Reducing the Contents of Free Phenol and Formaldehyde in Phenolic Foam

Wanli Li, Qiang Lin, Mingfa Yan, Yousi Zou

Department of Material Science and Engineering, Xiamen University, Xiamen, 361005, China

Received 24 September 2002; accepted 21 January 2003

ABSTRACT: The problem of overly high contents of remnant monomers (free phenol and free formaldehyde) in phenolic foam was studied. Free phenol was characterized by iodimetry, and free formaldehyde was characterized by a hydroxylamine hydrochloride method. The effect of the phenol/formaldehyde molar ratios and the reaction temperature on the contents of the remnant monomers was examined. The effect of adding urea on the content of free formaldehyde was investigated. The effect of the foaming process on the contents of the remnant monomers was examined in detail. Phenolic foams in which the content of free phenol was 0.09% and the content of free formaldehyde was less than 0.1% were successfully prepared. A prepolymer of polyurethane, which toughened the phenolic foam, lowered the contents of free phenol and free formaldehyde. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 2333–2336, 2003

INTRODUCTION

Typically, phenolic foams are made by the heating of a mixture of a resol, a liquid blowing agent, a surfactant, and an acid catalyst, which initiates a condensation reaction. The resols generally used are prepolymers of phenol and formaldehyde made under aqueous basic conditions with an excess of formaldehyde. Compared with rigid plastic insulation materials such as polystyrene, polyurethane, and polyethylene, phenolic foam has low smoke and flammability properties, which make it an excellent candidate for use in buildings, ships, and aircraft with promising developments in materials and new processing techniques.

However, phenolic resin contains overly high contents of free phenol and free formaldehyde that cannot be removed substantially. It is well-known that free phenol and free formaldehyde are toxic, and they are suspected to be carcinogens. They can also cause environmental problems. The recent public awareness of the hazards of free phenol and formaldehyde in phenolic foam will also undoubtedly lead to a decreased share of the insulation market for phenolic foam.

With deficiencies such as the mechanical strength, high open cell content, and corrosion having been resolved to a great extent (except for friability), this study was undertaken to reduce the overly high contents of free phenol and free formaldehyde in phenolic foam. A trend of decreasing free phenol and free formaldehyde during the synthesis of resols has been reported in recent years.[1–4] Manfredi et al.[5] gave the results of free phenol and free formaldehyde contents with different formaldehyde/phenol (F/P) molar ratios. We investigated the literature and found that there was little information on reducing the contents of free phenol and free formaldehyde in phenolic foam. Various methods of reducing the contents of free phenol and free formaldehyde in phenolic foam were studied.

Correspondence to: Y. S. Zou (yszou@jingxian.xmu.edu.cn).

Journal of Applied Polymer Science, Vol. 90, 2333–2336 (2003)

EXPERIMENTAL

Resin preparation

Formaldehyde (37% aqueous solution) and phenol (analytical reagent) in various molar ratios (F/P = 1.2, 1.5, 1.8, or 2.2) were added to a 250-mL, three-necked flask fitted with a condenser and a mechanical stirrer. The pH was adjusted to about 8–9 with an aqueous (50%) solution of sodium hydroxide. The mixture was heated to a preset temperature (heating rate = 1°C/min) with stirring and was maintained at that temperature for a certain period (at 90°C for 1.5 h or at 80°C for 5 h). The mixture was then cooled to room temperature, and the pH was adjusted to 7 with an aqueous (10%) solution of hydrochloric acid. The dehydration of the resol was performed inside the same flask *in vacuo* at 75–80°C until a viscosity of about 2500 mPa s at 20°C was obtained. The resols were kept at 4°C after the synthesis until they were used.

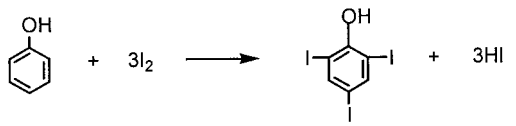
Foam formation

A foamable mixture was first prepared by the thorough mixing of 100 parts by weight resol, 4 parts tween 80 surfactant, and 8 parts petroleum ether blowing agent (boiling range = 30–60°C). An acid catalyst

mixture (8 parts 70% *p*-toluene sulfonic acid and 6 parts phosphoric acid) was then added to this mixture, and fast stirring was maintained for 1 min. The foamable mixture was immediately poured into a paper mold and placed in an oven set at 80°C for a period of 30 min.

Free phenol determination

Iodimetry was employed to determine the free phenol.[6] The resin (or milled foam) under study was mixed with an excess of an iodine solution in an acidic medium for a definite time:



After the reaction of free phenol and iodine was completed, the excess iodine was then titrated with a standard sodium hyposulfide solution with a starch solution as an indicator.

Free formaldehyde determination

The hydroxylamine hydrochloride method was employed to determine the free formaldehyde.[7] It is based on the liberation of hydrochloric acid on the addition of hydroxylamine hydrochloride to formaldehyde:

$$HCHO + NH_2OH \cdot HCl \rightarrow CH_2NOH + H_2O + HCl$$

The liberated hydrochloric acid was titrated with a potassium hydroxide solution with bromophenol blue as an indicator.

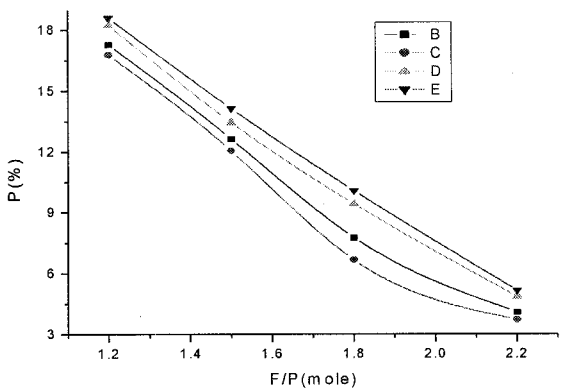


Figure 1 Content of free phenol in the resol under different conditions: (B) 92°C with 3 g of urea, (C) 92°C without urea, (D) 80°C without urea, and (E) 80°C with 3 g of urea.

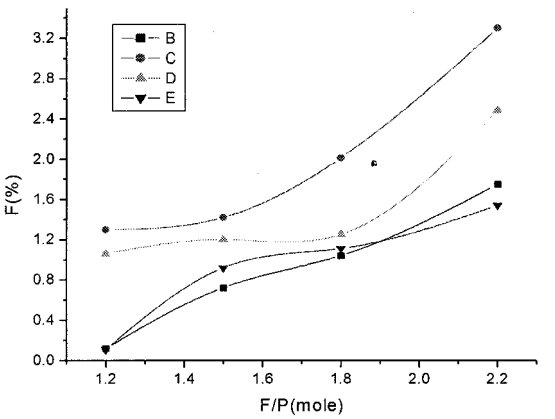


Figure 2 Content of free formaldehyde in the resol under different conditions: (B) 92°C with urea, (C) 92°C without urea, (D) 80°C without urea, and (E) 80°C with urea.

RESULTS AND DISCUSSION

To reduce the contents of free phenol and free formaldehyde in phenolic foam, we should first reduce their contents in phenolic resin.

Free phenol and free formaldehyde in the resol

The disappearance of phenol monomers is the condensation reaction between formaldehyde and aromatic (ortho) carbons and/or the condensation of hydroxymethyl groups on the same carbons.[8] The disappearance of phenol during the synthesis was quick during the first 25 min and almost stopped for the last 35 min of the reaction.[9] The most effective method for decreasing the content of free phenol is increasing the F/P molar ratio. We carried out a series of experiments for F/P molar ratios of 1.2, 1.5, 1.8, and 2.2 under a mild temperature condition (80°C). The results are shown in Figure 1(D). The content of free phenol obviously decreased with an increase in the F/P molar ratios. These results followed trends similar to the values obtained by Manfredi et al.[5] For an F/P molar ratio of 1.2, the content of free phenol was very high, about 18.24%. With increasing F/P molar ratios, the content of free phenol obviously decreased. The content of free phenol was only 4.85% at an F/P molar ratio of 2.2.

With an increasing reaction temperature, the reactivity of phenol increases. This is beneficial for reducing the content of free phenol. The resol was prepared at a relatively high temperature (92°C). We found that the content of free phenol in the resol prepared at 92°C was lower than that at 80°C. The content of free phenol was only 3.71% at an F/P molar ratio of 2.2 [Fig. 1(C)].

Figure 2 shows that the content of free formaldehyde increased slowly with increasing F/P molar ratios. As for free formaldehyde, 3 parts urea (in contrast

TABLE I
Contents of Free Phenol and Free Formaldehyde in Phenolic Resin and Foam

Conditions	Free phenol (%)		Free formaldehyde (%)	
	Phenolic resin	Phenolic foam	Phenolic resin	Phenolic foam
F/P = 1.5, 80°C, with urea	13.45	0.20	1.20	<0.1
F/P = 1.5, 80°C, without urea	14.14	0.24	0.92	<0.1
F/P = 2.2, 80°C, with urea	5.16	0.14	1.54	<0.1
F/P = 1.8, 92°C, without urea	6.67	0.13	2.01	<0.1
F/P = 1.8, 92°C, with urea	7.76	0.15	1.04	<0.1
F/P = 2.2, 92°C, with urea	4.08	0.09	1.75	<0.1
F/P = 1.8, 92 °C, with urea and prepolymer of polyurethane	4.08	Undetectable	1.75	Undetectable

to 100 parts phenol) was added as a formaldehyde catcher during the last 30 min of the reaction. It was obvious that adding urea had a significant effect on the free formaldehyde. For example, the content of free formaldehyde was only 0.11% at F/P = 1.2 and 1.54% at F/P = 2.2. This was because methylol urea groups were formed by the reaction of the postadded urea with the unreacted formaldehyde. Some remnant formaldehyde was reacted. The content of free formaldehyde varied little with an increasing reaction temperature [see Fig. 2(B,E) or Fig. 2(C,D)]. Adding urea had little effect on the free phenol [see Fig. 1(B,C) or Fig. 1(D,E)], but the resistance to temperature and humidity was relatively reduced.

Therefore, under these conditions at 92°C, with an F/P ratio of 1.8–2.2 and 3 g of urea, the smallest contents of both free phenol and formaldehyde were obtained, as well as an adequate balance between free sites and methylol groups available for the acid cure. The resin prepared under this condition was easy to foam and yielded a uniform product.

Free phenol and free formaldehyde in phenolic foam

The resols prepared under various conditions were foamed. The results are given in Table I. Except for the effect of the accessory ingredients (the surfactant, blowing agent, and mixed acid catalyst or modifier), the contents of free phenol and free formaldehyde in phenolic foam were lower than those in the resol. In particular, the contents of free formaldehyde were all lower than 0.1%. The content of free phenol was extremely low and practically undetectable for foam prepared by the resol (at 92°C with added urea and F/P = 2.2).

Typical resols used in foam preparation contain about 85% solids, and the volatile components consist mainly of water, formaldehyde, and phenol. As the foaming process was completed under 80°C, the free formaldehyde that originally existed in the resol emitted at temperatures close to 70°C,[10] and phenol also emitted partly. The weight of the mixture for foaming decreased 6% after foaming.

The prepolymer of polyurethane, which toughened the phenolic foam, lowered the contents of free phenol and free formaldehyde, as shown in Table I. The phenolic foam toughened by the prepolymer of polyurethane will be discussed in another article in detail.

CONCLUSIONS

We undertook this study to investigate the effects of various conditions on the contents of free phenol and free formaldehyde in phenolic foam. We reached the following conclusions:

1. With increasing F/P molar ratios, the content of free phenol obviously decreased, but the content of free formaldehyde increased slowly. Therefore, to reduce the content of free phenol, it would be beneficial to increase the F/P molar ratios. With a properly increasing reaction temperature, the reactivity of phenol increases, and the content of free phenol decreases.
2. Adding urea had a significant effect on the removal of free formaldehyde.
3. In an acidic medium during cure, a reaction between phenol and formaldehyde occurred, and so did a reaction between free phenol and monosubstituted methylol phenol. Moreover, the volatile components, consisting mainly of water, formaldehyde, and phenol, emitted under the foaming temperature. Therefore, a foaming process with an acid mixture as a catalyst at 80°C during cure can drastically reduce the contents of free phenol and free formaldehyde in phenolic foam.
4. The prepolymer of polyurethane, which toughened the phenolic foam, lowered the contents of free phenol and free formaldehyde.

Phenolic foams in which the contents of free phenol and free formaldehyde were less than 0.1% or even

undetectable were successfully prepared. We believe that phenolic foams will be widely applied in buildings when the problem of overly high contents of free phenol and free formaldehyde in phenolic foam is resolved. Further work is being carried out.

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