

STUDY ON THE TOUGHENING MECHANISM OF RUBBER TOUGHENED EPOXY

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ABSTRACT

The following factors affecting the rubber toughened epoxy resin system were studied: 1. kinds of curing agent used, 2. the $\bar{M}_c$ value of the matrix, 3. the bonding force between the dispersed phase and the matrix. Our experimental result indicates that the average chain length between crosslinks ($\bar{M}_c$) is a much more important affecting factor. Chemical bonding between the dispersed phase and the matrix is also important. A toughening mechanism of rubber toughened epoxy has been proposed. In the material with relatively low crosslinking density, extensive fracture process strip is formed which is induced by the combined stress field near the rubber particles. The chemical bonding between the dispersed phase and the matrix may increase the strength of the local stress field about the rubber particles which is in favor of broadening the fracture process area.

INTRODUCTION

Various kinds of rubbers are used to toughen the thermosets. The carboxyl terminated nitrile rubber (CTBN) toughened epoxy resin system has often been used for studying the mechanism of rubber modified thermosets. Three mechanisms have been proposed to explain the improved toughness of rubber modified thermosets; shear banding and crazing^[1,2], elastic deformation and tear of the rubber particles^[3], voiding and shear yielding^[4-6]. These previous studies on the toughening mechanisms usually emphasized on the toughening effect of rubber particles and frequently ignored the influential effect of the structure of epoxy resin on the rubber particles, and a specific kind of rubber modified epoxy material was chosen. By changing the loading velocity, experimental temperature etc., they proposed the toughening mechanism through the relationship between the mechanical properties and fracture behaviors of the above material, but it was only limited to the specific material. In the present research, we synthesized various kinds of rubber toughened epoxy resins with different phase separation conditions, different bond force between the dispersed phase and the matrix and with matrix of different $\bar{M}_c$ value. The properties and fracture morphologies of these materials were investigated. Thus a mechanism of rubber toughening which might be suitable for various kinds of thermosets was suggested.

EXPERIMENTAL

Material

Carboxyl terminated nitrile rubber (CTBN) made by this laboratory.

Nitrile 26 made by Lang-Zhu Chemistry Co., China.

Epoxy resins all made by Wu-Xi Resin Factory, China.

Epoxy 618# mol. wt. 403

Epoxy 634# mol. wt. 476

Epoxy 601# mol. wt. 1012

70* anhydride made by East Tianjin Chemical Industrial Factory, China. It is a eutectic mixture of four tetrahydrophthalic anhydrides.

Triethanolamine, piperidine, hexahydrophthalic anhydride, N,N-dimethyl benzyl amine, BF₃ monoethylamine and bisphenol A were all analytical reagents.

Testing methods

Fracture toughness. 230×40×6 (mm) simple slotted double cantilever beam specimen was used. Head cross speed 1.25 mm/min. Testing and calculating methods were given in reference [7].

Impact toughness. 55×6×4 (mm) unnotched specimen was used, tested with CXZ-40 type SSB impacting machine.

Dynamic mechanical property test with DDUREA Viscoelastometer, calculated the $\bar{M}_c$ value (average chain mol. wt. between two crosslinks) with the following equation: $\lg G = 7.0 + 293d/\bar{M}_c$, where G is the shear modulus at 30°C above its T_g , d is the density of the material at room temperature.

Electron microscopy observation. The fracture surface and vertical profile morphologies of the stress whitening and rapid crack growth regions were observed with JSM-U3 SEM.

RESULTS AND DISCUSSION

1. The influence of the curing agents

The properties of pure epoxy resins and 10 phr (phr means per hundred parts of epoxy resin) CTBN toughened epoxy resins cured by various curing agents are listed in Table 1. AN% of CTBN is 30.7%, the molecular weight of CTBN is 3170. The curing conditions of piperidine and triethanolamine are 100°C 2h, 120°C 16h. The curing conditions of hexahydrophthalic anhydride and 70* anhydride are 100°C 2h, 140°C 6h, and 1 phr N,N-dimethylbenzylamine is added. The curing condition of BF₃ monoethylamine is 120°C 2h, 150°C 3h.

From the experimental results (see Table 1) the following conclusion can be drawn. No matter what kind of curing agent is used, the addition of CTBN will enhance the fracture toughness of epoxy resin tremendously but raise the impact toughness moderately as long

as the rubber particles are dispersed in the epoxy matrix. The distortion temperature of the epoxy resin lowers a little. When curing agent BF_3 monoethylamine is used, pronounced decrease in distortion temperature of CTBN toughened epoxy resin is resulted, the material is transparent and no rubber particles are observed at the fracture surface with SEM. In this case most of the added rubber is solved instead of dispersed in it, then the matrix is flexibilized, the impact toughness of the material increases apparently. When the AN% of the added CTBN is 19% instead of 30.7%, both toughening and flexibilizing effect can be observed. The heat distortion temperature of unmodified epoxy resin cured by different kinds of catalytic curing agents are quite different. The lowest is 72°C and the highest is 148°C. This is probably owing to the different crosslinking density of the matrix. The higher the crosslinking density of the matrix is, the lower the impact and fracture toughness is observed.

Table 1 The properties of epoxy resin and CTBN toughened epoxy resin with different curing agent system

Kind of curing agent	Epoxy resin	Recipe (weight ratio)		Fracture toughness (J/m ²)	Impact toughness (kg-cm/cm ²)	Heat distortion temperature (°C)	Morphology
		CTBN	curing agent				
Piperidine	100	0	5	178	24	102	Homogeneous
	100	10	5	1023	25	90	With dispersed rubber phase
Triethanolamine	100	0	10	195	23	72	Homogeneous
	100	10	10	964	24	69	With dispersed rubber phase
Hexahydrophthalicanhydride	100	0	78.5	113	7.08	132	Homogeneous
	100	10	78.5	741	9.58	126	With dispersed rubber phase
70* anhydride	100	0	77.5	110	6.5	131	Homogeneous
	100	10	77.5	781.8	8.95	126	With dispersed rubber phase
BF_3 ethylamine	100	0	3	108	2.8	148	Homogeneous
	100	10	3	119	9.5	84	No dispersed rubber phase
	100	*10	3	294	5.2	105	With dispersed rubber phase but not clear

* AN% of this CTBN is 19% instead of 30.7%

2. The influence of the $\bar{M}_c$ value of epoxy matrix on the toughening effect of rubber

Sultan and McGarry^[2] found that a remarkable increase in the toughness could be

achieved by adding certain amount of bisphenol A, and they suggested that it was attributed to the bimodal distribution of the rubber particles in the matrix caused by the added bisphenol A. They proposed the shear banding and crazing mechanism to the rubber toughened system. However, according to our experimental results^[8,9] the following explanation might be more appropriate.⁶ While basic catalytic curing agents such as piperidine or triethanolamine is used, it predominately catalyses the reaction of bisphenol A and epoxy resin, therefore the molecular weight of epoxy resin increases in situ. The improvement of the impact and fracture toughness by adding bisphenol A is ascribed to the decreased crosslinking density of the epoxy resin network. In order to further investigate the influence of the $\bar{M}_c$ value of the epoxy matrix on the toughening effect of rubber, two types of epoxy resin and CTBN modified epoxy resin with similar structure but different crosslinking densities were made. The first type is epoxy resin 618* cured with different quantities of reactive curing agent 70* anhydride. The second type is epoxy resins with different molecular weight cured with 10 phr triethanolamine. Tables 2 and 3 are the $\bar{M}_c$ values and properties of these two types of epoxy resins and toughened epoxy resins. The AN% of CTBN is 23% and the molecular weight of CTBN is 3500. The curing conditions are the same as Table 1.

Table 2 The properties of epoxy resin of 70* anhydride cured systems

Epoxy 618*	Recipe (weight ratio)		$\bar{M}_c$	Fracture toughness (J/m ²)	Impact toughness (kg-cm/cm ²)	Tensile strength (kg/cm ²)	T_g (°C)
	CTBN	70* anhydride					
100	0	39	610	139	10.1	388	93
100	0	58	383	111	8.7	544	119
100	0	77	379	93	6.7	574	132
100	10	39		839	18.9	773	89
100	10	58		589	18.9	811	111
100	10	77	377	419	15.0	884	125

The experimental results reveal that the structure of epoxy resin, especially the $\bar{M}_c$ value of the cured network has a marked influence on the toughening effect of rubber. This influence appears to be much more important than the other factors such as the composition and the volume fraction of the dispersed phase, the distribution of rubber particle sizes.

As seen from SEM pictures of the fracture surface morphology of both the stress whitening and rapid crack growth regions, as well as the vertical surface morphology of the stress whitening surface associated with different $\bar{M}_c$ values, the rubber particles are visible as circular depressions on the fracture surface. The depressions in the stress whitening region are larger and deeper. The rubber particles near the stress whitening region are elongated. These pictures also show that a large amount of yielding and plastic flow exist just beneath the stress whitening region. Besides, several microcracks are distributed near the trunk of the main crack. The larger the $\bar{M}_c$ is, the more extensive is the above phenomena.

Table 3 The properties of epoxy resin of triethanolamine cured systems

Epoxy resin	Recipe (weight ratio)		$\overline{M}_c$	Fracture toughness (J/m ²)	Impact toughness (kg-cm/cm ²)	Tensile strength (kg/cm ²)	T_g (°C)
	CTBN	Triethanol-amine					
618* 100	0	10	546	128	18	769	82
634* 100	0	10	556	189	20.5	781	82
601* 100	0	10	1600	455	33.6	—	80
618* 100	10	10		1278	22.5	654	72
634* 100	10	10		1658	28.6	664	75
601* 100	10	10		6372	53.7	651	72

3. *The influence of the bonding force between the dispersed phase and the matrix on the toughening effect of rubber*

Two kinds of rubber, namely CTBN (AN%=23%) and liquid nitrile 26, were used to toughen epoxy resin. CTBN was reacted with epoxy 618 to form epoxy-CTBN-epoxy adduct before curing, therefore the chemical bonding between the rubber particles and the matrix are present. In the case of liquid nitrile 26, no such chemical bonding can exist between the two phases. The crosslinking density can be changed by adding a certain amount of bisphenol A. The fracture toughness of these materials are listed in Table 4.

Table 4 The relationship between the fracture toughness of the material and the bonding condition of the dispersed phase and the matrix

Epoxy 618*	Recipe (weight ratio)			Triethanol-amine	Fracture toughness (J/m ²)
	Bisphenol A	CTBN	Nitrile 26		
100	0	0	0	10	178
100	24	0	0	10	288
100	0	10	0	10	1082
100	0	0	10	10	764
100	24	10	0	10	7748
100	24	0	10	10	4736

From the above experimental results, the addition of CTBN or nitrile 26 can markedly raise the fracture toughness of the epoxy resin, especially for the bisphenol A modified epoxy resin system, because in the latter case the crosslinking density of the matrix is lower. The above results also reveal that the toughening effect of CTBN is obviously greater than that of nitrile 26. Hence the chemical bonding between the dispersed rubber phase and the matrix

will enhance the toughening effect of rubber considerably.

Based upon the foregoing results, we propose the following toughening mechanism:

As the thermo-cured specimen is cooled to room temperature a self-equilibrated local stress field will be developed in the neighborhood of the rubber particles, owing to the difference in thermo-expansion coefficients between the matrix and rubber particles. Specifically, the rubber particles are subject to tensile stress. The intensity of these local stress fields are influenced by the properties of the composing two phases, and this dependence is increased as the extent of bonding and phase-separation improves. Next, if one consider a crack flank propagates to the vicinity of the rubber particle under consideration, the associated stress field is superposed to these local stress fields, resulting void nucleation or cracking along rubber-matrix interfaces. These defects situated near the crack front stimulate crack branching or shear localization emitting from the main crack, creating a more extensive fracture process zone. Apparently, the epoxy matrix with larger value of $\bar{M}_c$ offers much weaker resistance against phenomena like crack branching or shear localization. Consequently, broaden fracture process zone will be produced in the material with rather low degree of crosslinking. Furthermore, a strong chemical bonding between matrix and rubber phase will intensify the local stress near rubber particles, in favor of spreading of the fracture process area. The above explanation is supported by the photographs taken by transmission and scanning electron microscope. In the slow-bonding process of the material, energy is partially absorbed by the extension and tearing of rubber themselves. The amount of this energy dissipation is substantial for the material with high crosslinking matrix, but becomes less important for the material with low crosslinking matrix.

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