High Toughness Liquid Crystalline Epoxy Resin

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1 Abstract

In recent years, increased fuel efficiency of moving vehicles has been demanded for the purpose of reducing the environmental burden, and resin composites are receiving attention as the lightweight and high-strength materials. However, resin composites are brittle compared with conventional metal materials, and so increased resin material toughness is required to address this issue. We have developed high-toughness liquid crystalline epoxy resins which can form higher order structures due to reaction-induced phase transitions in the cured materials. The resins show excellent handling properties in an un-cured state, and the cured resins exhibit fracture toughness 3 times greater than that of general-purpose epoxies as well as high heat resistance properties due to the formation of crosslinking structures. Therefore, the resins are suitable as matrix resins for high-strength composite materials.

2 Characteristics of the Product

- Crystallinity controlled by modification of a mesogenic epoxy resin to permit solvent-free coating of the uncured resin.
- Excellent fracture toughness, at least 3 times greater than general-purpose epoxy, as a material cured by liquid crystal domain formation.
- Cross-linked and fixed higher-order structure, superior in fracture toughness and heat resistance.

3 Background of the Development

In recent years, there has been an increased demand for lower fuel consumption of moving vehicles to reduce their environmental impact, and resin composites are attracting attention as lightweight and high-strength materials. There is a demand for tougher resins as resin composite materials are susceptible to brittle fracture and have a problem with impact resistance. Investigations into toughening the epoxy resins that are widely used as matrix resins for composite materials have been made by adding rubber or elastomer, or adding an engineering plastic[1), 2)]. However, the former often brings about a decrease in elastic modulus and strength, and the latter causes a drop in processability due to greater viscosity, so their effect of improving toughness is limited and further improvement is required. On the other hand, it is known that toughness can be greatly enhanced by introducing a mesogenic group into the epoxy resin to form a higher order structure in the cured resin[3), 4)]. However, the introduction of a mesogenic group increases the crystallinity of the material and often causes problems with handling, making industrial application difficult. Therefore, Hitachi Chemical attempted to develop a liquid crystalline epoxy resin that combines excellent handling in the uncured state with high toughness as a cured product.

4 Technical Details

We developed a new tough liquid crystalline epoxy resin by controlling the crystallinity and molecular orientation by multimerizing mesogenic epoxy monomers via aromatic units, as shown in **Figure 1**. **Figure 2** shows the temperature-viscosity curves for the mesogenic epoxy monomer and the developed resin.

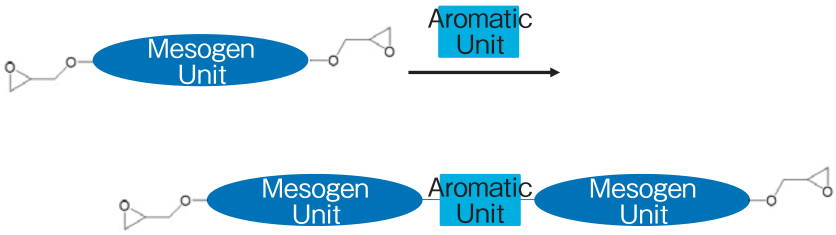


Figure 1 Modified mesogenic epoxy compounds

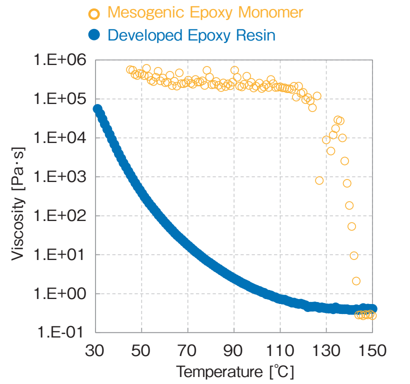
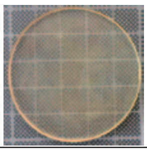
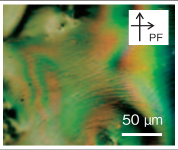
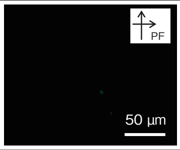


Figure 2 Temperature dependence of viscosity of monomer and developed epoxy resin

Unlike the monomer that crystallized at 130 °C or lower, the developed resin does not change phase in the temperature range of 30 to 150 °C, which makes solvent-free coating by heating easier. **Figure 3** shows the appearance of the developed resin and general-purpose epoxy resin cured with diaminodiphenylsulfone.

Item	Developed Epoxy Resin	General Epoxy Resin[1]
Appearance		
POM		

1) Diglycidylether of bisphenol A

Figure 3 Appearance and POM image of cured epoxy resin

The developed resin undergoes a reaction-induced phase transition to form liquid crystal domains in the cured product. The appearance became cloudy white and depolarization images were observed with the orthogonal Nicol optical system of a polarizing microscope. **Table 1** shows the properties of the developed resin and general-purpose epoxy resin cured with diaminodiphenylsulfone.

Table 1 Properties of cured epoxy resin[1]

Item	Unit	Developed Epoxy Resin	General Epoxy Resin	Note
Fracture Toughness	MPa·m$^{1/2}$	2.5	0.6	SENB[2] Test
Tg	℃	175	179	DMA
Modulus	GPa	2.7	2.8	Flexural Test
Water Absorption	%	1.6	2.4	48 h in 98 ℃ water

1) 150 ℃ 4 h, 2) Single Edge Notched Bend

Because the higher order structures formed by self-alignment are cross-linked and fixed, the developed resin exhibited an extremely high fracture structure toughness of 2.5 MPa.m$^{1/2}$ while maintaining high heat resistance as a thermosetting resin. Therefore, the developed resin is considered to be a suitable matrix resin for high-strength composite materials.

5 Future Business Development

・Investigation of applications to composite materials and development of applications

【References】

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