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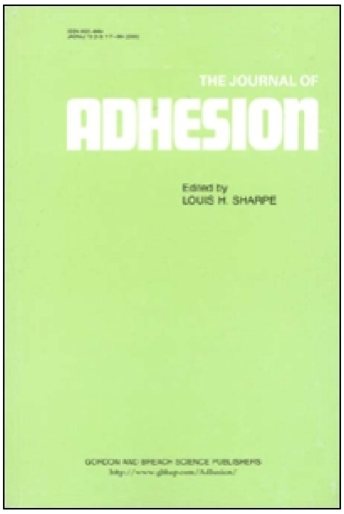

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On the Cure Acceleration of Oil-Phenol-Formaldehyde Resins with Different Catalysts

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Oil-phenol-formaldehyde (Oil-PF) resins containing 50 wt% replacement of petroleum phenol with bio-oil were prepared and different catalysts [sodium carbonate (Na_2CO_3), urea, and magnesium oxide (MgO)] were added in the synthesis process of resins to accelerate the cure. The cure-acceleration effects of catalysts on cure characteristics of oil-PF resins were investigated by using differential scanning calorimetry (DSC), gel time, and a plywood panels test. The results indicated that catalysts presented different accelerating effects on the cure of the oil-PF resin. Both Na_2CO_3 and MgO can accelerate the oil-PF resin cure at a low temperature; however, urea seemed to have no significant effect on the cure of the resin. The application of Na_2CO_3- and MgO-accelerated oil-PF resins reduced hot pressing time for the manufacture of three-layer plywood panels. Compared with MgO, Na_2CO_3 had more significant accelerating effect on the cure of the oil-PF resin.

Keywords: Catalysts; Cure characteristics; Cure-acceleration; Oil-phenol-formaldehyde resin

1. INTRODUCTION

Phenol-formaldehyde (PF) resins, as the first true synthetic polymers, have a wide range of commercial applications in industrial products such as impregnating resins, molding compounds, coatings, and wood binders [1]. In recent years, the rising cost and forseeable future scarcity of petrochemicals have driven researchers to investigate

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renewable resources as an alternative source for phenol in PF resins. Agricultural and forestry residues are abundant biomass resources and can be converted into phenolic chemicals by degradation/de-polymerization processes [2].

Fast pyrolysis is a relatively recent thermochemical conversion technology. It can convert biomass into low-molecular weight and phenolic-rich bio-oil that has the potential to replace partially or totally petroleum-based phenol in the production of PF type resins [3]. Therefore, many studies have been conducted in the past on the use of biomass pyrolysis oils for preparing PF resins [4–6]. Early work focused on the production of resols with phenolic fraction separated from pyrolysis bio-oil by solvent extraction [4,7]. However, such an extracting process involved a series of lengthy and complex liquid-liquid extraction steps, resulting in a relatively low yield of the phenolic fraction and a negative effect on the process economies that limited its industrial application. In addition, panels bonded with resins prepared with these separated fractions had poor mechanical properties. In recent years, some researchers used the whole oils without previous separation. Himmelblau and Grozdits [8] synthesized PF resins with a phenol substitution of 50% by bio-oil that was obtained from fast pyrolysis of mixed hardwoods (maple, birch, and beech). These resins showed nearly as well in making three-ply plywood of southern pine as a commercial resin. Oil-PF resols can be also prepared at phenol replacements of 25 and 50 wt% using bark-derived oils [6,9]. Strandboards manufactured with these resins exhibited comparable mechanical properties with those of panels made with commercial surface resins under the same pressing conditions. However, these PF resins containing a portion of pyrolysis oil required higher hot pressing temperature for good bonding strength when manufacturing wood-based composite panels as compared with pure PF resins. The cure of oil-PF resols was accelerated by mixing with a small concentration of propylene carbonate (PC); however, the PC did not significantly improve the mechanical properties of the panels [10].

The cure rate of PF resins can be accelerated by using various catalysts and additives such as carbonates, bivalent metallic ions, urea, etc. [11]. Higuchi *et al.* [12] found that both Na_2CO_3 and K_2CO_3 had an accelerating effect on the cure of PF resin. The resins with these additives had a shorter gel time than the control PF resins. Zhang *et al.* [13] showed that MgO-catalyzed PF resin can cure at a low temperature. Faster curing PF resins were also prepared by adding a certain amount of urea in the synthesis [14,15]. Although considerable work has been done on the chemistry, structure, and cure properties of cure-accelerated PF resins, study on the effect of the addition of basic catalysts on cure acceleration of oil-PF resins has not been reported in the literature.

In this work, in view of the goal of a price-competitive renewable resin, the crude pyrolysis bio-oil was directly used and oil-PF resins were prepared with 50 wt% replacement of petroleum phenol with bio-oil. Catalysts such as sodium carbonate (Na_2CO_3), urea, and magnesium oxide (MgO) were added in the synthesis process to accelerate the oil-PF resin cure. The cure characteristics and adhesive performance of the cure-accelerated oil-PF resins were investigated by Differential Scanning Calorimetry (DSC), gel time, and a plywood panels test.

2. MATERIALS AND METHODS

2.1. Materials

Phenol, formaldehyde aqueous solution (37%), Na_2CO_3, urea, MgO, and sodium hydroxide were commercial products supplied by Beijing Chemical Industries, Beijing, China and were used directly as raw materials without further purification. Bio-oil from fast pyrolysis of larch sawdust was supplied by the Institute of Wood Based Material, Beijing Forestry University. It is composed of 34% phenolic compounds, 30% water, 15% organic acids, and 21% other compounds including sugars, esters, ketones, etc. (wt% of total bio-oil).

2.2. PF Resin Preparation

To better study the cure characteristics of oil-PF resins, a neat PF resin with a F:P:NaOH molar ratio of 1.6:1:0.20 was prepared following a previous procedure [16].

2.3. Preparation of Oil-PF Resins

In the following experiments, crude bio-oil was used without any pre-treatment except for the remove of low molecular weight organic acids, and some amount of water, by vacuum distillation. The bio-oil contained about 18% by wt. moisture and its molar mass was assumed to be 94 g/mol. The control and cure-accelerated oil-PF resins had 50% by wt. phenol replacement by bio-oil.

The control oil-PF resin (traditional NaOH-catalyzed resin) was prepared with overall F:P:NaOH molar ratio of 0.9:1:0.23. The preparation procedure was as follows: 1 mol of phenol was mixed with 0.36 mol of 30% aqueous sodium hydroxide solution and 1.5 mol of formaldehyde in a three-neck reactor equipped with a stirrer, a thermometer, and a reflux condenser. After stirring for 10 min at 30°C, the reaction mixture was then heated to 80°C over a period of 25 min and maintained at this temperature for 30 min. After that, 0.7 mol of bio-oil was charged and the reaction was maintained at 80°C for 30 min. About 0.3 mol of bio-oil, 0.3 mol of formaldehyde, and 0.1 mol of 30% sodium hydroxide solution were added to the reactor and the temperature was kept at 85°C until the Gardner-Holdt viscosity (measured at 20°C) of the resin reached between 300 and 500 mpa · s.

The cure-accelerated oil-PF resins with different catalysts were based on this preparation procedure. The catalysts used were Na_2CO_3, urea, and MgO and the addition amount was 2 wt% of the total resin. Na_2CO_3 and MgO were added at the beginning of the resin reaction, together with the first part of sodium hydroxide solution. Urea was added when the resin reached between 300 and 500 mpa · s, and the mixture continued to react for about 15 min at 85°C. The resin was then cooled to 30–40°C in a cold water bath.

Viscosity and pH values were, respectively, obtained with a rotational viscometer (NDJ-5S, Shanghai Changji Geological Instruments Co. Ltd., Shanghai, China) and pH meter (PHS-3B, Shanghai Precision and Scientific Instrument Co. Ltd., Shanghai, China) at 20°C. Gel times were measured at 160°C and each value of gel time is an average of five test results. These properties of PF and Oil-PF resins are shown in Table 1.

2.4. DSC Analysis

All DSC analyses was made using a DSC-60/60A (Shimadzu, Tokyo, Japan) instrument and TA60 thermal analysis software. The equipment was calibrated with indium and zinc samples. About 10 mg of resin samples were sealed in a high-pressure stainless steel crucible that was capable of resisting up to 5 MPa pressure. Dynamic scans were carried out at a heating rate of 10°C/min in the range of

TABLE 1 Properties of Prepared PF and Oil-PF Resins

Resins	Solid content (%)	pH	Viscosity (mPa · s)	Gel time[a] (s)
PF resin	51.2	10.39	421	433
The control oil-PF resin	49.8	10.47	445	441
Na_2CO_3-accelerated oil-PF resin	50.0	10.72	414	352
Urea-accelerated oil-PF resin	50.4	10.58	457	450
MgO-accelerated oil-PF resin	50.1	10.45	478	375

[a] Measured at 160°C.

30–250°C. DSC runs were made with at least two replications per sample and the reproducibility of the data was ±3%. The result of onset temperature, peak temperature, and endset temperature was an average of replication tests.

2.5. Plywood Panels Preparation

Three-layer laboratory plywood panels of 400 × 400 × 4.5 mm were prepared using the control and cure-accelerated oil-PF resins, and rotary peeled poplar (*populus*) veneers. To each resin glue-mix 15% wheat flour by weight on the liquid resin was added. The adhesive-coated veneer was stacked between two uncoated veneers with the grain directions of two adjacent veneers perpendicular to each other. Three-layer plywood panels were prepared under the following conditions: moisture content of veneer 8–10%; glue spread 350–370 g/m^2 (double line); hot pressing temperature 150°C; hot pressing pressure 1.0 MPa; hot pressing time 3 and 5 min. The wet strength properties of plywood panels were measured by previous test methods [17]. Fifteen specimens were used for the wet strength test.

3. RESULTS AND DISCUSSION

3.1. Cure Characteristics

Figure 1 shows the DSC curves of PF resin and the control and cure-accelerated oil-PF resins. The cure characteristics of each resin are summarized in Table 2 in terms of characteristic curing temperatures (onset temperature, peak temperature, and endset temperature). The DSC curves give information about the curing process while the samples are subjected to a heating rate program. The curves in Fig. 1 show significant differences in the thermochemical cure characteristics of the compounds in terms of the shape and position of the reaction peaks. Pyrolysis bio-oil is a mixture of oligomeric as well as monomeric compounds of very diverse chemical nature. The bio-oils are composed mostly (~50%) of low-molecular weight phenolic-rich compounds including monomeric phenols, lignin, and tannin-based compounds. During synthesis of oil-PF resins, these phenolic compounds were able to react with formaldehyde or with methylol groups of phenolic compounds and further condensed into a series of oligomers that contained active reactivity sites such as methylol groups and unsubstituted phenolic sites. The DSC curves of PF resin and the control oil-PF resin present an exothermic peak with a maximum between 146 and 151°C, which indicated that they presented a similar curing process. This

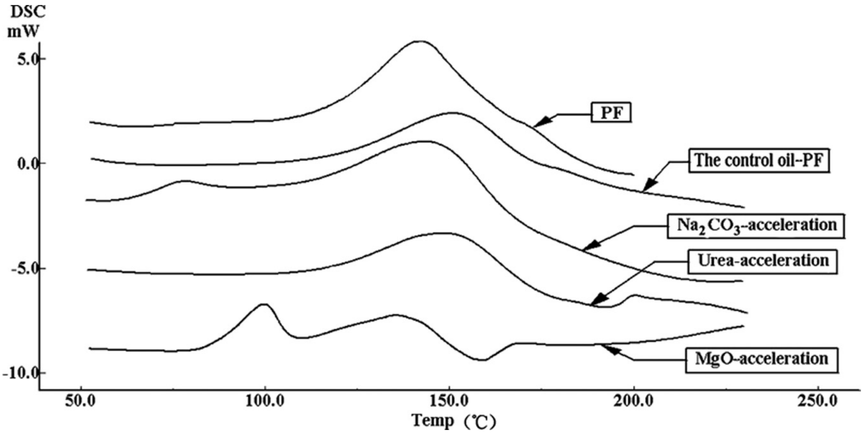

FIGURE 1 DSC curves of cure-accelerated oil-PF resins with different catalysts.

peak was associated with the condensation of methylol groups with phenolic units according to previous reports [9,18]. It is clearly seen from Fig. 1 and Table 2 that the control resin had a higher curing temperature than the PF resin. This was because petroleum-based phenol possessed more active sites than the bio-oil.

Both Na_2CO_3- and urea-accelerated oil-PF resins show two DSC exotherms. Higuchi *et al.* [12] reported that Na_2CO_3 appeared to present purely an accelerating effect on the polycondensation reaction

TABLE 2 Characteristic Curing Temperature of Cure-Accelerated Oil-PF Resins with Different Catalysts

Resins	Onset temperature (°C)	Peak temperature (°C)	Endset temperature (°C)
PF resin	114.6	146.7	178.2
The control oil-PF resin	117.7	151.0	194.3
Na_2CO_3-accelerated oil-PF resin			
Peak 1	64.9	78.4	87.8
Peak 2	113.6	144.3	176.8
Urea-accelerated oil-PF resin			
Peak 1	119.5	149.8	174.6
Peak 2	188.7	199.1	208.3
MgO-accelerated oil-PF resin			
Peak 1	86.9	99.9	105.9
Peak 2	113.8	136.5	154.6

of PF resin. Christiansen and Gollob [18] related the peak at 98–130°C to the methylolation reaction of free formaldehyde with free phenol. Therefore, taking into account that the control resin has no exothermic peak at 98–130°C in Fig. 1, the first peak at around 78.4°C in the curve of Na_2CO_3-accelerated oil-PF resin was possibly caused by the reaction of free formaldehyde with phenolic compounds of bio-oil due to the cure accelerating effect of Na_2CO_3. Another possible explanation of the first peak of Na_2CO_3-accelerated oil-PF resin was that low-reactivity phenolic compounds might react with each other under a cure accelerating condition such as having Na_2CO_3 as a catalyst. The second peak at around 144.3°C of Na_2CO_3-accelerated resin was due to the formation of methylene bridges. It is noticeable from Fig. 1 and Table 2 that Na_2CO_3-accelerated oil-PF resin shifted down to lower curing temperature when compared with the control resin, and had reactivities comparable with PF resin. As Fig. 1 and Table 2 show, the peak at around 150°C of urea-accelerated oil-PF resin was associated with the formation of methylene or dibenzyl ether bridges, which was similar to the corresponding peak in the PF, the control oil-PF, and Na_2CO_3-accelerated oil-PF resins. The small exothermic peak was attributed to further reactions such as the condensation of the dibenzyl ether bridges to methylene bridges with the elimination of formaldehyde [17]. Urea in PF resin has an accelerating effect on the resin cure by inducing an increase in molecular size of the polymer at equivalent viscosity attributable to a higher degree of branching [15]. But from Fig. 1 and Table 2 we can see that the addition of urea did not accelerate the cure of the oil-PF resin, but possibly retarded the cure. One possible explanation in this study was that at the end of the reaction added urea might have reacted with free formaldehyde in the resin to form methylolureas, or remained in free form. And those urea units needed relatively high apparent activation energy values when reacted with phenolic compounds of the oil-PF resin during curing. Another possibility might be that the added urea has a poor solubility in the bio-oil that caused the effect observed in Fig. 1 and Table 2.

The DSC curve of MgO-accelerated oil-PF resin also displays two exothermic peaks. The bivalent metallic salts can accelerate both the reaction of phenolic nuclei with formaldehyde and the condensation of methylolphenols with other phenolic nuclei by forming the metallic ions/phenols/formaldehyde complexes [19–21]. Thus, when compared with the exothermic peak of the control resin, the first peak of MgO-accelerated oil-PF resin was possibly associated with the addition reaction of free formaldehyde with phenolic compounds of bio-oil, or was caused by the faster reaction of low reactivity phenolic compounds due to the cure-acceleration effect of MgO. The second peak of the exotherm was caused by the condensation of methylol groups with phenolic compounds to form methylene bridges.

As Fig. 1 and Table 2 show, the MgO-accelerated oil-PF resin had a much lower curing temperature than the control resin, indicating that MgO can make the oil-PF resin cure at a lower temperature that was likely to result from the formation of high-*ortho* resins [19]. It was also known from the gel time in Table 1 that both Na_2CO_3 and MgO increased the curing rate of oil-PF resin; however, urea slightly inhibited the resin cure. Compared with curing characteristics of Na_2CO_3- and MgO-accelerated oil-PF resins, we can conclude that Na_2CO_3 had a more significant accelerating effect on the reaction of phenolic compounds of bio-oil with formaldehyde than MgO, and that the accelerating effect of MgO on the condensation of methylol groups was more marked than Na_2CO_3.

3.2. Adhesive Performance

The adhesive performances of oil-PF resins without and with the addition of catalysts were evaluated by testing the wet strength of plywood panels. The wet strength values of plywood panels bonded with oil-PF resins are summarized in Table 3, where the effects of hot pressing time are shown.

When hot pressing time was 5 min, the Na_2CO_3- and MgO-accelerated oil-PF resins had similar wet strength to the control resin; however, the urea-accelerated resin had a lower wet strength. This was possibly because urea-accelerated oil-PF resin had a much longer gel time than the control resin during curing (as shown in Table 1).

TABLE 3 Wet Strength Values of Plywood Panels Bonded with Cure-Accelerated Oil-PF Resins Under Different Hot Pressing Times

Resins	Hot press time (min)	Plywood shear strength, mean ± S.D.[a] (kgf/cm^2)
The control oil-PF resin	3	5.61 ± 0.16
	5	9.8 ± 0.18
Na_2CO_3-accelerated oil-PF resin	3	9.6 ± 0.08
	5	10.3 ± 0.11
Urea-accelerated oil-PF resin	3	4.1 ± 0.10
	5	8.3 ± 0.12
MgO-accelerated oil-PF resin	3	8.9 ± 0.14
	5	9.4 ± 0.13

[a] Fifteen replicates of each resin, S.D.: standard deviation.

Another possible explanation is that the urea-accelerated oil-PF resin had a certain amount of untreated urea due to poor solubility of urea in the bio-oil. The untreated unreacted as an unbound unit that was not easy to react with methylol groups of the phenolic compounds to form the oligomers during the resin curing process, thus, to decrease the tightness of the final hardened resin network. Previous research showed that the application of cure-accelerated PF resin by the addition of Na_2CO_3 can reduce total hot pressing time for the manufacture of three-layer MDF panels [22]. Pizzi [21] reported that when limited hot press time was involved, plywood glued with tannin/formaldehyde adhesives containing the metal ions were simply more cured and consequently presented higher strength, which was due to faster cure promoted by the presence of the metal ions. Therefore, when the hot pressing time was decreased to 3 min, the wet strength of Na_2CO_3- and MgO-accelerated resins decreased a little; however, the control resins significantly decreased from 9.8 to 5.6 kgf/cm^2. It is also observed from Table 3 that urea-accelerated oil-PF resin had the lowest wet strength when the hot pressing time was 3 min. This resulted from the urea-accelerated oil-PF resin being difficult to react adequately to form a highly cross-linked network during a 3-min curing time due to its much longer gel time. As Table 3 also shows, Na_2CO_3-accelerated oil-PF resin had the highest wet shear strength under the same hot press time regardless of whether it was 3 min or 5 min. This indicated that when a limited hot press time was involved, the cure-acceleration effect of Na_2CO_3 was more significant than that of the other catalysts.

In conclusion, the addition of Na_2CO_3 and MgO in the resins synthesis can reduce the hot pressing time of three-layer plywood panels bonded with oil-PF resins. Among all the catalysts, Na_2CO_3 had more a significant improving effect on both the cure and wet strength of oil-PF resin.

4. CONCLUSION

In this paper, cure-accelerated oil-PF resins with 50 wt% replacement of phenol with bio-oil were prepared using different catalysts such as Na_2CO_3, urea, and MgO. Both Na_2CO_3- and MgO-accelerated oil-PF resins shifted down to lower characteristic curing temperature; however, urea-accelerated resin presented a higher curing temperature compared with the control resin. The results of gel time also indicated that both Na_2CO_3 and MgO increased the curing rate of oil-PF resin; however, urea slightly inhibited the resin cure. The application of

Na_2CO_3- and MgO-accelerated oil-PF resins reduced the hot pressing time for the manufacture of three-layer plywood panels.

In conclusion, both Na_2CO_3 and MgO had an accelerating effect on the cure of the oil-PF resin; however, urea seemed to have no significant effect. Compared with MgO, Na_2CO_3 had a more significant cure-acceleration effect on the oil-PF resin.

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