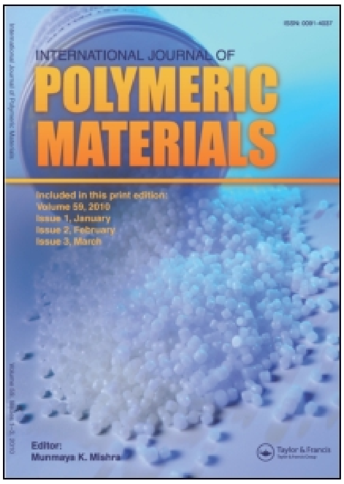

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Influence of Polar Monomers on the Performance of Wood Fiber Reinforced Polystyrene Composites. I. Evaluation of Critical Conditions

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Influence of Polar Monomers on the Performance of Wood Fiber Reinforced Polystyrene Composites.
I. Evaluation of Critical Conditions

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Wood fibers and nonpolar thermoplastics, e.g. polystyrene, are not the ideal partner for the preparation of composites because of a wide difference in their polarity. In the present study, polarity of the polystyrene was modified by the introduction of a —COOH group, through the reaction with maleic anhydride (MA) in the presence of an initiator (benzoyl peroxide: BPO) in a roll mill at the elevated temperatures. Optimum conditions for the preparation of polar polystyrene have been investigated. The temperature of the roll mill, i.e., the reaction temperature, and reaction time varied between 160–175°C and 10–15 min., respectively. The concentrations of the monomer, (MA) as well as the initiator (BPO), also varied: 0–10% and 0–2% (by weight of polymer), respectively. The mechanical properties of chemithermomechanical pulp (CTMP)-filled modified polystyrenes were evaluated. The effect of 3% coupling agent [e.g. poly(methylene (polyphenyl isocyanate))] (PMPPIC) on the mechanical properties of the same composites was also determined.

Generally, mechanical properties of the composite materials were enhanced when modified polymers were used as base polymers. Moreover, the extent of the improvement in mechanical properties depends on the reaction temperature and time, as well as on the concentrations of the monomer (maleic anhydride) and initiator. Maximum improvements in mechanical properties occur when the temperature was maintained at 175°C for 15 min. In addition, preferred concentrations of both the monomer and initiator were found to be 5% and 1% (by polymer weight), respectively. Once again, properties were further accelarated when coupling agent (e.g. PMPPIC) was used in addition to the modified polystyrene. The improvements in mechanical properties (over those of the original polymer and those of composites containing unmodified polymers) indicate that the compatibility between hydrophilic cellulosic fiber and hydrophobic polymer has increased.

Keywords: Thermoplastic composites, polystyrene, polar monomer, wood fiber, coupling agent, graft copolymerization, mechanical properties.

INTRODUCTION

Wood fiber reinforced thermoplastic composites are presently the subject of intense research.[1–8] Unfortunately, wood fibers and nonpolar thermoplastics, e.g.

polystyrene, are not the ideal partner for the preparation of composites because of a wide difference in their polarity. The compatibility between wood fibers and thermoplastics can be modified using a coupling agent or through graft copolymerization.[9-13] Compared to other methods, graft copolymerization is profitable because the polarity of either the fiber or the polymer can be modified chemically.[14-18] Moreover, a chemical affinity between the filler and the matrix can be established through the judicious selection of reactive groups among the grafted materials. In the present study, polar monomer units (e.g. —COOH group) have been introduced in the polystyrene matrix by grafting maleic anhydride. To obtain a satisfactory performance, processing conditions have also been optimized. Furthermore, the impact of the coupling agent-poly(methylene (polyphenyl isocyanate))-on the mechanical properties of the composites of modified polystyrene-chemithermomethanical pulp have been evaluated.

MATERIALS

Thermoplastics

i) high impact polystyrene (PS 525) and

ii) high heat crystal polystyrene (PS 201) were supplied by Polysar Limited, Sarnia, Ontario, Canada.

Fiber

Hardwood aspen (Populus Tremuloides Michx) was used in the form of chemithermomechanical pulp (CTMP). This pulp was prepared in a Sund Defibrator under the same conditions as described earlier.[9]

Coupling agent

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

Monomer

Maleic anhydride was supplied by Anachemia, Montreal, Canada.

EXPERIMENTAL

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

Graft copolymerization

Polymer, maleic anhydride (MA) and benzoyl peroxide (BPO) were mixed with a roll mill, C.W. Brabender Laboratory preparation Mill, Model 065. The temperature of the roll mill and the reaction time varied between 160–175°C for 10–15 min, respectively. The concentrations of the monomer, (MA) as well as the initiator (BPO), also varied: 0–10% and 0–2% (by weight of polymer), respectively. The resulting modified polymers were ground to mesh 20.

Preparation of the composites

Usually, a 25 gr mixture of modified polymer (with or without 3% of PMPPIC) and pulp (15–35% by weight of composite) were mixed at 175°C in a roll mill. After mixing 5–10 times, the resulting mixtures were 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 were: temperature, 175°C; pressure during heating and cooling, 3.8 MPa; heating time, 20 min; cooling time, 15 min. Width and thickness of each specimen were measured with the help of a micrometer.

Mechanical tests

The mechanical properties (e.g. tensile modulus, tensile strength at maximum point and the corresponding elongation and energy) of all the samples were measured with an Instron Tester (Model 4201). A standard general Tensile Test Program method, called "PLA 10," was used, and mechanical properties were automatically calculated by 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, un-notched) was tested with an Impact Tester (model TMI, no. 43-01), supplied by Testing Machines Inc., U.S.A. The samples were tested after conditioning at 23 ± 0.5°C and 50% R.H. for at least 18 hours in a controlled atmosphere. Mechanical properties were reported after taking the statistical average of six measurements. The coefficients of variation, 2.5–8.5%, were taken into account for each set of tests.

RESULTS AND DISCUSSION

Table I shows the effect of the reaction conditions, e.g. concentrations of monomer maleic anhydride (MA) and the benzoyl peroxide initiator (BPO), as well as reaction time and temperature, on the ultimate mechanical properties of these modified polystyrenes (PS 201 and PS 525). This table reveals that mechanical properties (except energy of the polymer containing 10% MA and 1% BPO) deteriorate because of the grafting of maleic anhydride. In the case of PS 525, however, all mechanical properties, except for modulus, improve. In order to remove the non-reacting maleic anhydride, only one modified PS 201 (which was

TABLE I

Effects of reaction conditions on the mechanical properties of maleic anhydride grafted polystyrene

Composition[a] (Wt.%)		Mixing conditions		Polystyrene 201				Polystyrene 525			
MA	BPO	Tempe-rature (°C)	Time (min)	Strength (MPa)	Elongation (%)	Energy (mJ)	Modulus (MPa)	Strength (MPa)	Elongation (%)	Energy (mJ)	Modulus (MPa)
—	—	[b]		41.5	3.3	80.5	1900.0	16.8	1.5	17.2	1420.0
5	1	160	15	36.3	2.7	69.4	1700.0	19.9	2.0	35.6	1239.0
5	1	160	30	36.6	2.6	64.0	1718.0	22.3	2.0	30.8	1405.0
5	1	175	15	34.1	2.3	55.9	1775.0	20.3	1.9	25.6	1373.0
5[c]	1	175	15	41.0	3.5	117.8	1666.7				
5	1	175	30	39.1	2.7	70.6	1807.0	21.6	2.0	30.0	1404.0
5	0.2	175	15	35.7	3.0	77.5	1766.6	15.4	1.7	20.5	1190.4
5	0.5	175	15	35.8	2.7	68.1	1708.6	17.9	1.8	22.3	1250.8
5	2.0	175	15	37.2	2.8	70.8	1831.8	20.4	1.9	28.6	1415.6
1	1	175	15	30.7	2.1	41.6	1821.9	18.1	1.9	26.7	1234.0
2	1	175	15	32.1	2.4	54.6	1711.1	18.4	1.9	26.7	1214.9
7	1	175	15	33.0	2.3	46.9	1834.9	20.0	2.0	27.0	1254.8
10	1	175	15	38.9	3.2	98.4	1593.9	19.3	2.0	26.7	1268.7

[a] By weight of polymer.
[b] Un-modified polymer.
[c] After extraction with boiling water for 24 hours.

prepared by reacting 5% of MA and 1% of BPO at 175°C for 15 min) underwent boiling water extraction for 24 hours. After this treatment, the gross loss in weight was determined as 1.92%. The mechanical properties of the extracted polymer are also included in Table I. The level of strength, in the case of this polymer, is close to that of the original polymer, but both elongation and energy improve while modulus weakens. The decrease in the mechanical properties of the non-extracted and modified polystyrene may be due to the presence of unreacting maleic anhydride.

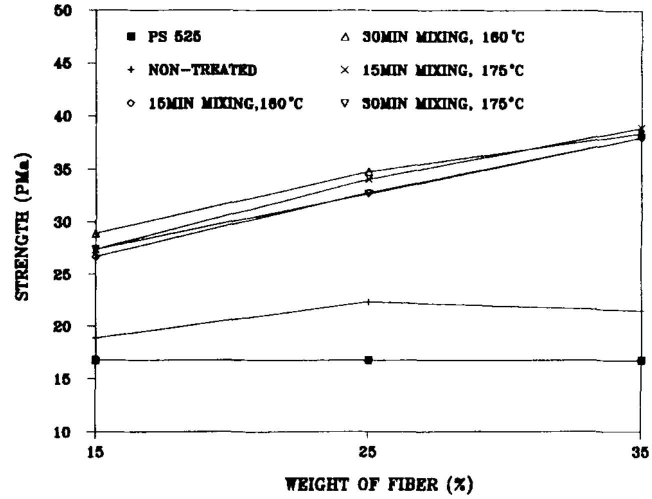


FIGURE 1a Effect of the reaction temperature and time on the strength of non-treated PS 525-CTMP composites. Concentrations of monomer and initiator are 5% and 1% respectively, according to the weight of the polymer.

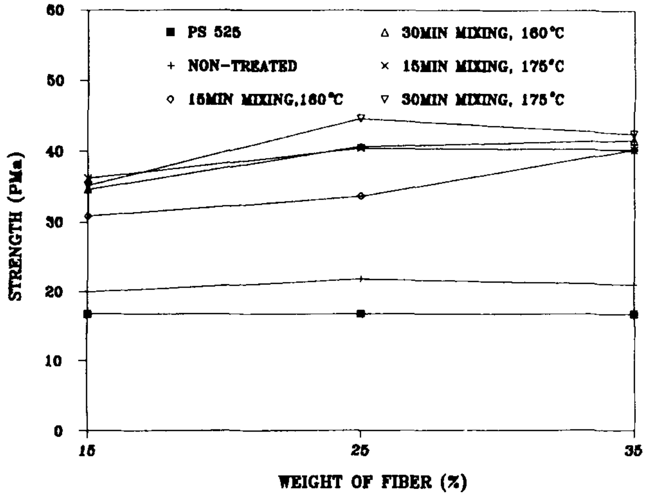


FIGURE 1b Effect of the reaction temperature and time on the strength of 3% PMPPIC treated PS 525-CTMP composites. Concentrations of monomer and initiator are 5% and 1% respectively, according to the weight of the polymer.

Figures 1a–4a provide the mechanical properties of composites of CTMP and modified PS 525 for which the reaction temperature and time varied (temperature: 160 and 175°C, time: 10 and 15 min) while the concentrations of monomer (5% by weight of polymer) and initiator (1% by weight of polymer) remained constant. Figures 1b–4b show the mechanical properties of the same composites which were treated with a 3% coupling agent poly(methylene (polyphenyl isocyanate)) (PMPPIC). These figures reveal that the mechanical properties,

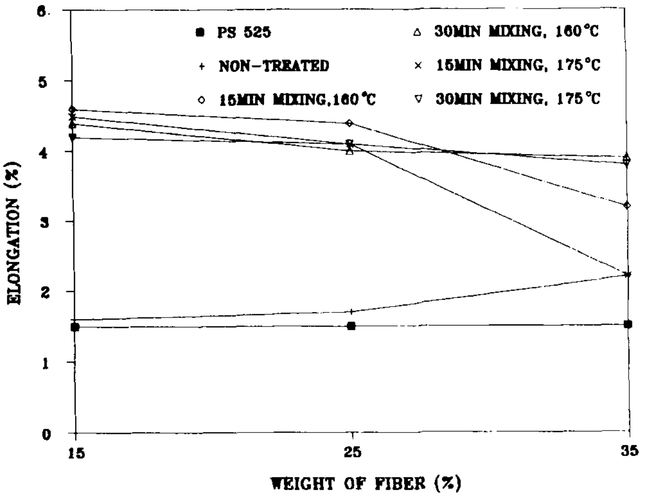


FIGURE 2a Effect of the reaction temperature and time on the elongation of non-treated PS 525-CTMP composites. Concentrations of monomer and initiator are 5% and 1% respectively, according to the weight of the polymer.

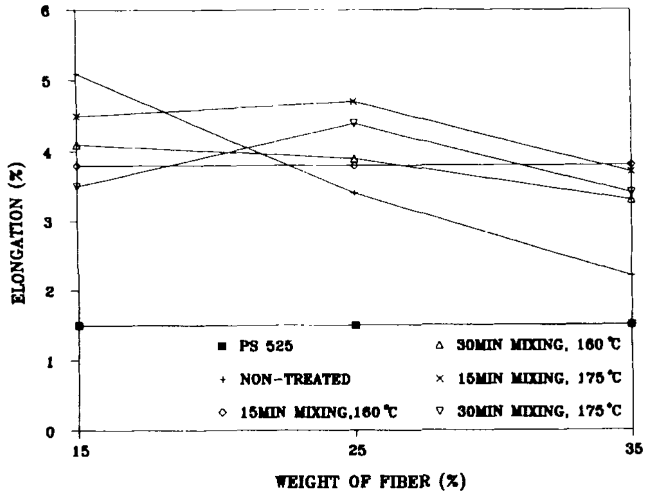


FIGURE 2b Effect of the reaction temperature and time on the elongation of 3% PMPPIC treated PS 525-CTMP composites. Concentrations of monomer and initiator are 5% and 1% respectively, according to the weight of the polymer.

except for modulus of the composites containing modified polystyrenes, improve compared to those of both the original polymer and the composites containing unmodified polystyrene. Once again, properties modified even more when a coupling agent PMPPIC was used in addition to the modified polystyrene. Although the modulus of untreated composites is inferior compared to that of unmodified polystyrene (Figure 4a), this situation is quite opposite in the case of isocyanate treated composites (Figure 4b). At a temperature of 175°C, results

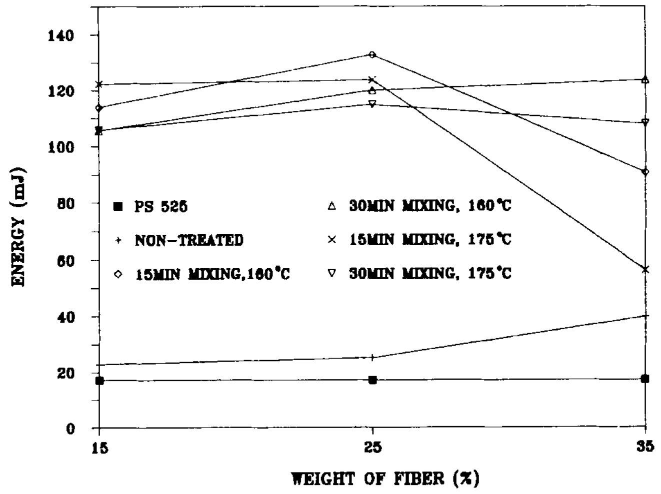


FIGURE 3a Effect of the reaction temperature and time on the energy of non-treated PS 525-CTMP composites. Concentrations of monomer and initiator are 5% and 1% respectively, according to the weight of the polymer.

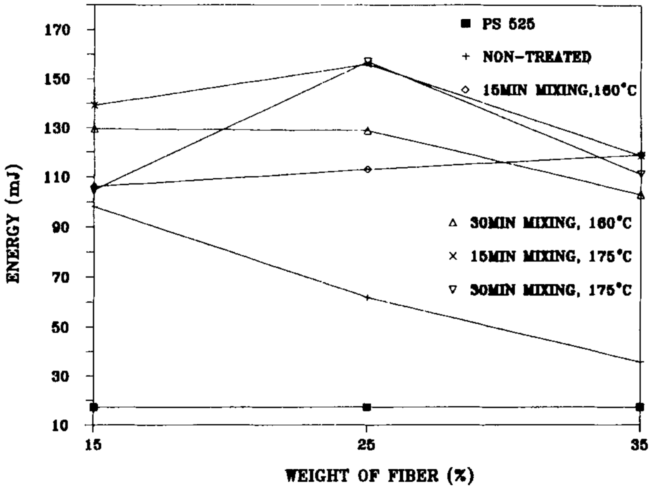


FIGURE 3b Effect of reaction the temperature and the time on the energy of 3% PMPPIC treated PS 525-CTMP composites. Concentrations of monomer and initiator are 5% and 1% respectively, according to the weight of the polymer.

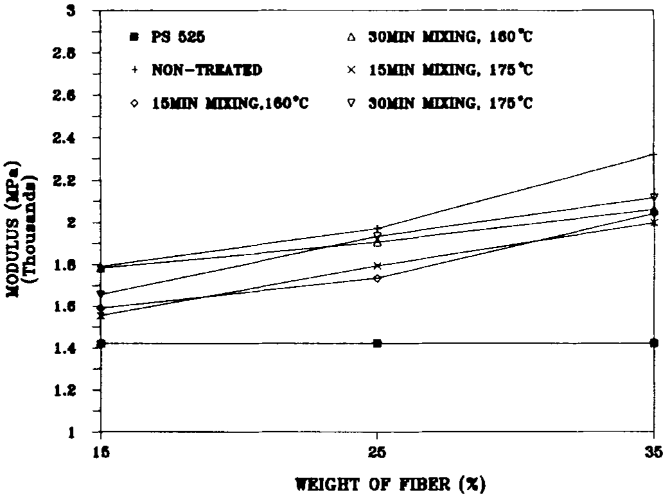


FIGURE 4a Effect of the reaction temperature and time on the modulus of non-treated PS 525-CTMP composites. Concentrations of monomer and initiator are 5% and 1% respectively, according to the weight of the polymer.

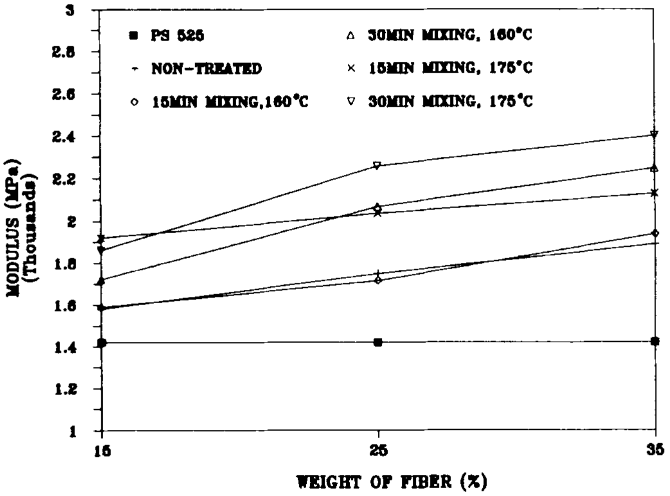


FIGURE 4b Effect of the reaction temperature and time on the modulus of 3% PMPPIC treated PS 525-CTMP composites. Concentrations of monomer and initiator are 5% and 1% respectively, according to the weight of the polymer.

appear superior to those registered at 160°C. In fact, a reaction time of 15 min is better for some properties while 30 min is better for others. It is indeed quite difficult to make a proper selection of lengths of time between these two. In order to avoid confusion, a similar study was performed taking PS 201 as a base polymer. The experimental results are illustrated in Table II which also indicates the positive influence of modified polystyrene as observed in the case of PS 525. It appears clearly that higher reaction time, e.g. 15 min, provide maximum

TABLE II

Effects of mixing temperature and time on the mechanical properties of maleic anhydride grafted PS 201-CTMP composites

Composition[a] (wt.%)		Mixing conditions		Strength (MPa)			Elongation (%)			Energy (J) × 10^3			Modulus (MPa)		
MA	BP (wt.% of Fiber)	Temp. (°C)	Time (min)	15	25	35	15	25	35	15	25	35	15	25	35
							Non-treated composites								
—	—	—	—		41.5[b]			3.3[b]			80.5[b]			1910.0[b]	
—	—	—	—	36.0	35.8	33.8	2.7	2.6	2.2	63.7	57.9	44.1	1920.0	2030.0	2200.0
5	1	160	15	40.8	43.3	45.3	2.5	2.8	2.6	73.9	78.3	66.1	1940.0	2270.0	2240.0
5	1	160	30	47.3	42.9	36.6	3.6	2.9	2.0	101.2	87.4	47.8	1962.0	2041.0	2121.7
5	1	175	15	42.4	47.3	45.0	2.7	2.8	2.6	73.9	85.3	80.7	2094.0	2216.0	2294.0
5[c]	1	175	15	43.0	44.6	42.3	2.8	3.2	2.6	85.4	120.8	85.1	1999.0	2056.3	2234.3
5	1	175	30	38.7	45.3	35.5	1.9	2.9	3.6	43.3	93.7	101.9	1917.0	2040.0	2072.0
							3% PMPPIC treated composites								
—	—	—	—	41.0	45.0	39.7	3.3	2.8	2.4	73.0	90.1	52.6	1950.0	2230.0	2240.0
5	1	160	15	39.2	42.1	44.5	2.3	2.6	2.4	62.2	60.6	67.9	1945.7	2148.4	2387.0
5	1	160	30	42.3	46.9	47.5	2.4	2.7	2.6	50.1	77.2	81.4	2009.6	2297.9	2400.7
5	1	175	15	47.0	49.2	46.9	2.8	2.7	2.5	80.3	81.9	82.3	2134.0	2224.9	2278.0
5[c]	1	175	15	44.7	45.8	49.7	2.6	2.8	2.5	65.6	67.9	67.0	2070.6	2429.4	2636.3
5	1	175	30	41.0	44.1	40.9	2.4	2.3	2.3	61.6	68.1	63.9	2244.5	2289.8	2453.0

[a] By weight of polymer.
[b] Un-modified polymer.
[c] After extraction with boiling water for 24 hours.

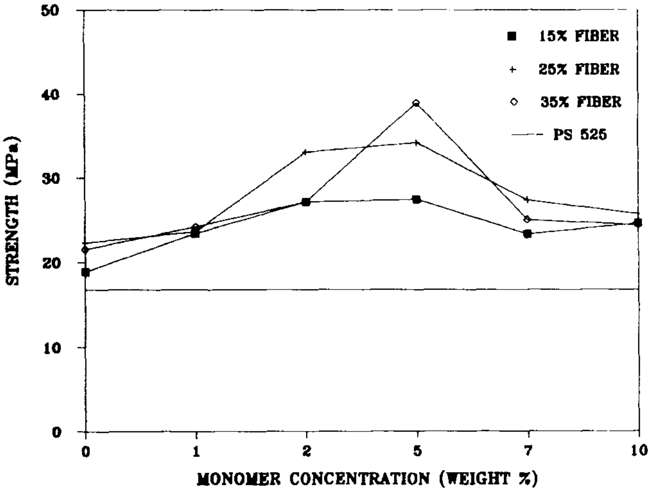


FIGURE 5a Effect of the monomer concentration on the strength of non-treated PS 525-CTMP composites. Reaction temperature and time are 175°C and 15 minutes, respectively, and the concentration of the initiator is 1% by weight of polymer.

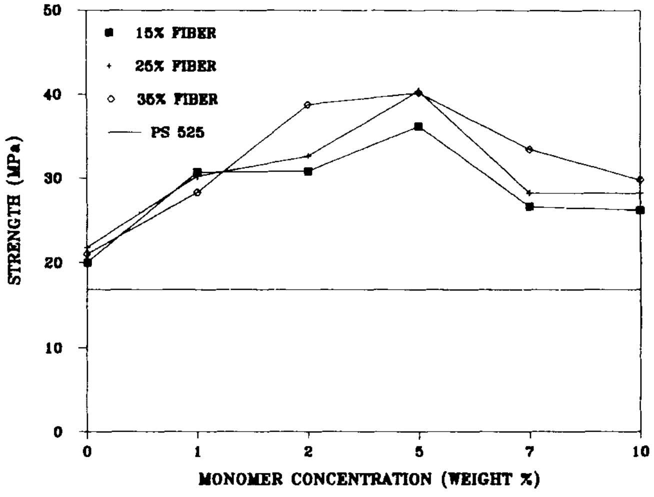


FIGURE 5b Effect of the monomer concentration on the strength of 3% PMPPIC treated PS 525-CTMP composites. Reaction temperature and time are 175°C and 15 minutes, respectively, and the concentration of the initiator is 1% by weight of polymer.

improvements. For further studies the standard (optimum) reaction conditions were determined to be: temperature 175°C for 15 min.

Once again, isocyanate provides some synergistic effect. The mechanical properties of the composites comprising modified and extracted polymer, as well as CTMP are also included in Table II. When one compares the properties of the composites containing unextracted, as well as extracted modified polymers, one observes that strength and modulus diminish due to extraction, whereas both

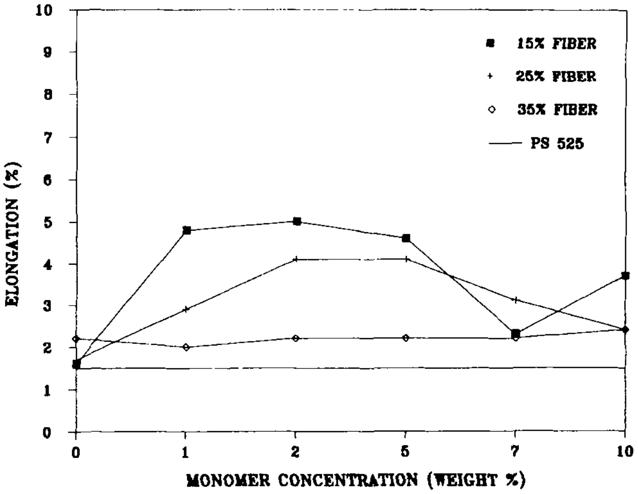


FIGURE 6a Effect of the monomer concentration on the elongation of non-treated PS 525-CTMP composites. Reaction temperature and time are 175°C and 15 minutes, respectively, and the concentration of the initiator is 1% by weight of polymer.

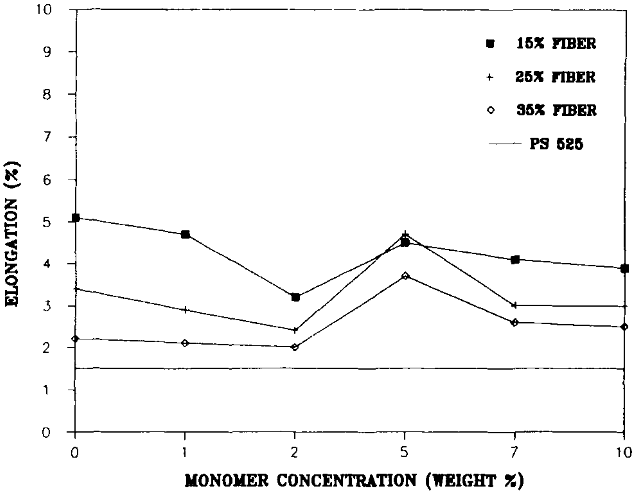


FIGURE 6b Effect of the monomer concentration on the elongation of 3% PMPPIC treated PS 525-CTMP composites. Reaction temperature and time are 175°C and 15 minutes, respectively, and the concentration of the initiator is 1% by weight of polymer.

elongation and energy increase for the same treatment. The opposite is true when isocyanate treated composites are compared.

Figures 5a–8a show the variation in mechanical properties accompanied by the change in monomer (MA) concentrations (varied from 0–10% of polymer weight) in the modified PS 525 of the composites comprising CTMP and PS 525. Results of a similar study with 3% of PMPPIC treated modified PS 525 are given in Figures 5b–8b. From these figures, it is obvious that most of the mechanical

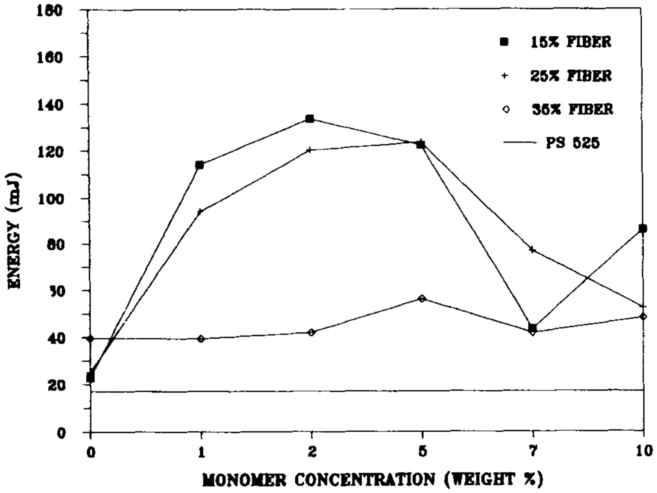


FIGURE 7a Effect of the monomer concentration on the energy of non-treated PS 525-CTMP composites. Reaction temperature and time are 175°C and 15 minutes respectively, and the concentration of the initiator is 1% by weight of polymer.

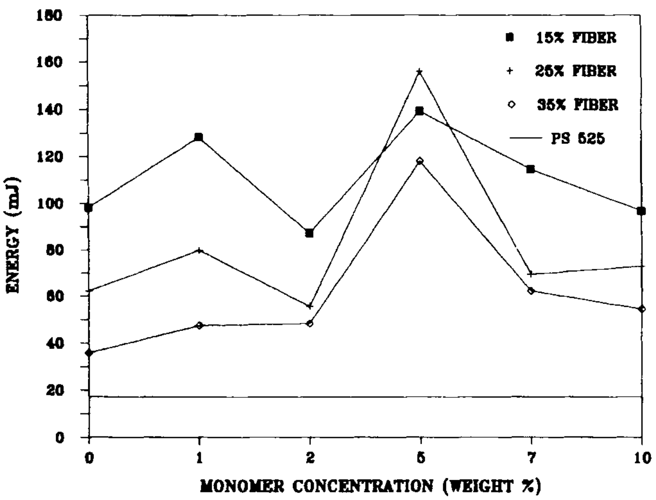


FIGURE 7b Effect of the monomer concentration on the energy of 3% PMPPIC treated PS 525-CTMP composites. Reaction temperature and time are 175°C and 15 minutes, respectively, and the concentration of the initiator is 1% by weight of polymer.

properties increase with a rise in the concentration of monomers in the initial phase, and decrease later on showing maxima around 2–5% concentration of maleic anhydride. When one considers the effect of adding fibers to composites, both strength and modulus increase (Figures 5a and 5b) when 35% of fibers are added to composites, as opposed to both elongation and energy of untreated composites. Both elongation and energy of treated composites increase with that

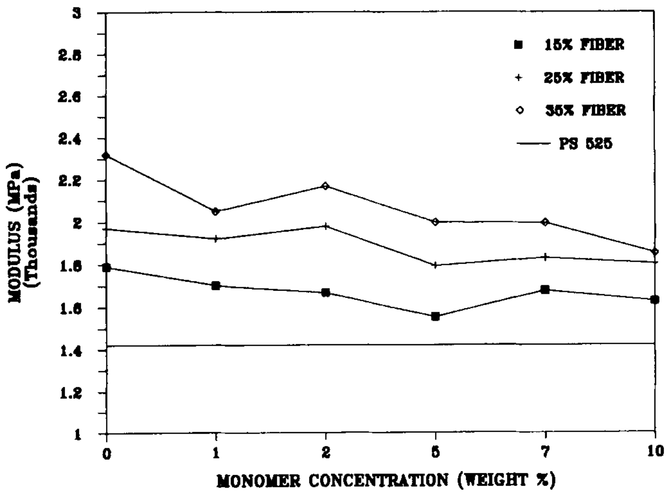


FIGURE 8a Effect of the monomer concentration on the modulus of non-treated PS 525-CTMP composites. Reaction temperature and time are 175°C and 15 minutes, respectively, and the concentration of the initiator is 1% by weight of polymer.

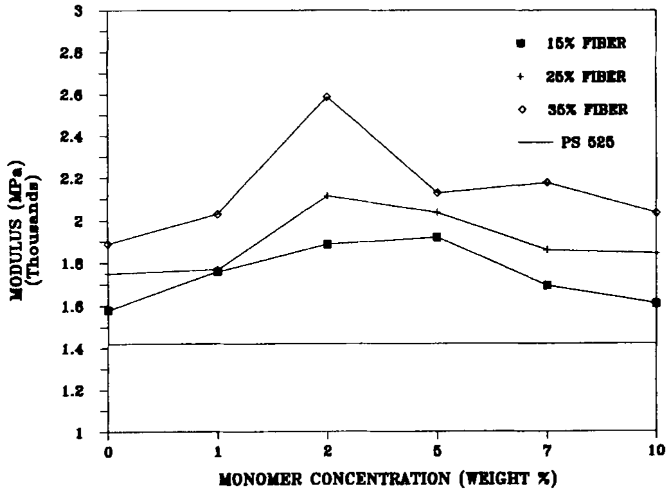


FIGURE 8b Effect of the monomer concentration on the modulus of 3% PMPPIC treated PS 525-CTMP composites. Reaction temperature and time are 175°C and 15 minutes, respectively, and the concentration of the initiator is 1% by weight of polymer.

of the weight percentage of fibers up to a 25% weight level. Moreover, properties are always superior to those of unmodified PS 525.

To verify the effect of increasing the amounts of monomer (MA), the monomer concentrations in PS 201 have also been varied in the same range, 0–10% and the mechanical properties of the composites comprising these modified polymers and CTMP (aspen) appear in Table III. As for modified polystyrenes of PS 525, the

TABLE III

Effects of monomer concentration on the mechanical properties of maleic anhydride grafted PS 201-CTMP composites

Composition[a] (wt.%) MA	BPO	Treatment	Strength (MPa)			Elongation (%)			Energy (J) × 10^3			Modulus (MPa)		
(wt.% of Fiber)			15	25	35	15	25	35	15	25	35	15	25	35
—	—	—		41.5[b]			3.3[b]			80.5[b]			1910.0[b]	
—	—	—	36.0	35.8	33.8	2.7	2.6	2.2	63.7	57.9	44.1	1920.0	2030.0	2200.0
1	1	—	33.7	34.6	27.6	2.3	2.1	1.7	52.7	45.0	33.8	2063.2	2154.9	2259.3
2	1	—	36.3	38.0	37.1	2.6	2.4	2.2	69.9	60.5	54.3	2036.4	2281.5	2393.8
5	1	—	42.4	47.3	45.0	2.7	2.8	2.6	73.9	85.3	80.7	2094.0	2216.0	2294.0
7	1	—	40.4	40.1	36.8	3.2	2.6	1.9	77.0	71.4	46.2	2190.0	2265.5	2338.9
10	1	—	39.9	36.9	33.4	2.8	2.4	1.9	82.9	64.5	47.0	2097.7	2187.7	2250.0
—	—	PMPPIC(3%)	41.0	45.0	39.7	3.3	2.8	2.4	73.0	90.1	52.6	1950.0	2230.0	2240.0
1	1	PMPPIC(3%)	35.1	37.8	35.9	2.1	2.1	2.0	46.2	48.4	44.5	2184.5	2243.6	2485.9
2	1	PMPPIC(3%)	37.5	38.9	38.9	2.2	2.4	2.2	55.7	56.1	67.9	2187.8	2197.7	2322.6
5	1	PMPPIC(3%)	47.0	49.2	46.9	2.8	2.8	2.5	80.3	81.9	82.3	2135.0	2224.9	2278.0
7	1	PMPPIC(3%)	42.5	39.3	36.3	2.6	2.4	2.2	68.9	64.8	55.3	2140.2	2214.1	2443.6
10	1	PMPPIC(3%)	40.3	37.4	36.0	2.6	2.3	2.1	67.6	55.8	45.8	2071.3	2197.0	2413.0

[a] By weight of polymer.

[b] Un-modified polymer.

Reaction conditions: mixing with roll mill at 175°C for 15 min.

mechanical properties in the present case also increase up to 5% of monomer. The mechanical properties, except for modulus, which increases continuously, rise with that of the concentration of fiber levels up to 25 weight precentages. The properties of the composites containing unmodified PS 201 and 3% of PMPPIC are also included in this table, and when results of these composites are compared to those of modified ones, modified polymers provide a better performance, even in the presence of isocyanate. The best concentrations of monomer were believed to be 5 weight percentages of polymer.

During the preparation of modified polymers, the concentrations of initiator are also an important factor in achieving a sufficient degree of graft copolymerization. In order to determine how the initiator concentration affects on the ultimate properties of composite materials, BOP concentrations were varied from 0–2% (by weight of polymer). The resulting mechanical properties of the composites including modified PS 525 as well as PS 201 and CTMP are shown in Figures 9a–12a and Table IV, respectively. The influence of isocyanate (3% by weight of polymer) on the composite properties of the respective polymers are illustrated in Figures 9b–12b and in Table 4. These figures and table reveal that mechanical properties are enhanced initially with the increase in the concentrations of the initiator and then decrease showing maxima around 0.5–1.0 wt.% of the initiator. Both strength and modulus of PS 525 based composites improve up to 35 wt.% of fiber content, whereas both elongation and energy for the same composites, and all properties of PS 201 based composites, increase only up to 25 wt.% in fiber content. The synergistic effect of PMPPIC is also observed in the present case. Once again, Table IV indicates that the properties of modified polymers (as opposed to unmodified polymer) are superior, whether they are used alone or along with isocyanate.

Percentage improvements in the mechanical properties of the composites (with respect to the original polymer) for the entire study are summarized in Tables V(A) and V(B). Positive values in most cases indicate clearly the accelerating role of maleic anhydride, as well as the synergistic effect of PMPPIC.

The Izod impact strength of un-notched samples of the composites under study were evaluated. Table VI provides the effect of variation in the concentrations of maleic anhydride and the initiator during the preparation of maleic anhydride grafted polystyrene at 175°C for 15 min, on the impact strength of the modified polystyrenes. Table VI reveals that the impact strength of the original polymer improves when 5% MA and 0.2% BPO are used. Impact strength reduces with the increase in the concentration of the initiator beyond 0.2% at a MA concentration level of 5%. This level is believed to be the optimum concentration. Due to the extraction of the modified polymer, the impact strength remained almost unaltered.

The concentrations of monomer (0–10 wt.%) and initiator (0–2 wt.%) on the Izod impact strength of CTMP-filled modified polystyrene composites are presented in Tables VII and VIII. Table VII shows that the mechanical properties of the composites improve only for polystyrene 201 modified polystyrene containing 5% or 7% of maleic anhydride. Impact strength of the same composites improves more when the polymer is extracted with boiling water.

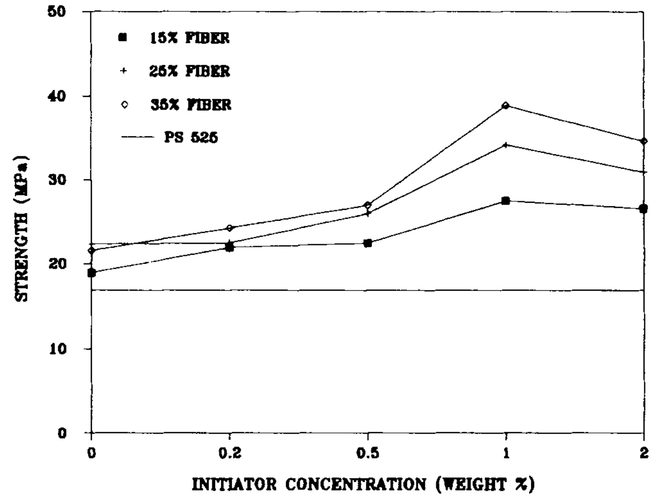


FIGURE 9a Effect of the initiator concentration on the strength of non-treated PS 525-CTMP composites. Reaction temperature and time are 175°C and 15 minutes, respectively, and the concentration of the monomer is 5% by weight of polymer.

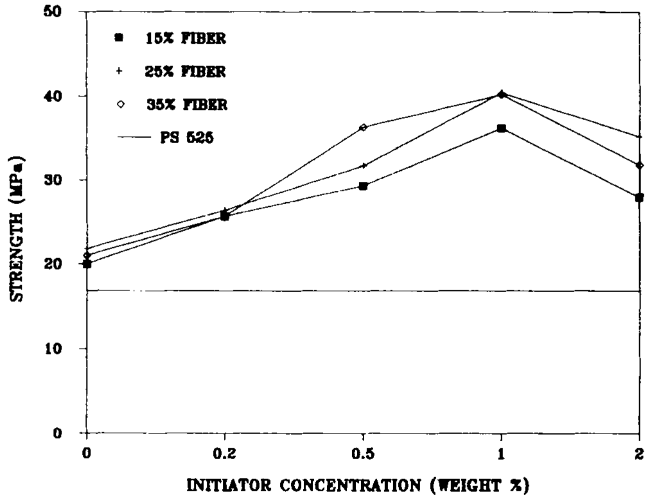


FIGURE 9b Effect of the initiator concentration on the strength of 3% PMPPIC treated PS 525-CTMP composites. Reaction temperature and time are 175°C and 15 minutes, respectively, and the concentration of the monomer is 5% by weight of polymer.

Similar to other mechanical properties, impact strength also increases up to 25% in fiber level and modified polystyrene showed superior behavior in the presence of PMPPIC. Unlike other mechanical properties, the impact strength of composites with PS 525 did not improve at all. In fact, it rather diminished.

When attention was paid to the effect of the concentration of the initiator on the composite properties of PS 201 (Table VIII), one observed that the impact

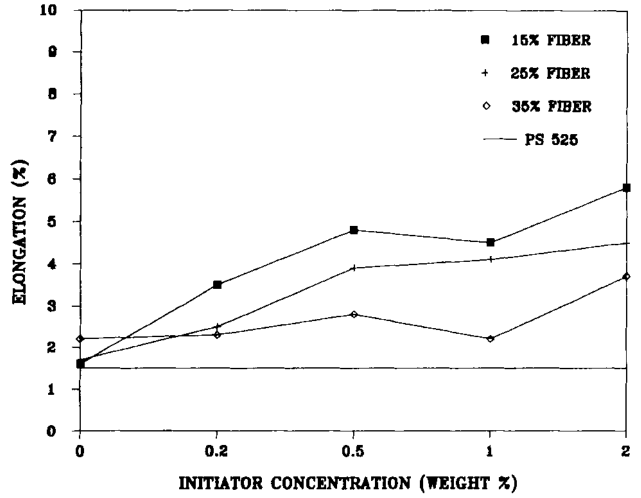


FIGURE 10a Effect of the initiator concentration on the elongation of non-treated PS 525-CTMP composites. Reaction temperature and time are 175°C and 15 minutes, respectively, and the concentration of the monomer is 5% by weight of polymer.

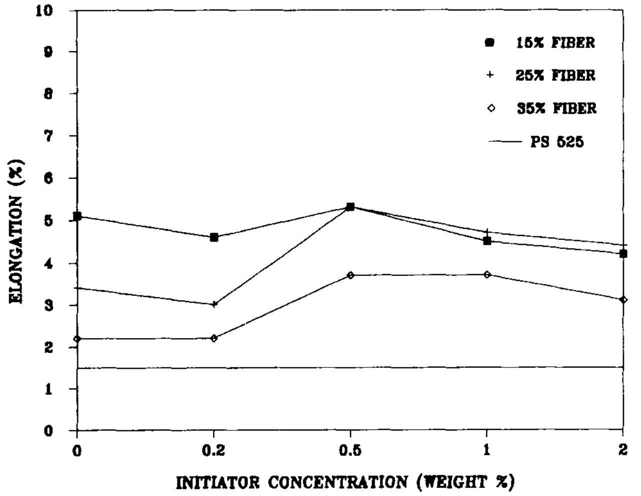


FIGURE 10b Effect of the initiator concentration on the elongation of 3% PMPPIC treated PS 525-CTMP composites. Reaction temperature and time are 175°C and 15 minutes, respectively, and the concentration of the monomer is 5% by weight of polymer.

strength increased with that of the concentration of the initiator, up to 1.0%, and then decreased. The results using only initiator concentrations of 0.5 and 1.0% exceed those of the original polymer. Impact strength also accelerated more when isocyanate was used as a coupling agent. Once again, these two tables reveal that similar to other mechanical properties, impact strength of the composites improve more for modified polystyrene prepared with a monomer and an initiator with concentrations of 5 and 1 wt.%, respectively.

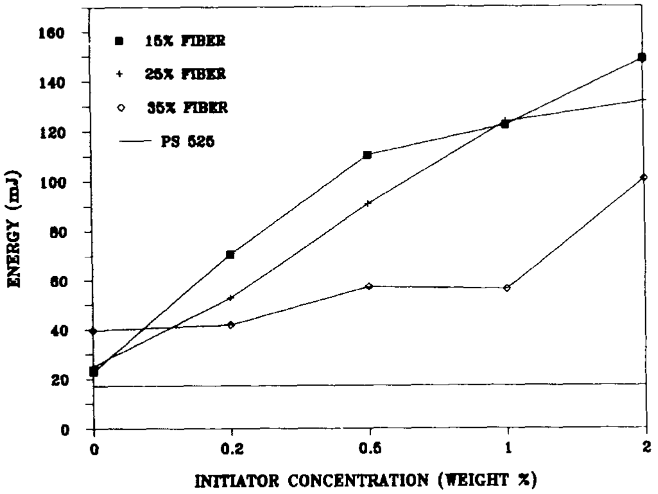


FIGURE 11a Effect of the initiator concentration on the energy of non-treated PS 525-CTMP composites. Reaction temperature and time are 175°C and 15 minutes, respectively, and the concentration of the monomer is 5% by weight of polymer.

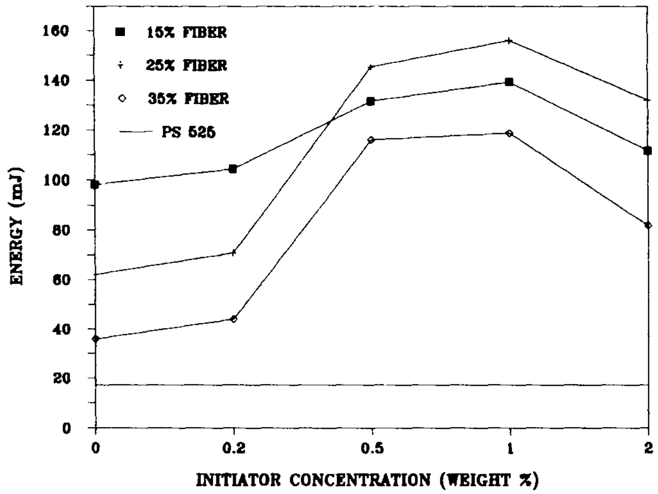


FIGURE 11b Effect of the initiator concentration on the energy of 3% PMPPIC treated PS 525-CTMP composites. Reaction temperature and time are 175°C and 15 minutes, respectively, and the concentration of the monomer is 5% by weight of polymer.

The improvements in mechanical properties (over those of the original polymer and those of composites containing unmodified polymers) indicate that the compatibility between hydrophilic cellulosic fiber and hydrophobic polymer has increased. As cellulose is a material containing —OH groups and PS was chemical modification by the grafting of MA, the polystyrene and cellulose are linked together by means of the MA forming a block copolymer containing a succinic half ester bridge between cellulose and polystyrene segments.[19,20] The

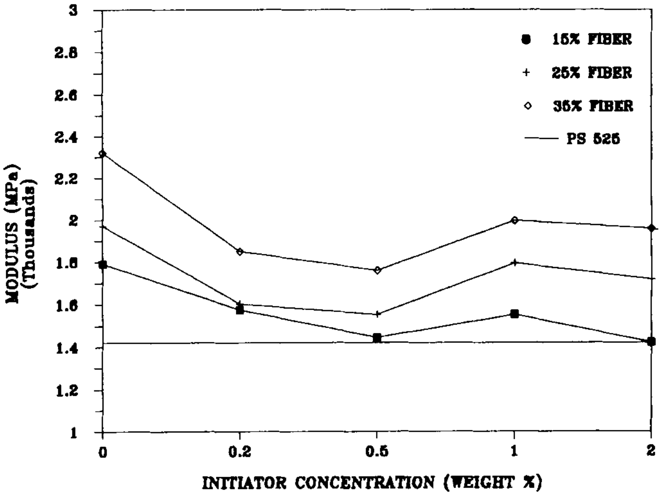


FIGURE 12a Effect of the initiator concentration on the modulus of non-treated PS 525-CTMP composites. Reaction temperature and time are 175°C and 15 minutes, respectively, and the concentration of the monomer is 5% by weight of polymer.

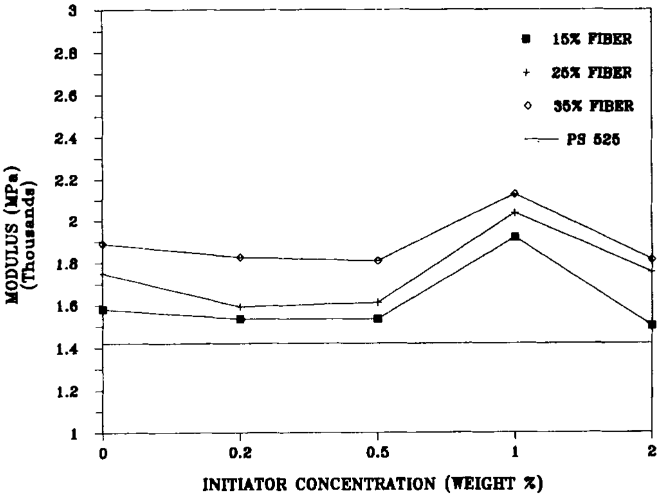


FIGURE 12b Effect of the initiator concentration on the modulus of 3% PMPPIC treated PS 525-CTMP composites. Reaction temperature and time are 175°C and 15 minutes, respectively, and the concentration of the monomer is 5% by weight of polymer.

polystyrene becomes, in this manner, a side chain of the cellulose. The reactions which occur may be represented in Figure 13. Moreover, the —OH group of cellulose also has the ability of forming hydrogen bonds with the —COOH group of modified polystyrene. The properties further accelerate when PMPPIC is used. In fact, PMPPIC behaves as a coupling agent. The functional group —N=C=O in isocyanate reacts chemically with the —OH group of cellulose, as well as with the —COOH group of modified polystyrene.[21]

TABLE IV

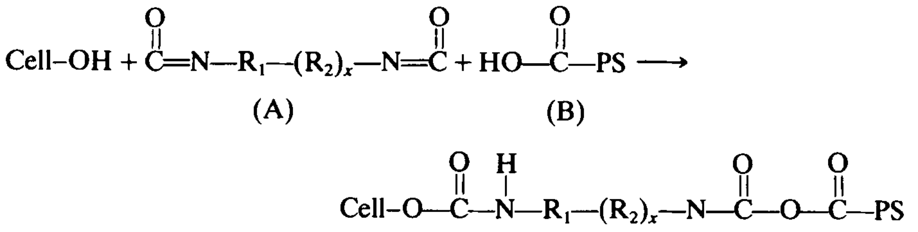
Effects of initiator concentration on the mechanical properties of maleic anhydride grafted PS 201-CTMP composites

Composition[a] (wt.%) MA	BPO	Treatment[a]	Strength (MPa)			Elongation (%)			Energy (J) × 10^3			Modulus (MPa)		
(wt.% of Fiber)			15	25	35	15	25	35	15	25	35	15	25	35
—	—	—		41.5[b]			3.3[b]			80.5[b]			1910.0[b]	
—	—	—	36.0	35.8	33.8	2.7	2.6	2.2	63.7	57.9	44.1	1920.0	2030.0	2200.0
5	0.2	—	39.8	41.2	38.7	2.7	2.5	2.4	71.5	64.9	64.5	1939.2	2247.7	2258.5
5	0.5	—	40.2	40.6	39.6	2.8	2.5	2.2	71.5	64.0	51.0	1878.1	2098.5	2302.2
5	1.0	—	42.4	47.3	45.0	2.7	2.8	2.6	73.9	85.3	80.7	2094.0	2216.0	2294.0
5	2.0	—	40.9	44.5	43.6	2.8	3.1	2.8	71.7	102.2	79.9	1922.8	1988.4	2210.9
—	—	PMPPIC(3%)	41.0	45.0	39.7	3.3	2.8	2.4	73.0	90.1	52.6	1950.0	2230.0	2240.0
5	0.2	PMPPIC(3%)	43.1	44.1	43.0	3.1	2.8	2.5	92.0	76.7	71.1	1962.6	2155.2	2170.2
5	0.5	PMPPIC(3%)	43.9	46.0	41.4	3.0	2.7	2.4	95.9	80.3	58.3	1849.3	2109.1	2266.1
5	1.0	PMPPIC(3%)	47.0	49.2	46.9	2.8	2.8	2.5	80.3	81.9	82.3	2135.0	2224.9	2278.0
5	2.0	PMPPIC(3%)	43.1	48.6	45.1	3.0	2.9	2.5	90.9	96.3	67.3	1788.4	2107.2	2346.9

[a] By weight of polymer.

[b] Un-modified polymer.

[c] Reaction condition: mixing with roll mill at 175°C for 15 min.



$$\text{Cell-OH} + \underset{(A)}{\overset{O}{\overset{\|}{C}}{=}N{-}R_1{-}(R_2)_x{-}N{=}\overset{O}{\overset{\|}{C}}} + \underset{(B)}{HO{-}\overset{O}{\overset{\|}{C}}{-}PS} \longrightarrow \text{Cell-O}{-}\overset{O}{\overset{\|}{C}}{-}\overset{H}{\overset{|}{N}}{-}R_1{-}(R_2)_x{-}N{-}\overset{O}{\overset{\|}{C}}{-}O{-}\overset{O}{\overset{\|}{C}}{-}PS \quad (1)$$

where (A) is the general formula of diisocyanate,[10] e.g. PMPPIC, and (B) is the modified polystyrene. Moreover, the delocalized π-electron of the benzene rings of both polystyrene and PMPPIC also provides a strong interaction.[9,10] As a result, PMPPIC develops an efficient interfacial contact between cellulose and thermoplastic matrices. On the other hand, when PMPPIC is used in unmodified polystyrene based composites, the polymer phase might be linked to PMPPIC only through π-electron interaction, which is opposed to covalent linkage as shown in the Eq. (1). This explains why modified polystyrene seems more efficient, even in the presence of PMPPIC. Once again, due to the extraction of modified polystyrene with boiling water, the weight of the polymer reduces (1.92%) whereas properties increase. This can be explained by the fact that the ungrafted maleic anhydride which is washed away with hot water, when present in the composites, does not improve any interfacial contacts.

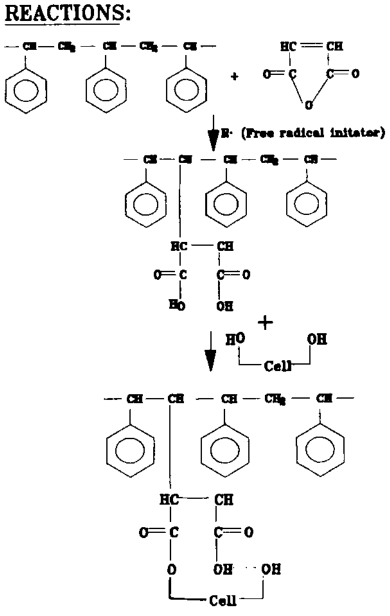


FIGURE 13 The chemical reactions of polystyrene–maleic anhydride–cellulose.

TABLE V(A)

Comparison of the improvement in mechanical properties of maleic anhydride grafted polystyrene-CTMP composites

Composition[a] (wt.%)				Improvement %					Improvement %			
MA	BPO	Treatment[a]	Fiber (wt.%)	Strength	Elongation	Energy	Modulus	Fiber (wt.%)	Strength	Elongation	Energy	Modulus
				Polystyrene 201					Polystyrene 525			
—	—	—	15	−13.3	−18.2	−20.9	+0.5	35	+28.0	+46.7	+130.8	+63.4
1	1	—	25	−16.6	−36.4	−44.1	+12.8	25	+40.5	+93.3	+446.5	+35.1
2	1	—	25	−8.4	−27.3	−24.8	+19.5	25	+96.4	+173.3	+598.8	+39.4
5	1	—	25	+13.9	−14.3	+6.0	+16.0	25	+103.1	+174.0	+618.8	+26.3
7	1	—	25	−3.4	−21.2	−11.3	+18.6	25	+62.5	+107.3	+346.5	+29.0
10	1	—	25	−11.1	−27.3	−19.9	+14.6	25	+53.0	+60.0	+204.7	+27.0
—	—	PMPPIC (3%)	25	+8.4	−15.2	+11.9	+16.8	25	+29.8	+126.7	+261.1	+23.2
1	1	PMPPIC (3%)	25	−8.9	−18.2	−39.9	+17.5	25	+80.0	+93.3	+364.5	+24.5
2	1	PMPPIC (3%)	25	−6.3	−27.3	−30.3	+15.1	25	+94.1	+60.0	+222.7	+48.9
5	1	PMPPIC (3%)	25	+18.6	−17.6	+17.9	+16.4	25	+140.4	+213.3	+807.0	+43.4
7	1	PMPPIC (3%)	25	−5.8	−27.3	−19.5	+15.9	25	+67.9	+100.0	+303.5	+30.9
10	1	PMPPIC (3%)	25	−9.9	−30.3	−30.7	+15.0	25	+67.9	+100.0	+323.8	+29.8

[a] By weight of polymer.

TABLE V(B)

Comparison of the improvement in mechanical properties of maleic anhydride grafted polystyrene-CTMP composites

Composition[a] (wt.%)				Improvement %					Improvement %			
MA	BPO	Treatment	Fiber (wt.%)	Strength	Elongation	Energy	Modulus	Fiber (wt.%)	Strength	Elongation	Energy	Modulus
					Polystyrene 201					Polystyrene 525		
—	—	—	15	−13.3	−18.2	−20.9	+0.5	35	+27.9	+46.7	+130.8	+63.4
5	0.2	—	25	−0.6	−23.9	−19.4	+17.7	25	+33.2	+64.7	+206.5	+12.8
5	0.5	—	25	−2.2	−24.9	−20.5	+9.9	25	+54.2	+157.3	+428.3	+9.4
5	1.0	—	25	+13.9	−14.2	+6.0	+16.0	25	+103.1	+174.0	+618.8	+26.3
5	2.0	—	25	+7.2	−6.4	+26.9	+4.1	25	+84.1	+200.0	+665.6	+20.9
—	—	PMPPIC(3%)	25	+8.4	−15.2	+11.9	+16.8	25	+29.8	+126.7	+261.1	+23.2
5	0.2	PMPPIC(3%)	25	+6.2	−13.9	−4.8	+12.8	25	+56.6	+101.3	+311.0	+12.1
5	0.5	PMPPIC(3%)	25	+10.8	−18.2	−0.3	+10.4	25	+88.9	+250.7	+745.6	+13.4
5	1.0	PMPPIC(3%)	25	+18.6	−17.6	+17.9	+16.4	25	+140.4	+213.3	+807.1	+43.4
5	2.0	PMPPIC(3%)	25	17.0	−11.8	+19.7	+10.3	25	+109.5	+192.0	+668.4	+23.6

[a] By weight of polymer.

TABLE VI

Effects of reaction conditions on the impact strength of maleic anhydride grafted polystyrene

Composition[a] (wt.%)		Conditions		Izod impact strength (Joules/meter)	
MA	BPO	Temperature (°C)	Time (min)	PS 201	PS 525
—	—	[b]		7.8	25.2
5.0	0.2	175	15	8.6	25.4
5.0	0.5	175	15	7.2	22.9
5.0	1.0	175	15	6.7	17.1
5.0[c]	1.0	175	15	6.6	
5.0	2.0	175	15	5.8	16.0
1.0	1.0	175	15	5.4	19.0
2.0	1.0	175	15	5.8	12.9
7.0	1.0	175	15	5.8	12.9
10.0	1.0	175	15	5.2	12.6

[a] By weight of polymer.

[b] Un-modified polymer.

[c] After extraction with boiling water for 24 hours. Reaction conditions: mixing with roll mill at 175°C for 15 min.

TABLE VII

Effect of monomer concentration on the impact strength of maleic anhydride grafted polystyrene-CTMP composites

Composition[a] (wt.%) MA	BPO	Treatment[a]	Izod impact strength (Jules/Meter)					
(wt.% of Fiber)			15	25	35	15	25	35
			Polystyrene 201			Polystyrene 525		
—	—	—		7.8[b]			25.2[b]	
—	—	—	6.3	6.1	4.9	12.0	11.3	7.0
1	1	—	6.7	6.5	7.1	9.0	10.2	11.8
2	1	—	6.9	7.5	7.4	9.6	12.6	8.4
5	1	—	7.9	8.1	7.4	9.4	10.1	9.1
5[c]	1	—	7.8	9.0	7.2			
7	1	—	6.0	9.1	6.2	8.5	9.1	9.5
10	1	—	6.2	6.2	6.5	8.0	8.4	9.3
—	—	PMPPIC(3%)	5.9	6.8	5.4	11.7	14.9	10.8
1	1	PMPPIC(3%)	6.1	6.4	6.4	8.6	9.0	9.4
2	1	PMPPIC(3%)	6.3	6.8	6.3	10.7	9.8	9.5
5	1	PMPPIC(3%)	7.3	8.5	7.3	10.3	11.1	9.2
5[c]	1	PMPPIC(3%)	7.7	9.0	7.5			
7	1	PMPPIC(3%)	6.4	7.4	7.6	9.8	9.3	7.2
10	1	PMPPIC(3%)	6.5	5.2	5.0	9.6	9.8	6.6

[a] By weight of polymer.

[b] Un-modified polymer.

[c] After extraction with boiling water for 24 hours.

Reaction conditions: mixing with roll mill at 175°C for 15 min.

TABLE VIII

Effect of initiator concentration on the impact strength of maleic anhydride grafted polystyrene-CTMP composites

Composition[a] (wt.%) MA	BPO	Treatment[a]	Izod impact strength (Jules/Meter)					
(wt.% of	Fiber)		15	25	35	15	25	35
			Polystyrene 201			Polystyrene 525		
—	—	—		7.8[b]			25.2[b]	
—	—	—	6.3	6.1	4.9	12.0	11.3	7.0
5	0.2	—	6.7	6.1	5.2	8.7	8.3	6.2
5	0.5	—	8.2	7.1	6.0	8.0	9.4	7.9
5	1.0	—	7.9	8.1	7.4	9.4	10.1	9.1
5	2.0	—	7.2	7.3	6.5	10.9	11.8	11.5
—	—	PMPPIC(3%)	5.9	6.8	5.4	11.7	14.9	10.8
5	0.2	PMPPIC(3%)	7.0	9.7	6.2	9.0	10.2	8.6
5	0.5	PMPPIC(3%)	8.7	10.1	7.2	10.5	10.7	10.6
5	1.0	PMPPIC(3%)	7.3	8.5	7.3	10.3	11.1	9.2
5	2.0	PMPPIC(3%)	8.6	11.5	7.5	11.2	14.2	11.4

[a] By weight of polymer.
[b] Un-modified polymer.
Reaction conditions: mixing with roll mill at 175°C for 15 min.

Acknowledgement

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References

1. A. Boldizar, C. Klason, J. Kubat, P. Naslund and P. Saha, *Intern. J. Polymeric Mater.*, **11**, 229 (1987).
2. R. T. Woodhams, G. Thomas and D. K. Rodgers, *Polym. Eng. Sci.*, **24**, 1166 (1984).
3. B. V. Kokta, P. D. Kamdem, A. D. Beshay and C. Daneault, *Polymer Composites*, B. Sedlácek, Ed., Walter de Gruyter and Co., Berlin, 251 (1986).
4. S. Sapieha, J. F. Pupo and H. P. Schreiber, *J. Appl. Polym. Sci.*, **37**, 233 (1989).
5. L. Czarnecki and J. L. White, *J. Appl. Poly. Sci.*, **25**, 1217 (1980).
6. A. W. McKenzie and J. P. Yuritta, *Appita*, **32**, 460 (1979).
7. G. R. Lightsey, P. H. Short and V. K. K. Sinha, *Polym. Eng. Sci.* **17**, 305 (1977).
8. B. V. Kokta, C. Daneault and A. D. Beshay, *Polym. Composites*, **7**, 337 (1986).
9. D. Maldas, B. V. Kokta and C. Daneault, *J. Appl. Polym. Sci.*, **37**, 751 (1989).
10. D. Maldas, B. V. Kokta, R. G. Raj and C. Daneault, *Polymer*, **29**, 1255 (1988).
11. D. Maldas, B. V. Kokta, R. G. Raj and S. T. Sean, *Mater. Sci. Eng.*, **A104**, 235 (1988).
12. C. Klason, J. Kubat and H.-E. Stromvall, *Intern. J. Polymeric Mater.*, **10**, 159 (1984).
13. H. Dalvag, C. Klason, and H.-E. Stromvall, *Intern. J. Polymeric Mater.*, **11**, 9 (1985).
14. N. G. Gaylord, U. S. Pat., 3 485 777 (Dec. 23, 1969).
15. Yu. A., Zoldners, R. R. Pauls and T. G. Borisova, *Khim. Drev.* (Riga), No. 5, 19 (Sept./Oct., 1978).
16. G. G. G. Gonzalez, Mississippi State Univ., Ph. D. Thesis, 125 p. (1979).
17. I. A. Gamova, T. V. Makhova, V. N. Vikhreva, A. V. Bryskovskaya, V. V. Mikhailova and E. V. Umanskaya, *Izv. VUZ, Lesnoi Zh.*, No. 2, 80 (1979).
18. M. Kodama and I. Karino, *J. Appl. Polym. Sci.*, **32**, 5057; 5345 (1986).
19. N. G. Gaylord, U.S. Pat., 3 645 939 (Feb. 29, 1972).
20. H. Kishi, M. Yoshioka, A. Yamanoi and N. Shiraishi, *J. Japan Wood Res. Soc.*, **34**, 133 (1988).
21. W. E. Johns, *Proc. Symp.* Particleboard, Washington State University, **14**, 177 (April, 1980).