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Cure mechanism and thermal properties of the phthalide-containing bismaleimide/epoxy system

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ABSTRACT

A series of novel resin systems were prepared using a novel thermosetting bismaleimide containing phthalide cardo structure (BMIP), diglycidyl ether of bisphenol A epoxy resin (DGEBA) and 4,4′-diamino diphenyl sulfone (DDS). The cure mechanism of the mixture was studied by Fourier transform infrared (FTIR) spectroscopy and differential scanning calorimetry (DSC). The FTIR results demonstrated the cure temperature of BMIP was reduced in the presence of epoxy group. The DSC thermogram of the blends showed three different cure regimes in the temperature range of 150–350 °C and the intensity and position of the exothermic peaks were varied with the blend formulation. The cause of their formation was analyzed in detail. Thermal properties of the cured network were characterized by dynamic mechanical analysis (DMA) and thermogravimetric analysis (TGA). Experimental results exhibited that the heat resistance and thermal stability were decreased with the epoxy content and the molar ratio of the BMIP and DDS exhibited little effect on them.

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1. Introduction

Epoxy (EP) and bismaleimide (BMI) resins are two most important classes of high performance thermosetting polymer. They have been evolved as foundational matrices for fiber-reinforced structural composites in the aircraft and aerospace industries and as adhesives or coatings used widely in the electronic/electrical and other related high-tech fields [1–4]. Despite the current popularity of two resin systems, they still suffer from some limitations, which hamper their further application. The high level moisture absorption and relatively lower heat-resistant temperature and thermostability are the main shortcoming of the cured EP networks [4–9]. Owing to superior chain rigidity, the fully cured BMI can provide a higher service temperature than the EP. However, the common BMI monomers have difficultly to process, because they are usually crystalline powder with high melting point (T_m) and thermal curing starts at temperatures just above T_m. On the other hand, the cured product of the unmodified BMI is so brittle that it is of little use due to the highly crosslinked network structure [10–13].

Thermoset/thermoset blend is a promising approach emerged recently, which can overcome the drawbacks of both components and produce considerable and unexpected improvements in some properties [6–8]. This is because the cured resins belong to inter-crosslinked or interpenetrated polymer networks, which often exhibits synergistic effects. Providing EP resins are incorporated into BMI resin, it can be as plasticizer to improve the stiffness and processing of BMI resin, in the same way, the thermal properties and hygroscopic characteristics of EP can be improved via the incorporation of BMI resins. Therefore, many efforts have been devoted to preparing improved matrices with advantageous combination of properties based on BMI and EP resins [4–13].

The modified resin systems based on BMI and EP usually contain another component, diamine (DA), which has dual function as a hardener of EP and a chain extender of BMI. The cure behavior, compatibility and thermal, mechanical and physical properties of the BMI/DA/EP blends have been investigated in detail [4–13]. However, there are still dispute in respect of the cure mechanism. It is actually not surprising when one considers the multitude and complexity of the BMI/DA/EP formulations. According to the reports, the following reactions were proposed in the curing process (Fig. 1): the ring-opening reaction of the EP ring and primary amines for producing chain growth and secondary amines for building chain branches, etherification of EP ring with a pendant hydroxyl group and homopolymerization of EP group at higher temperature in the absence of active N—H functionality, Michael addition of the primary amines and secondary amines to double bond in the maleimide groups and free radical polymerization of the BMI double bonds[5,7–14]. In principle, the above-mentioned reactions may occur, either simultaneously or at different stages of

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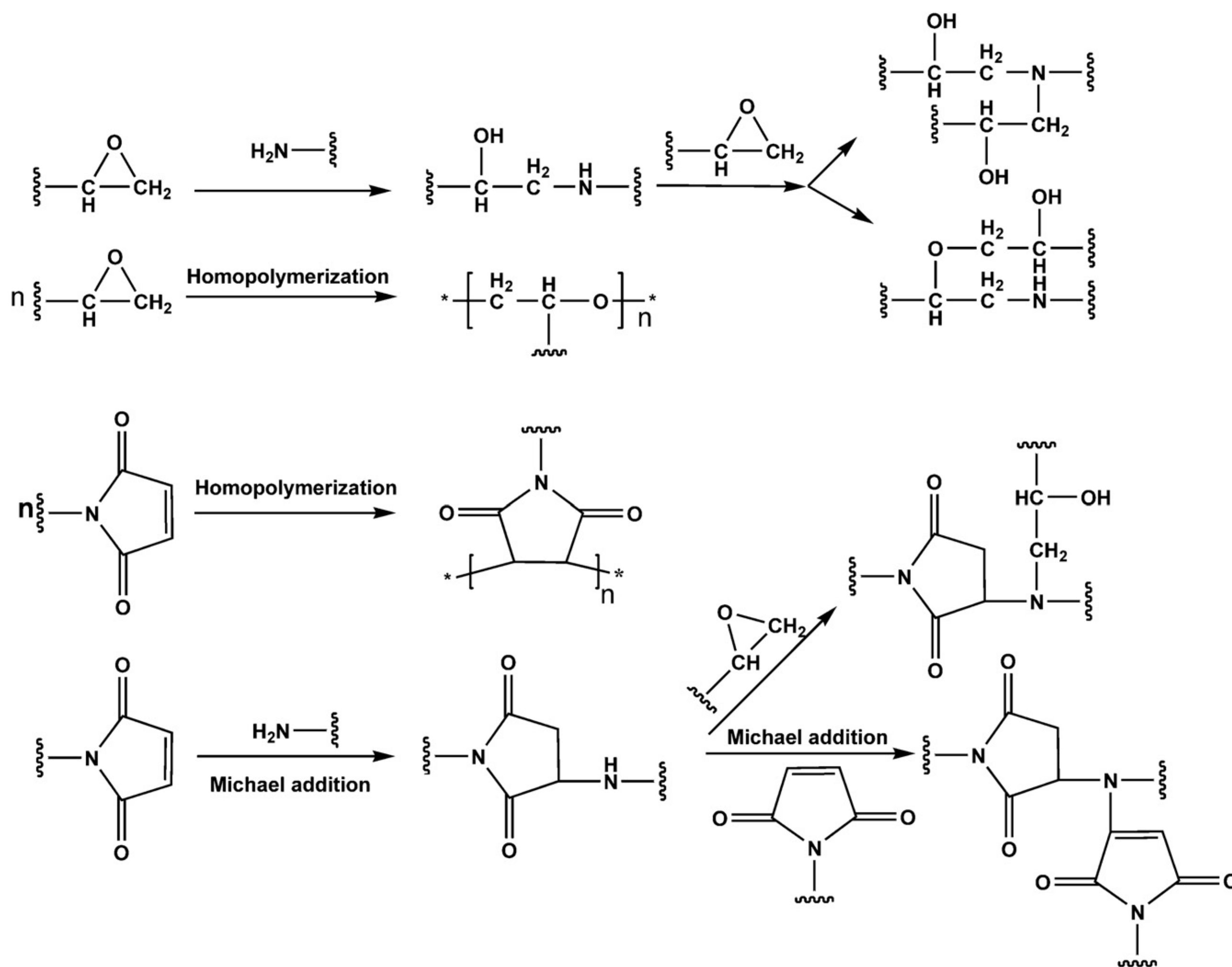

Fig. 1. Proposed curing pathways of BMIP/DDS/DGEBA resin.

the curing process, depending on the relative reactivity of the components and on the process temperature. Such as the neat EP/DA system, at lower temperature the reaction of the epoxy ring and primary amine is the only one occurring in the presence of primary amine and the secondary amine and pendant hydroxyl group reactions with glycidyl ether start to occur only when the concentration of primary amine groups becomes negligible, whereas the three reactions may occur almost simultaneously with increasing process temperature. Furthermore, the unreacted EP groups, trapped in the glassy polymeric network, may be catalyzed by the resultant tertiary amine group to self-polymerize to form a polyether at higher temperature [14,15]. In the presence of DAs, the BMIs may undergo two different reactions, Michael addition and radical homopolymerization. Many authors agree that the Michael addition between primary amines and double bond is faster and take place at lower temperature than the homoploymerization and Michael addition of secondary amines, however, some contributions give the opposite conclusion that the homoploymerization is of higher reactivity [5,7,13,16–18].

The ultimate properties of the polymeric material are determined mainly by the polymer structure and morphology, which depend on the type of cure reaction and the stage that it takes place during the processing operations [19–21]. Therefore, it is imperative to study the pathways of the cure reaction. The objective of this research is to provide the information about the cure mechanism of BMIP/DDS/DGEBA resin, which is composed of a novel thermosetting bismaleimide containing phthalide cardo structure (BMIP), diglycidylether of bisphenol A (DGEBA) and 4,4′-diamino diphenyl sulfone (DDS), investigated by FTIR and nonisothermal DSC. Furthermore, the thermal properties of the blend resins have been characterized by DMA and TGA.

2. Experimental

2.1. Materials

Commercially available diglycidylether of bisphenol A (DGEBA)-based epoxy resin, with an epoxy equivalent of about 185–210, was supplied by Wuxi Resin Works, China. The hardener used was 4,4′-diamino diphenyl sulfone (DDS) provided by Shanghai Huifeng Science and Trading Company (Shanghai, China). BMIP was synthesized according to the reported method [22]. The chemical structures of BMIP, DDS and DGEBA are shown in Fig. 2.

2.2. Sample preparation

The BMIP/DDS/DGEBA prepolymer was prepared by mixing crushed BMIP, DGEBA and DDS at 130 °C under vigorous mechanical stirring for about 10 min, and then a homogeneous, visually transparent mixture was obtained. Bubbles in the blends were drawn out in a vacuum oven at 130 °C. Then, the blends were introduced into preheated (130 °C) Teflon molds and thermally cured in an air convection oven at 150 °C for 1 h, 180 °C for 2 h, 200 °C for 4 h

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