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THERMAL BEHAVIOUR OF PHENOL-FORMALDEHYDE (PF) COMPOUNDS

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Abstract

The self-condensation reactions of 2- and 4-mono-methylol phenols (2-MMP and 4-MMP), in the presence of varying concentrations of NaOH, have been studied by differential scanning calorimetry (DSC). The reaction exotherms were analysed to derive the activation energy, E_a, and the heat of reaction, H_T, for the condensation reactions. In the case of 2-MMP an increase in NaOH:2-MMP molar ratio caused an increase in E_a and a decrease in H_T up to a molar ratio of 0.6:1. However, for 4-MMP, an increase in NaOH concentration caused an increase in E_a up to a molar ratio of 0.3:1 beyond which there appeared to be no further effect. The presence of NaOH had no effect on H_T for this compound. The results suggest that in the range of NaOH concentration used the effect of NaOH was substantially greater on 2-MMP compared to 4-MMP.

Keywords: activation energy, differential scanning calorimetry, heat of reaction, 2-mono-methylol phenol, 4-mono-methylol phenol

Introduction

The production of reconstituted wood products has become increasingly important as demands for wood and wood-based products continue to increase. The viability of reconstituted wood products greatly depends on the use of suitable wood adhesives. Some of the commonly used thermoset 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 of variations in anatomical features and wood substrate properties such as moisture content and density, which limit their allowable gluing conditions [1].

Generally, the synthesis of PF resins is a two-stage process. The first stage is the condensation of phenol with formaldehyde to form mono-methylol (MMP) [2], then di-methylol (DMP), and then tri-methylol (TMP) phenols. The second stage in-

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volves the reaction of the methylol groups with themselves and/or with unsubstituted phenol to form extensive branched tree-like structures. With alkaline catalyst and excess formaldehyde, resols are obtained of varying molecular size, and are used as wood adhesives. The nature of the resol is dependent on the type of catalyst and the molar ratio of the reactants. Further heating continues the condensation reactions resulting in the resin curing.

While the kinetics of the formation of initial condensation products from the reaction of phenol with formaldehyde has been widely investigated [3–9], there is limited understanding of the thermochemical properties of these products, as well as the dependence of these properties on the alkalinity of the reaction. There is limited published information on the effects of NaOH on the condensation reactions of monomethylols, particularly in terms of their thermochemical properties. Yeddanapalli and Francis [10] studied the kinetics of NaOH catalysed self-condensation of 2-MMP and 4-MMP using quantitative ascending paper chromatographic analysis of the reactants and products. However, they did not report on the effect of change in NaOH concentration on E_a. Knowledge in this area is important for the development of improved resin systems. As part of the research program, the thermochemical characteristics of MMP, DMP, TMP and other PF model compounds have been studied using differential scanning calorimetry (DSC).

In this paper, we present the results on the thermochemical properties of the two MMP condensation products, namely, 2-mono-methylol phenol (2-MMP) and 4-mono-methylol phenol (4-MMP) formed during the initial condensation of the synthesis process under various alkaline conditions.

Experimental

Materials and sample preparation

Compounds of 2-MMP (99% purity) and 4-MMP (>98% purity) were obtained from Aldrich Chemical Company, Inc., and MERCK-Schuchardt respectively. Sodium hydroxide (analytical grade) was obtained from BDH Chemicals Ltd.

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

Instrumental procedure and analysis of DSC scans

The DSC runs were carried out using a Perkin Elmer DSC (Pyris-1) under a constant purge of nitrogen gas (20 $cm^3 min^{-1}$). Temperature calibration was performed by determining the heats of fusion of pure indium metal (99.9% purity). The samples were weighed directly into the stainless steel pans specifically designed for DSC use and sealed (the mass of the samples ranged from 4 to 9 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 scan speeds of 5, 7, 10, 15 and 20°C min^{-1}

in the range 25–280°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%.

The DSC curves were analysed for heat of reaction, H_T, and activation energy, E_a. The calculation of H_T was based on the total area under the exotherm, which is assumed to be proportional to the heat of the reaction. The calculation was performed using the Pyris computer software.

The exothermic peak temperature (T_p) of a reaction increases with higher heating rate. Kissinger [11] has expressed the relationship between heating rate and peak exotherm by the equation:

$$-\ln(\varphi/T_p^2) = E_a/R(1/T_p) - \ln(AR/E_a)$$

where φ – heating rate (°C min^{-1}); T_p – peak temperature (K); E_a – Arrhenius activation energy (kJ mol^{-1}); R – universal gas constant; and A – frequency factor.

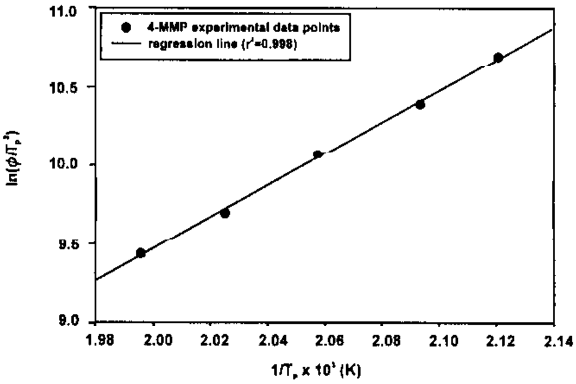

Fig. 1 Kissinger plot for 4-MMP in the absence of NaOH

DSC curves were obtained at five different scan rates for each sample. From the T_p of the reaction exotherm at each scan rate, graphs of $\ln(\varphi/T_p^2)$ *vs.* $1/T_p$ were drawn. Values of E_a for the condensation reactions were then calculated from the slopes of these graphs. Figure 1 shows an example of a plot of the Kissinger equation for the self-condensation reaction of 4-MMP in the absence of NaOH.

Results and discussion

Values for activation energy, E_a, and heat of reaction, H_T, for 2-MMP and 4-MMP in the presence of varying amount of NaOH were obtained. Figures 2 and 3 show the plots of E_a and H_T as functions of NaOH:MMP molar ratio, respectively, for both MMP compounds. In the uncatalysed condition, the results shown in Fig. 2 suggest that E_a for 2-MMP has a value of 96.4 kJ mol^{-1}, which is similar to the value of about 84 kJ mol^{-1} obtained by Sprung and Gladstone [12] who used titration

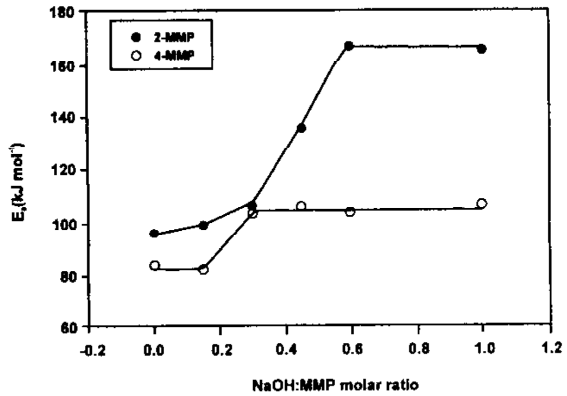

Fig. 2 Activation energy, E_a *vs.* NaOH:MMP molar ratio for 2-MMP and 4-MMP

methods. Katovic [13] used differential thermal analysis and infrared spectroscopy and reported an E_a value of 73 kJ mol^{-1}. For 4-MMP without NaOH, we obtained an E_a value of 84.2 kJ mol^{-1}, which is similar to the DSC work of Pizzi [14] who reported an E_a of 102 kJ mol^{-1}. The variations in the E_a values obtained by these authors may be due to the use of different analytical techniques.

Figure 2 indicates that for 2-MMP there was a distinct increase in E_a with increase in NaOH concentration until a NaOH:2-MMP molar ratio of 0.6:1 was reached. At this point, E_a appeared to reach a value of about 165 kJ mol^{-1} and was constant with increasing molar ratios. For 4-MMP, on the other hand, E_a increased to a value of about 103 kJ mol^{-1} when the NaOH:4-MMP molar ratio reached 0.3:1, and remained constant at that value with further increases in NaOH concentration. The effect of NaOH was substantially greater on the condensation reactions of 2-MMP than on the 4-MMP compounds. This was indicated by the higher value of E_a for 2-MMP than for 4-MMP in the range of NaOH concentrations used. In other words, a maximum molar ratio of 0.3:1 NaOH may be required to slow down the condensation reaction of 4-MMP. Further investigation is currently underway to determine the exact molar ratio of NaOH:MMP required to establish the maximum peak values of E_a for both 2-MMP and 4-MMP.

Figure 3 shows that H_T for 2-MMP in the uncatalysed condition was 526.5 J g^{-1} and decreased to approximately 425 J g^{-1} at the NaOH:2-MMP molar ratio of 0.6:1. This value of heat of reaction remained constant at higher molar ratios. This is also the molar ratio at which E_a for 2-MMP became steady. For 4-MMP, under these experimental conditions, there appeared to be no significant effect of NaOH concentration on H_T, which was approximately 440 J g^{-1}.

It was also observed that in the absence of NaOH, both monomers reached a fully cured state during the DSC scan resulting in a rigid material. This was confirmed by immersing the rigid material into methanol (solvent). These materials were unaffected by the solvent. On the other hand, the presence of NaOH had an effect on the curing behaviour of the monomers. Following the DSC scan, these materials ap-

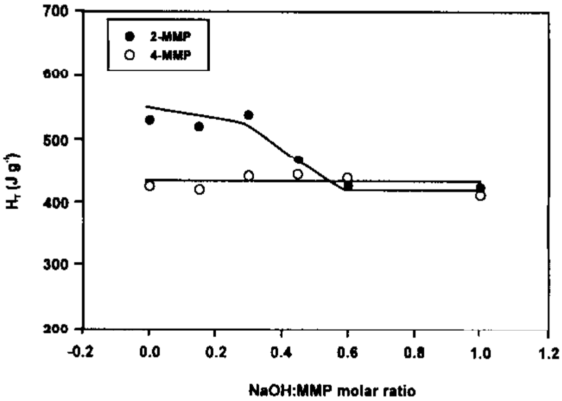

Fig. 3 Heat of reaction, H_T vs. NaOH:MMP molar ratio for 2-MMP and 4-MMP

peared to be fully cured. i.e. they became solid and rigid. However, when immersed in methanol they disintegrated into a gel-like substance. This demonstrates the complex nature of the condensation reactions of 2- and 4-mono-methylol phenols in the presence of NaOH. Further study is required to aid the current understanding of the effect of NaOH on the formation of stable methylene linkages, which is characteristic of a fully cured resole resin.

The results obtained in the present study show that in the range of increasing NaOH:MMP molar ratio examined, E_a values for both MMP compounds increased not over the whole range, but in a specific concentration interval. This is consistent with the accepted view [15] that in condensation reactions of the PF compounds NaOH has the effect of slowing down the rate of formation of methylene linkages between the mono-methylols.

Conclusions

DSC has proved to be a useful technique for studying the thermochemical properties of the self-condensation reactions of 2-MMP and 4-MMP. The results obtained strongly suggest that the presence of NaOH had a marked effect on the curing characteristics of these compounds. E_a values for 2-MMP were generally higher than for 4-MMP. 2-MMP was also more sensitive to the presence of NaOH, with a distinct increase in E_a until NaOH:2-MMP molar ratio of 0.6:1 was reached. At and above this point, E_a reached a constant value of approximately 165 kJ mol^{-1}. For 4-MMP, the effect of NaOH appeared to be less pronounced, with an increase of E_a to about 103 kJ mol^{-1} at the NaOH:4-MMP molar ratio of 0.3:1 and becoming constant at increasing ratios. It was also observed that H_T of the condensation reaction for 4-MMP appeared to be unaffected by the presence of NaOH, whereas for 2-MMP, H_T decreased with increase in NaOH:2-MMP ratio until the ratio of 0.6:1 was reached.

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