Polyolefin–Wood Filler Composite. I. Performance of *m*-Phenylene Bismaleimide-Modified Wood Fiber in Polypropylene Composite

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SYNOPSIS

The properties of the composite of polypropylene (PP) and chemithermomechanical pulp reactively treated with bismaleimide-modified PP or premodified pulp have been investigated. The results were compared with the properties of unmodified composites of PP and pulp. The effect of some flame retardants on the properties of composites was also studied. Premodifications of PP as well as pulp with *m*-phenylene bismaleimide provided a positive response with regard to the mechanical properties of the composites. The tensile strength of a 35 wt % pulp-filled PP composite was found to be much higher than that of the strength of pure PP. On the other hand, tensile strength decreased considerably with increase in the chemithermomechanical pulp content if unmodified PP was used. The occurrence of chemical grafting reactions between PP and bismaleimide as well as between pulp and bismaleimide have been suggested, which can explain the aforementioned difference in mechanical properties among different composites. *In situ* addition of sodium borate, boric acid, or phenolic resin during processing of the composite decreased the rate of burning of PP. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Wood powders, produced as waste material by wood and paper industries, have been burnt without meaningful utilization, used as fuel for boilers, or utilized as a relatively valueless product.[1] In the past, various attempts have been made to utilize waste wood powders and wood fibers. The plastic composites filled with various cellulosic fibers and other fillers have been used industrially. However, there is currently a great deal of interest to update the technology to incorporate cellulosics in plastic composites.

The strength of composite materials formed by incorporating randomly oriented wood fibers into a plastic matrix depends primarily on the strength of wood fiber and on how effectively the polymer matrix is able to transfer externally applied loads to the fibers. The interfacial zone between the wood fiber and the polymer matrix must satisfy several mechanical and chemical requirements to obtain a useful composite: (1) adequate bonding (preferably chemical) between fiber and matrix, (2) maximum surface area of contact between fiber and plastics, and (3) no chemical attack of the matrix by the fiber that would be detrimental to the strength of the composite or to the interfacial bonding.

Two major problems have been encountered to prepare wood fiber-filled polypropylene (PP) composite. First, the affinity and adhesion between PP and wood is poor.[1] Second, the rate of thermal decomposition of lignocellulosics increases exponentially with increase in temperature and reaches a significant level in the processing range of PP (180–200°C). This can result in the formation of tarlike products and acid products of pyrolysis, which can have various damaging effects not only on the processing machines but also on the ultimate properties of the composites.[2]

Several attempts have been made in the past to improve adhesion between polyolefin and wood fi-

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bers.[1,3-5] It has been reported that the use of maleic anhydride-grafted PP as coupling agent improves the strength of PP–wood fiber composite.[3,5]

Very little is known about the influence of maleated PP on the thermal stability of wood fiber during processing. Han et al.[3] reported that use of MgO as a processing stabilizer for wood flour-filled PP can reduce the influence of degradation on composite properties. A new technology to improve the heat stability of polyolefin-based elastoplastic blends is dynamic cross-linking of the elastomer phase using heat-stable multifunctional monomers.[6-8] The use of *m*-phenylene bismaleimide (BMI) as a heat-stable curative has been well established.[7,9] The beneficial effect of BMI is based on its ability to chemically react with many natural and synthetic polymers *in situ* during processing.

This article illustrates the function of BMI, which has been used in the preparation of PP–wood fiber composite. The importance of reactive processing to promote interfacial bonding between the wood fiber and PP is discussed.

EXPERIMENTAL

Materials

Polypropylene (PP, PM 6100) was supplied by Shell Chemical, Canada; the nominal melt flow index was 15.5 (g/10 min), and density, 0.905 (g/cc). A chemithermomechanical pulp (CTMP) was used as a filler. The average size and aspect ratio of the CTMP pulp were 0.38 mm and 14.8, respectively. CTMP was prepared in a Sund defibrator. The detailed conditions for fiber preparation have been described elsewhere.[10] Luperrox 500R (dicumyl peroxide, DCP) was supplied by Pennwalt Corp., U.S.A., and *m*-phenylene bismaleimide (BMI) (active matter content 93%) was obtained from VUOT, Perdubice, Czechoslovakia. The melting point of BMI was 200°C. Analytical-grade sodium borate ($Na_2B_4O_7$, $10H_2O$) and boric acid were used. Powder-grade phenolic resin (IB-215) was supplied by Reichhold Ltd., Canada; the resin used was a resol type with an approximate molecular weight of 400.

Bismaleimide Modification of PP

PP modified with BMI was prepared by impregnating powdered PP in acetone solution of BMI. One hundred grams of PP was added to a 5 wt % BMI solution in acetone and the mixture was heated slowly with constant stirring in a nitrogen atmosphere. When the reaction temperature reached 50°C, 2 g of DCP was added to the system and the reaction temperature was raised slowly to 140°C. The reaction was carried out for about 3 h. Although it was found that uncatalyzed BMI melted at 200°C, a differential scanning calorimetry study (Perkin-Elmer DSC-2) of a 5 : 2 mixture of BMI and DCP indicated that BMI decomposed even below 140°C with a high exothermic reaction in presence of DCP, which is shown in Figure 1. Moreover, no melting peak for BMI was found in DCP-activated BMI. The above fact suggests that a solid-state reaction between PP and BMI is possible in a peroxide-catalyzed system even at 140°C.

The product obtained after reaction was then thoroughly washed with acetone and finally extracted with hot acetone and dried under vacuum. The bismaleimide-modified polypropylene is designated as BPP.

Modification of Fiber

A mixture of 25 g CTMP and 5 g of PP was placed in a kneader (Brabender rollmill) thermostated at 170°C and rotated at 10 rpm for 3 min; then 5 g of BMI and 0.5 gm of DCP were added and kneading was continued for another 3 min. The stock was mixed for further 5 min. The modified CTMP fiber was removed from the kneader, extracted with acetone to remove unreacted peroxide and BMI, and reduced to small size (60 mesh) for use. This modified fiber is henceforth designated as BCTMP.

To determine the BMI and PP contents in BCTMP, two separate methods were employed: First, the amount of PP was determined by measuring the heat of fusion due to melting of PP in BCTMP ($\Delta H_{\mathrm{BCTMP}}$), with respect to the heat of fusion of virgin PP (ΔH_{PP}), by differential scanning calorimetry (DSC). Three samples were measured for each tested composition and an average of three results were used to calculate the heat of fusions. The standard errors were found to be 4.9% for BCTMP and 3% for PP. The fraction, χ, of PP in BCTMP was calculated from[11]

$$\chi = (\Delta H_{\mathrm{BCTMP}}/\Delta H_{\mathrm{PP}}) \cdot (W_{\mathrm{PP}}/W_{\mathrm{BCTMP}}) \qquad (1)$$

where W_{PP} is the weight of virgin PP, and W_{BCTMP}, the weight of BCTMP used for DSC analyses.

The amount of BMI chemically attached to BCTMP was determined by the analytical method based on the Gunning[12] modification of the well-known Kjeldahl procedure. A similar procedure for determining organic nitrogen in paper using mercury

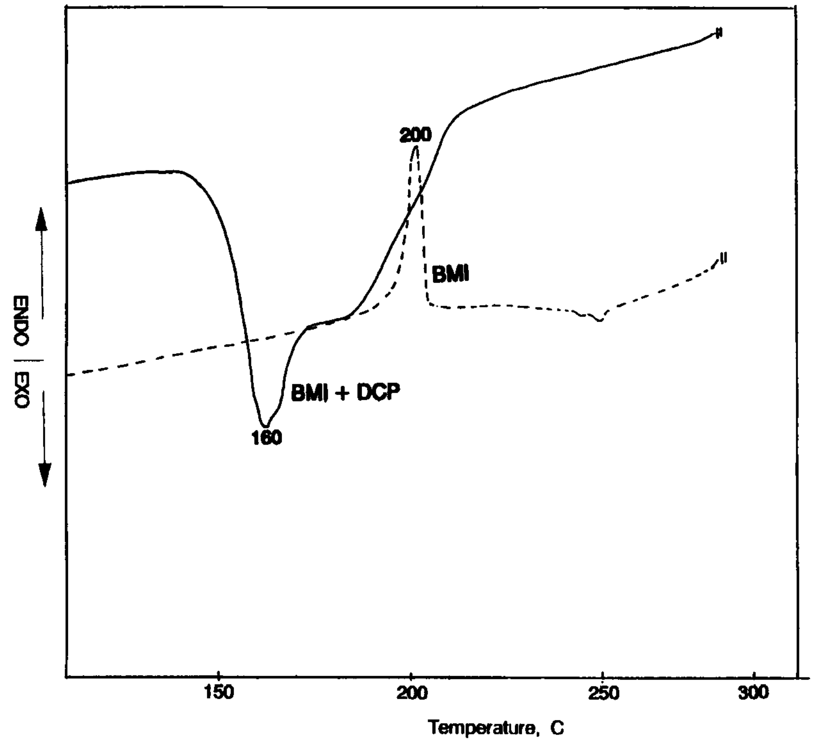


Figure 1 DSC thermograms of BMI with or without DCP.

and selenium oxychloride as the oxidizing catalyst is described in ASTM D 982-52.

The amount of nitrogen in the BCTMP as well as in the reference sample was calculated using the relationship

$$m_N = (S_0 - S) \cdot f \cdot R \cdot 0.07 \quad (2)$$

where m_N is the amount of nitrogen in the sample; S_0, the volume of NaOH required for blank titration; S, the volume of NaOH required for the BCTMP or for the reference sample; f, the normality factor for standard NaOH; and R, the dilution factor of the titrating solution.

The amount of grafted BMI in BCTMP was obtained by deducting the amount of nitrogen present in the reference sample from the amount of nitrogen present in BCTMP and then calculating the BMI weight equivalent of the residual nitrogen. Hence,

$$\text{Wt \% BMI attached to BCTMP} = (m_N \text{ for BCTMP} - m_N \text{ for the reference}) \times 957. \quad (3)$$

Composition of Modified or Unmodified CTMP with PP

A prescribed amount of modified and unmodified CTMP (vacuum dried at 60°C for 24 h) was placed in a two-roll mill along with a prescribed amount of modified and/or unmodified PP. The mixing was carried out for 6 min at 180–185°C after PP had melted. If used, sodium tetraborate, boric acid, and an *in situ* modifier (phenolic resin or BMI) were added after the melting of PP. The mixing speed was 20 rpm, but reduced if necessary to keep the stock temperature at or below 185°C. After mixing, the batches were removed from the mixer and remixed for about 2 min to improve dispersion. Finally, compositions were cooled by cold pressing to a thickness of about 3–5 mm, then cut into pieces for compression molding of 1–2 mm-thick test slabs. Molding was against well-released (by a fluorocarbon release agent) aluminum foils in frame-and-plate molds at 200°C. A molding cycle of 5 min preheating, 4 min molding under 3.5 MPa pressure, and 10 min cooling under pressure was used. One should note that the BMI *in situ* modifier is the same substance used above for the BMI modification of PP or CTMP.

Mechanical Tests

The mechanical properties of the composition were determined with test specimens described by ASTM procedure D 638. However, the test procedure was somewhat modified. The specimens were pulled in an Instron tensile tester at a crosshead speed of 1.5 mm min. Young's modulus (*E*) was estimated from the slope of the stress–strain curve near the origin. From the rest of the stress–strain curve, tensile strength (UTS), elongation at yield point (YE), and tensile toughness (area under the stress–strain curve) were determined. The unnotched Charpy impact strength was measured following the ASTM D 256 procedure with an Impact tester (Model TMI, No. 43-01) supplied by Testing Machines Inc., Amityville, NY. The impact strength was expressed as energy/area (kJ m^{-2}). For impact testing, unnotched specimens were clamped vertically in a sample vise with the thickness of the sample facing the direction of impact. The statistical average of the measurements on at least five test specimens was taken to obtain the mean value and standard deviation for all tests conducted. The coefficient of variations for the mechanical properties varied from 2.0 to 5.5%.

Infrared spectroscopic measurements were done in a Perkin-Elmer 283B IR spectrometer as well as in an FTIR analyzer (Bomum Co.) with a resolution of 4 cm^{-1}. The KBr disk technique was employed to prepare samples for measurements.

Flammability tests were carried out according to ASTM test method D 635-63. Test specimens of 152 mm in length, 12.5 mm in width, and over 1.3 mm in thickness were used. Three samples were tested for each specimen. The flammability of the composite is reported in terms of following parameters: average burning rate (mm/min), number of ignitions to burn 127 mm in length of the test specimen, and thickness of the test specimen.

A light microscope (Zeiss, Germany) was used to measure the length and diameter of CTMP fibers. For BCTMP and the composites, the samples were extracted with hot xylene by a Soxhlet extractor for 48 h. After dispersion of the extracted residues in ethanol, they were mounted on glass slides for measurements of fiber length and diameter. Dimensions of 200 fibers were noted. Aspect ratios of the fibers were calculated from length and diameter measurements.

RESULTS AND DISCUSSION

The value of χ calculated from relationship (1) using Figure 2 reveals that BCTMP used for preparation of composite contains 16.8 wt % PP. Such a determination of the PP fraction in BCTMP may not be accurate because the melting behavior of PP in BCTMP is also influenced by many other factors like thermal history, degree of crystallinity, etc. It is thought that the chemical reaction between PP and BMI, if any, would change the heat of fusion of

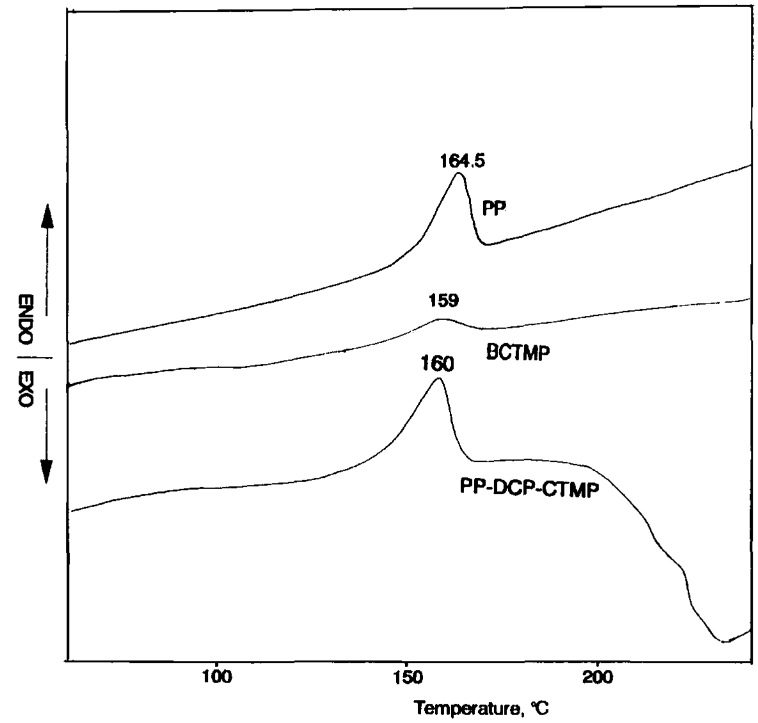


Figure 2 DSC thermograms of PP and BCTMP and PP–DCP–CTMP.

Table I Effect of Boron Compounds

	Compositions[a]							
	1	2	3	4	5	6	7	8
	PP–CTMP		PP–NaB–CTMP			PP–NaBH–CTMP		
PP	100	77	100	100	77	77	77	77
CTMP	0	23	0	0	23	23	23	23
Sodium borate	0	0	5	10	5	5	7.5	10
Boric acid	0	0	1	2	0	1	1.5	2
Properties								
UTS (MPa)	33.4	25.1	30.8	31.7	27.2	27.1	26.1	23.8
	(1.1)	(1.6)	(1.5)	(1.5)	(1.4)	(1.3)	(1.4)	(1.6)
YE (%)	7.6	6.4	9.3	9.3	6.6	5.9	5.4	5.3
	(0.4)	(0.5)	(0.7)	(0.5)	(0.4)	(0.5)	(0.6)	(0.6)
Young's modulus (GPa)	0.94	1.17	0.89	1.1	1.2	1.3	1.08	1.12
	(0.09)	(0.05)	(0.04)	(0.07)	(0.09)	(0.06)	(0.05)	(0.1)
Tensile toughness (MPa)	2.25	0.97	1.71	1.63	0.76	0.75	0.72	0.76
	(0.12)	(0.06)	(0.09)	(0.09)	(0.05)	(0.03)	(0.05)	(0.04)
Impact strength (kJ m^{-2})	7.4	13.5	7.7	6.4	12.1	12.2	11.3	9.2
	(0.7)	(1.3)	(0.5)	(0.4)	(1)	(0.9)	(0.7)	(0.5)
Flammability (ASTM D 635)								
buring rate	80	53	55	50	40	38	35	32
(mm/min)	4.1	1.9	2.4	2.6	1.8	1.9	2.2	1.5
Specimen thickness (mm)	1.41	1.52	1.4	1.43	1.49	1.47	1.51	1.48

[a] Compositions in wt %; values in the parentheses are the standard deviations.

PP on melting due surface-free energy effects and that might introduce error in such measurements. For this reason, this result was supported by our findings based on the gravimetric estimation of bound BMI calculated from eq. (3). Although the arithmetic average of three samples was taken in this estimation method, it was found that the sample-to-sample variation in this estimation process was relatively high. The amount of attached BMI in BCTMP was found to be 2.9 ± 0.7 wt %.

Effect of Boron Compounds

One of the problems in the preparation of wood fiber-filled PP composite is that, due to the presence of resin acids and hydrolyzable acetyl groups in wood components, kneaded PP/wood fiber compounds tend to become acidic, which affects the interface bonding and also discolors the appearance of the composite due to thermal degradation of the wood.[3] As their countermeasure, a mixture of sodium borate ($Na_2B_4O_7$, $10H_2O$) and boric acid (HBO_3) was used in the composites. Sodium borate liberates eight water molecules at 60°C; hence, two residual water molecules are retained by it even when PP/wood fiber compositions are processed at 180–185°C. Thus, sodium borate in combination with boric acid can work as a fire retardant. Moreover, the alkaline nature of sodium borate can also help to reduce the acidity of the composite.[13] The effect of sodium borate and boric acid on a 23 wt % CTMP-filled PP composite is given in Table I in relationship to their mechanical properties. The Young's modulus of pulp-filled composites practically remained uninfluenced by the addition of boron compounds. For the tensile strength, it practically remains uninfluenced by the added amount of sodium borate and boric acid or marginally decreases, particularly if the concentration of sodium borate in the composition exceeds 7.5 wt %. This observation may be attributed to the fact that sodium borate probably also acts as a nonreinforcing filler in the composite, particularly at higher loading. Moreover, a high concentration of boric acid lowers the pH of the composite.[13] Nevertheless, the rate of burning of the composite is decreased with the progressive addition of sodium

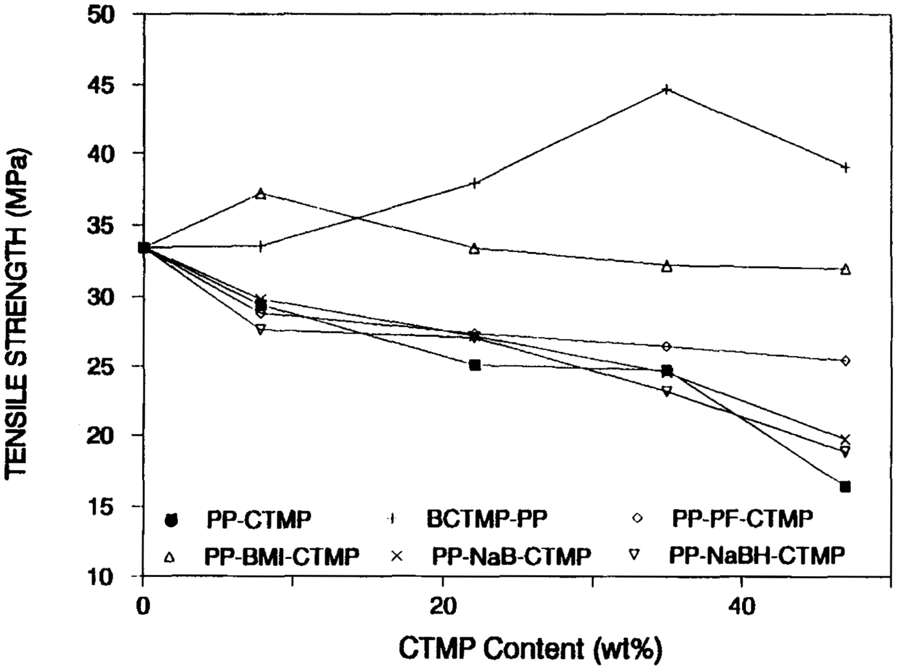


Figure 3 Variation of tensile strength with the filler content for unmodified and modified composites of CTMP-filled PP. PP–CTMP: composite without modification; PP–NaB–CTMP: PP + CTMP + 7.5 wt % sodium borate; PP–NaBH–CTMP: PP + CTMP + 7.5 wt % sodium borate + 1.5 wt % boric acid; PP–PF–CTMP: PP + CTMP + 2.0 wt % phenolic resin; PP–BMI–CTMP: PP + CTMP + 2.0 wt % BMI; PP–BCTMP: PP–CTMP composite with 30 wt % of CTMP replaced by BCTMP.

borate and boric acid in the composition showing improvement in flame retardance characteristics of the composites.

Effect of Modifiers

In this study, BCTMP and BPP were used as modifiers. The effect of these modifiers on the interaction between CTMP fiber and PP and their mechanism of action were studied through mechanical testing and IR spectroscopy study of the composites. Moreover, the effects of *in situ* modifications with uncatalyzed BMI and phenolic (PF) resin were also investigated on the properties of composites. Figure 3 exhibits the tensile strength of the composites. The UTS value of composite (composition: BCTMP–PP), prepared with a 70/30 (wt ratio) blend of CTMP and BCTMP fibers as one component and PP as a second component, were progressively increased with increasing total fiber content. The UTS value reached a maximum at 35 wt % of total fiber loading and then marginally decreased with further increase in fiber content. An insignificant change in the tensile strength of the composites was observed if BMI was directly added (*in situ*) to the roll mill during kneading of PP with CTMP (composition: PP–BMI–CTMP). A positive influence of the modified PP (BPP) on tensile strength of the composite (BPP–CTMP) is also evident from Table II. The Young's modulus and breaking elongation are also improved by adding BMI, BPP, or BCTMP as the modifier. The results in Figure 3 and Table II demonstrate the superiority of BPP as well as BCTMP-modified composites to the BMI-modified ones. Evidently, no reinforcing effect was observed if BMI was directly added to the roll mill (*in situ*) during kneading of PP and CTMP. Moreover, both the unmodified PP–CTMP composite as well as the composite containing sodium borate (composition: PP–NaBH–CTMP) significantly decrease in their UTS values with increase in the CTMP fiber content. Addition of PF resin during kneading of PP and CTMP was found to have no significant influence on the strength of the composite (composition: PP–PF–CTMP). Based on these findings, the empirical equations proposed by Hui[14] can be referred to:

$$\mathrm{UTS} = KV_fT_f(1 - L_c/2L) + (1 - V_f)T_m \quad (4)$$

Table II Effect of Nature of Modifier on Composite Properties

	Compositions[a]					
	9	10	11	12	13	14
	PP–PF	PP–CTMP	PP–PF–CTMP	PP–BMI–CTMP	BCTMP–PP	BPP–CTMP
PP	100	65	65	65	65	65
CTMP	0	35	35	35	24.5	35
PF resin	2	0	2	0	0	0
BMI	0	0	0	2	0	0
BCTMP	0	0	0	0	10.5	0
BPP	0	0	0	0	0	2
Properties						
UTS (MPa)	33.6	25.2	26.5	32	44.7	36.5
	(1.9)	(1.3)	(0.9)	(0.8)	(1.8)	(1.5)
YE (%)	10.2	4.3	6.2	4.9	5.2	5
	(0.8)	(0.3)	(0.3)	(0.4)	(0.3)	(0.4)
Young's modulus (GPa)	1	1.15	1.26	1.34	1.38	1.35
	(0.06)	(0.03)	(0.1)	(0.11)	(0.08)	(0.1)
Toughness (Mpa)	1.72	0.7	0.92	1.17	1.34	1.23
	(0.06)	(0.03)	(0.07)	(0.05)	(0.08)	(0.05)
Impact strength ($kJ\ m^{-2}$)	7.4	15.2	13.2	12.3	11.9	12.7
	(0.6)	(1.3)	(1.1)	(0.8)	1	(0.7)
Flammability	50	49	42	48	47	52
buring rate (mm/min)	2.4	1.9	2.7	2.2	2.5	2
Specimen thickness (mm)	1.48	1.51	1.56	1.49	1.51	1.5

[a] Compositions are in wt %; values in the parentheses are standard deviations.

and

$$L_c = DT_f/2\tau \qquad (5)$$

where UTS is the tensile strength of the composite; K, the empirical fiber efficiency parameter; V_f, the volume fraction of the fiber; T_f, the tensile strength of the fiber; T_m, the tensile strength of the PP matrix; L, the fiber length; L_c, the critical fiber length; D, the diameter of the fiber; and τ, the interface shear strength.

From these equations, it is apparent that tensile strength depends on two different factors: First, UTS is directly proportional to the interfacial strength (τ). This implies that the improvement of adhesion between CTMP and the PP matrix by replacing 30 wt % of the CTMP fiber with BCTMP can directly reflect an increase of the UTS of the composite. Besides interfacial strength, fiber length and diameter also influence the strength of the composites. Figure 4 shows the fiber length distribution as well as aspect ratio of fibers before and after composite preparations. Surprisingly, the aspect ratio of fibers marginally increased after modification and molding. This observed increase in the aspect ratio of the fibers can be attributed to the fiber shrinkage due to extraction of noncellulosic materials and/or compaction of the microfibrils during modification, compounding, molding, and solvent-extraction processes. It is apparent from Figure 5 that the structure of fiber starts diminishing [fiber rupture in Fig. 5(b)] and are somewhat pulverized after mixing, molding, and extraction. The effect of the marginal increase in the aspect ratio of fibers during processing operations is a corresponding increase in critical fiber length (L_c) that might help to prevent the loss of strength in composites.

Figures 6–8 demonstrate the effect of the CTMP fiber concentrations on some mechanical properties of unmodified as well as of various modified composites of CTMP-filled PP. In each case, the concentrations of modifiers were held constant. The impact strength of PP increases with increase in

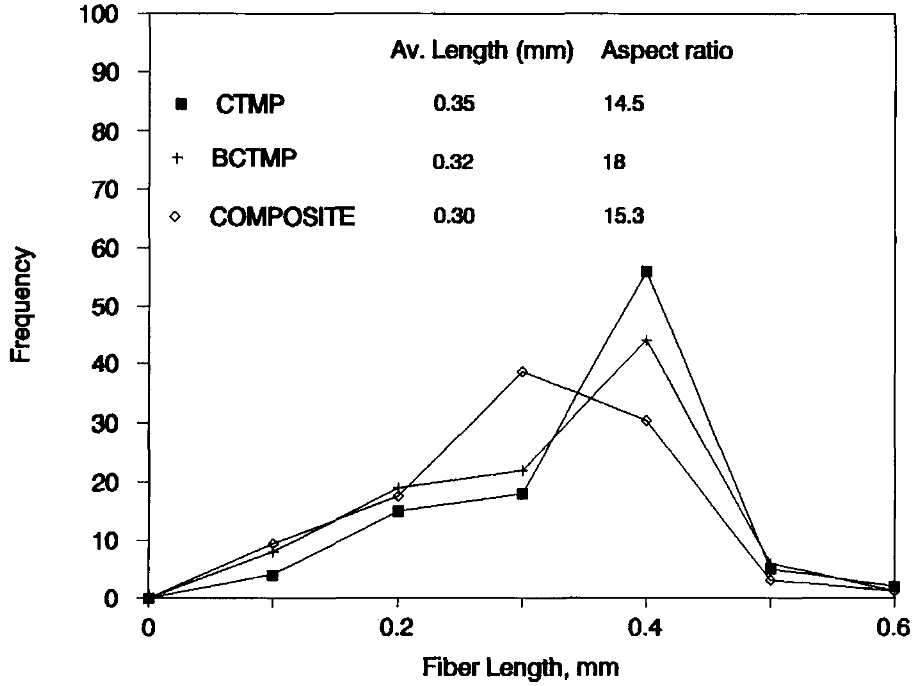


Figure 4 CTMP fiber length distribution: CTMP, in untreated fiber; BCTMP, in BCTMP-modified fiber; composite, in PP–BCTMP composite.

CTMP fiber concentration, which is evident from Figure 6. On the other hand, all composites containing modifiers, such as BCTMP, BMI, or PF resin, although having better impact strength than that of pure PP, are less resistant to impact compared to the unmodified ones. The reason for this observed effect of modifiers on the impact strength of the composites is not known. It is thought that an improved interaction at the interface between the PP matrix and the CTMP fiber could also inhibit polymer mobility and thereby could reduce the ability of the system to absorb energy during fracture propagation. A similar decrease in the impact strength of maleic anhydride-grafted PP-modified wood filler composite was also reported by Myers et al.[5]

The elongation at the yield point of composites is generally decreased due to incorporation of unmodified as well as modified wood fibers. However, it is interesting to note that PF resin modification of CTMP-filled PP composition improves the elongation of composites when the fiber loading is restricted to 23 wt %. To explain the reason for this observed increase in the elongation of the composite, the mechanical properties of the PF resin-modified unfilled PP is compared with the properties of the CTMP–PF–PP composite. Results in Table II reveal that the initial improvement of elongation in the lightly filled (23 wt %) CTMP–PF–PP composite is attributed to an increase in elongation of the PF resin-modified PP. A similar increase in elongation evidenced in a PF resin-modified blend of nitrile rubber and PP was also reported to be due to a chemical reaction between PP and PF resin.[8]

Tensile toughness, a measure of the ability to absorb energy of a material under load up to fracture, is expected to increase with an increase in the interfacial adhesion between PP and the CTMP fiber. The data of Table II as well as the trend displayed in Figure 8 characterize and compare the effects of modifiers and fiber loadings on the tensile toughness of unmodified and modified composites of CTMP-filled PP. Evidently, the addition of BCTMP as well as BPP as modifiers improved the tensile toughness of the composites. Although the same toughness property of the composites deteriorates with increasing loading of unmodified CTMP, a significant improvement of the above property was observed if a part of the unmodified CTMP is replaced by BCTMP.

Role of BCTMP as a Compatibilizer

To ellucidate the reason for imparting good physical properties of the BCTMP–PP composites compared to those found in the PP–CTMP composi-

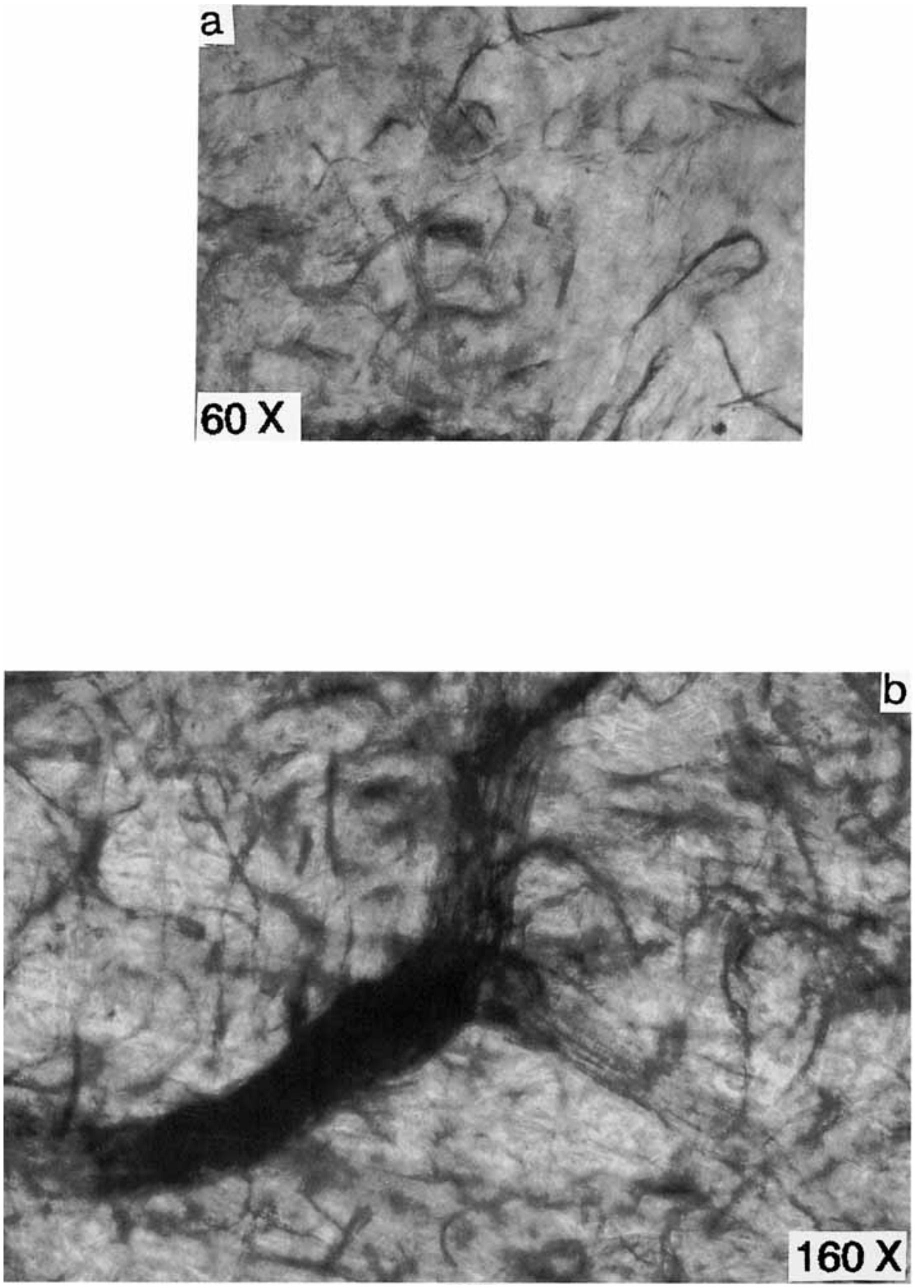


Figure 5 Light microscopy photographs of CTMP fibers: (a) fibers before melt-mixing with polymers; (b) xylene-extracted fibers after melt-mixing and molding operations.

tion, the possibility of the occurrence of a grafting reaction between BCTMP and PP is considered. This grafting can improve the adhesion between CTMP and PP.

In an attempt to investigate the possibility of the grafting reactions within the blended composition of CTMP, BMI, and PP in the presence of a peroxide catalyst, few experiments were conducted. First, PP and BMI were mixed in 10 : 1 proportion with 2.0 wt % of DCP in a kneader at 185°C for 5 min. The composition was extracted with hot acetone for 24 h. In another experiment, only PP and BMI were dry-blended in a 10 : 1 proportion and acetone extracted for 24 h. The extracted residues are vacuum-dried for 24 h at 60°C. The IR spectrum for the residues of both peroxide-catalyzed and uncatalyzed samples are in Figure 9. Although the spectrum for uncatalyzed sample resembles the spectrum of pure

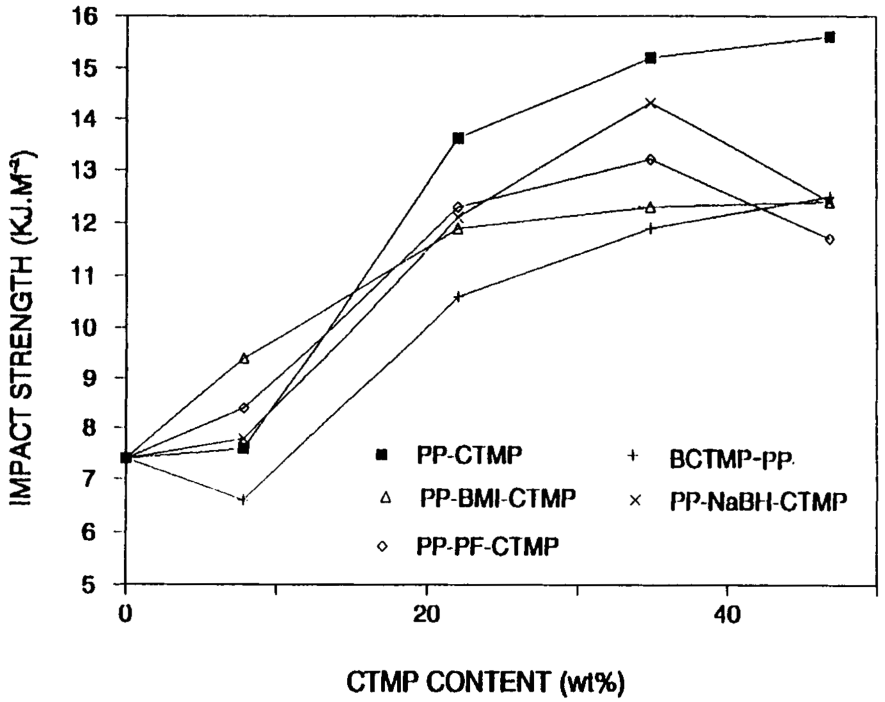


Figure 6 Variation of impact strength with the filler content for unmodified and modified composites of CTMP-filled PP. Compositions are the same as described in Figure 1.

PP, the peroxide-catalyzed sample shows a peak at 1741 cm^{-1} and a characteristic shoulder of the BMI moiety at 1715 cm^{-1} (peak for the unsaturated 5-membered cyclic imide group) in addition to the peaks attributable to PP. The peak at 1741 cm^{-1} may be attributed to either (a) the carbonyl group

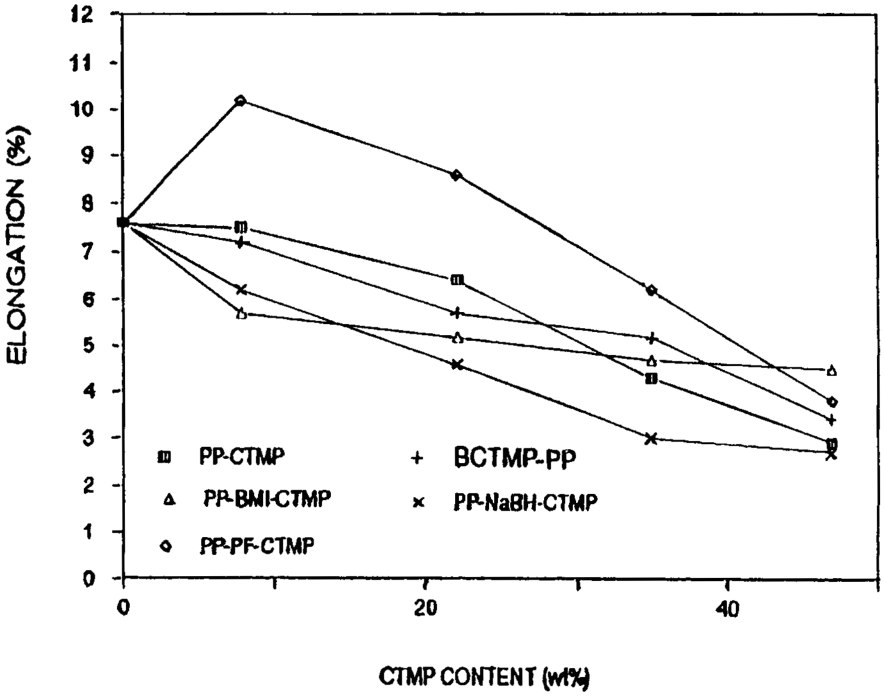


Figure 7 Variation of breaking elongation with filler content for unmodified and modified composites of CTMP-filled PP. Compositions are same as in Figure 1.

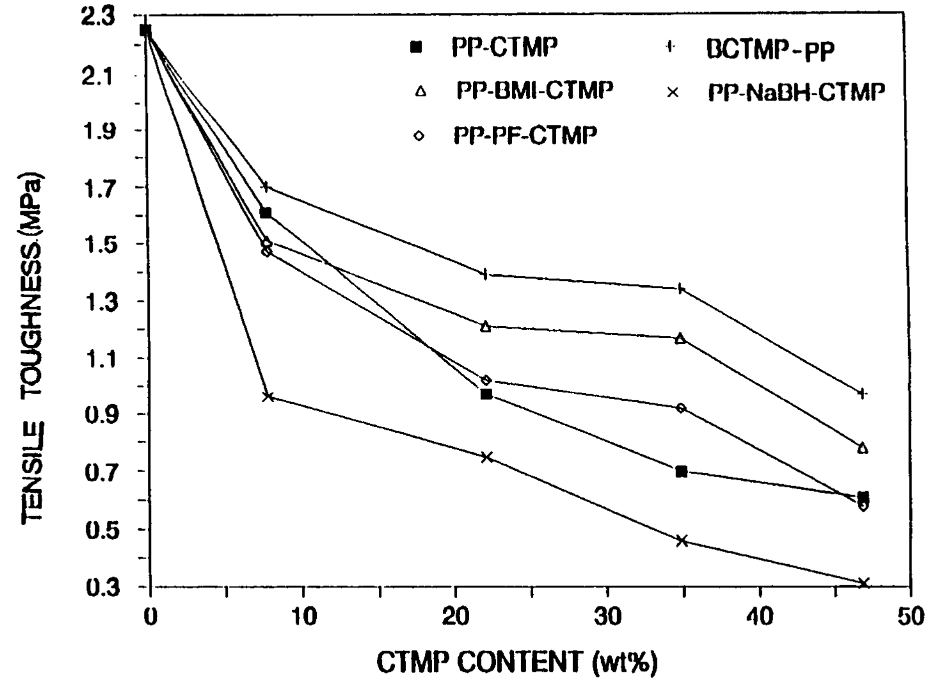


Figure 8 Variation of tensile toughness with filler content for unmodified and modified composites of CTMP-filled PP. Compositions are same as in Figure 1.

resulting from ketonic scission of the alkoxy radical formed on cleavage of the hydroperoxide from the reaction of the PP radical with oxygen or (b) unsaturation in some appended BMI units, due to termination by disproportion, as proposed with LDPE.[15]

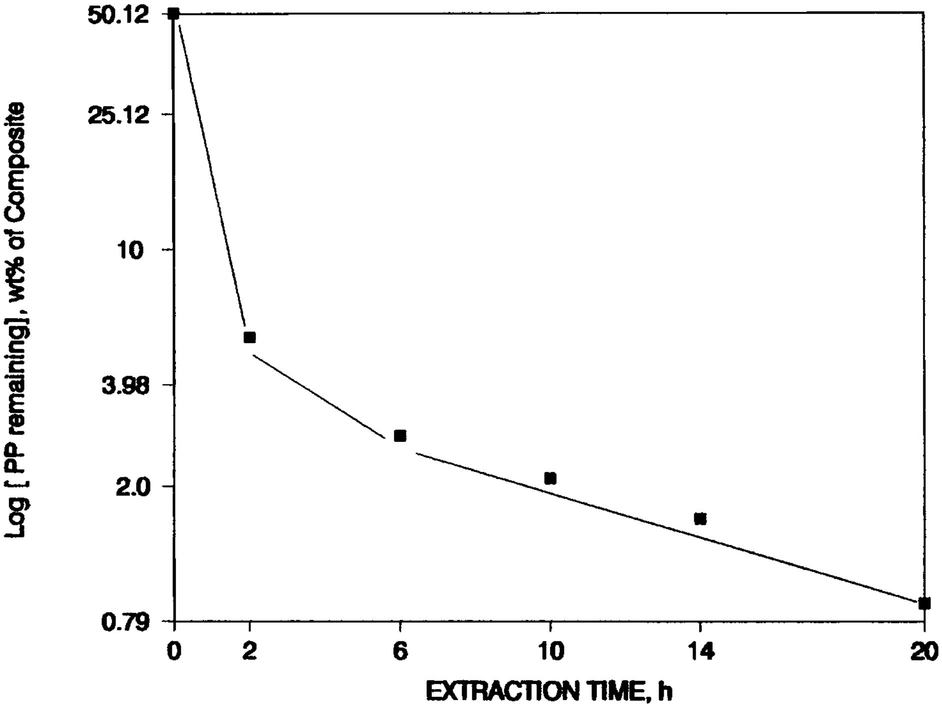


Figure 9 The concentration of PP remaining in a PP–CTMP composite as a function of hot xylene extraction time.

Table III **Weight Percent of the Composite Retained After Extractions**

Wt Ratio PP/CTMP	Wt Retention (%) PP–CTMP	BCTMP	PP–DCP–CTMP	Theoretical Value
1	49.4 (1.4)	54.4 (2.1)	48.9 (1.7)	50
0.5	65.7 (0.8)	68.9 (1.7)	65.3 (1.1)	66.6

[a] Both compositions of BCTMP contain 10 wt % BMI and 2 wt % DCP; both compositions of PP–DCP–CTMP contain 2 wt % DCP; values in parentheses are standard deviations.

In another set of experiments, CTMP and PP (designated as PP–CTMP), CTMP mixed with PP and DCP (designated as PP–DCP–CTMP), and CTMP mixed with PP, BMI, and DCP (designated as BCTMP) were compounded separately in various proportions in a two-roll mill at 185°C for 8 min. Each of these composites was first extracted in hot acetone and then in hot xylene; finally, they were washed with acetone to separate out unreacted BMI, peroxide, and PP. The residues were vacuum-dried at 60°C for 24 h and weighed. The gravimetric analysis results are shown in Table III together with the theoretical values calculated based on the assumption that no grafting occurs during kneading or dry blending.

A 24 h (overnight) extraction time in hot xylene was chosen, in view of the preliminary work exemplified by the data in Figure 9. In addition to being convenient, complete extraction appears to have occurred overnight. Very long extraction times might give misleading results since PP can slowly degrade if there is any free-radical-generating catalyst present. Much of this degraded PP, even though initially grafted to CTMP, would no longer be bound to it.

As the data in Table III shows, the residual weights of PP–CTMP and PP–DCP–CTMP compositions agree well with the theoretical values, whereas those of BCTMP compositions exceed the theoretical values, i.e., PP can be removed completely from the PP–CTMP and PP–DCP–CTMP compositions by extraction with xylene, whereas part of the PP remains within the residue if the BCTMP composition is subjected to extraction. Thus, the results of gravimetric analysis suggest that PP is chemically attached to the CTMP fiber. The above presumption could be visualized further in the IR spectrum of the residues after extractions. As an example, the IR spectra of the acetone- and xylene-extracted residue of PP–CTMP and BCTMP compositions, all initially containing PP and CTMP in 25 : 50 proportions, are shown in Figure 10 in comparison with those of pure PP, BMI-modified PP, and pure CTMP. The residue from the PP–CTMP composite resembles a spectrum very similar to that of the CTMP and does not reveal a peak attributable to PP. On the other hand, the IR spectrum of residue from the extracted BCTMP composition shows two shoulders at 1741 and 1610 cm^{-1} and two peaks at 1715 and 841 cm^{-1}, in addition to the peaks ascribable to the CTMP fiber. The shoulder at 1741 cm^{-1} and a peak at 1715 cm^{-1} are the same as those previously found in peroxide-catalyzed BMI-modified PP. However, an additional shoulder at 1610 cm^{-1} may be due to the formation of secondary amide groups by reaction of cellulosic —OH with cyclic imide as shown in reaction Scheme I and a peak at 841 cm^{-1} is characteristic to the vibrational band of crystalline PP.

Although two separate compositions, PP with peroxide-activated BMI and the BCTMP, showed development of a peak at 1715 cm^{-1} attributable to the unsaturated cyclic imide, it can be argued that this new peak may be due to the carbonyl group derived from peroxide-catalyzed autooxidative product in degraded PP. In an attempt to clarify the reason for the development of the peak at 1715 cm^{-1}, the DSC thermal analyses as well as FTIR spectra of BCTMP were compared with the FTIR spectrum of a reference sample prepared by compounding CTMP, PP, and DCP without BMI (PP–DCP–BMI). The proportion of PP, CTMP, and DCP in the reference composition was the same as that in BCTMP. The IR spectra of the reference sample and BCTMP were compared after extractions in hot acetone and hot xylene and they are shown in Figure 11 between the 1900 and 1600 cm^{-1} spectral range. It is clear from the spectra that the peak attributed to the unsaturated 5-membered cyclic imide is absent in the reference sample. However, in both the samples, a peak at 1741 cm^{-1} ascribable to the car-

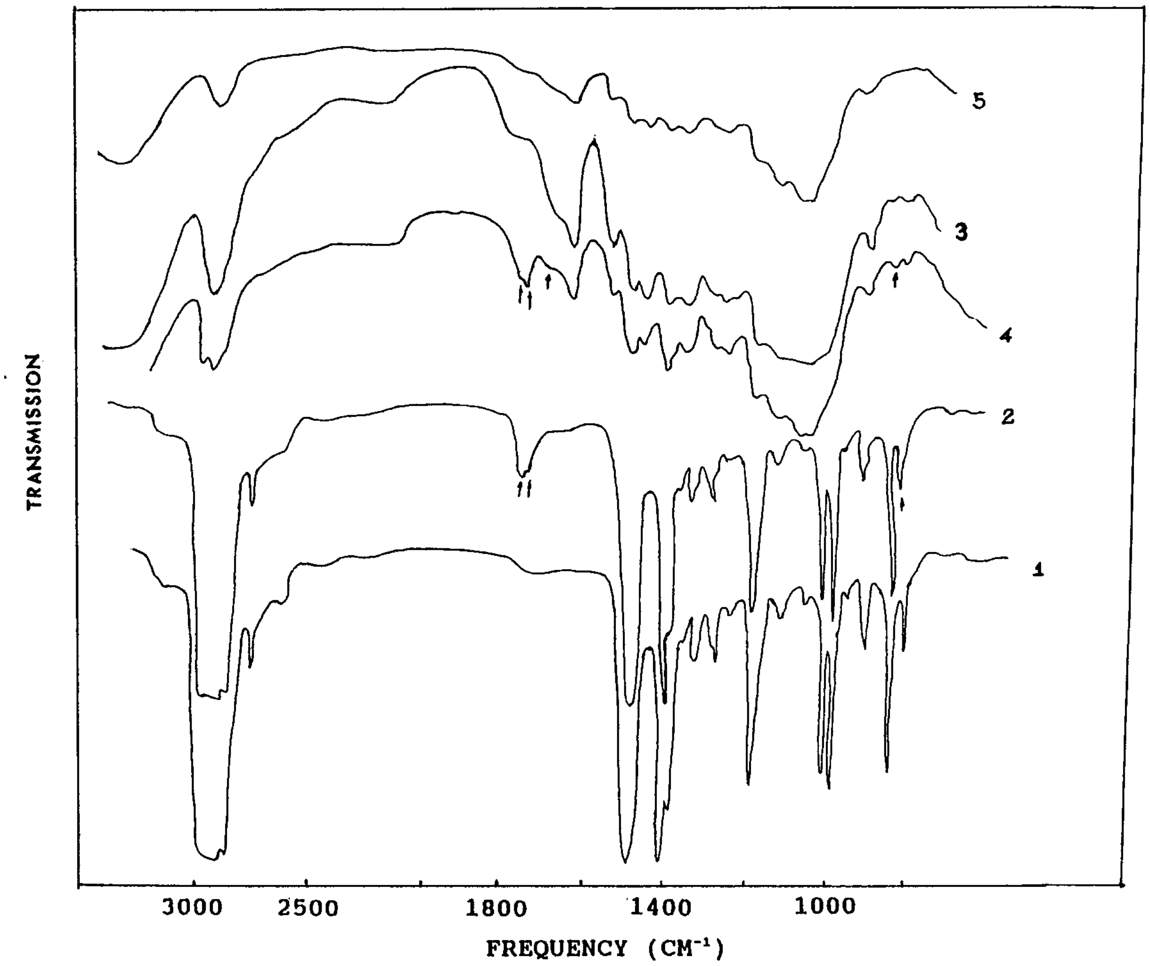
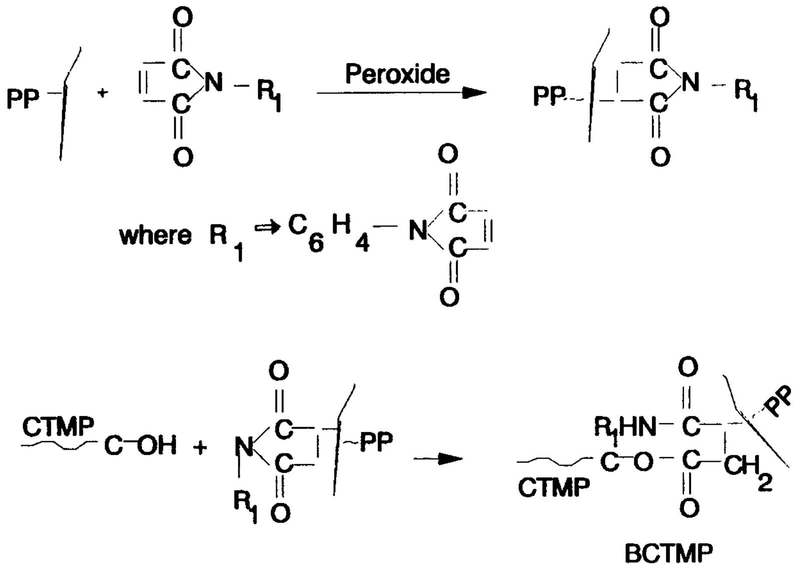


Figure 10 Infrared spectra for PP and composites of CTMP-filled PP: (1) pure PP; (2) BMI-modified PP; (3) PP–CTMP composite; (4) PP–BCTMP composite; (5) pure CTMP.



Scheme I

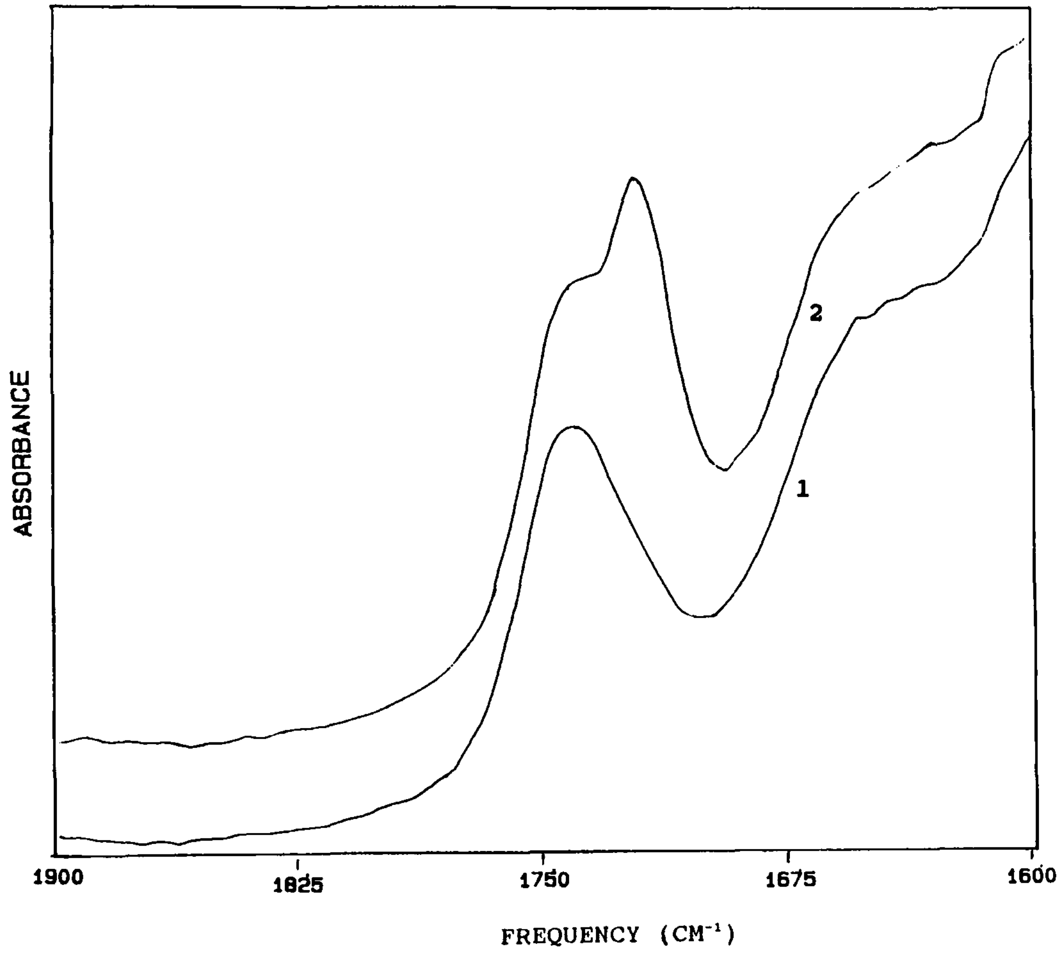


Figure 11 Infrared spectra for BCTMP and PP–DCP–CTMP in the absorbtion range 1900 to 1600 cm^{-1}.

bonyl group of oxidized PP or CTMP is present. It is further noted that the intensity of the carbonyl group peak in the sample without BMI is stronger than that of the BCTMP sample, indicating that the peroxide catalyst was a more effective oxidizing agent for PP and/or CTMP in the absence of BMI. This fact is further confirmed from the DSC thermograms shown in Figure 2. The initiation of a strong exothermeric decomposition reaction at 200°C indicates dominant thermal oxidation in PP–DCP–CTMP compared to that of BCTMP.

The data can be interpreted in a number of ways: (i) Chemical bonds, as indicated in Scheme I, form between the CTMP and PP molecule; (ii) both CTMP and PP molecules become partially cross-linked to the extent of reduced solubility but without the linkage of one kind of polymer molecule to the other; or (iii) because of physical and morphological constraints, extraction is incomplete. It is not likely that extraction is incomplete, since the attack of acetone on BMI is rapid (data obtained are not reported). It is also not likely that the PP, by itself, becomes insoluble by cross-linking. However, the PP could become cross-linked by a multiplicity of linkages per PP molecule to a multiplicity of CTMP molecules, each multilinked to different PP molecules. This would give a gelled network as proposed in reaction Scheme I. Moreover, this would reduce the solubility of PP, but as a result of the graft formation, not instead of it. The general point to be made here is that graft formation during peroxide-catalyzed kneading of CTMP, PP, and BMI is suggested.

CONCLUSION

CTMP wood fiber and PP can be mixed above the melting temperature of PP to give compositions that have useful properties. If the compositions are treated with sodium borate, boric acid, or phenolic resin, the chance of burning of the compositions during processing can be decreased.

Premodification of either PP or the fiber with BMI improves the strength of the composites without practically affecting the other useful properties. The reason for the improvement of strength for various BCTMP as well as BPP-modified composites appears to be that a chemical bond forms between the PP and the CTMP fiber.

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