Study on the Synthesis of Thiirane

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ABSTRACT: In this study, a thiirane resin was synthesized by the reaction of corresponding epoxy resin with KSCN. The synthetic conditions influencing the conversion of epoxy group were systematically investigated, such as the reaction temperature, reaction media, reaction time and the ratio of KSCN to epoxy group. It was found that the conversion of epoxy group increased with the increasing reaction temperature, improving the solubility of the mediate, extending reaction time, and the enhancing ratio of salt (KSCN) to epoxy group. Wherein, the reaction temperature and the ratio of the KSCN to epoxy group were more effective. For example, when the molar ratio of KSCN to epoxy group was equal to 2.0, the conversion of epoxy group got the maximum value, 0.65. In addition, the hot plate method was used to measure the gelling time of the resultant thiirane resin at different temperatures. It was found that the gelling time was reduced to 47–85% times as the corresponding epoxy resin depending on the conversion of the epoxy group, and the curing activation energy was diminished from 39 kJ/mol of epoxy resin to 17 kJ/mol. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 4023–4027, 2006

Key words: synthesis; adhesives; resins; FTIR; activation energy

INTRODUCTION

Standard epoxy resins have good mechanical properties, but their prolonged low-temperature curing limits their potential use in clinical as well as in industrial application. Episulfides are substances in which the oxygen in epoxy is replaced with sulfur. The sulfur-containing ring should be at higher energy level, and thus can be more easily opened, with low energy evolved.[1–3] Therefore, episulfides are theoretically appropriate for low-temperature rapid curing application and have become increasingly useful and important in organic synthesis, used advantageously in the pharmaceutical, polymer, pesticide, and herbicide industries.[4] Some methods of synthesizing thiirane compound have been widely reported.[1,2,5–13] However, the reactions of corresponding epoxy compound with potassium sulfocyanate (KSCN), or thiourea are considered to be convenient and practical methods.[1,2,5,12,13] Reaction was carried out in cosolvent of water and ethanol at low temperature, which successfully minimized the threat of toxic and volatile organic solvents to the environment. However, according to the previous works, this method suffered from a drawback of low yield of reaction and long reaction time. The highest overall yield is about 75–80%, and the reaction time is 10 or 12 h.[1,8] In this study, the thiirane resin was synthesized by the reaction of corresponding epoxy resin with KSCN, and the effect of reaction conditions on the conversion of epoxy group was systemically investigated by FTIR spectra. Some experimental data were quite different from those reported previously.

EXPERIMENTAL

Materials

Bisphenol A diglycidyl ether CYD128 and curing agent T31 were supplied by Yueyang petrifaction epoxy resin plant. Potassium sulfocyanate (KSCN) was supplied by Tianjing wen Da Xi Gui Agent Chemical Plant. Ethanol, toluene, sodium chloride, and $MgSO_4$ were supplied by Beijing Chemical Plant.

Synthesis of thiirane resin

A four-necked flask equipped with mechanical stirrer, condenser, thermometer, and drop funnel was charged into a solution of KSCN in ethanol and water. Epoxy resin, the trade name CYD128, diluted by ethanol was added dropwise into the flask within 1 h to react with KSCN, and stirred vigorously for 10 h, followed by stilling for 2 h or more. The water phase in upper layer was removed off. The crude product in the bottom layer was then dissolved in toluene, washed with aqueous NaCl (1 mol/L) for three times and twice with water, dried with $MgSO_4$, and allowed to stand for 12 h. A rotary evaporator was used to strip

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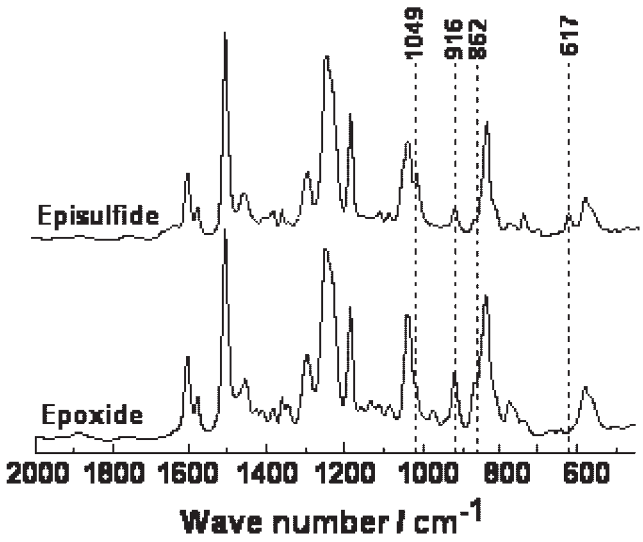


Figure 1 FTIR spectra of CYD 128 and resultant episulfide compound.

off toluene at 70°C, followed by drying under vacuum. The thiirane product with solid content of 99% was obtained.

Figure 1 shows the FTIR spectra comparing the starting epoxy and after reaction (thiirane). The characteristic absorption peak of epoxide group, symmetric and asymmetric ring deformation at 916 and 862 cm^{-1} were greatly decreased, and two new peaks occurred at 1049 and 617 cm^{-1}. They are symmetric and asymmetric deformation of thiirane ring, respectively, revealing the conversion of epoxy groups to thiirane groups successfully.

Analysis and measurement

The infrared spectra of the samples were recorded on Nicolet Nexus-670 spectroscopy. KBr pellet was used in measuring. The gelling time of thiiranes was estimated by a hot plate method; the different temperature was used; and the sample of 1 g was taken (compound:curing agent = 1:0.3 (wt)).

RESULTS AND DISCUSSION

Quantitative analysis of conversion of epoxy groups by FTIR spectra

Actually, the product was a mixture of epoxide compound and episulfide compound, and the quantitative assignment and distinguishing between them are difficult because of their extremely similar structures. Here, FTIR data were attempted to calculate the conversion of epoxy group to episulfide. The area of characteristic peak of symmetric epoxy ring deformation at 916 cm^{-1} was used to analyze the amount of epoxy resin in resultant mixture. To clarify the possibility of accuracy of this analysis, a series of sample were prepared by mixing the starting epoxy and the resultant thiirane with the epoxy ratio of 0, 5, 10, 15, 20, 30, 40, 50, 70, and 90% by weight, respectively. According to Lambert-Beer's Law, assuming that the volume of resin was unchanged after mixing in different ratio, the benzene ring stretching vibration absorbance was set as an internal standard, and the density of 916 cm^{-1} peak should be changed in straight linear with the variation of epoxy.

Figure 2 shows the dependences of area of peak 916 cm^{-1} on the added content of epoxy resin with different part of benzene ring absorbance peaks as reference, respectively. They both were linear lines with correlation coefficient of 0.99, 816 and 0.97, 535. The experimental data shows a good coincidence with the expected result, proving the quantitative analysis was reasonable.

Now, the upper linear line in Figure 2 can be used to calculate the conversion of epoxy groups. Suppose that the conversion of epoxy groups (wt %) in the prepared thiirane is α, which coincides with the point of $x = 0$ in Figure 2. Let's extrapolate the linear line, which will cross with the x-axis at the point -63.83 where the epoxy resin part in mixture is supposed to be zero (Scheme 1).

Therefore, a simple linear equation was deduced as:

$$100 - 100\alpha - 63.83\ \alpha = 0$$

That is,

$$100 - 163.83\ \alpha = 0 \qquad (1)$$

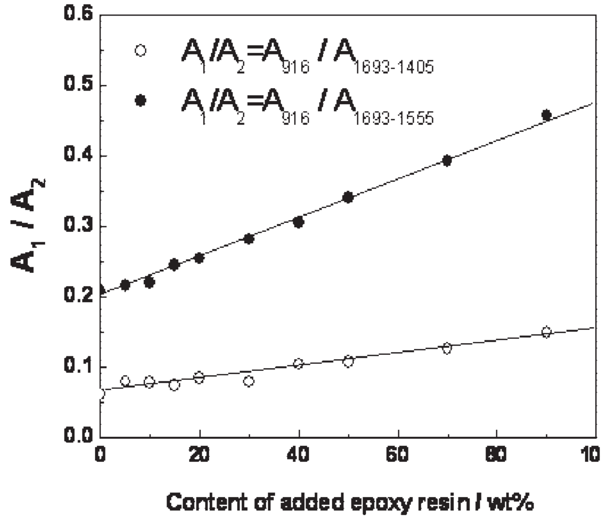
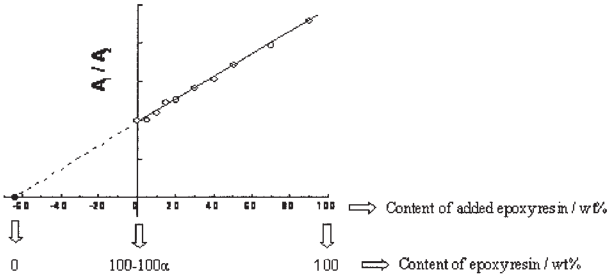


Figure 2 The dependence of area of peak 916 cm^{-1} on the added content of epoxy resin. A_1: the integral area of characteristic absorbance peak of epoxy group at 916 cm^{-1}; A_2: the integral area of characteristic absorbance peak of benzene ring.



Scheme 1 Diagram of calculation of conversion of epoxy groups. $A_1$and A_2: described in Figure 2

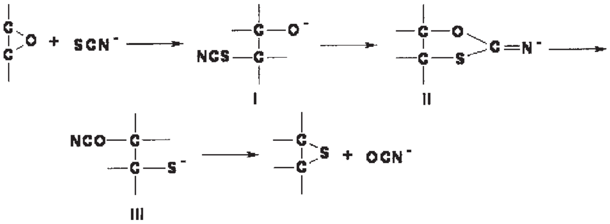
This equation can be used to calculate the absolute content of epoxy part in mixture.

Reaction time dependence of the conversion of epoxide groups

Figure 3 shows the epoxy groups conversion with reaction time. The samples were taken from reactant at some time interval and checked by FTIR.

It can be seen from Figure 3 that the reaction process came through three stages. At the initial stage, the steep increase of conversion rate of epoxy groups was revealed with slight increase of reaction time. In the second stage, a steady tendency grew up. At last, the conversion of epoxy groups became slower and slower. This phenomenon was more likely to be caused by the solid conglomeration of by-product salt with resin together, and prevented the contact probability of epoxy groups from KSCN.

On the other hand, the characteristic absorption peak at 616 cm^{-1} in the FTIR spectra did not appear at the first stage, although the conversion of epoxy groups was quite obvious. It is probably be explained by the mechanism of the reaction (Scheme 2). The rate of formation of episulfide is slower than that of the ring opening reaction; though the content of epoxy groups decreases rapidly, the thiirane groups do not obviously increase, but increases with prolonged reaction time.



Scheme 2 Mechanism of the reaction of epoxy with KSCN.[5]

Dependence of conversion of epoxy groups on ratio of KSCN to epoxy resin

Figure 4 shows the effect of the ratio of KSCN to epoxy resin on the conversion of epoxy groups. The conversion rate of epoxide groups increases with the increasing excessive content of KSCN. So, we can conclude that the synthesis reaction is not equivalent amount conversion as what was reported earlier,[2] but the excessive content of KSCN has a remarkable effect on the conversion of epoxy groups. When the ratio increased from 0.7 to 2.0, the conversion grew from 21 up to 63%.

This result is considered to have two aspect reasons: one is because the reaction system is heterogeneous, and the diffusion effect will influence the contact of KSCN and epoxy groups, and further the conversion. The other is related to the reaction mechanism in

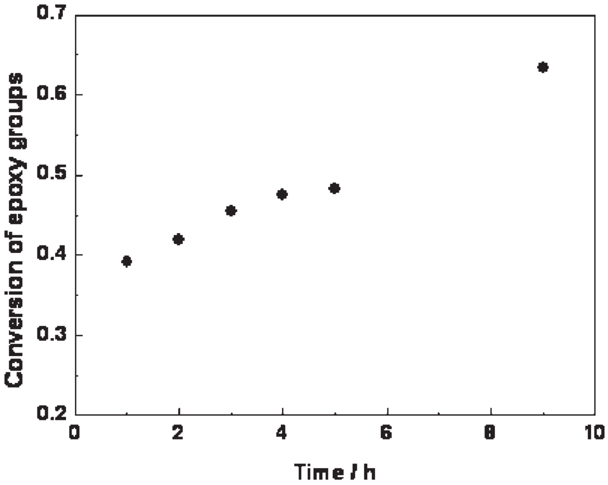


Figure 3 The reaction time dependence of the conversion of epoxy groups.

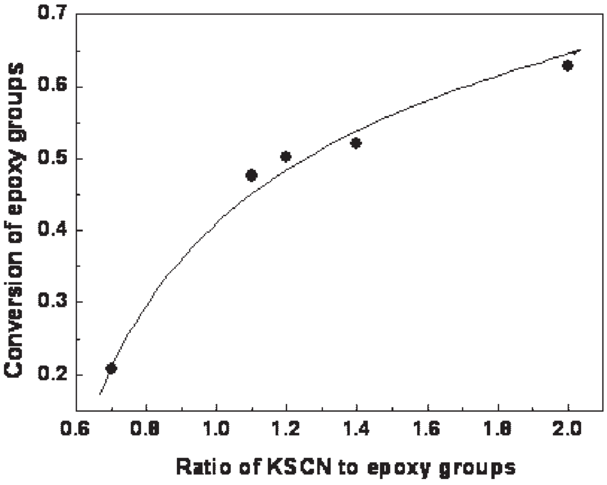


Figure 4 Plot of conversion of epoxy groups with ratio of materials.

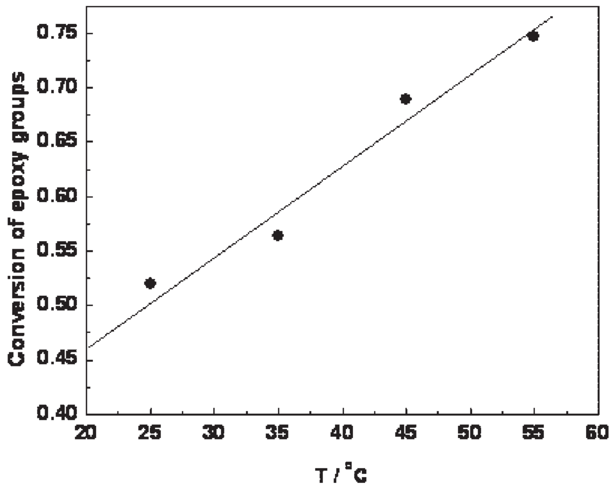


Figure 5 The dependence of conversion of epoxy groups on reaction temperature.

Scheme 2. To some extent, the reaction of KSCN and epoxy groups is reversible.

On the other hand, the episulfide absorbance peak did not emerge in the FTIR spectra until the ratio value of KSCN to epoxy resin is equal or higher than 1.1 (molar ratio of KSCN to epoxy groups), and increased with the increase of the ratio.

Dependence of conversion of epoxy groups on the reaction temperature

Figure 5 shows that the reaction temperature has a remarkable effect on the conversion rate of epoxy groups. Both the conversion rate of epoxy groups and the intensity of the episulfide characteristic absorption peak increases with the increasing of the reaction temperature. However, the intensity of the episulfide characteristic absorption peak has little increase when the reaction temperature is higher than 45°C. It may be caused by the disadvantage of high temperature for the closing ring and the advantage for polymerization and the side reaction. Then, 45°C is regarded as the most suitable reaction temperature.

TABLE I
The Gelling Time of Thiirane with Different Conversion of Epoxy Groups

Conversion of epoxy groups	*T* (°C)	Gelling time (min)	The gelling time of the corresponding pure epoxy resin (min)
0.21	14.5	53	84
0.48	13.5	23	89
0.50	11.5	16	100
0.52	12.0	14	97

Dependence of conversion of epoxy groups on the media

Reaction media were mixture of water and ethanol, with KSCN dissolved in water and epoxy resin diluted by ethanol. It can be seen from Figure 6 that the ratio of resin to ethanol influenced the conversion of epoxy groups more effectively than the ratio of water to ethanol. The presence of more ethanol solvent in the reaction system diluted the epoxy resin effectively and diminished viscosity of epoxy resin solution, which led to the essential and plentiful contact between the epoxy resin and KSCN.

Curing behavior of thiirane

The gelling time measured by hot plate method at different temperature was used to characterize the

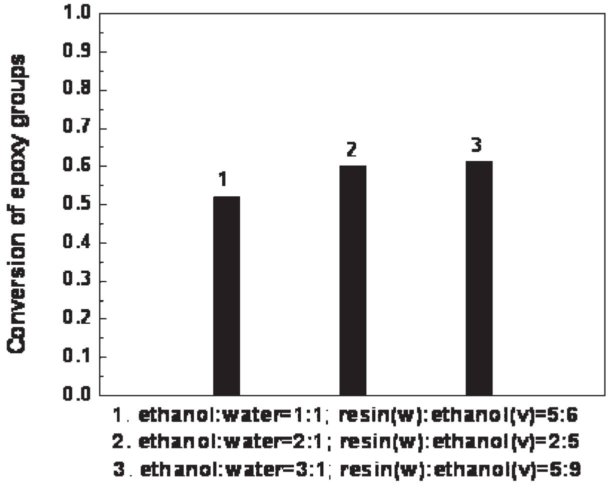


Figure 6 The effect of reaction media on the conversion of epoxy groups.

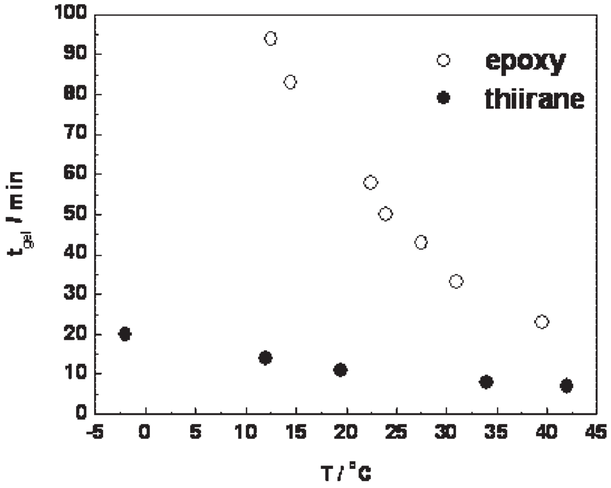


Figure 7 The temperature dependence of gelling time.

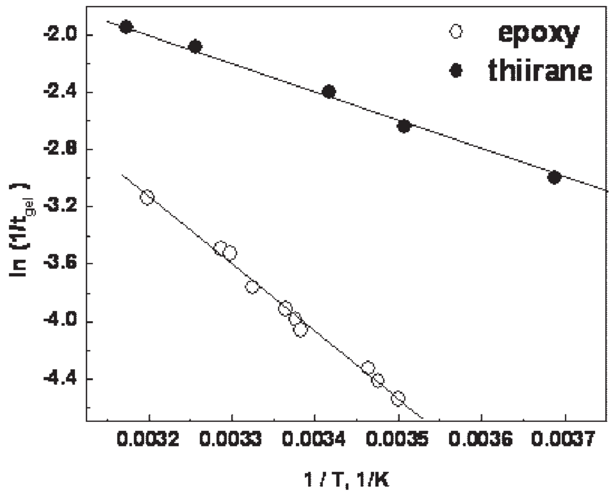


Figure 8 The relationship of ln ($1/t_{\mathrm{gel}}$) and $1/T$.

curing reaction. Table I shows the comparison of gelling time data between thiirane with different conversion of epoxy groups and the pure epoxy resin (CYD 128) at relatively low temperature.

It can be seen from Table I that the curing reaction rate of thiirane resin was accelerated drastically comparing with the pure epoxy resin and increased with the increasing conversion rate of the epoxy groups. When the conversion rate of epoxy groups increased from 0.21 to 0.52, the gelling time reduced from 0.63 to 0.15 times as that of pure epoxy resin.

Curing activation energy of thiirane resin and epoxy resin

2.5 g of mixture of the thiirane resin (100 parts, 0.46 conversion of epoxy groups) and curing agent T31 (30 parts) were taken on the hot plate to determine the gelling time. The temperature dependence of gelling time was plotted in Figure 7. According to Arrhenius eq. (2), the ln ($1/t_{\mathrm{gel}}$) was plotted against $1/T$ in Figure 8.

$$\ln (1/t_{\mathrm{gel}}) = \ln A_{(\mathrm{rheo})} - \frac{E}{RT} \tag{2}$$

The activation energies of epoxy resin and thiirane were calculated out from the slopes, respectively.

$$E_a \text{ (epoxy resin)} = 39.177 \pm 1.319 \text{ kJ/mol}$$

And,

$$E_a \text{ (thiirane resin)} = 17.263 \pm 0.564 \text{ kJ/mol}$$

It illuminates that the reactivity of thiirane resin is higher than its corresponding epoxy resin.

CONCLUSION

The reaction conditions were investigated systematically. The conversion of epoxide to thiirane was enhanced by increasing reaction temperature from ambient temperature to 45°C, ratio of KSCN to epoxy group from 0.7 to 2.0. The gelling time of the prepared thiirane resin was remarkably shorter than that of pure epoxy resin, and the activation energy was 17.263 kJ/mol, which was significantly smaller than that of pure epoxy compounds.

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