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Effect of three boron flame retardants on thermal curing behavior of urea formaldehyde resin

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Abstract The purpose of the study was to investigate the effects of three kinds of flame retardant (FR), boric acid, zinc borate, and borax on the thermal curing behavior of urea–formaldehyde (UF) resin. Both pH value and gel time were measured to study the curing characters of the UF resin with different loading levels of FR. In addition, differential thermal analysis was also used to obtain kinetic analyses parameter. The results showed that boric acid decreased pH value of UF resin, and reduced gel time of the UF resin. There are no significant changes of the UF resin curing characters with different loading levels of FR. The activation energies for curing reaction of UF resins in the presence of boric acid, zinc borate, and borax, were 84.37, 84.41, and 118.4 kJ/mol, respectively, higher than that of the control one (75.38 kJ/mol). All FRs showed adverse effect on the curing behavior of the UF resin.

Keywords Urea–formaldehyde resin · Flame retardant · Curing behavior · Activation energy

Introduction

With concern about the depletion of natural resources and environmental damage becoming serious all over the world, wood and wood-based panels are being paid more-than-ever attention due to their unique renewable and environmental advantages. They have long been material of choices for various industries (mostly construction and transportation industry). However, wood-based panels, being natural materials, also have several disadvantages when compared to materials like steel or concrete. The inherently flammable character of wood-based panels gives rise to high probability of fire hazard. In order to meet today's increasing stringent demands for fire safety, wood-based panels have to be treated with flame retardants (FRs) [1]. The manufacture methods of fire resistant wood-based panels involving post-treatment of boards with aqueous solutions of FR compounds and the blending of FR compounds with raw wooden material or adhesives prior to hot-pressing were widely used. The traditional post-treatment-manufactured fire resistant boards encounter some problems including irreversible thickness swell and/or negative influence of structural properties of treated composite panels. The addition of FR chemicals in the process of panels manufacture shows some advantages like insuring enough addition volume of FR to meet fire resistance and little change of processing steps during manufacture. Nevertheless, problems are often encountered when attempting addition of FR chemicals in the process of panel manufacture. The first relates to the interference of treatment chemicals with resin curing and bond development. This interference seems to either inhibit or alter the chemical mechanism required for the adhesives to bond together the panel constituents. The second problem relates to significant and negative effect of the internal bonding critical to structural performance of the panel resulting from addition of FR chemicals [2]. Boron compounds can be used to increase the resistance of composites of fire and biodegradation of wood and wood-based panels [3, 4]. The effectiveness of many boron compounds (e.g., boric acid, borax, zinc borate, etc.) used as FRs in wood-based panels such as oriented strand board (OSB) and plywood, has been reported [5–7]. The adverse effect of borates on the mechanical properties of wood-based panels has been

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presumed to be due to the reaction of borate ions with methylol groups which prevents the adhesives from forming effective bonds to these groups before gelation occurs [7].

In practice, for application, wood-based panels treated with FRs not only need enhancement of fire resistance but also should meet the requirement of physical and mechanical properties. It is well known that the curing behavior of resin determines the properties of wood-based panels. Therefore, knowledge about the effect of FR chemicals on adhesive resins is important for efficient use of adhesive and FR to achieve good bonding in the manufacture of wood-based panels.

Urea–formaldehyde (UF) resin is the most widely used polycondensation resins today in wood-based panels industry due to some advantages such as fast curing, good performance in the panel, and cost efficiency [8]. The curing process of UF resin adhesive is a fairly complicated process with numerous influencing factors. Although previous studies reported the influence of FR chemicals on physical and mechanical properties, the study about effect of FR chemicals on the curing behavior of UF resin will benefit to reach a balance between improvement of fire resistance and decrease of mechanical properties of panels. Currently, information available in the literature on curing behavior of UF resin affected by FR chemicals is limited. The purpose of this study was to investigate the effect of three boron compound FR on curing behavior of UF resin at different loading levels with the simultaneous TG-DTA technique and other methods. The result of this study should provide useful information on impact of FR on UF resin curing behavior and bonding in composite panel manufacturing.

Experimental

Materials

A commercial UF resin powder (after spraying dry from liquid UF resin) designed for particleboard was used in this study. The UF resin powder model No. 5100C was purchased from Bosson (Beijing) Chemical Co., Ltd. Ammonium chloride, and three boron compound FR Borax, Boric acid, Zinc borate were purchased from Beijing Chemical Plant, China.

Measurement of the pH value and gel time of UF resin

To compare the effect of FR chemical on reactivity of UF resin, the pH value and gel time of the UF resin were measured. The UF resin powder was dissolved in distilled water with a concentration of 50 wt%. As hardener 1% ammonium chloride (NH_4Cl 20 wt%) based on solid resin was added to liquid UF resin. Then three kinds of FR were added to the up liquid UF resin at 10, 20, and 30% loading levels, respectively, based on solid UF resin content. The pH value was measured with pH meter (PHS-3C, China) at 25 °C. The gel time of liquid UF resin mixed with FR were measured according to Chinese national standard GB/T 14074.7-93 [9]. An average of three replications was reported.

Thermal behavior of UF resin and FR mixture

Thermal analysis of UF resin mixed with different FR chemicals at various loading levels was carried out using simultaneous TG-DTA technique (DT-60, Shimadzu, Japan). DT-60 was also used to evaluate the curing behavior of UF resin blended with three different FR compound at 20% loading level, respectively, with four different heating rates (5, 10, 15, and 20 K/min). For each scan, about 7–10 mg of mixture was added to an aluminum crucible. An aluminum crucible with alumina powder was used as reference. Samples were heating from 30 °C to 200 °C in a 50 mL/min flow of N_2. For each heating rate, the onset temperature, peak temperature, and heat of reaction were recorded, and an average value, with at least two replications was represented.

Activation energy analysis

There are several methods for calculating the activation energy of resin curing. The Kissinger equation [10] was selected as the model equation because it could be used to calculate not only the activation energy but also the pre-exponential factor, as shown in Eq. 1. Unless stated otherwise, activation energy refers to the Kissinger activation energy:

$$-\ln\left(\frac{\beta}{T_p^2}\right) = \frac{E}{RT_p} - \ln\left(\frac{ZR}{E}\right) \quad (1)$$

where β is the heating rate (K/min), E_a is the activation energy (kJ/mol), R is the gas constant (8.314 J/mol/K), T_p is the peak temperature (K), and Z is the pre-exponential factor (1/s). On the basis of the equation, there was a straight line between $-\ln(\beta/T_p^2)$ and $1/T_p$; from this, the activation energy and pre-exponential factor could be calculated from the slop and the intercept, respectively.

Results and discussion

Gel time and pH values of UF resin-FR mixture

The curing behavior of UF resin showed great relationship with the pH values. The results of pH values and gel time measurements of the UF resin in the presence of different FR

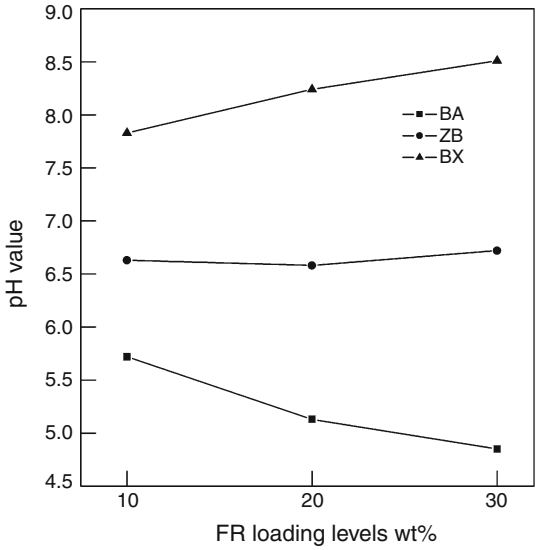

Fig. 1 Changes of pH value of UF in the presence of various different FR contents

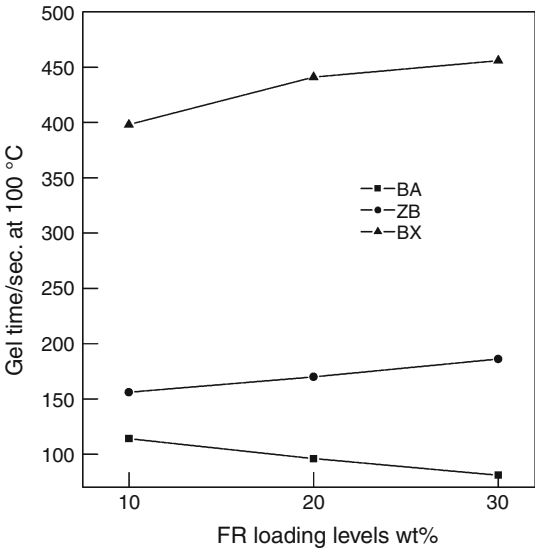

Fig. 2 Changes of gel time of UF in the presence of various different FR contents

chemicals with various loading levels were shown in Figs. 1 and 2, respectively. In the presence of FR boric acid, with the increase of loading levels from 10 to 30%, both pH values and gel time of UF resin rapidly decreased. In the curing process of UF resin, the polycondensation of methyl derivatives which formed in the stages of resin manufacturing leads to building the tridimensional network in acidic condition [11]. Stable complex was formed when boric acid was blended with polyhydroxy compounds. The pH value of aqueous solutions of boric acid is about 5.0, and the pH value of liquid UF resin blending with boric was about 5.7. It suggested that boric acid accelerated the curing rate of UF resin through catalyzing polycondensation between dihydroxylmethylurea and hydroxylmethylurea, and obviously promoted the gelation of the UF resin. It also showed that the UF resin blended with borax showed the longest gel time and the highest pH value 8.8 with 30 wt% of borax loading level, which might imply delaying the curing rate of the UF resin. For the reason was that the chemical condensation was prevented among methyl groups in the alkaline media [12], so borax prolonged the gel time of UF resin. It also confirms the fact that a higher temperature or increased time is needed to cure the UF resin blended with borax in practice. The pH values and gel time of UF resin showed no obvious changes with the presence of various zinc borate contents. These results also suggested that pH values of the UF resin should be adjusted in proper range, when it was used to manufacture fire resistance panels with FR chemicals.

UF resin curing in the presence of various FR chemicals with different contents

To compare the effect of FR chemicals on curing behavior of the UF resin, a series of DTA scans at a heating rate of 10 K/min were made for the UF resins with various FR contents ranging from 10 to 30 wt%, as shown in Table 1. Onset temperature, heat of reaction, and peak temperature were obtained. The onset point is defined as the extrapolated beginning point of any transition or phase change, determined from data analysis. Thus, the onset temperature may be expressed as an extrapolated and starting temperature of curing of UF resin.

As shown in Fig. 3, the onset temperature was not generally influenced with the increasing loading levels of FR. However, differences presented on the addition of different FR chemicals. The highest onset temperature, regardless of loading levels, was found at the UF resin mixed with borax, followed by the one with zinc borate, and then the one with boric acid. These results indicated that UF resin with boric acid provides lower onset temperature, which implies that the curing rate of the UF resin at the early stage was promoted in the acidic condition. While the onset temperature was enhanced, decreasing the curing rate of the UF resin.

Even though the onset temperature is an indicator cure or reactivity of the UF resin, the peak temperature is also an important parameter of comparing the reactivity of the UF resin [13]. The peak temperature is a temperature where the rate of cure reaches the maximum during a dynamic scan of the reaction. Figure 4 showed the changes of peak temperature of the UF resin with various different FR loading levels. The peak temperature presented similar changes to the onset temperature. Regardless of loading levels, UF mixed with boric acid appeared the lowest peak temperature, implying acceleration of curing rate of the UF resin, but the

Table 1 Curing parameters for the UF resin with various FR loading levels

FR types	Loading level/%	Onset temperature/°C	Peak temperature/°C	Heat of reaction/Jg^{-1} K^{-1}
None	0	74.32	88.83	20.4
Boric acid	10	51.03	67.09	7.51
	20	51.28	68.29	10.8
	30	52.05	69.02	17.3
Zinc borate	10	65.92	90.55	6.2
	20	71.89	89.23	5.48
	30	70.27	89.55	6.96
Borax	10	111.56	136.21	4.32
	20	112.42	137.58	3.87
	30	113.07	138.04	3.36

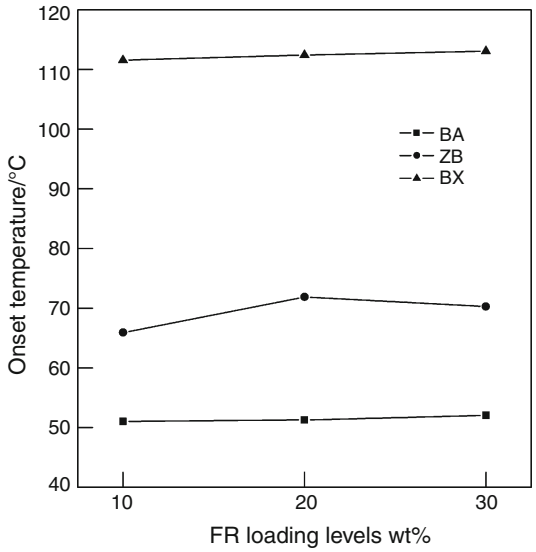

Fig. 3 Changes of onset temperature of UF resin depending on FR loading levels

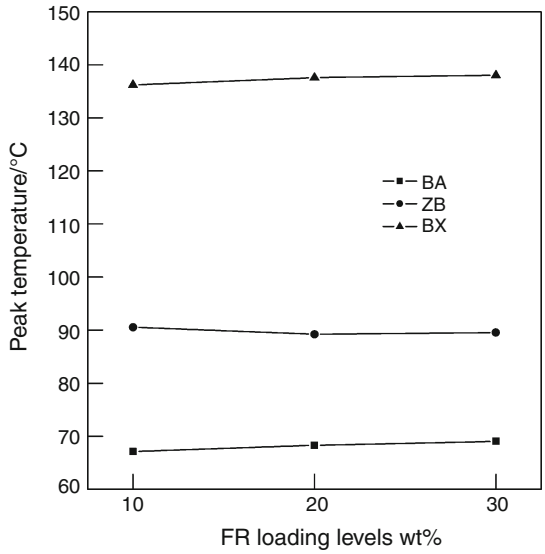

Fig. 4 Changes of peak temperature of UF resin depending on FR loading levels

borax appeared to reduce the curing rate of the UF resin. The reasons might be due to their pH values of mixture. The UF resin was easily cured on acidic conditions.

Table 1 also showed different heat reaction (ΔH) values of UF resins during their curing. The ΔH was the amount of energy required to complete the cure of a resin, which was the area under an exothermic DTA curve [14]. Although there were variations, differences between the ΔH values of the UF resin cure, the UF resin with borax showed the lowest ΔH value, suggesting curing delay. The ΔH of the UF resin with boric acid was the biggest, compared with those of the others.

Kinetic analyses of UF resin curing in the presence of different FR

Activation energy is a kinetic parameter independent of curing temperature, but it reflects the sensitivity of a resin to temperature. Activation energy is usually calculated from the changes in the level of DSC peak temperature as heating rate changes. Therefore, the resin curing with lower activation energy indicates that the curing rate is more sensitive to temperature change compares to that of a resin with higher activation energy. In addition, the activation energy could be used as a reference in the evaluation of curing behavior of the UF resin [15].

The results of DTA measurement with different FR chemicals and their kinetic analyses were summarized in Table 2. The curing peak temperature of UF resin in the presence of each FR chemical was in the range of 64.93–146.53 °C when the heating rate was 10 K/min. The sharp curing peaks were similar to control group, those of the UF resin cured with NH_4Cl. The peak temperature of the UF resin cured with boric acid appeared lower than the control ones. A plot of $-\ln\left(\beta/T_p^2\right)$ versus $1/T_p$, as shown in Fig. 5, was used to calculate the activation energies of

Table 2 Kinetic analyses of UF resin with different FR chemicals of 20 wt% content

FR types	T_p/K				E_a/kJ/mol	Z	R^2
	5/K/min	10/K/min	15/K/min	20/K/min			
AC (control)	359.55	366.7	367.92	369.8	75.38	5.95×10^{10}	0.9458
Boric acid	338.08	346.71	348.23	353.79	84.37	5.127×10^{12}	0.9589
Zinc borate	353.79	362.38	366.3	370.79	84.41	1.19×10^{12}	0.9956
Borax	403.76	411.19	416.04	419.68	118.4	9.28×10^{14}	0.9416

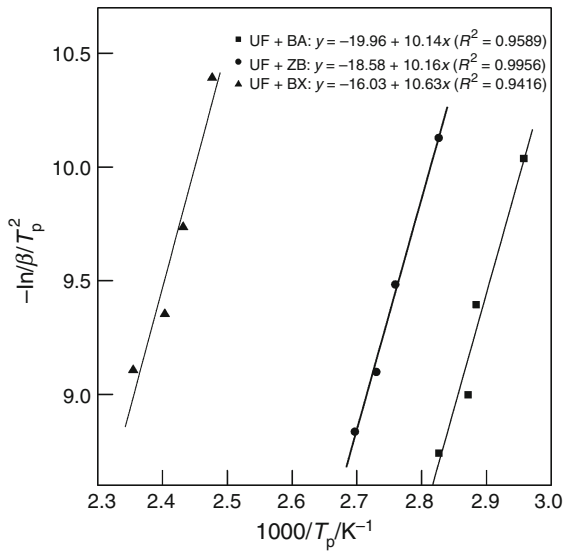

Fig. 5 Linear relationships between heating rate and peak temperature of UF resin with 20 wt% different FR chemicals

the UF resins cured in the presence of different kinds of 20 wt% FR chemicals.

It was found that the activation energy for cure reaction of the UF resin blended with ammonium chloride was 75.38 kJ/mol. For the cure reaction of the UF resin with the presence of boric acid, zinc borate, and borax, the activation energies were 84.37, 84.41, and 118.4 kJ/mol, respectively. The results indicated that FR chemicals appeared adverse effect on the curing behavior of the UF resin. The increased activation energy might due to the results of some energy consuming reactions accelerated by FR, such as decomposition.

The activation energy did not, however, reveal the whole picture of resin curing when certain FR was present; the activation energy was often influenced by the curing conditions. For example, the peak temperatures of the UF resin curing with addition of boric were lower than that with zinc borate at different heating rates. This indicated that the addition of boric acid had a stronger promotion effect on resin curing than the use of zinc borate. However, the activation energies of the UF resin with these two species were quite similar (84.37 and 84.41 kJ/mol). The case implied that other kinetic variables, such as the pre-exponential factor, should also be considered to better understand the cure kinetics of the UF resin in the presence of FR. According to the well-known Arrhenius equation, shown in Eq. 1, the rate constant of UF curing is determined by both the activation energy and the pre-exponential factor. The peak temperature corresponds to the curing rate of the UF resin or is directly proportional to the rate constant. According to the collision theory, the pre-exponential factor is equivalent to the total number of successful collisions that result in a reaction; these successful collisions occur as a result of reactant particles coming sufficiently into contact with each other [16].

For the pre-exponential factor Z, the cure reaction of the UF resin with zinc borate was 1.19×10^{12} that is a lower value than boric acid's 5.127×10^{12}. According to the collision theory, the lower Z value of the UF resin curing with zinc borate might have been a result of borate ions were unfavorable for resin curing behavior; as a result, a higher temperature was needed to ensure polycondensation. In addition, from Fig. 1, we could found that the UF resin mixed with borax showed the highest pH value. It is known to all that the acidy lower pH value was favorable for the UF resin curing. Therefore, to obtain a sufficient number of successful collisions for the curing reaction, the UF resin mixed with borax needed to be heated up to a higher reaction temperature. The result was well compatible with the gel time and peak temperature described above.

Conclusions

This study was conducted to investigate the effects of three boron compound FR chemicals on thermal curing behaviors of the UF resin, using non-isothermal method of DTA. The main findings drawn from this study can be summarized as follows.

All of the three kinds of boron compound FRs changed the pH values and gel time of aqueous solution of the UF resin. The addition of boric acid reduced the pH value and gel time of liquid UF resin the most, leading to acceleration of the UF resin cure. It also confirms the fact that a higher

temperature or increased time is needed to cure the UF resin blended with borax in practice. The pH values of the UF resin should be adjusted in proper range, when it was used to manufacture fire resistance panels with boron compound FR chemicals in practice. The loading levels of FR showed no significant effect on onset temperature, peak temperature, and reaction heat of cure reaction of the UF resin. The activation energies for curing reaction of the UF resins in the presence of boric acid, zinc borate, and borax, were 84.37, 84.41, and 118.4 kJ/mol, respectively, higher than that of the control one (75.38 kJ/mol). The activation energies and pre-exponential factor explained that all boron compound FR presented adverse effect on curing behavior of the UF resin.

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