A Positron Annihilation Study on the Microstructure of the Interpenetration Polymer Networks of Cyanate ester Resin/Epoxy Resin

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Abstract. Cyanate ester (CE) resin was blended with epoxy resin (EP) at different mass ratios (CE/EP: 100/0, 90/10, 70/30, 50/50, 30/70, 10/90, 0/100). The free volume size of CE/EP IPNs has been determined by positron annihilation lifetime spectroscopy (PALS). The size decreased as the epoxy resin content increased. The PALS results are consistent with the chemical structure changes for the copolymerizing between CE and EP. The crosslinking units of curing products (oxazoline, oxazolidinone, and polyether network) of the blends are all smaller in size than those of triazine ring structure from neat CE. Therefore, the free volume size of the blends decreases with increase of EP content. Examination of the mechanical properties, thermal stability, and morphology of the blend systems showed that addition of epoxy resin resulted in improved toughness but a little sacrifice in thermal stability when compared with pure CE. The correlations between the free volume properties and physical properties (thermal stability and mechanical properties) have been discussed.

1. Introduction
Cyanate ester resin (CE) is one of the most important kinds of thermosetting resins and has received more and more attentions for its superior mechanical properties, low water absorptivity, low outgassing in curing, high environmental resistance, and excellent dielectric properties. It has been widely used as adhesives and matrixes for composites. However, like most other thermosetting resins, it has a drawback of brittleness. The improvement of the toughness of CE while retaining its high thermal stability, modulus and dielectric properties has been an important issue in the past few decades. Current and prior attempts to improve toughness have been made through transforming the basic rigid-triazine structure into flexible structures by blending with thermoplastics and flexible rubbers, or copolymerization with other thermosetting resins like epoxy resin (EP), bismaleimides, etc. Among the blends, CE/EP has been explored as polymer matrix in high performance composites for aerospace and electronic applications. Blending these two resins allows for modification of properties such as glass transition temperature, mechanical properties and adhesion, while reducing the cost. For a CE-
rich system (EP as modifier), the addition of EP monomer can improve the processability and toughness of CE matrix. For an EP-rich system (CE as modifier), the addition of CE monomer can improve the thermal stability and modulus of EP matrix. Each of them can be utilized as latent catalysts to the other component.

Positron annihilation lifetime spectroscopy (PALS) is an innovative nuclear technique which has been carried out with the aim of characterizing free volume in polymeric materials during the last two decades. Free volume defined as the difference between the total volume and hypothetically occupied volume, has been considered as an intrinsic parameter that will correlate with microstructure and mechanical performance. In the present study, we present the results of the free volume properties of a real CE/EP blend system with different mass ratios obtained from PALS. The differences in the free volume properties must effectively reflect from the differences in the crosslinking network. The main purpose of this study is to use PALS as a probe to measure the free volume properties of the CE/EP blend and then examine the relationship between free volume holes and physical properties of the blend system.

2. Experimental

2.1. Materials
A phenolic-based CE resin (melting point: 76°C) was supplied by Jinan Special Structure Institute of China Aero-Industry (Jinan, China). Bisphenol A type epoxy resin (E-51) was purchased from Wuxi Huili Resin Factory (Jiangsu, China). Curing agent 4, 4-diaminodiphenyl methane (DDM) was purchased from Jiangying Huifeng Chemical Company (Jiangsu, China).

2.2. Preparation of the composites
CE/EP mixtures with different mass ratios (100/0, 90/10, 70/30, 50/50, 30/70, 10/90) were thoroughly blended at 90 °C for 30 min with constant stirring. After complete mixing, each mixture was quickly poured into a preheated steel mold coated with the mold release agent. After degasification under vacuum for 30 min at 110 °C, the mold temperature was kept in the following curing procedure: 130 °C/ 1hr +150 °C/ 1hr + 170 °C/ 1hr + 190 °C/ 1hr + 210 °C/ 1hr + 230 °C/ 1hr + 250 °C/ 1hr to form the specimens. Neat EP specimens were prepared with the process: An appropriate amount of DDM (curing agent, 10 wt%) was added to EP at 90 °C, stirred for several minutes, and quickly poured into a preheated steel mold coated with the release agent. After degasification at 90 °C for about half an hour, the sample was allowed to cure at 90 °C for 2 hr and then at 150 °C for 5 hr.

2.3. Characterization of the composites
The unnotched impact strength was measured with a Charpy impact tester (XJC-5, Chengde Testing Machine Co. Ltd., China). The tests were according to the Chinese national standard methods for impact resistance of resin casting body (GB/T 2571-1995) at 23±2 °C. The size of the samples for impact testing is about: 80 mm × 10 mm ×5 mm. The tensile properties were measured with a universal materials testing machine (SANS Testing Machine Co. Ltd., Shenzhen, China) with a crosshead speed of 2 mm/min. The tensile measurements were according to the Chinese national standard methods for tensile properties of resin casting body (GB/T 2568-1995) at 23±2 °C. The sample for tensile testing is dumbbell shaped and the scale distance is 50 mm. Five specimens of each group were prepared and tested.

Thermal gravimetric analysis (TGA) was performed using a NETZSCH STA 449C (NETZSCH Company, German) thermal analyzer. The samples were heated from 30 °C to 800 °C at a heating rate of 20 °C/ min under nitrogen atmosphere.

2.4. PALS measurement
Positron annihilation lifetime spectroscopy (PALS) was measured with an EG&G ORTEC fast-fast lifetime spectrometer (ORTEC Co., Tennessee, USA) with a FWHM=190 ps for a 60Co prompt peak.
of 1.18 MeV and 1.33 MeV γ rays. A $6 \times 10^5$ Bq of positron source ($^{22}$Na) was deposited between two Kapton films (3 µm in thickness), which was sandwiched between two identical composite samples. All PALS measurements were performed at room temperature. Every spectrum contained about $10^6$ counts. The resulting spectra were consistently modeled with a three-component fitting program PATFIT.

3. Results and Discussions

3.1. Free volume properties of the blend systems

Figure 1. The $\alpha$-Ps lifetime $\tau_3$ of CE/EP IPNs with different EP content.

Figure 2. The calculated free volume radius $R$ of CE/EP IPNs with different EP content.

Figure 3. The curing products structure of CE/EP IPNs.

The PALS spectra for all samples were analyzed with PATFIT for three or more components of lifetime. For all samples a three-component fit was much better with variances all below a value of 1.2. Usually, the shortest lifetime $\tau_1$ is attributed to $\alpha$-Ps annihilation. The intermediate lifetime $\tau_2$, is due to the free positron annihilation. The longest lifetime $\tau_3$, is assigned to $\alpha$-Ps annihilation. The EP content dependence of the $\alpha$-Ps lifetime $\tau_3$ is shown in Figure 1. The average radius $R$ (as shown in Figure 2)
of free volume holes has been calculated with a quantum mechanical model developed by Tao 11 as follow equation:

\[
1/\tau_s = 2\left[1 - R/(R + \Delta R) + \sin\left(2\pi R/(R + \Delta R)\right)/2\pi\right]
\]  

(1)

where \( R \) is the radius of the free volume hole, \( \Delta R \) (=0.1656 nm) is derived from fitting the observed \( o-Ps \) lifetimes in molecular solids with known hole sizes 12.

Previous studies 13, 14 have showed that in the case of thermosetting-based composites, chains are restricted in the rigid network structure (in which chain units connect with chemical bonds) and their mobility depends much more on the properties of the network, such as chemical structure and crosslinking density. Our recent works 15, 16 have shown that the mass ratio of CE/EP has great influences on the reaction routines of the interpenetration polymer networks (IPNs). In a CE-rich blend system, the main curing products are triazine ring networks and oxazoline, together with a small amount of oxazolidinone. In an EP-rich blend system, the main curing products are polyether network, oxazolidinone and isocyanurate, whereas the triazine ring network is rare for the lack of CE (as see in Figure 3).

**Figure 4.** The curing reaction of pure CE (a) and EP with DDM (b).

The changes of \( R \) are similar with changes of \( o-Ps \) lifetime of the composites. It is observed that the mean free volume hole size of the blend system decreases with the increase of EP content. Before a
discussion on this phenomenon, the difference of the free volume size of both crosslinked CE and EP (cured with DDM) should be mentioned. The free volume size of the matrix is determined by the crosslinking degree and the size of the crosslinking unit. As shown in Figure 4, pure CE forms a highly crosslinked network of triazine during the curing process. For comparing, the curing process of EP with DDM is also shown in Figure 4. It can be easily deduced from the structure of both curing products that the crosslinking unit of triazine is larger than that of cured EP. The smaller size of the free volume holes in EP cured with DDM should be mainly attributed to the smaller crosslinking unit.

Therefore, for CE/EP blend system, the decrease of the free volume size is due to the loss of the triazine structure in the blends with the increase of EP. As discussed above (Figure 3), cured products of oxazoline, oxazolidinone and polyethers increase with the EP content. The sizes of the crosslinking units of these curing products are all smaller than the crosslinking units of triazine ring structure. Therefore, the free volume size of the blend decreases with the EP content. In the case of CE/EP (10/90), its free volume size is even smaller than EP cured with DDM. This is caused by the different curing mechanism of EP curing process. In the case of CE/EP (10/90), the catalytic curing agent (oxazolidinone or CE) induces anionic ring-open addition polymerizations to form crosslinked polyether network (Figure 3). The catalytic curing agent does not appear in the structure of the curing products, whereas in EP cured with DDM, DDM has appeared in the structure of the curing products (as shown in Figure 4). This may be the main reason for the smaller free volume size in the case of CE/EP (10/90).

3.2. Thermal stability of the blend systems

![Figure 5](image_url)

**Figure 5.** The thermal stability of CE/EP IPNs with different EP content.

Figure 5 shows the thermal gravimetric (TG) curves for the cured CE/EP blends with different mass ratios. Neat CE has much higher thermal stability than EP cured with DDM. The thermal stability of all the blends is better than EP cured with DDM but worse than neat CE. The blend mass ratio has great influences on the thermal stability of the blends. It is believed that CE has more thermal stability than EP because of the triazine ring structure. For the cured CE/EP blends, the number of triazine unit decreases as the EP content increases. It seems that the thermal stability of CE/EP blend system should be reduced as the EP content increases. However, in our TG study, the results show that the EP-rich systems have higher thermal stability than CE-rich systems especially in the early stage of the tests. For example, the temperature of 10% weight loss: 100/0>10/90>30/70>90/10>70/30>50/50>EP (with
DDM). Similar results have been reported by Walters NR and Lyon RE\textsuperscript{17} who found that CE/EP (2/8) and CE/EP (4/6) had higher thermal stability than CE/EP (8/2) and CE/EP (6/4) in the early stage of the TG tests. To explain this phenomenon, we should make a careful examination of the crosslinking products of the blend system as the blend mass ratio changes. The significant differences of the blend in CE-rich systems and EP-rich systems are more oxazoline structures and triazine ring structures but fewer oxazolidinone, isocyanurate and polyether network structures formed in CE-rich systems. It is believed that the oxazoline structures degrade first and have an inferior effect on the composite\textsuperscript{17}. Oxazolidinone, isocyanurate, triazine ring and polyether network structures have higher thermal stability than oxazoline. Therefore, an EP-rich system even has higher thermal stability in the early stage of the tests than a CE/EP (90/10) system. The higher thermal stability of the polyether network than the oxazoline structure may be attributed to its higher crosslinking density and compactness of each crosslinking unit, which is in accord with the PALS results that the free volume size of CE/EP (10/90) blend is the smallest.

3.3. Mechanical properties of the blend systems
The impact strength and tensile strength of the blend systems have been shown in Figure 6 and Figure 7. A significant increase in the impact strength of all the samples added with EP is observed when compared to that of neat CE. The tensile strength of the blend system decreases firstly and then increases as the EP content increases. Pure CE has highly symmetrical triazine ring crosslinking backbone and exhibits low toughness and high stiffness. For CE-rich blends, the highly symmetrical triazine ring crosslinking backbone has been partially destroyed and replaced by some oxazoline and oxazolidinone structure. The oxazoline and oxazolidinone structures exhibit more thermoplastic character and reduce the tensile strength\textsuperscript{18}. Therefore, they have a higher toughness but lower stiffness than neat CE. For EP-rich blends, the main backbone of the crosslinking network is polyether network, together with some oxazolidinone structure and rare triazine ring structure. The increase in the tensile strength of the blends as EP content increases (EP content >30%) is due to the increase of the formation of polyether network with high crosslinking density. In the case of CE/EP (10/90), relatively lower toughness and higher stiffness is due to the highest crosslinking density of polyether network. The higher toughness of EP cured with DDM is mainly attributed to its bigger free volume size (DDM has appeared in the structure of the curing products), which can provide more room for the segmental motion.

![Figure 6. Impact strength of CE/EP IPNs with different EP content.](image)

![Figure 7. Tensile strength of CE/EP IPNs with different EP content.](image)
4. Conclusions
CE resin was blended with EP with different mass ratios. Investigation of the mechanical properties, thermal stability, and morphology showed that addition of epoxy resin resulted in improved toughness but a little sacrifice in thermal stability than neat CE. The free volume properties of the blend system determined by PALS are consistent with the chemical structure changes for the co-curing reactions between CE and EP. In addition, physical properties of the blend system can be estimated from the changes in the free volume properties of the blends.

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