Curing Kinetics of Cyanate Resin Modified by ESi

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Abstract. The kinetics of the curing reaction of cyanate resin modified by ESi was studied using DSC. The apparent activition energy, reaction order and frequency factor of the curing reaction of the resin were obtained as being E=68.58kJ·mol-1, A=2992.06 s-1, n= 0.89 respectively. In addition, the gel point, setting point, post cure temperature of this resin was found to be at 149.40°C, 180.72°C, 238.98°C.

1. Introduction

Cyanate ester (CE) resins are new high performance resin matrices that contain two or more cyanate functional groups. When polymerized, under heat and catalyst they can form a high MW macromolecule with a high degree of crosslinking containing triazine rings. The triazine ring in the polymer of is highly symmetric and it also has high steric hindrance, essentially, a spot polar group rotating in a small range. These attributes afford cyanate ester resins many advantages, such as excellent mechanical properties, high thermal stability, low dielectric constant (2.8~3.2), dielectric loss factor (a loss tangent of 0.002~0.008 at 10~50MHz) [1-3] and minimal water absorption. They are currently in widespread use for a variety of applications from structural aerospace composites to electronic insulation. Though cyanate resins are very tough in comparision to other high performance themosetting polymers, this toughness is still insufficient for some applications. Therefore, further improvement in toughness is currently a popular area of study [4-5]. Silanes exhibit many outstanding properties when used to modifiy epoxy resins [6-7]. Silanes have been introduced into epoxies by reaction between the epoxy group and the reactive hydroxy group, or amino group of silanes. The copolymer modification improved the nascent properties of pure epoxy and silane polymer, but also increased impact and tensile strength, and thermal stability by decreasing the crosslinking density. Recently, modification of a cyanate ester resin using epoxidized polysiloxane has been reported [8]. The resulting modified resins had the better processing properties, toughness and water resistance than the neat resins. The T_g and the initial degradation temperature of modified resins system were lower than those of original cyanate esters. However, the desirable flexural property of modified resin systems was retained. In the study, epoxidized silane (ESi) was used to modify bisphenol A dicyanate ester resins. The reaction mechanism and curing kinetics of the modified resins were studied. This research laid the foundation for further study of the mechanical properties and dielectric properties of this novel copolymer.

2. Experimental section

2.1. Materials
The resin belends comprised two commercially available materials: one, 2,2' -Bis(4-cyanatopheny) is opropylidene (BCE) (an industrial product with a write grainy crystal and melting point of 74 ℃)was supplied by Jinan Academy of Aviation Special Structure, China; the other γ-(2,3-epoxypropoxy) propyl silane (epoxy group silane) or ESi(transparent liquid industrial product) was purchased from Jinghan Fine Chemicals Company (Jingzhou/Hubei Province, China).

2.2. Preparation of BCE/ESi mixtures
Preparation of BCE/ESi mixtures by BCE dissolved in acetone. And then ESi was added to above the mixtures. When acetone could evaporate completely, the BCE/ESi mixtures and pure BCE would be 1:1 in a weight ratio. In the study, a catalyst must employ to initiate the polymerization.

3. Measurements

3.1. Gel time
Gel time was measured on a temperature-controlled hot plate by standard knife method [9]. The time when the resin cannot form filaments is defined as the gel time at a fix temperature.

3.2. Differential scanning calorimetry
DSC measurement was performed with a Perkin Elmer DSC-7 supported by a Perkin Elmer computer for data acquisition. The DSC was calibrated using high-purity indium. Polymer samples were weighed into small DSC aluminum pans and sealed with holed aluminum lids. The DSC analysis was conducted under a nitrogen flow of $20cm^3 min^{-1}$. All the samples were subjected to a dynamic DSC scan from room temperature to 300 ℃ and at a scan rate of 5 ℃ /min, 10 ℃ /min, 15 ℃ /min, 20 ℃ /min.
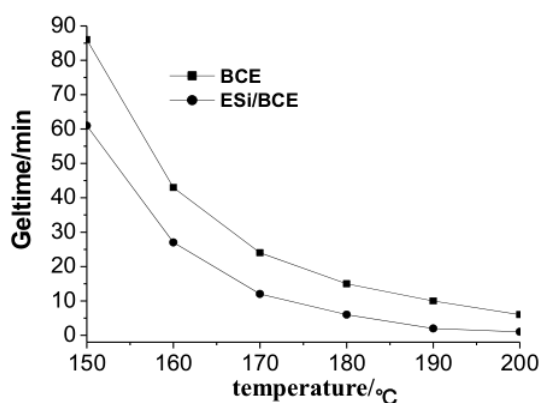
4. Results and discussion

4.1. Gel time

Figure 1. The dependency of gel time on temperature.

The results of the gel time analysis of the ESi/BCE composites and the neat BCE is shown in Figure 1. As can be seen, the results show reaction activity of resin matrix to temperature. Figure 1 shows that the ESi/BCE of gel time was shortened the time with addition of the ESi. The gel time of the ESi/BCE system was shortened to 25, 16, 6, 5 min, at 150, 160, 190, 200 ℃, respectively. As Figure 1 shows, each of these gel times for the ESi/BCE at the select temperature was significantly shorten than the gel times for the neat BCE. This result suggests that the combined resin matrix has excellent stability at low temperature but also a better reactivity at high temperature and improved reaction rate. The gel time of the ESi/BCE system changes quickly between 160 ℃ and 200 ℃.These results suggest that

curing reaction of ESi/BCE is sensitive to temperature range: therefore, the curing reaction of ESi/BCE was found to be in the range of 160 ℃ to 200 ℃.

4.2. Differential scanning calorimetry analysis
Figure 2 show the dynamic scanning thermograms (DSC) for the pure BCE and epoxy group silane/BCE system at a scan rate of 10 ℃ /min, among which the content of the epoxy group silane was 6.0%.The epoxy group silane/BCE system began to cure around 160 ℃ as shown in Figure 1,but the pure BCE began to cure around 180 ℃.This illustrates that the epoxy group silane had catalyzed the cure of the BCE resin thereby decreasing the Curing temperature.

   Figure 3 shows the dynamic scanning thermograms (DSC)of the ESi/BCE system at a scan rate of 5 ℃ /min, 10 ℃ /min and 20 ℃ /min, in which the content of ESi was 6.0%. In Figure 3, it can be seen that there is an endothermic melting peak at about 80 ℃ the quality of which is different for the three heating rates. With an increase in the heating rate, the endothermic melting peak became sharper and moved toward a higher temperature. The reason for this is because the polymers are thermal good conductors, so the difference between internal temperature and environmental temperature of the sample, except external surface. Therefore, the severer the production of thermal hysteresis, the faster heating rate. In addition, we see in Figure 3 that is only endothermic melting peak under three heating rate of it. The results show that was two possibilities of ESi/BCE system, which was only single reaction existing during the whole resin system, more reaction of exothermic peak coincide.
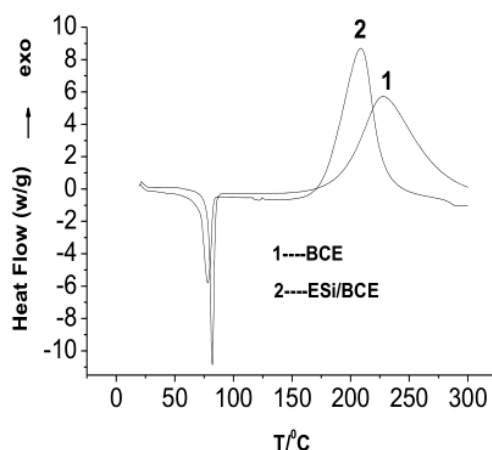

Figure 2. DSC thermograms of BCE and ESi /BCE system (at a scan rate of 10 ℃ /min).
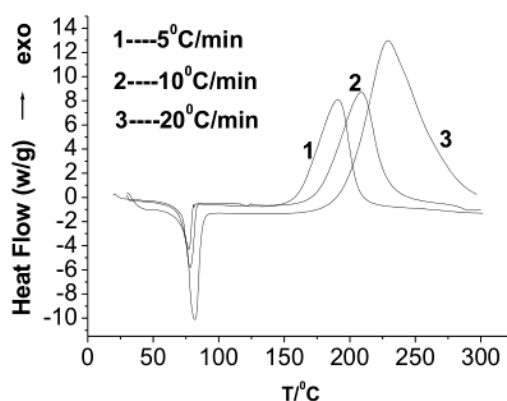

Figure 3. DSC thermograms of ESi /BCE at a different scan rate.

4.3. Curing kinetics of ESi/BCE
DSC is one of most commonly used methods for studying the curing kinetics of a resin. Compared with FTIR technique, DSC is more flexible in revealing fundamental chemical changes of

thermosetting resin systems. The DSC curing curve of the ESi/BCE system of exothermic peak temperatures at different heating rate are listed in Table 1.

Table 1. DSC curing curve of exothermic peak of peak temperature at different heating rate.

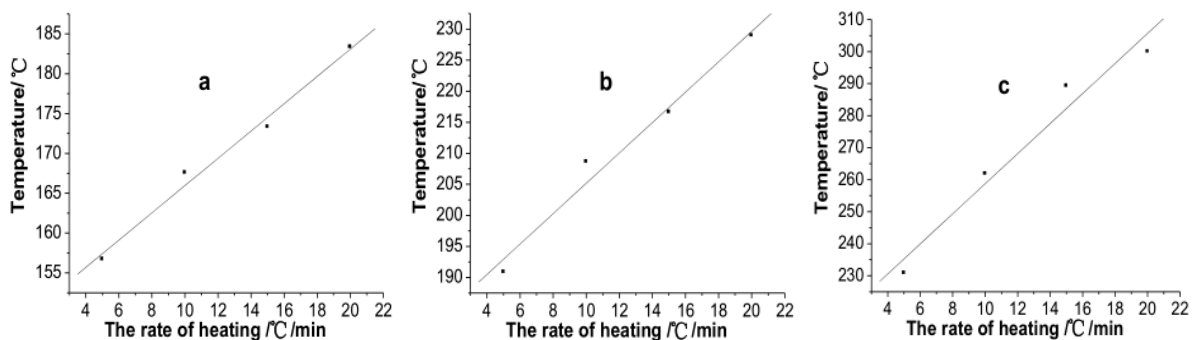| Heating rate ℃ /min	5	10	15	20
Temperature of onset/ ℃	160.04	176.7	182.9	197.97
Temperature of peak(T_m)/ ℃	190.89	208.65	216.64	229.00
Temperature of ending/ ℃	243.04	288.92	281.54	297.04

Figure 4. The linear regression graph of peak temperature. a. temperature of onset; b. temperature of peak; c. temperature of ending

The regression graph (see Figure 4) of the peak temperatures was obtained. The curing process parameters of system were determined preliminarily: gel temperature was 149.40 ℃, curing temperature was 180.72 ℃ and post-curing temperature was 238.98 ℃. The kinetics of the curing reaction of cyanate resin can be obtained from the DSC data by variety of means, including the. Kissinger, Ozawa, and Coats-Redfern methods. The apparent activation energy of curing reaction can be obtained by the Kissinger equation as shown below:

$$\frac{d\left[\ln\left(\beta/T_m^2\right)\right]}{d\left(1/T_m\right)} = -\Delta E/R \tag{1}$$

where, β is the heating rate(K/min), T_m is the temperature of peak(K), R is the gas constant(8.314J/mol·K), E is the apparent activation energy(J/mol). According to the Kissinger equation, the $\ln(\beta/T_m)$ and $1/T_m$ relationship is linear. So we can adopt the drawing of method with $-\ln(\beta/T_m^2)$ and $1/T_m$. Furthermore, through the line fitting got line slope and intercept are obtained, which yields the apparent activation energy of the curing reaction.
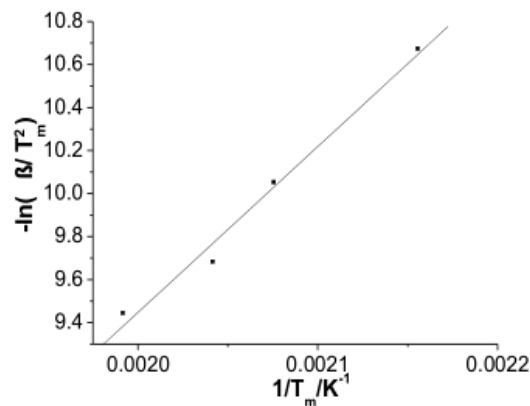
$$-\ln(\beta/T_m^2) = -5.9836 + 7715.25(1/T_m) \tag{2}$$
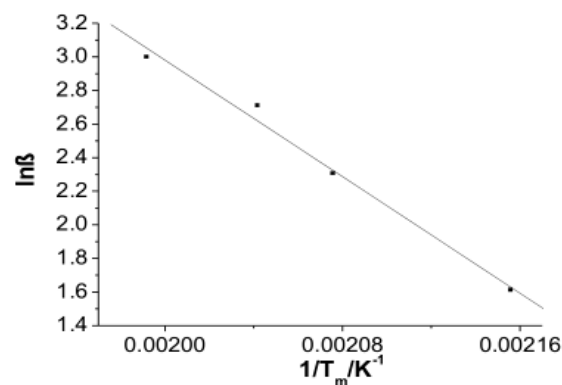
Figure 5. Relationship between -ln(β/T2m) and 1/Tm.

Figure 6. Relationship between lnβ and 1/Tm.

A straight line was obtained $-\ln(\beta/T_m^2)$ using plotted against 1/Tm as shown in Figure 5. Eq. (2) is a regression equation of the line. The apparent activation energy was found to be 64.14 kJ·mol^{-1} by the plot slope.

The Crane Equation can be derived from Kissinger Equation as shown in Eq. (3). Where, β is the heating rate (K/min), T_m is the temperature of peak(K), R is the gas constant(8.314J/mol·K), E is the apparent activation energy(J/mol). Because of $\Delta E/nR > 2T_m$, $2T_m$ can be ignored. Figure 6 was obtained $-\ln\beta$ using plotted against 1/Tm.

$$d\ln\beta / d\left(1/T_m\right) = \left(\Delta E / nR\right) - 2T_m \tag{3}$$

The linear regression equation can be properly described using Eq. (4). From Eq. (4), E can be calculated from line slope. Furthermore, the reaction order was found to be 0.89 which was a non-integer. The calculated results indicate that reaction mechanism in the cure of the ESi/BCE was very complex.

$$\ln\beta = 20.34 - 8677.57(1/T_m) \tag{4}$$

Eq. (5) was obtained using the Kissinger Method. From Eq. (5), the frequency factor A can be obtained which was 2992.06 s^{-1}.

$$A \approx \frac{E\beta\exp\left(E/RT_m\right)}{RT_m^{\ 2}} \tag{5}$$

The advantages of the Kissinger Method are that complex computation methods can be avoided. Meanwhile, the kinetic parameters of E, A, n can be obtained and the curing mechanism need not be known when calculating of E, A. This reduced the errors in calculating the reaction kinetic parameters.

5. Conclusions

The reaction mechanism and kinetic parameters in the curing process of a polymer system composed between ESi and BCE were studied using DSC. The results showed that the copolymerization between ESi and BCE occurred during the initial curing stage while the self-polymerization of BCE occurred during the later curing stage. Some of the parameters of the system were obtained using a non-isothermal DSC and were found to be the curing temperature 180.72 ℃, post-curing temperature 238.98 ℃ and gel temperature 149.40 ℃. The activation energy, frequency factor and reaction order were calculated using the Kissinger and Crane methods. Their values were $64.14kJ^{-1}$, $2992.06s^{-1}$ and 0.89, respectively.

6. Acknowledgments

7. References

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