

Modification on epoxy-based adhesive

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Abstract: This research adopted four methods to toughen epoxy adhesives. They were liquid hydroxyl group terminated polybutadiene (HTPB) rubber modification, silicon rubber modification, polyacrylate multiplicity elastomer particulates emulsion modification and chemical grafting modification. After modification, the shearing strength and the rupture elongation were tested. The interface and the chemical reaction between the modifiers and the epoxy were analyzed by scanning electron microscope (SEM) and infrared optical spectrum. The results show that the elastomer particulates modification and the chemical grafting modification can reach the better toughening effects.

Key words: epoxy adhesive; shearing strength; rupture elongation; modifiers

Epoxy adhesives have been extensively used to fasten bridges and buildings in civil engineering because they are high in adhesion strength, low in shrinkage, high in corrosion resistance and simple in processing. With the appearance of new pattern composite materials, the fastening method is also changing from traditional adhering steel plates to adhering fiber reinforced polymer (FRP) sheet. FRP strengthened concrete structures need to support large loads. So they called for adhesives with high intensity and toughness, good anti-creep performance, good fatigue resistance, and good impact resistance. But it's well known that epoxy resins are brittle after being cured, so it's very necessary to toughen epoxy adhesives.

There are many methods for toughening epoxy adhesives such as changing epoxy resin's structure; filling it with rubber, thermoplastic resins, inorganic fillers; and reacting with swell monomers.

This study adopted four methods to improve the shearing strength and the rupture elongation of epoxy adhesives. This study also used SEM and infrared optical spectrum to investigate not only the interaction between the modifiers and the epoxy resin but also the mechanisms of the improvement on adhesive properties.

1 Sample-Making and Testing Methods

1.1 Test on shearing strength

The resins, toughener, filler and plasticizer were

mixed together and agitated until the mixture was homogeneous. Then the curing agent was added and also agitated homogeneously. The adhesive was then coated on the steel plates until the coating was thin and bubbleless. The testing sample was made as Fig.1.

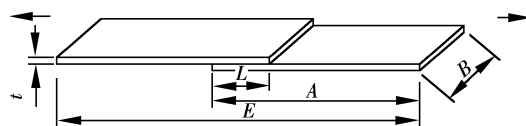


Fig.1 The sample for testing of shearing strength

In Fig.1, A is the length of steel plates (70 mm); B is the width of steel plates (20 mm); t is the thickness of steel plates (2 mm); L is the lapping length (15 mm); E is the whole length of the testing sample (125 mm). The two top arrows indicate the direction of the shearing. The shearing strength was tested by a universal testing machine.

1.2 Test on rupture elongation

When the adhesive was made, it was poured into a mold and then placed at room temperature for about 24 h. The sample was made as Fig.2. The rupture elongation was also tested by a universal testing machine.

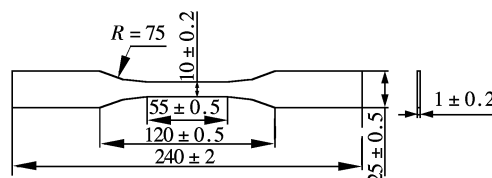


Fig.2 The sample for testing of rupture elongation (the unit is mm)

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2 **Modification by Liquid Hydroxyl Group Terminated Polybutadiene Rubber (HTPB)**

The molecular structure of liquid HTPB rubber can be indicated as $\text{HO} \left[\text{CH}_2\text{—CH=CH—CH}_2 \right]_n \text{OH}$. Its glass transition temperature is about $-80\text{ }^\circ\text{C}$, which is lower than other rubbers. This characteristic gives it a good low-temperature performance. And its long main chain has a nonpolar structure, which gives it a good electric performance. Besides, this rubber's price is relatively low, so it is prevalent a kind of modifier of epoxy adhesives.

In order to investigate the effect of the contents of HTPB rubber on the properties of the adhesives, the following recipe was selected.

$m(\text{E-44 epoxy resin}) : m(\text{E-51 epoxy resin}) : m(\text{663 epoxy resin}) : m(\text{Al}_2\text{O}_3 \text{ powder}) : m(\text{dibutyl phthalate}) : m(\text{rubber}) : m(\text{650 polyamide}) : m(\text{593 hardener}) : m(\text{KH-550 coupling agent}) = 50 : 50 : 10 : 50 : 5 : (5 - 30) : 100 : 15 : 2$. For results refer to Tab.1.

Tab.1 Influence of HTPB rubber contents on properties of the adhesives

Rubber content/g	Shearing strength/MPa	Rupture elongation/%
5	17.6	1.0
10	17.4	1.0
20	17.1	6.0
25	10.3	10.8
30	8.9	7.3

From Tab.1, the following conclusion can be withdrawn. When the content of HTPB is below 20 g, with the increase of the HTPB rubber content, the shearing strength of the hardened adhesive drops a little, but the rupture elongation increases dramatically; when the rubber content is above 20 g, both the shearing strength and the rupture elongation decrease significantly. Therefore the optimal content of rubber is 20 g within the range of this research.

3 **Silicone Rubber Modification**

Silicone rubber has good thermal-oxidative stability, a low glass transition temperature ($-123\text{ }^\circ\text{C}$), a low hydrophobicity, and a low stress concentration^[1]. So using silicone rubber to modify epoxy resins is a good way to reduce the internal stress of epoxy resins, and to improve heat stability and flame resistance of resins.

In this research, a 107 silicone rubber was selected to improve the shearing strength and the

rupture elongation of the epoxy-based adhesives. The compatibility of 107 silicone rubber is $7.4 - 7.8$. Therefore the silicone rubber cannot be dissolved in epoxy resins directly. To solve this problem, a KH-560 coupling agent was used to improve the compatibility between the epoxy matrix and the rubber.

The following recipe was used to investigate the influence of 107 silicon rubber:

$m(\text{E-44 epoxy resin}) : m(\text{E-51 epoxy resin}) : m(\text{663 epoxy resin}) : m(\text{Al}_2\text{O}_3 \text{ powder}) : m(\text{dibutyl phthalate}) : m(\text{rubber}) : m(\text{650 polyamide}) : m(\text{593 hardener}) : m(\text{KH-550 coupling agent}) = 50 : 50 : 10 : 50 : 5 : (0 - 40) : 100 : 15 : 2$. For results refer to Tab. 2.

Tab.2 Results of 107 silicone rubber modification

Rubber content/g	Shearing strength/MPa	Rupture elongation/%
0	17.6	1.0
10	17.2	4.8
20	16.8	13.6
25	14.0	16.0
35	9.8	16.8
40	7.0	12.4

It can be seen that the satisfactory content of silicone rubber is 20 g from both the shearing strength and the rupture elongation.

4 **Polyacrylate Multiplicity Elastomer Particulates Emulsion Modification**

Liquid rubber can effectively improve the toughness of epoxy resins^[2,3]. But the rubber phase will separate from the two-phase system. This rubber phase is controlled by the status of the rubber particulates, such as the rubber's content, size, and degree of cross-linking. Besides those factors, the thermal deformation temperature of cured adhesive will be lower than that of the pure epoxy resin. Through emulsion polymerization, the core and shell multiplicity elastomer particulates can be obtained. The core is the poly (*n*-butylacrylate) and the shell is poly (methy mechacrylate). The elastomer particulates' sizes can be controlled by adjusting the ratio between the core and the shell. Generally, the larger the ratio between the core and the shell is, the smaller the particulates' sizes are. By adding the multiplicity particulates, with the proper ratio between the core and shell, the modified system can be improved in anti-impact strength and shearing strength. Furthermore, its internal stress may be reduced^[4].

In order to determine the best ratio of core to shell, it is necessary to study the modified effect of different elastomers with different core-shell ratios firstly.

4.1 Core to shell ratio

In this research, the effects of five different elastomers were studied. Tab.3 gives the research results.

Tab.3 Modified results of polyacrylate elastomers with different core-shell mass ratios

$m(\text{core}) : m(\text{shell})$	Shearing strength/MPa	Rupture elongation/%
20 : 80	9.3	6.4
40 : 60	10.6	7.8
60 : 40	14.3	10.3
70 : 30	12.1	9.0
80 : 20	9.8	6.3

From Tab.3, it can be seen that the rupture elongation of the modified system is improved largely when the core-shell mass ratio is 60 : 40. And the shearing strength reaches its highest. When the ratio is above 60 : 40, the shearing strength and the rupture elongation decrease. These results can be explained as follows: When the core-shell ratio increases, the shell will not encase the core well, and the particulates will aggregate. Thus, the system’s mechanical property will be reduced.

4.2 Results of modification

The core-shell mass ratio 60 : 40 of the elastomer was selected to study the satisfactory content of the modifier. It can be seen from Tab.4 that the best content of the elastomer is 10 g.

Tab.4 Results of modification with different contents of polyacrylate elastomers

Elastomer’s content/g	Shearing strength/MPa	Rupture elongation/%
0	17.6	1.0
5	17.5	7.8
10	16.8	14.0
15	14.3	10.3
20	11.0	3.7

5 Chemical Grafting Modification

Organic silicon resins have several advantages, such as toughness at low temperature, low in surface energy, high in heat resistance and so on. So they cannot only reduce internal stress but also improve

heat-resistance^[4].

In this research, a 208 hydroxyl group organosilicon was selected to modify epoxy resin. The results may be seen in Tab.5.

Tab.5 Modification results with organic silicon resin

Modifier’s content/g	Shearing strength/MPa	Rupture elongation/%
0	17.6	1.0
5	17.0	2.7
15	15.8	9.0
20	15.2	13.1
35	14.6	17.8
40	9.2	14.0

From Tab.5, it can be seen that the organic silicon resin can toughen epoxy resins effectively, but the shearing strength drops more than in the other methods introduced above. The best content is 35 g per 100 g epoxy resin.

When the four modified methods mentioned above are analyzed, it can be seen that the latter two yield more satisfactory results. So, their modification mechanisms are discussed in the following section.

6 Discussion on Modification Mechanism

6.1 Mechanism of elastomer modified epoxy

Fig.3 shows the morphology of elastomer modified epoxy by SEM. Its recipe was selected as follows:

$m(\text{E-44 epoxy resin}) : m(\text{E-51 epoxy resin}) : m(663 \text{ epoxy resin}) : m(\text{Al}_2\text{O}_3 \text{ powder}) : m(\text{dibutyl phthalate}) : m(\text{elastomer}) : m(650 \text{ polyamide}) : m(593 \text{ hardener}) : m(\text{KH-550 coupling agent}) = 50 : 50 : 10 : 50 : 5 : 10 : 100 : 15 : 2$.

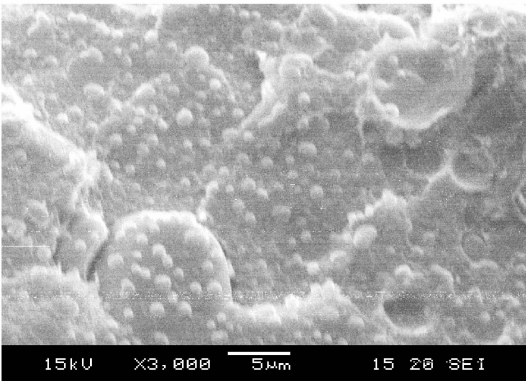


Fig.3 SEM observed morphology of elastomer modified epoxy

From Fig.3 and Tab.4, it can be seen that when the elastomer’s content is 10 g per 100 g epoxy, the particulates disperse as individual particles, which results in satisfactory properties. When the content is above 10 g, these particulates may aggregate together. At this time, the elastomers can only act as filler, and

From the reactions, it can be seen that the organosilicon resin modification can introduce a flexible chain into the epoxy groups. The stable Si—O—C bond is then formed. After curing, the modification system can form a two-phases structure with satisfactory performance.

7 Conclusion

This research adopted four methods to toughen epoxy-based adhesives. All of them can reach the satisfactory toughening effect. But when the epoxy resins are modified by liquid rubbers, the rubber phase will separate from the two-phase system. So it's hard to reach the best two-phase system. Moreover, when the rupture elongations of modified adhesives are analyzed, the latter two methods have the more satisfactory results. When 100 g epoxy resins are modified by 10 g polyacrylate multiplicity elastomer particulates, the shearing strength can reach 16.8 MPa, meanwhile the rupture elongation is as high as 14.0%. The mechanism of the elastomer modification is that the elastomer particulates, which disperse in the epoxy resins, act as a stress-concentrated body. They can

release the elastic stress energy of a matrix. In this way, the epoxy resins are toughened. When 100 g epoxy resins are modified by organosilicon resin, the optimal content is 35 g, the shearing can reach 14.3 MPa, and the rupture elongation can be as high as 17.8%. The modification mechanism is that the organosilicon resin can introduce a flexible chain into the epoxy groups, which produces a block copolymer. This copolymer can reduce the surface stress effectively and make polysiloxane disperse in epoxy matrix well.

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环氧树脂胶粘剂的改性

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摘要 采用了4种方法增韧环氧树脂胶粘剂,分别是端羟基聚丁二烯液体橡胶改性、硅橡胶改性、聚丙烯酸酯复合弹性体微粒乳液改性及化学接枝共聚改性.研究过程中测试了剪切强度和断裂伸长率,并分别运用了扫描电镜图和红外光谱图分析了界面特性及改性剂与环氧树脂间的化学反应.研究表明,复合弹性体微粒改性和化学接枝改性能够取得更好的效果.

关键词 环氧树脂胶粘剂;剪切强度;断裂伸长率;改性剂

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