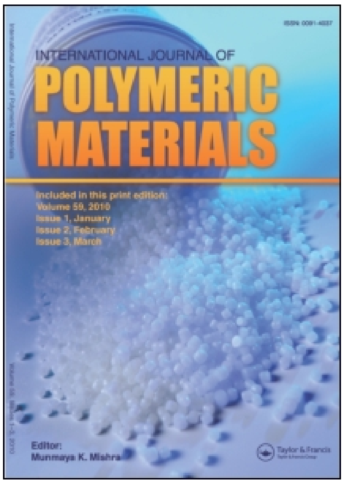

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

Role of Coupling Agents on the Performance of Woodflour-Filled Polypropylene Composites

D. Maldas[a]; B. V. Kokta[a]
[a] Université du Québec, Centre de Recherche en Ptes et Papiers C.P. 500, Québec, Canada

To cite this Article Maldas, D. and Kokta, B. V.(1994) 'Role of Coupling Agents on the Performance of Woodflour-Filled Polypropylene Composites', International Journal of Polymeric Materials, 27: 1, 77 — 88
To link to this Article: DOI: 10.1080/00914039408038294
URL: http://dx.doi.org/10.1080/00914039408038294

Intern. J. Polymeric Mater., 1994, Vol. 27, pp. 77-88
Reprints available directly from the publisher
Photocopying permitted by license only

Role of Coupling Agents on the Performance of Woodflour-Filled Polypropylene Composites

D. MALDAS and B. V. KOKTA

Université du Québec, Centre de Recherche en Pâtes et Papiers C.P. 500, Trois-Rivières, Québec G9A 5H7, Canada

(Received June 18, 1994)

Composite materials were prepared from waste woodflour and polypropylene (PP). In order to enhance the chemical affinity between hydrophilic woodflour and hydrophobic polymer, the surface of the filler was modified by coating with a mixture of PP and a polymeric isocyanate, while PP was mixed with two types of maleated PP, before being mixed the woodflour with polymer. The effects of coupling agents (i.e., individually or their mixtures) on the mechanical properties and void content of the composites have been evaluated. In the presence of coupling agents the composites showed superior mechanical properties compared to those of non-treated composites and to those of unmodified polymer. The extent of improvement in mechanical properties depends on the nature, addition levels, and compositions of coupling agents. As far as mechanical properties of the composites were concerned, the mixtures of coupling agents showed better performance compared to those of coupling agents used individually.

KEY WORDS Modified PP, isocyanate, surface modification, coupling agent, adhesion, coupling reaction, mechanical properties, void content.

INTRODUCTION

In the last few years, there has been a growing interest in the use of cellulosic materials in plastic composites, because of their low cost, their versatility, their low density relative to inorganic reinforcements, and because they are a renewable resource.[1] However, incompatibility of polar cellulosics and nonpolar plastics leads to poor adhesion which results in composite materials with poor mechanical properties. One promising method of enhancing adhesion in such composite systems is through the use of coupling agents, which generally improve the bonding between fillers and matrix.[2] A wide variety of coupling agents, e.g. isocyanates, organic acids and anhydrides, and silanes, have been used in cellulose fiber-filled thermoplastic composites.[3,4]

Generally, voids, or bubbles, are formed in short-fiber-filled thermoplastic composites because of entrapment of air, or the release of moisture and volatiles in the compounding and molding steps. Void can also be the result of the uneven shrinkage during cooling of fillers and matrix having wide differences in their thermal conductivities, and expansion coefficients. The presence of even a small amount of voids is detrimental to the mechanical properties of polymer composites.[5,6]

In the present study, the effects of three different coupling agents (i.e. one polymeric isocyanate and two types of maleated polypropylene), and void content, on the mechanical properties of the woodflour-filled polypropylene composites have been evaluated.

EXPERIMENTAL

Woodflour of hard wood aspen having mesh size 60 was used as filler and polypropylene (Profax 8301, supplied by Himont, Canada) [PP] was used as matrix. Poly(methylene(polyphenyl isocyanate)) [PMPPIC] (Polysciences Inc.), and two grades of maleated PP: Epolene E-43 (Eastman) and Polybond PB-3001 (BP Chemicals) were used as coupling agents. The woodflour was surface modified with the mixtures of PP (10%/weight of woodflour) and PMPPIC (1.77%/weight of composite) in a heated roll mill (180°C) for 10 min. The coated woodflour was allowed to cool to room temperature and was then ground to mesh size of 20. The mixtures of non-coated and coated woodflour and/or PP were melt blended with E-43 and/or PB-3001, at 180°C in the roll mill. In each batch, the concentration of coupling agents was varied, while the concentration of woodflour remained constant (i.e., 15 vol.%). After mixing, the batches were removed from the roll mill and remixed 5–10 times (for about 6–8 min.) to improve dispersion. Finally, the batches were removed and were allowed to cool to room temperature by cold pressing, and were then broken into small pieces for compression molding. Dumbbell-shaped test specimens (ASTM D638, Type V) were prepared in a Carver Laboratory Press. The molding cycle was: 5 min. preheating, 10 min. molding at 180°C under 2.2 MPa pressure, and 10 min. water cooling under pressure.

The mechanical properties [e.g. tensile strength, elongation at break, toughness (fracture energy ÷ volume) and Young's modulus) of all the samples were measured with an Instron Tester (Model 4201) following ASTM D-638. The strain rate was 1 mm/min. The statistical average of the measurements on at least 5 specimens was taken to obtain a reliable average and standard deviation.

The void content in the composites was estimated by comparing the theoretical density with its actual density[7]:

$$v_v = [d_c - d]/d_c \quad (1)$$

where v_v = volume fraction of void; d_c = theoretical density, calculated from following Equation (2); d = actual density, measured experimentally on composite specimens.

Theoretical density:

$$d_c = 1/[(w_f/d_f) + (1 - w_f)/d_m] \quad (2)$$

where w_f = woodflour weight fraction; $(1 - w_f)$ = PP weight fraction; d_f = woodflour density; d_m = PP density (i.e. 0.934 g/cc). However, the densities of the coated woodflour for different coating compositions were calculated by taking the densities of non-coated woodflour = 1.45 g/cc, PMPPIC = 1.22 g/cc; E-43 = 0.934 g/cc; and PB-3001 = 0.91 g/cc.

RESULTS

Figure 1 shows the variation in tensile strength and elongation at break with the concentration of E-43 in unfilled PP and woodflour-filled PP composites. The effect of coating the woodflour with PMPPIC on the properties of the composites is also presented in the same figure. The influence of coupling agents on the tensile toughness and Young's modulus for the same composites is presented in Figure 2. Figure 1 reveals that in the presence of only 2 wt.% E-43 tensile strength of unfilled PP increased compared to those without E-43. The tensile strength of E-43-treated woodflour-filled composites were superior to those of non-treated ones. The tensile strength reaches its maximum value even after addition of only 1 wt.% E-43, and then it remained almost constant. The tensile strength for non-treated composites improved slightly when PMPPIC-coated woodflour was used. Due to the addition of E-43 in the same composites, tensile strength diminished slightly at the initial level of E-43 (i.e. 1–2 wt.%) and then it increased and exceeded those with only E-43, showing a maxima at 3 wt.% E-43. However, the tensile strength of the composites with 1.77 PMPPIC and 3 wt.% E-43 was similar to that of unfilled PP with 2 wt.% E-43. The elongation of unfilled PP decreased, except at 2 wt.% E-43, with the addition of E-43. Moreover, there was not much difference in elon-

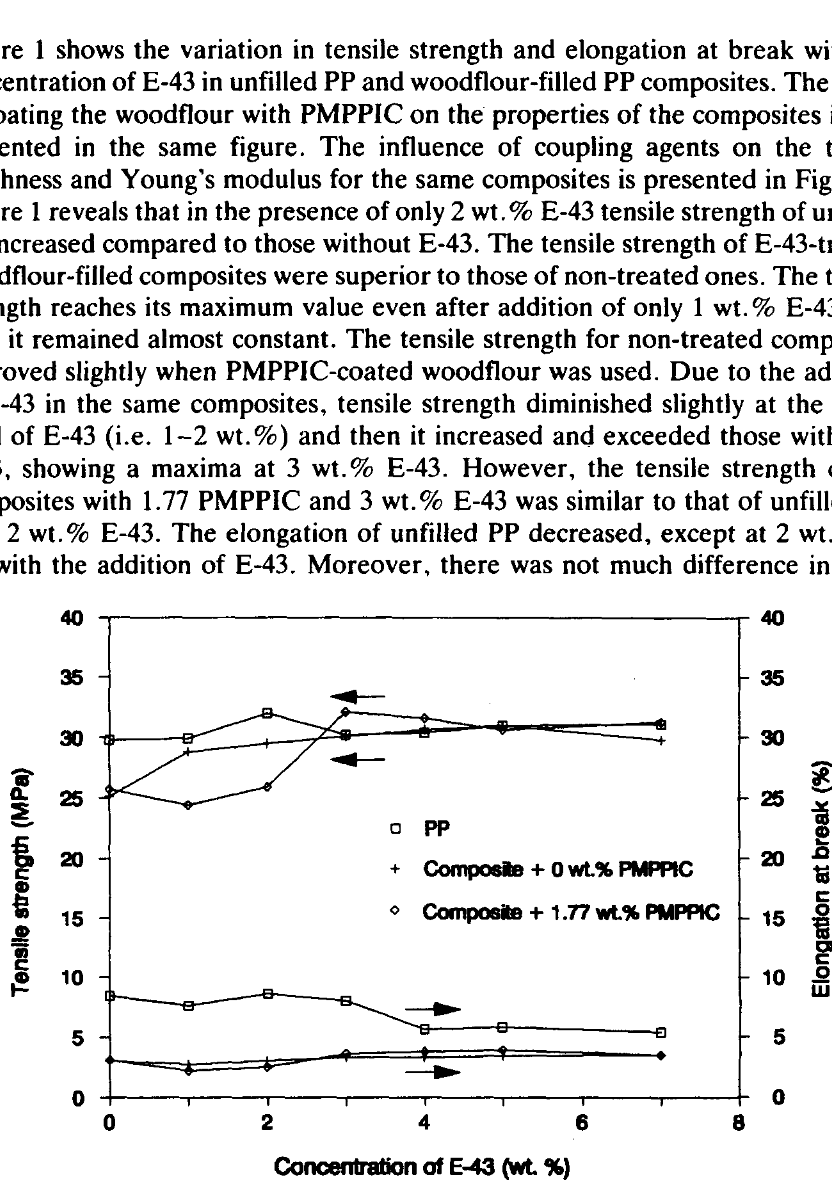

FIGURE 1 Variation of tensile strength and elongation at break with the concentrations of E-43 and PMPPIC for woodflour-filled PP composites.

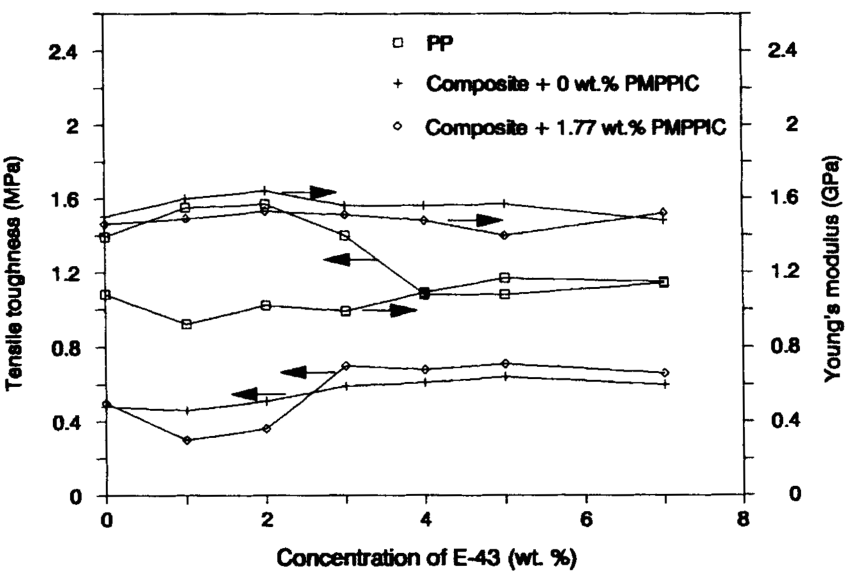

FIGURE 2 Variation of tensile toughness and Young's modulus with the concentrations of E-43 and PMPPIC for woodflour-filled PP composites.

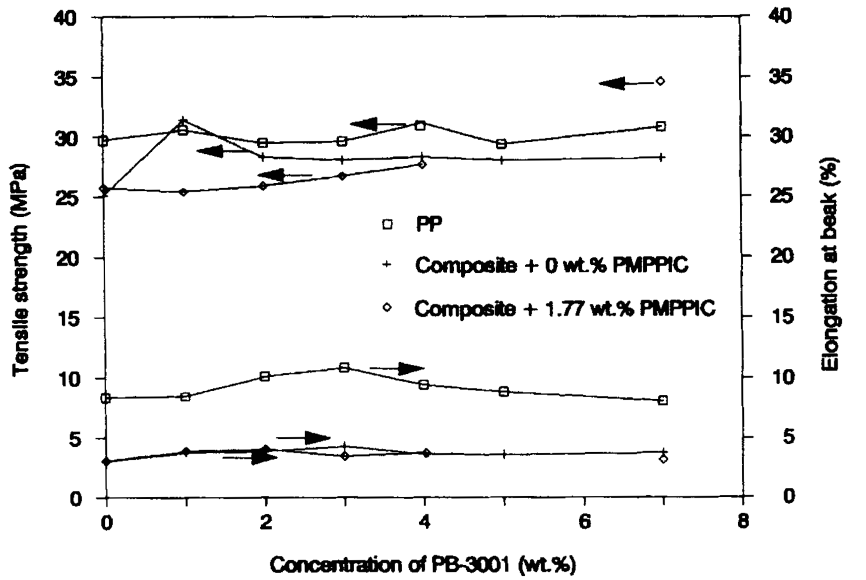

FIGURE 3 Variation of tensile strength and elongation at break with the concentrations of PB-3001 and PMPPIC for woodflour-filled PP composites.

gation values between non-coated, E-43-treated, and mixture of E-43 + PMPPIC-coated woodflour-filled composites.

Figure 2 shows that tensile toughness of unfilled PP increased up to 2 wt.% E-43, and then decreased. The toughness of woodflour-filled composites is, however, lower compared to that of unfilled PP. Tensile toughness for E-43-treated wood-

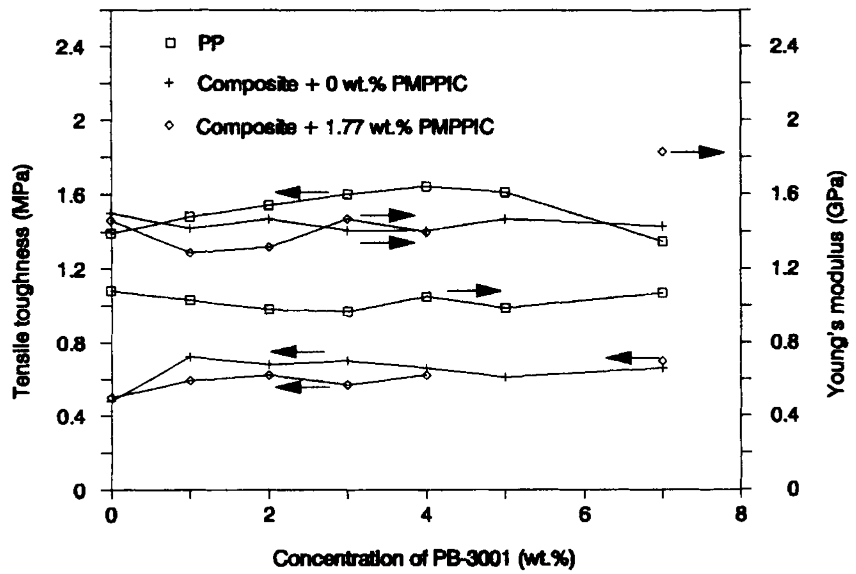

FIGURE 4 Variation of tensile toughness and Young's modulus with the concentrations of PB-3001 and PMPPIC for woodflour-filled PP composites.

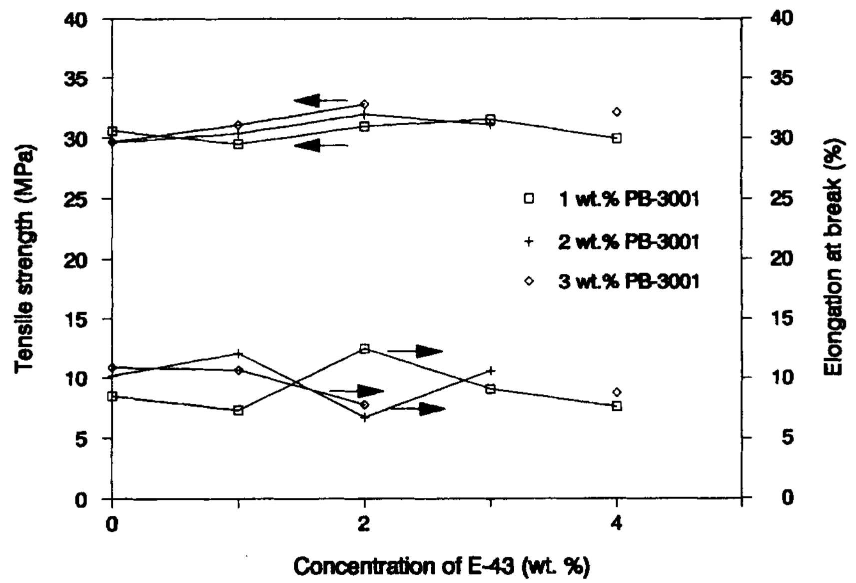

FIGURE 5 Variation of tensile strength and elongation at break with the concentrations of E-43 and PB-3001 for unfilled PP.

flour-filled composites did not show any improvement over those of non-treated ones. The tensile toughness for E-43 + PMPPIC-coated woodflour-filled composites increased compared to those of non-treated or only PMPPIC-coated ones only when the concentration of E-43 was more than about 2.7 wt.%. The modulus of unfilled PP was inferior to that of composites. Moreover, compared to non-

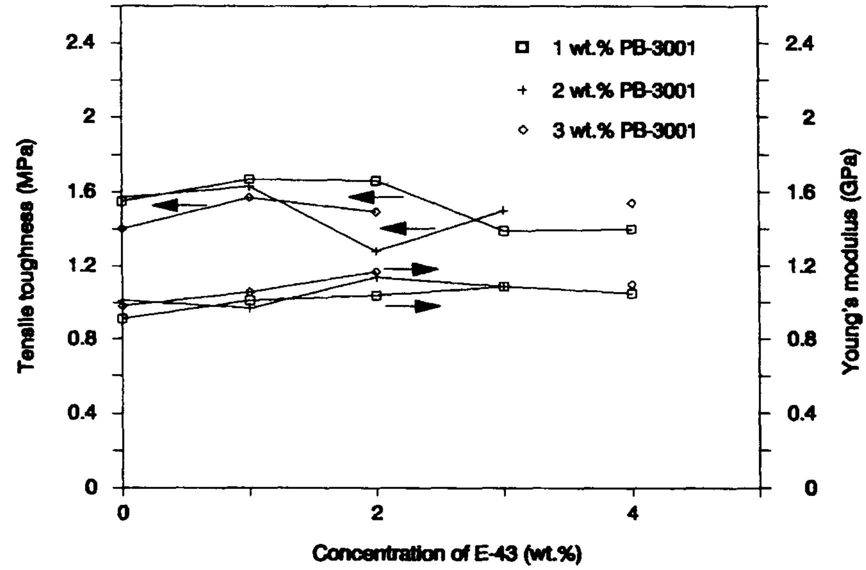

FIGURE 6 Variation of tensile toughness and Young's modulus with the concentrations of E-43 and PB-3001 for unfilled PP.

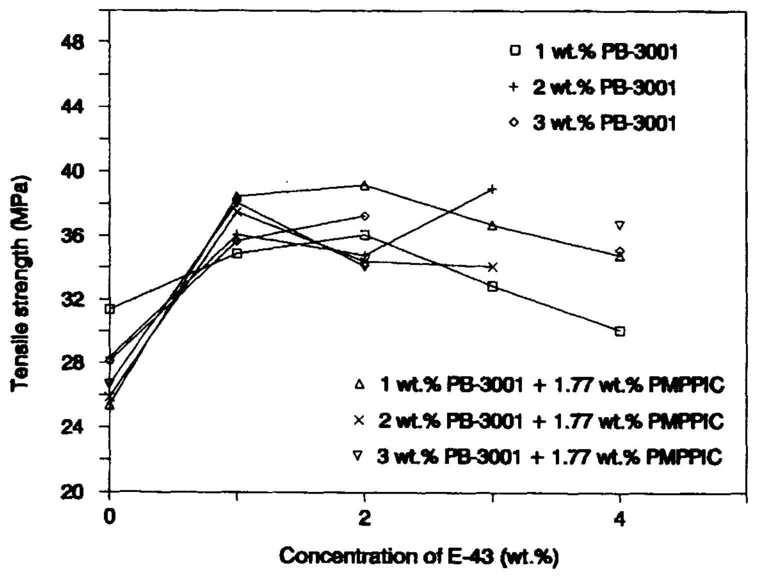

FIGURE 7 Variation of tensile strength with the concentrations of E-43, PB-3001 and PMPPIC for woodflour-filled PP composites.

treated PP the modulus diminished slightly up to 3 wt.% of E-43. The modulus of only E-43-treated woodflour-filled composites was better than that of E-43 + PMPPIC-coated ones. The same property, except for 2 wt.% of E-43, did not improve in comparison to those of non-treated woodflour-filled composites.

The effects of PB-3001 and PMPPIC on the mechanical properties of woodflour-filled PP composites are presented in Figures 3 and 4. It is evident from Figure 3

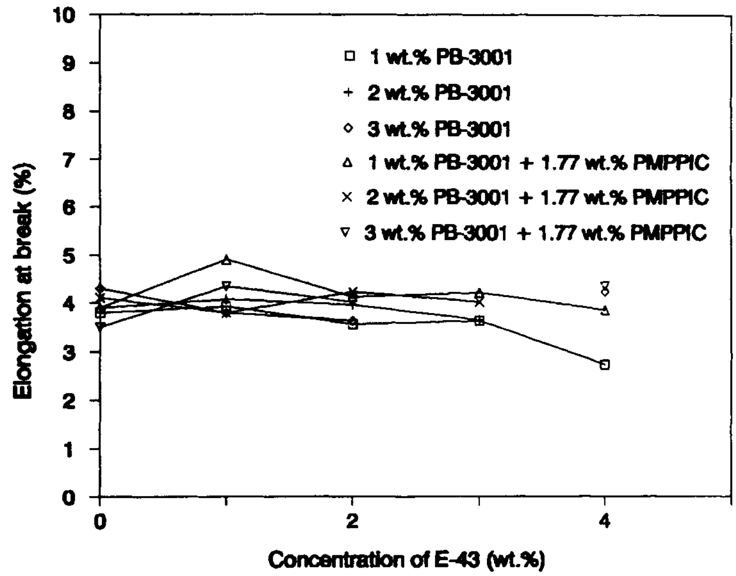

FIGURE 8 Variation of elongation at break with the concentrations of E-43, PB-3001 and PMPPIC for woodflour-filled PP composites.

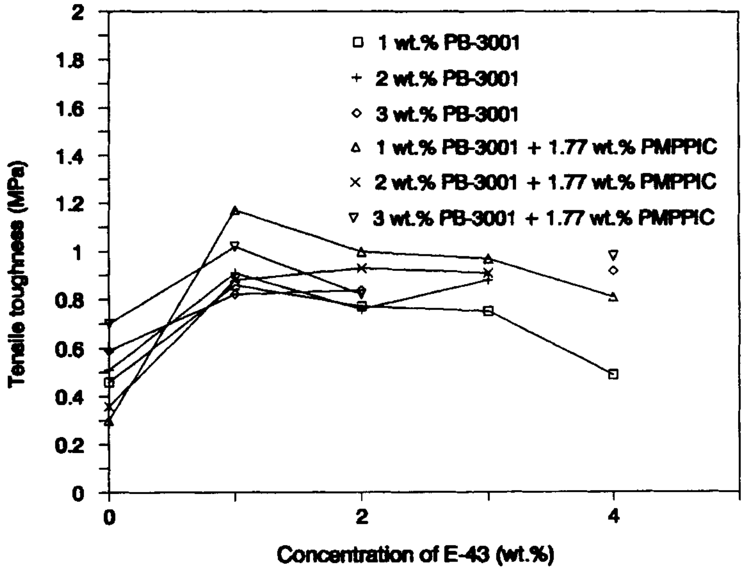

FIGURE 9 Variation of tensile toughness with the concentrations of E-43, PB-3001 and PMPPIC for woodflour-filled PP composites.

that tensile strength for unfilled PP, except at 4 wt.% PB-3001, remained unaltered for the change in PB-3001 concentration. However, for the composites with woodflour-treated with lower levels of PB-3001 (e.g. 1 wt.%), the tensile strength was superior even to that of the unfilled PP, and remained almost constant at higher PB-3001 levels. In the presence of both PB-3001 and PMPPIC, tensile strength

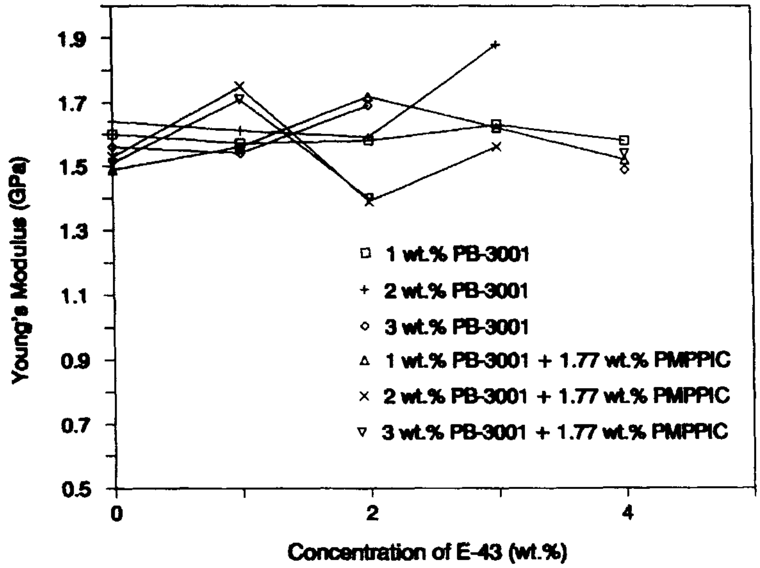

FIGURE 10 Variation of Young's modulus with the concentrations of E-43, PB-3001 and PMPPIC for woodflour-filled PP composites.

increased slowly with increasing PB-3001 concentration. The spectrum of elongation at break vs. concentration of PB-3001 (Figure 3) followed a more or less similar trend to that of elongation at break vs. concentration of E-43 (Figure 1). The tensile toughness (Figure 4) for unfilled PP was, however superior to that of woodflour-filled composites. Unlike E-43-treated woodflour-filled composites, the tensile toughness for PB-treated ones was superior to those of non-treated woodflour-filled and PB-3001 + PMPPIC-coated woodflour-filled composites. Moreover, about 1 wt.% PB-3001 was sufficient to reach the maximum value in tensile toughness. The modulus (Figure 4) of unfilled PP was inferior to those of woodflour-filled composites, and it did not change significantly with a change in concentration of PB-3001. At the initial level of PB-3001 concentration (e.g. 1 wt.%), the modulus for both PB-3001-treated and PB-3001 + PMPPIC-coated woodflour-filled composites decreased. However, with the further increase in concentration of PB-3001 the modulus for PB-3001-treated woodflour-filled composites remained more or less constant, while the same property for PB-3001 + PMPPIC-coated ones increased.

Figures 5 and 6 show the variation in mechanical properties accompanied by the change in both E-43 and PB-3001 concentrations in unfilled PP. From these figures, it is obvious that most of the mechanical properties increased with the rise in the concentrations of either E-43 or PB-3001 in their mixtures only up to certain concentrations (e.g. 3% PB-3001 + 2% E-43 for both tensile strength and Young's modulus, and 1% PB-3001 + 2% E-43 for both elongation and tensile toughness). The effects of coating of woodflour with the mixtures of three coupling agents, e.g. PB-3001, E-43 and PMPPIC, simultaneously on the mechanical properties of the composites are presented in Figures 7–10. Similar to unfilled PP, the mechanical properties of the composites increased with the rise in the concentrations of coupling

TABLE I

Effects of E-43 and PMPPIC on the density and void content of woodflour-filled polypropylene composites

Concentration (wt %) of coupling agent in		Density (g/cc)				Void content (%)	
Polymer	Woodflour	Theoretical		Experimental			
E-43	PMPPIC	Volume % of fiber: 0	15	0	15	0	15
-	-	0.903	0.985	0.824	0.941	8.75	4.44
-	1.77	-	0.982	-	0.903	-	8.09
1	-	0.903	0.986	0.831	0.913	8.00	7.32
1	1.77	-	0.982	-	0.939	-	4.42
2	-	0.904	0.986	0.837	0.937	7.38	4.98
2	1.77	-	0.983	-	0.940	-	4.39
3	-	0.904	.0.986	0.811	0.938	10.33	4.83
3	1.77	-	0.983	-	0.920	-	6.43
4	-	0.904	0.986	0.846	0.925	6.41	6.16
4	1.77	-	0.983	-	0.934	-	4.95
5	-	0.905	0.987	0.820	0.944	9.44	4.36
5	1.77	-	0.984	-	0.937	-	4.77
7	-	0.905	0.987	0.834	0.927	7.87	6.11

agents in the initial phase, and decreased later after showing maxima for different compositions of coupling agents and for different mechanical properties. In general, a mixture of 1% PB-3001 + 1.77% PMPPIC + 1% E-43 offered the best tensile strength, elongation and tensile toughness, but mixture of 2% PB-3001 + 1.77% PMPPIC + 1% E-43 offered the best Young's modulus. Once again, mixture of 2% PB-3001 + 3% E-43 gave the best results for both tensile strength and modulus. However, both the tensile strength and the modulus of the treated woodflour-filled composites were superior to those of unfilled PP, while the reverse was true as far as elongation and tensile toughness were concerned.

The effects of E-43 and PMPPIC on the density and void contents of unfilled PP and woodflour-filled PP composites are listed in Table I. Table I reveals that experimental density was always less than that of calculated ones. However, the void content did not follow any regular pattern with an increase in E-43 concentrations or due to the addition of PMPPIC. In general, the void content of unfilled PP was higher than that of woodflour-filled composites. For unfilled PP the void content varied from 6.41% to 10.33%, while for woodflour-filled composites it varied from 4.36% to 8.09%.

DISCUSSION

The general improvements in mechanical properties, except modulus, of treated-woodflour-filled composites (over those of composites containing non-treated woodflour) indicate that the compatibility between hydrophilic cellulosic fiber and modified PP has increased. The tensile strength of short fiber reinforced composites is strongly dependent on the degree of adhesion between fibers and matrix. However, modulus is strongly affected by the orientation of the fiber and less by the polymer-fiber adhesion.[8] It is also evident from the above-mentioned results that both tensile strength and modulus increased, while both elongation at break and tensile toughness declined for the treated woodflour-filled composites in comparison with those of original PP. Generally, as the tensile strength increases, a given product increases in stiffness; this usually occurs at the expense of elongation properties.[9] As both E-43 and PB-3001 used maleic anhydride grafted PP, the anhydride groups of these modified PP (MPP) can link to the surface —OH groups of cellulose and its counterpart lignin through the formation of a block copolymer containing a succinic half ester bridge between cellulose and PP segments.[9,10] However, the chemical interactions of cellulose-MPP-PP and their interphase have already been characterized and established by FTIR, ESCA, SEM, TEM and X-ray.[2,11-15]

The properties are further improved when PMPPIC is used. In fact, PMPPIC also behaves as a coupling agent. The functional group —N=C=O in the isocyanate reacts chemically with the —OH group of the cellulose, as well as with the —COOH groups of MPP.[10,16,17,18] Incidentally, Farrissey[19] used FTIR to investigate the surface of isocyanate-treated flakes. He was able to show the presence of polyurea bonds with a strong absorption band at 1650 cm^{-1}. Also seen, but less obvious, was the presence of a urethane absorption band at 1725 cm^{-1}. Both of these bands are associated with the relevant carbonyl group. A band at 1530 cm^{-1} was also noted. This band is associated with an amide II group and is unique to the binder and not the wood substrate. Moreover, prior coating of the woodflour with PP and PMPPIC assists in the formation of a soft film of hydrophobic materials on the surface of the hydrophilic woodflour.[16] In addition, strong fiber-fiber interaction due to intermolecular hydrogen bonding has also been diluted, which leads to better dispersion of the woodflour.

The mechanical properties improve independently of the concentrations of coupling agents because with the increase in concentrations of coupling agents in the composites, the possibility of the formation of interfacial contact increases. In most cases, higher concentrations of coupling agents are detrimental. Once again, the extent of improvement varies with the change in the nature of coupling agents. When comparing the performance of MPP and PMPPIC, one observes that PMPPIC links the cellulose matrix through a chain of urethane bonds,[17] whereas MPP forms ester linkages and hydrogen bonds. The former types of linkages are believed to be more stable than that of the latter types. Moreover, the polymeric nature of PMPPIC helps to link the cellulose phase and the polymeric phase (i.e. MPP) *continuously* at the interface, while the discrete nature of MPP alone makes it inferior in this respect. The mechanical properties of the composites also vary for the two MPP. In fact, the coupling action of MPP depends on the extent of maleic anhydride grafted onto PP. However, the two MPP (i.e. E-43 and PB-3001) supplied by two different companies, contain different amounts of maleic anhydride (e.g. ~4.1 and ~6%, respectively). As a result, PB-3001 showed slightly better coupling action compared to that of E-43.

Generally, the void content of unfilled PP is higher than that of woodflour-filled composites. This may happen as a result of uneven shrinkage of the unfilled PP due to temperature gradients involved in the solidification step by cooling, or because of restrained volume shrinkage of the core region of the polymer by the already solidified external skin.[6] This fact may be more pronounced in unfilled PP compared to woodflour-filled PP composites. Once again, Table I reveals that generally, composites with coated woodflour, show higher void content compared to that with non-coated woodflour. This fact implies that due to the good adhesion of cellulosic filler and PP in the presence of coupling agents, even with higher amount of void content offer better mechanical properties. As void content does not follow any regular pattern with the increase in concentrations of coupling agents, it is difficult to make any conclusion on the effect of void content on the mechanical properties of the composites. However, in order to justify this point further systematic study is required.

CONCLUSION

The tensile strength and modulus of MPP-treated woodflour-filled PP composites were generally better than those of unfilled PP. Except for modulus, the other mechanical properties of MPP-treated composites were improved compared to those of non-treated woodflour-filled composites. The properties improved along with the increase in the concentrations of the MPP until the optimal concentrations were reached. Properties also varied with the nature of MPP. Properties were further improved when PMPPIC was used in addition to MPP. Mixture of coupling agents showed some positive influence on the mechanical properties of the composites over those of the coupling agents used individually. Generally, the void content of unfilled PP was higher than that of woodflour-filled composites.

Acknowledgments

The authors wish to thank the NSERC and Forestry Department of Canada, FCAR of Québec, Canadian Liquid Air Ltd., and Lands and Wildlife of Alberta for their financial support.

References

1. D. Maldas and B. V. Kokta, *Trends in Polym. Sci.*, **1**, 174 (1993).
2. D. Maldas and B. V. Kokta, *Compos. Interf.*, **1**, 87 (1993).
3. D. Maldas and B. V. Kokta, in: "Wood Fiber/Polymer Composites: Fundamental Concepts, Process, and Material Options," M. P. Wolcott (Ed.), p. 112, Forest Products Society, U.S.A., 1993.

4. D. Maldas and B. V. Kokta, in: "Macromolecules 1992," J. Kohovec (Ed.), p. 349, VSP International Publishers, The Netherland, 1993.
5. N. C. W. Judd and W. W. Wright, *SAMPE Journal*, **14**, 10 (1978).
6. A. Vaxman, M. Narkis, A. Siegmann and S. Kenig, *Polym. Comp.*, **10**, 449 (1989).
7. P. Mallick, "Fiber-Reinforced Composites: Materials, Manufacturing, and Design," p. 63, Marcel Dekker, Inc., New York, 1988.
8. D. M. Bigg, D. F. Hiscock, J. R. Preston and E. J. Bradbury, *J. Therm. Compos. Mater.*, **1**, 146 (1988).
9. D. Maldas, B. V. Kokta and J. Nizio, *Int. J. Polym. Mater.*, **17**, 1 (1992).
10. D. Maldas and B. V. Kokta, *Inter. J. Polymeric Mater.*, **14**, 165 (1990).
11. J. M. Felix and P. Gatenholm, *J. Appl. Polym. Sci.*, **42**, 609 (1991).
12. H. Kishi, M. Yoshioka, A. Kamanoi and N. Shiraishi, *Jpn. Wood. Res. Soc. J.*, **34**, 133 (1988).
13. S. Takase and N. Shiraishi, *J. Appl. Polym. Sci.*, **37**, 645 (1989).
14. G. S. Han, S. Saka and N. Shiraishi, *Jpn. Wood Res. Soc. J.*, **37**, 241 (1991).
15. C. Klason, J. Kubat and P. Gatenholm, in: "Viscoelasticity of Biomaterials," W. Glasser and H. Hatakeyama (Eds.), ACS Symp. Ser. No. 489, p. 82, American Chemical Society, U.S.A. (1992).
16. D. Maldas and B. V. Kokta, *Polymer J.*, **23**, 1163 (1991).
17. D. Maldas, B. V. Kokta, R. G. Raj and C. Daneault, *Polymer*, **29**, 1255 (1988).
18. W. Johns, *J. Adhesion*, **15**, 59 (1982).
19. W. Farrisey, 1st Annual Interl. Symp. Adhesion and Adhesives for Structural Materials, Pullman, WA, 1981.