Effect of Ammonium Pentaborate on Curing of Aqueous Phenol Formaldehyde Resin

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ABSTRACT

Ammonium pentaborate (APB) is used as fire retardant in polymers or additive in producing wood-based composites. In order to understand the reactions between APB and aqueous phenol formaldehyde (PF) resin to provide a reasonable explanation of the properties of wood composites made with APB modified PF resin, the effect of APB on curing behaviour of aqueous PF resin was investigated, by using dynamic differential scanning calorimetry (DSC) and Fourier transform infrared spectrometry (FTIR) studies. Activation energies at each conversion point of PF resin reference and its mixtures were calculated by Kissinger-Akahira-Sunose (KAS) algorithm according to isoconversional kinetic method. The enthalpy change of reaction, the conversion progress with temperature, and the chemical groups in PF resin formed by APB were analyzed at the same time. The results showed that addition of APB at about 3.20 wt% brought about a minute distinction between addition and condensation reactions. However, as the loading of APB increased to 8.88 wt%, another exothermal peak was observed at temperature around 172°C. The consistent data of activation energy and enthalpy suggested that this peak was caused by the second curing process in APB modified PF resin systems, which helped the completion of cure reaction but delayed the curing time. This second curing process was considered to include the following features: the formation of more stable methylene bridges, addition reactions between eliminated formaldehyde and active groups on PF resin and the formation of hexamine which were consistent with FTIR results characterized by the altered network.

INTRODUCTION

Phenol formaldehyde (PF) resin is used in many applications such as adhesives, coatings, composites, etc. [1,2]. It is one of the most important adhesives applied in producing wood-based composites. The properties of the adhesive itself and its interaction with wood have a great influence on the properties of the wood-based composites. In order to improve the performance of wood-based composites e.g., the fire retardancy, the formaldehyde emission control and the termite resistance, some additives are required in the wood-adhesive system.

Boron or borates are among the main effective ingredients in many fire retardant and water-borne preservative formulations for wood or wood-based composites [3,4].
The effectiveness of many borates (e.g., boric acid, borax, zinc borate, calcium borate, etc.) used as fungicide, mouldicide or insecticide in wood-based composites such as oriented strand board (OSB) has been reported [5-7]. However, it is also reported that borates have adverse effect on the mechanical properties of wood composites [8], which have been presumed to be due to the methylol groups (-CH2OH) reaction with borate ions forcing the resin to gel before it is able to develop an effective bond [9-11]. The curing process of resin is a fairly complicated process with numerous influencing factors. The addition of borates may have great influence on the curing kinetics of PF resin. Lei et al. [12] have studied the influence of zinc borate (ZB) on the curing kinetics of PF resin, and found that although ZB accelerated the addition reaction of PF resin, it in fact delayed the entire cure reactions by hindering the condensation reaction. Hitherto, the influence of any other boron compounds except ZB on the curing kinetics of PF resin has not been reported yet.

Ammonium pentaborate (APB) is a kind of metal-free borate. It is reported that strand boards made with APB modified PF resin show lower formaldehyde emission level and produce higher termite resistance. The mechanical properties of strand board are also decreased, though not significantly as compared with those modified with ZB and disodium octaborate tetrahydrate (DOT) at the same BAE (boric acid equivalent) level [13]. Therefore, it can be conjectured that APB has an effect on cure kinetics of PF resin and this effect should be different from that of ZB or other metal-containing borates. In our preliminary research we found that an appropriate amount of APB added in powdered PF resin could clearly reduce the activation energy of PF reactant systems but the mechanism is still unclear [14].

In this study, the curing behaviour of PF resin at different loading levels of APB was investigated by using differential scanning calorimetry (DSC). Fourier transform infrared spectrometry (FTIR) was also used to study the changing network of PF resin on addition of APB. The results of this study can be helpful to understand the reaction between APB and PF resin and thus provide a reasonable explanation of the properties of wood composites made with APB modified PF resin.

**Experimental**

**Materials**

Solid phenol, C₆H₆O (AR) and formaldehyde, HCHO, (AR, 37.0 w/v%) were obtained from Xilong Co., China. Sodium hydroxide, NaOH, (AR) was purchased from Beijing Chemical Plant. Ammonium pentaborate, NH₄B₅O₈·4H₂O (AR, with molecular weight of 272.15) was obtained from Sinopharm Chemical Reagent Co. Ltd., Shanghai, China.

**Preparation of PF/APB Mixtures (PAM)**

The PF resin used in this study was synthesized in laboratory by using solid phenol, formaldehyde (37.0 w/v%) and sodium hydroxide (NaOH). The solid content of the synthesized resin was about 46.4 wt% with a pH value between 10.5 and 11.5. Then, the aqueous PF resin was frozen, dried at a vacuum of 21 Pa and a cold trap temperature of -54°C for 17 h, after which its solid content increased to 87.1 wt%. Afterwards, it was ground to powder. PAM (the mixture of PF resin and APB) samples were prepared by mechanical mixing APB (NH₄B₅O₈·4H₂O, AR) with PF powder at APB/PF ratios of 3.20, 6.04, 8.88, and 15.00 wt%, which correspond to the BAE levels of 0.4, 0.7, 1.0, and 1.8 wt%, assuming the target density of the wood composite is 700 kg.m⁻³, that of PF resin is 54 kg.m⁻³, and the moisture content of the composite is 7 wt%. The APB/PF ratios were determined on the considerations that the effective BAE level must be 5 wt% based on the oven dry weight of wood flakes [15,16], and the results of our pilot experiments showed that in order to avoid endothermic effect, the APB addition into PF resin should not go beyond 15 wt%.

**Differential Scanning Calorimetry Analysis**

A DSC60 (Shimadzu, Japan) equipped with a TA-60 thermal analysis system was used to analyze the cure reactions of pure PF resin, APB and PAM systems. Before DSC test, the calorimeter was calibrated by using standard substances of indium, tin, lead and zinc. Then 5-7 mg sample was taken and placed in a hermetically sealed aluminium capsule with vapour pressure limit of 4.9 MPa. The DSC process started after the samples reached room temperature. The weight of the samples was measured before and after...
each run to ensure that there was no mass loss during thermal studies. The samples were heated from 40 to 250°C in the presence of nitrogen gas (10 mL/min) at different heating rates (5, 10, and 20°C/min, respectively) to obtain dynamic DSC curves. Three replicates were scanned for each testing condition.

The total area under the exothermal curve, based on the extrapolated baseline, was used to calculate the heat of cure. Both degree of conversion ($\alpha$) and conversion rate ($d\alpha/dt$) at a certain curing time ($t$) were calculated according to eqns (1) and (2). The conversion of PF resin can be defined as the transform of small molecules to large molecules through the process of chain extension, chain branching and cross-linking, which finally result in a three-dimensional network of infinite molecular weight [17,18].

$$\alpha = \frac{\Delta H(t)}{\Delta H_{RXN}} \quad (1)$$

$$\frac{d\alpha}{dt} = \frac{dH}{d\Delta H_{RXN}} \quad (2)$$

where, $\Delta H(t)$ is the heat of reaction at a certain curing time ($t$), $\Delta H_{RXN}$ is the total heat of reaction and $dH/dt$ is the heat flow.

**Dynamic DSC Kinetic Theory**

Based on the above dynamic DSC results, it is possible to estimate the activation energy at a given degree of conversion, $E_{\alpha}$, according to the following procedures. The relationship between $\alpha$ and $k$ can be expressed as eqn (3).

$$\frac{d\alpha}{dt} = k (1-\alpha)^n \quad (3)$$

$$k = A\exp\left(-\frac{E}{RT}\right) \quad (4)$$

where, $k$ is the reaction rate (s$^{-1}$), $n$ is the reaction order, $A$ is the pre-exponential factor (s$^{-1}$), $E$ is the activation energy (J/mol), $R$ is the universal gas constant (8.314 J/mol·K), and $T$ is the absolute temperature (K).

The basic assumption of the isoconversional method is that the reaction rate at constant rate of conversion is only a function of temperature [19]. For model free analysis, the kinetics start with the basic rate equation that relates the rate of conversion at constant temperature, $d\alpha/dt$, to a function of reactants concentrations, $f(\alpha)$, through the reaction rate constant, $k$. If $k$ is dependent on reaction temperature through the Arrhenius relationship, then by replacement with eqn (3), a relationship may be obtained as follows:

$$\frac{d\alpha}{dT} = \frac{f(\alpha)}{\Phi} A\exp\left(-\frac{E}{RT}\right) \quad (5)$$

where, $\Phi = dT/dt$ is the heating rate (K/min). In the isoconversional kinetic method, the parameters are independent of the heating rates, thus, corresponding parameters at different heating rates can be obtained. The differential of eqn (5) is expressed as eqn (6).

$$d\ln(d\alpha/dt) / dT^{-1} = -E_{\alpha} / R \quad (6)$$

where, $E_{\alpha}$ is the activation energy at a given degree of conversion. Based on eqn (6), several methods have been suggested to calculate the $E_{\alpha}$ value, which include the Kissinger-Akahira-Sunose (KAS) algorithm [20,21] and the method proposed by Vyazovkin [22,23].

In this study, the KAS algorithm was used to calculate $E_{\alpha}$ as expressed in eqn (7).

$$\ln \Phi / T_i^2 = -\frac{E_{\alpha}}{RT_i} + \ln(RA / E_{\alpha}) \quad (7)$$

where, $T_i$ is the temperature required to reach a given degree of conversion. From the linear relationship between $\ln\Phi/T_i^2$ and $1/T_i$, the activation energy $E_{\alpha}$ and the pre-exponential factor $A$ can be obtained. The model free kinetics technique follows every point of conversion, obtaining the activation energy at each point. Therefore, it can reveal the dependence of $E_{\alpha}$ on $\alpha$ and the complexity of the curing process [23].

**FTIR Analysis**

Infrared spectra were obtained on a Bruker Tensor 27 (Germany) Fourier transform infrared spectrometer...
Figure 1. Dynamic DSC curves of: (a) pure PF resin, (f) APB, and PAM samples with ammonium pentaborate (APB) loading levels of (b) 3.20%, (c) 6.04%, (d) 8.88%, and (e) 15.0% at a heating rate of 5°C/min.

(FTIR). All samples were heated at 120°C for 4 h and then ground to powder. FTIR measurements were performed with a homogenized mixture of sample and KBr. In each measurement 32 scans were accumulated at 4 cm⁻¹ resolution. To obtain the background contribution, the KBr spectrum was measured for automatic background subtraction.

RESULTS AND DISCUSSION

Effect of APB on the Curing Process of PF Resin

Dynamic DSC is a common technique to analyze the curing kinetics of thermosetting resins [24]. Figure 1 shows the dynamic DSC curves of pure PF resin (PF control), APB, and PAM systems at a heating rate of 5°C/min. It can be found that there is only one

Figure 2. Dynamic DSC curves of: (a) pure PF resin and PAM samples at APB loading levels of (b) 3.20%, (c) 8.88%, and (d) 15.00% at heating rates of 5, 10, and 20°C/min, respectively.
exothermal peak at about 132°C for pure PF resin. With the addition of APB, this peak tends to decrease and a very weak peak begins to appear within the temperature range of 70-95°C. As the APB loading is increased to 8.88 wt%, another exothermal peak emerges at temperature around 172°C, which can also be observed at other heating rates as shown in Figure 2. The exothermal peak of within 70-95°C was reported before for PF resin incorporated with borates which was considered to be caused by distinctive addition and condensation reactions in the curing process of PF resin [12]. As suggested in previous investigations, curing of PF resin is accomplished in a two-step process [25-27]. The first step involves the addition of formaldehyde to phenol to form hydroxyl methylphenol, and the second step is the condensation of hydroxyl methylphenols to form methylene and methylene-ether-bridged di- or high-molecular compounds. Since the exothermal peak observed in this temperature range is very weak and can be even neglected, it is concluded that APB has little effect on the separation of the addition and condensation reactions in the curing process of PF resin.

However, up to present, there is no report concerning the exothermic peaks at temperatures higher than 170°C in the curing process of PF resin containing borates. Therefore, it is of great interest to explain the appearance of the strong exothermic peak for PAM at APB loading levels of 8.88 wt% and 15 wt% at temperatures higher than 170°C. For APB control system, there are three endothermic peaks which have appeared at 135°C, 167°C, and 185°C, respectively, therefore, there must be some complex reactions occurring in the PAM systems during the heating process. One possible reason responsible for this peak is the occurrence of a second cure reaction while a certain amount of APB is added to PF resin. We have tried to verify this claim via the following kinetic analysis on activation energy and exothermic heat.

Cure Kinetic Analysis
The variation of activation energy ($E_\alpha$) against the degree of conversion was calculated on the basis of the model free hypothesis. As shown in Figure 3, all the curves except that of PAM with 15 wt% APB begin with a sudden increase and then a decrease, indicating that the curing process is accomplished in two stages for these samples. A kinetic process involves parallel reactions or reactions that occur simultaneously as the curves initially increase [28]. Afterwards, as the curves decrease with a convex shape, it is presumed that there is a change in the mechanism from kinetic to diffusion mode.

Generally speaking, the cure reaction systems undergo gelation (from liquid to rubber) and vitrification (from rubber to glass) transitions, and cross-linking process to reduce molecular mobility and result in a change from a chemical kinetic to a diffusion regime during the curing of thermosetting resins [29]. As $E_\alpha$ reaches rapidly to a maximum value at a low degree of conversion, it is reasonable to conclude that the addition reactions are few and almost completed [30]. It is clear that the systems of PF control and PAM with less than 6.04 wt% APB loading are consistent with this theory where the addition reactions are few. Furthermore, the initial values of $E_\alpha$ for PAM, except the value for 15 wt% APB loading are slightly lower than that of PF control system, indicating that APB has some effects on accelerating the addition reaction of PF curing process, which is consistent with the weak peak appearing in the temperature range of 70-95°C as shown in Figure 1.

However, the activation energy of PAM resin at an
APB loading of 8.88 wt% showed quite different trends compared with other samples. For PAM system with 8.88 wt% APB, the $E_\alpha$ reaches its maximum at around 120 kJ/mol by a high conversion degree of around 40% followed by an abrupt decrease and a small convex. An increase and a decrease in the appeared $E_\alpha$ peak are considered to be the results of some energy consuming reactions accelerated by APB, such as the decomposition of methylene ether bridges (Scheme II). During these reactions, some active molecules such as formaldehyde are released leading to exothermic condensation reactions which may occur among these active molecules, and finally result in sharp fall in $E_\alpha$.

This deduction can be strengthened by the enthalpy change shown in Figure 4. As the cure reactions of PF resin are typically exothermic, it can be confirmed that the reaction enthalpy, in other words, the amount of heat released in the reaction is proportional to the degree of conversion during the curing process or the cross-linking created in the adhesive self-condensation process [31]. The maximum reaction enthalpy was observed at APB loading of 8.88 wt% which indicates that cure reactions were more completed. Since APB has very

\[2\text{NH}_4\text{B}_5\text{O}_8\cdot4\text{H}_2\text{O} \xrightarrow{\Delta} 5\text{B}_2\text{O}_3 + 2(\text{NH}_3)(\text{gas}) + 5(\text{H}_2\text{O})(\text{gas})\]

**Scheme I.** The decomposition of APB and elimination of ammonium [35].

\[
\begin{array}{c}
\text{OH} \\
\text{CH}_2\text{O} \\
\text{O} \\
\text{CH}_2\text{OH} \\
\text{OH} \\
\end{array} \xrightarrow{\text{B}_2\text{O}_3} 
\begin{array}{c}
\text{OH} \\
\text{CH}_2\text{OH} \\
\text{OH} \\
\text{CH}_2\text{OH} \\
\end{array} + \text{CH}_2\text{O}
\]

**Scheme II.** The decomposition of methylene ether bridge and elimination of formaldehyde [32].

\[
\begin{array}{c}
\text{OH} \\
\text{CH}_2\text{O} \\
\text{O} \\
\text{CH}_2\text{OH} \\
\text{OH} \\
\end{array} \xrightarrow{\text{B}_2\text{O}_3} 
\begin{array}{c}
\text{OH} \\
\text{CH}_2\text{OH} \\
\text{OH} \\
\text{CH}_2\text{OH} \\
\end{array} + \text{CH}_2\text{O}
\]

**Scheme III.** The functional groups and possible reaction sites with formaldehyde in PF resin [32].

\[
\begin{array}{c}
\text{H} \\
\text{O} \\
\text{N} \\
\end{array} \xrightarrow{\Delta} 
\begin{array}{c}
\text{N} \\
\text{N} \\
\text{N} \\
\end{array}
\]

**Scheme IV.** The formation of hexamine from formaldehyde and ammonia [36].

**Figure 4.** Enthalpy of the PF resin and PAM at different APB loading levels.
little effect on the addition reactions of curing process as shown by the small peaks in Figure 1, this increase in enthalpy is considered to be mainly resulted from the second curing process at higher temperature range. The previous research indicated that methylene ether bridges may also exist in commercial powdered resol phenolic resins [32]. King et al. [33] and Kenny et al. [34] reported that the dibenzyl ether bridges formed by the condensation of two methyol groups break to create more stable methylene bridges and eliminate formaldehyde at higher temperatures. These reactions may be promoted by APB at 8.88 wt% loading, considering the effect of boron oxide generated from APB as shown in Scheme I.

Then, the second curing characterized by (1) formation of more stable methylene bridges (Scheme II), (2) the later addition reaction between eliminated formaldehyde and the active groups on PF resin (Scheme III), and (3) the reaction between released ammonia and formaldehyde to produce hexamethylene tetramine (hexamine) (Scheme IV). It is reasonable that the consumption of formaldehyde in Scheme IV accelerates the decomposition of methylene ether bridges, which meanwhile eliminates a lot more formaldehyde by reacting with the active sites on the PF resin network.

To complete these cure reactions, more time is required. As shown in Figure 5, the conversion degree of PAM at 8.88 wt% APB loading is lower than other systems, especially at higher temperatures. It can be found in Figure 2c that the second cure reaction takes place at higher temperatures. Therefore, the total curing process is prolonged.

However, for PAM at 15 wt% APB loading, the endothermic action of APB exceeds the second curing reaction effect on PF resin. This is an indication of a relatively small peak at 172°C shown in Figure 1 and small decrease of $E_A$ shown in Figure 3 while compared with that of PAM at 8.88% APB loading. Therefore, the influence of APB on PF cure can be summarized as two aspects: catalytic activation and endothermic effect. At low APB loading level, both aspects are negligible. When the APB loading reaches a certain value, the catalytic activation becomes predominant and a second curing process takes place. If the APB loading continues to increase and exceeds the critical point, the endothermic effect would be prevalent and inhibit the second curing process. Further study is needed to analyze the relationship between these two effects, quantitatively.

**FTIR Spectrum Analysis**

The effect of APB on the changes of chemical groups in PF resin during the curing process was analyzed by FTIR. Figure 6 shows the FTIR spectra of pure PF resin and PAM after curing. The absorptions are assigned in Table 1 according the literature [27,37-39].

There are some differences between the results in Figure 6 and the reported data in Table 1, which are mostly attributed to different formulations and synthesizing process of PF resins. Compared to PF
control, the absorption at 1475.5 cm⁻¹, due to the stretching and deformation absorptions of C-H bonds in aliphatic methylene obviously decreased for PAM samples at APB loading from 3.20 wt% to 15.0 wt%. Meanwhile, the absorption at 1145.6 cm⁻¹ corresponding to the C-O stretching vibration of alkyl ethers is also reduced significantly. These changes provide a strong evidence for the decomposition of methylene ether bridges as shown in Scheme II. The previous research indicated that the absorptions corresponding to B-O vibrations of borate crystal and the C-N and C-H vibrations of hexamine appeared in the frequency ranges of 782-1432 cm⁻¹ [40] and 1050-1450 cm⁻¹ [41], respectively. This is a wide absorption range which may be overlapped with the absorption of PF resin itself. As APB is increased, the absorption at 1436.9 cm⁻¹ is increased synchronously. The shape and strength of absorptions at 2842.9 cm⁻¹ to 3006.8 cm⁻¹ assigned to -CH₂- groups in PAM are distinct from those of pure PF resin, which confirm the existence of -B-O- groups in hydroxyl methyl positions and the formation of hexamine during the heating process. This discloses the mechanism that the complex reaction between APB and PF resin takes place in the position of phenolic hydroxyl groups in aromatic ring and/or phenolic hydroxymethyl groups.

These results are consistent with the results obtained from dynamic DSC. The prevailed argument is that the decomposition of methylene ether bridges, the reaction between -B-O- groups and hydroxyl methyl functionalities, and formation of hexamine have all contributed to the second curing process, which were characterized by the second exothermic peaks occurred at higher temperature shown in Figures 1 and 2. This is confirmed by increase in the enthalpy of reaction which is presented in Figure 4, as well.

## CONCLUSION

APB showed quite different effect on the curing kinetics of PF resin compared with other borates used in previous studies, which was characterized by a second curing process appeared at relatively high temperature range. This process is considered to be a result of the formation of more stable methylene bridges, the precedent addition reaction of formerly eliminated formaldehyde groups with active sites in PF resin, and the formation of hexamine from ammonia and formaldehyde. With the second curing process, a more complete curing reaction of PF resin would be achieved. However, the loading level of APB is very critical. At low APB loading levels, the second curing process can hardly happen, while at excessive APB loading, it will also be overwhelmed by the endothermic effect. The optimal loading level of APB is considered to be 8.88% in this study. Since the APB modified PF resin is supposed to be used in wood-based composites, wood may also have an

### Table 1. Assignment of absorption bands of phenol formaldehyde resin.

<table>
<thead>
<tr>
<th>Functional group</th>
<th>Absorption</th>
<th>Wavenumber (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-O/phenolic &amp; methylol</td>
<td>Stretching</td>
<td>3352.1</td>
</tr>
<tr>
<td>C-H/aromatic</td>
<td>Stretching</td>
<td>3006.8</td>
</tr>
<tr>
<td>C-H/aliphatic</td>
<td>Stretching</td>
<td>2910.4</td>
</tr>
<tr>
<td>C=C/benzene ring</td>
<td>Stretching</td>
<td>1635.5</td>
</tr>
<tr>
<td>C-H/aliphatic</td>
<td>Deformation</td>
<td>1475.5</td>
</tr>
<tr>
<td>B-O</td>
<td>Stretching</td>
<td>1436.9</td>
</tr>
<tr>
<td>C-O/phenolic</td>
<td>Stretching</td>
<td>1213.2</td>
</tr>
<tr>
<td>C-O/aliphatic</td>
<td>Stretching</td>
<td>1145.6</td>
</tr>
<tr>
<td>C-H/adjacent 2H, para-substituted</td>
<td>Deformation</td>
<td>879.50</td>
</tr>
<tr>
<td>C-H/adjacent 4H, ortho-substituted</td>
<td>Deformation</td>
<td>773.40</td>
</tr>
</tbody>
</table>

*Experimental and Reference values from literature.*
influence on the curing behaviour of APB modified PF resin. In this study, the effect of wood was not included which would be the focus of further study.

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