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Preparation of Waterborne Epoxy Resin for Carbon Fibers Sizing Agent

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In this paper, according to the molecular design, a waterborne epoxy resin for carbon fiber sizing agent was synthesized with poly-functional group novolac epoxy resin (F-51) and diethanolamine by self-emulsifying method. The effects of reaction temperature and time on the structure of modified resin were investigated. Fourier transforms infrared spectrum was used to characterize the molecular structure of the modified resin. To investigate the conversion rate of epoxy group, the epoxy value (EV) of the modified and unmodified resin was measured by hydrochloric acid-actetone method. The water-solubility of the modified epoxy resin was also studied. The results showed that the optimum reaction temperature and time were 80 ºC and 2 h, respectively. The modified epoxy resin has good water-solubility and high storage stability, which was suitable as sizing agent for carbon fibers.

Key Words: Carbon fibers, Sizing agent, Waterborne epoxy, Self-emulsifying method.

INTRODUCTION

Epoxy resin type emulsion made by self-emulsifying method is gaining popularity due to its high storage stability and no emulsifiers[1-3]. Self-emulsifying method, also be named chemistry modified method, is to introduce hydrophilic groups or chain segments into epoxy resin molecular structure utilized activated reaction groups in epoxy resin molecule structure, such as epoxy bases, second hydroxy groups and hydrogen atoms on the hypo-methyl groups[4-6]. Therefore, the epoxy resin becomes amphiphilic and its water-solubility is improved. Amine modified epoxy resin is obtained by reaction of chemical compounds contained amino groups (diethanolamine, 2-amino ethyl-2-hydroxyl ethyl ether, tris(hydroxymethyl)-aminomethane, *etc*.) with epoxy resin[7]. A waterborne cation system contained alkaline-rich groups is obtained by following acid neutralizing reaction. This system can be prepared as water solution or emulsion. This type of waterborne epoxy resin have good stability due to the absence of hydrolyzable chemical bond.

In this paper, according to the molecular design, a modified epoxy resin which have both epoxy groups and hydrophilic groups was synthesized with poly-functional group novolac epoxy resin (F-51) and diethanolamine. After neutralized by acid, the modified epoxy resin could be dispersed into water and a waterborne epoxy resin system with excellent stability was gained. This waterborne epoxy resin is suitable for carbon fiber sizing agent. There are many epoxy groups reserved in epoxy molecular structure, which have excellent compatibility with epoxy resin matrix. On the other hand, the absence of hydrolyzable chemical bond in waterborne epoxy resin made sized carbon fibers have enough water resistance.

EXPERIMENTAL

Novolac epoxy resin (F-51) was supplied by Yisheng resin factory China (viscosity of 6.8 Pa·s, epoxy value of 0.50-0.55). Absolute alcohol, ethylene glycol monobutyl ether, diethanolamine and acetic acid were bought from Tianjin Guangcheng chemical reagent corporation China.

Preparation of modified epoxy resin emulsion: A calculated amount of F-51 resin was added into 3-neck flask and heated for 10 min at 60 ºC under a constant stirring rate. A certain percentage of mixed solvent consist of absolute ethyl alcohol and ethylene glycol monobutyl ether was added into the flask to dissolve resin. The system was warmed to setting temperature, then, a calculated amount of diethanolamine solution (ethyl alcohol as solvent) was dripped into it. After dripping is finished, keeping on stirring 0.5 h at constant temperature. The solvent is removed by a rotary evaporator. Thereafter, a quantity of 60 wt % acetic acid solution is dripped into modified resin under a constant stirring rate at salified temperature. Keeping on stirring 0.5 h under constant temperature after acid is dripped. Finally, water was added into it until solid content to 40 wt %, the waterborne novolac epoxy resin system was obtained.

Characterization: The chemical structure and composition of modified epoxy resin were analyzed by the Nicolet 380 infrared spectrometer (Thermo electron corporation, United States).

The epoxy value (EV) of modified epoxy resin and unmodified F-51 were measured by hydrochloric acid-acetone method according to GB 1677-81. Then, the percent conversion of epoxy groups (α %) can be calculated by formula (1):

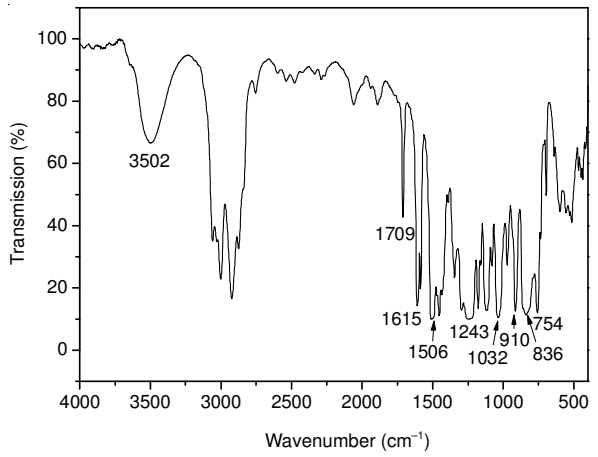
$$\alpha\,(\%) = \frac{X_0 - X_i}{X_0} \times 100\,\% \quad (1)$$

X_0: epoxy value of unmodified F-51, X_i: epoxy value of modified F-51.

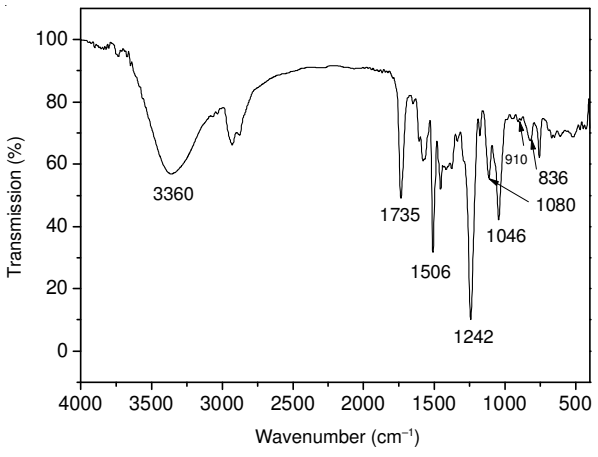
Water was dripped slowly into 10 g modified resin until it became muddy. The volume (mL) of water was recorded exactly. The more water was added, the better hydrophilic modified epoxy resin would be.

RESULTS AND DISCUSSION

Chemical structure of modified F-51: Fig. 1a is the FTIR spectra of unmodified F-51 resin. 910 and 836 cm^{-1} are the characteristics absorption peaks of the epoxy groups. 1032 cm^{-1} is the absorption peak of primary alcohol's (C-O) stretching vibration. 1243 cm^{-1} is the absorption peak of aryloxide. 1615 and 1506 cm^{-1} are the characteristics absorption peaks of benzene ring. 3502 cm^{-1} is the absorption peak of hydroxyl group.



(a) Unmodified F-51 resin



(b) Modified F-51 resin

Fig. 1. FTIR spectra of F-51 resin

Fig. 1b is the FTIR spectra of modified F-51 resin. Due to the addition reaction between diethanolamine and F-51, part of epoxy groups took ring-opening reaction. It led to the decrease of the absorption peak of epoxy groups at 910 and 836 cm^{-1}. Meanwhile, the absorption peak of hydroxyl at 3500 cm^{-1} grows deeper and wider due to introduction of hydroxyl produced by ring-opening reaction and diethanolamine. The characteristics absorption peak at 1080 cm^{-1} represents the structure of tertiary amine groups. These results prove that the reaction has happened according to the molecular design.

Influence of reaction temperature on the epoxy groups ring-opening reaction: The reaction between F-51 and diethanolamine belongs to etherification reaction which is an exothermic reaction. During the reaction the effect of reaction is directly influenced by the temperature. $n_{epoxy\ group}$:$n_{diethanol\ amine}$ = 1:1 was adopted in the system. The influence of different temperatures on the epoxy groups' conversion rate was investigated. The result is shown in Table-1.

TABLE-1
INFLUENCE OF REACTION TEMPERATURE ON THE EPOXY GROUPS RING-OPENING REACTION

Temperature (ºC)	60	70	80	90
Conversion rate of epoxy groups (%)	58.19	79.70	90.50	Gel

It can be concluded from Table-1 that the conversion rate of the epoxy groups increases suddenly with temperature increase. When temperature increases, system viscosity decreases. The chances of contact and collision between the molecules of F-51 and diethanolamine increase and the effective collisions go up which improves the reaction speed.

When the reaction temperature is high and the reaction becomes fast, the absorption of heat and reaction heat will be in the internal system and can hardly give off. This will cause temperature of system continues to rise.

As for epoxy resin F-51, the reaction between diethanolamine and epoxy resin changes secondary amine group into tertiary amine structure which can accelerate crosslinking cure of epoxy resin. Therefore, high temperature within the system will lead to the hot polymerization, form three dimensional network polymer structure and gel structure, resulting in failure. In this experiment, when the temperature of system was above 90 ºC, gel phenomenon would appear. Inversely, if the reaction temperature was too low, system became very sticky. The molecules could not get effective collisions, which would influence the reaction speed. The experimental results and the analysis indicate that the reaction temperature 80 ºC should be advisable.

Influence of reaction time on the epoxy groups ring-opening reaction: The influence of different reaction times on the epoxy groups' conversion rate at 80 ºC was investigated (Fig. 2). It can be seen that the reaction speed is rapid. The epoxy groups' conversion rate reaches 82.18 % after 1.5 h. It reaches 88.52 % after 2 h. Then the conversion rate increases very slowly.

At the earlier stage of reaction the concentration of reactants was high. After heated under 80 ºC the system viscosity decreased, moleculars' diffusion was fast which could improve effective impact rate among the molecules. The reaction

TABLE-2
WATER-SOLUBILITY OF THE MODIFIED F-51

Diethanolamine dosage (g/100gF-51)	Conversion rate of epoxy groups (%)	Water volume (mL)	Storage stability	Appearance
20	38.7	Infinity	≥ 12 months	Faint yellow, homogeneous transparent

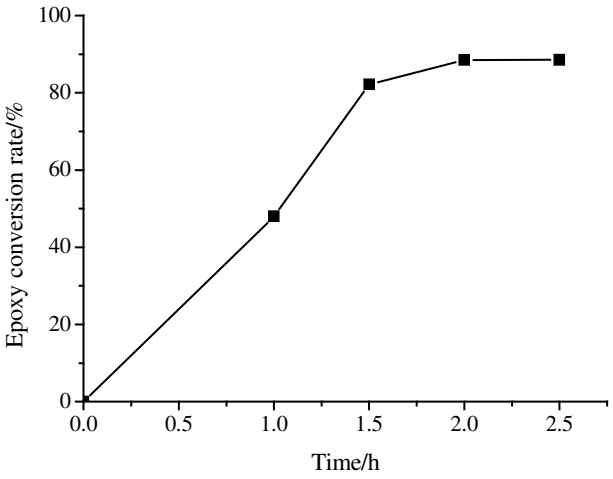


Fig. 2. Curve of epoxy groups' conversion rate *versus* reaction time

is relatively easier. After a period of time, diethanolamine and epoxy groups relatively decreased because they were massively consumed. At the same time, the system viscosity increased and the effective impact rate among the molecules decreased which led to the decrease of reaction speed. From the observation and characterization the epoxy groups' ring-opening rate of growth appears stable. The experimental results indicate that at 80 ºC, the reaction time controlled in 2 h is appropriate.

Water-solubility of the modified F-51: Although the epoxy resin F-51 was modified by diethanolamine and the hydrophilic hydroxyls were introduced into the resin, the modified resin still could not be scattered in the water due to the force among the molecules of resin and the association of hydroxyls. Adding acid, change the molecules of modified F-51 into tertiary amine salt structure. Its essence is H^+ in the acid and the nitrogen atoms of tertiary amine in modified F-51 in coordination with coordinate bond and the process of tertiary amine cation. In this way, on one hand, the strong hydrophilic tertiary amine cations were introduced to the modified F-51. On the other hand, the same electric charge of the resin molecules, gay charge of repulsed each other which would break the association among the resin molecules. It made the resin could be scattered in the water. The formula of modified resin after salified is shown by Fig. 3. The water-solubility of the modified F-51 was shown in Table-2.

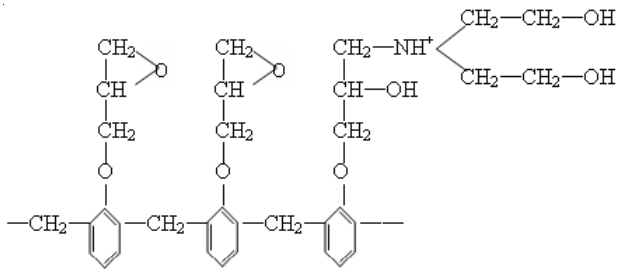


Fig. 3. Formula of modified resin after salified

Conclusion

A self-emulsifying waterborne epoxy resin for carbon fiber sizing agent was synthesized with poly-functional group novolac epoxy resin (F-51) and diethanolamine. FTIR proved that the modified epoxy resin was obtained according to the molecular design. The hydrophilic group was introduced into epoxy resin molecular and suitable amount of epoxy groups were reserved. The main factors influencing the epoxy group conversion rate are reaction temperature and time. The optimum reaction temperature and time are 80 ºC and 2 h. The modified epoxy resin has good water-solubility and high storage stability.

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