



Characteristic correlation between liquid crystalline epoxy and alumina filler on thermal conducting properties



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ABSTRACT

As a promising matrix for developing efficient heat-dissipating materials, liquid crystalline epoxy resins (LCERs) have received much attention for a decade. Here, we present a comprehensive study including the synthesis, fabrication, and characterization of polymer/inorganic composites with a representative LCER, 4,4'-diglycidylxybiphenyl (BP) epoxy. The thermal conducting properties of composites are systematically investigated by preparing a series of samples with various epoxy resins and alumina fillers. Notably, liquid crystalline BP composites show approximately 30% higher thermal conductivity compared to the composites of commercial epoxy with the same type of filler owing to the highly aligned microstructure of the LCER. In addition, the threshold loading of filler content required to construct an effective thermally conducting path in our system is in the range of 40–50 wt%. Furthermore, the thermal conductivity of BP composites can be controlled by incorporating various fillers differentiated by size and shape. In particular, the highest thermal conductivity among the BP composites with 80 wt% content of alumina is 6.66 W/m·K, which is significantly high for epoxy/alumina composites. The experimental results which agree well with the theory by Agari model reveal that the highly aligned microstructure of the LCER is essential requirement that should be considered to improve thermal conductivity of composites.

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1. Introduction

Recently, increasing demands for light-weight, thinner, and multi-functional electronic devices in our daily life have been accelerating the development of highly integrated circuits generating significant heat during operation [1,2,3]. The accumulated heat energy in the circuit causes problems in operation such as deterioration in the device performance as well as malfunction and a decrease in durability. Therefore, the development of more efficient heat dissipating materials has been a critical issue [4,5,6]. To alleviate the problem, many studies on developing thermally conductive and electrically insulating materials have been

proposed [7,8]. The compounding of organic polymers and thermally conducting fillers such as carbon material and ceramics has been considered as a promising solution [9–12]. Although the thermal conductivity of polymeric resins can be improved significantly by addition of fillers, some important physical properties of composites such as processability and mechanical strength (durability) are significantly diminished by the use of fillers with high concentration [13,14]. To address the problems caused by high filler concentration, new approaches such as synthesis of thermally conducting resins [15,16], processing commercial polymers to have a thermally conductive state [17,18], and orienting inorganic fillers within composites [19,20], have been reported and, developing heat-dissipating materials with low filler loading has been a development trend in field of materials sciences [21,22].

Liquid crystalline polymers (LCPs) have been spotlighted as a promising matrix for heat-dissipating materials because LCPs have a highly oriented microstructure, which enables efficient heat

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transfer through phonon vibration [23,24]. In this regard, several types of liquid crystalline polymers including epoxy [25], acrylate [26], and maleimide [27] have been reported. In composite industry, epoxy resins have been widely used for fabrication of thermally conducting composites due to their good adhesive strength through strong interfacial interaction with inorganic fillers as well as superior physical and chemical properties [28,29]. However, because their intrinsic thermal conductivity is low ($<0.3 \text{ W/m}\cdot\text{K}$), some attempts to apply the liquid crystal moiety to epoxy resins have been reported as a method for improving thermal conductivity [30]. For example, the Harada and Ochi group synthesized a series of liquid crystalline epoxy resins (LCERs) using terphenyl [31], methyl stilbene [32], and terephthalylidene [33] as a mesogen core. In the case of terephthalylidene-type LCER (DGE-TAM/DDM system), the values of thermal conductivity were $0.43 \text{ W/m}\cdot\text{K}$ in the isotropic and $0.89 \text{ W/m}\cdot\text{K}$ in the aligned direction (cured in a magnetic field) [34]. In this regard, LCERs exhibit significantly higher thermal conductivity compared to common epoxy resin. However, the complexity in synthesis and expensive starting materials of the above-mentioned LCERs needs to be improved for commercialization. In addition, only few systems related to composites prepared with LCERs have been investigated. Specifically, the studies on composites using alumina which is the most generally used thermal conductive filler have been limited.

In this study, we designed a composites system using LCER as a matrix, which is easy to synthesize, and commonly available alumina as a filler. The LCER, oligomeric 4,4'-diglycidyloxybiphenyl (BP), was synthesized from 4,4'-biphenol and epichlorohydrin as starting materials via a one-step reaction. Composites of LCER and alumina filler were prepared through a solvent-free dry process using 4,4'-diaminodiphenylsulfone (DDS) as a hardener. The effects of crystal order of LCER and characteristics of the filler such as size and shape on thermal conductivity were correlated via both systematic investigation of thermal properties of composites and theoretical study. To our knowledge, this is the first scientific report that identifies the relationship and interaction between LCER and filler moieties with respect to heat conduction.

2. Experimental section

2.1. Materials

4,4'-Biphenol and benzyltrimethylammonium bromide were purchased from Wako Chemical (Japan) and Sigma-Aldrich (USA), respectively. In addition, epichlorohydrin and common reagents were obtained from Daejung (Korea). 4,4'-Diglycidyloxybiphenyl (BP) epoxy was synthesized in our laboratory and the detailed synthetic procedure and characterization were described in supporting information. 4,4'-Diglycidyloxy-3,3',5,5'-tetramethylbiphenyl (TMBP) was purchased from Shin-A T&C (Korea). Commercial epoxy resin and curing reagent, diglycidyl ether of bisphenol-A (DGEBA) and 4,4'-diaminodiphenylsulfone (DDS), were received from Kukdo Chemical (Korea). The values of epoxy equivalent weight (EEW) of TMBP and DGEBA were 183.8 g/eq and 187 g/eq , respectively. Chemical structures of the resins were shown in Fig. 1. In addition, three types of alumina; first one is irregular shape and $45 \mu\text{m}$ size ($\text{Al}_{45,\text{ir}}$), second is spherical shape and $45 \mu\text{m}$ size ($\text{Al}_{45,\text{sp}}$), and last is spherical shape and $70 \mu\text{m}$ size ($\text{Al}_{70,\text{sp}}$), were purchased from Sigma-Aldrich (USA), Denka (Japan), and Denka (Japan), respectively.

2.2. Preparation of epoxy composites

Powder type epoxy composites (BP and TMBP) were prepared by following method. First, the mixture of epoxy resin, curing

agent, and alumina was grinded by Lab Mill with $100 \mu\text{m}$ sieve. Second, the mixture of the obtained fine powder was mixed by thinky mixer. Finally, after the mixture was inserted in a SUS mold, cured for 2 h by hot press under 20 MPa pressure. The curing temperatures are varied; for BP at $170 \text{ }^\circ\text{C}$, for TMBP at $190 \text{ }^\circ\text{C}$, and for DGEBA at $190 \text{ }^\circ\text{C}$. In addition, DGEBA samples were fabricated without crushing procedure by the Lab Mill because DGEBA is a liquid type resin at room temperature. A typical procedure for making BP epoxy composite with alumina of 10 wt% was demonstrated as follows. The mixture of BP epoxy (30.0 g), DDS (9.80 g), and alumina (4.42 g) was pulverized and mixed by Lab Mill. In addition, after the mixture was blended by planetary centrifugal mixer, the specimen was cured in a circular SUS mold (inner 20 mm) at $170 \text{ }^\circ\text{C}$ for 2 h. After cooled to room temperature, the cured epoxy composite was obtained.

2.3. Characterization

^1H NMR spectra were measured with a 600 MHz Premium COMPACT NMR spectrometer (Agilent, USA). In addition, ^1H NMR spectra were obtained by using tetramethylsilane (TMS) as an internal standard and $\text{DMSO-}d_6$ as a solvent. The molecular weights of epoxy resins were measured by a high temperature gel permeation chromatography (HT-GPC) PL-220 (Agilent, USA) at $80 \text{ }^\circ\text{C}$ in dimethylformamide with 0.05 wt% LiBr as an eluent. Thermogravimetric analysis (TGA) was carried out with a Q50 (TA Instruments, USA) under nitrogen gas flow at a heating rate of $10 \text{ }^\circ\text{C}/\text{min}$. Glass transition temperatures (T_g), liquid crystalline behaviors, and curing studies of epoxy resins were observed by a differential scanning calorimetry (DSC) Auto-Q20 (TA Instruments, USA) under nitrogen gas flow at a heating rate of 10 or $20 \text{ }^\circ\text{C}/\text{min}$. Dynamic mechanical analyses (DMA) were evaluated from rectangular samples (40 mm length, 10 mm wide, and 4 mm thickness) on a DMA (TA Instruments, DMA Q800, USA) at a heating rate of $3 \text{ }^\circ\text{C}/\text{min}$ with a load frequency of 1 Hz in air by using cantilever clamp. Microscope observation was carried out under crossed nicols by using a Carl Zeiss AXIO IMAGER MIM polarizing optical microscope

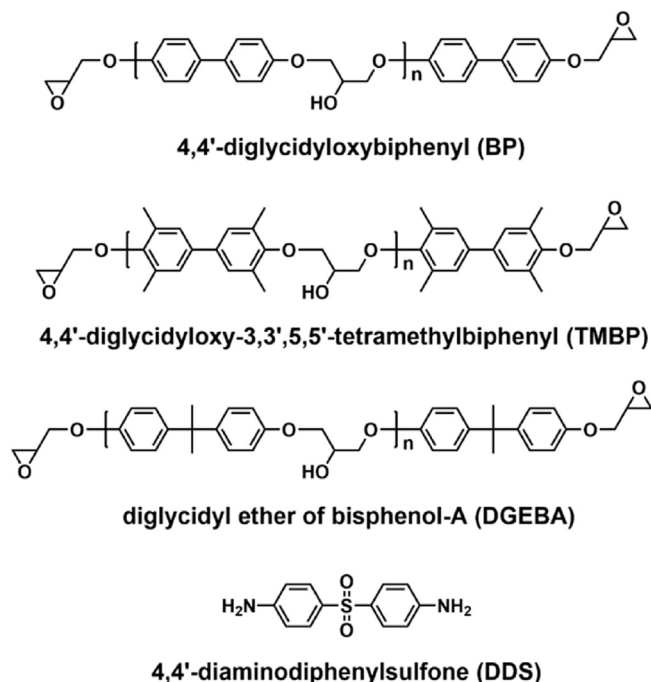


Fig. 1. Chemical structures of epoxy resins.

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