

Simultaneously Enhanced Cryogenic Tensile Strength, Ductility and Impact Resistance of Epoxy Resins by Polyethylene Glycol

Qingping Feng, Jiaoping Yang, Yu Liu, Hongmei Xiao, Shaoyun Fu*

Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing 100190, China

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Rubbers have been well accepted for modifying brittle epoxies but rubber modified epoxies usually possess lowered tensile strength though enhanced ductility and fracture resistance. In this work, a polyethylene glycol (PEG-4000) is used to modify diglycidyl ether of bisphenol A/methyltetrahydrophthalic anhydride system for enhancing cryogenic tensile strength, ductility and impact resistance. The results display that the cryogenic tensile strength, ductility (failure strain) and fracture resistance (impact strength) are all enhanced for the modified epoxy system at proper PEG contents. The maximum tensile strength (127.8 MPa) at the cryogenic temperature (77 K) with an improvement of 30.1% is observed for the modified system with the 15 wt% PEG content. The ductility and impact resistance at both room temperature and cryogenic temperature are all improved for the modified epoxy system with proper PEG-4000 contents. These observations are explained by the positron annihilation lifetime spectroscopy results and scanning electron microscopy results. Moreover, the glass transition temperature decreases slightly with increasing PEG content.

KEY WORDS: Epoxy resin; Modification; Polymer composite; Tensile strength

1. Introduction

Due to their easy fabrication, good electric insulating and mechanical properties *etc.*, thermosetting epoxy resins have been well accepted as matrices for fiber reinforced composites applied in cryogenic engineering fields in the temperature range of liquid helium (4.2 K), liquid hydrogen (20 K), liquid nitrogen (77 K), liquid oxygen (90 K), and liquid methane (112 K)^[1–7]. However, as a kind of thermosetting resins, the intercrossed molecular chains make epoxy resins rigid and brittle, thus micro-cracking and even fracture of epoxy resins might happen when their thermal-stress induced stress intensity factor exceeded their fracture toughness as temperature decreased down from room temperature to cryogenic temperature^[3,8]. This would result in the permeation of medium molecules such as helium, hydrogen, nitrogen, oxygen or methane molecules along the cracking passages when epoxy resins were used as matrices for composites^[9]. Therefore, it is necessary to improve the cryogenic mechanical performance of epoxy resins to meet the high requirements by cryogenic engineering applications.

Blending of polymers with rubbers is an important area of research activity^[10]. Rubbers are often used to modify brittle epoxy resins. Epoxy resins aimed for cryogenic engineering applications are also modified by using rubbers. Ueki et al.^[3] designed several epoxy systems with different chemical structures and employed carboxyl-terminated butadiene–acrylonitrile rubber copolymer to modify epoxy resins. Nobelen et al.^[7] used two carboxyl-terminated butadiene–acrylonitrile rubbers as modifiers to improve the cryogenic mechanical performance and investigated their cryogenic micro-cracking behavior. However, rubber modified epoxies showed enhanced ductility and fracture resistance such as impact strength but generally exhibited lowered tensile strength.

In this work, polyethylene glycol (PEG) with the molecular weight of 4000 g/mol (PEG-4000) is employed to modify the epoxy system of diglycidyl ether of bisphenol A (DGEBA)/methyltetrahydrophthalic anhydride (MeTHPA) to enhance their cryogenic tensile strength, ductility and impact resistance. First, the hydroxyls at the ends of PEG-4000 molecules would react with the curing agent (MeTHPA) and hence the PEG-4000 molecules would enter and control the network structure of the cured epoxy system. Second, the flexible PEG-4000 polymer chains, which are composed of ether bonds, are expected to improve the impact resistance at cryogenic temperature of cured epoxy resins. However, to our best knowledge, no work has been done so far on the cryogenic mechanical properties of epoxy resins modified by PEG-4000. Therefore, in this work, the

* Corresponding author. Prof., Ph.D.; Tel./Fax: +86 10 82543752; E-mail address: syfu@mail.ipc.ac.cn (S. Fu).

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cryogenic mechanical behaviors at 77 K of MeTHPA/DGEBA system modified by PEG-4000 are reported in terms of their cryogenic tensile and impact properties. The liquid nitrogen was used to create a cryogenic temperature (77 K) environment due to its less expensiveness compared to other cryogenic media. The mechanical properties at room temperature (RT) were also investigated for comparison.

2. Experimental

2.1. Materials and sample preparation

The epoxy resin, DGEBA (CYD-128) with an epoxide equivalent of 184–194, was provided by Yueyang Refinery Plant, China. The curing agent, methyltetrahydrophthalic anhydride (MeTHPA), was bought from Shanghai Li Yi Sci. & Technol. Development Co. Ltd, China. Benzyl dimethylamine (BDMA) as the accelerator was obtained from Shijiazhuang Wells Electronic Material Co., Ltd, China. The PEG-4000 with the molecular weight of 4000 g/mol used in this work was purchased from Beijing Chemical Reagent Company. The chemical structure of PEG-4000 was shown in Fig. 1. The chemical structures of DGEBA and MeTHPA have been given in our previous paper^[11].

60.0 g DGEBA was firstly mixed with 3.2, 6.7, 10.6 and 15.0 g PEG-4000, respectively and stirred at 60 °C for 30 min until a homogenous mixture was observed. The PEG-4000 content in the blended mixtures varied from 0, 5, 10, 15 and 20 wt%. 60 g MeTHPA and 1.5 g BDMA were added to the PEG-4000/epoxy mixtures at 60 °C, respectively, which were then degassed under vacuum for 30 min. Homogenous solutions were obtained, and casted in a preheated steel mold at 80 °C, then cured at 130 °C for 2 h, 150 °C for 10 h, and post-cured at 170 °C for 5 h. The dumbbell-shaped tensile specimens were prepared according to the ASTM D638-96. The impact specimens were prepared with the dimensions of 4 mm (thickness) × 10 mm (width) × 80 mm (length) according to the ASTM D-256.

2.2. Instruments and measurements

The PALS characterization was conducted by an EG&G-ORTEC fast–slow coincidence system with a resolution of 180 ps at room temperature. The source of ²²Na (5 × 10⁵ Bq) was sandwiched between two pieces of the samples and three million counts were collected for each spectrum. The positron lifetime (τ_3) and intensity (I_3) of the long-lived components were analyzed by the computer program “POSFIT88”.

The glass transition temperature (T_g) of the cured specimens was measured *via* NETZSCH STA 409 PC at a heating rate of 10 °C/min under nitrogen atmosphere. The heating temperature ranges from 30 to 200 °C. The tensile properties of the cured samples were tested at RT and 77 K by an RGT-20A Reger mechanical tester, by using a 10 kN load cell with a crosshead speed of 2 mm/min. The clamps and the samples were dipped in

a liquid nitrogen filled cryostat designed in our laboratory when the tensile samples were tested at 77 K.

The impact strength of the cured specimens was measured with a REGER impact tester. At least five specimens were tested for each composition. When the impact testing was performed at 77 K, the specimens were dipped in a liquid nitrogen filled cryostat for over 10 min, then the impact testing was quickly completed within a couple of seconds after taking the specimens out from the cryostat. During the impact testing, the temperature inside the samples would show no obvious change after the specimens were taken out from the cryostat for a few seconds and the temperature was approximately considered as 77 K^[12]. The micrographs of the fracture surfaces of the impact specimens were taken by scanning electron microscopy (SEM, HITACHI S-4300). The fracture surfaces were cleaned with alcohol and spray coated with a thin layer of evaporated gold to improve their conductivity before the examination.

3. Results and Discussion

3.1. Characterization of PALS and DSC

Positron annihilation lifetime spectroscopy (PALS) is an effective technique to evaluate the free volume of polymers and has been widely used in studying polymer systems at molecular level. The free volume is an important parameter for describing the structure of a polymer and has great influences on the mechanical properties of the polymer, mainly depending on the ability of the polymer segments to pack together by the rigidity of the backbone and the cross-link density. This technique utilizes the interactions between the positrons and the electrons from the host material to elucidate the free volume hole dimensions, which range from about 0.1 to 1 nm. The positronium lifetime (τ_3) has a strong correlation with the size of the free volume and is an indication of the average size of free volumes; the intensity (I_3) is an indication of the concentration of free volumes within the cured epoxy networks^[7,11,13–15].

The measured results by PALS for the positronium lifetime (τ_3) and the intensity (I_3) as a function of PEG-4000 content are exhibited in Table 1. It can be seen from Table 1 that the τ_3 value increases with increasing PEG-4000 content, which indicates that the average size of the free volumes within the PEG-4000 modified epoxy systems increases with increasing PEG-4000 content. And the I_3 value for the modified epoxy systems is obviously larger than that for the unmodified epoxy system, which displays that the concentration of free volumes in the PEG-4000 modified epoxy networks is higher than that in the unmodified epoxy system. Fig. 2(a) and (b) shows the size of the simulated structures of single PEG-4000, DGEBA and MeTHPA molecule by using the well known Chemoffice3D Ultra 10.0

Table 1 Positronium lifetime τ_3 , intensity I_3 and glass transition temperature (T_g) of unmodified and PEG-4000 modified epoxy resins

PEG-4000 content (wt%)	τ_3 (ns)	I_3 (%)	T_g (°C)
0	1.72 ± 0.01	20.7 ± 0.2	118.5
5	1.82 ± 0.01	22.7 ± 0.2	116.2
10	1.84 ± 0.01	22.3 ± 0.2	112.9
15	1.86 ± 0.01	22.2 ± 0.2	104.9
20	1.94 ± 0.01	23.5 ± 0.2	102.4

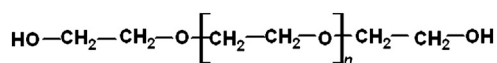


Fig. 1 Chemical structure of polyethylene glycol PEG-4000.

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