea that interfacial area increases even more when coated fibres are further treated with isocyanate. It is well known that cellulose fibres always contain some adsorbed water molecules,

Table 4 Composites of isocyanate and polymer coated sawdust (aspen) fibre[a]

Treatment																		
Coating (wt% of fibre wt)		Post (wt% of polymer wt)	Stress (MPa)				Elongation (%)				Energy (J) × 10^3				Modulus (MPa) × 10^{-2}			
Polymer	PMPPIC	PMPPIC	10	20	30	40	10	20	30	40	10	20	30	40	10	20	30	40
PS201			36.3				2.6				46.6				16.4			
Non-coated		–	35.6	33.3	28.8	24.3	2.4	2.1	1.8	1.3	41.2	32.2	24.2	14.7	19.5	20.5	20.7	23.4
Non-coated		4	38.3	38.3	39.0	34.1	2.8	2.4	2.3	2.0	51.0	39.6	41.4	31.9	18.4	19.6	21.8	22.2
10	8	–	35.5	38.6	40.9	36.8	2.6	2.5	2.6	2.1	43.5	44.4	54.6	40.5	18.2	20.1	20.5	21.1
5	8	–	40.5	39.3	39.9	38.2	3.1	2.5	2.4	2.3	62.4	47.5	46.8	45.2	18.0	19.9	20.0	21.4
5	4	–	39.0	37.3	37.8	34.5	2.6	2.4	2.2	2.0	53.1	45.2	37.5	31.4	18.3	19.9	21.3	21.5
5	4	1	40.1	40.7	44.6	39.5	2.9	2.5	2.7	2.3	59.5	48.7	61.4	47.0	18.8	20.2	20.7	20.9
PS525			15.2				1.6				12.8				10.9			
Non-coated		–	16.3	16.3	15.8	16.5	1.4	1.9	1.4	1.3	11.3	18.9	12.1	12.1	14.2	15.6	16.8	17.9
Non-coated		4	16.8	18.2	21.1	19.1	5.6	3.9	3.2	2.0	66.9	48.7	42.9	23.6	14.2	15.7	17.1	17.7
10	8	–	15.4	16.0	17.2	20.6	4.2	3.4	2.6	2.6	49.4	36.4	34.8	33.3	13.5	14.2	15.5	17.3
5	8	–	15.4	16.9	18.5	19.7	5.4	3.2	2.5	2.3	63.3	36.5	32.7	29.9	13.3	14.9	15.9	17.1
5	8	1	15.9	18.8	17.8	16.9	7.4	4.7	3.2	2.0	99.1	67.2	38.2	20.9	13.1	14.2	15.2	16.1

[a] Mesh size 60

Table 5 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% fibre+2% PMPPIC (wt% of polymer)	1.4
(b)	30% fibre+3% PMPPIC (wt% of polymer)	2.1
(c)	30% fibre+4% PMPPIC (wt% of polymer)	2.8
(d)	30% fibre coated with 5% polymer +4% PMPPIC	1.2
(e)	30% fibre coated with 5% polymer+4% PMPPIC+post-treatment with 1% PMPPIC (wt% of polymer)	1.9
(f)	30% fibre coated with 5 or 10% polymer+8% PMPPIC	2.4
(g)	30% fibre coated with 5 or 10% polymer+8% PMPPIC+post-treatment with 1% PMPPIC (wt% of polymer)	3.1

Table 6 Composites of PS685D sawdust (birch) fibre[a]. Effect of the silane treatment

	Stress (MPa)				Elongation (%)				Energy (J) × 10^3				Modulus (MPa) × 10^{-2}			
	10	20	30	40	10	20	30	40	10	20	30	40	10	20	30	40
4% silane A-172	38.2	35.8	34.5	35.7	2.8	2.2	2.1	2.0	51.3	35.4	36.3	34.6	17.8	19.6	20.0	21.9
4% silane A-174	37.8	35.7	37.0	36.2	2.8	2.4	2.4	2.1	52.5	42.9	40.8	35.6	17.7	18.8	21.1	22.7
4% silane A-1100	39.2	39.0	39.3	37.0	3.1	2.8	2.5	2.2	59.5	52.5	46.1	39.0	16.7	19.5	18.8	21.6
Non-treated	38.7	38.3	35.2	36.2	2.7	2.6	2.1	2.0	51.1	48.7	34.6	32.2	18.3	17.7	20.7	22.0
PS685D	40.3				3.3				67.3				15.2			

[a] Mesh size 60

which are eliminated[26] at about 150°C. Again, isocyanates are susceptible to water already contained in the wood sample, forming polyurea[22,27]. As a result, during coating or treatment with isocyanate at 175°C, most of the adsorbed water should be eliminated and the formation of by-product polyurea should end. Therefore, post-treatment of coated fibres with isocyanate offers a better opportunity to make more 'bridges' between fibre and polymer, as discussed earlier.

Effect of silane coating

Sawdust (birch) fibres were coated with 4% each of silanes A-172, A-174 and A-1100. The mechanical properties of the silane-treated fibres and PS685D are shown in *Table 6*. From this table, it is obvious that, compared to untreated fibres, there are some improvements in mechanical properties of silane-treated fibres. Unfortunately, except for modulus, there is no significant improvement in other mechanical properties if compared to the original polymer. In fact, the hydroxy (–OH) groups, which can be produced by the hydrolysis of alkoxy groups of silanes with adsorbed water, as well as alkoxy groups, are supposed to link to the cellulose matrix with the formation of hydrogen bonds with the –OH groups of cellulose and lignin. However, the remaining chain of silanes can adhere to polystyrene with the help of a Van der Waals type of weak interaction. In this way, silane acts as a coupling agent to make a link between fibre and polymer. As a result, mechanical properties are improved with respect to uncoated fibre composites. But the hydrogen bonds and Van der Waals type of weak forces are insufficient to make a strong 'bridge' between fibre and polymer, so that stress transfer between denser hardwood fibre (birch) and polystyrene can take place easily.

Table 7 Composites of grafted sawdust (aspen) fibre[a]

Add-on (%)		Stress (MPa)				Elongation (%)				Energy (J) × 10^3				Modulus (MPa) × 10^{-2}			
Graft	Homopolymer	10	20	30	40	10	20	30	40	10	20	30	40	10	20	30	40
	PS201	36.3				2.6				46.6				16.4			
–	–	35.6	33.3	28.8	24.3	2.4	2.1	1.8	1.3	41.2	32.2	24.2	14.7	19.5	20.5	20.7	23.4
14.7	8.9	37.9	34.0	34.4	30.3	2.7	2.3	2.1	1.6	50.5	38.7	33.9	22.3	17.9	18.8	20.5	20.9
14.7	–	38.6	36.6	36.2	35.7	2.7	2.3	2.1	2.0	53.7	41.7	36.1	32.2	18.2	19.0	20.8	21.9
5.5	7.3	37.1	34.8	28.8	26.2	2.6	2.2	1.6	1.5	48.1	38.5	22.1	18.6	17.8	19.9	21.3	22.7
5.5	–	36.8	35.0	33.9	32.5	2.6	2.4	2.1	1.7	43.9	39.7	34.0	28.5	17.9	19.2	19.9	23.4
	PS525	15.2				1.6				12.8				10.9			
–	–	16.3	16.3	15.8	16.5	1.4	1.9	1.4	1.3	11.3	18.9	12.1	12.1	14.2	15.6	16.8	17.9
14.7	8.9	15.5	16.5	17.1	16.8	1.5	1.8	1.7	1.5	13.2	19.2	16.2	13.3	13.4	14.7	16.2	17.3
14.7	–	15.4	16.7	18.1	18.2	1.5	2.2	1.7	1.7	14.0	23.5	18.2	17.6	13.4	14.7	17.5	18.0
5.5	7.3	15.1	14.9	16.6	17.3	1.4	1.5	1.5	1.4	10.9	11.9	14.9	14.2	13.6	15.1	16.8	17.8
5.5	–	15.9	16.5	17.0	17.7	14.7	2.1	1.8	1.5	12.6	24.1	17.5	14.8	13.8	15.1	15.8	17.4

[a] Mesh size 60

Table 8 Comparison of the property improvement of composites of PS667 and PS685D

Composition (%) of composites	Improvement (%) of			
	Stress	Elongation	Energy	Modulus
	Polystyrene 667			
Spruce 20 mesh (30%)	+3.2	−23.0	−25.2	+35.8
Spruce 20 mesh (30%) +PMPPIC (2%)	+19.9	−19.2	−5.0	+40.9
Spruce 20 mesh (30%) +TDIC (2%)	+12.0	−26.9	−18.9	+27.7
Spruce 20 mesh (20%) +HMDIC (2%)	−2.9	−34.6	−41.0	+15.1
Spruce 60 mesh (20%)	+9.1	−3.8	+4.2	+13.8
Spruce 60 mesh (30%) +PMPPIC (2%)	+22.2	−19.2	+5.9	+32.7
Spruce 60 mesh (30%) +TDIC (2%)	+14.3	−26.9	−12.0	+37.7
Spruce 60 mesh (30%) +HMDIC (2%)	+6.1	−38.5	−30.4	+35.8
Aspen 20 mesh (20%)	−7.9	−23.1	−29.0	+18.2
Aspen 20 mesh (30%) +PMPPIC (2%)	+10.2	−26.9	−22.9	+39.0
Aspen 60 mesh (10%)	+1.8	+3.8	−8.3	+13.2
Aspen 60 mesh (30%) +PMPPIC (2%)	+17.5	−23.1	−8.0	+40.3
Aspen (CTMP) 60 mesh (30%)	+11.7	−11.5	−1.7	+28.9
Aspen (CTMP) 60 mesh (30%)+PMPPIC (2%)	+31.6	+34.6	+93.2	+34.6
	Polystyrene 685D			
Spruce 20 mesh (30%)	−11.7	−48.5	−47.1	+30.3
Spruce 20 mesh (20%) +PMPPIC (2%)	−1.5	−24.2	−28.7	+25.7
Spruce 20 mesh (20%) +TDIC (2%)	−4.5	−21.2	−26.2	+11.8
Spruce 20 mesh (20%) +HMDIC (2%)	−2.5	−21.2	−33.7	+25.0
Spruce 60 mesh (20%)	−3.0	−24.2	−26.4	+19.7
Spruce 60 mesh (20%) +PMPPIC (2%)	+9.2	−6.1	−8.1	+22.4
Spruce 60 mesh (20%) +TDIC (2%)	+4.0	−15.2	−14.4	+18.4
Spruce 60 mesh (20%) +HMDIC (2%)	+4.0	−21.2	−28.6	+15.1
Aspen 20 mesh (10%)	−12.7	−27.3	−43.0	+16.5
Aspen 20 mesh (10%) +PMPPIC (2%)	+0.5	−18.2	−26.7	+19.7
Aspen 60 mesh (20%)	−9.7	−27.3	−40.4	+21.7
Aspen 60 mesh (30%) +PMPPIC (2%)	+6.2	−21.2	−17.7	+29.6
Birch 60 mesh (10%)	−4.0	−18.2	−24.7	+20.4
Birch 60 mesh (10%) +silane A-172 (4%)	−5.2	−15.2	−24.4	+17.1
Birch 60 mesh (10%) +silane A-174 (4%)	−6.2	−15.2	−22.7	+16.5
Birch 60 mesh (10%) +silane A-1100 (4%)	−2.7	−6.1	−12.4	+9.9
Aspen (CTMP) 60 mesh (30%)	+1.0	−27.0	−32.4	+40.8
Aspen (CTMP) 60 mesh (30%)+PMPPIC (2%)	+22.3	−3.0	+14.6	+37.5

Effect of grafting

Sawdust (aspen) fibres having mesh size 60 were grafted with polystyrene with the help of the xanthate method of grafting. *Table 7* shows the mechanical properties of the composites of PS201 or PS525 comprising grafted fibres having both higher and lower levels of polymer addition. These fibres are also examined when ungrafted homopolymers are either present or absent. It is obvious from study of the table that mechanical properties are improved due to the higher level of grafting. Again, the mechanical properties of the composites with extracted (only graft) fibres are superior to those of unextracted (graft plus homopolymer) fibres. These results are consistent with our previous communication[28] as well as with other publications reported by Kokta *et al.*[17–20]. Grafting is a method by which polymer (polystyrene) can

Table 9 Comparison of the property improvement of composites of PS201 and PS525

Composition (%) of composites	Improvement (%) of				Composition (%) of composites	Improvement (%) of			
	Stress	Elongation	Energy	Modulus		Stress	Elongation	Energy	Modulus
	Polystyrene 201					Polystyrene 525			
Aspen 60 mesh (10%)	− 1.9	− 7.7	−11.6	+18.9	Aspen 60 mesh (20%)	+ 7.2	+18.8	+47.7	+43.1
Aspen 60 mesh (30%) +PMPPIC (4%)	+ 7.4	−11.5	−11.2	+32.9	Aspen 60 mesh (30%) +PMPPIC (4%)	+38.8	+100.0	+235.2	+56.9
Aspen 60 mesh (coated 10% PS+8% PMPPIC) (30%)	+12.7	0.0	+17.2	+25.0	Aspen 60 mesh (coated 10% PS+8% PMPPIC) (30%)	+13.1	+62.5	+171.9	+42.2
Aspen 60 mesh (coated 5% PS+4% PMPPIC) (30%)+PMPPIC (1%)	+22.9	+ 3.8	+31.8	+26.2	Aspen 60 mesh (coated 5% PS+4% PMPPIC) (20%)+PMPPIC (1%)	+23.7	+100.0	+425.0	+30.3
Aspen 60 mesh (10%) grafted with PS (14.7%)	+ 6.3	+ 3.8	+15.2	+11.0	Aspen 60 mesh (30%) grafted with PS (14.7%)	+19.1	+ 6.3	+42.0	+60.6
Aspen (CTMP) 60 mesh (20%)	+ 5.5	+ 3.8	+ 7.3	+17.7	Aspen (CTMP) 60 mesh (30%)	+23.0	+37.5	+115.6	+48.6
Aspen (CTMP) 60 mesh (30%) +PMPPIC (3%)	+14.9	+ 3.8	+27.3	−25.6	Aspen (CTMP) 60 mesh (30%) +PMPPIC (3%)	+32.9	+112.5	+248.4	+49.5
Aspen (CTMP) 60 mesh (coated 10% PS+8% PMPPIC) (30%)	+15.4	− 3.8	+19.3	+25.0	Aspen (CTMP) 60 mesh (coated 10% PS+8% PMPPIC) (30%)	+24.3	+100.0	+249.2	+44.0
Aspen (CTMP) 60 mesh (coated 5% PS+4% PMPPIC) (30%)+PMPPIC (1%)	+16.5	0.0	+14.2	+31.1	Aspen (CTMP) 60 mesh (coated 5% PS+8% PMPPIC) (30%)+PMPPIC (1%)	+54.6	+106.3	+292.2	+59.6
Aspen (CTMP) 60 mesh (20%) grafted with PS (56.2%)	+13.2	+ 3.8	+22.3	+20.1	Aspen (CTMP) 60 mesh (30%) grafted with PS (56.2%)	+34.2	+56.3	+200.0	+59.6

be directly linked to the cellulose matrix by the formation of a chain of covalent chemical bonds.

Owing to the cohesive force between grafted polystyrene and reinforced polystyrene, phase separation between cellulose and polymer can be overcome to some extent. The presence of ungrafted low-molecular-weight homopolymer, which does not form any chemical bond with the cellulose matrix, shows inferior mechanical properties.

CONCLUSIONS

It is useful to summarize the results by calculating the percentage of best improvements in mechanical properties of each of the different systems investigated. The calculated results are shown in *Tables 8* and *9*. The comparison of the mechanical properties of the sawdust-based composites with those of chemithermomechanical pulp (CTMP) of aspen appears in the same tables. Based on the results of *Tables 8* and *9*, one may conclude that:

(i) best mechanical properties can be reached with a fibre loading of ~30%;

(ii) mechanical properties of composites with finer particles (mesh 60) are superior to those of coarse ones (mesh 20);

(iii) CTMP is better than sawdust and the reinforcing property of softwood sawdust (spruce fibre) is slightly better than hardwood sawdust (aspen fibre);

(iv) about 3% isocyanate in the composite brings about maximum improvement in mechanical properties;

(v) the accelerating effect of isocyanates decreases in the order PMPPIC, TDIC and HMDIC;

(vi) among different treatments, coating followed by isocyanate treatment is best of all;

(vii) improvement due to grafting of fibres is comparable to that of the isocyanate treatment;

(viii) high-impact polystyrene (PS525) is also best to improve mechanical properties compared to other varieties of polystyrenes.

In addition, the modification of the interfacial bond between reinforcing fibres and polymer matrix by using some selective coupling agents and/or some treatments, e.g. grafting, plays a significant role in improving the mechanical properties of the composites.

ACKNOWLEDGEMENTS

The financial support of NSERC, FCAR as well as the cooperation and financial support provided by Polysar Ltd are appreciated.

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