Influence of Phthalic Anhydride as a Coupling Agent on the Mechanical Behavior of Wood Fiber–Polystyrene Composites

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Synopsis

The performance of phthalic anhydride used as a coupling agent in wood fiber-filled polystyrene composites have been verified by evaluating the mechanical properties of the composite materials. Generally, mechanical properties improved along with the increase in concentrations of the coupling agent as well as wood fiber in the composites up to a certain limit and then decreased at the higher concentrations. The concentrations of phthalic anhydride and fibers which produce maximum improvements in mechanical properties differ with the change in wood species and pulping techniques. Compared to other efficient coupling agents (e.g., isocyanate), phathlic anhydride's performance seemed inferior.

INTRODUCTION

It is now a well established fact that the compatibility between hydrophilic wood fibers and thermoplastics can be modified by using coupling agents,[1–6] (e.g., isocyanate). Generally, coupling agents facilitate the optimum stress transfer at the interface between filler and matrix. In fact, strength and modulus of the composite materials improved, but at the same time toughness deteriorated. The selection of a coupling agent which can combine both strength and toughness to a considerable degree, is an important art of formulation of a composite material. In the present investigation, phthalic anhydride was selected as a coupling agent for wood fiber-polystyrene composites. The benzene ring of phthalic anhydride can interact with the benzene ring of polystyrene used as a base polymer and, on the other hand, an anhydride group can link to the —OH group of cellulose. As a result, it may be hoped that phthalic anhydride would have the effect of marrying to the fiber/plastic components of the composite systems to produce an "interfacial bridge."

MATERIALS

Thermoplastics

1. High impact polystyrene (PS 525); and
2. High heat crystal polystyrene (PS 201) were supplied by Polysar Limited, Sarnia, Ontario, Canada.

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Fiber

In the present study, two different varieties of wood species, viz. hardwood species aspen (*Populus Tremuloides Michx*), and softwood species mixtures (75% black spruce, 20% balsam, and 5% aspen) were used in the form of wood flour (sawdust) and chemithermomechanical pulp (CTMP). CTMP was prepared in a Sund Defibrator under the same conditions as described earlier.[6]

Coupling Agent

Phthalic anhydride was supplied by Anachemia, Montreal, Canada.

EXPERIMENTAL

CTMP aspen pulp and chips for making sawdust were dried in an air-circulating oven 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, with a Granu Grinder, C. W. Brabender, Instruments Inc., U.S.A.

Preparation of the Composites

Usually, a 25 g mixture of polymer, phthalic anhydride (0–10% by weight of composite) and pulp (15–35% by weight of composite) were mixed with the roll mill at 175°C. For better results, the resulting mixtures were mixed repeatedly 5–10 times. After mixing, the mixtures were allowed to cool to room temperature and then reground to mesh size 20. The mixtures were then molded (24 at a time) into shoulder-shaped test specimens (ASTM D638, Type V). Standard molding conditions are: 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 a 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), suppied by Testing Machines Inc., U.S.A. The samples were tested after conditioning at 23 ± 0.5°C and 50% R.H. 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 were taken into account for each set of tests (2.5–8.5%).

RESULTS

Figure 1 shows the effect of the concentrations of phthalic anhydride on the mechanical properties (e.g., strength, elongation, energy, and modulus) of

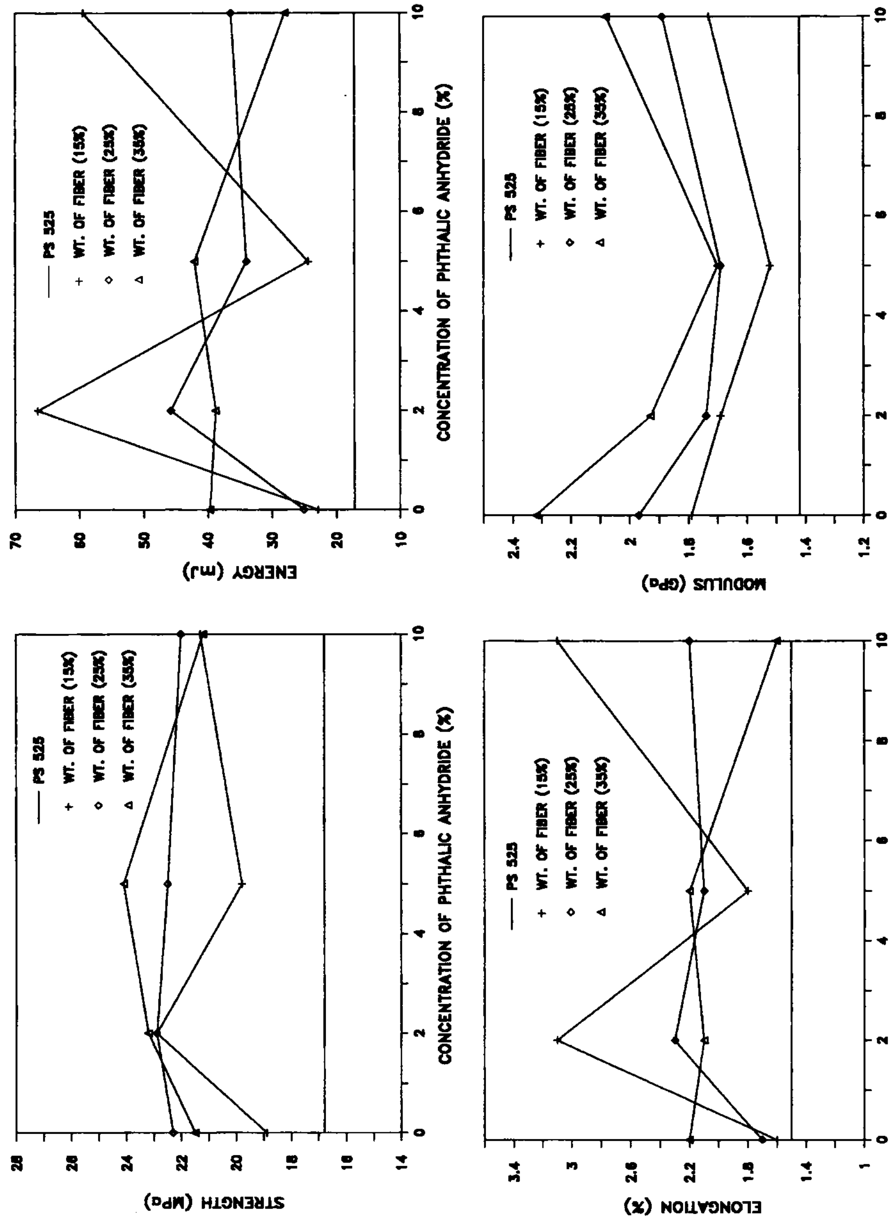


Fig. 1. Variation of mechanical properties with the concentrations of phthalic anhydride and filler for PS 525–CTMP composites.

CTMP filled-polystyrene composites. It is obvious from this figure that the tensile strength of phthalic anhydride treated composites improved compared to the original polymer as well as nontreated ones. Moreover, it increased independently of fiber content at the beginning and then leveled off around 25–35% of fiber loading. Again, tensile strength also increased with the concentration of the coupling agent up to 5% of phthalic anhydride in the composites, and then decreased at higher concentrations.

The same figure reveals that both elongation and energy increase linearly with the rise in fiber content in the composites containing 5% of phthalic anhydride. Although these properties are superior to the original polymer as well as to nontreated ones at lower fiber and phthalic anhydride concentrations, they are inferior when higher concentrations of both fiber and phthalic anhydride are incorporated into the composites. The modulus, in general, increases with the rise in fiber content in the composites. Moreover, a spectrum of treated composites lies between those of the original polymer and of nontreated ones. Five percent phthalic anhydride treated composites show the least improvement in modulus compared to other concentrations.

The variation of mechanical properties versus the concentrations of phthalic anhydride in sawdust (aspen)-filled PS 525 composites is presented in Figure 2. Unlike CTMP filled composites, strength of sawdust-filled composites improved up to the 10% level of phthalic anhydride. On the other hand, 25% fiber loading offers maximum improvements in the strength of composite materials. Elongation and energy of 2% phthalic anhydride treated composites show an inferior behavior compared to nontreated ones, and even to the original composites, particularly at higher fiber levels (e.g., 35%). Modulus of such composites indicates that fiber-filled composites produce a superior behavior when compared to the original composites, but only 10% phthalic anhydride treated composites are superior as far as nontreated composites are concerned.

Figure 3 represents the variation in strength, elongation, energy, and modulus with the concentration of phthalic anhydride and a fiber content of PS 525—sawdust (spruce) composites. The mechanical properties improve due to the addition of phthalic anhydride in the composites, and 2% phthalic anhydride offers the best improvement, while 5% gives the least. Furthermore, it is obvious from this figure that both elongation and energy of 5% treated composites, especially when composites contain higher percentages of fiber, are inferior even compared to nontreated composites. Modulus follows nearly the same trend as that of sawdust (aspen)-filled composites (e.g., 10% phthalic anhydride treated composites offer superior behavior and 5% phthalic anhydride treated composites are inferior in this respect).

Likewise, attention was paid to discover the influence of phthalic anhydride as a couling agent on the mechanical properties of PS 201 composites filled with CTMP (aspen) and sawdust (both aspen and spruce). The experimental results are listed in Table I. For CTMP (aspen)-filled composites, the best improvement in the mechanical properties are found when 10% of phthalic anhydride and 35% of fiber are present in the composite materials. However, the strength of sawdust (aspen)-filled composites improves most when composites comprise 15% of fiber and 2% of phthalic anhydride. Elongation and energy values are superior when composites contain the same percentage of fiber and 10% of phthalic anhydride. Modulus increases continuously up to the

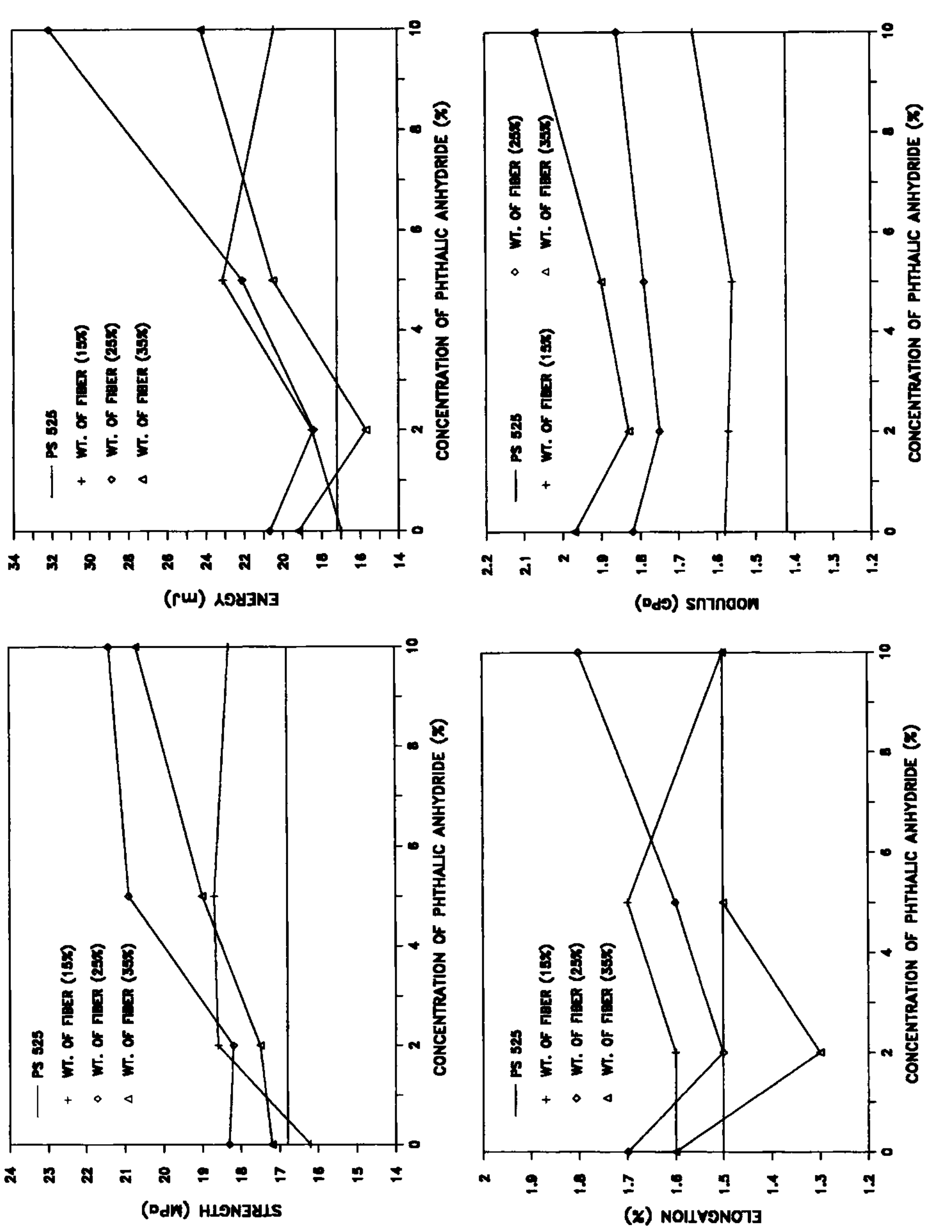


Fig. 2. Variation of mechanical properties with the concentrations of phthalic anhydride and filler for PS 525–sawdust (aspen) composites.

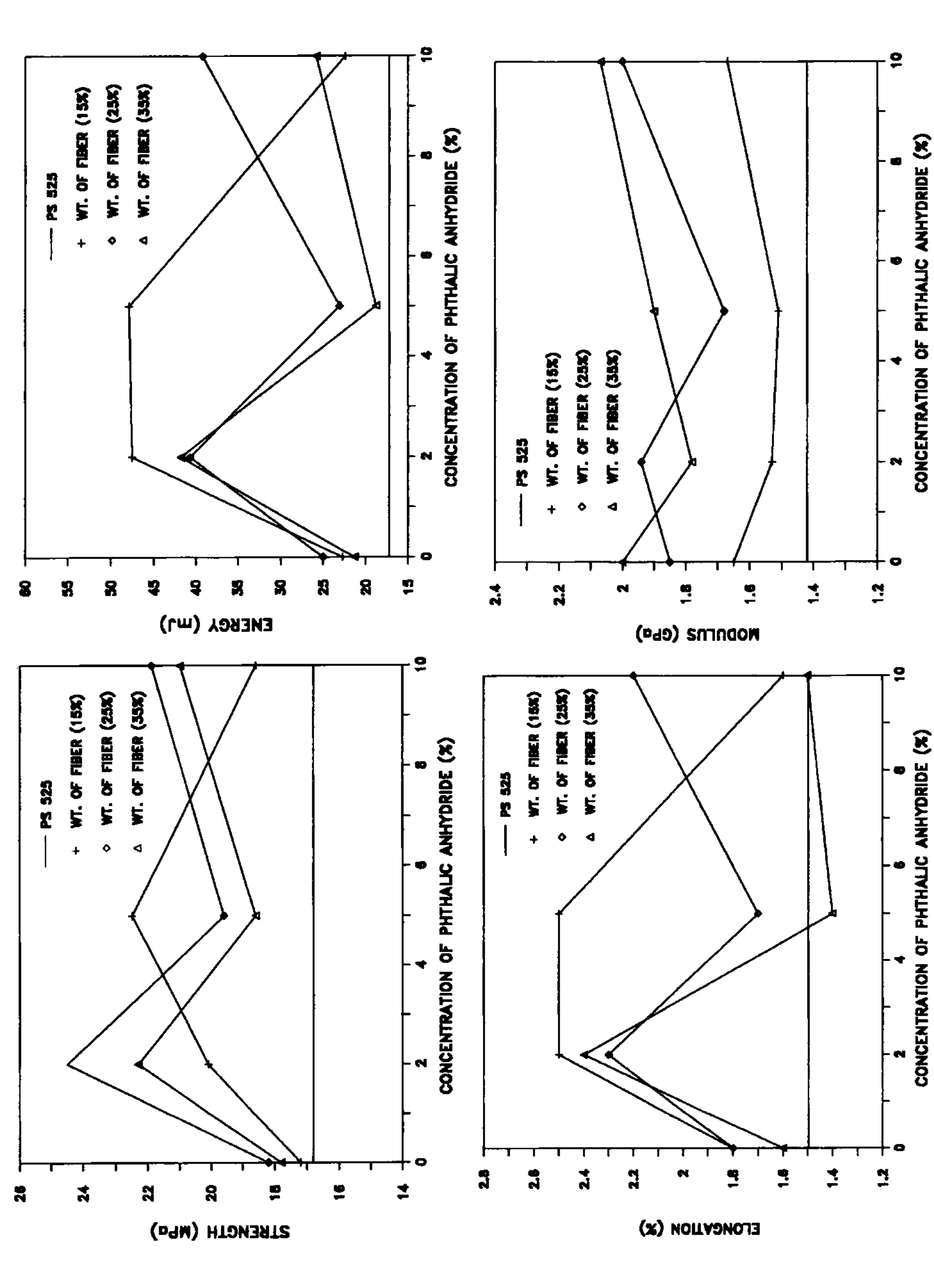


Fig. 3. Variation of mechanical properties with the concentrations of phthalic anhydride and filler for PS 525–sawdust (spruce) composites.

TABLE I
Variation of Mechanical Properties of PS 201–Wood Fiber Composites on the Concentration of Phthalic Anhydride

Composite		Strength (MPa)			Elongation (%)			Energy (mJ)			Modulus (MPa)		
Polymer/fiber (wt % of fiber)	PHA (wt %)	15	25	35	15	25	35	15	25	35	15	25	35
PS 201	—	41.5			3.3			80.5			1910.0		
CTMP	—	36.0	35.8	33.8	2.7	2.6	2.2	63.7	57.9	44.1	1920.0	2030.0	2200.0
CTMP	2	36.5	40.0	41.8	2.4	2.6	2.3	51.1	68.5	59.8	1835.7	1936.7	2208.9
CTMP	5	36.4	40.7	31.1	2.3	2.6	1.8	49.3	70.7	37.9	1952.3	2026.0	2223.1
CTMP	10	35.9	41.7	46.9	2.4	2.5	2.6	60.1	64.1	80.9	1970.4	2249.2	2476.4
Sawdust (aspen)	—	35.6	32.5	30.6	2.5	2.2	2.1	54.7	49.1	40.1	2160.0	2260.0	2420.0
Sawdust (aspen)	2	40.5	38.8	37.6	2.6	2.3	2.0	65.4	57.6	45.8	1926.2	2049.1	2434.9
Sawdust (aspen)	5	36.8	35.2	33.5	2.5	2.2	2.1	62.3	46.9	40.8	2002.0	2018.6	2136.8
Sawdust (aspen)	10	38.8	36.5	36.4	2.7	2.2	2.1	69.3	49.8	45.9	2061.5	2237.0	2411.2
Sawdust (spruce)	—	38.4	38.1	33.3	2.8	2.7	2.3	71.0	66.9	51.6	1950.0	2030.0	2190.0
Sawdust (spruce)	2	38.4	41.5	40.5	2.3	2.5	2.1	53.3	64.8	49.4	1999.3	2084.6	2198.6
Sawdust (spruce)	5	39.9	42.8	33.2	2.5	2.5	1.9	62.4	70.4	40.7	1864.4	2037.9	2138.5
Sawdust (spruce)	10	41.1	41.1	32.8	2.7	2.9	2.1	74.9	88.8	46.5	1978.1	1980.6	2291.4

35% level of fiber and 10% level of phthalic anhydride. Once again, the best improvement in the strength of sawdust (spruce) fiber-filled composites is observed for 25% fiber and 5% phthalic anhydride. Both elongation and energy are superior when composites contain 25% fiber and 10% phthalic anhydride. Modulus follows the same trend as that of other composites. It is important to note that the elongation of wood fiber-filled composites improves compared to nontreated ones rather than the original polymer.

In order to summarize the results, the improvement percentages of the mechanical properties compared to those of the original polymers are listed in Table II. In addition, improvement percentages of the composites containing 3% poly[mthylene (polyphenyl isocyanate)] (PMPPIC) which is believed[5–7] to be an efficient coupling agent are also listed in the same table. When one compares the performance of these two coupling agents, one concludes that phthalic anhydride is indeed inferior.

Table III shows the impact strength of nontreated and treated composites of both PS 201 and PS 525 composites comprising CTMP (aspen) and sawdust (aspen and spruce). The impact strength of composite materials is generally inferior compared to the original polymers (except for PS 201-based composites with 15% of either CTMP (aspen) and sawdust (spruce) and 2% phthalic anhydride).

DISCUSSION

The above mentioned results indicate that most of the mechanical properties (except elongation and impact strength) improved due to the addition of phthalic anhydride. Once again, compared to nontreated composites even elongation and impact strength of the treated composites are enhanced. Incidentally, Viswanathan and Gilton[8] showed that the addition of phthalic anhydride sig-

TABLE II
Comparison of the Improvement in Mechanical Properties of Polystyrene–Wood Fiber Composites

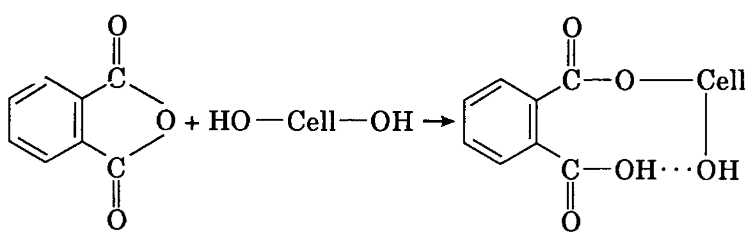
Composition (wt %)			Improvement %					Improvement %			
PULP	PHA	Fiber (wt %)	Strength	Elongation	Energy	Modulus	Fiber (wt %)	Strength	Elongation	Energy	Modulus
				Polystyrene 201					*Polystyrene 525*		
CTMP	—	15	−13.3	−18.2	−20.9	+0.5	25	+28.0	+46.7	+130.8	+63.4
CTMP	2	25	−3.6	−21.2	−14.9	+1.4	15	+36.3	+106.7	+28.7	+19.1
CTMP	5	25	−1.9	−21.7	−12.2	+6.1	35	+43.5	+46.7	+144.8	+20.1
CTMP	10	35	+13.0	−21.7	+0.5	+29.6	15	+26.8	+100.0	+248.3	+22.1
CTMP	3*	25	+8.4	−15.2	+11.9	+16.8	25	+29.8	+126.7	+261.0	+23.2
Sawdust (aspen)	—	15	−14.2	−24.2	−32.0	+13.1	25	+8.9	+13.3	+20.3	+28.2
Sawdust (aspen)	2	15	−2.4	−21.2	−18.8	+0.8	25	+8.3	0.0	+7.0	+22.9
Sawdust (aspen)	5	15	−11.3	−24.2	−22.6	+4.8	25	+24.4	0.0	+28.5	+26.4
Sawdust (aspen)	10	15	−6.5	−18.2	−13.9	+7.9	25	+27.4	+20.0	+86.6	+30.9
Sawdust (aspen)	3*	25	+1.2	−18.2	−19.9	+4.7	35	+36.3	+66.7	+176.2	+40.1
Sawdust (spruce)	—	15	−7.5	−15.2	−11.8	+2.1	25	+8.3	+20.0	+45.3	+30.3
Sawdust (spruce)	2	25	0	−24.2	−19.5	+9.1	25	+45.8	+46.7	+136.6	+36.4
Sawdust (spruce)	5	25	+3.1	−24.2	−12.5	+6.7	15	+33.9	+66.7	+178.5	+6.2
Sawdust (spruce)	10	25	−1.0	−12.1	+10.3	+3.7	25	+29.8	+46.7	+127.9	+39.3
Sawdust (spruce)	3*	25	+8.7	−9.1	−0.4	+18.3	15	+29.2	+140.0	+283.7	+15.5

* Poly[methylene (polyphyl isocyanate)] (by weight of polymer).

TABLE III
Variation of Impact Strength of Polystyrene-Wood Fiber Composites on the Concentration of Phthalic Anhydride

Composite: Polymer/fiber (weight % of fiber)	Composite: PHA (wt %)	Izod impact strength (joules/meter): 15	25	35	15	25	35
		Polystyrene 201			*Polystyrene 525*		
Polymer	—		7.2			21.7	
CTMP	—	6.5	6.4	4.6	15.8	14.4	11.5
CTMP	2	8.9	6.5	5.8	13.6	11.8	10.9
CTMP	5	6.6	6.6	6.1	14.0	12.2	6.2
CTMP	10	6.6	6.6	5.7	14.2	6.7	6.3
Sawdust (aspen)	—	6.3	6.2	5.5	14.8	9.3	7.1
Sawdust (aspen)	2	6.6	6.4	5.7	16.5	11.9	7.7
Sawdust (aspen)	5	6.9	6.7	5.7	10.8	7.2	6.2
Sawdust (aspen)	10	6.2	5.3	5.1	11.3	7.1	6.4
Sawdust (spruce)	—	6.6	6.2	4.9	17.4	10.7	7.6
Sawdust (spruce)	2	8.4	6.5	6.0	14.1	11.7	7.6
Sawdust (spruce)	5	7.8	7.7	6.1	9.1	11.3	6.4
Sawdust (spruce)	10	6.1	6.5	4.9	16.4	7.4	6.1

nificantly increase in internal bond strength of high-density particle boards made from the resins. When phthalic anhydride was used as a coupling agent, the anhydride group chemically reacted with —OH group of cellulose or lignin to form an ester linkage during pressing and heating.[9,10] In addition, since carboxy or ester groups are polar in nature they can link to —OH groups through hydrogen bondings. The reaction which occurs may be presented as follows:[11]



However, π-electron of benzene rings of phthalic anhydride as well as polystyrene can interact. As a result, phthalic anhydride can produce a "bridge" between cellulose and polystyrene matrices in the interface.

Generally, mechanical properties increase along with the concentrations of phthalic anhydride up to a certain limit and then decrease at higher concentrations. The appearance of maxima at different fiber levels and at different phthalic anhydride concentrations varies. In fact, the morphology of various wood species is different.[12-15] Moreover, softwood spruce is more flexible, whereas hardwood aspen is stiffer. The aspect ratio of two wood species also differs. Once again, CTMP which was prepared through the combination of chemical and mechanical methods provides a greater specific surface area compared to mechanical pulps (e.g., sawdust). These might be the cause of disparity in performance in the mechanical properties of various wood fiber-filled composites.

Again, comparing the results for PMPPIC and phthalic anhydride, it can be observed that the extent of improvement is greater in the case of the former. We already discussed in our previous publications[5–7] that isocyanate links with the fiber matrix through the chain of stable urethane bonds which are supposed to be more stable compared to an ester linkage. Furthermore, owing to the polymeric nature of PMPPIC, the cellulose phase and thermoplastic (polystyrene) phase are continuously linked by it at the interphase, while the discrete nature of phthalic anhydride makes it inferior in this respect.

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