The Effects of Fillers and Extenders on the Cure Properties of Phenol–Formaldehyde Resin as Determined by the Application of Thermal Techniques

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SYNOPSIS

The techniques of dynamic mechanical thermal analysis (DMTA) and differential scanning calorimetry (DSC) were used to examine the effects of the addition of various fillers and extenders (clay, pecan shell flour, and wheat flour) on the curing mechanism of a phenol–formaldehyde resol. The DMTA results indicated that the curing process was unaffected by any of the additives. The DSC thermograms showed a single exothermic peak that was not influenced to a great extent by the fillers or extenders. Comparison of viscosity measurements and gel time determinations showed slight differences in the physical properties of the uncured resins.

INTRODUCTION

Due to the high cost of petrochemicals, it has become increasingly desirable to reduce the amount of adhesive required in the manufacture of wood composites. One alternative bonding system that has been developed in plywood manufacture involves the combination of a filler or extender with phenol–formaldehyde resin.[1] It is reasonable to assume that similar systems may be used for bonding flakeboard; however, there are no reports of the use of filled or extended adhesives for flakeboard manufacture. A filler may be defined as a relatively nonadhesive substance added to an adhesive binder to improve its working properties, strength, or other qualities, whereas extenders generally exhibit some adhesive properties.[2] Proteinaceous and amylaceous substances are classified as extenders, whereas lignocellulosic and inorganic substances are classified as fillers.[1] The main objective for the use of such substances is to reduce the amount of primary binder that is required per unit area. Any resulting improvement in the board properties is also desirable.

Ebewele et al.[3] have examined the effects of various inorganic and organic fillers on the properties of phenol–resorcinol–formaldehyde adhesives. It was reported that these fillers had no effect on adhesive cure; however, the use of the filled adhesives showed a pronounced effect on the morphology of the wood–adhesive interphase and on the bulk adhesive properties. In a study conducted by Gollob et al.,[4] fillers were found to alter stress distribution in adhesive joints, thus improving fracture toughness.

The current report is concerned with the effects of a filler or extender on the properties of phenol–formaldehyde resin to be used for bonding flakeboard, with emphasis placed on examining the curing process. Thermosetting polymers such as the phenol–formaldehyde system undergo a complex curing process, which is dependent upon time, temperature and adhesive formulation.[5–7]

In this study, the techniques of dynamic mechanical thermal analysis (DMTA) and differential scanning calorimetry (DSC) were used to examine differences among the cure properties of the adhesives, while viscosity and gel time measurements were used to monitor physical properties of the ad-

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hesives. Dynamic mechanical methods which have been developed in the past two decades are quite effective for studying the curing process of thermosetting polymers. Techniques such as dynamic mechanical analysis (DMA)[6] and torsional braid analysis (TBA)[7,8] have been used to examine phenol–formaldehyde resins and urea–formaldehyde resins. Although these methods measure changes in mechanical properties during cure, DSC is used to examine thermal behavior during cure. DSC has been used to determine the influence of free formaldehyde content on the reaction occurring in phenol–formaldehyde resoles[9] and the effects of fillers on the curing process of a phenol–resorcinol–formaldehyde adhesive.[3]

MATERIALS AND METHODS

Adhesive Formulations

The phenol–formaldehyde (PF) resin that was used in the study was GP-3195 (55.9% solids) supplied by Georgia Pacific Resin (Conway, NC). This adhesive, as obtained from the manufacturer, was an A-stage resol, in which the phenol had been previously reacted with formaldehyde in the presence of an alkaline catalyst, such that reactive methylol groups were added to the phenolic molecules.

The fillers used in the study included pecan shell flour (Lignoflex) supplied by the Robertson Corp. (Brownstown, IN) and clay (Betagloss) supplied by E.C.C. America (Anglo-American Clays, Sandersville, GA). The extender used in the study was wheat flour (Glu-x) supplied by Robertson Corp. Each filler or extender was added to the resin at levels of 25 and 33% (clay and wheat flour) or 25 and 40% (pecan shell flour). It was originally intended to add each filler or extender at various levels up to 50%; however, the increased viscosities of the filled adhesives precluded the use of the higher levels. Water was added to adjust the total solids to 50–52%, and in some cases a small amount of 50% sodium hydroxide solution was added to decrease the viscosity. The resin formulations are summarized in Table I. The resin as delivered from the manufacturer was used as a control.

Viscosity and Gel Time

The viscosity was determined with a Brookfield LVT viscometer at 25°C and was measured immediately after each adhesive was mixed and after storage at room temperature for 24 h.

The gel time was determined with a Sunshine gel time apparatus with the sample tube immersed in a boiling water bath at 100°C.

Dynamic Mechanical Thermal Analysis (DMTA)

For DMTA, a Polymer Laboratories dynamic mechanical thermal analyzer was used. Several drops of the adhesive mix were transferred to a glass fabric, spread to form a uniform layer, and the sample was wrapped in a square of aluminum foil. The instrument was operated in the dual cantilever bending mode with an applied frequency of 10 Hz. The temperature was scanned from 30 to 175–200°C at a rate of 2.5°C/min.

Differential Scanning Calorimetry (DSC)

The DSC data were obtained with a Perkin-Elmer DSC-7 differential scanning calorimeter. A portion (5.0–15.0 mg) of each sample was sealed in a stainless steel, large-volume capsule following the procedure reported in Ref. 5, and an empty capsule was

Table I Formulations of Phenol–Formaldehyde Adhesives

	Amount of Component (g)				
Adhesive	Water	Filler or Extender	PF Resin	50% NaOH	% Solids
PF resin (control)					55.9
25% Clay	685	490	2625		51.6
25% Pecan shell flour	700	490	2625	10	51.4
25% Wheat flour	700	490	2625		51.4
33% Clay	900	647	2345		50.4
40% Pecan shell flour	900	784	2100	30	51.8
33% Wheat flour	900	647	2345		50.4

used as a reference. The temperature of the instrument was programmed from 40 to 200°C at a scan rate of 10°C/min. The instrument was calibrated with indium.

RESULTS AND DISCUSSION

The results of the viscosity and gel time measurements are presented in Table II. The initial viscosity gives an indication of the effect of the filler or extender on the properties of the resin before curing. If the viscosity is greater than 0.600 Pa s, difficulties will be encountered in achieving adequate adhesive distribution when spraying flakes. As would be expected, there is an increase in viscosity with the addition of a filler or extender. It was found that those adhesives having high viscosities could be warmed to 40°C, giving acceptable spraying properties. The 24-h viscosity measurements give an indication of the effects of the fillers or extender on the storage properties of the resin, which would not be expected to change appreciably after 24 h. Only slight increases in the viscosity were observed after 24 h.

Gel time is a technique that is used to measure the cure time of thermosetting polymers at a constant temperature, and may be considered a relative measure of the rate of bond formation in fiberboard.[10] The gel times of the resins containing clay or pecan shell flour fillers were within acceptable limits. The resins containing wheat flour extender displayed greatly decreased gel times, and further examination by DMTA and DSC was deemed necessary to investigate the nature of these differences.

Dynamic mechanical thermal analysis (DMTA) gives a description of the viscoelastic behavior of an adhesive throughout the curing process. The DMTA curves (log E' and tan δ) for the experimental adhesives (Figs. 1–3) show only minor differences. Duplicate DMTA runs of the samples gave reproducible results. It should be noted that each of the filled and extended resins, which exists initially as a viscous liquid, shows a higher initial storage modulus (log E') than the control, due to the higher viscosity and to added rigidity from the filler or extender. As the temperature is increased, the curve has a slight downward slope due to the slight decrease in viscosity. This portion of the curve is somewhat erratic, because the sample lacks stiffness. As the resin undergoes gelation followed by vitrification to form a glassy solid, there is a sharp inflection in the curve. A further increase in temperature causes softening of the solid, revealed by the downward slope of the curve. These results indicate that the addition of a filler or extender has no effect on the curing process. Additional evidence is provided by comparing the loss tangent (tan δ) curves (Figs. 1–3) of the filled and extended resins to that of the control. A single transition is exhibited in the tem-

Table II Viscosity and Gel Time Measurements of the Phenol–Formaldehyde Adhesives

Adhesive	Viscosity (Pa s) (25°C) Initial	24 h	Gel Time (min) (100°C)
PF resin (control)	0.265		23.1
25% Clay	0.700	0.720	27.6
25% Wheat flour	0.514	0.500	16.2
25% Pecan shell flour	0.370	0.375	24.2
33% Clay	1.200	1.200	29.5
33% Wheat flour	0.665	0.610	2.0
40% Pecan shell flour	1.540	1.940	25.6

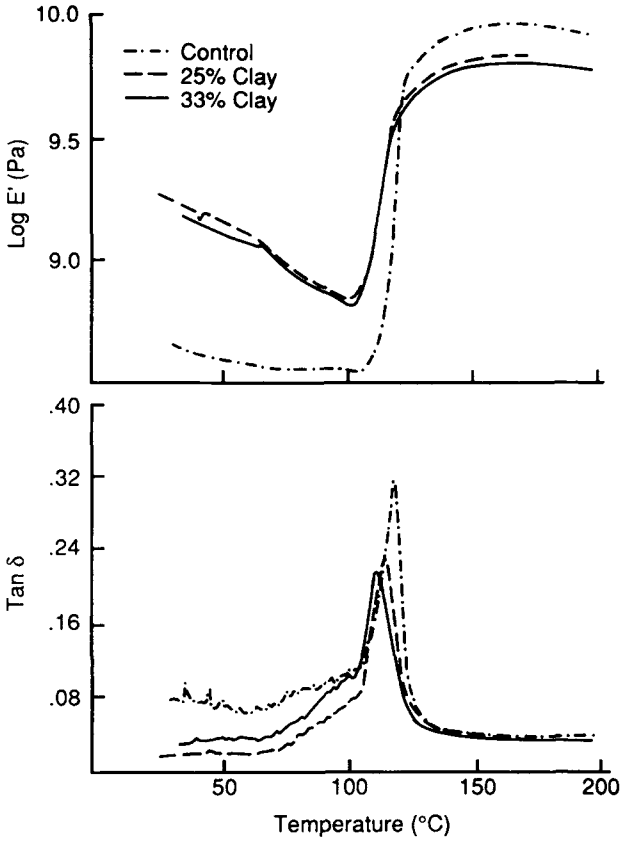

Figure 1 DMTA curves of phenol–formaldehyde adhesive containing clay filler.

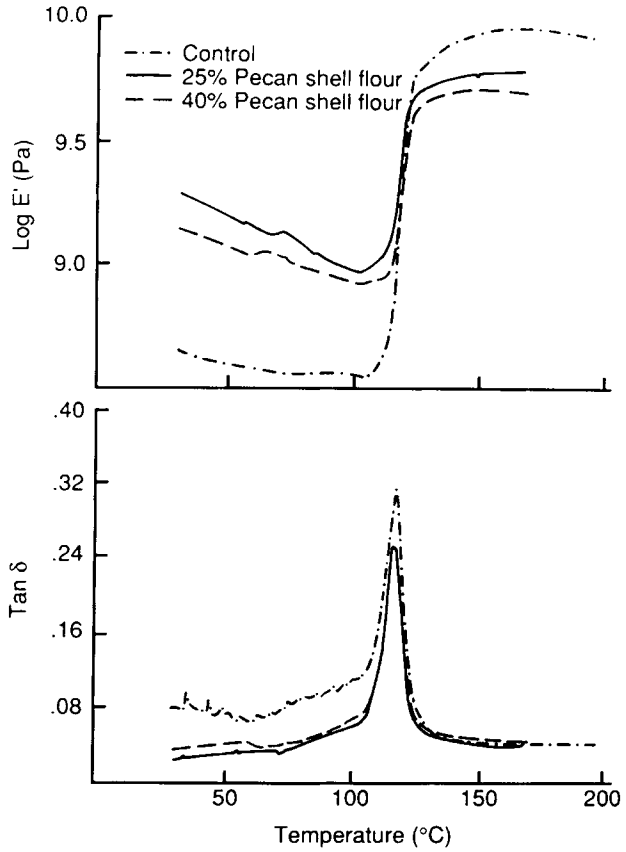

Figure 2 DMTA curves of phenol–formaldehyde adhesive containing pecan shell flour filler.

perature range of 115–120°C in each case, with no peak broadening, shoulders, or other irregularities that would indicate atypical behavior.

The results of differential scanning calorimetry are presented in Figures 4 and 5. The repeatability of the results was established by running a duplicate of each sample. The control and the resins containing clay or wheat flour exhibit similar thermograms, with a sharp exothermic peak in the range of 140–150°C. In a previous report,[9] the DSC thermograms of phenol–formaldehyde resoles showed an exothermic peak between 98 and 129°C corresponding to the addition of formaldehyde to the phenolic rings to form hydroxymethylphenols, and an exotherm in the range of 139–151°C corresponding to the crosslinking reactions. The intensity of each of these peaks was related to the resin formulation (concentration of NaOH and molar ratio of formaldehyde-to-phenol). The single peak in each of the thermograms shown in Figures 4 and 5 corresponds to the occurrence of the condensation reaction. This interpretation is supported by two pieces of information. First, the resin that was obtained for use in the experiment was an A-stage resol, in which the addition reaction had already occurred. Also, the temperature of the peak in each thermogram is within the range previously reported for the crosslinking reaction.

Examination of the DMTA and DSC data for the resins to which wheat flour has been added indicate that the extender does not affect the mechanism of the curing reaction, in contrast to the gel time results. A plausible explanation is that the irregularities observed in the gel times may be due to the occurrence of physical changes, such as swelling and thickening, upon heating. Sellers[1] has noted that proteinaceous and amylaceous extenders may impart important rheological properties to adhesive mixes, including a tackier consistency. He reports that under alkaline conditions and at slightly elevated temperatures, such extenders in phenol–formaldehyde mixes will tend to gel, which is in agreement with the results reported here.

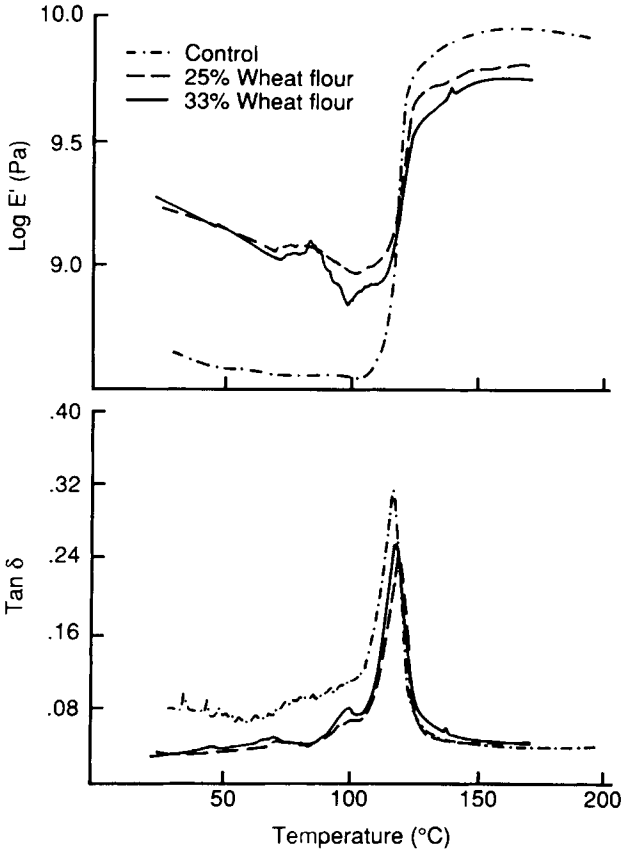

Figure 3 DMTA curves of phenol–formaldehyde adhesive containing wheat flour extender.

The DSC thermograms for the resin containing pecan shell flour show some anomalous behavior. The peaks in these thermograms are broadened and occur at slightly increased temperatures. The extent of deviation from the control is related to the level of the filler. Nutshell flours, which are classified as lignocellulosic fillers,[1] generally do not exhibit adhesive properties. It is suggested that tannins, which are present in the pecan shell flour, may be participating in the reaction, thus affecting the thermogram. Condensed tannin extracts from nutshells have been used as a replacement for a portion of the phenol in wood adhesives.[11,12] Under similar conditions to those used in processing phenol–formaldehyde adhesives, condensed tannins may react rapidly with formaldehyde.[13] The presence of tannins in a phenol–formaldehyde adhesive would thus influence the reaction of phenol with formaldehyde and would be evident in the DSC results; however, unless there were an effect on the mechanical properties of the adhesive, the DMTA scans would not be expected to show any differences.

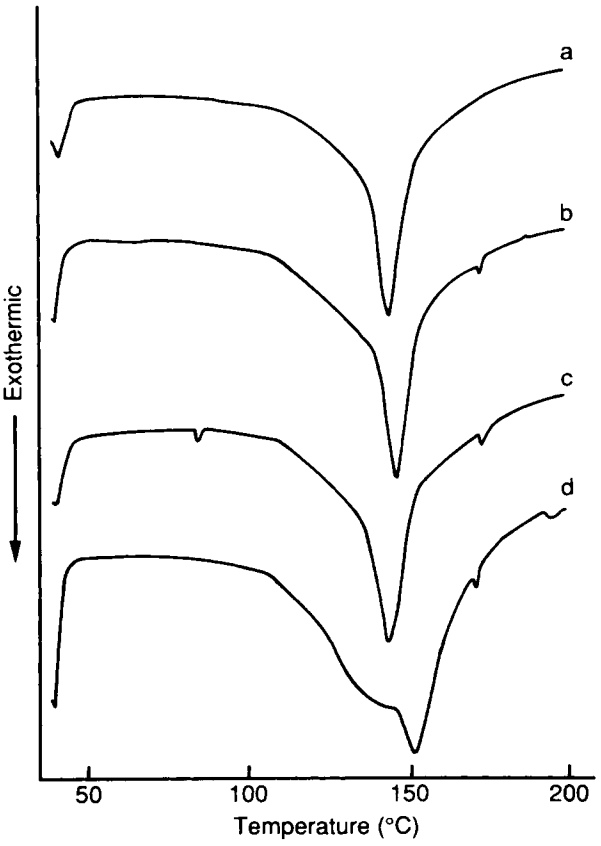

Figure 4 DSC thermograms of phenol–formaldehyde adhesives containing 25% filler or extender: (a) control; (b) clay; (c) wheat flour; (d) pecan shell flour.

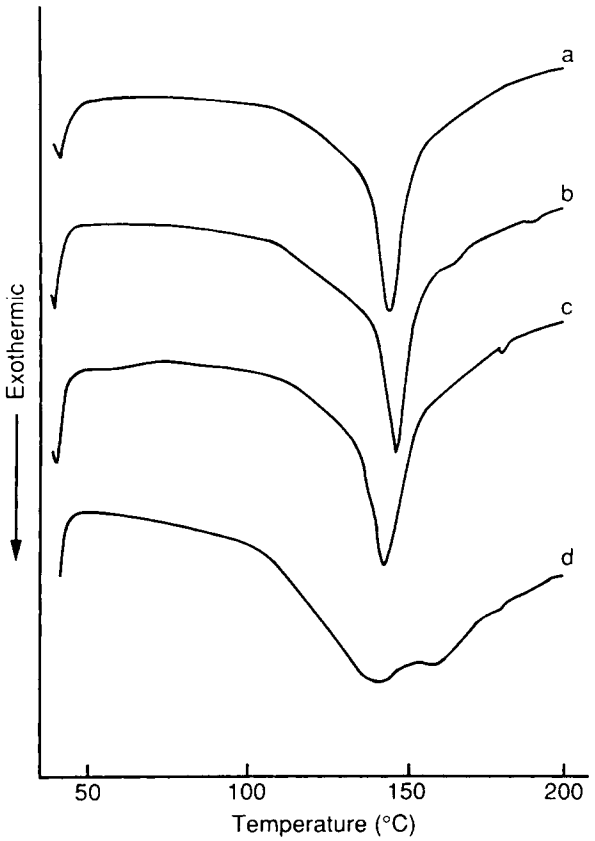

Figure 5 DSC thermograms of phenol–formaldehyde adhesives containing 33% or 40% filler or extenders: (a) control; (b) 33% clay; (c) 33% wheat flour; (d) 40% pecan shell flour.

The DMTA curves, the DSC results, the viscosities, and the gel time data for the resin blends containing the clay filler showed no significant irregularities upon comparison to the control. Because clay is classified as an inert, inorganic filler,[1] these results are indicative of the expected behavior, such that the main effect and chief purpose of the addition of clay to the phenol–formaldehyde resin is as a diluent to the primary binder.

CONCLUSIONS

Experimental results indicate that the addition of a filler or extender to a phenol–formaldehyde resin has little or no effect on the curing properties of the resin. The information obtained from dynamic mechanical thermal analysis and differential scanning calorimetry show that the mechanism of the curing process is essentially unchanged by the additives.

Irregularities in the DSC curves of the adhesives containing the pecan shell flour filler suggested that there may be some participation of the filler in the curing reaction due to the presence of condensed tannins. The results of viscosity and gel time measurements indicate slight differences in the physical properties of the uncured experimental resins. These may be of consequence in working with the resin, but are not important in the curing process.

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