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Improved surface quality and hygrothermal performance of epoxy based prepreg by liquefied dicyandiamide with enhanced solubility and dispersibility

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ABSTRACT

Liquefied dicyandiamide (L-DICY) was fabricated by pretreatment of DICY with polyetheramine (PEA)/diglycidyl ether of bisphenol A (DGEBA) adduct, and physicochemical properties of L-DICY, mechanical, thermal and optical properties of L-DICY cured epoxy resins and hygrothermal performance of L-DICY cured epoxy based prepregs were evaluated to compare with those of DICY and PEA/DICY blends. Amine hydrogen equivalent weight of L-DICY was increased with inferior reactivity to PEA/DICY. The solubility of PEA/DICY and L-DICY in epoxy resin was increased due to good dissolving ability of PEA and PEA/DGEBA adduct. The dispersibility of PEA/DICY and L-DICY in epoxy resins was improved, while dispersion stability of L-DICY was superior to that of PEA/DICY. The mechanical and thermal properties of three kinds of resin matrix changed little, while transparency of L-DICY cured resin films was higher than those of DICY and PEA/DICY. The surface qualities and hygrothermal properties of epoxy based prepreg composites were improved notably, which was attributed to DICY crystal reduction in cured resin films resulted from enhanced solubility and dispersibility of L-DICY.

1. Introduction

Carbon fiber/epoxy prepregs as the intermediate-product of composites were widely used in large-scale components such as aerospace and automotive parts, which were mainly based on carbon fiber fabric impregnated by B-staged epoxy matrix [1–3]. Hot-melt impregnation was the prevalent method to prepare epoxy based prepregs, which consisted of applying a uniform resin film to a release paper and further impregnating the fiber bed by the upper and lower resin film with hot-pressing [4,5]. Therefore, the uniformity of surface appearance and curing behavior of resin films were one of the key indexes for prepreg quality control, which was dependent on the homogeneity of resin matrix made up of epoxy resin and curing system [6–8]. Dicyandiamide (DICY) was the most commonly used latent curing agent in intermediate temperature curing prepreg system [9,10]. However, the poor solubility of DICY in non-polar epoxy resin resulted in the tendency to separate and form a white precipitate on prepreg surface [7,11], and the sedimentation of DICY crystals would affect the degree of crosslinking as well as the hygrothermal properties of DICY cured composites [12,13]. Generally, the chemical modification by molecular design or physical dissolving by liquid curing agent was a feasible way to improve the solubility and compatibility between DICY and epoxy resin.

The reactivity and compatibility between epoxy resin and DICY chemically modified by aromatic or aliphatic amine have been much improved [14,15], but the higher reactivity led to the reduction of out time and shelf life of prepregs. DICY solution was obtained by dissolving it in a liquid multifunctional amine such as aliphatic amine [16], which possessed good dissolving ability and compatibility with epoxy resin. The solution could prevent crystal separation taking place during the impregnation of fiber fabrics and curing process of the impregnated prepregs. However, the combination of DICY and liquid aliphatic amine also increased the curing rate of resin mixture due to the high reactivity of aliphatic amine. In view of the high volatility and reactivity of aliphatic amine with low molecular weight, the aliphatic amine adducts of increased molecular chain have been developed by addition reaction between aliphatic amine and epoxide compound [17,18], which led to reduced reactivity, improved handling safety and surface appearance of epoxy resin films. Also, the soluble aliphatic amine adducts with amphiphilic structure could promote the solubility of DICY in epoxy resin, which was due to the favorable solvent environment (i.e., higher dielectric constant, hydrogen bonding) [19].

Therefore, to obtain well-balanced solubility and curing rate of modified DICY in epoxy resins, the adducts of polyetheramine (PEA) and diglycidyl ether of bisphenol A (DGEBA) were synthesized for preparing the liquefied DICY (L-DICY), and the reactivity and solubility of L-DICY

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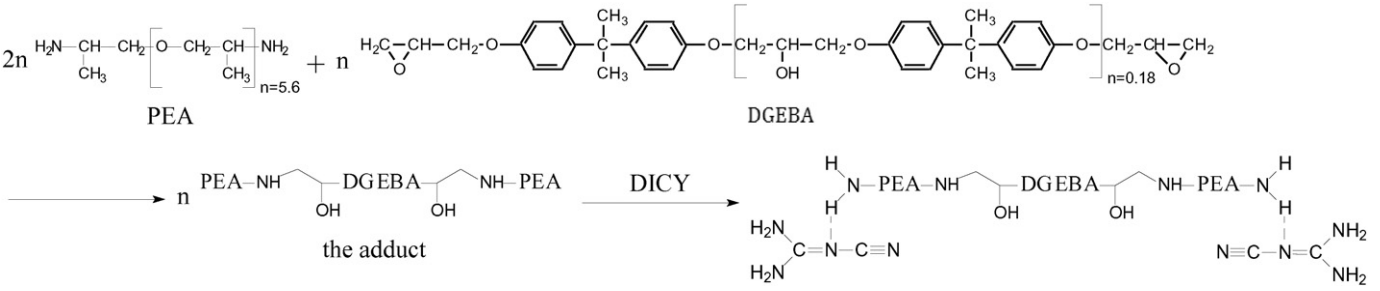

Fig. 1. The schematic of preparation procedure of liquefied DICY (L-DICY).

were studied in comparison of pure DICY and the blend of PEA/DICY. The storage stability and dispersibility of L-DICY in epoxy resins were investigated, and the schematic dispersion models of DICY, PEA/DICY and L-DICY were proposed. The mechanical and thermal properties of L-DICY cured epoxy resins, surface transparency of cured resin films and hygrothermal properties of epoxy based prepreg composites were also discussed.

2. Experimental

2.1. Materials

Diglycidyl ether of bisphenol A (DGEBA, NPES-128, NPES-901) was supplied from Nanya Epoxy Resin Co., Ltd. Dicyandiamide (DICY, Dyhard 100S, Degussa) and polyetheramine (PEA, D400, Huntsman) were used in this paper. 2-Methyl Imidazole (2-MZ) was purchased from Beijing Reagent Co., Ltd. Carbon fiber fabric (T300-3K, plain weave, areal density: 200 g/m^2) was kindly provided by Jiangsu Tianniao high and new technique Co. Ltd.

2.2. Preparation of liquefied DICY (L-DICY)

To improve the compatibility between DICY and epoxy resin, the liquefied DICY (L-DICY) was prepared through two steps. Fig. 1 shows the schematic of preparation procedure of PEA/DGEBA adduct. The reaction of diglycidyl ether of bisphenol A and polyetheramine was performed for 2 h at 80 °C, in which the mole ratio of epoxide to amide (N—H) was 1:2. Then DICY was added into the above adduct and stirred for 4 h at 80 °C. In comparison, the blend of PEA/DICY with the same mole ratio was obtained by partially dissolving DICY in PEA under stirring for 1 h at 80 °C.

2.3. Preparation of resin matrix and carbon fiber prepreg

Three kinds of resin matrix were prepared by mixing DICY, PEA/DICY and L-DICY into 100 g DGEBA (60 g NPES-128 + 40 g NPES-901) at 70 °C under mechanical stirring, respectively, in which the usage of DICY was fixed at 6 g. In addition, 2-MZ (0.2 g) was added into each resin matrix as an accelerator.

The resin films (areal density: 82 g/m^2) of three kinds of resin matrix were applied to a release paper with a reverse roller coater at 73 ± 2 °C. Carbon fiber fabric were placed between the upper and lower resin films and further impregnated at 105 °C to fabricate carbon fiber prepreg (areal density: 364 g/m^2).

2.4. Characterization

According to ISO 9702:1999, the total amine group nitrogen content (X_T) was determined by potentiometric titration against hydrobromic or perchloric acid in glacial acetic acid [20]. The primary amine groups were reacted with a measured excess of salicylaldehyde to form H_2O, and the primary amine group nitrogen content (X_{L1}) was calculated from the generated mass of H_2O. The amine hydrogen (N—H) equivalent weight (AHEW) can be calculated as follows:

$$\mathrm{AHEW} = \frac{14}{X_T + X_{L1}}.$$

Fourier transform infra-red spectroscopy of PEA and PEA/DGEBA adduct was performed on Nexus 5700 FT-IR spectrophotometer (Nicolet Instruments, USA), which recorded the wavenumber from 4000 to 400 cm^{-1}. X-ray diffraction patterns of DICY, PEA/DICY and L-DICY were collected using a wide angle X-ray diffractometer (XRD, Rigaku D/max 2500 VB2 +/PC) operating at 40 kV and 200 mA with Cu Ka radiation. The melting point and fusion enthalpy of DICY, PEA/DICY and L-DICY were measured by differential scanning calorimeter (DSC-7, Perkin Elmer) at 10 °C/min heating rate under nitrogen flow of 20 ml/min.

Three kinds of resin matrix were cured at 90 °C/0.5 h + 120 °C/2 h。 The tensile and flexural properties were measured by tensile testing machine (Instron 1121), according to GB 2568 and GB 2570, respectively. Dynamic mechanical thermal analysis was performed by three-point bending mode (DMTA-*V*, Rheometrics Scientific Co. USA). The heating rate was 10 °C/min from 50 °C to 250 °C, and the fixed frequency was 1 Hz. The T_g was measured from the peak of the tanδ spectrum. The transparency of the completely cured resin films were measured with an UV/VIS/NIR spectrometer.

12 plies of carbon fiber prepregs (80 mm × 80 mm size) were stacked on the laboratory-made mold, and cured with flat-plate vulcanizer at 90 °C/0.5 h + 120 °C/2 h at 8 MPa molding pressure. Interlaminar shear strength (ILSS) and flexural properties were measured by three-point bending test with 2 mm/min crosshead speed using tensile

Table 1
Total amine group nitrogen content (X_T), primary amine group nitrogen content (X_{L1}) and amine hydrogen equivalent weight (AHEW) of DICY, PEA/DICY and L-DICY.

	DICY		PEA/DICY		L-DICY	
	Theoretical value	Measured value	Theoretical value	Measured value	Theoretical value	Measured value
X_T/%	50.2	51.2	28.5	29.4	19.7	20.2
X_{L1}/%	16.7	17.1	11.8	12.2	7.1	7.3
AHEW/g/eq	21.0	20.3	34.7	34.1	52.1	51.8