Study on the mixed system of liquid crystalline epoxy/epoxy resin

CHEN LIXIN, WANG RUMIN, CHAN PENGSHAN, QI SHUHUA
Department of Applied Chemistry, Science of School, Northwestern Polytechnical University, Xi'an 710072, People's Republic of China
E-mail: chen-lixin@mail.china.com

Epoxy resin (EP), owing to its outstanding advantages of strength, high modulus and processability for advanced resin matrix, has been widely used in the fields of high technology, such as aviation, spaceship, etc. However, EP is limited in utilizing high performance structural composites because of its insufficient toughness after curing. Modification on this thermosetting resins currently is very active.

The route of toughening EP, at present, is mainly focused on rubber [1, 2], thermoplastic [3, 4], chain-extending and thermotropic crystalline polymers [5, 6] modification. These methods, however, have disadvantages to various extents. In order to overcome these problems, liquid crystalline epoxy is used to self-reinforce *in situ* to improve the toughness of cured resin. At the same time, as liquid crystalline epoxy is compatible with EP, it links EP with strong chemical bond by chain-extending of ammoniac cure agent [7]. Moreover, the addition of liquid crystalline epoxy with low-molecular weight could not lead to the problem of poor processability.

Liquid crystalline epoxy resin with the aromatic ester mesogen—the diglycidylether of 4-hydroxyphenyl—4-hydroxybenzoate (PHBHQ) is synthesized, and the effect of synthesis and extraction on product yield has been discussed. The structure and phase behaviors of synthesized PHBHQ have been characterized by Differential Scanning Calorimetry (DSC) (see Fig. 1). The results indicate that PHBHQ emerges in the state of nematic phase during the cooling process at temperature of 131–94 °C.

The curing reaction characteristics, heat resistance and mechanical properties of cured PHBHQ resin have been studied (see Table I). It is discovered that different curing agents can form eutectic mixture, but DDS could not. The comprehensive performance of cured resin of PHBHQ/DDM and PHBHQ/mixed aromatic diamine 4# is better, and the microstructure is observed by SEM, POM and Wide-angle X-Ray Diffraction (WAXD).

The curing mechanism and kinetics of PHBHQ, reacted with DDM, are studied by FTIR. The curing reaction was proceeding with auto-accelerating mechanism, and is accelerated by the hydroxyl group produced in the curing process. The isothermal curing processes of PHBHQ/DDM system at different temperatures are monitored by FTIR. The kinetics parameters of each step of curing reaction are calculated: $Ea_1 = 66.51$ kJ/mol, $Ea_2 = 69.05$ kJ/mol.

The toughness of CYD-128 resin system increases by adding PHBHQ. The impact strength and glass transition temperature of cured PHBHQ/CYD-128/mixed aromatic diamine 4# system are 40.2 kJ/m^2 and 182.9 °C, respectively, when the content of PHBHQ is 50%; the impact strength and glass transition temperature of cured PHBHQ/CYD-128/DDM are raised to 29.5 kJ/m^2 and 165 °C, respectively, when the content of PHBHQ is 23% (see Figs 2 and 3).

The system of PHBHQ/CYD-128/ aromatic diamine is a partial compatible system while during the curing process PHBHQ phase is separated according to the analysis of Dynamic Thermomechanical Analysis (DMTA) (see Fig. 4). The SEM photos show that the ordered structure of PHBHQ in the cured network can initiate, branch and terminate the crack dispersed in the

TABLE I The properties of cured PHBHQ

Ingredient	Impact strength (kJ/m^2)	Bending strength (MPa)	Heat distorion tempetature (°C)	Moleculer weight between crosslinks
CYD-128/DDM	20.1	94.9	152	
PHBHQ/DDM	28.3	112.3	154	294.0
CYD-128/DDS	10.9	111.7	174	
PHBHQ/DDS	18.9	107.7	168	301.3
CYD-128/DDBA	38.6	86.7	158	
PHBHQ/DDBA	46.1	87.1	149	346.7
CYD-128/4#	23.4	91.5	132	
PHBHQ/4#	38.6	96.4	158	

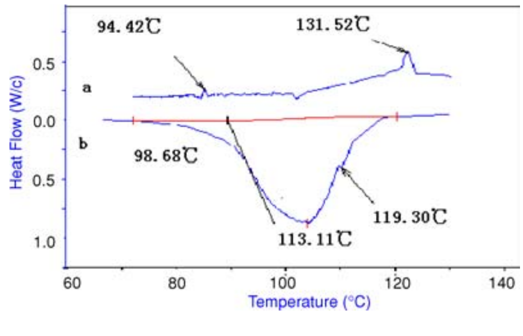

Figure 1 The DSC curve of PHBHQ at 10 °C/min ramping rate (a: decreasing, b: increasing).

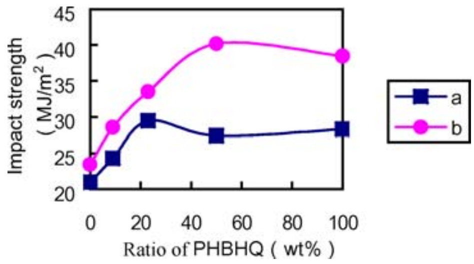

Figure 2 The effect of PHBHQ content on impact strength.

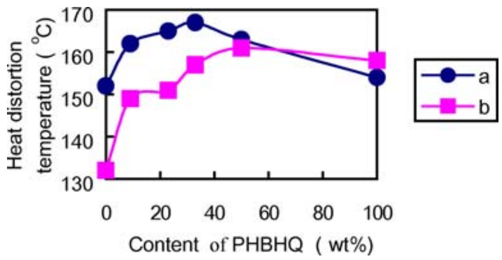

Figure 3 The effect of PHBHQ content on HDT.

continuous epoxy matrix, and can make the toughened resin system have good dynamic property and outstanding heat resistance.

Note: In Figs 2 and 3, a is PHBHQ/CYD-128/DDM, b is PHBHQ/CYD-128/ mixed aromatic diamine4#.)

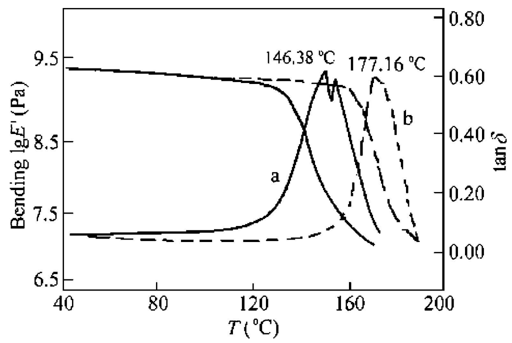

Figure 4 DMTA curve of cured PHBHQ/CYD-128/4# (a: 0 wt% PHBHQ; b: 9 wt% PHBHQ).

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