Modified Synthesis of Phenolic Novolac by Biomass Pyrolysis Oil

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(Received on 21st October 2008, accepted in revised form 31st May 2010)

Summary: The possibility of synthesis of fast curing phenolic novolac has been studied under the catalyst of HCl/ $Zn(AC)_2$. Synthesis of high-ortho novolac resins modified with different concentration (10, 20, 30 and 40 wt %) of biomass pyrolysis oil have been performed according to the reaction conditions of novolac production from pure phenol and formaldehyde. Curing reaction of resins indicated that resins modified with biomass pyrolysis oil (10 wt %) provide fast curing property with cure time ranges from 40 to 50 s and suitable softening point range from 85 ℃-95 ℃. The structure of fast curing novolac was characterized by FT-IR and DSC.

Introduction

Phenolic resins are typically cross-linkable polymeric resins made from phenol and aldehydes (formaldehyde). Novolac is one of the phenolic resins made under acidic conditions using excess phenol; the acid catalyzes the reaction of phenol and formaldehyde to form the cross-linkable polymeric resin. It is widely used for the formation of molded pieces and articles [1].

As one of raw materials in novolac production, phenol is primarily obtained from petroleum and its price is expensive because of the shortage of energy source. Therefore, a number of attempts have thus been made in recent years to at least partially substitute the petroleum-based phenol in phenolic resins with inexpensive phenols derived from biomass [2-5].

Biomass has been recognized as a sustainable replacement for its cleanness and substantial sources. Besides, zero emission of CO_2 can be achieved because CO_2 released from biomass will be revolved into the plants by photosynthesis quantitatively. Pyrolysis of biomass materials is known to produce a complex mixture of phenols and their alkylated compounds, which are derived primarily from the lignin contained in the feedstock. Biomass can be utilized as a source for valuable chemicals like phenols in synthesis of phenolic resins.

In this work, we have investigated the possibility of synthesis of fast curing novolac resins (PPF, resins from Pyrolysis oil- Phenol-Formaldehyde) using biomass pyrolysis oil, phenol and formaldehyde as starting materials under acidic conditions. Resins obtained have been characterized by several techniques.

Results and Discussions

Synthesis of Novolac from Pure Phenol and Formaldehyde (PF)

Ortho-connection and contra-connection in novolac had a great influence on the cure time because the contra-position of phenol shown higher activity than ortho-position of phenol [6]. Compared with conventional novolac, using $Zn(AC)_2$ as the catalyst gave high ortho novolac with short cure time because $Zn(AC)_2$ can promote the ortho-position connection in novolac [6]. However, the yield and soft point of obtained novolac was not satisfied. On the other hand, using HCl as catalyst, the resin obtained was in high contra connection with high yield and soft point. Therefore, we tried to combine the advantages of these two catalysts to achieve an efficient method in synthesis of fast curing phenolic resins. The results of novolac from pure phenol and formaldehyde are shown in Table-1. It was found that the soft point and cure time of novolac were promoted by this methodology. By using both of the catalysts, it was possible to modify a suitable ratio of ortho connection and contra connection in resin.

The differences between ortho- connection and contra-connection in phenolic resin were studied by

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Table-1: Properties of novolac from pure phenol and formaldehyde

Catalyst	Reaction time(h)	Yield (%)	Soft point (℃)	Cure time (s)
HCl	**2**	**91.6**	**98**	**108**
$Zn(AC)_2$	**7**	**67.8**	**47**	**68**
$HCl / Zn(AC)_2$[a]	**3**	**90.3**	**93.5**	**46.0**

a. Reaction time of resin synthesized by $HCl / Zn(AC)_2$ = reaction time 1(0.5 h) + reaction time 2(2.5 h)

FT-IR, the results are shown in Fig. 1. The absorption band of ortho-connection in resin is observed at 755 cm^{-1} and the band of contra-connection is observed at 850 cm^{-1}. From Fig. 1, it can be seen that the novolac catalyzed by HCl / $Zn(AC)_2$ shown higher ortho-connection than the novolac catalyzed by HCl but lower ortho-connection than the novolac catalyzed by $Zn(AC)_2$.

DSC-thermograms were obtained for novolacs obtained with different catalyst are shown in Fig. 2. Compared with resin obtain by strong acid (HCl), it was indicated that the cure reaction of resin catalyzed by $HCl/Zn(AC)_2$ occurs at lower temperature. This conclusion was in good agreement with the result of FT-IR spectra in Fig. 1.

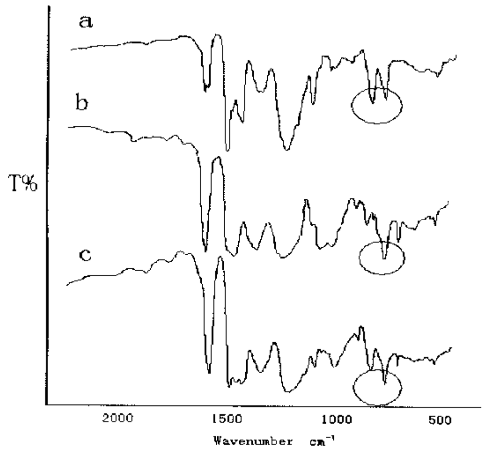

Fig. 1: FT-IR spectra of novolacs (a, catalyst: HCl; b, catalyst: $Zn(AC)_2$; c, catalyst: $HCl/ Zn(AC)_2$).

Synthesis of Novolac with Different Concentration of Biomass Pyrolysis Oil (PPF)

In GC-MS analysis (see Table-2), it was determined that the pyrolysis oil from biomass materials produces a complex mixture of phenolic compounds. Therefore, such a complex mixture of phenolic compounds could be used as a substitute for the petroleum-based phenol in the synthesis of phenolic resins.

Table-2: Main components in biomass pyrolysis oil.

Composition	wt%
Phenol,-3-methyl-	**1.980**
Phenol, -2-methoxy-	**6.314**
Phenol, -4-ethyl-	**4.272**
Phenol,-2-methoxy-4-methyl	**3.367**
Benzenediol,-3-methyl-	**1.277**
Hydroquinone	**1.610**
Phenol,-4-ethyl-2-methoxy-	**1.857**
1,2-Benzenediol, -4-methyl-	**2.372**
2-Methoxy-4-vinylphenol	**2.663**
Vanillin	**3.479**
Phenol,-2-methoxy-4-(1-propenyl)-	**4.061**
4-Hydroxy-2-methoxycinnamaldehyde	**3.798**

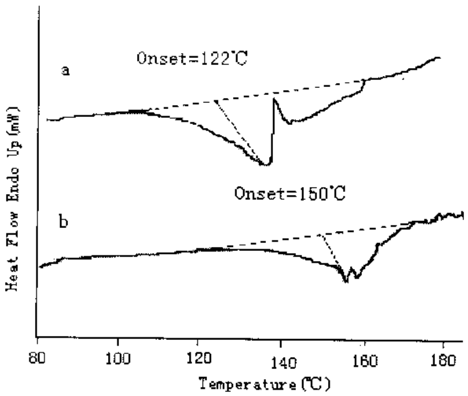

Fig. 2: DSC thermograms of novolac s.(a catalyst: $HCl/ Zn(AC)_2$); b catalyst: HCl) with 10 wt % hexamine

In this paper, in order to investigate the effect of biomass pyrolysis oil on synthesis of fast curing novolac, we attempted to using phenol, formaldehyde and biomass pyrolysis oil as starting materials in the presence of $HCl/Zn(AC)_2$ as catalyst. The results of substitute ratio on the properties of novolac are shown in Table-3.

From Table-3, it can be seen that with the increasing usage of biomass pyrolysis oil, the reaction time and catalyst used in reaction were also increased in order to obtain the novolac resin with good yield and suitable soft point. In previous GC-MS analysis, most of the components identified

Table-3: Effect of substitute ratio on novolac resins.

m(phenol) : m(insoluble fraction)	Reaction time 1 /h	Reaction time 2 /h	Catalyst,HCl/ $Zn(AC)_2$ ª	Yield/%	Soft point/℃	Cure time/s
0	0.5	2.5	0.1% / 1.5%	90.4	92.5	43.5
1 : 9	1.5	1.5	0.1% / 1.5%	90.5	93.5	56.0
2 : 8	2.0	2.5	0.2% / 1.5%	85.6	90.0	89.5
3 : 7	2.0	2.5	0.3% / 1.5%	83.7	85.0	95
4 : 6	1.5	2.5	0.4% / 1.5%	88.3	93.0	100

Mole ratio of HCl and $Zn(AC)_2$ to phenol

were oligomeric lignin-derived components. Compared with pure phenol, ortho-position and contra-position or both of position in these lignin derivatives were taken place by methyl, methoxy, propenyl, ketones, and aldehyde groups. Therefore, it was difficult to react with formaldehyde because these phenol derivatives did not provide enough reaction positions in molecular structure. Moreover, there were other components without phenolic structure in biomass pyrolysis oil. Therefore, biomass pyrolysis oil used in synthesis of novolac resin was not in good reactivity. In our future work, we aim to extract phenol rich compounds from biomass pyrolysis oil to use as phenol substitute.

The different substitute ratio of biomass pyrolysis oil in resins is shown in Fig. 3. Compared with FT-IR spectra in Fig. 1, there is appearance of new bands at about 1700 cm^{-1}. These bands must be attributed to the biomass pyrolysis oil present in the resins because they are not present in reference resin spectra (Fig. 1). It was also found that using biomass pyrolysis oil from biomass pyrolysis oil as phenol substitute, the obtained novolac still remain its high ortho-connection.

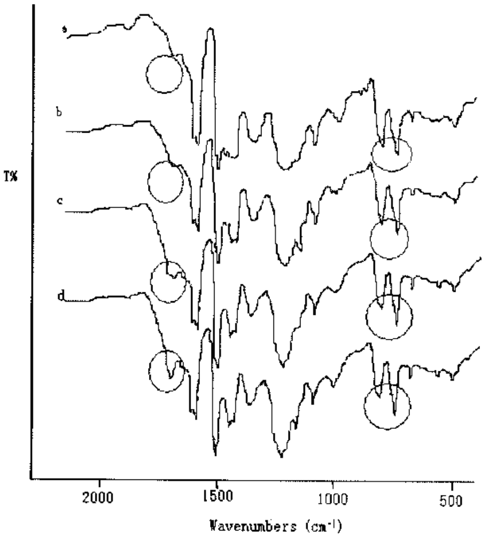

Fig. 3: FT-IR spectra of novolac s in different substitute ratio (a : 10%; b : 20%; c : 30%; d : 40%)

Experimental

General

The fast pyrolysis bio-oil from biomass used in experiment was the same as in literature [7,8]. The feedstock of pyrolysis was rice husks, they were produced from Anhui province, China. They stored for one year before production of bio-oil. The rice husks were dried (moisture 7.7%) and milled (average diameter 0.3192 cm) before pyrolysis. The yield of bio-oil was 56%, charcoal was 24% and gas was 20%. The bio-oil was used in experiment without any pretreatment and the bio-oil was held in a refrigerator for 3 month before its upgrading.

FT-IR spectra (max in cm^{-1}) were recorded on a MAGNA-IR 550 spectrophotometer. Gas chromatography-mass spectrometry (Agilent 6890N/5973N) was conducted to analyze the composition of bio-oil. The separation was done using column of HP-5, 30 m ×0.25 mm×0.25 um.

Cure time : The cure time of resins was determined (HG 5-1338-80, China). Each resin (1.0 g) with 10 wt % hexamine was placed into the grooves at 150℃ and the time for the formation of gel was determined.

Thermal analysis : Thermal analysis was carried out with Pyris Diamond (PerkinElmer) differential scanning calorimeter (DSC). A 5-10 mg sample was sealed in a medium pressure capsule pan and scanning temperature ranges from 25 to 280 °C was

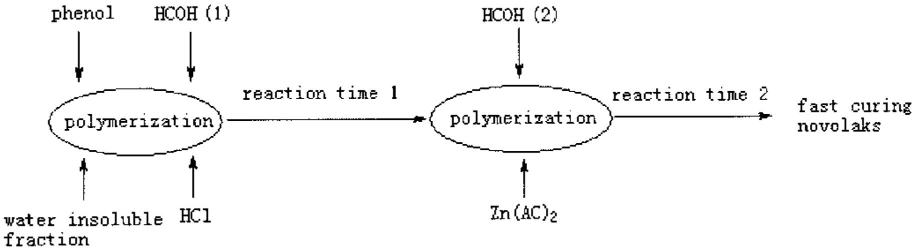

Fig. 4: Scheme for synthesis of fast curing novolac.

employed for thermal characterization. The sample crucibles were heated at 10 °C min^{-1}.

Experimental Setup and Procedure

The process of synthesis of fast curing novolac (PPF) substitute by biomass pyrolysis oil is shown in Fig. 4. Biomass pyrolysis oil was added in several concentrations (10, 20, 30, and 40 wt %) according to total amount of phenol used in synthesis of PPF. F1 (formaldehyde used in first step, HCOH(1)) : F2 (formaldehyde used in second step, HCOH(2)) = 3 : 2. The reaction mixture was stirred and refluxed in the first step catalyzed by HCl and catalyzed by $Zn(AC)_2$ in the second step. Water was stripped off by distillation under vacuum at the end of the synthesis.

Novolac from pure phenol and formaldehyde (PF) was synthesized and characterized as reference. The synthesis process was the same as PPF.

Conclusions

1. Synthesis of novolac with fast curing property from pure phenol and formaldehyde was studied and shows that the novolac catalyzed by HCl / $Zn(AC)_2$ give suitable soft point and fast cure time.
2. The possibility of using biomass pyrolysis oil as partial substitute of phenol in synthesis of phenolic novolac has been proved using FT-IR.
3. It was found that biomass pyrolysis oil gave negative effect on fast curing property of novolac. In order to obtain novolac with cure time ranges from 40 to 50 s, suitable amount of biomass pyrolysis oil used in resins was below 10 %.

Acknowledgements

The authors would like to thank the National Natural Science Foundation of China (30671649) and Special Fund for Fundamental Research of CAF(200904008, CAFINT2010C04, INT2008C03) for the financial support during this investigation.

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