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Physicochemical and mechanical interfacial properties of trifluorometryl groups containing epoxy resin cured with amine

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Abstract

A phenyl-trifluoromethyl (-Ph-CF_3) groups modified epoxy resin, diglycidylether of bisphenol A-fluorine (DGEBA-F), was synthesized and the physical properties, such as curing behaviors, thermal stabilities, and dielectric constant of the DGEBA-F/4,4′-diaminodiphenyl methane (DDM) system were investigated and compared with commercial DGEBA/DDM system. For the mechanical behaviors of the specimens, the fracture toughness and impact tests were performed, and their fractured surfaces were examined by using a scanning electron microscope (SEM). The dielectric constant values of the DGEBA-F/DDM system were lower than those of the DGEBA/DDM system and the mechanical properties of the casting DGEBA-F specimens were higher than those of the DGEBA specimens. This was probably due to the fact that the introduction of the -Ph-CF_3 groups into the side chain of the epoxy resin resulted in improving the electrical properties and toughness of the cured DGEBA-F epoxy resin.
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Keywords: Synthesis; Activation energy; Thermal properties; Dielectric properties; Fracture toughness

1. Introduction

Epoxy resins of diglycidyl ether of bisphenol A (DGEBA) are one of the most important classes of thermosetting polymers with outstanding properties, including good heat resistance, high modulus, good heat resistance, and high electrical resistance. They are widely used in matrices for composite materials, coatings, structural adhesives, and microelectronics [1]. However, highly cross-linked DGEBA epoxy resins show low impact and fracture toughness. Hence many attempts have been made to modify the epoxy resins. The modification of epoxy resins has two pathways, one is the blending with toughening agents, such as reactive rubber, other thermosetting resins, and thermoplastics, and another is the synthesis of new epoxy resins. Use of toughening agents, including epoxidized natural rubber, sulfone-containing epoxy resins, poly(sulfone), poly(ether sulfone imide), and poly(ether imide) has been recently reported [2–6]. Newly synthesized epoxy resins, such as siloxane-incorporating epoxy copolymers, thiodiphenol modified epoxy resins, phosphate modified epoxy copolymers, and poly(vinyl methyl ether) modified epoxy resins have been explored and the properties of the epoxy resins, including thermal stabilities, electrical, and mechanical properties have been investigated [7–10].

The carbon–fluorine bond is one of the strongest organic bonds. The introduction of phenyl-trifluoromethyl (-Ph-CF_3) groups into polymers improves chemical resistance, surface, electrical, mechanical, and optical properties of the polymers compared to the nonfluorinated materials [11,12]. Therefore it is of interest to incorporate -Ph-CF_3 groups into the chain of epoxy resins and to study the physical properties of the resultant epoxy resins.

In this work, the -Ph-CF_3 groups modified epoxy resin, diglycidylether of bisphenol A-fluorine (DGEBA-F), is synthesized and the effect of the -Ph-CF_3 groups on the curing behaviors, thermal, electrical and mechanical properties of the

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diglycidylether of bisphenol A-fluorine (DGEBA-F)/DDM system is discussed as determined by differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), thermogravimetric analysis (TGA), dielectric spectrometry, a united test machine (UTM), impact tester and scanning electron microscope (SEM).

2. Experimental

2.1. Materials

Epoxy resin used in this study was diglycidylether of bisphenol-A (DGEBA) supplied by Kukdo Chem. of Korea (YD-128), which had an epoxide equivalent weight of 185–190 g eq^{-1} and a density of about 1.16 g cm^{-3} at 25 °C. Tetraisopropyl titanate (TPT) and 4-chlorobenzotrifluoride (CBTF) were purchased from Jin Chem. of Korea and Aldrich Chem., respectively. The curing agent was diaminodiphenyl methane (DDM) and was purchased from Aldrich Chem. These materials were used as supplied without further purification. DGEBA-F epoxy resin was synthesized throughout the recent work. The chemical structures of DGEBA, DGEBA-F, and DDM are shown in Fig. 1.

2.2. Synthesis of DGEBA-F epoxy resin

The -Ph-CF_3 groups modified DGEBA-F epoxy resin was synthesized with a hot-melt condensation method and the procedure of the synthesis was as follows [7]:

DGEBA (152.3 g, 0.2 mol), 4-chlorobenzotrifluoride (17.1 g, 0.1 mol) and tetraisopropyl titanate (0.4 g) were placed in a 500 ml four-neck round flask equipped with mechanical stirrer, thermometer and reflux condenser. The mixtures were heated and reacted at 110 °C for 2 h. After the reaction was completed, the crude product was washed with distilled water repeatedly and dissolved in chloroform. Then

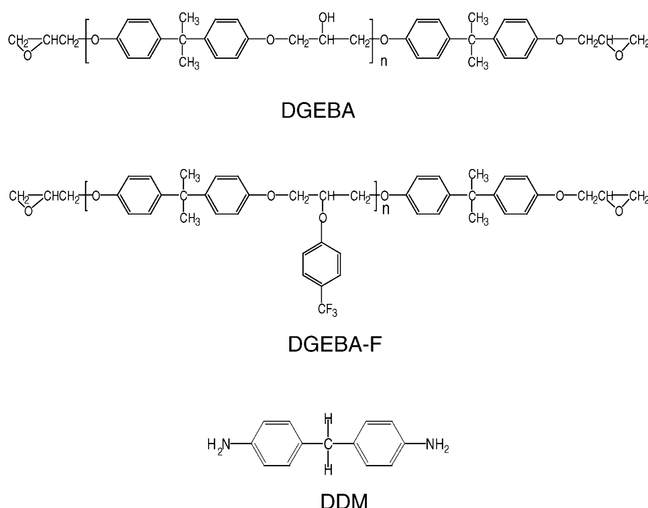

Fig. 1. Chemical structures of the materials used.

the chloroform and unreacted reactant were distilled off at 138 °C. Finally, the product was dried in a vacuum oven at 110 °C for 8 h. The yield of the obtained DGEBA-F epoxy resin was 84%. The epoxy equivalent weight was 212 g/eq.

IR (KBr): 1110 cm^{-1} (CF_3 group), 1387 cm^{-1} ($(CH_3)_2C$ group), 833, 914 cm^{-1} (epoxide group).

^{13}C NMR (chloroform-d): δ = 42.1, 31.3 ppm ($(CH_3)_2C$ group), 128.4 ppm (CF_3 group), 69.9, 50.5, 44.3 ppm (epoxide group), 157.4, 144.1, 114.6 ppm (aromatic ring).

^{19}F NMR (chloroform-d): $\delta = -62.0$ ppm (CF_3 group).

2.3. Sample preparation

The epoxy resin (DGEBA-F or DGEBA) were mixed with stoichiometric amount of curing agent (DDM). The epoxy resin was melted in an oil bath at 100 °C for 1 h and then the DDM was added to the resins. The mixtures were stirred by a mechanical stirrer and degassed in a vacuum oven to eliminate air bubbles before measuring. The preparation of the specimens for the electrical and mechanical tests was as follows: bubble-free mixtures were poured into the mold and cured at 110 °C for 1 h, at 140 °C for 2 h, and at 170 °C for 1 h in a convection oven.

2.4. Characterization and measurements

The structure of the epoxy resin was characterized by FT-IR, ^{13}C NMR, and ^{19}F NMR spectroscopy. IR spectrum was recorded with a Bio-Rad Co. digilab FTS-165 spectrometer by using KBr pellets. ^{13}C NMR and ^{19}F NMR spectra were determined on a BRUKER Co. DRX300 spectrometer operated at 300 MHz in chloroform-d. The epoxy equivalent weight was determined by the pyridinium chloride method described in the literature [13].

The cure behaviors of the DGEBA-F/DDM and DGEBA/DDM systems were determined with a dynamic differential scanning calorimeter (Perkin Elmer, DSC6) under the nitrogen flow of 30 ml/min.

The temperature dependence of the storage modulus (E') and the loss factor ($\tan\delta$) for the DGEBA-F/DDM and DGEBA/DDM systems were measured using a dynamic mechanical analyzer (RDS-II, Rheometrics Co.) at a frequency of 1 Hz and over a temperature range from 35 to 250 °C at a heating rate of 5 °C/min. The sample size was approximately 3 mm × 12 mm × 60 mm.

Thermogravimetric analysis was performed with a Du Pont TGA-2950 analyzer to investigate the thermal stabilities of the cured DGEBA-F/DDM and DGEBA/DDM systems from 30 to 850 °C at a heating rate of 10 °C/min in a nitrogen atmosphere.

The dielectric constant of the DGEBA-F/DDM and DGEBA/DDM systems was measured over a frequency range from 1 to 10 GHz at room temperature using a dielectric spectrometer (Novocontrol GmbH, Model: CONCEPT 40).

The fracture toughness parameters, critical stress intensity factor (K_{IC}) and specific fracture energy (G_{IC}) of the

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