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EFFECTS OF INITIAL PHENOL-FORMALDEHYDE (PF) REACTION PRODUCTS ON THE CURING PROPERTIES OF PF RESIN

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Abstract

Differential scanning calorimetry (DSC) was used to study the effects of varying NaOH concentrations on the thermochemical curing properties of 2,4-dimethylol phenol (2,4-DMP), and 2,6-dimethylol phenol (2,6-DMP). Analysis of the DSC curves showed significant differences in the thermochemical curing behavior of these compounds with increasing NaOH : DMP molar ratios, in terms of the peak shape, position of the reaction peaks, (T_p), along the temperature scale and energy of activation, E. The curves consisted of either a single, two or three exothermic peaks which indicated the occurrence of multiple reactions. One of these peaks was observed for the entire range of NaOH molar ratios, and is attributed to the self-condensation reaction. For the 2,4-DMP, NaOH had the effect of lowering the T_p of curing from 212°C in the uncatalyzed state to 135°C between 0.15–0.75 molar ratios. The lowest value of E, however, was 111 kJ mole^{-1}, only through 0.45–0.60 molar ratios and this combined with the above, points to this concentration range as the optimum NaOH level. Similarly, the T_p of curing for the 2,6-DMP was lowered from 211°C in the uncatalyzed state, to a minimum of 116°C at the NaOH : 2,6-DMP molar ratio of 0.45. At this ratio, E also had the lowest value of 117 kJ mole^{-1} and this suggests that 0.45 molar ratio is the optimum NaOH level.

Keywords: activation energy, differential scanning calorimetry, 2,4-dimethylol phenol, 2,6-dimethylol phenol, thermochemical

Introduction

Rapidly diminishing availability of high quality large-diameter logs has led to increasing demands for the production of reconstituted wood products such as particle board and plywood. The viability of reconstituted wood products industries greatly depend on the use of suitable wood adhesives. Some of the commonly used thermoset

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wood adhesives in Australia are phenol-formaldehyde (PF), resorcinol-formaldehyde (RF), melamine-urea-formaldehyde (MUF) and urea-formaldehyde (UF).

Of these, the PF type adhesives are environmentally more acceptable because of negligible formaldehyde emission. They are structurally the most durable, provide high quality wood bonding, and are suitable for use under all climatic conditions. However, conventional PF adhesives are slower curing, require higher cure temperature, and are less tolerant to variations in anatomical features and wood substrate properties such as moisture content and density, which limit their gluing capacity [1].

It is generally agreed that the initial polymerization in the phenol-formaldehyde reaction is a two-stage process. According to the reaction scheme in Fig. 1 [2], in the first-stage phenol reacts with formaldehyde to form five addition reaction products, i.e. two monomethylol-(MMP) phenols and then two dimethylol-(DMP) phenols and finally a trimethylol-(TMP) phenol (reaction 1). The second stage of the reaction involves the condensation reaction between two molecules (reactions 2 to 4). At this stage, three major mechanisms may occur depending on the initial reaction condi-

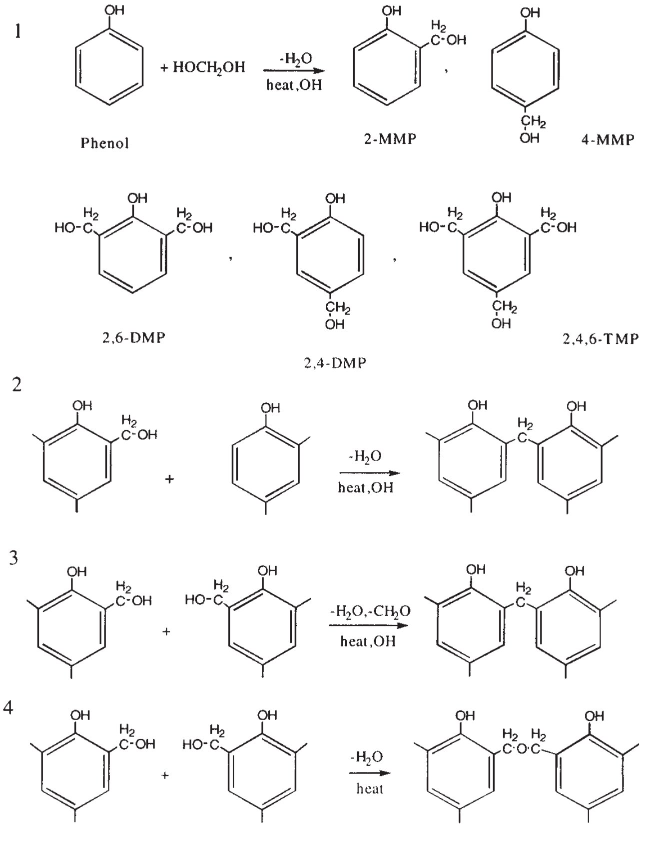

Fig. 1 Reaction mechanisms during the phenol-formaldehyde (PF) resol formation: 1 – addition reactions; 2–4 – condensation reactions

tions. One involves the condensation of the methylol groups with active protons on unsubstituted phenols to form higher order reaction products linked via a methylene bridge (reaction 2). The other possible scheme is the condensation reaction between methylol groups on different phenols (reaction 3). Both reactions are accompanied by the release of one molecule of water per reaction, and in the latter scheme formaldehyde is also released which may further add to unreacted phenols and hence cause additional condensation. The third mechanism is similar to reaction 3, however, in this case dibenzyl ether linkages are formed and similarly water is released (reaction 4). The formation of ether links, are rare in alkaline catalyzed PF reactions but occur in neutral or slightly acidic conditions. With alkaline catalyst and excess formaldehyde the condensation reactions are allowed to proceed to form a resol which is a mixture of various low and high molecular mass PF condensation products, but still water soluble. The resols are applied as wood adhesives. Further heating continues the condensation reactions to form an insoluble three dimensionally cross-linked structure.

It has been established that the mechanism and kinetics for the formation of the five initial addition products and hence their condensation to form higher order prepolymers is dependent on the initial formulation parameters, namely, the type and amount of catalyst, reaction temperature and the molar ratio of the reactants. These factors determine the structure of the higher molecular mass PF products comprising the resol, and hence effect the thermochemical curing properties of the mixture, namely the rate of resinification. The determination of reliable kinetic data for phenolic resin formation is complicated, and therefore, reported data differ considerably, because a slight change in the reaction conditions profoundly influences the kinetic results obtained [3].

Approaches taken to gain further understanding of the kinetics of PF resol formation have included the variation of the synthesis parameters, particularly the phenol to formaldehyde ratio and less intensely, the type and amount of catalyst [2, 4–16]. The most common techniques employed for the investigations have been quantitative paper chromatography (PC), high-performance liquid chromatography (HPLC), gel permeation chromatography (GPC), nuclear magnetic resonance (NMR) and infrared spectroscopy (IR) and to a lesser extent differential scanning calorimetry (DSC). In these studies, the rates of formation and condensation of the five initial addition products in the PF reaction were monitored and some of the condensation products formed identified. Freeman and Lewis [8] in particular carried out an intensive study and found the relative reaction rates for the formation and disappearance of 2-MMP, 4-MMP, 2,4-DMP and 2,6-DMP.

The results obtained for the above studies are mostly based on specific reaction parameters such as a particular temperature and alkalinity level. Despite the fact that the rate constants for the reactions of some of the methylol phenols, particularly 2,6-DMP, are relatively large, GPC results have identified unreacted mono-, di- and tri-substituted phenols and dimers in addition to low molecular mass oligomers in the resol. This indicates that the reaction conditions may influence the reactivities of these compounds to form higher order oligomers and further to this, their presence in the resol may have an effect on the overall curing property.

Little is known about the thermochemical properties of the initial PF addition and condensation products and the effects of their presence in the resin during the curing reaction. There is also limited information on the effect of NaOH level on the curing process. In a series of studies using model compounds of the initial addition and condensation products, our group examined the thermochemical properties of the 5 addition monomer compounds individually with and without the presence of NaOH to better understand the effect of NaOH level on the condensation reactions. The results for the monomers, 2-MMP and 4-MMP in the presence of varying amounts of NaOH have been previously reported [17].

In this paper we discuss the effects of the presence of NaOH on the thermochemical curing properties of 2,4-DMP and 2,6-DMP. DSC was used for the study and the resulting curves analyzed in terms of peak shapes, peak temperature, T_p, of curing and energy of activation, E, of the curing reaction.

Experimental

Materials and sample preparation

Compounds of 2,4- and 2,6-DMP were synthesized according to the method of Freeman [18]. Sodium hydroxide (analytical grade) was obtained from BDH Chemicals Ltd.

Aqueous solutions (0.040 M) of 2,4-DMP and 2,6-DMP, together with solutions of 0.006, 0.012, 0.018, 0.024, 0.030 and 0.040 M aqueous sodium hydroxide were prepared and mixed at room temperature to form molar ratios of NaOH:DMP ranging from 0.15 to 1.0. These mixtures were freeze dried and stored at –5°C prior to DSC runs.

Instrumental procedure

The DSC runs were carried out using a Perkin Elmer DSC (Pyris1) under a constant purge of nitrogen gas (20 cc min^{-1}). Temperature calibration was performed by determining the heats of fusion of pure indium metal (99.9% purity). The freeze dried samples were weighed directly into the stainless steel pans specifically designed for DSC use and sealed (the mass of the samples ranged from 1 to 4 mg). The sealed samples were heated in the DSC using an empty sample pan as reference. These sealed pans can withstand pressures up to 24 atm and, hence, reactive volatiles were able to be contained. DSC curves were recorded at four scan speeds ranging between 2.5 to 20°C min^{-1} in the range 40–200°C. Baselines were obtained by re-scanning the cured sample and subtracting from the sample scan using relevant Pyris computer software. DSC runs were made in duplicate and the reproducibility of the data was ±5%.

Analysis of the DSC scans

The DSC curves were analyzed for peak shape, peak temperature, T_p, and for kinetic parameter, E. Values for E were obtained according to Kissinger’s relationship between heating rate and peak exotherm as discussed previously [17].

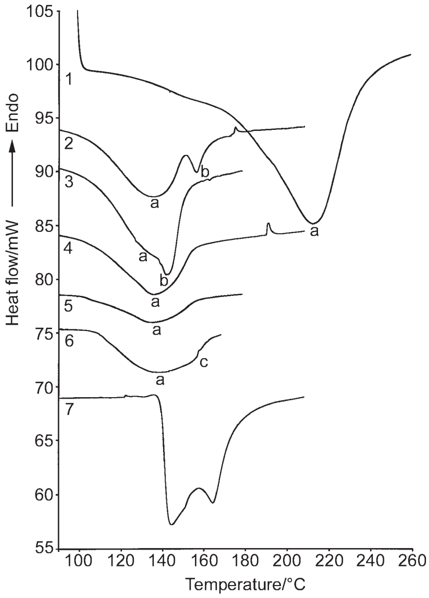

Fig. 2 DSC curves for the self-condensation of 2,4-DMP in the presence of varying NaOH : 2,4-DMP molar ratio obtained at 10°C min^{-1} scan rate. Curves: 1 – 0.00, 2 – 0.15, 3 – 0.30, 4 – 0.45, 5 – 0.60, 6 – 0.75, 7 – 1.00

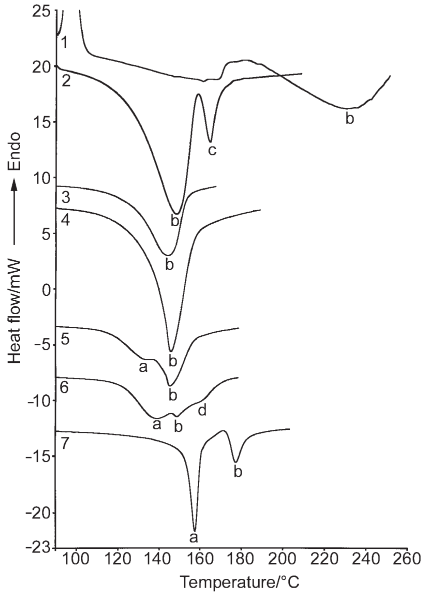

Fig. 3 DSC curves for the self-condensation of 2,6-DMP in the presence of varying NaOH : 2,4-DMP molar ratio obtained at 10°C min^{-1} scan rate. Curves: 1 – 0.00, 2 – 0.15, 3 – 0.30, 4 – 0.45, 5 – 0.60, 6 – 0.75, 7 – 1.00

Results and discussion

Figures 2 and 3 show the DSC curves obtained for 2,4-DMP and 2,6-DMP, respectively, in the presence of varying amounts of NaOH. The curing characteristics of each sample are summarized in Tables 1 and 2 in terms of peak temperature of curing, (T_p), and energy of activation, E, of the reactions corresponding to the particular T_p.

The DSC traces give information about the crosslinking reactions that occur while the samples are subjected to a heating rate program. The curves in the figures show significant differences in the thermochemical curing behavior of the compounds, as the NaOH concentration is increased, in terms of the shape and position of the reaction peaks along the temperature scale. The curves consist of either a single, two or three observable exothermic peaks indicating the occurrence of multiple reactions possibly in sequence or parallel to the main reaction. This renders a full analysis of the DSC curves difficult so only a broad and general interpretation of the curves are presented at this stage.

Table 1 Curing characteristics of 2,4-DMP at various NaOH:2,4-DMP molar ratios. T_p values obtained at 10°C min^{-1} scan rate

NaOH : 2,4-DMP molar ratio	$T_{p\,(a)}$/	$T_{p\,(b)}$/	$T_{p\,(c)}$/	$E_{(a)}$/	$E_{(b)}$/	$E_{(c)}$/
	°C			kJ mol^{-1}		
0.00	212	–	–	66	–	–
0.15	135	156	–	102	136	–
0.30	134	142	–	130	108	–
0.45	136	–	–	111	–	–
0.60	135	–	–	112	–	–
0.75	137	–	153	110	–	131
1.00	144 and 163			151 and 106		

Table 2 Curing characteristics of 2,6-DMP at various NaOH:2,6-DMP molar ratios. T_p values obtained at 10°C min^{-1} scan rate

NaOH : 2,6-DMP molar ratio	$T_{p\,(a)}$/	$T_{p\,(b)}$/	$T_{p\,(c)}$/	$T_{p\,(d)}$/	$E_{(a)}$/	$E_{(b)}$/	$E_{(c)}$/	$E_{(d)}$/
	°C				kJ mol^{-1}			
0.00	–	211	–	–	–	57	–	–
0.15	–	148	164	–	–	97	131	–
0.30	–	145	–	–	–	131	–	–
0.45	–	143	–	–	–	117	–	–
0.60	134	145	–	–	127	116	–	–
0.75	139	149	–	161	105	116	–	134
1.00	163	177	–	–	167	218	–	–

Following the DSC scans, all the samples, except the samples with 1.0 molar ratio of NaOH, became rigid materials and hence appeared to have fully cured. To confirm this observation, they were immersed in acetone (solvent) to check for solubility and as they were unaffected by the solvent confirmed that they were cured. The sample with 1.0 molar ratio of NaOH did not melt and remained a powder even following the curing process. These samples were also immersed in the solvent and did not dissolve, confirming that they had also been cured. It therefore appears that the reaction peaks at $T_{\mathrm{p\,(a)}}$ for the 2,4-DMP (Fig. 2, curves 1 to 6) and peaks at $T_{\mathrm{p\,(b)}}$ in the case of the 2,6-DMP (Fig. 3, curves 1 to 7), are due to the self-condensation (curing) reactions between the methylol groups on the phenol, because of the observed consistent appearance of these peaks for the entire range of experimental conditions. For the 2,4-DMP at the 1.0 molar concentration of NaOH, the two peaks in Fig. 2, curve 7, are not assigned at this stage, due to uncertainty as to which of the two peaks can be attributed to the curing reaction.

Following the analysis of the DSC curves, a number of interesting differences and similarities can be observed, in terms of the positions of the reaction exotherms, T_{p}, and for the values of their corresponding activation energies, E (Figs 2 and 3 and Tables 1 and 2). In the uncatalyzed condition both compounds had one characteristic peak exotherm at approximately 211°C, $T_{\mathrm{p\,(a)}}$ for the 2,4-DMP (Fig. 2, curve 1) and $T_{\mathrm{p\,(b)}}$ for the 2,6-DMP (Fig. 3, curve 1). At the NaOH : DMP molar ratio of 0.15, the position of the peaks shifted significantly to lower temperatures, approximately to 135°C for 2,4-DMP (Fig. 2, curve 2 and Table 1) and to 145°C for the 2,6-DMP (Fig. 3, curve 2 and Table 2). For both compounds these T_{p} values remained constant until the ratio of 1.00 was reached, at which concentration the peak shapes again changed significantly (Fig. 2, curve 7 and Fig. 3, curve 7). The E values corresponding to these peaks, on the other hand, increased at the NaOH:DMP molar ratio of 0.15, from 66 to 102 kJ mol^{-1}, for the 2,4-DMP (Table 1) and from 57 to 97 kJ mol^{-1} for the 2,6-DMP (Table 2) and for both compounds, the values continued to increase to a peak of 130 kJ mol^{-1}, until 0.30 molar ratio was attained (Tables 1 and 2). This result is consistent with the view [3] that at higher alkali concentrations, the rate of formaldehyde addition to the phenolic ring is increased, while the rate of formation of methylene linkages between the methylol groups are decreased. Between 0.30 and 0.45 ratios, the E values for this reaction decreased to 111 kJ mol^{-1} for the 2,4-DMP and to 117 kJ mol^{-1} for the 2,6-DMP (Tables 1 and 2). These values remained constant in the range of 0.45 to 0.75 molar ratios. At 1.00 molar concentration, there was a marked increase in the activation energies for both compounds. This may be due to the fact that the samples did not melt during the DSC temperature scan and hence the contact between molecules to form the cross-linking reactions could not be achieved as efficiently as for the samples that melted prior to the curing reaction.

A further observation is the appearance and disappearance of other smaller reaction exotherms at particular molar ratios. As indicated in Fig. 2 and Table 1, for the 2,4-DMP, these appeared at higher temperature regions and at the molar ratios of 0.15, 0.30 and 0.75. At 0.15 molar ratio, an additional peak, $T_{\mathrm{p\,(b)}}$, at 156°C emerged (curve 2), with a corresponding $E_{(b)}$ value of 136 kJ mol^{-1}. This was significantly higher than $E_{(a)}$ for the peak at $T_{p\ (a)}$. It thus appears that at this particular NaOH concentration of 0.15, the reaction at peak $T_{p\ (a)}$ (with the lower $E_{(a)}$ value) is the dominant reaction. At 0.30 molar ratio (curve 3), the $T_{p\ (b)}$ shifted to a lower temperature of 142°C, partly overlapping with the peak at (a). E values of 130 and 108 kJ mol^{-1} for the reactions at $T_{p\ (a)}$ and $T_{p\ (b)}$ respectively, indicate that at this molar ratio, there is a reverse in the dominance of the reactions, with the reaction at $T_{p\ (a)}$ perhaps inhibited by the reaction at $T_{p\ (b)}$. At 0.75 level (curve 6), a broad shoulder at $T_{p\ (c)}$ at 153°C became evident with a higher $E_{(c)}$ value of 131 kJ mol^{-1}.

According to Fig. 3 and Table 2, for the case of the 2,6-DMP, additional peaks became evident at NaOH concentration levels of 0.15, 0.60, 0.75 and 1.00. At 0.15 concentration (curve 2), the peak shapes are similar to the 2,4-DMP, indicating that similar types of reactions may have occurred. Similarities between the 2,4-DMP and the 2,6-DMP in terms of the shapes of these additional reaction peaks, diverged at the NaOH : 2,6-DMP molar ratio of 0.30 and beyond. By 0.30 molar ratio (curve 3), the peak at $T_{p\ (c)}$ from curve 2, disappeared. At 0.60 ratio (curve 5), a reaction peak, $T_{p\ (a)}$ emerged and preceded the curing peak $T_{p\ (b)}$. The corresponding $E_{(a)}$ value for the reaction at $T_{p\ (a)}$ was 127 kJ mol^{-1}. This reaction is enhanced by the rise in NaOH molar ratio to 0.75 (curve 6), as can be observed in the increased intensity of this peak and equivalent decrease in $E_{(a)}$ value to 105 kJ mol^{-1}. At this same concentration level, another consecutive reaction emerged marked by an obvious shoulder at $T_{p\ (d)}$ positioned at 160°C along the temperature scale. This reaction appears to have ceased with further increase in NaOH molar ratios. At the ratio of 1.00 (curve 7), there are two very distinct and sharp peaks. As for the 2,4-DMP, the assignment of these latter peaks to the precise reactions, need to be confirmed by further studies. However, by superimposing the scans, it is believed that the lower temperature peak is still on account of the reaction occurring at $T_{p\ (a)}$ from curve 6 and the higher temperature peak is due to reaction at $T_{p\ (b)}$. Both peaks shifted to higher temperature values. It would perhaps be useful to repeat the experiment for both compounds at NaOH:DMP molar ratio of 0.90 to follow the evolution of these peaks.

The other reactions, as revealed in the presence of additional exotherms at certain NaOH : DMP molar ratios, are uncertain at this stage and work is currently being undertaken using IR and HPLC techniques to identify these reactions.

Results so far have indicated that the self-condensation characteristics of 2,4-DMP and 2,6-DMP without and with the presence of varying molar ratios of NaOH is governed by complex reaction mechanisms and is affected by the varying levels of NaOH molar ratios.

Conclusions

DSC was an effective technique to study the self-condensation reactions of 2,4-DMP and 2,6-DMP with and without the presence of NaOH. Results of this study suggest that the presence of NaOH had a marked influence on the thermochemical curing characteristics of these compounds.

The DSC curves indicated several reactions as observed by the presence of one, two or three peaks at different alkalinity levels. One of these peaks was observed for the entire range of NaOH molar ratios examined, and was attributed to the self-condensation curing reaction. The additional peaks appeared only at specific NaOH concentration levels, and were due to other types of reactions occurring in sequence or parallel with the main curing reaction. Whether these are related to decomposition of intermediate products has yet to be determined and is currently being investigated, together with the mechanism governing the curing process. At the 1.0 molar ratio, both compounds depicted a significant change in the self-condensation reaction mechanism. This was illustrated by a substantial variation in the peak shapes, which occurred at higher temperatures with correspondingly higher E values as compared with the reactions at the other mole ratios.

A major effect of the presence of NaOH with both compounds, 2,4-DMP and 2,6-DMP, was the shift of the curing T_p, to significantly lower values at NaOH:DMP molar ratio of 0.15 which remained constant until molar ratio of 0.75. The effect, however, was more pronounced on the 2,4-DMP as evidenced by the greater shift of the T_p to lower values.

The energies of activation for the self-condensation reaction of both compounds showed similar trends. There was an initial increase between 0.15–0.30 molar ratios, followed by a significant lowering at 0.45 ratio, then remained steady until 0.75.

Thus far, the results tend towards an optimal NaOH:DMP molar ratio of approximately 0.50 for the self-condensation reactions of both compounds. On the other hand, the effects of the increasing NaOH:DMP molar ratios on the structural changes during the self-condensation reactions, also needs to be examined.

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