Thermal Degradation and Stability of Accelerated-curing Phenol-formaldehyde Resin

Yuzhu Chen, Dongbin Fan, * Tefu Qin and Fuxiang Chu *

In order to study the thermal stability of accelerated-curing PF resin, the curing behavior of fresh PF resin was investigated in the presence of single accelerator of methylolurea derivatives (MMU), magnesium hydrate ($Mg(OH)_2$), 25% aqueous solution of sodium carbonate (Na_2CO_3), and propylene carbonate (PC). Also their optimum combination was added in fresh PF resin. The thermal stability of cured phenol-formaldehyde (PF) resins was studied using thermogravimetric analysis TG/DTA in air with heating rates of 5, 10, 15, and 20 °C min^{-1}. Thermal degradation kinetics were investigated using the Kissinger and Flynn-Wall-Ozawa methods. The results show that these accelerators can promote fresh PF resin fast curing, and the degradation of accelerated-curing cured PF resin can be divided into three stages. Single accelerator MMU, $Mg(OH)_2$, and Na_2CO_3 can promote fresh PF curing at low temperatures in the first stage, while the structure of PF resin which was added with MMU and PC was more rigid, according to thermal degradation kinetics. A novel fast curing agent which is compound with MMU+Na_2CO_3 for PF resin is proposed; not only can it maintain the advantage of fast curing of the single accelerator Na_2CO_3, but it also improves the thermal stability of PF resin.

Keywords: Accelerators; Kinetics; Phenol-formaldehyde resin; Thermal degradation

*Contact information: Research Institute of Wood Industry, Chinese Academy of Forestry, Beijing, 100091, P.R. China; *Corresponding author: fandongbin8@163.com; chufuxiang@caf.ac.cn*.

INTRODUCTION

Phenol-formaldehyde (PF) resin is one of the most suitable resins for producing exterior-grade wood composites, especially as PF offers the characteristics of high fire resistance, high char yield, and solvent resistance. PF resin can offer better shear strength and wood failure percentage (WFP) after curing crosslinking with hot pressing temperatures of 130 °C to 150 °C. However, its main drawback is a slower curing rate than other amino-type resins, which could consume more energy or time to achieve the basic mechanical properties requirement, leading to a reduction in the production efficiency. Many attempts have been made to accelerate the curing processes of PF resins, such as using different catalysts, additives, or modified resin formulas. Adding catalysts, such as carbonates, divalent metal ions, and esters, has been shown to be simple and effective.

Sodium carbonate (Na_2CO_3) has been shown to be the most effective catalyst to promote the curing of PF resin by shortening 30% of curing time (Kim *et al.* 2008). Fan *et al.* (2010) also found that Na_2CO_3 can accelerate oil-PF resin curing at a low temperature, leading to a shorter hot pressing time of only three minutes for the manufacture of three-layer plywood panels that has higher shear strength than the control oil-PF resin.

Some research has focused on fast-curing phenolic resins by introducing metallic ion catalysts such as Mg^{2+}, Ca^{2+}, and Ba^{2+} that promote the addition formaldehyde onto phenol in the ortho position and generate ortho-methylol groups. Grenier-Loustalot *et al.*

(1996) found a positive relationship between the characteristics of the catalyst (size and valence of cation) and the reaction rate.

The addition of ester- and lactone-based accelerators such as ethyl formate, propylene carbonate, γ-butyrolactone, and triacetin after synthetic processing of PF resins can also significantly increase the rate of condensation reactions. However, the curing accelerators are consumed during the reaction, indicating that they act not only as true catalysts but that they are also involved in self-condensation (Conner *et al.* 2002). Therefore, the application of propylene carbonate (PC) in accelerated-curing PF resins with this mechanism not only causes the reduction of resin consume, but also can reduce the hot-pressing time for the manufacture of panel products such as medium density fiberboard (MDF) (Park and Riedl 2000). Other studies on the effect of urea addition to PF resins after condensation found that urea addition could lower the free formaldehyde content and increase the degree of polymerization, while the curing rates at first increased and then decreased due to an increase in the amount of low-molecular weight methylolureas (Fan 2009; He and Riedl 2003).

The fast curing process of PF resins may lead to changes in micro cross-linking within the cured resin system, which has implications with respect to the thermal properties, thermal stability, durability, and service life of wood composites. Although most efforts studied the thermal curing of PF resins relative to accelerators, structures, and curing mechanisms of faster-curing resins, the effect of acceleration curing modification on thermal properties was not clear. The aim of this work was to obtain the optimal accelerators which could maintain or improve the thermal property of PF resin. The relationship between the PF curing properties and thermal degradation kinetics was also investigated.

EXPERIMENTAL

Materials

Phenol (> 99%), urea (≥ 99%), and formaldehyde (37% aqueous solution) were purchased from Beijing Yili Fine Chemicals Co. Ltd. (Beijing, China). Magnesium hydroxide (98%) and propylene carbonate (≥ 99%) were purchased from Tianjin Guangfu Fine Chemical Research Institute (Tianjin, China). Sodium carbonate (≥ 99%) was purchased from Sinopharm Chemical Reagent Co. Ltd. (Beijing, China). All chemicals used were of analytical reagent grade.

Methods

Synthesis of mixture of methylolureas (MMU)

Methylolureas of formaldehyde and urea with molar ratios of 1.0 and 1.2, respectively, were developed. The mixtures were processed in a tri-neck flask equipped with a thermometer, a stirrer, and a reflux condenser. The mixtures were stirred as the temperature increased from room temperature to 90 °C in 30 to 40 min, and then this temperature was maintained for an additional 30 min while the pH value was maintained from 8.0 to 8.5. Then, the mixtures were cooled to room temperature as the MMU product formed.

Synthesis of resins with and without accelerators

Phenol (99% purity; 291 g), formaldehyde solution (37%; 403 g), sodium hydroxide solution (30%; 124 g) (ratio of 1:1.6:0.3), and distilled water (30 g) were added to a tri-neck flask and heated to 95 °C over 30 to 40 min. After maintaining temperature for the 30-min synthesis reaction, the mixtures were cooled to 75 °C. Additional formaldehyde (124 g) and sodium hydroxide (62 g) were then added before the viscosity of the mixtures reached a dynamic viscosity between 300 and 500 mPa·s (measured at 20 °C), which should lead to a mixture temperature of approximately 70 °C. At this time, the final portions of distilled water (96 g) and sodium hydroxide (16 g) were added and the reaction product slowly cooled to room temperature (25 °C). The final pH and solid content of the PF resin were 10.0 (± 0.1) and 46% (± 1%), respectively. The final product served as the control PF resin.

The fast curing PF resins were developed by adding the accelerators magnesium hydrate ($Mg(OH)_2$), 25% aqueous solution of sodium carbonate (Na_2CO_3), propylene carbonate (PC) (1% to 5 % of total resin weight) to the controls, and the methylolureas (MMU) were mixed into the PF resin. The loading of MMU ranged from 1% to 10%, depending on the weight of total resin.

Measurement of gel time

About 5 g of the resin mixture was placed into a 16 mm × 180 mm test tube, and a thin wire spring was placed in the tube to manually mix the contents. The test tube was placed in an oil bath at a constant temperature of 138 °C, and the contents were mixed until gelation occurred; the gelation time was recorded. Three replicates were performed for each combination.

Measurement of thermal degradation

The PF resin and its blends of different accelerators were dried for 3 h at 120 °C until cured, then cooled to room temperature and ground into powders. Non-isothermal measurements were performed with a DTG-60 Thermogravimetry/Differential Thermal Analyzer (Shimadzu; Japan) at heating rates (β) of 5, 10, 15, and 20 °C min^{-1} from 30 to 550 °C. For each scan, approximately 7 to 10 mg of each mixture was added to an aluminum crucible, with an empty aluminum crucible used as a reference. The peak temperature, the percentage of weight loss at different temperatures, the temperatures of corresponding mass loss, and char residuals at 500 °C were obtained from the TG curves.

Activation energy analysis

Kinetic characterization is important for understanding structural changes of the degradation of phenolic resins during the different phases of degradation, which could be used to predict and improve the industrial performance of resin (Alonso *et al.* 2011). Based on dynamic analysis, isoconversional methods were used in this work. Kissinger (Jiang *et al.* 2011) and Flynn-Wall-Ozawa methods (He *et al.* 2004) were used for interpreting resin degradation kinetics, as shown in Eqs. 1 and 2, respectively,

$$-\ln\left(\frac{\beta}{T_{\mathrm{p}}^{\ 2}}\right) = \frac{E_a}{RT_{\mathrm{p}}} - \ln\left(\frac{ZR}{E}\right) \tag{1}$$

where β is the heating rate (K/min), T_{p} is the peak temperature, E_a is the activation energy (kJ/mol), R is the gas constant (8.314 J/mol/K), and Z is the pre-exponential factor (1/s).

On the basis of Eq. (1), there was a straight line between $-\ln(\beta/T_p^2)$ and $1/T_p$; therefore, the activation energy and pre-exponential factor can be calculated from the slope and the intercept, respectively.

From the Flynn-Wall-Ozawa equation (Eq. 2),

$$\ln\beta = C - 1.0516\left(\frac{E}{RT_p}\right) \tag{2}$$

there is linear relation between ln (β) and $1/T_p$, so the activation energy can be calculated from the slope of the linear equation.

RESULTS AND DISCUSSION

Gel Time of PF Resin with Single Accelerators

The gel times of the PF resin in the presence of MMU, $Mg(OH)_2$, Na_2CO_3, and PC with various loading levels are given in Fig. 1. As shown in Fig. 1a, the addition of MMU resulted in an acceleration of the curing process; the gel times of all MMU-PF resins with different F/U molar ratios and different loadings of MMU were much lower than those of the control resin, indicating that methylolurea derivatives may have promoted the polycondensation of PF resins to form three-dimensional networks. At the MMU loading of 1%, the gel time of PF resins with the F/U of 1.0 and 1.2 were 0.83 and 0.88 times that of the control resin, respectively. The curing times consistently decreased as the loading of MMU increased; the curing time decreased from 344 to 327 s for a 1.0 F/U molar ratio and from 362 to 347 s for a 1.2 F/U molar ratio when the loading was increased from 1% to 5%. The PF resin with MMU at 5% and a F/U molar ratio of 1.0 had the shortest gel time among all combinations tested.

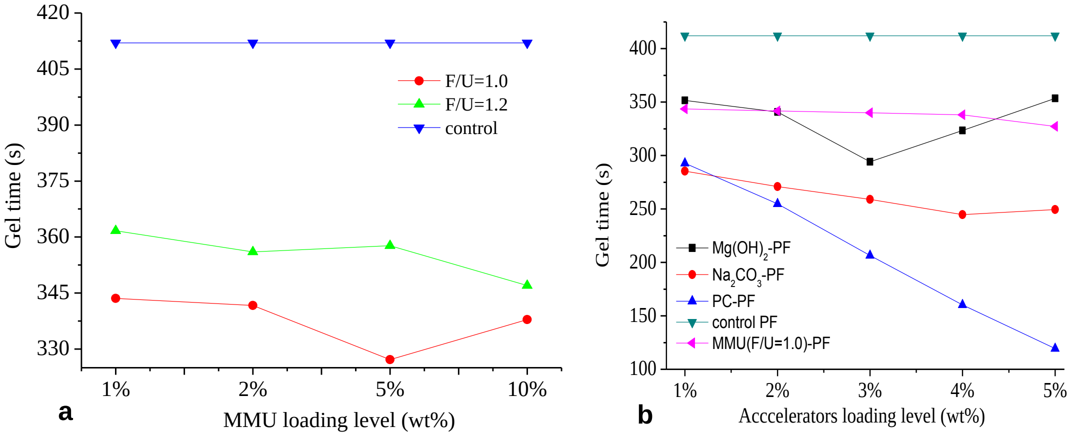

Fig. 1. Gel time of PF resins at 135 °C with different accelerator and different loading level

Urea in PF resin has an accelerating effect on resin curing by increasing the molecular size of the polymer at an equivalent viscosity, which is attributable to a higher degree of branching (Zhao *et al.* 1999). Methylolphenols appeared to react faster with urea than their auto-condensation. The properties of PF resins prepared with the addition of small amounts of urea appear to be consistent with what is observed in the reactions of the model compounds, *e.g.*, their gel times become shorter and viscosity increases with the addition of increasing amounts of urea (Pizzi *et al.* 1993).

The addition of $Mg(OH)_2$, Na_2CO_3, and PC also had a promoting effect on the curing process of PF resins (Fig. 1b). For the same loading of accelerators, PC was the most effective, leading to the shortest gel time. The ranking order of the efficacy was PC > Na_2CO_3 > $Mg(OH)_2$ > MMU > control resin. The effect of loading level of the accelerators was also very different between the types of the accelerators; an increase of loading level from 1 to 5% resulted in a decrease in the gel time from 280 to 125 s for the PC-accelerated PF resin, from 286 to 250 s for the Na_2CO_3-accelerated PF resin, from 352 to 294 s for the $Mg(OH)_2$-accelerated resin, and from 344 to 327 s for the MMU-accelerated resin.

These results indicate that transesterification of the PC may have taken place, which resulted in an increase in the reactivity of the ortho-hydroxymethyl groups. It has been reported that the esters or residue of their decomposition could attack the negatively charged phenolic nuclei in a polycondensation reaction, resulting in a higher functionality to activate methylol groups and hence increasing the curing speed and reducing the gel time of PF resin (Park and Riedl 2000; Pizzi and Stephanou 1994). Moreover, the bivalent metallic salts can accelerate both the action of phenolic nuclei with formaldehyde and the condensation of methylolphenols with other phenolic nuclei by forming metallic ion/phenol/formaldehyde complexes (Pizzi 1979a,b), resulting in an accelerating effect of Mg^{2+} on gelation of PF resin.

Thermal Stability (Degradation) of PF Mixtures with Single Accelerators

To compare the effect of accelerators on the degradation of PF resins, a series of TG-DTA scans was performed to test the cured resins with heating rates of 5, 10, 15, and 20 °C min^{-1}. The measurements of the amount and rate (velocity) of change in the mass (mass loss) of a sample as a function of temperature or time in a controlled atmosphere are used primarily to determine the oxidative stabilities of materials as well as their compositional properties. The TG technique can analyze materials that exhibit mass loss due to the decomposition, oxidation, and/or loss of volatiles (such as moisture) (Chen *et al.* 2008). The peak temperature, the percentage of weight loss at different temperatures, the temperature of corresponding mass loss, and char residuals at 550 °C obtained from the DTG curves are shown in Table 1.

There were three peak temperatures: peak I range from 57 to 96 °C, peak II from 374 to 404 °C, and peak III from 494 to 529 °C, depending on the accelerated PF mixtures. It is apparent that with the heating rate increase, the three peaks shifted to higher temperatures (Table 1). Taking a heating rate of 10 °C min^{-1} as an example, the degradation of the accelerated PF resins occurred in three steps, as shown in Fig. 2. There was a peak below 100 °C (*i.e.*, 65 °C for PC-PF, 68 °C for MMU-PF, 72 °C for PF, 69 °C for Na_2CO_3, and 76 °C for $Mg(OH)_2$). According to the common sense that no peak appeared around 100°C after drying for 3 h. An explanation for this phenomenon may be that the surface layer of resin was completely cured while the released water or formaldehyde from the core layer were sealed. Once the samples were taken out of beaker and then ground into powder immediately, these low molecular weight compounds may have been absorbed onto the surface of the powders, so the mass loss was apparent, associated with these low weight monomers becoming released as the temperature was elevated.

The temperature range of the second stage reaction was from 100 to 400 °C, and the changes in PF resin with the addition of accelerators during this stage were complex due to multiple reactions that occurred simultaneously, that is, the release of main contributors to the weight loss, such as free phenol, aldehyde, short oligomers, and water (Zhao *et al.* 2013). Moreover, methylene bridges decompose into methyl groups that yield both phenol and cresol homologs (Chen *et al.* 2008). Furthermore, auto-oxidation reactions have been proposed to take place by producing either -OH radicals or water, followed by the evolution of CO_2 (Costa *et al.* 1997; O'Connor and Blum 1987); although Chen *et al.* (2008) disputed the idea of the auto-oxidation reaction, noting that such a scheme is made difficult due to oxygen stripped during the first degradation stage.

Table 1. Peak Temperature Obtained from the DTG Curves of PF Mixture

Heating rate		Peak Temperature (°C)			Corresponding Mass loss (%)			Corresponding Temperature (°C)				Char residual (%) at 550 °C
					Temperature (°C）			Mass loss (%)				
	-	I	II	III	RT-100	100-400	400-550	5	10	20	30	
0	5	63	378	496	9.885	14.096	11.347	67	101	338	492	64.672
	10	72	392	509	8.75	13.869	12.775	75	111	358	509	64.606
	15	78	399	523	9.649	14.102	12.867	73	102	324	510	63.36
	20	85	401	526	4.894	13.381	13.164	101	186	429	537	68.561
1	5	59	382	502	7.915	13.579	12.104	72	138	382	507	66.497
	10	76	391	519	5.328	13.8	13.451	97	190	412	525	67.455
	15	85	399	526	4.146	13.138	14.802	112	215	440	535	67.914
	20	93	404	540	2.977	12.774	15.15	132	247	467	544	69.099
2	5	66	374	497	9.309	14.736	11.648	69	108	342	490	64.307
	10	68	389	506	10.714	14.712	11.888	68	95	319	485	62.783
	15	80	396	518	8.608	14.315	11.966	78	113	353	511	65.136
	20	85	400	526	7.528	14.329	12.406	83	125	369	522	65.737
3	5	63	382	496	6.383	12.767	10.891	87	163	417	547	69.959
	10	69	390	512	7.242	12.937	12.271	81	136	396	522	67.55
	15	86	399	524	5.137	13.41	12.991	98	178	426	532	68.462
	20	97	401	530	2.907	12.305	13.573	129	239	500	549	71.215
4	5	62	377	494	5.19	16.295	11.004	97	222	393	511	63.45
	10	65	392	506	7.751	15.081	11.794	77	140	373	513	64.176
	15	74	399	513	2.945	15.337	11.939	141	275	460	548	63.86
	20	81	401	522	5.564	15.34	12.612	96	194	406	532	65.038

0 = PF, 1 = PF+$Mg(OH)_2$ (3%), 2 = PF+MMU (5%), 3 = PF+Na_2CO_3 (2%), 4 = PF+PC (2%)

Taking the PF resin with MMU as an example, co-condensation between the hydroxymethyphenols and the methylolureas occurred between 170 and 176 °C, whereas self-condensation of hydroxymethyphenols occurred between 140 and 145 °C; the linkages may break down between the hydroxymethyphenols and the methylolureas as temperature rises due to weak thermal stability, and accelerators may self-decompose (*e.g.*, $Mg(OH)_2$ decomposes into MgO at around 390 °C due to heat absorption). In this temperature range from 100 °C to 400 °C, the mass loss of the MMU-PF resin was higher than that of the other four with the same heating rate, as shown in Table 1, with the higher degree of branching of MMU increasing the alkyl chain length, which may result in lower thermal stability of the resin. The length of the alkyl chain is longer or the content of alkyl-substituted phenol in the polymer is higher, and the decline in weight during this step is steeper (although the position of the substituent of the ring has only a minor effect) (O'Connor and Blum 1987).

When the temperature increased from 400 °C to 550 °C, the major polymer decomposition took place. The degradation of the polymeric molecules and the formation of small and volatile molecules, such as CO, CO_2, benzaldehyde, and phenol can account for the weight loss and contribute to the initial formation of char (Chetan *et al.* 1993a,b; Shulman *et al.* 1996). Li *et al.* (2010) found that char residuals increased with increasing heating rate, but this change was not noticeable. The reason for this variation may require further investigation. However, elevating the heat too quickly causes the reaction to occur at a higher temperature, resulting in an incomplete reaction; therefore, a slow rise in temperature is beneficial to the separation of each stage.

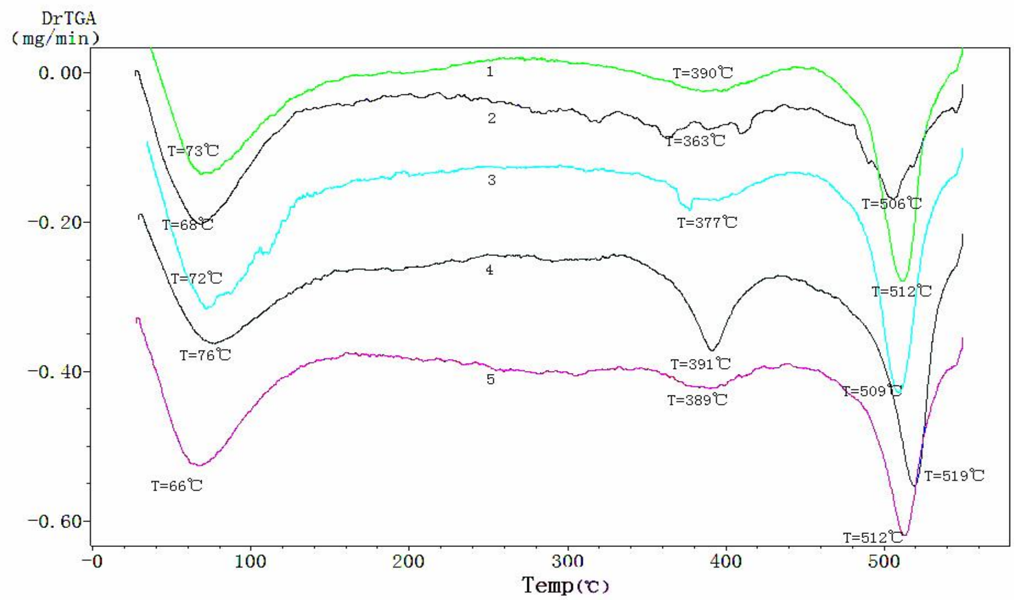

Fig. 2. The DTG 1st derivative curves of PF with accelerators with heating rate 10 °C /min. 1 = Na_2CO_3-PF, 2 = MMU-PF, 3 = PF, 4 = $Mg(OH)_2$-PF, 5 = PC-PF

Degradation Kinetic Analyses of PF Resin with Single Accelerators

Activation energy (E_a) is a kinetic parameter that reflects the sensitivity of a material to temperature and can be used as a reference to evaluate the curing rate of PF resin. A resin with a lower activation energy has a curing rate that is more sensitive to a temperature change. 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 (He and Riedl 2004; Li *et al.* 2010). Therefore, the pre-exponential factor was used to better understand the cure kinetics of the PF resin in the presence of accelerators.

Table 2 gives the peak temperatures at different heating rates, the activation energy (E_a) values calculated by the Kissinger method and their corresponding regression coefficient (R_a^2), the pre-exponential factor A, and the activation energy (E_k) values calculated by the Flynn-Wall-Ozawa equation and their corresponding regression coefficient (R_k^2).

It is apparent that the values of E and R^2 obtained by both methods were very similar, and there were only slight differences in the regression coefficients, between 0.03% and 4.14%. This means that the curing kinetic parameters calculated by both methods were credible and consistent. Moreover, similar to those of the pure PF resins, the decomposing processes of the accelerated PF resins can also be described by *n*th-order kinetics, following the Kissinger method. The differences in E_a and E_k between PF and the accelerated PF resins were within 8% except PF-Na_2CO_3 for 13%, indicating that their reaction mechanisms, active sites, or reaction paths may be very similar.

Table 2. Kinetic Parameters and Correlation Coefficients of the Thermal Degradation of PF and Addition of Accelerators by Kissinger (K) and Flynn-Wall-Ozawa (O) Methods

		PF types	PF	PF-$Mg(OH)_2$ (3%)	PF-MMU (5%)	PF-Na_2CO_3 (2%)	PF-PC (2%)
I	K	E_a	58	36	55	32	63
		Z	3.673×10^5	7.934×10^1	1.058×10^5	1.930×10^1	2.403×10^6
		R_a^2	0.9836	0.9986	0.8229	0.8633	0.7054
	O	E_k	61	39	58	36	66
		R_k^2	0.9866	0.9989	0.8504	0.899	0.7403
II	K	E_a	197	218	178	238	179
		Z	1.779×10^{12}	8.020×10^{13}	5.880×10^{10}	3.475×10^{15}	5.973×10^{10}
		R_a^2	0.9751	0.9909	0.9893	0.9751	0.9817
	O	E_k	198	218	180	237	180
		R_k^2	0.9775	0.9918	0.9904	0.9772	0.9837
III	K	E_a	207	183	222	192	235
		Z	2.499×10^{10}	4.430×10^8	3.072×10^{11}	2.280×10^9	1.763×10^{12}
		R_a^2	0.9762	0.9702	0.958	0.9971	0.9903
	O	E_k	209	187	209	195	236
		R_k^2	0.9789	0.9741	0.9789	0.9975	0.9913

During the first stage, while the peak temperatures of all resins were below 100 °C (Table 1), the E_a and E_k values of $Mg(OH)_2$ and Na_2CO_3-PF resins were much lower than that of the PF resin (Table 2). This means that $Mg(OH)_2$ and Na_2CO_3 can promote PF curing at low temperatures. With the reaction proceeding into the second stage, there is no obvious boundary between post-curing and degradation. The main reactions of components may occur between MMU, PC, and PF resins at this stage because the E_a and E_k values of MMU-PF and PC-PF resins were much lower than those of the PF resin.

Heating resins to around 500 °C resulted in higher values of the activation energy for MMU-PF and PC-PF resins than for the control PF resin, indicating that the structures of these two kinds of accelerated PF resins may be more ordered than that of others, requiring more energy to break the linkages.

The Z values are also given in Table 2. According to the collision theory, the Z value is correlated with the number of active sites and collision possibilities (Jinxue *et al.* 2011). It can been seen that both $Mg(OH)_2$- and Na_2CO_3-accelerated PF resin in the third stage have lower Z values than that of the control PF resin, which may illustrate that active sites such as methylene bridges were stripped during the course of the temperature rising to 500 °C and still reserve the quantity of active sites in the residue of PF resin with the added MMU and PC. Otherwise stated, the structure of accelerated PF resin with $Mg(OH)_2$ and Na_2CO_3 was less rigid and resulted in lower thermal stability.

Gel Time and Degradation Kinetics of PF Resin with Compound Accelerators

Compound accelerators may be used to see if there is an advantage over a single accelerator. Previous research by the authors showed that the viscosity increase due to PF+PC was too fast to meet the manufacture requirement which refers to the pot life being at least 4 h. Meanwhile the dispersity of $Mg(OH)_2$ in PF resin was poor, so that stratification appeared after standing for several minutes, so MMU and Na_2CO_3 were still present and able to compose the compound accelerators (Table 3). The gel time of PF resin with MMU + Na_2CO_3 were much lower than that of the control PF resin, though similar to that of MMU-PF resin, indicating that the addition of Na_2CO_3 had no accelerating effect on the curing of PF+MMU+Na_2CO_3.

Table 3. Gel Time of PF Resins with Compound Accelerators

Resin	Gel time (s)
PF	412
PF+Na_2CO_3 (2%)	271
PF+MMU (5%)	327
PF+MMU (5%)+Na_2CO_3 (2%)	338

The thermal degradation properties of PF resin with the compound accelerator MMU+Na_2CO_3 with heating rates of 5, 10, 15, and 20 °C min^{-1} are given in Table 4. With the heating rate rising, the trend of peak temperature PF+MMU and PF+Na_2CO_3 went up in Table 2, and changes of that of PF+MMU+Na_2CO_3 were the same in Table 4. The peak temperature of PF added with compound accelerator went up with heating rate rising in Table 4. This result was the same as for PF added with single accelerator MMU or Na_2CO_3. With a heating rate of 10 °C min^{-1}, for example, the ranking order of the peak I temperature was MMU+Na_2CO_3 > PF > Na_2CO_3 > MMU, whereas when the heating rate was 5 °C min^{-1}, the peak I temperature of PF resin with MMU was the highest, which shows that the different heating rate had a different peak temperature.

Table 4. Thermal Degradation Analysis with TG of PF Resins with the Compound Accelerator MMU (5%) + Na_2CO_3 (2%)

Heating rate	Peak Temperature (°C)			Corresponding Mass loss (%)			Corresponding Temperature (°C)				Char residual (%) at 550 °C
				Temperature(°C)			Mass loss (%)				
	I	II	III	RT-100	100-400	400-550	5%	10%	20%	30%	
5	57	392	499	6.768	14.594	10.116	83	189	383	513	68.522
10	76	398	512	5.257	14.162	11.727	98	225	407	529	68.854
15	80	403	523	5.965	14.139	12.161	91	176	398	528	67.735
20	96	402	529	3.081	13.786	12.02	131	277	450	552	71.113

When the temperature was raised to 100 °C, similar values of the mass loss of PF resin with MMU+Na_2CO_3 and Na_2CO_3 were observed (*i.e.*, the average values were 5.3% for MMU+Na_2CO_3-PF and 5.4% for Na_2CO_3-PF, with both lower than that of the control and PF with MMU). When the reaction proceeded into the second stage, the mass loss of MMU+Na_2CO_3-PF was up to 14.2%, similar to that of MMU-PF at 14.5% and higher than the 12.8% of Na_2CO_3-PF. When heat-treated to 500 °C, the mass loss of MMU+Na_2CO_3-PF was lower than that of the others, and its average value of char residuals was 69%, which was similar to that of Na_2CO_3-PF at 69.3%, and was higher than the others. In short, in the first and third stage, the reaction course of PF with MMU+Na_2CO_3 was similar to that of PF with Na_2CO_3, while MMU of compound accelerators was the main component that decomposed in the second stage.

The degradation kinetic parameters of PF resin with MMU+Na_2CO_3 are given in Table 5. In the first stage, the E_a value of MMU+Na_2CO_3-PF was 31 kJ/mol, similar to the 32 kJ/mol of Na_2CO_3-PF, both of which were much lower than the 58 kJ/mol for the control PF resin and 55 kJ/mol for the MMU-PF resin. This showed that the compounds (MMU+Na_2CO_3) accelerated the PF resin curing and seemed to be able to maintain the advantages of the single accelerator Na_2CO_3.

Table 5. Kinetic Parameters and Correlation Coefficients of the Thermal Degradation of PF with Compound Accelerators by Kissinger (K) and Flynn-Wall-Ozawa (O) Methods

		PF types	PF-MMU (5%)-Na_2CO_3 (2%)
I	K	E_a/ (kJ/mol)	31
		Z	1.5933×10^{1}
		R^2	0.9398
	O	E_k/ (kJ/mol)	35
		R^2	0.9569
II	K	*Ea*/ (kJ/mol)	422
		Z	7.7571×10^{29}
		R^2	0.921
	O	E_k/ (kJ/mol)	412
		R^2	0.9248
III	K	E_a/ (KJ/mol)	221
		Z	1.9612×10^{11}
		R^2	0.9944
	O	*E*k/ (kJ/mol)	222
		R^2	0.995

As mentioned before, both the higher degree of branching of MMU and Na_2CO_3 exist in the same PF resin, which requires more energy to cross-link or form methylene bridges breakdown into methyl groups. Therefore, the E_a value of MMU+Na_2CO_3-PF was 422 kJ/mol and the Z value was 7.7571×10^{29} in the second stage, both higher when compared to that of PF added single accelerator MMU or Na_2CO_3. In the third stage, the double effect of MMU and Na_2CO_3 may result in many low weight molecules in the system after degradation, which results in higher thermal stability, similar to Na_2CO_3-PF and higher than that of the control and MMU-PF.

CONCLUSIONS

1. Four kinds of single accelerators, *i.e.*, MMU, $Mg(OH)_2$, Na_2CO_3, and PC, show an obvious promoting effect on the curing of PF resin. The ranking order of the efficacy is PC > Na_2CO_3 > $Mg(OH)_2$ > MMU > the control resin.
2. The degradation of thermal PF resin accelerated by a single accelerator can be divided into three stages. In the first stage, the peak I temperature range was 57 to 96 °C, and MMU, $Mg(OH)_2$, and Na_2CO_3 promoted PF curing at lower temperature due to their lower E_a values. In the second stage, the peak II temperature ranged from 374 to 404 °C, and peak III of third stage from 494 to 529 °C, mostly due to the breakages of the methylene bridge and the degradation of phenolic resin, respectively. The structure of MMU-PF and PC-PF resins were more rigid than the control, and $Mg(OH)_2$ and Na_2CO_3 added resin due to their higher E_a and Z values. With a heating rate increase, the three peaks shifted to higher temperatures.
3. The degradation of thermal PF resin accelerated by a compound accelerator was also divided into three stages. In the first and third stages, Na_2CO_3 had a more obvious effect on mass loss than did MMU, while MMU had the predominant effect in the second stage. The E_a and Z values of PF+MMU+Na_2CO_3 were higher in comparison to the control and single accelerator resin, due to the different accelerating mechanisms of Na_2CO_3 and MMU. In the third stage, many low-weight molecules still exist in the system after degradation. In short, the optimal compound accelerator MMU+Na_2CO_3 maintained the advantage of fast curing of the single accelerator Na_2CO_3, while also improving thermal stability to be better as single accelerator MMU added in PF resin.

ACKNOWLEDGEMENTS

The authors are very grateful for financial support from National Natural Science Foundation of China (Project No. 31200441) and National Key Technology R&D Program of China (Project No. 2012BAD24B04).

REFERENCES CITED

Alonso, M. V., Oliet, M., Dominguez, J. C., Rojo, E., and Rodriguez, F. (2011). "Thermal degradation of lignin-phenol-formaldehyde and phenol-formaldehyde resol resins," *Journal of Thermal Analysis and Calorimetry* 105(1), 349-356.

Chen, Y. F., Chen, Z. Q., Xiao, S. Y., and Liu, H. B. (2008). "A novel thermal degradation mechanism of phenol-formaldehyde type resins," *Thermochimica Acta* 476(1), 39-43.

Chetan, M. S., Ghadage, R. S., Rajan, C. R., Gunjikar, V. G., and Ponrathnam, S. (1993a). "Thermolysis of orthonovolacs. Part 1. Phenol-formaldehyde and m-cresol formaldehyde resins," *Thermochim. Acta* 228, 261-270.

Chetan, M. S., Ghadage, R. S., Rajan, C. R., Gunjikar, V. G., and Ponrathnam, S. (1993b). "Thermolysis of orthonovolacs. Part 2. Phenol-formaldehyde and α-naphthol-formaldehyde resins," *J. Appl. Polym. Sci* 50, 685-692.

Conner, A. H., Lorenz, L. F., and Hirth, K. C. (2002). "Accelerated cure of phenol-formaldehyde resins: Studies with model compounds," *Journal of Applied Polymer Science* 86(13), 3256-3263.

Costa, L., Di Montelera, L. R., Camino, G., Weil, E. D., and Pearce, E. M. (1997). "Structure-charring relationship in phenol-formaldehyde type resins," *Polymer Degradation and Stability* 56(1), 23-35.

Fan, D. B. (2009). "Synthesis, structure, and properties of urea- or biomass oil-phenol-formaldehyde cocondensed resins," Beijing Forestry University, pp. 41-55.

Fan, D. B., Chang, J. M., Gou, J. S., Xia, B. H., and Ren, X. Y. (2010). "On the cure acceleration of oil-phenol-formaldehyde resins with different catalysts," *Journal of Adhesion* 86(8), 836-845.

Grenier-Loustalot, M., Larroque, S., Grande, D., Grenier, P., and Bedel, D. (1996). "Phenolic resins: 2. Influence of catalyst type on reaction mechanisms and kinetics," *Polymer* 37(8), 1363-1369.

He, G. B., and Riedl, B. (2003). "Phenol-urea-formaldehyde cocondensed resol resins: Their synthesis, curing kinetics, and network properties," *Journal of Polymer Science Part B-Polymer Physics* 41(16), 1929-1938.

He, G., and Riedl, B. (2004). "Curing kinetics of phenol formaldehyde resin and wood-resin interactions in the presence of wood substrates," *Wood Science and Technology* 38(1), 69-81.

He, G., and Y, N. (2004)."Influence of the synthesis conditions on the curing behavior of phenol-urea-formaldehyde resol resins," *Journal of Polymer Science* 95(6), 1368-1375.

Jiang, J., Yang, Y., Li, Ch., and Li, J. (2011). "Effect of three boron flame retardants on thermal curing behavior of urea formaldehyde resin," *Journal of Thermal Analysis and Calorimetry* 105(1), 223-228.

Kim, S., Kim, H., Kim, H., and Yang, H. (2008). "Fast curing PF resin mixed with various resins and accelerators for building composite materials*," Construction and Building Materials* 22(10), 2141-2146.

Li, X., Gao, J. G., and Sun, B. B. (2010). "Thermal degradation kinetics of boron-containing phenol formaldehyde resin by paraformaldehyde method," *Thermosetting Resin* 25(6), 10-13.

O'Connor, D., and Blum, F. D. (1987). "Thermal stability of substituted phenol-formaldehyde resins," *Journal of Applied Polymer Science* 33(6), 1933-1941.

Park, B. D., and Riedl, B. (2000). "C-13-NMR study on cure-accelerated phenol-formaldehyde resins with carbonates," *Journal of Applied Polymer Science* 77(6), 1284-1293.

Pizzi, A. (1979a). "Phenolic and tannin-based adhesive resins by reactions of coordinated metal ligands. I. Phenolic chelates," *Journal of Applied Polymer Science* 24(5), 1247-1255.

Pizzi, A. (1979b). "Phenolic and tannin-based adhesive resins by reactions of coordinated metal ligands. II. Tannin adhesive preparation, characteristics, and application," *Journal of Applied Polymer Science* 24(5), 1257-1268.
Pizzi, A., and Stephanou, A. (1994). "Phenol-formaldehyde wood adhesives under very alkaline conditions. 2. Esters curing acceleration, its mechanism and applied results," *Holzforschung* 48(2), 150-156.
Pizzi, A., Stephanou, A., Antunes, I., and de Beer, G. (1993). "Alkaline PF resins linear extension by urea condensation with hydroxybenzylalcohol groups," *Journal of Applied Polymer Science* 50(12), 2201-2207.
Shulman, G. P., Lochte, H. W. (1996). "Thermal degradation of polymers. 2. Mass spectrometric thermal analysis of phenol-formaldehyde polycondensates," *J. Appl. Polym. Sci.* 10, 619-635.
Zhao, C., Pizzi, A., and Garnier, S. (1999). "Fast advancement and hardening acceleration of low-condensation alkaline PF resins by esters and copolymerized urea," *Journal of Applied Polymer Science* 74(2), 359-378.
Zhao, Y., Yan, N., and Feng, M. W. (2013). "Thermal degradation characteristics of phenol-formaldehyde resin derived from beetle infested pine barks," *Thermochaimica Acta* 555, 46-52.

Article submitted: March 17, 2014; Peer review completed: April 22, 2014; Revised version received and accepted: April 28, 2014; Published: May 16, 2014.