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Toughened Thermoplastic Composite. I. Cross-Linkable Phenol Formaldehyde and Epoxy Resins-Coated Cellulosic-Filled Polypropylene Composites

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SYNOPSIS

Composites of polypropylene (PP) or maleic-anhydride-modified polypropylene (MAH-PP) with uncoated or thermosetting resin-coated sawdust or explosion pulp (V-pulp) were prepared by dynamic cross-linking and their properties were compared to those of unmodified and uncross-linked composites. The effects of modification and dynamic cross-linking on the interfacial adhesion between polymer and filler have also been investigated by a solvent extraction study and microscopic analysis. The new method of dynamic cross-linking in combination with the additional effect of compatibilization suggests a practical route to obtain high-strength, toughened thermoplastic composites. Dynamically cross-linked epoxy- or phenolic resin-coated sawdust or V-pulp that can be grafted or can have affinity to MAH-PP was found to improve tensile strength as well as elongation at yield point. The tensile toughness of the dynamically cross-linked-compatibilized composites is better than that of an uncross-linked composite of MAH-PP and sawdust. The improved toughness of the dynamically cured composites appears to be that further chemical bonds form between coated filler and MAH-PP in addition to grafting of MAH-PP onto cellulose chain. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

It was not too long ago that thermoplastic material research and thermoset research were just about mutually exclusive. In recent years, however, the driving line between these two disciplines has been disappearing. Classical thermosets rely upon a cross-linked network, developed during the curing process, to provide high strength and dimensional stability. Nevertheless, easy recyclability and excellent fracture toughness of thermoplastics can be incorporated into a thermoset if these two different kinds of resins are mixed together. However, there must be some form of interaction between the two phases if useful properties are to be realized.

Recently, investigations were carried out to use various high-performance thermoplastics, e.g.,

polyetherimide and polyhydantoin, to improve fracture toughness of epoxy resins. A follow-on test using polyetherimide with a composite system was performed using carbon fiber.¹ Test results showed that composite fracture toughness markedly improved by adding them. A similar approach was also made in the past to prepare reprocessable rubber vulcanizates by adding thermoplastic into the system.²⁻⁷ A technically compatible yet reprocessable nitrile rubber/polypropylene vulcanizate has improved hot oil resistance.⁸ More recently, it has been found in our laboratories that cellulosic-filled and dynamically cross-linked epoxy as well as phenolic resin compositions that are fabricable as thermoplastic composite can be prepared.⁸ Such compositions, referred to here as thermoplasto-thermoset composites, have superior strength, good thermal resistance, improved tensile toughness, better resistance to flaming, etc. This report outlines the novel compositions of cellulosic-filled polypropylene with two different thermosetting resins. Tensile strength, elongation, and

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tensile toughness values of epoxy-coated or phenolic resin-coated cellulosic-filled maleated polypropylene composites, in which thermosetting resin is cross-linked, are higher than those of an uncross-linked composite. It is suspected that the surprisingly good properties might be due to chemical graft formation or interlinking among cross-linked thermoset, maleated polypropylene and cellulose during melt-mixing and molding. The presence of such interlinked or coupled molecules, particularly at thermoplastic-cellulose interfaces, could have the effect of reducing the surface energy mismatch between polypropylene and cellulose and promoting adhesion between the phases. Experiments suggesting the graft formation are described.

MATERIALS

Resin

Two different types of thermosetting resins used in these experiments are as follows: (I) liquid epoxy resin (Epon 812, Shell Chemical Co., Canada), and (II) Phenolic resin (IB-334, Reichhold Ltd., Canada). Stabilized granulated polypropylene (PM 6100, Shell Chemicals, Canada) was used as the thermoplastic resin.

Filler

In the present study, two different kinds of wood fibers were used, e.g., a softwood aspen in the form of explosion pulp (V-pulp) and a hardwood maple in the form of sawdust. Sawdust was ground to four different particle sizes (1.2, 0.63, 0.50, and 0.27 mm) before mixing with the resins.

V-pulp was prepared by high-temperature treatment of wood chips using the following technique: 24 h immersion in 8% Na_2SO_3 ; immersion temperature, 60°C; and exposure to steam at 190°C for 4 min. The exploded chips were washed thoroughly with water and then refined in a blender for 1 min at high speed. The pulp was ground to an average size of 0.45 mm and dried in vacuum at 60°C for 24 h before use.

Curing Agent and Modifier

Dodecenyl succinic anhydride (DDSA) was used as curing agent for epoxy resin. Hexamethylene tetramine was used to cure phenolic resin.

Maleated polypropylene (MAH-PP) was used as a modifier. MAH-PP had been prepared by reacting

5 wt % technical grade maleic anhydride with powdered polypropylene (Profax 6301, Himont, Canada). A *t*-butyl peroxyester (Esperox-R10, Witco, USA), 3 wt %, was used as initiator. The following reaction conditions were used: temperature, 120–130°C; and reaction time, 2 h in an inert atmosphere. A similar method to prepare MAH-PP had been used earlier.⁹

Coating Treatment

Sawdust was pretreated with phenolic resin in a roll mill. No curative was added in phenolic resin-coated sawdust in this stage. The coating condition for phenolic resin treatment was 150°C for 15 min. On the other hand, sawdust as well as V-pulp were separately coated with epoxy resin at room temperature in a laboratory blender. Epoxy resin-coated sawdust or V-pulp, used for dynamic cross-linking, was also treated with DDSA curative during the coating operation; however, DDSA curative was not added in epoxy-coated sawdust used to prepare uncross-linked composites.

Preparation of Thermoplastic Composition without Cross-linking

Composites were prepared by adding polypropylene (PP) and phenolic or epoxy resin-coated sawdust or V-pulp without any curing agent (as indicated in Table I) on a two-roll mill with an oil bath temperature of 180–185°C. The mixing speed was 40 rpm until the PP was melted and 30 rpm thereafter. After the PP had melted, cellulosic filler was added and mixing continued for 15 min. The resulting composition was then removed from the mixer, cooled, and made into small chips in a granulator for further use. The chips were then compression-molded in a frame-and-plate molder at 200°C. The following molding cycle was used: preheating: 3 min without pressure; molding: 5 min at 35 MPa, and cooling to 60°C under pressure for a period of 10 min.

Preparation of Thermoplastic Composites by Dynamic Cross-linking

The preparation of thermoplastic resin composites containing cross-linked rubber, by dynamic vulcanization, has been described by Gessler.¹⁰ The procedure was later used by Fischer¹¹ to prepare compositions of partially cured EPDM-polyolefins. Dynamic cross-linking differs from the more common static cross-linking in that cross-linking occurs during mixing of the composition being prepared. If

Table I Mechanical Properties of Uncross-linked Compositions^a

	Composition No.							
	01	02	03	04	05	06	07	08
Ingredients, parts by wt								
PP	65	65	55	55	55	55	70	70
Sawdust ^b	35	35	35	45	45	45	—	—
V-pulp ^b	—	—	—	—	—	—	30	30
Epoxy resin	—	—	—	5	10	5	—	15
Phenolic resin	1	5	5	—	—	—	—	—
MAH-PP	—	—	10	—	—	5	—	—
Properties								
Max tensile strength	23.1	21.9	34.3	16.5	16.0	33.4	23.6	24.6
(MPa)	(1.3)	(1.0)	(1.2)	(1.0)	(1.2)	(0.6)	(0.8)	(0.7)
Strain at yield point	5.9	4.6	4.8	3.7	3.0	4.1	4.1	5.4
(%)	(0.5)	(0.4)	(0.3)	(0.3)	(0.3)	(0.2)	(0.3)	(0.3)
Young's modulus	1.54	1.60	1.50	1.6	1.54	1.69	1.39	1.30
(GPa)	(0.12)	(0.1)	(0.05)	(0.09)	(0.1)	(0.07)	(0.07)	(0.11)
Tensile toughness	0.63	0.59	1.04	0.5	0.45	0.70	0.62	0.68
(MPa)	(0.07)	(0.05)	(0.03)	(0.04)	(0.02)	(0.03)	(0.05)	(0.04)
Impact strength (kJ	9.1	8.7	9.7	8.6	8.7	9.2	12.4	11.5
m ⁻²)	(0.7)	(0.7)	(0.65)	(0.72)	(0.83)	(0.92)	(1.1)	(0.10)

^a Values in parentheses are coefficients of variation.^b Average particle sizes of sawdust and V-pulp are 0.27 and 0.45 mm, respectively.

enough of a thermoplastic resin is present in a molten state, the mixture does not lose processability as a result of cross-linking. This is true even when the thermosetting resin is fully cured. Thus, products with good strength and dimensional stability yet fabricable as thermoplastics can be prepared. This occurs within a certain range of proportions of thermoset and thermoplastic. In the resulting compositions, cured thermoset particles appear to be dispersed in the thermoplastic matrix. If enough thermoset phase is present, particles may interfere with one another to give a somewhat continuous thermoset phase.

In the present work, a dodecenyl succinic anhydride cross-linking agent was used in a 1 : 1 proportion with epoxy resin for all composites containing cross-linkable epoxy-coated cellulosic filler. Similarly, composites containing cross-linkable phenolic resin-treated cellulosic filler were cured with 10 wt % hexamethylene tetramine by weight of phenolic resin. The resin-coated fiber and PP were mixed (rate, 40 rpm) on a two-roll mill with the oil bath controlled at 180–190°C. Two to three minutes after melting of the resin, the curatives were added. Curing then occurred and was indicated by an increase in viscosity of the molten mass on the roll mill. Mixing was continued for 15 min. It was ex-

pected that this mixing time should be enough for a sufficient cross-linking reaction to occur (as indicated in Fig. 1). The composition was then removed and made into small chips in a granulator. The chips were then compression-molded in a frame (1.5 mm thick) between plates in a platen press at 200°C. The molding cycle was same as that used for uncross-linked compositions. Aluminum foil (0.1 mm thick) was used between the molded samples and plates. Depressions on the surface of the molded samples (shrink marks) were thus minimized.

Determination of Extent of Cross-linking of the Thermoset Resins

The extent of cross-linking of the epoxy or phenolic particles in composite after the mixing operation was estimated from values of dimethylene chloride-extracted residues. About 2 g of each sample was extracted overnight in hot dimethylene chloride, vacuum-dried at 60°C for 48 h, and weighed. The residual content after extraction and drying was estimated for various mixing time intervals. Major effects of change in the extent of cross-linking for two compositions containing 50 wt % PP, 25 wt % sawdust, and 25 wt % phenolic or epoxy composition (composition includes both the resin and the cu-

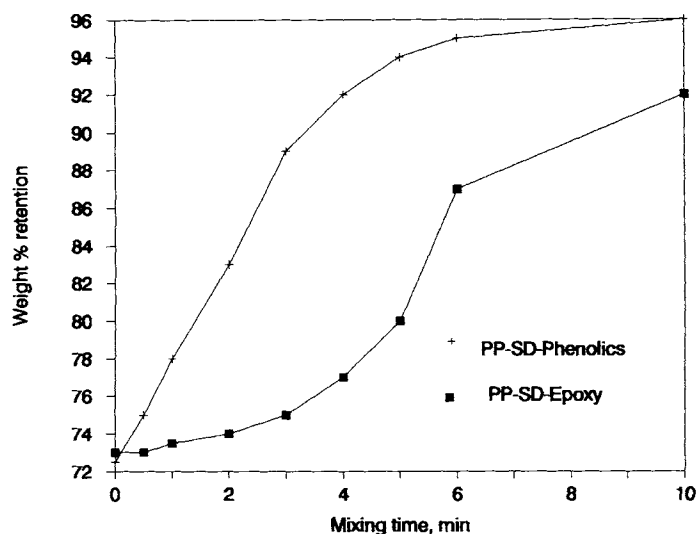


Figure 1 Effect of mixing time on residual content of composites after 24 h extraction in hot methylene chloride; PP-SD-phenolics: composite containing PP, sawdust, and phenolic resin with curative; PP-SD-epoxy: composite-containing PP, sawdust, and epoxy resin with curative.

rative) are given in Figure 1. It may be argued that the dimethylene chloride-extractable natural resin components present in cellulose would affect the result. However, in this particular series of measurements, cellulosic fillers were preextracted with dimethylene chloride before being mixed with resins. We have further found that the epoxy- or phenolic resin-coated cellulosic filler without the resin curing agent is essentially completely extractable from the composite matrix by hot dimethylene chloride.

Mechanical Testing

The mechanical properties (maximum tensile strength and strain at yield point, which are designated as yield strength and yield strain, respectively, Young's modulus, and tensile toughness (which is a measure of energy per unit area under the stress-strain curve) of the samples were measured with an Instron Tester (Model 4201). All these properties were automatically calculated by computer using the Instron 2412005 general tensile test program (under the name "PLA"). The strain rate was 1.5 mm/min.

The impact strength (Charpy, unnotched) was tested with an impact tester (Model TMI, No. 43-01) supplied by Testing Machines Inc. The samples were tested after conditioning at $23 \pm 0.5^\circ\text{C}$ and 50% RH for at least 18 h in a controlled atmosphere. Statistical averages of six measurements were taken for each sample.

Aging resistance of selective compositions was evaluated by determining the change in tensile strength of the respective compositions after 72 h exposure to hot circulating air at 150°C . Flammability tests have been carried out according to ASTM test method D635-63. Test specimens of 152 mm in length, 12.5 mm in width, and over 1.3 mm in thickness were used. The flammability of the composite is reported as follows: rate of burning (mm/min) to burn 127 mm in length of the test specimen and thickness of the test specimen.

Extraction and Infrared Spectroscopy Study

Both uncoated as well as thermosetting resin-coated thermoplastic composites of Tables I and II were each extracted overnight by dimethylene chloride. Dimethylene chloride is a good solvent for the phenolic and epoxy resins used in our compositions. After each extraction, by a relatively large amount of solvent, each specimen was dried to a constant weight (under vacuum at 60°C), with loss of weight being noted.

Infrared spectra of the samples were taken by a Perkin-Elmer 283B infrared spectrometer. Spectra were recorded in transmittance units in the range $400\text{--}4000\text{ cm}^{-1}$ with 4 cm^{-1} resolution. Composite samples, both extracted and unextracted, were dispersed in a tablet of KBr prepared by grinding 1.5 mg of sample with 100 mg of KBr and compressing

Table II Properties of Cellulosic-filled Cross-linked Composites^a

Composition No.	Composition ^b PP/SD/Coated-SD/ MAH-PP (by Weight)	Average Fiber Size (mm)	Yield Strength (MPa)	Yield Strain (%)	Young's Modulus (GPa)	Tensile Toughness (MPa)	Impact Strength (kJ m ⁻²)
1	65/35/0/0	1.20	17.3 (1.2)	2.1 (0.1)	1.1 (0.05)	0.42 (0.01)	11.1 (0.9)
2	65/35/0/0	0.63	20.8 (1.1)	2.9 (0.13)	1.2 (0.03)	0.40 (0.02)	10.8 (0.7)
3	65/35/0/0	0.50	22.0 (0.7)	3.7 (0.21)	1.5 (0.07)	0.51 (0.02)	10.6 (1.2)
4	65/35/0/0	0.27	22.1 (0.6)	7.4 (0.32)	1.64 (0.09)	0.69 (0.05)	9.2 (0.8)
5	55/45/0/0	0.28	16.5 (0.5)	3.0 (0.24)	1.78 (0.12)	0.49 (0.03)	8.9 (0.7)
6	65/26/9/0	0.29	23.2 (1.1)	4.8 (0.12)	1.73 (0.06)	0.51 (0.04)	10.9 (0.9)
7	65/18/17/0	0.32	22.3 (1.2)	7.0 (0.43)	1.50 (0.04)	0.60 (0.05)	9.9 (0.8)
8	65/9/26/0	0.33	21.7 (1.1)	5.6 (0.32)	1.74 (0.07)	0.49 (0.02)	8.4 (0.8)
9	65/0/35/0	0.36	22.9 (1.7)	6.6 (0.51)	1.25 (0.05)	0.59 (0.05)	9.5 (0.7)
10	55/35/0/10	0.28	39.0 (1.6)	5.9 (0.41)	1.68 (0.04)	1.45 (0.06)	10.3 (0.4)
11	55/0/35/10	0.34	40.0 (1.1)	8.5 (0.32)	1.53 (0.04)	2.21 (0.08)	11.7 (0.5)
12 ^c	60/0/30/10	0.50	36.6 (1.3)	5.1 (0.5)	1.31 (0.06)	1.21 (0.07)	11.8 (0.4)
13	55/0/45/0	1.17	16.6 (1.1)	1.9 (0.12)	1.48 (0.06)	0.29 (0.02)	12.4 (0.9)
14	55/0/45/0	0.33	26.9 (1.7)	7.1 (0.42)	1.51 (0.05)	0.85 (0.05)	7.9 (0.8)
15	50/0/45/5	0.32	37.1 (1.6)	5.3 (0.15)	1.89 (0.07)	1.05 (0.04)	6.3 (0.6)

^a Values in the parentheses are coefficients of variation.

^b SD, unmodified sawdust; coated-SD, sawdust treated with 15% epoxy resin and 15% DDSA or sawdust treated with 5% phenolic resin and 0.5% hexamethylene tetramine; compositions 6–9 and 11 are with epoxy-coated sawdust; compositions 13–15 are with phenolic-coated sawdust.

^c In composition 12, 15% epoxy and 15% DDSA-coated V-pulp is used instead of sawdust.

the whole into a transparent tablet. Compression time and pressure were 2 min and 10 MPa.

Microscopic Study of Composite Morphology

An optical microscope was used to determine the average size of about 100–150 (Zeiss, Germany) cellulose particles for some compositions prepared by melt-mixing uncoated or coated cellulosic filler with PP resin.

For microphotographs of samples under a known applied strain, thin films of selective compositions were separately clamped in a specimen grip and each film was elongated to a series of predetermined strains (1, 2, and 5%, if any) until the breaking point was reached. The change in matrix morphology in each stage of applied strain as well as the microstructure of the fractured film were photographed using an optical microscope.

RESULTS AND DISCUSSION

Were it not for their gross mutual incompatibility, a combination of a polyolefin resin, such as PP with

cellulosic filler, and epoxy or phenolic resin might be a good choice of materials from which to prepare high-strength, toughened thermoplastic composites by dynamic cross-linking. Properties of the uncross-linked as well as dynamically cross-linked composites of epoxy as well as phenolic resin-coated-cellulosic fillers with PP in Tables I and II demonstrate very little success in obtaining good mechanical properties for such composites. The effect of cross-linking of the thermoset resin during melt-mixing (dynamic cross-linking) is a marginal improvement in the mechanical properties of composites. This increase is indicated by the properties of compositions 02 and 04 in Table I compared to those of compositions 9 and 14 in Table II. It is likely that large surface energy differences between the two types of polymers (PP and thermoset resin) as well as between the polyolefin and cellulosic filler are the reasons for the insignificant effect of coating and cross-linking operations on the mechanical properties of the composites. Mutual wetting among PP, thermosetting resin, and cellulosic filler appeared incomplete; relatively large particles of cured thermosetting resin-coated cellulosic filler dispersed in polyolefin formed during mixing and dynamic cross-linking. An approach to technological compatibili-

zation, in addition to dynamic cross-linking, was thus sought.

It is now generally accepted that an interphase modifier with selective reactive functionality can compatibilize mixtures of polymers and filler. We have found that a MAH-PP can be used to technologically compatibilize a mixture of PP, cellulosic filler, and phenolic or epoxy resin, quite possibly by the formation (*in situ*) of a graft terpolymer of MAH-PP cellulose, and epoxy or phenolic resin. Data indicating technological compatibilization are given in Tables I and II.

The mechanical properties of the uncross-linked composite of cellulosic-filled MAH-PP with epoxy or phenolic resin (compositions 03 and 06 in Table I) are improved, in comparison to the composition of unmodified PP (compositions 02 and 04 in Table I). Tensile strength of the composite is improved and this improvement is also reflected in tensile toughness of the modified composites. The mechanism of improvement could be the formation of only a compatibilizing amount of a PP-cellulosic filler,¹² because uncross-linked epoxy or phenolic resin can be quantitatively extracted from these improved composites by hot dimethylene chloride.

In composition 11 of Table II, dodecenylsuccinic anhydride (DDSA) is added during the coating operation of sawdust with epoxy resin. The DDSA is added as a curing agent for the epoxy resin to cure the resin during continued melt-mixing (dynamic cross-linking), rather than as a reactant to further modify the PP. However, it is possible that epoxy resin with a terminal epoxy group might chemically react with sawdust in the presence of DDSA to form another chemical bridge between cross-linked epoxy and cellulosic filler.^{13,14} The effect of cross-linking, as before, is to further improve the mechanical properties of the composites. Thus, an epoxy-coated sawdust-filled PP composite with as high as 20% improved tensile strength and strain at yield point, and with a tensile toughness equal to that of the unfilled PP (2.2 MPa),¹⁵ can be obtained by suitable technological compatibilization and dynamic cross-linking.

With technological compatibilization by MAH-PP, a similar effect on the properties of dynamically cross-linked composite is also noticed if phenolic resin-coated sawdust is used instead of epoxy resin-coated sawdust. However, it is found that unlike epoxy-coated sawdust the tensile toughness of composite based on phenolic resin-coated sawdust and MAH-PP is inferior to unfilled PP (2.2 MPa). This is indicated by the properties of composite 15 of Table II. The improvement in mechanical properties may be due to a reaction between PP and phenolic

resin catalyzed by hexamethylene tetramine and/or between MAH-PP and phenolic resin via quinone methide formation.⁶

The data in Tables I and II also demonstrate the effect of change in the nature of the cellulosic filler (sawdust is replaced by V-pulp). The properties of composition 12 in Table II are much better than those of composition 08 in Table I where DDSA as well as the MAH-PP are absent. It is presumed that two effects, i.e., technical compatibilization and dynamic cross-linking, play a major role in developing good properties in the composites and the effect of the nature of cellulose fiber on properties of composite is not very significant. On the other hand, it is noted that the particle size of the filler influences the mechanical properties. Surprisingly, resin-coated cellulosic particles are, although higher in sizes compared to those of the uncoated ones, better in mechanical properties (composition 10 compared to composition 11 in Table II). It is possible that the decrease in mechanical properties due to increase in stress concentration associated with higher flaw (particle) sizes in uncoated compositions is more than compensated by the improved stress distribution due to better interfacial bonding in coated composites.

Evidence for Graft Formation

IR spectra of solvent-extracted samples of selected composites were analyzed in comparison with the spectra of unextracted composites that were used to construct a calibration curve. Examples of spectra are given in Figures 2 and 3; pertinent absorbances are given in Tables III and IV. The calibration for weight ratio, [PP]/[SD], of polypropylene (PP), and sawdust (SD) in a composite is illustrated by Figure 4; thus:

$$[\text{PP}]/[\text{SD}] = 59.6 (A_{1155})/(A_{1453}) - 14.95$$

Here, the absorbance at 1155 wave number (A_{1155}) is attributed to the polypropylene and A_{1453} is due to the cellulose.¹⁶

A 24-h extraction time was chosen in view of preliminary work exemplified by the data in Figure 5. In addition to being convenient, complete extraction appears to have occurred overnight. Very long extraction times might give misleading results since cellulose can slowly degrade under the high-temperature condition with the liberation of acid products of pyrolysis. Much of this degraded cellulose, even though initially grafted to resin, would no longer be bound thereto.

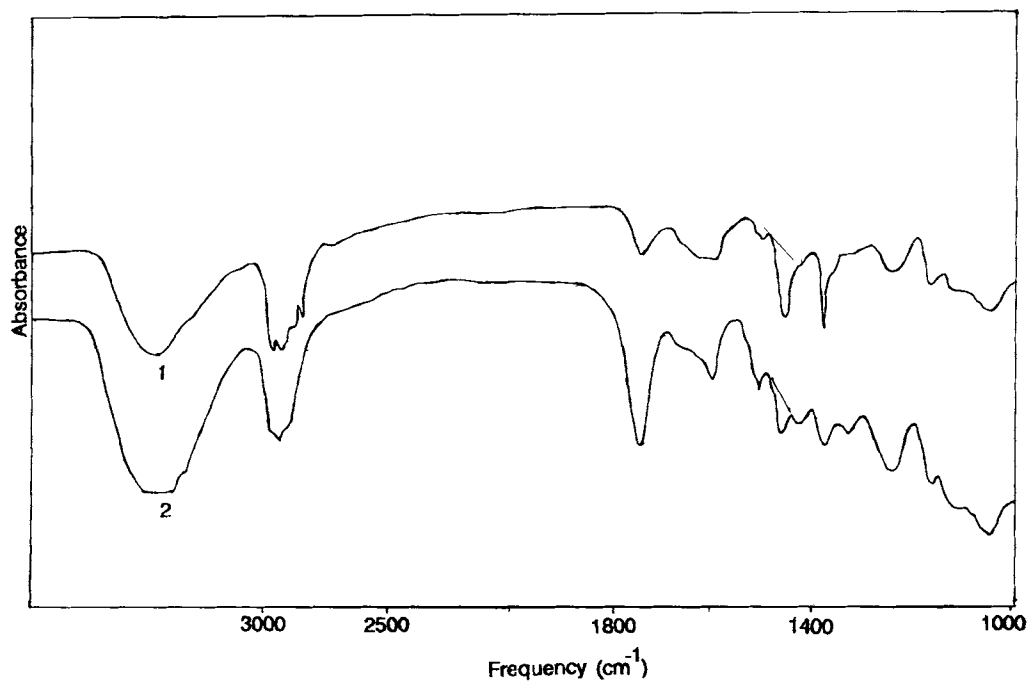


Figure 2 IR spectrum of dynamically cross-linked epoxy coated-sawdust-filled PP composites: (1) unextracted composition containing 65% PP, 31% sawdust, and 4% epoxy resin by weight; (2) hot methylene chloride followed by hot xylene-extracted composite containing 55% PP, 10% MAH-PP, 27% sawdust, and 8% epoxy resin by weight.

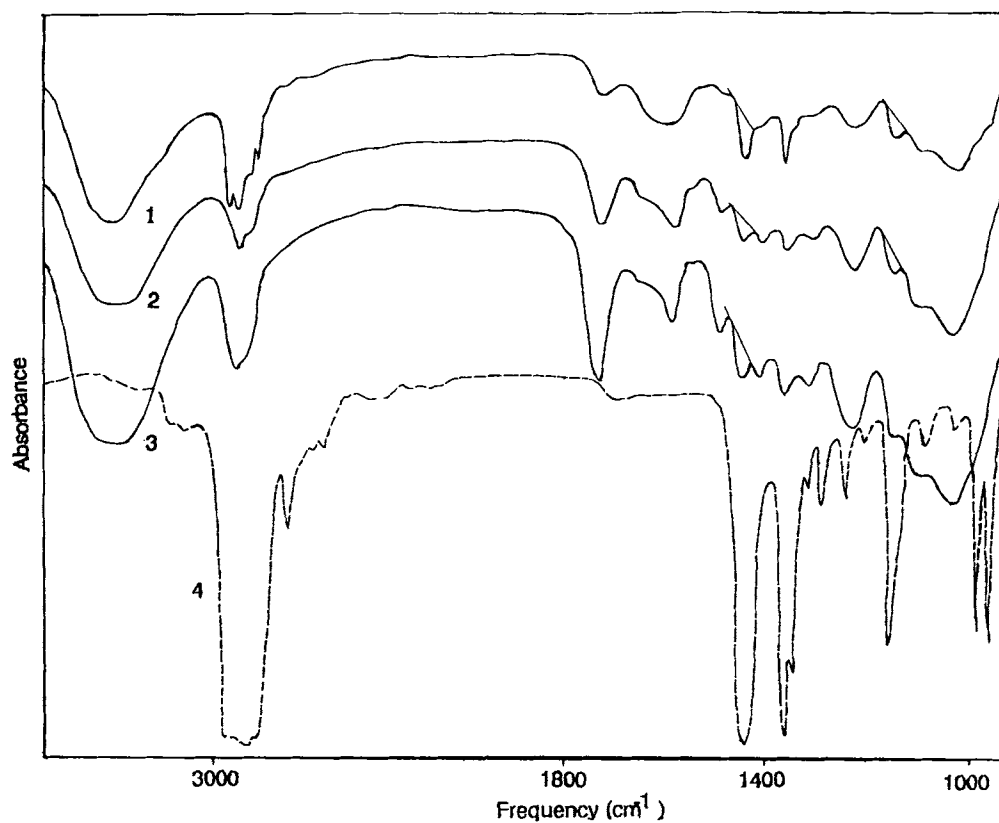


Figure 3 IR spectrum of dynamically cross-linked phenolic resin-coated sawdust-filled PP composites: (1) unextracted composition containing 45% PP, 5% MAH-PP, 45% sawdust, and 5% phenolic resin; (2) hot methylene chloride and then hot xylene extracted composite with the same composition as in (1); (3) hot methylene chloride followed by hot xylene-extracted sample of a composite containing 50% PP, 45% sawdust, and 5% phenolic resin without curative; (4) PP extracted from a composite with the same composition as in (3).

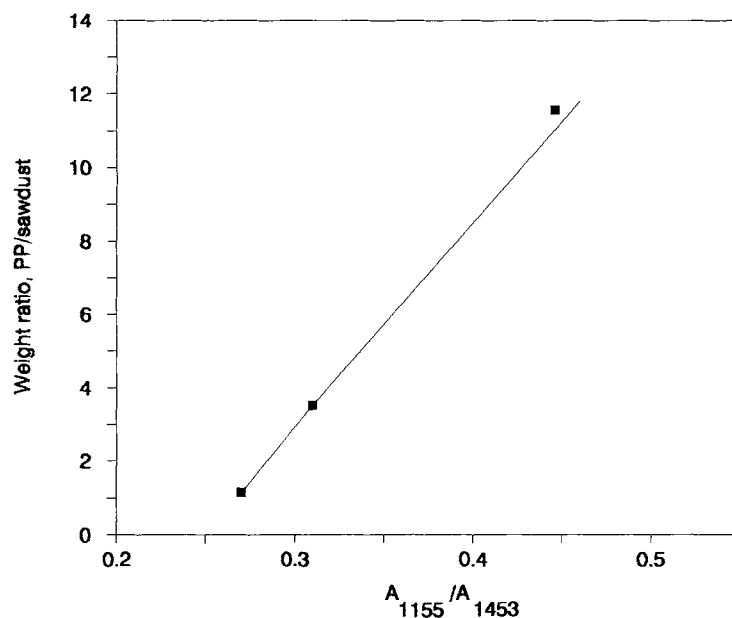


Figure 4 Calibration. Weight ratio of PP and sawdust as a function of IR spectra absorbances.

The data in Table II indicate that for either the 65/0/35/0 (composition 9 in Table II) or the 55/0/35/10 (composition 11 of Table II) PP/SD/epoxy-coated SD/MAH-PP composites a significant amount of the epoxy resin becomes insoluble. If the composites are further extracted by hot xylene, PP is lost and only about 35% of the initial unextracted composite remains from the 65/0/35/0 PP/SD/epoxy-coated SD/MAH-PP composite (composition 9 in Table II). On the other hand, about 38.2% of the unextracted composite remains insoluble in hot xylene extractant from 55/0/35/10 PP/SD/epoxy-coated SD/MAH-PP composite (composition 11 in Table II). This final remaining material, insoluble in both extractants, from the PP/epoxy-coated SD/MAH-PP composite (composition 11 of Table II), contains about 24.6% PP.

Similarly, IR spectra analysis and solvent extraction data of phenolic resin-coated sawdust-filled PP composite in Table IV indicate that about 17.2% PP becomes bound to sawdust and/or cross-linked phenolic resin in the 50/0/45/5 PP/SD/phenolic resin-coated SD/MAH-PP composite (composition 15 in Table II). It should be noted that the MAH-PP used in this work is extractable in hot xylene and the sawdust used in the present investigation contains about 2.5% of soluble material in dimethylene chloride.

The data can be interpreted in a number of ways: (i) Chemical bonds form between the sawdust and PP molecules; (ii) chemical bonds form between

cross-linked thermosetting resin (epoxy or phenolic, as applicable) and PP or MAH-PP; (iii) chemical linkages form between epoxy resin and sawdust that might further react with PP; (iv) besides dynamic cross-linking of the thermosetting resin, both PP and cellulose molecules becomes partially cross-linked to the extent of reduced solubility but without the linkage among different kind of molecules; or (v) because of physical and morphological constraints, extraction is incomplete. It is not likely that extraction is incomplete, since the attack of hot xylene on PP is rapid, removing almost 95% of the extractable PP in only 2 h (Fig. 5). It is also not likely that the PP, by itself, would become insoluble by cross-linking. However, the PP could become cross-linked by a multiplicity of linkages per PP molecule to a multiplicity of cellulose molecules in MAH-PP, each multilinked to different thermosetting resins and/or PP molecules. It is also presumed in the earlier part of our discussion that in case of phenolic resin-coated sawdust-filled composite an additional linkage might be expected between phenolic resin and PP resin. Many similar reactions between PP or rubber molecules and phenolic resin have been proposed long ago.^{6,17-19}

Morphology of Strain-induced Composites

The difference in mechanical properties in Tables I and II, between dynamically cross-linked cellulosic-filled, MAH-PP composite and uncross-linked

Table III Solvent Extraction Studies

Wt % Ratio, PP : SD : Epoxy, Initially in Compound	Treatment	Wt % of Compound Remaining after Treatment	Absorbance		Amount of PP ^c in Compound after Treatment (% of Compound)
			A ₁₁₅₅ ^a	A ₁₄₅₃ ^b	
Calibration					
92 : 8 : 0	None	100.0	0.070	0.160	92.0
79 : 21 : 0	None	100.0	0.055	0.175	79.0
65 : 35 : 0	None	100.0	0.045	0.160	65.0
56 : 44 : 0	None	100.0	0.030	0.110	57.0
65 : 33 : 2	None	100.0	0.042	0.147	66.0
65 : 31 : 4	None	100.0	0.0200	0.070	64.7
Determination ^d					
65 : 35 : 0	(4) Extracted by methylene chloride overnight	98.0	0.045	0.160	64.3
	Extracted by methylene chloride overnight, then xylene	36.0	0.016	0.064	0.0
65 : 33 : 2	(6) Extracted by methylene chloride overnight	97.0	0.042	0.150	65.3
	Extracted by methylene chloride overnight, then xylene	37.0	0.017	0.068	0.0
65 : 31 : 4	(7) Extracted by methylene chloride overnight	98.0	0.031	0.109	62.9
	Extracted by methylene chloride overnight, then xylene	36.8	0.013	0.052	0.0
65 : 29 : 6	(8) Extracted by methylene chloride overnight	96.0	0.53	0.182	62.3
	Extracted by methylene chloride overnight, then xylene	31.0	0.010	0.058	0.0
65 : 27 : 8	(9) Extracted by methylene chloride overnight	98.0	0.047	0.158	61.5
	Extracted by methylene chloride overnight, then xylene	35.0	0.012	0.050	0.0
65 : 27 : 8	(11) ^e Extracted by methylene chloride overnight	98.0	0.049	0.164	61.9
	Extracted by methylene chloride overnight, then xylene	38.2	0.018	0.070	24.6
65 : 35 : 0	(10) ^e Extracted by methylene chloride overnight	99.0	0.040	0.141	66.0
	Extracted by methylene chloride overnight, then xylene	40.0	0.013	0.051	18.8

^a Due to PP.^b Due to sawdust (SD).^c Average error in estimation, 2.5%.^d Nos. in parentheses indicate composition nos. in Table II.^e Compositions modified with 10 wt % maleated PP.

composites, is presumably due to their differences in the degree of heterogeneity. It is apparent from the solvent extraction study and IR analysis that the changes in mechanical properties are associated with a change in interfacial adhesion between PP and cellulosic filler. This conclusion was further supported by the results of the investigation of mor-

phology of the composites by an optical microscope under an externally applied strain. The microphotographs of four selective composites under the application of a series of gradually increasing strains are shown in Figures 6-8 in comparison with the optical microphotographs of unstrained composites. A comparison of the uncross-linked composites with

Table IV Solvent Extraction Studies

Wt % Ratio, PP : SD : Phenolic Resin, Initially in Compound	Treatment	Wt % of Compound Remaining after Treatment	Absorbance		Amount of PP ^c in Compound after Treatment (% of Compound)
			A ₁₁₅₅ ^a	A ₁₄₅₃ ^b	
Calibration					
92 : 8 : 0	None	100	0.070	0.160	92.0
79 : 21 : 0	None	100	0.055	0.175	79.0
65 : 35 : 0	None	100	0.045	0.160	65.0
56 : 44 : 0	None	100	0.030	0.110	57.0
50 : 45 : 5	None	100	0.025	0.092	50.0
Determination					
50 : 45 : 5	(15) ^d Extracted by methylene chloride overnight	96	0.028	0.103	48.2
	Extracted by methylene chloride overnight, then xylene	48	0.011	0.043	17.2

^a Due to PP.^b Due to sawdust (SD).^c Average error in estimation, 2.5%.^d No. in parentheses indicates composition no. corresponding to Table II.

the dynamically cross-linked ones indicates a difference in the degree of heterogeneity in composite matrices. The cross-linked resin-coated cellulosic particles in composites [Figs. 7(a) and 9(a)] apparently give more uniform particle-size distributions compared to that of the uncross-linked composites [Figs. 6(a) and 8(a)]. It is evident from photographs that unmodified composites contain

large particle agglomerates, which accounts for the poor strength of such composites.

It is thought that application of an external strain on the composite might change the morphology of the individual matrices as well as the morphology of polymer-filler interface. Keeping this assumption in mind, we have focused our microscopic analysis on selective polymer-filler interfaces visibly large

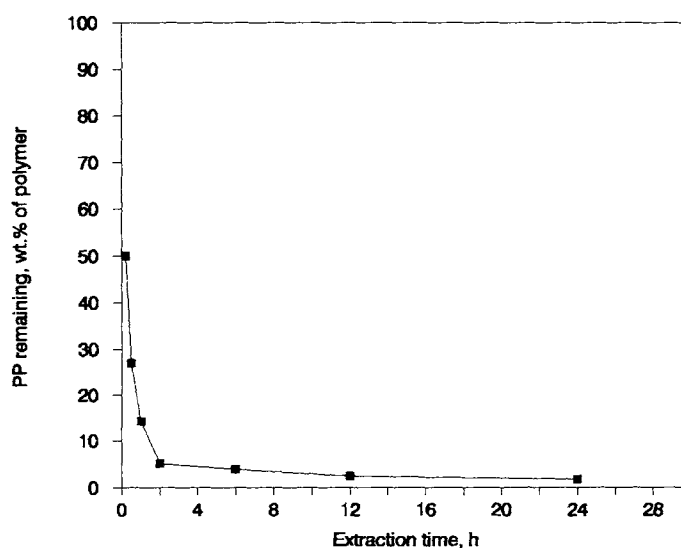


Figure 5 The concentration of PP remaining in a composite as a function of xylene extraction time at boiling temperature of xylene.

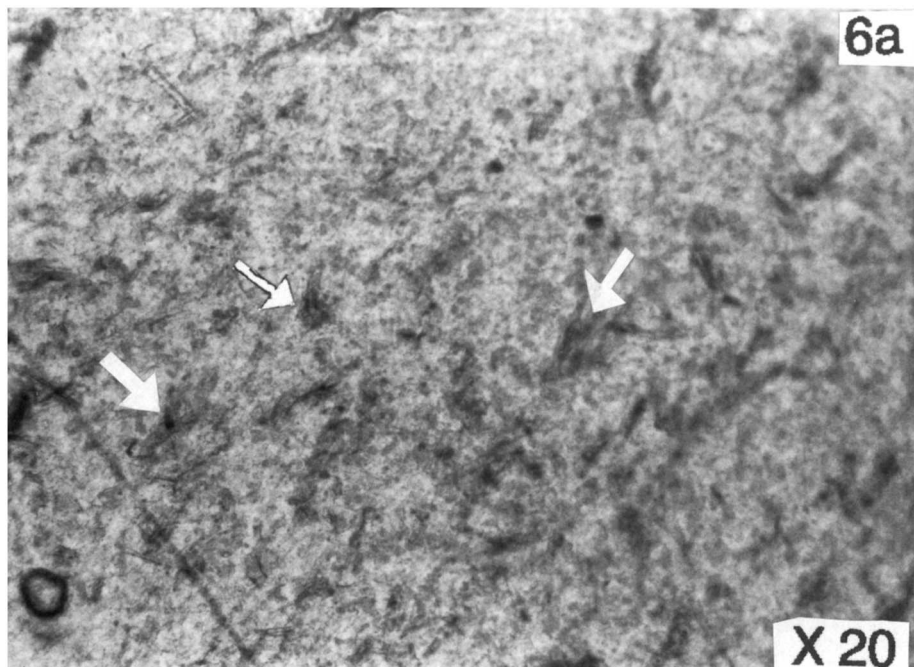


Figure 6 Optical microscopy photographs of unmodified V-pulp-filled PP composite (PP/V-pulp, 70/30): (a) no externally applied strain; (b) after an externally applied strain of 5% (very close to the breaking strain).

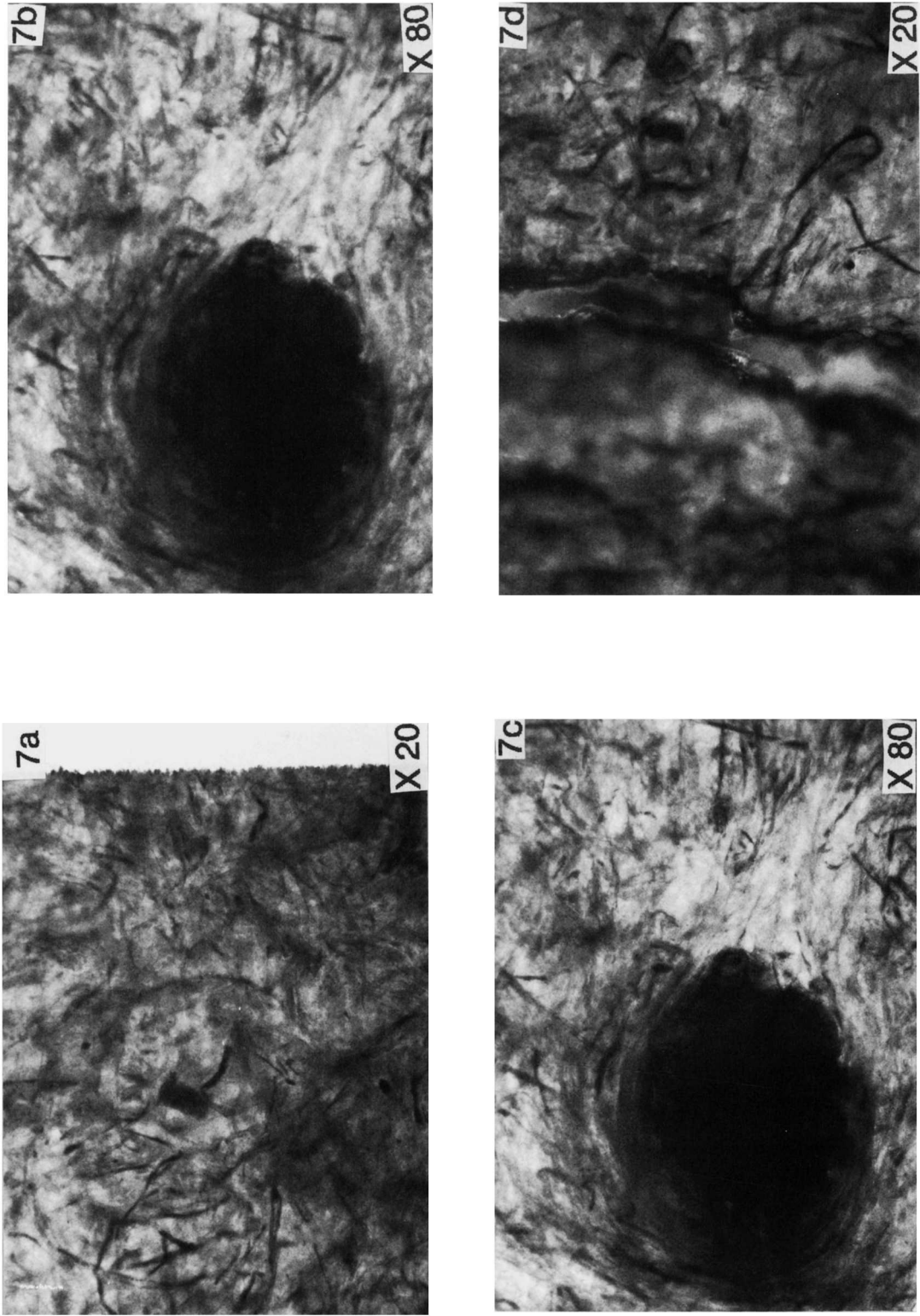


Figure 7 Optical microscopy photographs of dynamically cured epoxy resin-coated V-pulp-filled MAH-PP composite (composition 12 in Table II): (a) no external strain; (b) after 2% elongation; (c) after 5% elongation; (d) after failure.

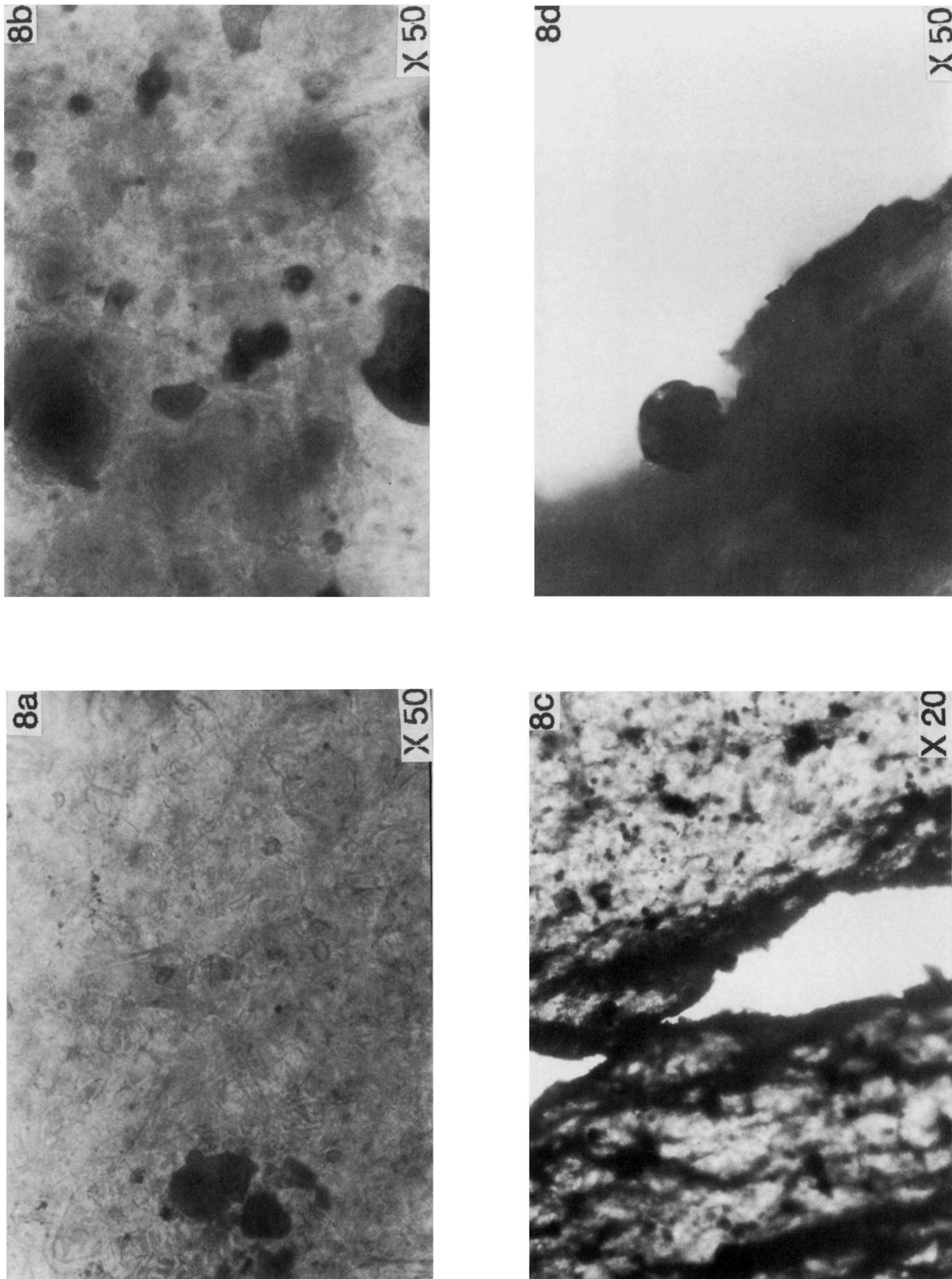


Figure 8 Optical microscopy photographs of unmodified and uncross-linked phenolic resin-coated sawdust-filled PP composite (composition 02 in Table I): (a) no external strain; (b) after 2% elongation; (c) after elongated to breaking point; (d) failure surface.

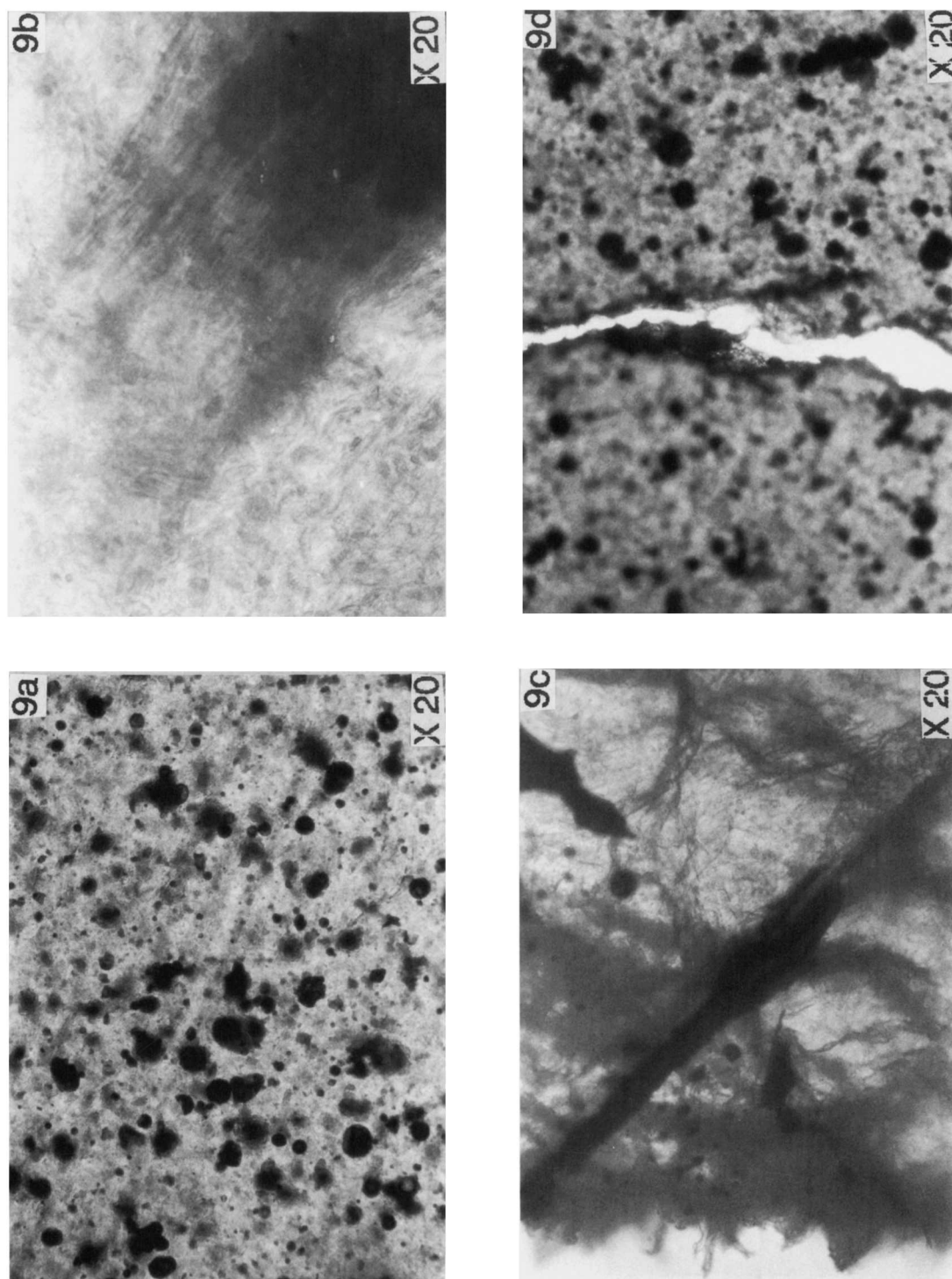


Figure 9 Optical microscopy photographs of dynamically cross-linked phenolic resin-coated sawdust-filled MAH-PP composite (composition 15 in Table II): (a) no external strain; (b) after 2% elongation; (c) after 5% elongation; (d) after failure.

enough to initiate flaws under the application of an external strain. Some of our observations are shown in Figures 6–9. It is evident that the failure mechanisms of unmodified and modified composites are different. The cracks are developed at the polymer–filler interfaces in unmodified composites at a very low strain level with hardly any plastic deformation of the polymer matrix [Figs. 6(b), 8(b), and 8(c)]. When the applied strain reaches the breaking point, the filler particles separate out from the matrix interface, indicating poor adhesion between the PP and the cellulosic filler [Figs. 6(b) and 8(d)]. On the other hand, in MAH–PP-modified composites, the polymer–filler interface is not the site for crack initiation [Figs. 7(b), 7(c), 9(b), and 9(c)]. In this case, stress due to externally applied strain induces a plastic deformation in the composite and orients the PP molecules along the direction of the applied strain until the sample breaks. The larger is the strain level, the greater is the molecular orientation. Thus, in modified composite matrix, stress due to applied strain apparently does not concen-

trate on the polymer–filler interface, since applied strain results in an “ordered” molecular arrangement surrounding the large filler particle surface. This observed orientation of plastic molecules is one of the possible reasons for the high strength of such composites.

Figures 7(d) and 9(d) are the optical microphotographs of the strain-induced failure surfaces of the modified composites. It is evident that the failures are ductile in nature with practically no “dropping out” of filler particles from the fractured composite surface.

Thermal Aging Resistance and Flame Retardancy

The thermal aging resistance and flame-retardance characteristics of selective modified and dynamically cross-linked sawdust-filled PP composites are given in Figure 10 and Table V, respectively. Though the phenolic resin-coated sawdust-filled PP composites offer good resistant to thermal aging and flame, the aging performance of epoxy-coated sawdust-filled

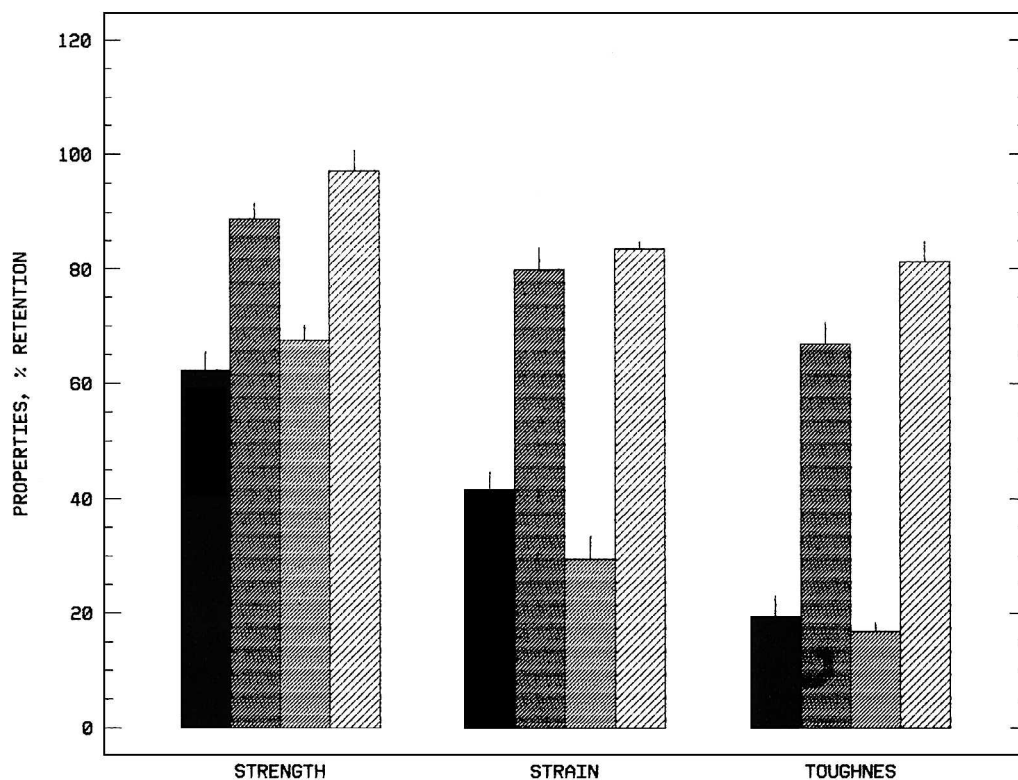


Figure 10 Aging resistance of various compositions in % retention of initial properties: (■) 35 wt % sawdust-filled PP (unmodified); (▨) 35 wt % sawdust-filled MAH–PP composite (composition 10); (▧) 35 wt % epoxy-coated sawdust-filled MAH–PP composite; (▩) 45 wt % phenolic resin-coated sawdust-filled MAH–PP composite (composition 15). Strength: max tensile strength; strain: strain at yield point; toughness: tensile toughness.

Table V Flame-resistant Properties of Composites

Composition No.	Composition ^a PP/SD/Coated-SD/MAH-PP	Sample Thickness (mm)	No. Ignition (ASTM D-635)	Burning Rate (mm/min)
4	65/35/0/0	1.53	1	46
6	64/25/9/0	1.45	1	51
7	65/18/17/0	1.52	1	39
8	65/9/26/0	1.52	1	37
9	65/0/35/0	1.40	1	38
10	55/35/0/10	1.43	1	43
11	55/0/35/10	1.44	1	41
15	55/0/45/5	1.57	1	38

^a Compositions are the same as given in Table II.

composites is somewhat lacking. The reason for this unusual thermal behavior of epoxy-coated sawdust-filled composite is not known. However, a marginal improvement in flame-retardance characteristics of the later composite is possibly due to the better anti-flaming property of the epoxy resin compared to that of the virgin PP.²⁰

CONCLUSIONS

The results of this work suggest a practical route to high-toughness thermoplastic composites based on PP and thermosetting resin-coated cellulosic fillers. Dynamic cross-linking (during melt-mixing) of a maleated-PP compatibilized and thermosetting resin-coated cellulose-filled PP composition produces a thermoplastic composite with tensile strength higher than that of unfilled PP and tensile toughness about as good as that of PP. The compatibilizing maleic anhydride graft PP might act by reducing (molten state) interfacial tension at the cellulose-PP as well as at the thermosetting resin-PP interfaces and also by increasing the interfacial adhesion in the "solidified-state" composite during its use.

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