High Thermal Conductive Resin Composites with Controlled Nanostructures for Electric Devices

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Keywords: thermal conductivity, high-order structure, epoxy resin, mesogen, laminates

We studied four kinds of diepoxy monomers, with or without so-called 'mesogens'- molecular groups that cause self-ordering - and cured them with an amine curing agent, 4,4'-diaminodiphenylmethane (DDM). The monomers are a conventional bis-phenol A type monomer (bis-A type), as a reference material, a 'mono-mesogen' type monomer (MM type), and two kinds of 'twin-mesogen' type monomers (TM-A and TM-B types). Thermal conductivities of cured resins are shown in Table 1. The resins containing mesogens showed higher thermal conductivities. We believe that the mesogens formed nanoscopic high-order structures and the structures formed mezoscopic structures, which were covalently bound together, suppressing phonon scattering. Such resin system is therefore considered to be a kind of polymer-polymer composite with controlled nanostructures. We confirmed the existence of crystal-like structures in the epoxy resins directly by transmission electron microscope (TEM) observation. We also observed mezoscopic structures in the resins with an atomic force microscope (AFM). TEM images of the MM/DDM and TM-B/DDM, and AFM images of the bis-A/DDM, MM/DDM, TM-A/DDM and TM-B/DDM resins are shown in Figure 1. A resin having larger domains of order structures and sharper boundaries between the domains tends to have the higher thermal conductivity. The results suggest a novel method to improve the thermal conductivities of insulating resins themselves by controlling the nanoscopic high-order structures.

Subsequently, laminates were prepared with the developed resin composite consisting of a kind of epoxy resins with mesogens and ceramic fillers, and tested as a part of a feasibility study.

The thermal conductivities of the test pieces were more than 10 times that of commercial FR-4 laminates. This result shows that controlling the nanoscopic high-order structure of the resins is effective in improving the thermal conductivity of resin composites, and the heat dissipation of electric devices as well.

Table 1.  Thermal conductivities of the epoxy resin samples evaluated at room temperature by a method based on the ac calorimetric method

<table>
<thead>
<tr>
<th>No.</th>
<th>Resin system</th>
<th>Monomer</th>
<th>Curing agent</th>
<th>Thermal conductivity [W/mK]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>bis-A type</td>
<td>DDM</td>
<td></td>
<td>0.19</td>
</tr>
<tr>
<td>2</td>
<td>MM type</td>
<td>DDM</td>
<td></td>
<td>0.27</td>
</tr>
<tr>
<td>3</td>
<td>TM-A type</td>
<td>DDM</td>
<td></td>
<td>0.54</td>
</tr>
<tr>
<td>4</td>
<td>TM-B type</td>
<td>DDM</td>
<td></td>
<td>0.85</td>
</tr>
</tbody>
</table>

Fig. 1. AFM images and TEM images of: (a) bis-A/DDM, (b) MM/DDM, (c) TM-A/DDM and (d) TM-B/DDM resin systems. Inset shows possible schematic image of high thermal conductivity in order-structure.
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We studied certain kinds of diepoxy monomers, with so-called 'mesogens'-molecular groups that cause self-ordering - and cured them with appropriate curing agents. Their thermal conductivities were up to 5 times higher than those of conventional epoxy resins. We believe that the mesogens formed nanoscopic high-order structures and the structures formed mesoscopic structures, which were covalently bound together, suppressing phonon scattering. Such resin system is therefore considered to be a kind of polymer-polymer composite with controlled nanostructures. We confirmed the existence of crystal-like structures in the epoxy resins directly by transmission electron microscope (TEM) observation. We also observed mesoscopic structures in the resins with an atomic force microscope (AFM). The results suggest a novel method to improve the thermal conductivities of insulating resins themselves by controlling the nanoscopic high-order structures.

Subsequently, laminates were prepared with the developed resin composite consisting of a kind of epoxy resin with mesogens and ceramic fillers, and tested as a part of a feasibility study. The thermal conductivities of the test pieces were more than 10 times that of commercial FR-4 laminates. This result shows that controlling the nanoscopic high-order structure of the resins is effective in improving the thermal conductivity of resin composites, and the heat dissipation of electric devices as well.

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1. Introduction

The improvement of heat dissipation in electric devices has become a very important issue recently, because operating currents and circuit densities in the devices show a consistent tendency to go up in various electrical systems. Moreover, it is a fact that the low thermal conductivity of insulating resins can be a blocking factor in the improvement of heat dissipation. Ceramic fillers are usually added to make up for such a lack of thermal conductivity. The thermal conductivity of a composite is improved with the increase of filler content and/or increase of thermal conductivity of the actual filler material. However, there is a certain limit to the improvement of heat dissipation by adding fillers, because the amount of filler added is limited by the practical requirements of the fabrication process conditions and of other properties. Therefore we have tuned our attention to the improvement of the thermal conductivities of the resins themselves.

Heat conduction through dielectric solids having no free electrons such as ceramics and organic insulating resins is usually discussed as 'phonon transport'. The thermal conductivities of such insulators are described by the Debye equation:

\[
\lambda = (1/3) c_v u l \quad \text{.......................................................(1)}
\]

where \(\lambda\) 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 characteristics of the resin such as its density, and cannot be changed drastically, \(l\) is determined by the degree of phonon scattering and can vary over a wide range\(^{[3]}\). Organic insulating resins in particular scatter phonons markedly due to the lack of ordering in their amorphous structure, which makes their thermal conductivities usually 1-3 orders lower than those of ceramics and metals. There are some studies on the thermal conductivity of anisotropically oriented polyethylene\(^{(1)(2)}\), and of model calculations of the thermal conductivity\(^{(3)(4)}\). Furthermore, the thermal conductivities and their anisotropy of some kinds of highly cross-linked liquid-crystalline polymers with the macroscopic orientation were also studied\(^{(5)}\). In these studies, thermal conductivity properties were anisotropic and thermal conductivities along the molecular chain direction and/or the macroscopic orientation direction could be much higher than those in the perpendicular direction. These studies tell us that the thermal conductivities of resins can be improved by the macroscopic orientation of molecular chain and the degree of improvement depends on molecular structures, forming conditions, and so on. However, it was not considered that some techniques introducing macroscopic uniform orientation to resins, for example rubbing technique, work well for the purpose of exceeding a limit to the improvement of heat dissipation of...
electrical insulating resins. Because the resins would be used as composites with certain amount of other materials, including ceramic fillers or glass fabrics, and/or a possible direction of the macroscopic orientation would be not necessarily correspond to a required direction of heat dissipation in many cases. Therefore we have been tried to develop resin systems having macroscopic isotropy of thermal, structural and mechanical properties and microscopic high-order structures, which suppress phonon scattering and improve the thermal conductivity.

We previously studied the thermal conductivity properties of certain resin systems consisting of selected liquid crystalline epoxy resins, which contained mesogens -molecular groups that cause self-ordering. In that study, we looked at certain kinds of diepox monomers, either with a biphenyl group or two phenyl benzoate groups as mesogens, and cured them with appropriate curing agents. The former type of monomer could be called a ‘mono-mesogen (MM) type’, and the latter type of monomer could be called a ‘twin-mesogen (TM) type’ after a number of mesogens in each monomer molecule. We found that the thermal conductivities of insulating epoxy resins could be raised by introducing a crystal-like order structure having microscopic anisotropy while maintaining their macroscopic isotropy(5). Thermal conductivities up to 5 times higher than those of conventional epoxy resins were obtained for the resin systems. The schematic representation of our approach to afford macroscopic isotropic resins with high thermal conductivities is shown in Fig. 1.

In this paper, we observed microscopic structures in the epoxy resins directly using a transmission electron microscope (TEM), and also observed mesoscopic structures in the resins using an atomic force microscope (AFM). Subsequently, laminates were prepared with the developed resin composite consisting of a biphenyl type epoxy resin and ceramic fillers, and tested as a part of a feasibility study.

2. Experimental

2.1 Fabrication and Tests of Resin Plates

We used four kinds of diepox monomers to make the resin samples in this study. They are a conventional bis-phenol A type monomer (bis-A type), as a reference material, a mono-mesogen type monomer (MM type), and two kinds of twin-mesogen type monomers (TM-A and TM-B types). Epoxy resin plates were made by curing the mixture of each diepox monomer and the stoichiometric amount of an amine curing agent, 4,4’-diaminodiphenylmethane (DDM), at 175°C for 4 h. Test pieces were obtained by cutting these bulk materials into appropriate sizes for evaluation and observation.

The thermal conductivities of the samples were calculated by multiplying the corresponding thermal diffusivity and volumetric heat capacity together. Thermal diffusivities and volumetric heat capacities at room temperature were evaluated for plate specimens cut from the bulk materials using a thermal diffusivity / conductivity meter based on a light irradiated ac calorimetric technique(8)(9) (SHINKU-RIKO Inc. model PIT-1). The thermal diffusivities parallel to the plate surface were measured by the method, where the thickness of the specimen was 0.1 - 0.2 mm, and the frequency was 0.2 Hz.

Observations of the microscopic structures of the resins were carried out using a transmission electron microscope (Hitachi TEM model H-7600 and H-9000NAR). For TEM observations, the samples were prepared by 0.5%-RuO4 vapor absorption after being cut to approximately 50nm thickness by a microtome and were observed under an acceleration voltage of 100 kV. The mesoscopic structure of the resins was also observed using an atomic force microscope (Seiko Instruments Inc. model SPI3000N/SPA300).

Changes of thermal conductivities after a thermal degradation, at 180-230°C and for up to 1500h, were measured for MM type/DDM resin plates and bis-A type/DDM resin plates. The degradation test was carried out to ascertain the presence or absence of any structure changes, which influence the thermal conductivities, after a thermal degradation. The samples were 5mm thick disks with diameter of 50mm. In the test, the thermal conductivities along through-thickness direction were measured by means of a guarded comparative longitudinal heat flow technique (ASTM E 1225, DYNATEC R/D COMPANY model C-MATIC).

2.2 Fabrication and Tests of Laminates

Laminates were fabricated with a MM type monomer, which is a mixture of biphenyl type epoxy monomers, 4,4’-Biphenol diglycidyl ether and 3,3’,5,5’-tetramethyl-4,4’-biphenol diglycidyl ether (Japan Epoxy Resins Co. Ltd.), and 1,5-diaminonaphthalene (1,5-DAN) as a curing agent, and certain kinds of ceramic fillers. 1,5-DAN was obtained from Nippon Steel Chemical Co., Ltd. Figure 2 shows a schematic drawing of the fabrication process on a laboratory scale. Prepregs were made by dipping glass fabrics into a varnish, a mixture of the above-mentioned materials and a solvent, and then drying them in a drying oven. The prepregs were cut into pieces, stacked between copper foils and then vacuum-pressed at 4MPa and 175°C. For comparison, laminates were also prepared with a conventional epoxy resin using the same process. The thermal conductivities of the laminates were measured by the hot wire method by using a quick thermal conductivity meter (Kyoto Electronics Manufacturing Co., Ltd. model QTM-D3).

We tested responsiveness to heating and cooling for some typical laminate samples using the apparatus shown in Fig. 3 to...
demonstrate the effect of the improvement in thermal conductivity of laminates. Changes of the surface temperatures of the laminates were measured while a Peltier device heated and cooled one structure in the AFM image of the bis-A/DDM system. Many TM-B/DDM resins are shown in Fig. 4. There is no mesoscopic image of the bis-A/DDM, MM/DDM, TM-A/DDM and TM-B/DDM systems. The results of direct observations of the mesoscopic structure of the TM-A/DDM system is considered to be in the intermediate state between the MM/DDM and TM-B/DDM systems. The results of direct observations of the morphologies of the resins are consistent with those of the thermal conductivity measurements. In short, the existence of higher order structures in the resins definitely improves their thermal conductivities and the degrees of the improvement depend on the state of the ordering, more specifically, the sizes, the amounts and the connectivity of domains of the ordered structures. It is considered that the mesogens forms nanoscopic high-order structures and the structures forms mesoscopic structures, which are covalently bound together, suppressing phonon scattering. Such resin system is therefore considered to be a kind of polymer-polymer composite with controlled nanostructures.

3. Results and Discussion

3.1 Observation of Higher Order Structures in Epoxy Resin

The thermal conductivities of the epoxy resin plates measured by the light irradiated ac calorimetric technique are shown in Table 1. The thermal conductivity of the MM/DDM system were 0.27 W/m•K, which was 1.4 times higher than that of conventional epoxy resin, the bis-A/DDM system, which is 0.19 W/m•K. On the other hand, the thermal conductivities of the epoxy resins of the TM-A/DDM, and TM-B/DDM systems were 0.54 and 0.85 W/m•K, respectively, that were 2.8 and 4.5 times higher than that of the bis-A/DDM system. Although the thermal conductivities of all the present resin systems are higher than those of commercial epoxy resins, which is represented by the bis-A/DDM system, the degree of improvement of thermal conductivities for the TM/DDM systems is much larger than that for the MM/DDM system. The results suggest that higher order structures, which suppress phonon scattering, were induced in the resins in all the present systems and that the degrees of ordering in the TM/DDM systems are much larger than that for the MM/DDM system. To obtain evidence for this hypothesis, we carried out direct observations at mesoscopic scales for the bis-A/DDM, MM/DDM, TM-A/DDM and TM-B/DDM systems by using AFM. And we also carried out observations at microscopic scales for the MM/DDM and TM-B/DDM systems by using TEM.

TEM images of the MM/DDM and TM-B/DDM, and AFM images of the bis-A/DDM, MM/DDM, TM-A/DDM and TM-B/DDM resins are shown in Fig. 4. There is no mesoscopic structure in the AFM image of the bis-A/DDM system. Many domains of order-structures can be recognized in the TEM image of MM/DDM resin, however, the sizes of the domains are 20nm at most and there is no mesoscopic structure in the AFM image. On the other hand, the TM-B/DDM system shows an obvious lattice structure in the TEM image and large domains with sizes of about several micrometers in the AFM image. Furthermore, the domains form ‘honeycomb’ structures with clear boundaries, not ‘island’ structures in the amorphous matrix, suggesting that most of the regions of the TM-B/DDM resin have higher order structures. In the AFM image of the TM-A/DDM system, large domains with sizes of about several micrometers are also observed, however, there is no sharp boundaries between the domains. The mesoscopic structure of the TM-A/DDM system is considered to be in the intermediate state between the MM/DDM and TM-B/DDM systems. The results of direct observations of the morphologies of the resins are consistent with those of the thermal conductivity measurements. In short, the existence of higher order structures in the resins definitely improves their thermal conductivities and the degrees of the improvement depend on the state of the ordering, more specifically, the sizes, the amounts and the connectivity of domains of the ordered structures. It is considered that the mesogens forms nanoscopic high-order structures and the structures forms mesoscopic structures, which are covalently bound together, suppressing phonon scattering. Such resin system is therefore considered to be a kind of polymer-polymer composite with controlled nanostructures.

3.2 Thermal Conductivity after Thermal Degradation

Figure 5 shows the changes of thermal conductivities for MM type/DDM and bis-A type/DDM resin plates after thermal degradation in air. The thermal conductivities were normalized with each starting value for comparison of degradation rates. However the thermal conductivities of both MM type/DDM and bis-A type/DDM resins gradually decreased with degradation time at temperatures of both 200 and 230°C, the degradation rates were almost the same between the two resin systems. The result suggests that the high-order structure formed in MM type/DDM resin system, which is considered to improve their thermal conductivity, was not broken by thermal degradation at temperature below at least 230°C.

3.3 Fabrication and Properties of Laminates

Figure 6 shows the variations in thermal conductivities as a function of the filler content for two typical series of laminate samples fabricated with different resin systems but with the same filler system. In the figure, the filler content is defined as a volume fraction of the filler in the laminates, excluding glass fiber. The thermal conductivities of the laminates without filler for a biphenyl type epoxy resin, containing a mesogen, and a conventional epoxy resin were 0.50 and 0.43 W/m•K, respectively. Here, the conventional epoxy resin sample without filler corresponds to a
The difference of these values for samples without filler is not large, however, the difference increases dramatically with an increase in filler content. For example, the thermal conductivities of the biphenyl type laminates reach more than twice that of a conventional one. Furthermore, a maximum thermal conductivity of more than 7 W/m·K was achieved, which is more than 10 times higher than that of ordinary epoxy resin laminates such as FR-4. Although this feasibility study used fillers with relatively high thermal conductivities, consisting mainly of boron nitride, such large thermal conductivities can be realized only by the improvement of the base resin. In other words, the potential for high thermal conductive fillers can be maximized by using high thermal conductive resins with a controlled higher order structure. From the results of the trial manufacture of the laminates, it was confirmed that the control of the higher order structure of the resin is sufficiently effective in improving thermal conductivity even in composite materials.

Figure 7 shows the changes of the surface temperatures of typical laminate samples while one surface was heated and cooled alternately at 15-second intervals using a Peltier device. Here, T₁ and T₂ are the temperatures on an upper and a lower surfaces of the laminates respectively, and ΔT is a temperature difference between the two sides. ΔT for a high thermal conductive laminate (thermal conductivity \( \lambda = 4.5 \text{ W/m·K} \)) is much smaller than that for a conventional one (\( \lambda = 0.43 \text{ W/m·K} \)). The result clearly demonstrates the effect of components consisting of high thermal conductivity.

**Fig. 4.** AFM images and TEM images of: (a) bis-A/DDM, (b) MM/DDM, (c) TM-A/DDM and (d) TM-B/DDM resin systems. Inset shows possible schematic image of high thermal conductivity in order-structure.

FR-4 grade laminate. The difference of these values for samples without filler is not large, however, the difference increases dramatically with an increase in filler content. For example, the thermal conductivities of the biphenyl type laminates reach more than twice that of a conventional one. Furthermore, a maximum thermal conductivity of more than 7 W/m·K was achieved, which is more than 10 times higher than that of ordinary epoxy resin laminates such as FR-4. Although this feasibility study used fillers with relatively high thermal conductivities, consisting mainly of boron nitride, such large thermal conductivities can be realized only by the improvement of the base resin. In other words, the potential for high thermal conductive fillers can be maximized by using high thermal conductive resins with a controlled higher order structure. From the results of the trial manufacture of the laminates, it was confirmed that the control of the higher order structure of the resin is sufficiently effective in improving thermal conductivity even in composite materials.

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conductive epoxy resins (laminates, in this case) in the improvement of heat dissipation in electric devices.

4. Conclusions

We confirmed the existence of crystal-like structures in several kinds of high thermal conductive epoxy resins containing mesogen through TEM and AFM observations. A resin having larger domains of order structures and sharper boundaries between the domains tends to have the higher thermal conductivity. The results suggest a novel method for improving the thermal conductivities of insulating resins themselves by controlling the high-order structures. Furthermore, laminates were prepared with an MM type epoxy resin, containing a biphenyl group mesogen, and ceramic fillers as a part of a feasibility study. Thermal conductivities more than 10 times higher than those of ordinary epoxy resin laminates were obtained for test pieces of the laminates. This result shows that controlling the nanoscopic high-order structure of the resins is effective in improving the thermal conductivity of resin composites. Measurement of surface temperature changes for typical laminate samples during alternate heating and cooling supports the view that the high thermal conductive epoxy resins are effective in the improvement of heat dissipation in various electrical systems.

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References


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