Study of High Thermal Conductive Epoxy Resins Containing Controlled High-Order Structures

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ABSTRACT: Heat is transported by phonons through dielectric solids such as ceramics and organic insulating resins. Especially in organic insulating resins, phonons scatter intensely mainly by their amorphous structure, which affects their thermal conductivities, usually 1 to 3 orders lower than those of ceramics and metals. Here, we show that by the thermosetting resin system with a crystal-like structure that is microscopic anisotropy, the thermal conductivities of the resin themselves can be improved while keeping their macroscopic isotropy. We studied four kinds of diepoxy monomers with a biphenyl group or two phenyl benzoate groups as mesogens, and cured them thermally with an aromatic diamine curing agent. These thermal conductivities were maximally 5 times higher than that of conventional epoxy resins because mesogens were highly ordered to form crystal-like structures to suppress phonon scattering. We also succeeded in the direct confirmation of the existence of crystal-like structures in the epoxy resins by TEM observation. These results suggest a novel strategy to improve thermal conductivities of insulating resins themselves by controlling the high-order structures. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 2464–2467, 2003

Key words: resins; liquid-crystalline polymers; microstructure; thermal properties; TEM

INTRODUCTION

Both electric and electronic apparatuses have recently been improved in size and performance with increasing quantity of heat from the internal conductor and have been designed to diffuse the heat efficiently. Although the thermosets are mainly used for insulating materials with thermal resistance, they have quite low thermal conductivities, usually 1 to 3 orders lower than those of ceramics and metals, that substantially prevent the heat from diffusing. A technical key point of the apparatus should be to use insulating materials that have higher thermal conductivities. One generally known approach is used to apply composites of thermosets with inorganic ceramic powders having high thermal conductivities, which is effective for heat diffusion to some degree, although it usually affects working, molding, and processing given their high elastic moduli and low flexibilities. A recent study showed that ceramic powder might also affect the curing reaction of the resin,[1] which would create additional problems that would need to be addressed.

One solution would be to improve the thermal conductivities of the insulating resins themselves, which would afford composites with higher thermal conductivity with equal amounts of ceramic powder and composites with lower thermal conductivity with lesser amounts of ceramic powder. Heat conduction in insulating resins is discussed in terms of the Debye equation:

$$\lambda = (1/3)c_v u l$$

where λ is the thermal conductivity, c_v is the volumetric heat capacity, u is the sound velocity, and l is the mean free path of a phonon. Although c_v is mainly determined by the character of the resin such as density, the l is determined by the crystallinity and orientation direction of the resin, that is, the degree of phonon scattering.[2] Phonon scattering occurs by such phenomena as the anharmonicity of molecular and lattice vibrations, boundary surface, and defects in the resin. Heat is transported rapidly through the molecular chain direction if the resin is ordered. There are some studies of the thermal conductivity of anisotropically oriented polyethylene,[2,3] and of the model calculation of the thermal conductivity.[4,5] Crosslinked anisotropic polymers of oriented liquid crystalline diacrylates initiated with a photoinitiator were also studied.[6] In these studies, thermal conductivity properties were also anisotropic and the values of thermal conductivities through the molecular chain direction could be much higher than those of the perpendicular direction. However, the thermal conductivities of the anisotropic resin through the perpendicular direction of oriented molecular chains were nearly equal to or lower than those of the corresponding isotropic ones.

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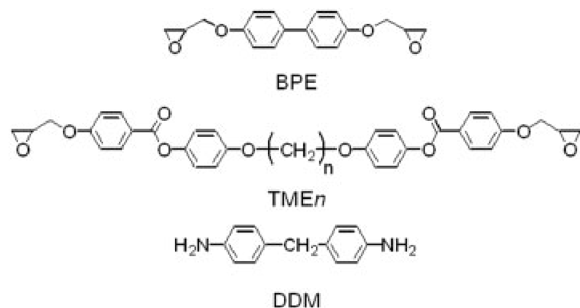

Figure 1 Structures of diepoxy monomers, BPE and TME*n* (*n* = 4, 6, 8), and a diamine curing agent, DDM. The *n* of TME*n* represents the number of $–CH_2$ – groups connecting two phenyl benzoate groups.

The purpose of this study was to suggest a novel strategy to improve the thermal conductivity of isotropic resins themselves by controlling and verifying the high-order structure.

EXPERIMENTAL

Materials

4,4′-Biphenol diglycidyl ether (BPE) was obtained by fractional recrystallization from the mixture of BPE and 3,3′,5,5′-tetramethyl-4,4′-biphenol diglycidyl ether obtained from Japan Epoxy Resins Co. Diepoxy monomers with two phenyl benzoate units (TME*n*) were synthesized on the basis of the method described in a previous study.[7] These diepoxy monomers had a purity $>$ 94%, as determined by chromatography. 4,4′-Diaminodiphenylmethane (DDM; Wako Pure Chemicals, Osaka, Japan) was used as a curing agent without further purification. These structures are illustrated in Figure 1.

Curing reaction

Epoxy resin plates were made by curing the mixture of the diepoxy monomer and stoichiometric DDM at 175°C for 4 h in an oven without any treatment. These epoxy resin plates were cut and polished suitably for evaluating the properties of the resins.

Measurement

Thermal conductivities of epoxy resins were calculated by multiplying the corresponding thermal diffusivity and volumetric heat capacity. Thermal diffusivities and volumetric heat capacities were evaluated by the method based on the ac calorimetric method,[8–11] where the thickness of the specimen was approximately 0.2 mm, the frequency was 0.2 Hz, and the temperature was approximately 30°C. Although these thermal diffusivities and thermal conductivities were the values determined in the lattice direction, they may be considered to represent the thermal conductivity in all directions because the epoxy resin plates were made without any treatment with respect to macroscopic isotropy. Structure analyses of the epoxy resins were carried out by polarizing optical microscope observations (Nikon Optiphot-II-Pol, Tokyo, Japan) or transmission electron microscope (Hitachi TEM model H-7600, Japan). In TEM observations, the samples were prepared by 0.5% RuO_4 vapor absorption after being cut by microtome to an approximately 50 nm thickness and observed under an acceleration voltage of 100 kV.

RESULTS AND DISCUSSION

Synthesis and evaluation of controlled high-order structure of epoxy resins

Figure 2 shows the schematic representation of the high-order structure of the resin to afford macroscopic isotropy and high thermal conductivity. The resin was characterized by the three following features: (1) in the resin there are microscopic anisotropic crystal-like structures by oriented mesogens in diepoxy monomers; (2) the macroscopic isotropy of the resin is achieved by disordering the domains of the crystal-like structure; and (3) the crystal-like structure is linked with the internal amorphous structure by covalent bonds that allow an indistinct boundary between them. This high-order structure would suppress phonon scattering, thus affording high thermal conductivity of the resin. The resin has an amorphous region that, on the one hand, is disadvantageous for improving thermal conductivity, but on the other hand is advantageous for favoring good working, good molding, and processing conditions, and high flexibilities that are desirable and important properties of the resins for manufacturing use.

For this purpose, we selected liquid crystalline epoxy resin systems and prepared four diepoxy monomers and a diamine curing agent, as shown in Figure

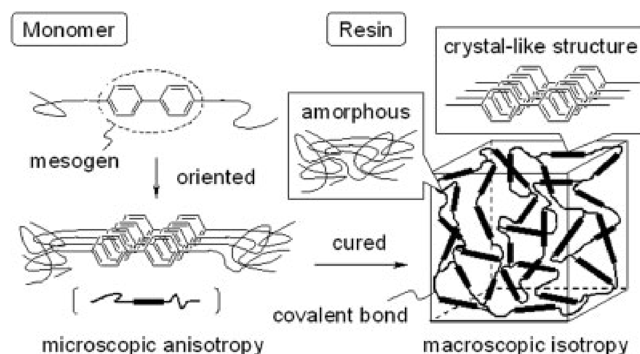

Figure 2 Schematic representation of the strategy to afford macroscopic isotropic resin having high thermal conductivity.

TABLE I
Thermal Conductivity of Studied and Conventional Resins

Run	Resin	Thermal conductivity ($W\ m^{-1}\ K^{-1}$)
1	BPE/DDM	0.30
2	TME8/DDM	0.85
3	TME6/DDM	0.89
4	TME4/DDM	0.96
5[a]	EP[b]	0.17–0.21
6[a]	HDPE[c]	0.46–0.51

[a] Value of conventional resin in ref. 16.
[b] Epoxy resin.
[c] High-density polyethylene.

1. The monomer BPE has a biphenyl group that is the smallest of all mesogens generally known. When cured with diamine or catechol Novolac as the curing agent, the epoxy resins are known to have no distinct glass-transition temperatures and very high tensile moduli in the rubbery region because the micro-Brownian motion is highly suppressed by the microstructure into which biphenyl groups formed.[12–15] A series of TME*n* (n = 4, 6, 8, where n is the number of $-CH_2-$ groups in the spacer) were the glycidyl ether type diepoxy monomer containing two mesogens of phenyl benzoate group connected by an alkylene spacer. TME8 is known to form a smecticlike structure when cured with diamine curing agents because of the flexible aliphatic chain.[7] These monomers were crystalline at room temperature and have high melting points of 155–180°C. The TME*n* series were characterized by the range of a nematic phase over the melting temperature. DDM was selected for a curing agent.

We first investigated the epoxy resins of BPE cured with DDM to confirm our strategy. The epoxy resin was light yellow and transparent, which usually means that the resin is homogeneous and amorphous. However, the epoxy resin showed an interference fringe-like Schlieren texture observed by polarizing optical microscopy under a crossed nicol situation, compared to the absence of texture observed for conventional bisphenol-A type epoxy resins. This result meant that the epoxy resins contained a crystal-like structure of highly oriented biphenyl groups, giving rise to birefringence. The thermal conductivities of the epoxy resins of BPE/DDM systems were 0.30 $W\ m^{-1}\ K^{-1}$ (Table I, run 1) that were approximately 1.5 times higher than those of conventional epoxy resins of 0.17–0.21 $W\ m^{-1}\ K^{-1}$ (Table I, run 5).[16] This result implied that the crystal-like structure by oriented biphenyl groups would have the effect of suppressing phonon scattering, following our strategy to improve the thermal conductivity.

Next, we investigated diepoxy monomers consisting of two larger mesogens, a series of TME*n*. The epoxy resins cured with DDM were all yellowish milky white and opaque, which meant the existence of large domains with a refractive index different from that of the matrix. In this case, the existence of large domains of smecticlike structures that would effectively suppress phonon scattering would be expected. The thermal conductivities of the epoxy resins of TME8/DDM, TME6/DDM, and TME4/DDM systems were 0.85, 0.89, and 0.96 $W\ m^{-1}\ K^{-1}$ (Table I, runs 2–4), respectively, that were 4.5–5.0 times higher than those of conventional epoxy resins of 0.17–0.21 $W\ m^{-1}\ K^{-1}$ (Table I, run 5) .[16] Furthermore, it was noted that these values were higher than those of conventional high-density polyethylenes of 0.46–0.51 $W\ m^{-1}\ K^{-1}$ (Table I, run 6), known to have the highest thermal conductivities of all the insulating, organic, and macroscopic isotropic compounds.[16] The spacer length of the TME*n* was effective in the thermal conductivities to some degree, given that a shorter spacer length such as TME4 afforded a higher concentration of phenyl benzoate groups that formed the crystal-like structures. From the preceding results, our novel strategy for improving the thermal conductivity of resin by forming the crystal-like structure was proved experimentally, yielding epoxy resins of quite high thermal conductivity.

TEM observation of high-order structure in epoxy resins

We further investigated the structural analyses by TEM, to confirm the existence of crystal-like structures

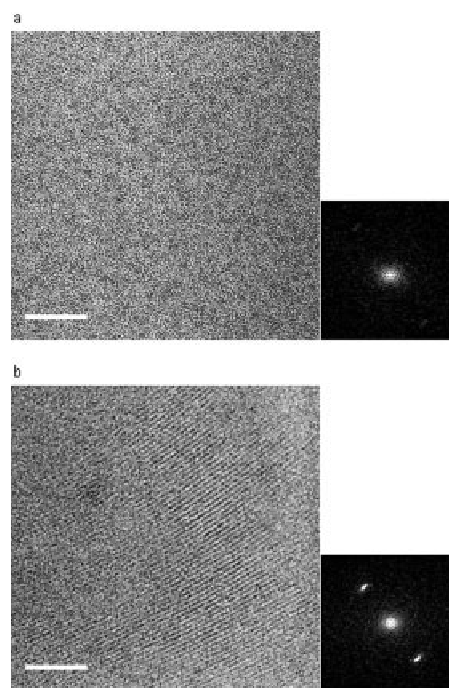

Figure 3 TEM images and Fourier transform of: (a) bisphenol-A type epoxy resin and (b) TME8/DDM. Scale bar = 20 nm.

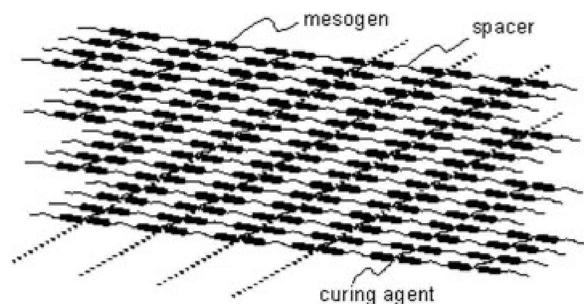

Figure 4 Possible schematic image of microstructure from Figure 3(b). Dotted lines represent the lattice plane of smectic-like structure with the space of approximately 4 nm.

as a proof of our strategy. Figure 3 shows the high-resolution TEM images of a specimen of the conventional bisphenol-A type epoxy resin and TME8/DDM system. Although the bisphenol-A type epoxy resin clearly showed a homogeneous and amorphous structure, the TME8/DDM system showed a lattice image. From the Fourier transform, the lattice was quite regular and directional. The lattice spacing estimated from the high-resolution image was approximately 4 nm, which corresponded to the *d*-spaces of a smectic-like structure estimated by wide-angle X-ray diffraction.[7] From these results, the lattice spacing of Figure 3(b) would correspond to the smecticlike structure formed in the TME8/DDM system, possibly represented by the schematic image of Figure 4. We also confirmed the existence of an intermediate state between the crystal and amorphous states in the TME8/DDM system by the distribution of electron beam diffraction patterns. The above supported our strategy for improving the thermal conductivities of resins themselves by means of controlling the high-order structures.

CONCLUSIONS

We suggested a novel strategy to improve the thermal conductivity of isotropic resins themselves by controlling the high-order structure, which could suppress phonon scattering. It was established that the epoxy resins with the controlled high-order structures had high thermal conductivities to yield the highest value of all isotropic insulating resins. We also directly confirmed crystal-like structures by TEM observation.

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