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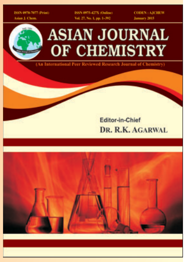

Study on Cyanate Ester Resin Modified with Epoxy Group Silane

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Bisphenol A dicyanate ester (BCE) was modified with epoxy group silane *i.e.*, γ-(2,3-epoxypropoxy)propyl silane (ESi) to improve impact strength of pure resin. The results showed the mechanical properties were improved mainly by the reaction of epoxy group in γ-(2,3-epoxypropoxy)propyl silane and cyanate group in bisphenol A dicyanate ester. The morphology of the cured materials was investigated by scanning electron microscopy techniques. The ESi/BCE composites were shown to have better impact strength and flexural strength properties. When the value of T_g is not significantly changed, impact and flexural strength of modified resins were increased from 10.1 kJ/m^2 and 94.11 MPa to 14.49 kJ/m^2 and 123.93 MPa, respectively.

Keywords: Cyanate resin, Epoxy group silane, Toughening, Mechanical properties.

INTRODUCTION

Cyanate esters with two or more cyanate functional groups are novel high performance matrix resins[1-3]. It will homopolymerize with the addition of heat and a catalyst through cyclotrimerization to from a 3-dimensional high crosslinking density network. Due to their high symmetry and high steric hindrance of cyclotrimerization, only small polar group can rotate in the small range. Cyanate esters can be retain low dielectric constant (with a dielectric constant of 2.8-3.2), dielectric loss factor (with a loss tangent of 0.002-0.008) when the frequency was at 10-50 MHz and at the range of wide temperature (0-220 °C)[4]. They have been widely used in aviation, aerospace and electronic industry as high performance matrix for composites for their superior comprehensive properties and processability[5]. Though cyanate resins are most tough compared with other high performance themosetting polymers. However, their toughness can't be satisfied in many application situations. Therefore, improved toughness are important study field of research on cyanate esters composites[6-9]. Silane exhibited many outstanding properties in this aspect modification epoxy resin[10,11] and the organic chain segment in silane were introduced by reaction between epoxy group with reactive end group of reactive silence such as hydroxy group, amino group. The experiment showed that modified epoxy resins not only improved compatibilities of epoxy resin and siloxane but also increased impact and tensile strength, thermal stability by decreasing crosslinking density[12,13]. At present, modification of cyanate ester resin by epoxidized polysiloxane has been reported[14]. The modified resins had the better processing property, toughness and water resistance than neat resins. Glass transition temperature and the initial degradation temperture of modified resins systems were lower than those of original cyanate esters. And then, desirable flexural property of modified resins systems was retained. In our experiment, the low molecular weight γ-(2,3-epoxypropoxy)propyl silane (ESi) were used to modify cyanate ester resins and their static and dynamic mechanical analysis were studied. We found that ESi/BCE composities of toughening improved, when the appropriate addition of ESi was selected.

EXPERIMENTAL

The resin blends comprised two commercially available materials: one, a bisphenol A dicyanate ester (BCE) (an industrial product with white or light yellow granular crystal and melting point of 74 °C) was supplied by Jinan Academy of Aviation Special Structure, China; the other γ-(2,3-epoxypropoxy)-propyl silane (ESi) (an industrial product with achromatism transparent liquid) was purchased from Jinghan Fine Chemicals Company (Jingzhou/Hubei Province, China).

Preparation of ESi/BCE composites: Bisphenol A dicyanate ester (BCE) and γ-(2,3-epoxypropoxy)propyl silane (ESi) were added by heating at 80 °C and under constant stirring. After prepolymerization for 30 min till 150 °C, prepolymer of ESi/BCE system was put into a preheated mold by degassing at 150 °C for 30 min in a vacuum oven. Then the modified resins were cured and post-cured by the procedures of 160 °C/2 h + 180 °C/2 h + 200 °C/2 h and 230 °C/2 h. At last, the mold was cooled to room temperature and demolded to get the sample of ESi/BCE system.

Property tests of ESi/BCE: Impact strength and flexural strength of modified resins were measured according to GB/T2571-1981. The sample dimension was 15 mm × 10 mm × 4 mm. The average value each testing 10 sample was adopted as the test result.

Scanning electron microscopy: Scanning electron microscopy (SEM) was used by HITACHIS-570 to investigate BCE/ESi by imaging modified resins fractured at room temperature. To reduce charging the fracture surface was coated with a thin sputtered layer of gold.

Dynamic mechanical analysis: Dynamic mechanical analysis was performed with a DMAQ800 dynamic analyser at a heating rate of 3 °C min^{-1}. Samples were heated from 25 °C to 300 °C at a fixed frequency of 1 Hz.

RESULTS AND DISCUSSION

Mechanical properties: Fig.1 shows the effect of the content of epoxy group silane on impact strength and flexural strength of modified resins. Impact strength and flexural strength of modified resins increased with the content of epoxy group silane being less than 6 wt. %, then reached the maximum value when the content of epoxy group silane being 6 wt. %, namely impact strength and flexural strength were, respectively increased from 94.11 Mpa and 10.1 kJ/m^2 to 123.93 Mpa and 14.49 kJ/m^2, after decreased with the content of epoxy group silane being more than 6 wt. %. The epoxy group of ESi can deep-set key in crosslinking density network of BCE by chemical bond, when composities are impacted by energy, which can disperse stress and transfer load, so that the toughness and strength of materials can be increased. When the content of ESi were less, the formation of chemical bonds were less, the effect which the materials were toughness increased was not evident. However, when the content of ESi were 8 wt. %, excessive methoxy groups on the other end of ESi was connected with triazine ring to form crosslinking points chain termination of cyanate esters of cross-linking network which is easy fracture when post high temperature treatment, make the mechanical properties of curing system of ESi/BCE reduced. Therefore, an appropriate (amount) of ESi (6 wt. %) can form chemical bond on curing network and reach the best effect of reasonable distribution in Network, which is toughening and reinforcing.

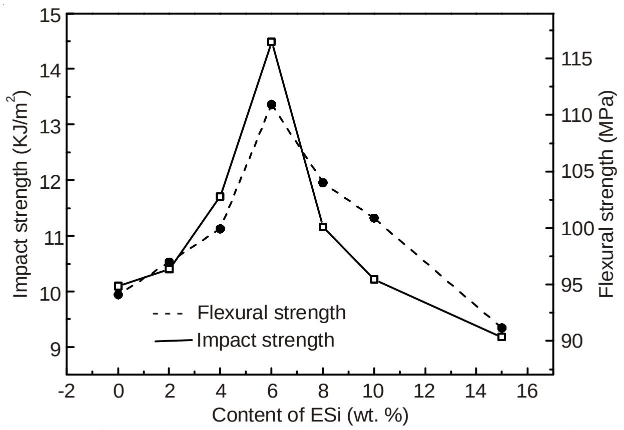

Fig. 1. Effect of the content of ESi on impact strength and flexural strength of modified resins

It can be seen from Fig. 2a-d that the microstructures of the failure specimens impact tests. Their have dimple zones and river pattern zones about SEM micrographs of pure BCE and ESi/BCE, respectively. Fracture surface of the original BCE (Fig. 2a) is a typical brittle fracture. With the increase of ESi, namely the content of epoxy group silane being 6 wt. %, as can be observed from the microstructures of fracture zone. When compared to pure BCE, river pattern zones of ESi/BCE showed larger aspect ratio and white pulling out can hinder growing cracks on river pattern zones. On dimple zones had fish scale concave convex surface and dimple per unit area are more than pure BCE, toughness showed more obviously.

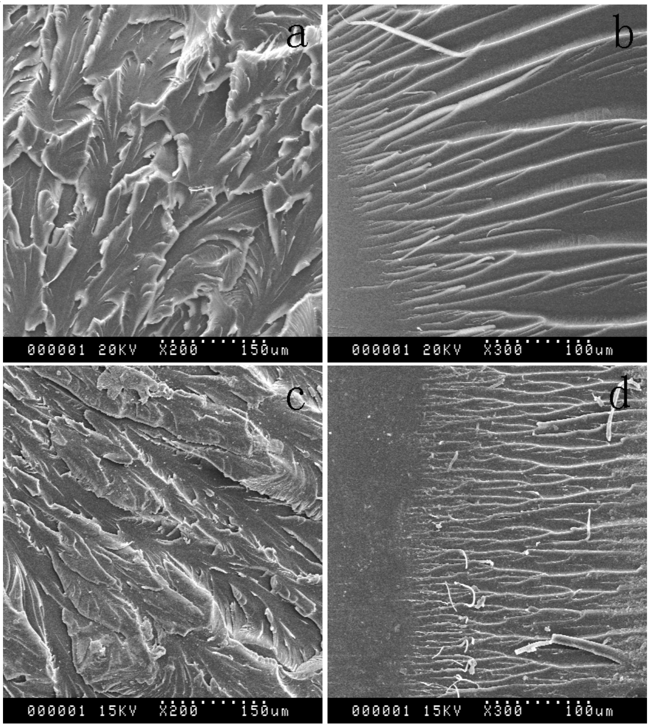

Fig. 2. SEM of fracture surfaces in the impact test of cured ESi/BCE (a, b: pure BCE; c, d: ESi/BCE)

Dynamic mechanical analysis: Figs. 3 and 4 show dynamic mechanical analysis curves of ESi/BCE composites and the effect of BCE on the tan δ is clearly observed. As shown in Fig. 3, the storage modulus of ESi/BCE composites a little decrease as the temperature of ESi/BCE increase from 22 to 175 °C. The storage modulus of ESi/BCE composites is lowest, when the amount of ESi was 6 wt. %. The storage modulus reflects hardness of materials. Their storage modulus are lower than pure BCE due to flexibility chain of the ESi, so their hardness decreased. This is consistent which the ESi/BCE composites of toughening is best, composites can obtain optimum crosslinking density, because of ESi of flexibility chain when the content of ESi is 6 wt. %. Thermosetting resin of T$_g$ is relatively important physical paramerers. It represents highest used temperature. In general, compared with DSC, thermosetting resin of T$_g$ which represents by tan δ of dynamic mechanical analysis is easy to obtain. Fig. 4 represents the effect of the content of ESi on tan δ of ESi/BCE composites. It can be seen from Fig. 4 that pure BCE of T$_g$ is 250.41 °C and ESi/BCE composites of T$_g$ are decreased with the increasing amount of

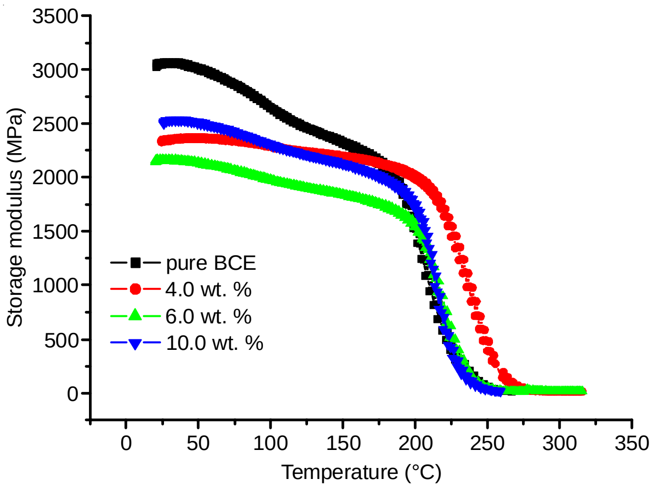

Fig. 3. Effect of the content of ESi on storage modulus E of modified resins

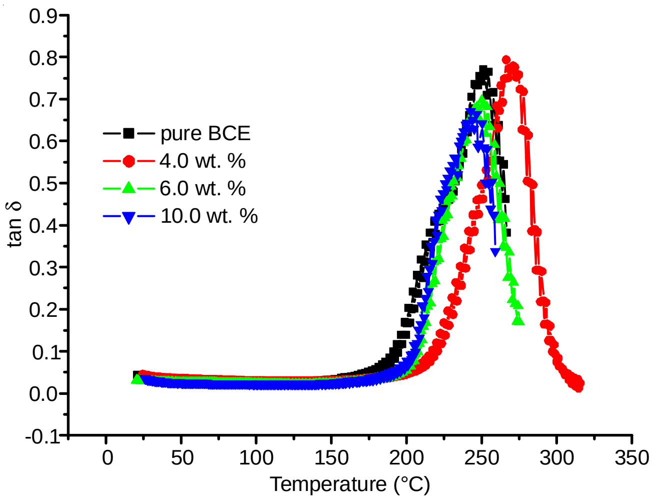

Fig. 4. Effect of the content of ESi on tan δ of modified resins

ESi (from 4 to 10 wt. %). But compared with pure BCE, the value of T_g is not significantly changed, the storage modulus is lowest and toughening improved, when the content is 6 wt. % of ESi. The reason is that BCE of decreasing crosslinking density, between crosslinking point and net chain become longer and the flexibility of ESi can protect restriction of chain segment which of two ends by crosslinking point. So the storage modulus, tan δ and T_g of compositites were all decreased.

Conclusion

ESi/BCE composites were successfully prepared. Results show that composites display improved mechanical properties. Impact and flexural strength of modified resins were increased by 43.5 and 31.7 %, respectively. Adding ESi increases interaction and entanglement of inter-molecules of BCE, resulting in a network structure. The SEM images confirmed the uniform and homogeneous dispersion of ESi in the BCE composites, but also their failure morphology transits from brittle fracture to toughness fracture. The value of T_g is not significantly changed, the storage modulus is lowest of and toughening improved, when the content is 6 wt. % of ESi.

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