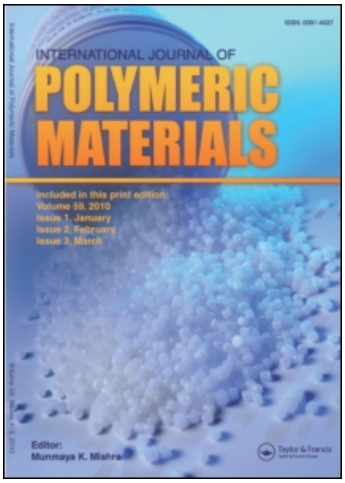

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

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To cite this Article Maldas, D. , Kokta, B. V. and Daneault, C.(1989) 'The Mechanical Properties of Wood Fiber-reinforced Polymethylmethacrylate', International Journal of Polymeric Materials, 12: 4, 297 — 323
To link to this Article: DOI: 10.1080/00914038908031509
URL: http://dx.doi.org/10.1080/00914038908031509

Intern. J. Polymeric Mater., 1989, Vol. 12, pp. 297–323
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Printed in the United Kingdom

The Mechanical Properties of Wood Fiber-reinforced Polymethylmethacrylate

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The mechanical properties, e.g. tensile modulus (at 0.1% strain), tensile strength at maximum point and corresponding elongation and breaking energy, as well as impact strength, of compression molded PMMA and PMMA filled with wood fibers (10%–40% by weight of composite) have been investigated. Optimization of molding conditions, (e.g. temperature, time, pressure and mixing aids) was carried out. In optimum conditions of mixing and molding, the effect of different parameters, (e.g. nature and concentration of coupling agents (isocyanates), coating treatment, nature of wood species in the form of various pulps) on the mechanical properties of the resulting composites were evaluated. PMPPIC having 2%–4% (by weight of polymer) was found to behave as a true coupling agent because modulus as well as the tensile and impact strengths were improved. Moreover, PMPPIC acted as a coupling agent even when it was used for treatment of PMMA and fiber or to precoat the fiber. A distinct effect of the morphology of wood species and fiber-making techniques on the mechanical properties of wood fiber-filled composites was also observed.

KEYWORDS: Thermoplastic composites, PMMA, Wood species, Wood pulp, Mechanical properties, Coupling agents.

INTRODUCTION

Many outstanding properties of thermoplastics are well-known.[1] But single component materials are no longer sufficient to meet all the prerequisite demands of today's advanced technologies.[2] On the other hand, a wide variation of mechanical and physical properties can be incorporated into thermoplastics through the judicious

compounding of polymer and filler. Various materials, e.g. non-metallic minerals, metallic powder or organic compounds, are used as a filler.[3] Compared to inorganic fillers, cellulosic raw materials offer some additional advantages.[3-5] moreover, cellulosic materials are renewable sources. The literature[4-11] reveals that a number of common thermoplastics, e.g. polyethylene, polypropylene, polystyrene, polyvinylchloride, polymethylmethacrylate, etc., are suitable for making composites containing cellulose fibers.

A poor chemical affinity between common thermoplastics and cellulose fibers keeps them away to develop an efficient interface which is of paramount importance to transfer stress between two different phases. Generally, to improve the filler/matrix interface, various additives,[7,10] coupling agents,[7-11] or special treatments,[5,11] are used. Apart from this, standardization of the method of preparation of composites also plays an important role on the ultimate properties of the composites.

In the present study, attempts have been made to standardize the mixing and molding conditions of the composites of PMMA filled with different pulps of various wood species. To improve the adhesion between polymer and fiber, coupling agent, e.g. isocyanates have also been used. The mechanical properties of the composites under study have been evaluated.

PMMA has been selected as a thermoplastic because PMMA filled with wood fibers have scarcely been studied. A brief review of the literature is as follows. Nagaty *et al.*[12] studied some physical and chemical behaviors of composites prepared by impregnation, or grafting of bagasse with PMMA. They reported that the properties of the composites were affected by both polymer loading and mesh size of the ground bagasse. Klason and Kubât[6] presented the results of a systematic study of processing and mechanical parameters of some composites based on a number of common thermoplastics along with PMMA and various cellulosic fillers and lignin, Kokta *et al.*[5] showed the improvements in composites' mechanical properties due to the grafting of wood fibers, e.g. birch or aspen in the form of chemithermomechanical pulps with PMMA.

MATERIALS

Polymer: polymethylmethacrylate was supplied by Scientific Polymer Products Inc., Ontario.

Filler

In this study, three different varieties of wood species, e.g. hardwood species white birch (Betula Papyrifera Marsh), aspen (Populus Tremuloides Michx)—and softwood species—spruce (mixture of 75% black spruce + 20% balsam + 5% aspen) in the form of chemithermomechanical pulps (CTMP), explosion pulps (V-pulp), Ontario Paper Company's pulp (OPCO-pulp) and sawdust, have been used as fillers.

Coupling agent

Three isocyanates were used as coupling agent:

i) Poly [methylene (polyphenyl isocyanate)] (PMPPIC);
ii) Tolulene 2,4-diisocyanate (TDIC) and
iii) Hexamethylene diisocyanate (HMDIC) were supplied by Poly Science Inc., U.S.A.

EXPERIMENTAL

Preparation of filler

i) *Chemithermomechanical pulp* (*CTMP*) was prepared in a Sund Defibrator: temperature, 126°C; retention time, 5 min, pressure, 0.12 MPa; refining energy, 5.26 MJ/kg; Na_2SO_3, 5%; NaOH, 5%; pH, 12.9. The characteristics of such pulp are: yield, 92%, lignin 17.9%, average fiber length, 0.75 mm; drainage index (CSF), 119 ml; breaking length, 4.46 km; tear index, 7.2 mN m^2/g.
ii) *Explosion pulp* (*V-pulp*) was prepared by an explosion technique: Na_2SO_3, 8%, immersion time 24 h, immersion temperature, 60°C; explosion time, 4 min; and explosion temperature 190°C. The explosed chips were washed thoroughly with water and then refined in a blender for 1 minute at high speed.
iii) *Ontario Paper Company's pulp* (*OPCO-pulp*) was supplied by the same company.

All these pulps and chips for sawdust were dried in a circulating air

oven at 55°C and then ground to mesh size 60 with a Granu Grinder, C. W. Brabender, Instruments, Inc., U.S.A.

Treatment with isocyanates

Fiber, polymer and isocyanates (2%–8% by weight of polymer) were mixed with a roll mill, C. W. Brabender Laboratory Prep. Mill, Model No. 065, at 185°C.

Coating treatment

Polymer (10% by weight of fiber) and PMPPIC (2% and 8% by weight of fiber) were mixed with fiber with the help of a roll mill at 185°C. The mixtures were collected and mixed repeatedly for 8 to 10 times for homogeneous coating. Finally the coated fibers were ground to mesh size 20.

Compounding and compression molding

Mixture of polymer and pulp/coated pulp having 10%–40% by weight of composite and isocyanate (in the case of isocyanate treated composites) were mixed repeatedly (for 5 to 6 times) with a roll mill at 185°C. The resulting mixtures were then allowed to cool to room temperature and then reground to mesh size 20. Polymer was also mixed with fibers in a laboratory blender, pulse operated 12 times with a one-second interval.

The mixtures were molded into shoulder shaped specimens in a mold which was covered by metal plates on both sides. The mold was heated under pressure in a Carver Laboratory press. Molding temperature, pressure during heating and cooling varies from 175°C–195°C and 1.10–4.34 MPa, respectively. The heating and cooling time of the mold in press also varied, e.g. 15–35 min and 7.5–30 min, respectively. To enable a comparative study to be carried out, standard molding conditions, e.g. heating temperature, 187°C, heating time, 20 min, molding pressure, 3.5 MPa, cooling time, 15 min were followed.

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

Mechanical testing

The mechanical properties (tensile modulus, tensile strength at the break point and the corresponding elongation and energy) of the samples were measured with an Instron tensile tester (Model 4201). All these properties were automatically calculated by a computer using the Instron 2412005 General Tensile Test Program (under the name "PLA"). The strain rate was 1 cm/min and tensile modulus was reported at 0.1 percent 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% RH for at least 18 hours in the testing room. Dimensions of all specimens were measured with a micrometer. Statistical averages of each 5–6 measurements were taken. The coefficients of variations, 2.5–8.5% were taken into account for each set of tests.

RESULTS AND DISCUSSION

Effect of molding temperature and time

It is well established[11,13] that compoundg conditions have a substantial effect on the mechanical properties of the composites. Figure 1 (a–d) shows the effect of molding temperature and heating time on the mechanical properties of the PMMA as well as composites having 10–40 wt.% of filler (CTMP). Figure 1a reveals that strength of PMMA first rises with the increase in temperature and then decreases at higher temperatures, e.g. 195°C. In all cases, e.g. either in polymer or in composites, strength increases with that of heating time, especially at lower temperatures, e.g. 175°C. But the pattern of the curves of strength vs. molding temperature changes with the increase in heating time. Moreover, the pattern also changes in different wt.% of fiber. In general, strength decreases with the increase fiber content in the composite.

Figures 1b and 1c show the effect of molding temperature and time on elongation and breaking energy of the composites, respectively. Similar to strength, elongation and breaking energy increase with that of heating time at lower temperatures, e.g. up to 185°C. But at a higher temperature, the elongation values for higher

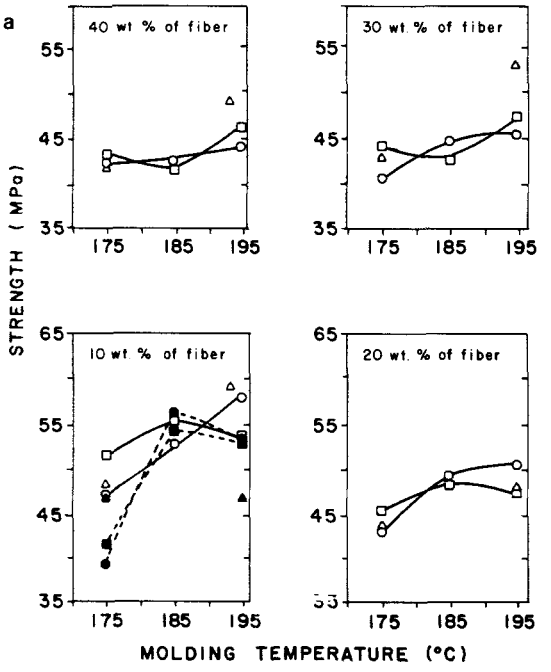


FIGURE 1a Effect of molding temperature for different durations of time on stress of PMMA and PMMA filled with CTMP (aspen) (10%–40% by weight of composite). The dashed lines and solid symbols indicate the properties of PMMA. The solid lines and hollow symbols indicate the properties of PMMA filled with CTMP (aspen). (●) and (○), heating time, 15 min; (▲) and (△), heating time, 25 min; (■) and (□), heating time, 35 min. Other molding conditions: molding pressure, 4.34 MPa; cooling time, 15 min.

heating time are either less, or nearly equal, to that of lower heating time. Elongation and breaking energy also decrease with the increase of fiber content in the composite. However, the modulus (shown in Figure 1d) increases with the increase of fiber percentage in the composite. In addition, modulus with lower heating time as well as with higher heating time shows a very marginal difference at both 175°C and 195°C. But at 185°C, modulus is higher for lower heating time, e.g. 15 min, compared to that of higher heating time, e.g. 35 min.

The anomalous behavior of mechanical properties especially at a higher temperature and higher heating time can be explained by the

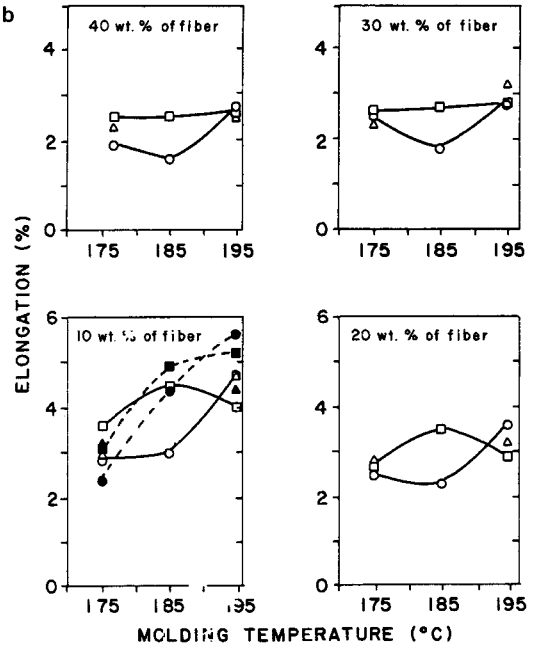


FIGURE 1b Effect of molding temperature for different durations of time on elongation of PMMA and PMMA filled with CTMP (aspen) (10%–40% by weight of composite). The dashed lines and solid symbols indicate the properties of PMMA. The solid lines and hollow symbols indicate the properties of PMMA filled with CTMP (aspen). (●) and (○), heating time, 15 min; (▲) and (△) heating time, 25 min; (■) and (□), heating time, 35 min. Other molding conditions: molding pressure, 4.34 MPa; cooling time, 15 min.

fact that most of the components of unbleached wood fibers, e.g. lignin, hemicellulose, etc., other than cellulose, degradate[10] at a higher temperature, viz. above 200°C.

Effect of molding pressure

Figure 2 shows the variation of mechanical properties with a change in molding pressure during molding of PMMA and PMMA filled with CTMP (10%–40% by weight of composite) while other molding conditions remain stable. Strength of PMMA has no effect on molding pressure. But elongation, breaking energy and modulus

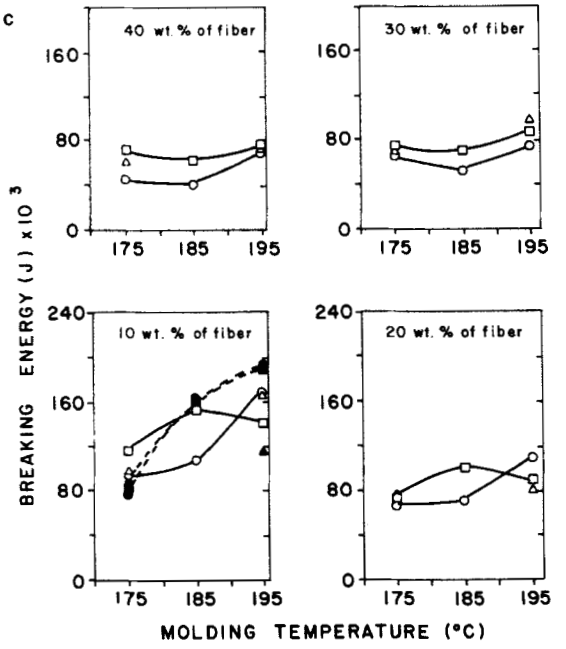


FIGURE 1c Effect of molding temperature for different durations of time on energy of PMMA and PMMA filled with CTMP (aspen) (10%–40% by weight of composite). The dashed lines and solid symbols indicate the properties of PMMA. The solid lines and hollow symbols indicate the properties of PMMA filled with CTMP (aspen). (●) and (○), heating time, 15 min; (▲) and (△), heating time, 25 min; (■) and (□), heating time, 35 min. Other molding conditions: molding pressure, 4.34 MPa; cooling time, 15 min.

decrease and then increase with a continuous increase in pressure. The strength of composites first increases and then remains constant with an increase in pressure, but elongation and breaking energy of the composite increase with that of pressure. Modulus at the beginning remains nearly constant and then decreases with the increase in pressure. Figure 2 indicates that optimum pressure is ≈3.5 MPa. Incidentally, Beshay, Kokta and Daneault[11] reported the optimum pressure to be 3.3 to 3.8 MPa for wood fiber filled polyethylene composites.

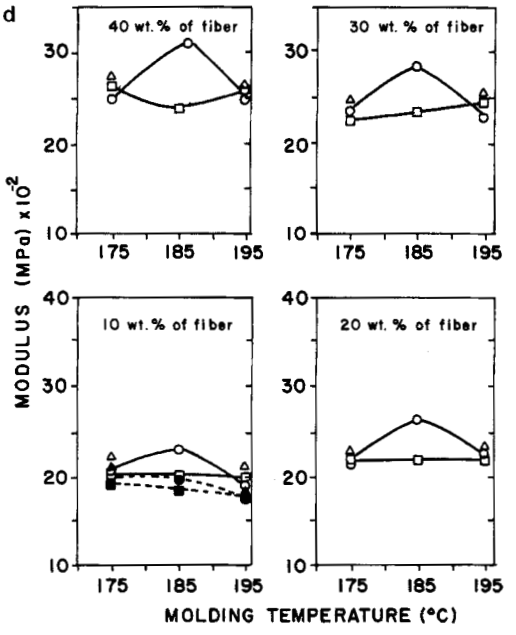


FIGURE 1d Effect of molding temperature for different durations of time on modulus of PMMA and PMMA filled with CTMP (aspen) (10%–40% by weight of composite). The dashed lines and solid symbols indicate the properties of PMMA. The solid lines and hollow symbols indicate the properties of PMMA filled with CTMP (aspen). (●) and (○), heating time, 15 min; (▲) and (△), heating time, 25 min; (■) and (□), heating time, 35 min. Other molding conditions: molding pressure, 4.34 MPa; cooling time, 15 min.

Effect of cooling time

Finding out optimum cooling time is also important because the expansion coefficients[14] of fiber and polymer are not same. Unmatched expansion coefficient results in numerous voids or micro-cracks in the composites if proper care is not taken. The effect of cooling time on the mechanical properties of PMMA and PMMA filled with CTMP (10%–40% by weight of composite) is shown in Figure 3. This figure reveals that modulus of PMMA is lower when cooling time is 15 min compared to that of 7.5 and

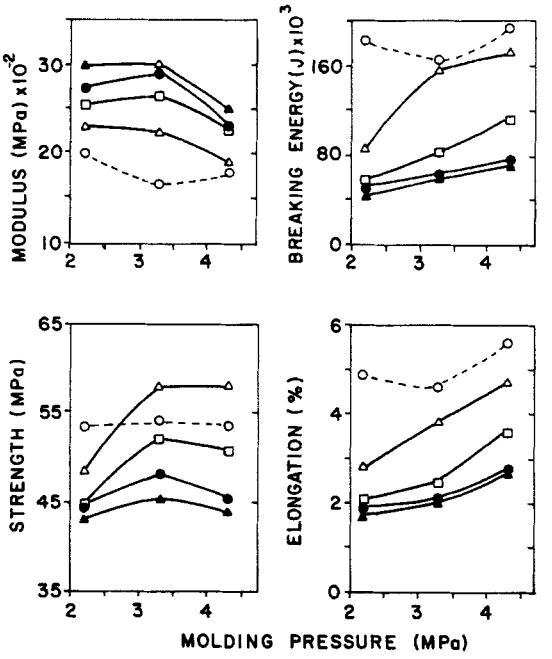


FIGURE 2 Effect of molding pressure on the mechanical properties of PMMA and PMMA filled with CTMP (aspen) (10%–40% by weight of composite). The dashed lines indicate the properties of PMMA. (△), 10 wt.% of fiber; (□), 20 wt. of % of fiber; (●), 30 wt.% of fiber; (▲), 40 wt.% of fiber. Other molding conditions: temperature, 195°C; heating time, 15 min; cooling time, 15 min.

30 min. Except in a few cases, the mechanical properties slightly increase with that of cooling time. But after 15 min of cooling time, most of the mechanical properties remain constant.

Upon examination of the effect of different operating conditions on composite preparation, the following optimum conditions were followed for molding samples for other studies: molding temperature, 187°C; heating time, 20 min; pressure, 3.3–3.5 MPa and cooling time, 15 min.

Effect of mixing with a roll mill and laboratory blender

The effect of mixing aid on the mechanical properties of PMMA-wood fiber composites, two different pulps, e.g. CTMP and sawdust

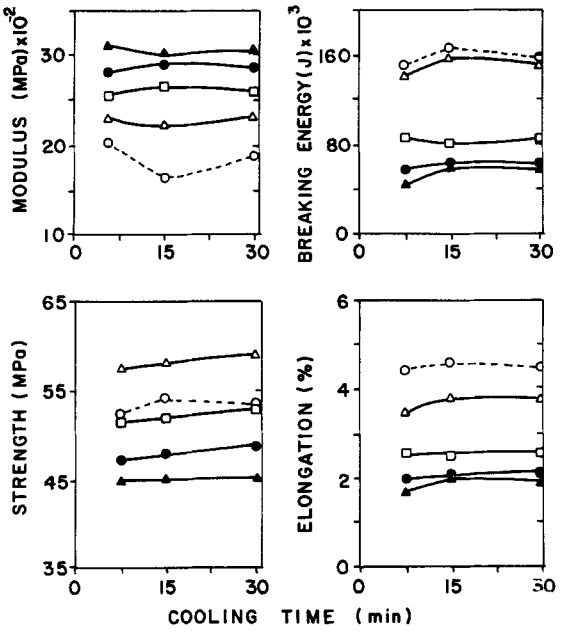


FIGURE 3 Effect of cooling time of the specimens in the mold on the mechanical properties of PMMA and PMMA filled with CTMP (aspen) (10%–40% by weight of composite). The dashed lines indicate the properties of PMMA. (△), 10 wt.% of fiber; (□), 20 wt.% of fiber; (●), 30 wt.% of fiber; (▲), 40 wt.% of fiber. Other molding conditions: temperature, 195°C; heating time, 15 min; molding pressure, 3.3 MPa.

of aspen are listed in Table I. From Table I, one observes that mechanical properties of untreated PMMA are better than PMMA treated with a roll mill at 185°C. This can be explained by the fact that during mixing of PMMA alone with a roll mill at a higher temperature the following phenomenon may occur, e.g. i) slow oxidation (in the presence of air), and/or ii) degradation of the main chain, and/or iii) cross linking among the chains. As a result, mechanical properties are reduced.

When PMMA and fibers were mixed with a roll mill, better mechanical properties were obtained compared to the use of a blender. Unfortunately, only modulus of composites based on CTMP (10–40 wt.% of fiber) and sawdust (40 wt.% of fiber) resulted in a slightly superior behavior when mixed with a blender.

TABLE I

Effect of mixing on the mechanical properties of PMMA filled with CTMP (aspen) and sawdust (aspen) fibers

Composite (wt.% of fiber)	Strength (MPa)				Elongation (%)				Breaking energy (J) × 10^3				Modulus (MPa) × 10^{-2}			
	10	20	30	40	10	20	30	40	10	20	30	40	10	20	30	40
a) PMMA			52.8				4.8				147.7				18.3	
b) PMMA			56.9				5.0				203.6				19.5	
a) PMMA + CTMP(aspen)	54.7	48.4	47.4	41.0	3.2	2.3	2.0	1.6	125.9	71.9	65.2	41.1	22.2	24.4	27.3	27.6
b) PMMA + CTMP(aspen)	48.8	44.9	44.7	39.0	3.4	2.3	2.0	1.6	132.6	72.3	57.4	42.4	23.2	25.5	26.8	29.5
a) PMA + Sawdust (aspen)	49.6	43.2	39.0	37.6	2.9	2.2	1.8	1.7	92.8	60.7	43.8	40.8	23.6	25.8	27.6	27.8
b) PMMA + Sawdust	46.7	42.9	37.7	35.7	2.5	2.1	1.6	1.6	87.3	60.6	39.6	36.2	23.4	25.7	27.6	28.5

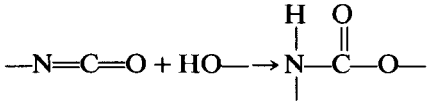
a) Mixed with roll mill at 185°C;
b) Mixed in a laboratory blender, pulse operated 12 times with a one-second interval.

When mixing fiber and polymer with a roll mill at a temperature (say, 185°C) above the melting point of polymer, the result is rather homogeneous compared to that with a blender at room temperature. Intimate mixing in a roll mill revealed better mechanical properties of the composites. In a similar study, Kokta *et al.*[5] reported some abnormal behaviour due to insufficient mixing of wood fiber and PMMA in a blender.

Effect of coupling agent

In order to verify the role of isocyanate as a coupling agent, three isocyanates (PMPPIC, TDIC and HMDIC having different chemical structures) have been studied. Mechanical properties of composites of PMMA along with two different wood fibers of aspen, e.g. CTMP and sawdust and with 2% (by weight of polymer) each of isocyanates, have been evaluated and listed in Table II. This table shows that strength of PMPPIC treated CTMP fiber filled composites is improved up to 30% of fiber level. But when TDIC is used as a coupling agent, strength is improved up to 10% of fiber level. On the other hand, strength of HMDIC treated PMMA–CTMP composite as well as PMMA-sawdust composites are inferior compared to that of the original thermoplastic. Again, elongation and breaking energy are also lower in all cases. The modulus values of the isocyanate treated composites are always superior to those of the original thermoplastic and nontreated composites.

Again, from Table II, we can easily say that PMPPIC is the best coupling agent among the three isocyanates, and TDIC is also better, but HMDIC is not at all good. This behavior can be attributed to a difference in the chemical structure of the three isocyanates. The functional group, —N=C=O of all these isocyanates, reacts with —OH group of cellulose.



But the link of the remaining part of isocyanates with PMMA differs because the remaining groups are hexamethylene, tolylene, poly [methylene (poly phenyl)] of HMDIC, TDIC and PMPPIC

TABLE II

Effect of nature of isocyanates on the mechanical properties of PMMA filled with CTMP (aspen) and sawdust (aspen) fibers

Composite (wt.% of fiber)	Strength (MPa)				Elongation (%)				Breaking energy (J) × 10^3				Modulus (MPa) × 10^{-2}			
	10	20	30	40	10	20	30	40	10	20	30	40	10	20	30	40
PMMA	52.3				4.3				147.7				18.3			
PMMA + CTMP (aspen)	54.7	48.4	47.4	41.0	3.2	2.3	2.0	1.6	125.9	71.9	65.2	41.1	22.2	24.4	27.3	27.6
[PMMA + 2% PMPPIC] + CTMP (aspen)	57.8	58.1	59.8	48.4	3.1	2.7	2.6	1.9	126.3	101.4	99.1	60.4	23.5	26.5	28.7	30.5
[PMMA + 2% TDIC] + CTMP (aspen)	58.2	48.7	49.8	41.2	3.1	2.2	2.1	1.5	117.1	65.6	61.3	34.9	23.4	26.4	28.5	29.9
[PMMA + 2% HMDIC] + CTMP (aspen)	49.3	43.5	37.1	37.1	3.2	2.2	1.5	1.4	114.3	64.0	36.1	32.6	22.5	25.5	27.0	27.6
PMMA + Sawdust (aspen)	49.6	43.2	39.0	37.6	2.9	2.2	1.8	1.7	92.8	60.7	43.8	40.8	23.6	25.8	27.6	27.8
[PMMA + 2% PMPPIC] + Sawdust (aspen)	51.6	48.6	45.2	42.8	2.7	2.3	1.8	1.6	89.6	71.6	54.6	42.8	24.4	25.8	27.1	30.3
[PMMA + 2% TDIC] + Sawdust (aspen)	49.8	40.3	35.8	35.3	2.6	2.0	1.7	1.4	87.8	53.0	39.7	31.8	23.6	25.8	25.6	28.5
[PMMA + 2% HMDIC] + Sawdust (aspen)	45.2	42.2	40.4	37.5	2.6	2.3	1.9	1.6	78.9	63.0	48.1	36.9	23.9	25.6	28.2	29.2

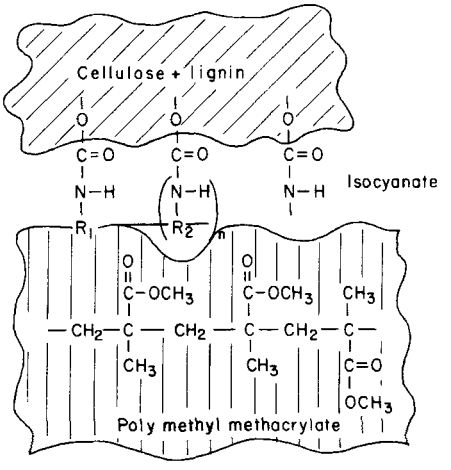


FIGURE 4 Hypothetical chemical formula of interfacial area of Cellulose–Isocyanate–Polymethylmethacrylate.

respectively. The hexamethylene group of HMDIC can offer only a Van der Walls type of weak adhesive force to link with PMMA on the interface. The delocalized π-electrons of the benzene ring in both tolylene and poly [methylene (polyphenyl)] groups of TDIC and PMPPIC can provide a small amount of polarity which can interact to the ester group (of PMMA) which also has slight polarity. In addition, the polymeric nature of PMPPIC, the cellulose and polymer phases (PMMA) are continuously linked by it on the interface, while the discrete nature of TDIC provides it inferior in this respect.

On the basis of the above discussion and with the help of the general formula[16] for isocyanates, the hypothetical chemical formula of the interfacial area of cellulose-isocyanate–polymethyl methacrylate can be proposed (as shown in Figure 4).

Effect of concentration of isocyanate

The variation in mechanical properties along with the change of isocyanate (PMPPIC) concentration (0–8% by weight of polymer) in the composite of PMMA and CTMP (aspen) (10%–40% by weight of composite) are shown in Figure 5. From this figure, one

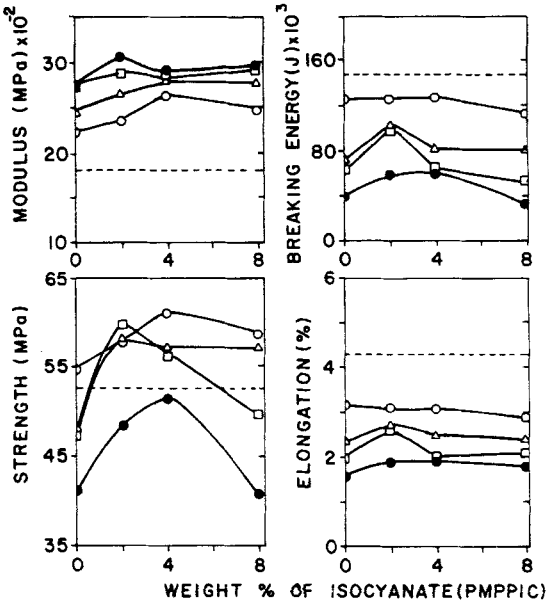


FIGURE 5 Effect of concentration of isocyanate, PMPPIC (percentage by weight of polymer) on the mechanical properties of PMMA filled with CTMP (aspen) (10%–40% by weight of composite). The dashed lines indicate the properties of PMMA. (○), 10 wt.% of fiber; (△), 20 wt.% of fiber; (□), 30 wt.% of fiber; (●), 40 wt.% of fiber. Molding conditions: temperature, 187°C; heating time, 20 min; molding pressure, 3.5 MPa; cooling time, 15 min.

finds that all the mechanical properties increase with the increase in the isocyanate concentration from 0% (i.e. untreated composite) to attain maximum between 2%–4% of isocyanate and then either decrease or level off. The strength of the treated composites is improved up to 30% of fiber content. But elongation and breaking energy are lower than the original polymer, and increases with the addition of more and more fibers in the composite. One must note however that other mechanical properties decrease with the increase of fiber level.

With the increase of the isocyanate concentration, the interfacial bonding (as discussed earlier) increases, as a result of which mechanical properties are improved continuously. With a higher concentration of PMPPIC, the mechanical properties either level off or decrease because isocyanate molecules can react among them-

selves to form various by-products[15]. As the chances of formation of by-products increase with the increase of isocyanate concentration, the properties are affected accordingly.

Effect of coating treatment

In order to improve the interfacial contact between hydrophilic wood fibers and hydrophobic polymer matrix, CTMP and sawdust of aspen wood were precoated with polymer (10% by weight of fiber) and PMPPIC (2% and 8% by weight of fiber). Table III presents the mechanical properties of the resulting composites. It is clear from this table that similar to PMPPIC treated composites, mechanical properties improve with the increase of concentration of isocyanate in the coated fiber. For CTMP fibers, mechanical properties are improved more when fibers are coated with 2% PMPPIC compared to 8% PMPPIC. On the contrary, in the case of sawdust coated fibers some mechanical properties perform even better for 8% PMPPIC as compared to non-coated fibers. Table III also shows that the overall trend of the results are similar to the effect of the concentration of PMPPIC. The above-mentioned results indicate that PMPPIC also acts as a good coupling agent even when it is applied to precoate the fibers along with the polymer.

Effect of wood species and nature of pulps

In order to discover the performance of different wood species, (e.g. hard wood such as aspen and birch, and soft wood such as spruce in the form of various pulps, e.g. CTMP, V-pulp, OPCO-pulp and sawdust, as a reinforcing filler), the composites of PMMA containing these wood fibers were made. Table IV illustrates the mechanical properties of the resulting composites. This table reveals that strength is improved up to 10% of fiber only when CTMP (aspen), V-pulp (aspen) and sawdust (birch) fibers are used as a filler. But elongation and energy values are inferior when compared to the original polymer. On the other hand, modulus had some positive effects.

This result can be explained by the fact that the ester group of PMPPA can form a hydrogen bond with —OH group of cellulose.

TABLE III

Effect of coating of fibers with isocyanate and polymer on the mechanical properties of PMMA filled with coated CTMP (aspen) and sawdust (aspen) fibers

Composite (wt.% of fiber)	Strength (MPa)				Elongation (%)				Breaking energy (J) × 10^3				Modulus (MPa) × 10^{-2}			
	10	20	30	40	10	20	30	40	10	20	30	40	10	20	30	40
PMMA	52.8				4.3				147.7				18.3			
PMMA + CTMP (aspen)	54.7	48.4	47.4	41.0	3.2	2.3	2.0	1.6	125.9	71.9	65.2	41.1	22.2	24.4	27.3	27.6
PMMA + CTMP[coated: PMMA (10%) + PMPPIC (2%)	60.8	59.8	50.5	38.0	3.5	2.9	2.2	1.5	145.7	111.4	74.1	33.1	23.7	26.1	28.0	28.6
PMMA + CTMP + [coated: PMMA (10%) + PMPPIC (8%)]	57.6	55.3	57.6	53.6	3.0	2.5	2.4	2.1	109.6	78.5	77.4	64.9	24.2	26.5	29.2	29.9
PMMA + Sawdust (aspen)	49.6	43.2	39.0	37.6	2.9	2.2	1.8	1.7	92.8	60.7	43.8	40.8	23.6	25.8	27.6	27.8
PMMA + Sawdust [coated: PMMA (10%) + PMPPIC (2%)]	48.9	46.9	42.3	41.4	2.6	2.4	1.8	1.7	84.3	78.0	55.8	45.1	24.2	26.5	27.5	28.8
PMMA + Sawdust [coated: PMMA (10%) + PMPPIC (8%)]	52.8	47.5	42.6	42.2	2.9	2.2	2.2	1.7	98.8	62.8	47.4	40.8	23.5	25.5	27.2	28.9

TABLE IV

Effect of nature of pulp on the mechanical properties of non-treated PMMA filled with different wood fibers

Composite (wt. % of fiber)	Strength (MPa)				Elongation (%)				Breaking energy (J) × 10^3				Modulus (MPa) × 10^{-2}			
	10	20	30	40	10	20	30	40	10	20	30	40	10	20	30	40
PMMA	52.8				4.3				147.7				18.3			
PMMA + CTMP (aspen)	54.7	48.4	47.4	41.0	3.2	2.3	2.0	1.6	125.9	71.9	65.2	41.1	22.2	24.4	27.3	27.6
PMMA + V-Pulp (aspen)	53.8	44.8	43.0	37.9	3.1	2.3	2.0	1.6	116.0	67.0	49.1	37.4	22.8	23.7	26.0	26.8
PMMA + V-Pulp (softwood)	51.1	48.8	42.8	39.0	3.1	2.5	1.9	1.6	99.4	77.9	49.4	37.0	22.1	24.4	25.7	28.0
PMMA + OPCO-Pulp (softwood)	50.7	46.2	40.4	—	2.4	2.2	1.7	—	104.5	64.5	40.7	—	21.5	24.7	26.4	—
PMMA + Sawdust (softwood)	49.8	45.6	43.6	30.1	2.9	2.3	1.9	1.2	105.4	70.3	51.0	24.1	21.9	25.1	28.3	28.8
PMMA + Sawdust (birch)	53.8	48.8	42.8	40.0	3.0	2.5	1.9	1.6	102.0	74.6	49.8	41.8	23.4	25.1	26.4	28.3
PMMA + Sawdust (aspen)	49.6	43.2	39.0	37.6	2.9	2.2	1.8	1.7	92.8	60.7	43.8	40.8	23.6	25.8	27.6	27.8

Thus, in a few cases, strength improved to a small extent. But due to lack of strong chemical bonding between hydrophobic polymer and hydrophilic wood fibers, mechanical properties did not improve in most cases.

To compare the reinforcement performance of these wood species in the form of various pulp in the presence of a coupling agent, PMPPIC (2% by weight of polymer), composites were made. The mechanical properties of these composites appear in Table V. It is clear from this table that the isocyanate treatment leads to some positive effects on stress for most of the wood fibers, except sawdust (aspen) fiber filled composites. In general, strength improved up to 10% of fiber level. But improvements reach 30% of fiber for CTMP (aspen) and V-pulp (soft wood) and 20% of fiber for OPCO-pulp (soft wood). In all cases, modulus also improved up to 40% of fiber. Elongation and breaking energy values did not improve compared to the original polymer.

The improvement in strength and modulus in the presence of a coupling agent is consistent with our results as discussed earlier in the case of the effect of the coupling agent. If one compares the effect of different wood species, one finds that hardwood (birch) is slightly better than softwood (spruce), as far as sawdust is concerned. When different pulps of softwood (spruce) are compared, OPCO-pulp is viewed as the best and V-pulp ranks better than sawdust. Again, when different pulps of hardwood (aspen) are compared, CTMP is considered best and V-pulp scores better than sawdust. This type of behavior was also observed earlier by Kokta *et al.*[5,17] and by us[18]. Depending on the origin, i.e. wood species, the characteristics of various kinds of pulps differs to a large extent,[19] e.g. softwood (spruce): long, medium slender, medium walled; hardwood (aspen): short, slender, medium walled, with thin walled vessels; hardwood (birch): short, very slender, medium walled, with thin walled vessels. Moreover, softwood fibers (spruce) are flexible compared to hardwood (aspen or birch). Again, between aspen and birch, the latter is denser. Once again, different pulping techniques offer various ways to separate fibers from the wood chips[18–21] (e.g. sawdust is prepared by separating fibers mechanically, V-pulps by combination of chemical and physical methods while both chemical and mechanical methods are used to CTMP. Accordingly, surface quality, physical and mechanical

TABLE V

Effect of nature of pulp on the mechanical properties of isocyanate (PMPPIC) treated PMMA filled with different wood fibers

Composite (wt.% of fiber)	Strength (MPa)				Elongation (%)				Breaking energy (J) × 10^3				Modulus (MPa) × 10^{-2}			
	10	20	30	40	10	20	30	40	10	20	30	40	10	20	30	40
PMMA	52.8				4.3				147.7				18.3			
[PMMA + 2% PMPPIC] + CTMP (aspen)	57.8	58.1	59.8	48.4	3.1	2.7	2.6	1.9	126.3	101.4	99.1	60.4	23.5	26.5	28.7	30.5
[PMMA + 2% PMPPIC] + V-Pulp (aspen)	58.1	49.4	46.6	42.6	3.1	2.2	1.9	1.6	118.1	70.0	54.2	43.0	23.5	25.4	28.0	29.2
[PMMA + 2% PMPPIC] + V-Pulp (softwood)	57.5	48.7	54.1	46.8	2.7	2.1	2.2	1.7	107.9	58.4	72.2	47.9	24.1	24.5	26.5	29.1
[PMMA + 2% PMPPIC] + OPCO-Pulp (softwood)	61.3	56.2	43.5	41.0	3.3	2.5	1.7	1.6	131.3	85.6	47.1	44.6	24.6	26.6	27.8	28.4
[PMMA + 2% PMPPIC] + Sawdust (softwood)	56.2	49.3	45.3	41.3	3.0	2.4	2.0	1.6	111.3	75.8	55.6	39.9	23.8	24.6	26.0	30.0
[PMMA + 2% PMPPIC] + Sawdust (birch)	56.6	50.0	45.6	40.7	2.9	2.4	2.0	1.6	100.9	72.8	55.0	39.2	24.5	26.2	26.9	27.3
[PMMA + 2% PMPPIC] + Sawdust (aspen)	51.6	48.6	45.2	42.8	2.7	2.3	1.8	1.6	89.6	71.6	54.6	42.8	24.4	25.8	27.1	30.4

properties of different pulps varies widely, e.g. CTMP provides higher specific surface area compared to mechanical pulps while sawdust is coarser than other pulps. Moreover, CTMP and other pulps ar more flexible than sawdust. As a result, the force required to separate the adhering materials changes.

Effect of coupling agent on the impact strength

The impact strength of PMMA and PMMA filled with aspen fibers of CTMP (non-treated and treated with PMPPIC (2%–8%, TDIC and HMDIC, each of 2%) and sawdust (non-treated and treated with PMPPIC, TDIC and HMDIC, each of 2% by weight of polymer) were evaluated and listed in Table VI. It is evident from this table that impact strength follows nearly the same trend as shown by other mechanical properties (as discussed earlier). For example, impact strength of PMMA treated with a roll mill at 185°C is lower than untreated PMMA. Again, the impact strength of non-treated composites are inferior when compared to the original polymer. When composites of both the fibers are treated with 2%

TABLE VI

Impact strength (izod, un-notched) for PMMA, non-treated and isocyanate (PMPPIC) treated PMMA filled with CTMP (aspen)

	Izod impact strength (Joules/meters)							
	CTMP (aspen)				Sawdust (aspen)			
(wt.% of fiber)	10	20	30	40	10	20	30	40
PMMA	10.3*				16.6†			
PMMA + fiber	9.6	8.5	5.7	3.8	8.0	7.4	5.5	4.3
[PMMA + 2% PMPPIC] + fiber	12.0	7.0	5.9	4.3	9.3	8.0	4.5	4.4
[PMMA + 4% PMPPIC] + fiber	12.6	9.1	6.8	6.1				
[PMMA + 8% PMPPIC] + fiber	9.0	7.9	7.0	6.6				
[PMMA + 2% TDIC] + fiber	8.8	7.5	6.5	3.5	7.3	6.2	5.9	3.3
[PMMA + 2% HMDIC] + fiber	8.7	7.4	5.6	3.8	7.3	7.0	5.3	4.0

* Mixed with roll mill.
† Without mixing with roll mill.

PMPPIC, impact strength improves up to 10% of fiber level compared to untreated composite. In the case of CTMP fiber, impact strength of the composite comprising 10% of fiber improved with the increase of the PMPPIC concentration up to 4% and then decreases. This result is also quite consistent with what was observed for other mechanical properties. Impact strength of TDIC and HMDIC treated composites is inferior compared to that of the original polymer. Improvement in impact strength with the increase of isocyanate, PMPPIC concentration (up to 4%) also supports the proposition that PMPPIC forms an efficient interfacial area between the fiber and the polymer.

CONCLUSION

To summarize the results of the systematic study of the various parameters under optimum conditions of molding, the percentage improvement in mechanical properties based on the mechanical properties of the original polymer, at best improvement points, were calculated and shown in Table VII (A–C). Based on the results of Table VII and our previous discussion, the following conslusions can be drawn:

i) modulus is improved in all cases (up to 40% fiber level), but it can be improved even more by treatment or coating of fiber with a coupling agent;

ii) after the optimization of the parameters, strength can be improved up to 30% of fiber level in the composite, e.g. 2% PMPPIC treated PMMA–CTMP (aspen) or V-pulp (softwood) or CTMP coated with PMMA (10%) and PMPPIC (8%);

iii) the selection of a coupling agent is essential for the formulation of composites of improved mechanical properties;

iv) PMPPIC plays a superior role when compared to other isocyanates;

v) 2%–4% concentration of PMPPIC is enough to improve the maximum level of mechanical properties;

vi) inherent morphology and fiber making techniques also play an important role in the performance of wood fiber as a filler.

TABLE VII(A)

Comparison of the improvement in mechanical properties of PMMA filled with CTMP (aspen) and sawdust (aspen) fibers

Composites	Improvement % of				Composites	Improvement % of			
	Strength	Elongation	Breaking energy	Modulus		Strength	Elongation	Breaking energy	Modulus
PMMA + CTMP (aspen) (10%)	+3.6	−25.6	−14.8	+21.3	PMMA + Sawdust (aspen) (10%)	−6.1	−32.6	−37.2	+29.0
[PMMA + 2% PMPPIC] + CTMP (aspen) (30%)	+13.3	−39.5	−32.9	+56.8	[PMMA + 2% PMPPIC] + Sawdust (aspen) (10%)	−2.3	−37.2	−39.3	−33.3
[PMMA + 2% TDIC] + CTMP (aspen) (10%)	+10.2	−27.9	−20.7	+27.9	[PMMA + 2% TDIC] + Sawdust (aspen) (10%)	−5.7	−39.5	−40.6	+29.0
[PMMA + 2% HMDIC] + CTMP (aspen) (10%)	−6.6	−25.6	−22.6	+23.0	[PMMA + 2% HMDIC] + Sawdust (aspen) (10%)	−14.4	−39.5	−46.6	+30.6
[PMMA + 4% PMPPIC] + CTMP (aspen) (10%)	+15.5	−27.9	−12.8	+43.2	PMMA + Sawdust [coated: PMMA (10%) + PMPPIC (2%)] (10%)	−7.4	−39.5	−42.9	+32.2
[PMMA + 8% PMPPIC] + CTMP (aspen) (10%)	+11.4	−32.6	−23.5	+35.5	PMMA + Sawdust [coated: PMMA (10%) + PMPPIC (8%) (10%)	0	−39.5	−33.1	+28.4
PMMA + CTMP [coated: PMMA (10%) + PMPPIC (2%)] (20%)	+13.3	−32.6	−24.6	+42.6					
PMMA + CTMP [coated: PMMA (10%) + PMPPIC (8%)] (30%)	+9.1	−44.2	−47.6	+59.6					

TABLE VIII(B)

Comparison of the improvement in mechanical properties of PMMA filled with different wood fibers

Composites	Improvement % of				Composites	Improvement % of			
	Strength	Elongation	Breaking energy	Modulus		Strength	Elongation	Breaking energy	Modulus
PMMA + CTMP (aspen) (10%)	+3.6	−25.6	−14.8	+21.3	[PMMA + 2% PMPPIC] + CTMP (aspen) (30%)	+13.3	−39.5	−32.9	+56.8
PMMA + V-pulp (aspen) (10%)	+1.9	−27.9	−21.5	+24.6	[PMMA + 2% PMPPIC] + V-pulp (aspen) (10%)	+10.0	−27.9	−20.1	+28.4
PMMA + V-pulp (softwood) (10%)	−3.2	−27.9	−32.7	+20.8	[PMMA + 2% PMPPIC] + V-pulp (softwood) (30%)	+2.5	−48.8	−51.1	+44.8
PMMA + OPCO-Pulp (softwood) (10%)	−4.0	−44.2	−29.3	+17.3	[PMMA + 2% PMPPIC] + OPCO-Pulp (softwood (10%)	+16.1	−23.3	−11.1	+34.4
PMMA + Sawdust (softwood) (10%)	−5.7	−32.6	−28.6	+19.7	[PMMA + 2% PMPPIC] + Sawdust (softwood) (10%)	+6.4	−30.2	−24.6	+30.1
PMMA + Sawdust (birch) (10%)	+1.9	−30.2	−30.9	+27.9	[PMMA + 2% PMPPIC] + Sawdust (birch) (10%)	+7.2	−32.6	−31.7	+33.9
PMMA + Sawdust (aspen) (10%)	−6.1	−32.6	−37.2	+29.0	[PMMA + 2% PMPPIC] + Sawdust (aspen) (10%)	−2.3	−37.2	−39.3	+33.3

TABLE VII(C)

Comparison of the improvement in impact strength (izod, un-notched of PMMA filled with CTMP (aspen) and sawdust (aspen) fibers

Composites	Improvement % of izod impact strength	
	CTMP (aspen)	Sawdust (aspen)
PMMA + fiber (10%)	−6.8	−22.3
[PMMA + 2% PMPPIC] + fiber (10%)	+16.5	−9.7
[PMMA + 4% PMPPIC] + fiber (10%)	+22.3	—
[PMMA + 8% PMPPIC] + fiber (10%)	−12.6	—
[PMMA + 2% TDIC] + fiber (10%)	−14.6	−29.1
[PMMA + 2% HMDIC] + fiber (10%)	−15.5	−29.1

Acknowledgments

The authors acknowledge with thanks the financial support of the Natural Sciences and Engineering Research Council of Canada.

References

1. R. E. Jones, Tappi Eng. Conf. (Atlanta) Proc., (Book 1), 243 (1985).
2. L. E. Nielsen (ed)., "Mechanical Properties of Polymer and Composites", Marcel Dekker Inc., New York., V. 2, C. 7. p. 379, (1974).
3. F. J. Washabaugh, "Fillers/Extenders", *Modern Plast. Encyl.*, **63,** 144 (1986–1987).
4. A. W. McKenzie and J. P. Yuritta, *Appita,* **32(6),** 460 (1979).
5. 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).
6. C. Klason and J. Kubát, Ibid., 153 (1986).
7. H. Dalvag, C. Klason and H.-E. Stromvall, *Intern. J. Polymeric Mater.*, **11,** 9 (1985).
8. L. A. Goettler, U.S. Pat., 4,376,144, March (1983).
9. M. H. Schneider and K. I. Brebner, *Wood Sci. Technol.*, **19**(1), 67 (1985).
10. R. T. Woodhams, G. Thomas and D. K. Rodgers, *Polym. Eng. Sci.*, **24(15),** 1166 (1984).
11. A. D. Beshay, B. V. Kokta and C. Daneault, *Polym. Composites,* **6**(4), 261 (1985).
12. A. Nagaty, A. B. Mustafa and O. Y. Mansour, *J. Appl. Polym. Sci.*, **23,** 3263 (1979).
13. D. Maldas, B. V. Kokta and C. Daneault, *J. Appl. Polym. Sci.*, **37,** 751 (1989).
14. A. Ruvo and E. Alfthan, *Polymer,* **19(8),** 872 (1978).
15. W. E. Johns, *J. Adhesion,* **15,** 59 (1982).
16. D. Maldas, B. V. Kokta, R. G. Raj and C. Daneault, *Polymer,* **29,** 1255 (1988).
17. B. V. Kokta, R. Chen, C. Daneault and J. L. Valade, *Polym. Composites,* **4(4),** 229 (1983).

18. D. Maldas, B. V. Kokta and C. Daneault, *J. Appl. Polym. Sci.*, **37** (1989).
19. J. A. Clark, "Pulp Technology and Treatment for Paper", 2nd Ed., Chap. 9, Miller Freeman Publications, Inc., San Francisco, 184 (1985).
20. B. V. Kokta, J. L. Valade and C. Daneault, *Transactions*, TR59 (Sept. 1979).
21. P. Zadorecki, H. Karnerfars and S. Linderfors, *Compos. Sci. Technol.*, **27**, 291 (1986).