

Effect of Solvent on the Chain Conformation and Cure Behavior of Phenolic Resin

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ABSTRACT: The research indicates that in comparison with other solvents, such as ethanol, propanol, butyl alcohol and acetone, which are usually selected as the solvent in phenolic solution, methanol can increase curing rate and enhance crosslinking density of phenolic resins. Therefore, the chain conformations of resole dissolved in different solvents are investigated by using viscosity method. It shows that the chain conformation of resoles changes from loose coil to compact ball, as the strength of hydrogen bond between resole and solvent drops along with the decrease of polarity of solvents. The transition of the chain conformation causes the decrease of reaction probability and reaction rate between functional groups of resoles. The number of unreacted molecules increases, and the crosslinking den-

sity of cured resins decreases. The differential scanning calorimetric analysis shows that compared with the resins in methanol, ethanol, propanol, and butyl alcohol, exothermic peak of resole in acetone is obviously wider, and its peak exothermic temperature is lower. Both optical microscope pictures and atomic force microscope pictures demonstrate that the crosslinking density of resins in methanol is higher than those in other solvents. The research concludes that the type of solvent has a great influence on the curing rate and curing degree of resoles. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 3009–3015, 2008

Key words: phenolic resin; solution properties; viscosity; conformation analysis; curing of polymer

INTRODUCTION

Phenolic resins are used across a range of industries, and their many different applications reflect the way in which this superficially system can be adapted to meet different requirements. A large amount of phenolic resin solutions are used in coatings, adhesives, composite wood materials, industrial laminates, and paper impregnation. And reinforced by glass fiber or carbon fiber, phenolic resins can be converted into high performance composite materials. The selection of solvent may affect dissolvability of the phenolic resin and its chain conformations, and consequently affect its curing reaction and final properties.

Solution properties of phenolic resins are quite dependent upon solvent type, interaction between the solvent and resins, and molecular conformation of the resins. Although a lot of research on the chain conformation of polymers has been made,^{1–3} phenolic resin's solution properties are less reported. And most solution properties are limited to novolac resins. Tobiason et al.⁴ determined the Mark-Houwink-Sakurada (MHS) equation for random novolac, and obtained the values of α in acetone, tetrahydrofuran,

and 1N NaOH aqueous solution, respectively. However, it was pointed out that the wide molecular weight distribution resulted from successive precipitational fractionation increased the value of exponent α . Kamide and Miyakawa⁵ reported $\alpha = 0.5$ for high ortho novolac and $\alpha = 0.28$ for random novolac in acetone. Sue concluded that the MHS exponent in acetone for ortho-cresol novolac, which was rich in ortho-para methylene linkages, was larger than the one for the all-ortho novolac and para-cresol novolac, which were rich in ortho-ortho methylene linkages. Sue also found that the MHS value α for acetylated phenolic resin is larger than the value α for branched one.^{6,7}

By comparing to novolac, the structure of resole is more complicated, which has many branched chains and reactive methylol end groups. Sometimes, resole is even more important than novolac in thermoset resin industry. Therefore, it is much meaningful to study the resole's chain conformations in different solvents, as well as the effect of the conformation transition on curing reaction of the resins. Although there has been a lot of research on the curing reaction of the phenolic resins involving synthesis parameters, curing time, temperature, hardener concentration, and resin pH, etc.,^{8–10} the study of the solvent influence on the property of the phenolic resins solution and curing reaction is still not found, to our best knowledge.

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Ethanol or acetone is usually selected to be solvent for phenolic solution. However, our research indicated that by comparing to other solvents, methanol can increase curing rate and enhance crosslinking density of the phenolic resin. To explain such difference, the chain conformation of the resoles in different solvent and the effect of its conformation transition on the curing rate and curing degree are investigated in this study. Viscosity measurement is used to evaluate the effect of solvents, namely methanol, ethanol, propanol, butyl alcohol and acetone, on the chain conformation of the resins. The influence of conformation transition on the curing rate is analyzed by using differential scanning calorimetry (DSC), and crosslinking density of the resins is further discussed according to optical microscope pictures and atomic force microscope (AFM) pictures.

EXPERIMENTAL

Materials

Phenolic resins were synthesized by a standard method. Essentially, phenol and formaldehyde solution were used as monomers in a polycondensation reaction with ammonia employed as a catalyst. A molar ratio of phenol to formaldehyde of 1 : 1.3 was applied. The resins with different number-average-molecular weight (\bar{M}_n) were prepared by controlling condensation time.

Molecular weight measurement

The number-average-molecular weight of the resins was determined using a KNAUER K-7000 vapor pressure osmometer operating at 100°C with *N,N*-dimethyl formamide as the solvent. Calibration standard was benzyl ($M_n = 210.23$).

Viscosity measurements

Viscosity measurements or flow times of dilute solutions of the resoles in solvents were obtained in Ubbelohde dilution viscometers at a constant temperature of 25°C ± 0.1°C. Analytical reagent grade methanol, ethanol, propanol, butyl alcohol, and acetone were used as the solvents.

Differential scanning calorimetric measurements

Thermal analysis was conducted on a NETZSCH STA 449C coupled to a computerized data station. A sample solution of 5 mg was placed in aluminum pan, in the air for 2 h without cover. Samples are heated in inert nitrogen atmosphere from room temperature to 80°C at constant heating rate of 2°C/min, and held for 10 min at 80°C to volatilize solvent.

Then dynamic scans were conducted with a temperature range from 80 to 300°C with heating rate 10°C/min.

Optical microscopic measurements

The surface morphologies of resoles in methanol, ethanol, propanol, and butyl alcohol were observed on Nikon TE2000-U inverted microscopy, respectively. The resole solution on glass plates was cured at 165°C for 4 h.

Atomic force microscopic measurements

AFM measurements were performed with Veeco NanoScope IIIa MultiMode instrument. The surface morphologies of resoles in methanol and acetone were further compared by AFM. The resins were treated as described earlier.

Fourier-transform infra-red spectroscopic analysis

Fourier-transform infra-red (FTIR) spectra of cured samples were recorded on a Nicolet Magna-IR 550 infra-red spectrophotometer, using KBr pellet, in the wave length range of 500–4000 cm⁻¹.

RESULTS AND DISCUSSION

The solvent influences on the conformation of resole chains

The phenolic resins solution is used in many fields such as coating, adhesive, casting. The chain conformation of the resins may be effected by the solvents. To investigate the influence of the solvents on the chain conformation of the phenolic resins, various solvents, such as, methanol, ethanol, propanol, butyl alcohol, and acetone, were used in viscosity measurements.

In solution, a polymer molecule is a randomly coiling mass and most of its conformation occupies many times the volume of its segments alone. The size of the molecular coil is very much influenced by the polymer-solvent interaction forces. In a thermodynamically "good" solvent, where polymer-solvent contacts are highly favored, the coils are relatively extended. In a "poor" solvent they are relatively contracted. The viscosity behavior and the chain conformations of the resins in solution are usually studied by MHS eq. (1).

$$[\eta] = KM^\alpha \quad (1)$$

where $[\eta]$ is the intrinsic viscosity, M the molecular weight, K is the Huggins constant, and α the exponent. For given polymer-solvent system and temperature, the value of the intrinsic viscosity is only

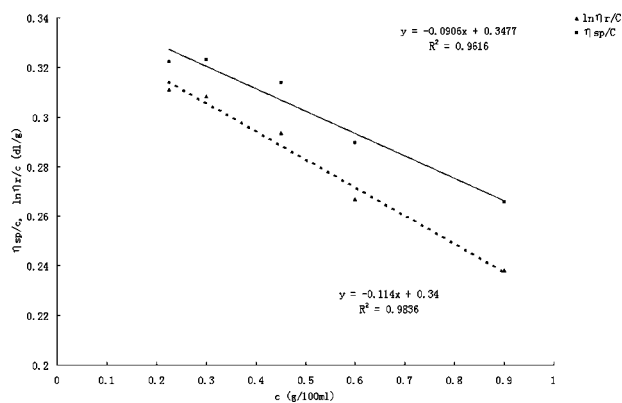


Figure 1 η_{sp}/c as function of concentration (a) and $(\ln\eta_r)/c$ as function of concentration (b) for a series of resoles in ethanol with different molecular weight.

determined by the resin's molecular weight. Therefore, for the sample with same molecular weight, its chain conformations in the solution can be studied by comparing the value of intrinsic viscosity $[\eta]$ in different solvents.

The viscosity of the polymer solution is usually related to its concentration except for the intrinsic viscosity $[\eta]$. The values of $[\eta]$ can be obtained according to the Huggins equation (2) and Kraemer equation (3):

$$\eta_{sp}/c = [\eta] + k'[\eta]^2c \quad (2)$$

$$(\ln\eta_r)/c = [\eta] - \beta[\eta]^2c \quad (3)$$

where c is the concentration of the resin's solution, η_{sp} is specific viscosity, η_r is relative viscosity, and intrinsic viscosities $[\eta]$ in deciliters per gram are determined by a least-squares extrapolation of η_{sp}/c from the Huggins equation and $(\ln\eta_r)/c$ from Kraemer equation to zero concentration. Figure 1 shows the plots of η_{sp}/c as function of concentration, $(\ln\eta_r)/c$ as function of concentration for a series of resoles in ethanol with different molecular weight. According to eq. (2), the intrinsic viscosity of the resole in ethanol is 0.348 dL/g based on η_{sp}/c plotted versus concentration c , extrapolated to zero concentration. According to eq. (3), $[\eta]$ is 0.340 dL/g. The results of two methods are quite similar. Since less approximation is used in eq. (2), the value of $[\eta]$ used in this study is calculated according to eq. (2).

Table I lists the intrinsic viscosities of resoles with different molecular weight in ethanol. The logarithm intrinsic viscosities of resoles in ethanol as a function of the logarithm number-average-molecular weight illustrated by the MHS equation are shown in Figure 2. The slope of the plot is α . There is no good linear relationship between the $\log[\eta]$ and $\log M_n$. The main reason of such deviation is originated from the

TABLE I
The Intrinsic Viscosities of Resoles with Different Molecular Weight in Ethanol

Molecular weight	$[\eta]$ (dL/g)
316	0.401
343	0.311
344	0.395
355	0.348
367	0.397

MHS equation itself, the mathematic model of which is based on flexible and high-molecular-weight polymer. However, there are many benzyl rings and many hydroxymethyl phenols groups cross linking together in resole resins, which makes its chains much stiff. The MHS equation is not suitable for phenolic resin, whose chains are more rigid and molecular weight are lower (usually <2000). On the other hand, the determination of constant K and α from the intrinsic viscosity data requires using a series of monodisperse polymers. The samples in this experiment are polydisperse resoles with wider range of molecular weight. Furthermore, the wide distribution of molecular weight of the resoles makes the value of M_n not precise. To obtain accurate MHS equation parameters K and α , the resole should be fragmented first and the MHS equation should be revised^{11,12} too. Here, we are most interested in the influence of the solvent on the resin's chain conformation, especially its further influence on the curing reaction process and crosslinking density of resins, other than the precise parameters of MHS equation. So the value of intrinsic viscosity is selected to characterize molecular size and conformation of the resole chains in different solvents.

The intrinsic viscosities of resoles with different molecular weight in different solvents are listed in Table II. The chain conformation of resoles in the solution is usually related to the flexibility of chain and the interaction between resin and solvent. When

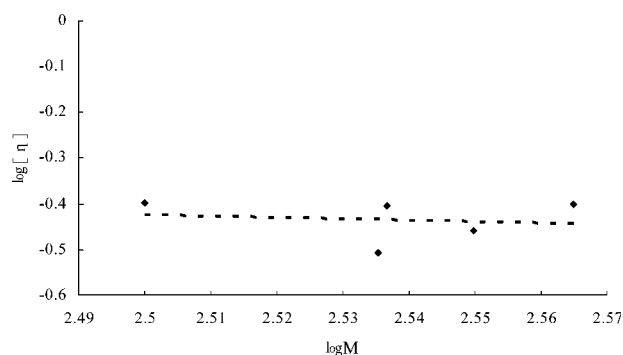


Figure 2 Dependence of $\log[\eta]$ of resoles in ethanol on $\log M_n$.

TABLE II
The Intrinsic Viscosities $[\eta]$ of the Resoles with Different Molecular Weight in Methanol, Ethanol, Propanol, Butyl Alcohol, and Acetone

No.	\bar{M}_n	$[\eta]$ (dL/g)				
		Methanol	Ethanol	Propanol	Butyl alcohol	Acetone
1	316	0.592	0.401	0.098	0.056	0.095
2	343	0.527	0.311	0.064	0.059	0.073
3	344	0.584	0.395	0.100	0.053	0.093
4	367	0.576	0.397	0.086	0.041	0.091

the interaction between resin and solvent were much stronger than that among the resin groups themselves, the chains of resins tend to be open and extended. Then the chain conformations of resins would act as loose coil, consequently to result in higher $[\eta]$. On the contrary, when the interaction among resin's molecular themselves is more powerful, the chains of resins would shrink up, and the chains act as compact ball, and the value of $[\eta]$ is lower. The intrinsic viscosities of resoles in different solvents are summarized in Table II. As displayed in Table II, the intrinsic viscosities of resins in methanol are higher than those in other alcohol solvents. It indicates that the value of $[\eta]$ drops with the increasing of the number of hydrocarbon group of alcohol solvent. In addition, the intrinsic viscosities of resins in acetone are lower than those in ethanol and propanol, but higher than those in butyl alcohol.

Such transition is mainly caused by the interaction change between resin and solvent. The resole in A-stage consists of many hydroxymethyl phenol groups, which have very strong intermolecular hydrogen bond among themselves. The solvent like alcohol not only can provide proton to form hydrogen bond with other groups, but also form hydrogen bond with other proton donor; that is, the solvent of this kind can form very strong hydrogen bond with the resole molecule. From methanol, ethanol, propanol to butyl alcohol, the polarity of the solvent is decreasing with the increasing of hydrocarbon group. And the hydrogen bond strength between solvent and hydroxymethyl phenol groups in resole is decreasing slowly. Gradually, the interaction force between resin and solvent is becoming weaker than that among the resin's molecules themselves. Therefore, the chains of resoles shrink tighter and tighter, and the resins' molecules become compact balls.

As for acetone, its carbonyl group (C=O) can interact with the hydroxyl group of phenolic resin to form intramolecular hydrogen bond, too. Although solvent like alcohol can provide proton, and its oxygen atom tend to form hydrogen bonds with hydroxymethyl phenol. The sketch maps of hydrogen bonds between phenolic resin and solvents,

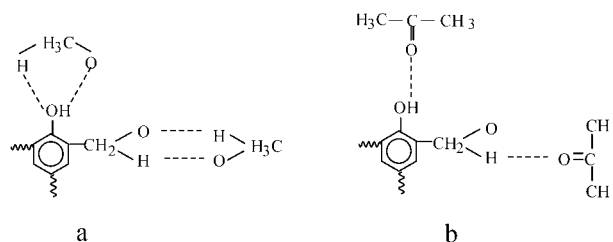


Figure 3 Sketch maps of hydrogen bonds between phenolic resin and solvents: (a) methanol and (b) acetone, respectively.

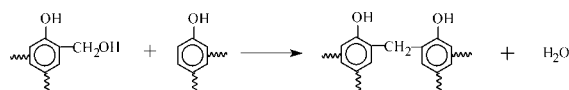
methanol and acetone, are shown in Figure 3. The interaction between phenolic resin and alcohol solvents such as methanol and ethanol, are stronger than that of acetone. So the intrinsic viscosities of resins in acetone are lower than those in ethanol and propanol, but higher than those in butyl alcohol.

The solvent influences on the curing behavior of resole

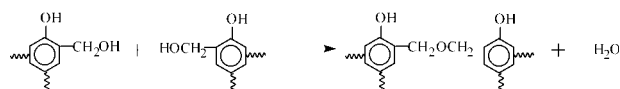
The solvents can change chain conformation of resoles in the solution. Such transition further affects curing behavior of the resole. The curing reaction of phenolic resin is shown in Scheme 1.

The reaction rate and degree of phenolic resins are usually determined by the reactivity and diffusion rate of functional groups. The motion freedom of reactive molecules and functional groups decreases as the resin's molecular weight increases, especially with gelation, vitrification, and crosslinking phenomena. At a certain degree of conversion, unreacted molecules and functional groups are restricted in their movement and collide with each other because of substantially greater viscosity and network formed in the curing systems. This probably leads to an early termination of curing reactions before reactive functional groups are consumed. Therefore, the mobility of reactants is very important to the curing reaction progress, especially, when system viscosity becomes higher and higher. When the interaction

Methylphenols and phenol produce a methylene bridge:



Methylphenols themselves produced an ether bridge:



Scheme 1 The curing reaction mechanism of the phenolic resin.

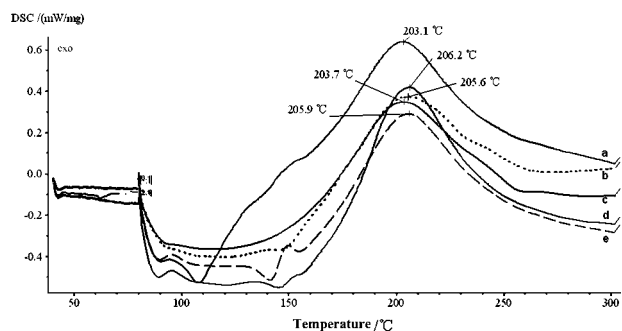


Figure 4 DSC analysis curves of the resoles in (a) acetone, (b) propanol, (c) butyl alcohol, (d) methanol, (e) ethanol.

force between resin and solvent is smaller than that among resin molecules, the chains of resole would shift from loose coils into compact balls. Reactive functional groups, hydroxymethyl phenol groups, and active hydrogens of phenol, may be entrapped in the compact chains, which may retard the moving velocity of the groups and decrease the collision probability of reactive groups. Hence, the curing rate of resin decrease and the curing degree gets lower too. On the contrary, the loose chain has more motion freedom. It brings more chances for functional groups to react with each other. And loose coils chains can penetrate each other, which would further enhance the crosslinking density. So the cur-

ing reaction of resole with loose chain is more complete, and the crosslinking density of final product is much higher.

Furthermore, according to thermodynamic expression (4), the driving force of the curing reaction is the change in Gibbs' free energy, ΔG , that is,

$$\Delta G = \Delta H - T\Delta S \quad (4)$$

where T is the temperature, ΔH is enthalpy associated with reaction, and ΔS is the entropy of reaction. The contribution for the entropy derives from two parts, that is, from rotational degree of freedom, ΔS_{rot} , and translational degree of freedom, ΔS_{tran} . Therefore, eq. (4) can be written as,

$$\Delta G = \Delta H - T(\Delta S_{\text{rot}} + \Delta S_{\text{tran}}) \quad (5)$$

For curing reaction to be feasible, the Gibbs free-energy change must be negative, that is, $\Delta G < 0$. Any factor that lowers the enthalpy or raises the entropy of a particular species in the system will shift the equilibrium to favor that species. For curing reaction of the given phenolic resin which has same ΔH (for curing reaction, ΔH is negative), the value of ΔS will determine the feasibility of reaction. The molecules of resin in methanol, whose chain conformation is random coil, have much more rotation freedom and translation freedom. It means that the molecules of resin in methanol before curing is more

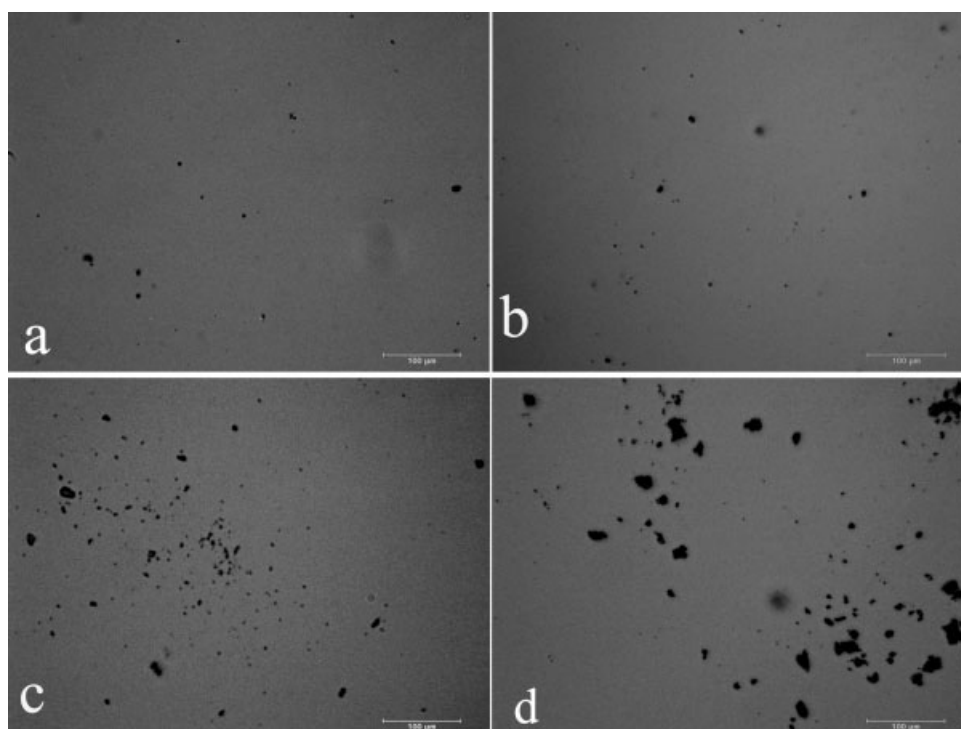


Figure 5 Surface morphologies of cured resins by optical microscopy in various solvents: (a) methanol, (b) ethanol, (c) propanol, and (d) butyl alcohol, respectively.

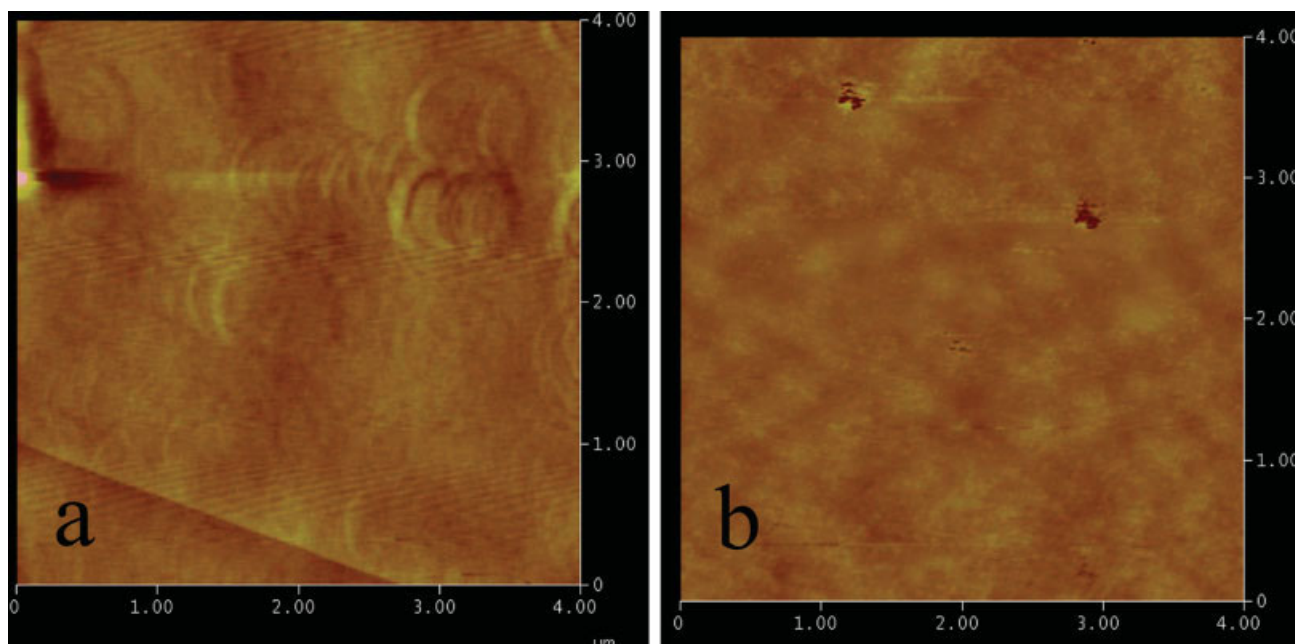


Figure 6 Surface morphologies of cured resins by AFM analysis in methanol (a) and acetone (b). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

“randomized.” Its ΔS_{rot} and ΔS_{tran} values are larger than others. Consequently, the curing reaction of resin in methanol is much easier and more complete than that in others.

To further investigate the influence of solvent type on the curing reaction of resole, DSC analysis of resole in different solvents were conducted and the results are shown in Figure 4. The whole cure processes of the resoles in different solvents are similar. Nevertheless, the peak exothermic temperature of resole in methanol is 206.2°C, 205.9°C in ethanol, 205.6°C in propanol, 203.7°C in butyl alcohol, and 203.1°C in acetone. Furthermore, the exothermic peaks of resole get wider successively when the resin is cured in different solvents, i.e., methanol, ethanol, propanol, butyl alcohol, and acetone. It implies that the curing rate of resin in methanol is the fastest, and that in acetone is the slowest. The curing exotherm of resoles is not discussed here because of the disturbance from endothermic vaporization of condensation by-products such as water and formaldehyde in the system.

Figure 5 shows the surface morphologies of cured resoles in different alcohol solvents. From methanol, ethanol, propanol to butyl alcohol, porosity content of the resin increases and porosity size is enlarged gradually. Surface morphologies of cured resoles in methanol and in acetone are further compared by AFM pictures in Figure 6. There exist a lot of cracks on the surface of cured resin in acetone whose cross-linking density is lower, while the surface of cured resin in methanol is much smoother with little cracks.

The pictures demonstrate that the curing degree of phenolic resins drop off with the decrease of hydrogen bond strength between resins and solvent. The curing reaction of resole in methanol is most complete, and crosslinking density is the highest.

IR spectra of cured resoles in different solvents shown in Figure 7 are very similar. It means that there is no new compound formed, that is, the solvent molecule does not react with the molecule of phenolic resin. The curing reaction is still the reaction of the hydroxymethyl phenol groups with phenol or hydroxymethyl phenol groups themselves. In fact, the solvent affects curing rate and curing degree of the resole only by changing its chain conformation in the solution.

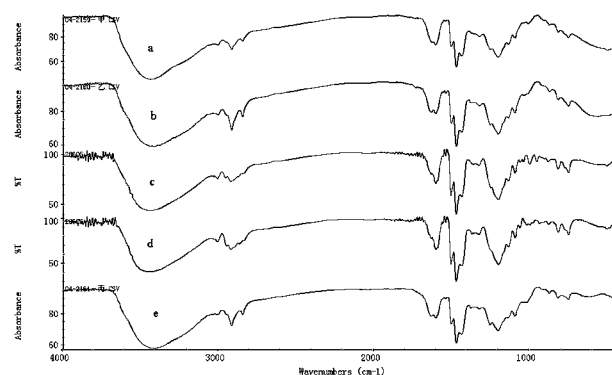


Figure 7 FTIR spectra of cured resole resins in (a) methanol, (b) ethanol, (c) propanol, (d) butyl alcohol, and (e) acetone, respectively.

CONCLUSIONS

The conformations of the resole chains in different solvents are quite different. With the increase of hydrocarbon groups of solvent and the decrease of polarity of solvent, the chain conformation of resoles transits from loose coil to compact ball. The intrinsic viscosities of resole decrease from 0.584 dL/g in methanol to 0.053 dL/g in butyl alcohol as the strength of intramolecular hydrogen bond between resole and solvent decreases.

The chains conformation of resole in solvent has great influence on its curing behavior. With the chains transiting from compact balls to loose coils, curing reaction probability increases and chains penetrate each other. Hence, the curing reaction rate of phenolic resins increases and curing reaction degree gets more complete. In addition, IR analysis shows that solvent dose not react with resole molecules at all.

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