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Preparation and mechanical properties of modified epoxy resins with flexible diamines

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Abstract

Diglycidyl ether of bisphenol A (DGEBA) is one of the most widely used epoxy resins for many industrial applications, including cryogenic engineering. In this paper, diethyl toluene diamine (DETD) cured DGEBA epoxy resin has been modified by two flexible diamines (D-230 and D-400). The cryogenic mechanical behaviors of the modified epoxy resins are studied in terms of the tensile properties and Charpy impact strength at cryogenic temperature (77 K) and compared to their corresponding properties at room temperature (RT). The results show that the addition of flexible diamines generally improves the elongation at break and impact strength at both RT and 77 K. The exception is the impact strength at 77 K filled with 21 wt% and 49 wt% D-400. Further, two interesting observations are made: (a) the cryogenic tensile strength increases with increasing the flexible diamine content; and (b) the RT tensile strength can only be improved by adding a proper content of flexible diamines. It is concluded that the addition of a selected amount namely 21–78 wt% of D-230 can simultaneously strengthen and toughen DGEBA epoxy resins at both RT and 77 K. However, only the addition of 21 wt% D-400 can simultaneously enhance the strength and ductility/impact strength of DGEBA epoxy resins at RT. The impact fracture surfaces are examined using scanning electron microscopy (SEM) to explain the impact strength results. Finally, differential scanning calorimetry (DSC) analysis shows that the glass transition temperature (T_g) decreases with increasing the flexible diamine content. The presence of a single T_g reveals that the flexible diamine-modified epoxy resins have a homogeneous phase structure.

Keywords: Epoxy resin; Flexible diamines; Cryogenic mechanical properties

1. Introduction

Epoxy resins are a most important class of thermosetting resins for many engineering applications because of their high strength and stiffness, good dielectric behavior, resistance to chemicals, corrosion and microbial organisms, low shrinkage during cure and good thermal characteristics [1–7]. With the rapid developments in spacecraft and superconducting cable technologies, and large cryogenic engineering projects such as the International Thermonuclear Experimental Reactor (ITER) etc., epoxy resins have been increasingly employed in cryogenic engineering technologies as impregnating materials, adhesives or matrices for fiber-reinforced composites [8–10]. In cryogenic engineering, liquid nitrogen or liquid helium is often employed as cooling media and hence the environment temperature is 77 K or 4.2 K, respectively. The cryogenic temperature in scientific research on cryogenic properties of materials refers more often to 77 K since liquid nitrogen (77 K) is much cheaper than liquid helium (4.2 K). Epoxy resins normally have poor crack resistance at room temperature [11,12] and are also highly brittle at cryogenic temperature [13], which makes them unsuitable for many cryogenic engineering applications. Thus, it is necessary to improve the toughness and ductility of epoxy resins so that they can be gainfully used in such cryogenic technologies.

Diglycidyl ether of bisphenol A (DGEBA) is one of the most widely used epoxy resins and it has found many cryogenic engineering applications [14]. Liquid aromatic amine (DETD) has low viscosity and low toxicity and is often used as a hardener

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for curing DGEBA. Therefore, DGEBA and DETD will be employed, respectively, as epoxy precursor and hardener in this study. Though DETD cured DGEBA system shows the high mechanical strength, it is brittle, particularly at cryogenic temperature. Hence, it is important to modify this epoxy system to broaden its acceptance for applications in cryogenic engineering.

The most common approach to toughen brittle epoxy resins is introduction of a toughening agent into the epoxy network. Toughening agents, such as epoxidized natural rubber [15], poly(sulfone) [16], polysiloxane [17], polyetherimide [18–20], poly(ether sulfone) [21–23], and poly(ether ether ketone) [24,25] etc., have been reported to improve the toughness of epoxy resins. Modification of the epoxy structure is also an effective method to improve crack toughness, including for example, chemical modification from a given rigid epoxy backbone to a more flexible backbone structure, increase of epoxy monomer molecular weight, decrease of crosslink density of a cured resin [26–28], etc. However, most past investigations were focused on the improvement of toughness at room temperature (RT), and very few studies at cryogenic temperature [29]. Moreover, among the above-mentioned toughening methods, rubber toughening might also lead to significant reduction in Young's modulus and tensile strength, which is undesirable for engineering applications at cryogenic temperature. Also, RT mechanical behaviors of materials are generally very different from those at cryogenic temperature so that their mechanical properties obtained at RT cannot simply be transferred to the cryogenic case.

Very low molecular weight polyether diamines such as D-230, D-400 and D-418 have been used as curing agents for DGEBA epoxy resins [30–33]. These include studies on cure kinetics by DSC [30], cure reactions by fluorescence and IR spectroscopic techniques [31], and by dynamic-mechanical behavior [32]. DGEBA resins cured with a mixture of two agents (mPDA and D-230) were also conducted [33]. Addition of a small amount of aliphatic amine increases the toughness but decreases the rigidity and the glass transition temperature. At a cryogenic temperature such as liquid hydrogen temperature (77 K), most chain segments of polymers are frozen and are brittle but the polyether chain segments are not completely frozen and rotational freedom is still permitted [34]. Hence, it is likely that polyether diamines can improve the cryogenic toughness of DGEBA epoxy resins. However, little work has been done to-date on the cryogenic mechanical properties of DETD cured DGEBA based epoxy resins modified by polyether diamines. This is the main purpose of the present paper.

Here, two flexible polyoxypropylene diamines (D-230 and D-400) are selected to modify DETD cured DGEBA epoxy resins due to their compatibility and ease of mixing. Also, flexible polyoxypropylene diamines can be simply incorporated into the epoxy cured network structure via normal cure reaction between amine and epoxy. The mechanical behaviors at RT and 77 K of the cured epoxy resins are studied in terms of the tensile properties and impact strength by taking into account the effects of the flexible diamine content. The glass transition temperature (T_g) as a function of the flexible diamine content is examined by DSC analysis.

2. Experimental work

2.1. Materials and preparation of samples

The epoxy resin CYD128 used in this study was a low molecular weight liquid diglycidyl ether of bisphenol A (DGEBA) with an epoxide equivalent weight of 184–194 purchased from YueYang Baling Petrochemical Technology Ltd. Diethyl toluene diamine (DETD) (ETHACURE-100), which existed as a mixture of the two DETD isomers (74–80% 2,4-isomer and 18–24% 2,6-isomer, amine equivalent weight = 44.3), was purchased from Albemarle Corporation, USA. The flexible diamines, namely polyoxypropylene diamines including Jeffamine D-230 (molecular weight (MW) = 230, amine equivalent weight = 57.5) and D-400 (MW = 400, amine equivalent weight = 100), were obtained from Huntsman Chemical Co. The chain length of D-400 is larger than that of D-230. The chemical structures of epoxy, DETD and polyoxypropylene diamines are shown in Fig. 1.

The hardener DETD was first mixed with flexible diamines homogeneously and the relative flexible diamine content in the mixed system varied from 0 to 100% in weight. The mixtures of two diamines served as the hardener. Then the equal equivalent amount of epoxy resin was added. Namely, the stoichiometric ratio of epoxy/amine, $[E]/\{[H]_{\mathrm{DETD}} + ([H]_{\mathrm{D\text{-}230}}$ or $[H]_{\mathrm{D\text{-}400}})\} = 1$, was used for this study, where $[E] = \mathrm{weight}_{\mathrm{CYD128}}$/epoxide equivalent weight, $[H]_{\mathrm{DETD}} = \mathrm{weight}_{\mathrm{DETD}}/\mathrm{amine}_{\mathrm{DETD}}$ equivalent weight, $[H]_{\mathrm{D\text{-}230}} = \mathrm{weight}_{\mathrm{D\text{-}230}}/\mathrm{amine}_{\mathrm{D\text{-}230}}$ equivalent weight and $[H]_{\mathrm{D\text{-}400}} = \mathrm{weight}_{\mathrm{D\text{-}400}}/\mathrm{amine}_{\mathrm{D\text{-}400}}$ equivalent weight. Formulas employed in this study are listed in Table 1. The resultant materials were completely mixed by a mechanical stirrer and degassed with a vacuum pump to eliminate air bubbles. The bubble-free mixtures were then poured into the preheated steel mold in an oven. The inner geometry of the steel mold is following the recommendation of ASTM D638-96 for making tensile specimens. The dimensions of tensile specimens are 4 mm × 6 mm in the working section. The inner dimensions of the steel mold for making impact specimens are 4 mm × 10 mm × 80 mm. The modified epoxy resins were cured at 60 °C for 8 h, then 100 °C for 12 h at normal pressure, while the unmodified epoxy resin was cured at 80 °C for 8 h, then 130 °C for 12 h at normal pressure. It should be pointed out here that it was also tried to cure the unmodified epoxy system at 100 °C but it was unsuccessful. In the later discussion, it will be clarified that the effect of curing temperature difference can be ignored on mechanical properties. The samples were dried in an oven before mechanical testing.

2.2. Measurement and characterization

The tensile samples were prepared according to the recommendation of ASTM D638-96. The tensile properties were measured on a RGT-20A REGER mechanical tester under