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Practical Technology of Toughening Epoxy Resin: Influence of Toughening Agents on Mechanical and Heat Properties

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Abstract: This research studies the effect of several toughening agents, such as carboxyl-terminated polyether (CTPE), carboxyl-terminated polytetrahydrofuran (CTPF), carboxyl-terminated liquid nitrile rubber (CTBN), random-base liquid nitrile-butadiene rubber (RBNR) and core-shell polymer (CSP) containing polybutadiene, on epoxy resin. These epoxy resin systems containing various toughening agents showed different viscosity, in which the viscosity of CTPE and CTPF systems nearly unchanged and the viscosity of CTBN, RNBR and CSP systems increased significantly. The impact resistance of modified epoxy systems had been improved significantly, especially the CTPF system raised by 257.2%. Meanwhile, the heat resistance of epoxy systems containing different toughening agents showed different results. Compared with the pure sample, the hardness of all toughened systems decreased. CTPE and CTBN systems decreased significantly, while CTPF and CSP remained fundamentally unchanged. Toughness modification resulted in reduction of tensile strength and the retention ratio was CSP > RNBR > CTPF > CTBN > CTPE. Toughness modification resulted in reduction of compression strength and the retention ratio was RNBR > CSP > CTPF > CTBN > CTPE. All of the toughening systems kept the shear strength basically unchanged. The shear strength of the CSP system was even improved. In terms of peel strength, all of toughening systems had improved.

Keywords: Epoxy Resin, Toughening, CTPE, CTPF, CTBN, RBNR, CSP

1. Introduction

Epoxy resin are used extensively in electronic, electrical, mechanical, architectural and even aerospace field due to their excellent mechanical properties, low shrinkage, chemical resistance and electrical insulation. Because of high cross-linking density, the non-toughened epoxy resin has some shortcomings, such as brittleness, poor fatigue resistance and impact toughness, which limited the application of epoxy resin. It's difficult to meet the requirements of engineering technology. Consequently, the toughening modification of epoxy resin has been a hotspot in the industry, and a considerable amount of research has been conducted to improve the toughness of epoxy polymers.

Reactive liquid rubber [1-5] can improve the fracture energy and impact performance of epoxy system. Thermoplastic resin [6, 7] can enhance the bending strength and impact performance of materials. The addition of thermogenic liquid crystal [8, 9] can also effectively increase the impact strength of epoxy resin. It can also be toughened by core/shell polymer [10, 11], grapheme [12-14] and nano particle filler [15-17].

Among all kinds of epoxy toughening modification researches, some of them are practical and some frontier researches are novel and prospective [18, 19]. However, due to technical difficulty or cost factors, it's hard to be widely used in the development of conventional epoxy products, especially civil products.

China Bluestar Chengrand Chemical Industry Co., Ltd. is a long-term commitment to the application research of epoxy resin. We have developed several special toughening materials for epoxy resins, which have been commercialized. This study summarizes and compares these practical toughening techniques in order to provide some reference and help to peers.

2. Experimental Section

2.1. Experimental Material

The main materials used in this paper were shown in table 1.

Table 1. *Main materials.*

Name and model	Composition and specification	Manufacture
Epoxy resin 128R	epoxy equivalent: 190g/eq, Viscosity: 12000~15000 mPa·s (25°C)	Taiwan South Asia company
Diluent 692	epoxy equivalent: 220g/eq, Viscosity: 2~8mPa·s (25°C)	Anhui hengyuan new material co., Ltd.
CTPE	Carboxyl-terminated polyether toughening agent	China Bluestar Chengrand Chemical Co., Ltd.
CTPF	Carboxyl polytetrahydrofuran toughening agent	China Bluestar Chengrand Chemical Co., Ltd.
CTBN	Carboxyl-terminated liquid nitrile butadiene rubber toughening agent	BASF
RNBR	Random-base liquid nitrile-butadiene rubber	Lanzhou rubber factory
CSP	Core-shell polymer toughening agent containing polybutadiene	US
5210B	Modified aliphatic amine curing agent, active hydrogen equivalent: 100 g/eq, Viscosity: 11000 mPa·s (25°C)	China Bluestar Chengrand Chemical Co., Ltd.
EC301	Modified aliphatic amine curing agent, active hydrogen equivalent: 61 g/eq, Viscosity: 10 mPa·s (25°C)	BASF

2.2. Experiment Instrument

INSTON 5569 electronic universal material testing machine, INSTRON company, USA (shear strength and compression strength test); INSTON 5967 testing machine, INSTRON company, USA (tensile strength and breaking elongation test); INSTRON WOLPERR impact testing machine, INSTRON company, USA (impact strength test); INSTRON 4302 testing machine, American INSTRON company (peeling strength test); Lx-d rubber hardness tester, Wuxi qianzhou measuring instrument factory; DSC 200 F3 differential scanning calorimeter, NETZSCH, Germany.

2.3. Preparation

2.3.1. Preparation of Toughened Epoxy Resin

To prepare modified epoxy resin, different toughening agents had different curing process. They wouldn't be covered in this article. For comparison, the mass fraction of toughening agents in all epoxy resins was 18%, as shown in table 2.

Table 2. *Components of toughening epoxy resin.*

Sample	1#R	2#R	3#R	4#R	5#R	6#R
128R (g)	72	72	72	72	72	72
CTPE (g)	-	18	-	-	-	-
CTPF (g)	-	-	18	-	-	-
CTBN (g)	-	-	-	18	-	-
RNBR (g)	-	-	-	-	18	-
CSP (g)	-	-	-	-	-	18
692 (g)	10	10	10	10	10	10
Appearance	Colorless, transparent and syrupy liquid	Translucent milky liquid	Pale creamy yellow liquid	Light yellow viscous liquid	Light yellow viscous liquid	Milky white viscous liquid
Viscosity (mPa·s)	1750	4100	5000	19000	20000	12300

2.3.2. Adhesive Curing and Sample Preparation

Toughened epoxy resin was mixed with curing agent accordance with the prescribed ratio. The specified samples were cured at 80°C for 3h.

2.4. Characterization Techniques

(1) Shear experiments were carried out at room temperature according to Chinese National Standard GB/T 7124-2008 *determination method of adhesive tensile shear strength (rigid material to rigid material)*. The carbon steel sample dimensions were 100mm×25mm×2mm. And the length of the bonding surface was 12.5mm.

(2) Impact strength, tensile strength, elongation at break and compression strength were measured according to Chinese National Standard GB/T 2567-2008 *resin casting performance test method*. The impact strength sample was 80mm×10mm×4mm without notch. The specimens for tensile strength and elongation at break tests were dumbbell shaped, with an external dimension of 250mm×20mm×4mm and a tensile width of 10mm. Cylindrical specimens of compression strength were Φ 10mm x 25mm.

(3) The glass transition temperatures (T_{gDSC}) of samples were tested by DSC.

(4) Peeling strength were measured according to GB/T 2791-1995 *test method for adhesive T peeling strength - flexible material to flexible material*. Aluminum foil bonding test was conducted with 200mm×25mm×0.3mm. And the length of the bonding surface was 150mm.

3. Results and Discussion

3.1. Influence of Toughening Agent on Hardness, Compression Strength and Other Properties

The performance comparison between the above toughening agent cured by modified amine curing agent 5210B was shown in table 3. Compared with non-toughened systems, the hardness of all modified systems decreased. And the decrease of CTPE and CTBN was obvious. CTPF and CSP did not change much.

Table 3. *Hardness, compression and other properties of curing agent 5210B.*

Sample	1#P	2#P	3#P	4#P	5#P	6#P
Shore D hardness	80	65	70	65	76	75
Compression strength/MPa	80.5	14.2	24.1	26	59	44.1
Compression failure mode	Failure	25%	25%	25%	25%	25%
Shear strength/MPa	22.4	21.7	22.3	23.1	22.1	29.3
Elastic modulus/MPa	2299	117	278	581	1850	1394
T_{gDSC}/°C	80.9	61.7	68.5	81.5	66.8	84.5

3.2. Influence of Toughening Agent on Compressive Properties and Elastic Modulus

It could be seen that the influence of several toughening agents on compression performance was obvious. The untoughened system was a rigid yield failure with high strength. The compression strength was lost at 25% compression. The retention ratio was RNBR > CSP > CTBN > CTPF > CTPE, and the elastic modulus demonstrated the same regularity as well.

3.3. Effect of Toughening Agent on Impact Strength, Tensile Strength and Elongation at Break

An important role of toughening agent introduced into epoxy resin was to improve the impact resistance of materials. The toughness of materials can be characterized from different aspects such as impact strength and elongation at break. These performance of modified epoxy systems cured by EC301 were shown in table 4. Low viscosity curing agent EC301 was used to obtain suitable casting specimens.

Table 4. *Impact strength, tensile strength and other properties of curing agent EC301.*

Sample	1#S	2#S	3#S	4#S	5#S	6#S
Un-notched Charpy Impact Strength /(KJ/m$^{2)}$	17.3	35.6	61.8	36.5	56.2	38.5
Tensile strength/MPa	49.3	18.0	29.5	28.4	36.0	38.9
Elongation at break /%	2.44	13.60	3.94	2.57	3.02	5.58
Peel strength/(KN/m)	0.09	0.15	0.23	0.21	0.18	0.38

As shown in tables 4, 5 and figure 1, several toughening agents had increased the impact strength by more than 100%, while CTPF system even exceeded 200%. The elongation at break and the peel strength represented the toughening effect of the material from another aspect. In general, the toughened epoxy resin was significantly improved in impact strength, peel strength and elongation at break.

The tensile strength of the toughened systems decreased as shown in table 4. Conservation ratio of tensile strength was CSP > RNBR>CTPF > CTBN > CTPE.

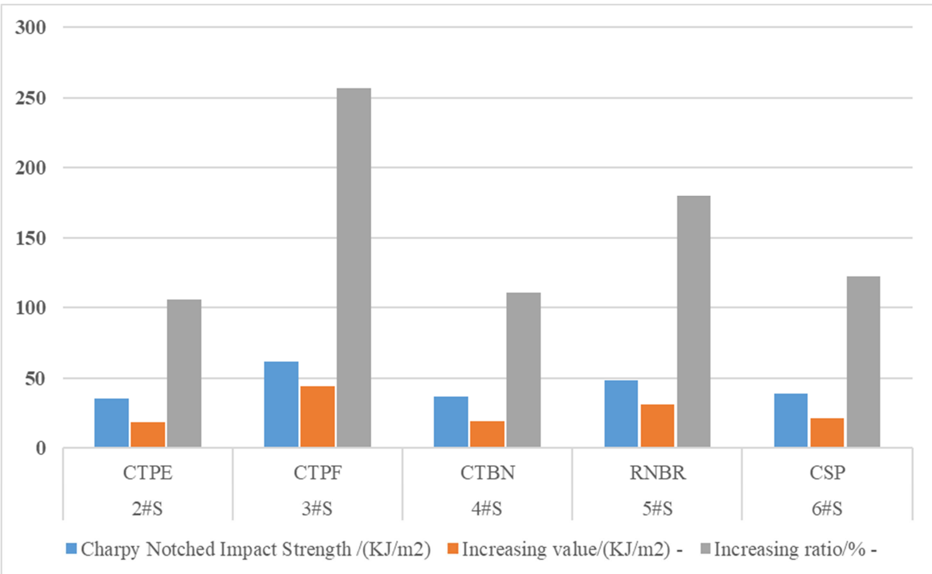

Figure 1. *Impact properties histogram of modified epoxy systems.*

Table 5. *Effects of toughening agents on impact properties.*

Sample	1#S	2#S	3#S	4#S	5#S	6#S
Modified system	-	CTPE	CTPF	CTBN	RNBR	CSP
Un-notched Charpy Impact Strength /(KJ/m^2)	17.3	35.6	61.8	36.5	48.5	38.5
Increasing value/(KJ/m^2)	-	18.3	44.5	19.2	31.2	21.2
Increasing ratio/%	-	105.8	257.2	111.0	180.3	122.5

3.4. Effect of Toughening Agent on Adhesive Performance

The improvement of shear strength and peel strength was an important indicator pursued by adhesives practitioners. As shown in tables 3 and 4, the toughening method adopted in this paper keeps the shear strength of the system basically unchanged. The shear strength of the CSP system was even improved. In terms of peel strength, all of toughening systems had improved.

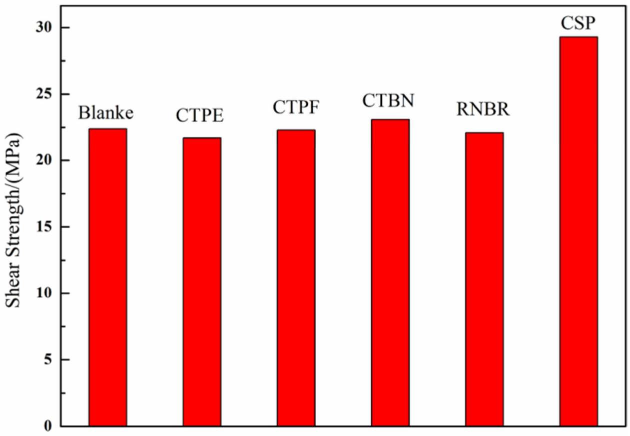

Figure 2. *Shear Strength histogram of modified epoxy systems.*

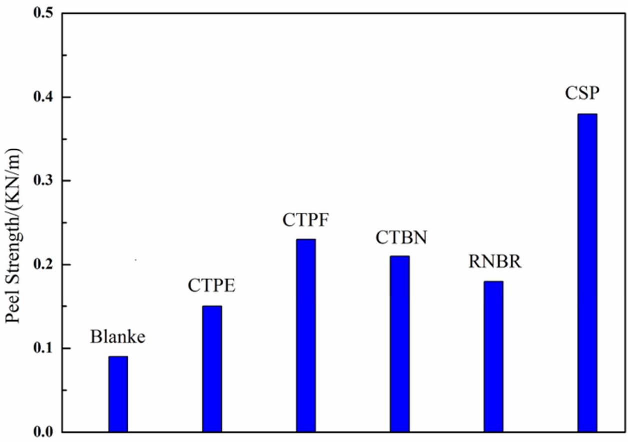

Figure 3. *Peel Strength histogram of modified epoxy systems.*

4. Conclusion

CTPE, CTPF, CTBN, RNBR, CSP and other toughening agents had obvious toughening effect on epoxy resin. For the influence of heat resistance, CTPE, CTPF and RNBR would cause T_{gDSC} to decrease, while CTBN and CSP had little effect on heat resistance. Toughening resulted in a reduction of compression strength and elastic modulus. And the retention ratio was RNBR > CSP > CTBN > CTPF > CTPE. The improvement of impact strength was CTPF > RNBR > CSP > CTPE > CTBN. Furthermore, it was noteworthy that the impact strength of CTPF modified resin increased by 257.2%. Toughening resulted in reduction of tensile strength and the retention ratio was CSP > RNBR > CTPF > CTBN > CTPE. All of the toughening systems kept the shear strength basically unchanged. The shear strength of the CSP system was even improved. In terms of peel strength, all of toughening systems had improved.

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