Compatibilizing Effect of Different Anhydrides on Cane Bagasse Pith and Melamine–Formaldehyde-Resin Composites

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ABSTRACT: Melamine–formaldehyde-resin-based wood–polymer composites were prepared with cane bagasse pith as a filler. The filler was treated with 1% maleic, phthalic, and succinic anhydrides in xylene separately. The treatment was carried out for different time periods. The effects of the treatment were determined from the acid and ester values of the filler material after every treatment time. Therefore, treated and untreated filler materials (60 wt %) were separately employed for the composite preparation with melamine–formaldehyde as a matrix (40%). Various mechanical tests of the prepared composites showed the effect of the treatment. The mechanical properties were improved by the anhydride treatments up to a particular period of the treatment. Each of the anhydrides had a profound effect on the peculiar mechanical properties. Of the three anhydrides, succinic anhydride and phthalic anhydride appeared to be better compatibilizers for a treatment period of 2 h at a concentration of 1% in xylene. The inconsistency in the acid values and mechanical properties beyond 2 h of treatment with the anhydrides was due to chemisorption and desorption phenomena. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 88: 1768–1774, 2003

Key words: biomaterials; compatibilization; composite; esterification; mechanical properties; resin

INTRODUCTION

The effect of moisture absorption on the mechanochemical performance of wood–polymer composites is well known.[1–6] Wood–polymer composites face the problem of phase separation because of the polar nature of the filler and the nonpolar nature of the matrix. This phase separation gives a pathway for moisture to enter. Moisture results in further separation of the filler and matrix. Therefore, the composite no longer remains a unique structure. It requires the introduction of agents that enhance the compatibility through chemical bond formation. Chemical bonding restricts the penetration of water molecules in composites by converting the two phases into one. Kokta et al.[7–15] reported the effect of a compatibilizing agent and the nature of adhesion in composites of cellulosic fibers and polypropylene. They also studied the effect of phthalic anhydride (PA) as a compatibilizer on the mechanical properties of wood-fiber-reinforced polystyrene composites.

Lignocellulose is the basic building material present in all naturally occurring fibers. —OH is the functional group for these materials. Therefore, a reaction with an anhydride may transform the —OH functional group, which is prone to moisture absorption and ultimately phase separation, decreasing the possibility of moisture absorption. Maleic anhydride (MA) has been reported as a compatibilizer for the preparation of wood–polymer composites.[16,17] Moreover, maleated matrices, such as maleated polystyrene, are readily available in the market. Anhydrides tend to incorporate —COOH groups onto the lignocellulose filler, and this results in the formation of an ester linkage per acid group.[18] In a polar matrix such as novolac, maleation imparts linking between the lignocellulose filler and matrix resin.[17] The fiber loading capacity also increases when MA is used as a compatibilizer. A few technologies have been developed to modify a resin by the incorporation of lignin during resin synthesis.[19] Also, a review of adhesive innovation and production is available that may help researchers to work appropriately.[20] In an earlier work,[21] the capability of MA as a compatibilizer for composites based on thermosets and thermoplastic matrices was reported.

In this study, to set the optimum processing conditions, we ran the process of maleation for different periods of time. The results obtained from the mechanical testing of composites with an incorporated filler (cane bagasse pith) were compared among themselves (with respect to the treatment period) and with the untreated filler-filled composites. To verify MA as a compatibilizer, we also compared it with succinic

TABLE I
Proximate Analysis of Untreated Cane Bagasse Pith Employed as a Filler for the Preparation of Melamine–Formaldehyde-Based Wood–Polymer Composites

	Content					
	Moisture	Cellulose	Pentose	Lignin	Sugar	Ash
Wt %	50	45	28	20	5	2

anhydride (SA) and PA in the same manner with mechanical testing. With respect to the acid value of the treated filler, the results obtained from tensile, flexural, impact, and hardness testing provided evidence of the degree of compatibility attributed to specific properties of the anhydride to the composites prepared.

EXPERIMENTAL

Composites based on cane bagasse pith were prepared with melamine–formaldehyde resin with a pith/matrix ratio of 60/40 (w/w). The resin synthesis and preparation of cane bagasse pith as a ready filler material are discussed next.

Materials

The chemicals employed for the synthesis of the melamine–formaldehyde resin, melamine and formaldehyde, as well as MA, PA, and SA, which were used for the treatment of cane bagasse pith, were acquired from S.D. Fine Chemicals, Ltd. (Mumbai, India).

Cane bagasse pith, employed as a filler material for the preparation of the composites, was procured readily from a cooperative sugar factory, Shri Satpuda Sahakari Sakhar Karkhana, Ltd., located in Shahada, India. Table I presents an analysis of the pith used as a filler.[22]

Methods

Resin synthesis

Melamine was dissolved in formaldehyde in a molar ratio of 1/3. An acidic pH was maintained with oxalic acid. The reaction was continued at 110°C until a resin layer formed. The completion of the reaction was confirmed by the measurement of the appropriate number of water molecules formed. The resin layer was collected in a tray and dried in a hot-air oven at 70°C. After the drying was complete, the resin was converted into a powder form.

Treatment of the filler material

The pith was treated with MA, PA, and SA separately for different time periods (1, 2, 4, 6, 8, and 10 h). Before the treatment, the pith was dried at 60°C so that the removal of moisture (if any) would be ensured because moisture could interrupt the reaction between the filler and the treatment reagent. The anhydride concentration was kept at 1% in xylene for 100 g of pith. For the treatment, the requisite amount of oven-dried cane bagasse pith was placed in a round-bottom flask initially containing a 1% anhydride solution in xylene (1/20 w/v) and equipped with a water condenser. The reaction was carried out for 1, 2, 4, 6, 8, and 10 h with MA, SA, and PA separately, as stated earlier.

Determination of the acid value

For the determination of the acid values of pith samples separately treated for different time periods with the three anhydrides, the filler material was digested in neutral alcohol, and the acid value was found via titration against standardized alkali. The following relation was used to determine the acid value:

$$\text{Acid value} = [\text{Burette reading (mL)}$$
$$\times \text{Normality of alcoholic KOH}]/$$
$$[\text{Weight of sample (g)}]$$

Determination of the saponification value

An accurately weighed amount of cane bagasse pith treated separately with different anhydrides was placed in a round-bottom flask containing 50 mL of alcoholic KOH and provided with a water condenser. The digestion of the sample was attained by reflux for 1 h. The reaction mixture was titrated against a standardized acid solution. The following relation was employed to determine the number of groups that could be saponified:

$$\text{Saponification value} = [(\text{Blank} - \text{Back})$$
$$\times \text{Normality of acid}]/[\text{Sample weight (g)}]$$

Ester production took place along with an acid with respect to the conversion of every —OH group of the filler material. Therefore, the saponification of one —OH group should correspond to one acid plus one ester (i.e., the saponification value is the acid value plus the ester value, or twice the acid value).

Preparation of the composites

The oven-dried treated and untreated filler materials were mixed with powdered melamine–formaldehyde resin in a weight ratio of 60/40. Oxalic acid was used as a crosslinking agent at a concentration of 1.5% of the weight of the filler. The material was mixed well
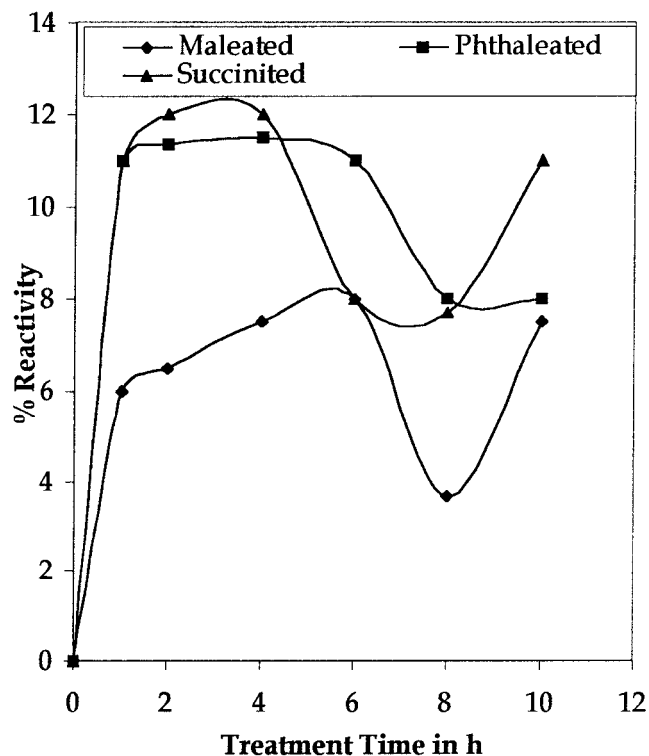
Figure 1 Reactivity of the three anhydrides with respect to the treatment time.

manually and poured into a die (10 cm × 10 cm × 0.5 cm). The die was then subjected to a compression-molding machine for curing and crosslinking. The curing time was 10 min under a pressure of 150 kg/cm² at 160°C. The die was allowed to cool down, and the sheet was ejected. Samples (10 cm × 1 cm × 0.5 cm) were cut with a power saw. A sample of each composite was used for tensile, flexural, impact, and hardness testing.

RESULTS AND DISCUSSION

Because of the treatments of the filler by the different anhydrides, the prepared composites appeared brownish black initially. There was no color difference between the composites with the three anhydride-treated fillers and the composites with untreated filler. However, the pith was gray, and the resin was white. This color change occurred because of the curing of the resin and the crosslinking between the filler and matrix and the resin chains. The composite with the phthaleated filler became yellow after lying on a shelf for 1 year. This happened because of the absorption of ultraviolet rays from the atmosphere by the phenyl ring present in PA.

Reactivity of the anhydrides

From Figure 1, it is very clear that the reactivity of the

anhydrides continued increasing with respect to the increasing treatment time up to a certain period, depending on the capacity of the anhydrides to incorporate the —COOH group at a given concentration.

SA tended to show a higher reactivity for the initial 2 h of the treatment that remained the same for a further 2-h treatment period. It decreased suddenly during the next treatment period and reached its lowest value after 8 h of treatment.

PA attained the maximum and minimum reactivity values, which lay nearer to those shown by SA. However, the achievements were gradual in comparison with SA. Also, after the lowest reactivity value was attained at the end of 8 h of treatment, there was no further change in the reactivity for the next 2 h of PA treatment, as found for MA and SA. MA was reported to be the most effective compatibilizer, but at this concentration, it appeared to be the least reactive compatibilizer. Also, it attained maximum reactivity later than the other two anhydrides. The achievement of the highest reactivity after 6 h of treatment increased with the treatment time. The value of the reactivity during this period of the treatment matched the corresponding value attained by SA. It showed a sudden decline in reactivity after 8 h of treatment, and this was the lowest of all three anhydrides. The reactivity of MA increased from 8 to 10 h. However, for phthaleation, the reactivity remained the same for that period, whereas succinition and maleation attained a higher activity. During this period of the treatment, the order of reactivity was as follows: SA > PA > MA.

Figure 2 illustrates the acid value of the filler after the treatments with the various anhydrides. Phthaleation proceeded with a more stable modification of the filler in comparison with the treatments by the other two anhydrides, as the change in the acid value was constantly in increasing order. SA showed major variations in the acid value for different treatment periods, although it achieved its highest acid value with a very short period of treatment. MA showed the lowest acid value with a lower degree of variation in the reactivity for all the reaction periods.

This trend was due to the fact that PA involved a phenyl ring present in the structure. This ring structure was more stable than the structures containing carbon–carbon double bonds and carbon–carbon single bonds for the stabilization of delocalized electrons in the ring by resonance.

MA, with its carbon–carbon double bond, increased the susceptibility of the bond breaking between carbon and oxygen by imparting more stability than SA, which contained a only carbon–carbon single bond.

The saturation of the anhydrides, by weight, in xylene was in the following order: MA > PA > SA. Therefore, a molar solution of MA in xylene was the most concentrated and that of SA was the most dilute for a concentration of 1 wt %, as SA was least soluble
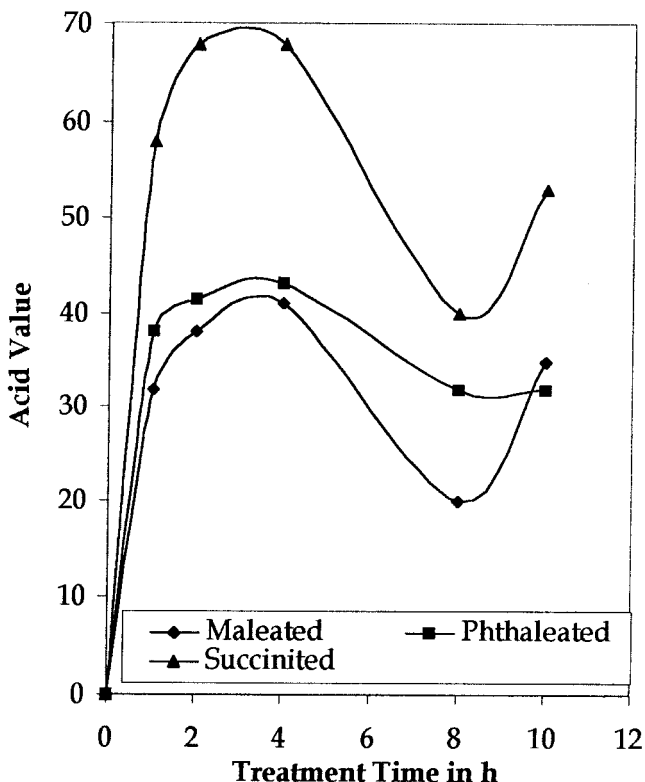
Figure 2 Acid value of cane bagasse pith after treatments with different anhydrides for different time periods.

of the three anhydrides in xylene. PA tended to produce more concentrated acid after hydrolysis by distilled water, whereas MA did not. Figure 3 shows the
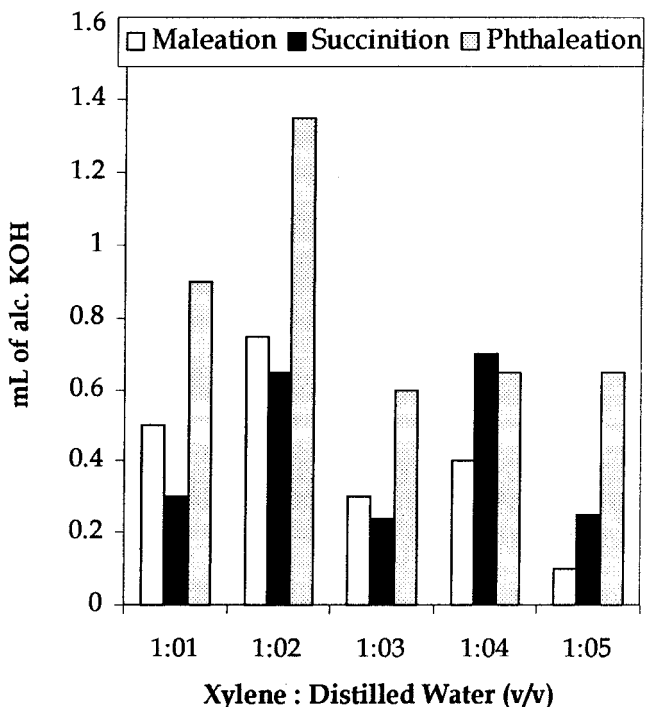

Figure 3 Capability of each anhydride used for treatment to impart acids after hydrolysis at its saturation in xylene.
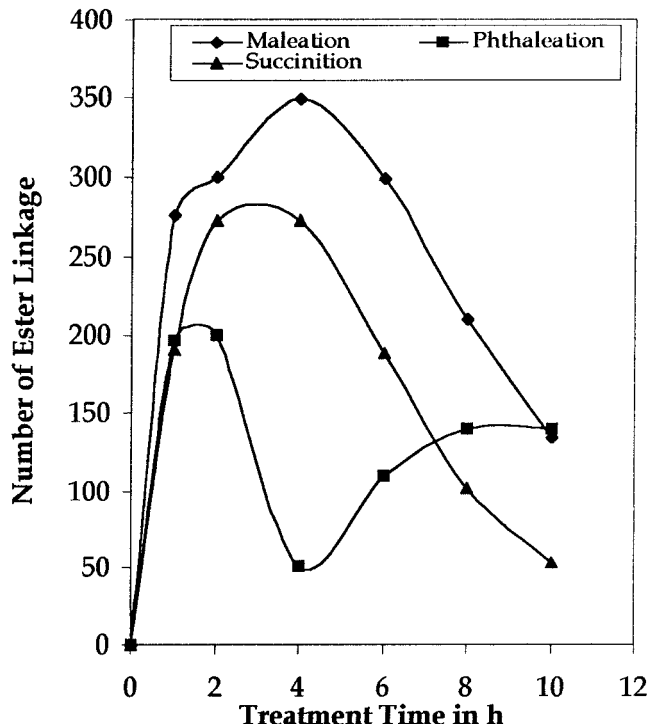

Figure 4 Excess esterification of cane bagasse pith by different anhydride treatments for various treatment times.

amount of alkali required to neutralize the acid produced at the saturation point of the anhydrides in xylene for various dilutions with distilled water. As the reaction proceeded, the dissolved amount of SA continued decreasing with respect to the time period of the treatment. The undissolved SA tended to dissolve more and, therefore, provided a greater molar concentration for treatment. This favored the treatment reaction kinetics being completed within a period of time even shorter than that required by PA. PA, which had moderate dissolution in xylene, tended to moderate reactivity, as shown in Figure 1.

As mentioned earlier, an ester linkage due to the anhydride treatment appeared. For the exact determination of the desorption, saponification of the treated material was followed. The acid group and ester could be saponified. It is also clear from Figures 1, 2, and 4 that all three of the anhydrides reacted readily for the initial period of treatment and tended to approach the complete esterification of the hydroxyl groups present on the surface. Once most of the hydroxyl groups converted into esters, the concentration of the hydroxyl groups decreased, and the rate of the treatment reaction also decreased with the available concentration of anhydride groups. As some of the SA remained undissolved at a 1% concentration, the dissolution of that undissolved anhydride continued with the use of dissolved anhydride for the production of acids along with the esterification of hydroxyl groups available in the filler. Therefore, SA tended to achieve the highest

reactivity. Figure 1 also shows that except for phthaleation, no trend was observed in the reactivity after the achievement of the highest reactivity. This was due to the ring structure present in PA. As is well known, the esterification of the —OH group with an anhydride is a chemisorption reaction.[23] Also, the hydroxyl groups in cellulose have a different reactivity.[24] The hydroxyl at C-2 is reported to be slightly more reactive than that at C, 6 which is about four times more reactive than the hydroxyl group at C-3. Reactions of cellulose lead to a nonuniform distribution of reacted groups.[25] Another report showed no reactivity difference between C-2 and C-3.[26] For the modification of cellulose via the xanthation of hydroxyl groups, the —OH groups at C-2 and C-3 are reported to be favored kinetically, but —OH at C-6 is favored thermodynamically.[27] Complete esterification was halted because of the spatial arrangement. Once the maximum conversion of available —OH groups was achieved, being reversible, the reaction desorption of —COOH groups started immediately.

The disrobed —COOH group resulted in the freed valence of the carbon atom. This carbon tended to have further bonding with unreacted —OH groups from the filler material. This increased the ester value, and so the compactness resulted in the structure of the composite.

Ester production took place along with an acid with respect to the conversion of every —OH group of the filler material. Therefore, saponification of one —OH group should correspond to the production of one acid plus one ester (the saponification value is equal to the acid value plus the ester value, or twice the acid value). However, in practice, no such correlation was found. The anhydride treatments tended to produce more ester linkages after a 2-h treatment period, as evidenced by the decreasing acid value, but more esterification was imparted with an increase in the treatment time for each of the anhydrides (Figs. 2 and 4).

Effect of different anhydride treatments on the various mechanical properties of wood–polymer composites prepared with cane bagasse pith and melamine–formaldehyde resin

Tensile properties

For phthaleated composites, the tensile strength continued increasing for up to 8 h of treatment, yielding the highest value at that point (69.2857 MPa). The composite containing 2-h-treated filler was observed to have the highest tensile strength (62.8571 MPa) for succinited composites. With an increase in the succinition of the filler from 4 to 10 h, the tensile strength of the composites decreased (Fig. 5).

For maleation, the highest value of the tensile strength was 57.1429 MPa for composites with 2- and 10-h-maleated filler. However, the tensile strengths
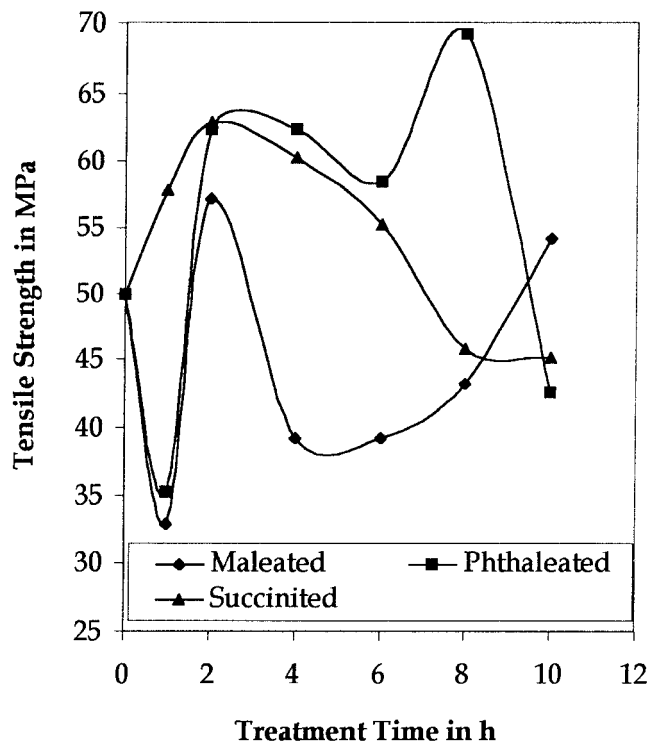

Figure 5 Tensile strength of wood–polymer composites prepared with cane bagasse pith and melamine–formaldehyde resin.

achieved with 4-, 6-, and 8-h-maleated filler were less than those of composites with 2-h-treated filler. However, the trend for the tensile strength for these composites was increasing up to 10 h. In comparison with the tensile strengths of SA and PA, the tensile strength for 2–8 h of MA treatment was less, but at 10 h, it was greater.

Young's modulus for the composites incorporated with the filler treated by MA, SA, and PA separately was also increasing with respect to the treatment time (Fig. 6). Succinition imparted the highest modulus of elasticity, whereas phthaleation imparted the lowest modulus value.

Flexural properties

As shown in Table II, the flexural strengths of the composites with maleated and phthaleated filler were of increasing order with respect to the increase in the treatment period. Succinition imparted an increase in the flexural strength for up to 4 h of treatment.

The flexural modulus (Table II) increased for up to 8 h of treatment for all three anhydrides. Succinition and maleation exhibited the maximum and minimum values of the flexural modulus of the composites, respectively, with a shorter range of variations in the flexural modulus values for the whole period of treatment. The strength of the composites with the maleated filler decreased with respect to the treatment
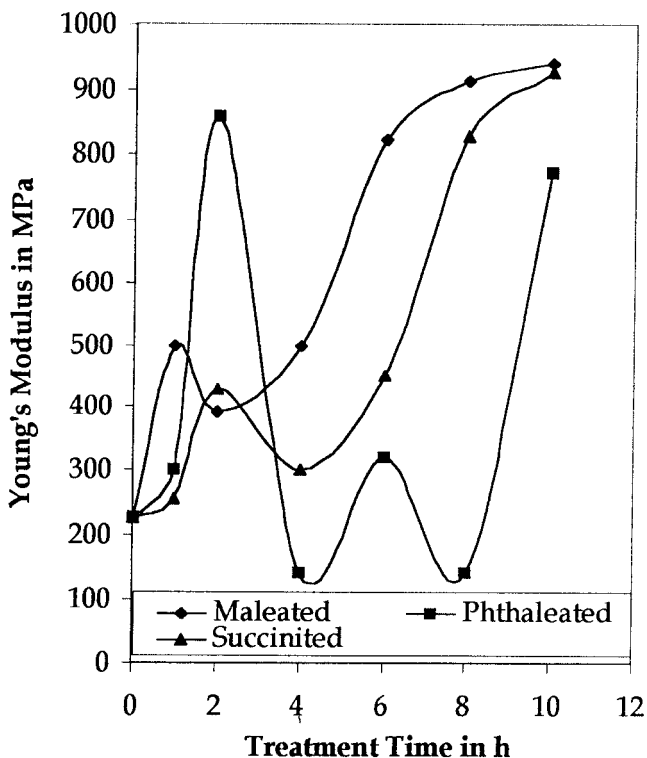
Figure 6 Young's modulus of wood–polymer composites prepared with cane bagasse pith and melamine–formaldehyde resin.
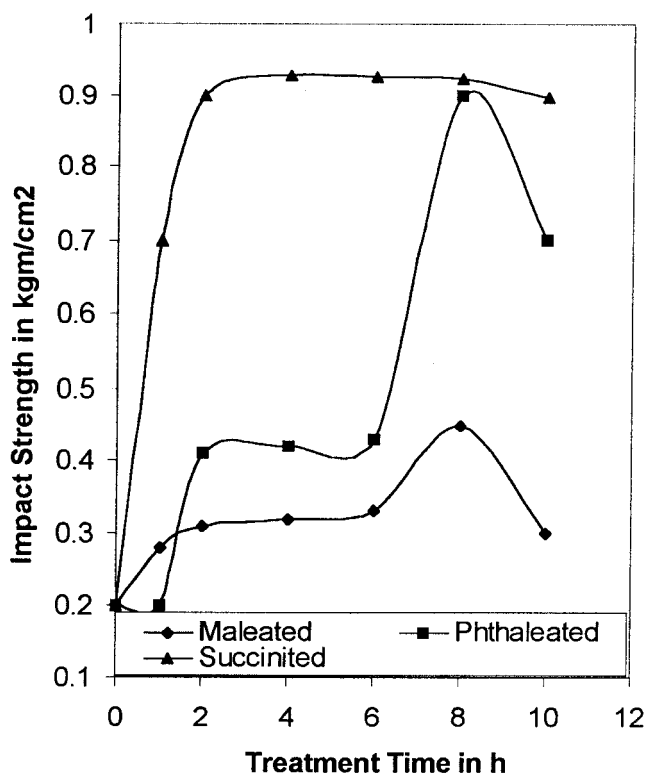

Figure 7 Impact strength of wood–polymer composites prepared with cane bagasse pith and melamine–formaldehyde resin.

time. The increasing trend in the modulus values clearly indicated that more esterification occurred.

Impact strength properties

Figure 7 illustrates the capacity for compensation with a sudden shock of composites prepared with cane bagasse pith treated for various periods of time with various anhydrides. It is very clear that phthaleation imparted the highest energy, followed by succinition and maleation. The higher energy of the composites from phthaleation was due to the ring structure. Also, the variation in the energy range by maleation was less than that of succinition.

TABLE II
Flexural Properties of Cane Bagasse Pith-Filled
Melamine–Formaldehyde Composites Treated
with Different Anhydrides

Time (h)	Flexural strength (MPa)			Flexural modulus (MPa)		
	MA	SA	PA	MA	SA	PA
0	13.2	13.2	13.2	140	140	140
1	41.0	31.0	13.0	185	160	170
2	37.0	34.0	24.6	468	430	420
4	29.0	38.0	19.5	460	420	390
6	28.5	14.0	31.0	420	300	430
8	21.5	32.5	41.5	427	600	470
10	20.0	11.5	41.8	433	400	385

Shore D hardness properties

Figure 8 illustrates the Shore D hardness values for the composites prepared with the filler treated separately with various anhydrides for different periods of time. It also shows that phthaleation conferred the hardest structure. For the initial period of the treatment time (1 h), the composites with the succinited filler exhibited the hardest structure because the reaction kinetics were faster. The composites with the succinited filler continued to be harder up to a filler treatment period of 8 h. However, at the end of the treatment (i.e., at 10 h), the composites with the phthaleated filler showed the greatest hardness. For up to 8 h of treatment, the order of the hardness was SA > PA > MA; this changed to PA > SA > MA by the end of the treatment period.

The reaction between the —OH groups from the filler and anhydride was a surface reaction, and it produced ester linkages along with the production of acid. The ester linkages resulted in an increased degree of crosslinking between the filler and matrix. Chemisorption and desorption affected the concentration of the acid that formed there. As esterification is a unidirectional reaction, the crosslinking via the ester linkages remained permanent even after the desorption of the —COOH group imparted by the anhydride. Therefore, as shown in Figures 5–8 and Table II, no similar trends were observed for the mechano-
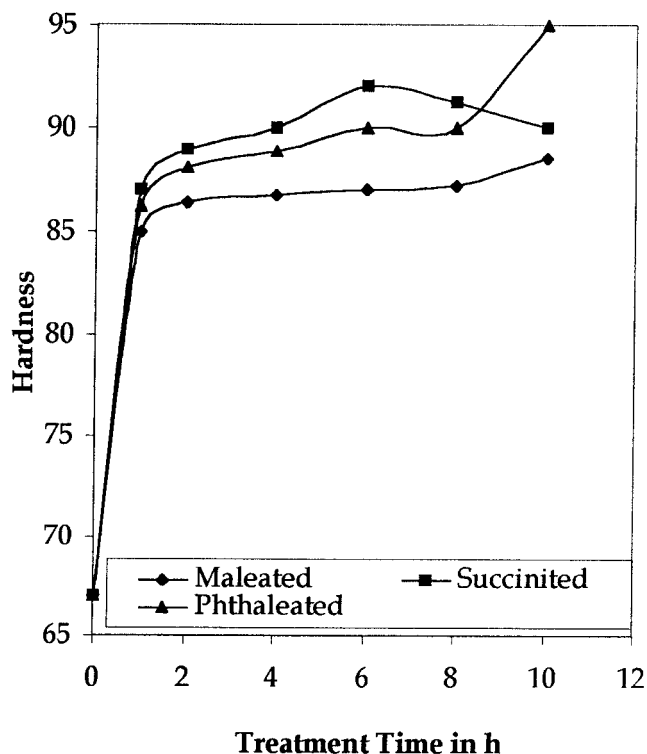
Figure 8 Shore D hardness of wood–polymer composites prepared with cane bagasse pith and melamine–formaldehyde resin.

chemical behavior of the composites prepared with the filler treated with the anhydrides. As explained earlier concerning the succinition of the filler, the undissolved SA provided more moles for further reaction by dissolution. As phthaleation proceeded with the formation of a stable modification in the filler material, the desorption of —COOH was controlled. This is clearly shown in Figure 4 by the constant acid values for treatment periods of 8 and 10 h. As the desorption of the —COOH groups tended toward more esterification, maleation attained the maximum degree of esterification. This was evidenced by the tensile strength and Young's modulus values for the composites prepared (Figs. 5 and 6). As the desorption started beyond a 2-h treatment time for all the anhydrides, treatment was given only for 2 h for better compatibilization at a 1% concentration of the anhydrides.

CONCLUSIONS

The following conclusions can be made from this study:

- MA, PA, and SA acted as compatibilizers for the wood–polymer composites.
- The incorporation of the —COOH group into the lignocellulose filler material by the anhydrides was a chemisorption-type mechanism.

- PA was the most stable treatment reagent and imparted greater hardness and impact strength, along with yellowing, to the composites.
- SA imparted a greater flexural property, as there was moderate esterification with a moderate liberation of —COOH groups.
- The carbon–carbon double bond present in MA facilitated a greater treatment reaction with freed carbon sites and free —OH groups from the filler, resulting more favorably in extra esterification and, therefore, a continuous increase in the tensile properties with increasing crystallinity.
- On the basis of the esterification trend, 2 h was the optimum time for treatment because, beyond this, the desorption of acid groups started in all the anhydride treatments.

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