Mechanical properties and microstructure of coordination toughened epoxy based composites

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Abstract. In this paper, toughening epoxy based composites were fabricated, the mechanical properties were measured and the microstructure was observed, the performance changes of epoxy casting system under different components were compared and analysed, coordination effect of multi-toughened was also investigated. Results showed that, the toughening agent and fumed silica as toughening fillers had the best strengthening and toughening effect on epoxy matrix with the addition of 4wt.% and 3wt.% respectively. Finally, by combining the different influence mechanism of the two fillers on the matrix, the comprehensive properties of the epoxy casting insulating materials were further improved. The results showed that the synergistic effect was obtained when the two fillers were blended with 3 wt.% toughener and 1 wt.% fumed silica. The tensile strength and impact strength were 67.42MPa and 13.69kJ/m², which were 67.51% and 37.15% higher than those of pure epoxy.

1. Introduction

Epoxy resin is widely used in the winding casting insulation of various power equipment because of its excellent dielectric properties and processing performance. However, the mechanical properties of the cured products are insufficient. Alicyclic epoxy resin has good heat resistance, but it lacks toughness because of its high crosslinking density and high glass transition temperature. In conclusion, it is necessary to toughen and modify it to prepare epoxy resin casting insulation material system with excellent mechanical properties.

At present, the second phase particle physical blending toughening method is widely used in epoxy materials. The commonly used toughening agents in this method are rubber elastomer[2,3], thermoplastic resin[4,5], inorganic rigid particle[6,7], core-shell structure polymer[8] and block copolymer[1]. The toughening modification of epoxy material is still the research hotspot of scholars at home and abroad. The mechanical properties of cured epoxy castable can be effectively improved by using appropriate toughening agent. However, there are few reports about the synergistic effect of nano fillers and tougheners on the mechanical properties of epoxy materials with united modification, so this study can be used for reference for the modification of epoxy system.

In this paper, alicyclic epoxy resin was used as basic resin, Methyltetrahydrophthalic anhydride as curing agent, and toughening agent and nano filler (fumed silica) were selected to toughen and modify them. The experimental materials and preparation methods for preparing epoxy composite insulation materials were determined, and the mechanical properties of the prepared samples were tested. Then...
the performance changes of epoxy pouring system under different components of single filler were compared and analyzed, and finally the comprehensive properties of epoxy pouring insulation materials were improved by combining the different influence mechanisms of the two fillers.

2. Experimental procedure

2.1 Materials

The epoxy resin was chosen Alicyclic epoxy resin. Typical properties for the resin include: a viscosity of 200-350cps, epoxy equivalent of 128-140g / mol. The MeTHPA (viscosity<45cps, anhydride equivalent=166g / mol) was used as a curing agent. DBU was used as amidine accelerator. A commercially available toughening agent was also chosen. The toughening agent was suitable for amines, dicyandiamide, anhydrides and phenols curing epoxy system. The fumed silica, manufactured by aerosol, was selected for this study with 20nm particle diameter and basically spherical.

2.2 Sample preparation

In single component study, toughening agent were mixed with epoxy in different weight ratios, 2wt.%, 4wt.%, 6wt.% and 8wt.%. The fumed silica were mixed with epoxy in weight ratios, 1wt.%, 2wt.%, 3wt.%, 4wt.%, 6wt.% and 8wt.%. In the multi-component study, keeping the total amount of filler 4wt.% unchanged, changing the ratio of the two fillers respectively. Using glass rod to preliminarily stir epoxy resin, curing agent and filler (toughening agent or fumed silica) weighed according to the proportion.

The mixing process of the epoxy resin with toughening agent or fumed silica was carried out using vacuum pump for degassing and high-speed mechanical stirring for 20min after mechanically stirring for about 10 min in water bath at 70 °C. Then accelerator were added to continuously high-speed stirring for degassing for 10min; the epoxy resin blend were poured along the inner wall of the mold. The mould was put into the oven and cured by step isothermal curing (90 °C / 2h + 110 °C / 2h + 150 °C / 3h + 180 °C / 5h).

2.3 Test

Tensile testing was carried out on samples (GB/T 2567-2008) using a universal testing machine (CMT-5504, Meister Industrial System Co Ltd, China). The shape of the sample was dumbbell type with a total length of 150 mm, a thickness of 4 mm, a width of 20 mm at the end, a width of 10 mm at the narrow part, and a gauge distance of 60 mm. The tensile rate was 2 mm / min. Impact test was carried out on samples (GB/T 2567-2008) using a simple support beam pendulum impact tester (MC009-XJJ-50, Shanghai Yanrun Optical Machinery Tech. Co. Ltd, China). The sample is a 120mm × 15mm × 10mm-non notched strip sample. The test was carried out at room temperature, with a span of 70mm and a pendulum energy of 7.5J.

Tensile and fracture surfaces of samples with different toughening agent or fumed silica contents were coated with gold and then analyzed using scanning electron microscope (SEM, E-9800, Keyence Ltd, Japan).

3. Results and discussions

3.1 Effect of single component filler on mechanical properties of the system

The Stress-strain relationship of pure epoxy, 4wt.% toughener and 3wt.% gaseous SiO2 are shown in Fig. 1(a). In addition, the effects of the toughening agent or fumed silica content on elongation at break, toughness and the Young's modulus of the epoxy resin composite for the different Filler content investigated are shown in Fig.1(b), Fig. 1(c), Fig. 1(d), respectively.

In Figure 1, the stress-strain curves of pure epoxy and toughened epoxy show typical brittle fracture, which shows that the stress first increases linearly. After slight bending, the sample breaks before reaching the yield point, no necking phenomenon and a large number of cracks are found on the tensile sample, and the fracture mechanism of epoxy resin may be dominated by micro shear deformation[9]. However, the tensile strength and elongation at break of the toughened epoxy
materials have been improved in varying degrees, the area surrounded by the stress-strain curve has increased significantly, and the fracture energy has also increased, indicating that the strength, ductility and toughness of the material have been improved.

![Stress-strain curve](image)

**Figure 1.** (a) Stress strain curve. (b) elastic modulus. (c) Tensile strength. (d) elongation at break of toughener or fumed silica at different weight fractions.

It can be seen from the Fig.1(b)-(d) that, the elastic modulus decreases with increasing toughening agent content, which is not obvious at low content, but rapidly decreases when the toughening agent content exceeds 4wt.%; the elastic modulus increases fastest when the content of fumed silica is less than 1wt.%. The tensile strength and elongation change synchronously. With increasing toughening agent and fumed silica content, both of them increased firstly and then decreased. When the toughening agent content was 4wt.% and fumed silica content was 3wt.%, respectively, the tensile strength increased by 54.22% and 52.46%, and the elongation ratio increased by 89.71% and 46.05%, respectively. When the content of fumed silica is less than 1 wt.%, the properties change most, and the toughening effect of the toughening agent changes more evenly. The effect of toughening agent and fumed silica on tensile strength is similar, but for elongation ratio, the effect of toughening agent is significantly higher than that of fumed silica.

![Microstructure](image)

Fig. 2(a)-(c) show microstructure of fracture surface after tensile test taken by SEM. According to the propagation of fracture, the tensile section of pure epoxy and epoxy containing toughener can be divided into mirror area, mist area and comb area, and the epoxy containing fumed silica is flat and smooth. Only the microstructure of comb like area is shown in the figure. On the section of pure epoxy, the fluvial craze and zigzag structure formed by crack collapse and micro shear zone can be observed. It is a typical section structure of brittle materials. However, in the epoxy cross section containing 4wt.% toughener, the striations and serrations zone are denser and arranged irregularly, and cracks are terminated at the end, which changes the development direction to form fan-shaped structure, and the cross section appears delamination and dimple phenomenon, which indicates that the ductility and toughness of the material are improved to a certain extent. The toughening agent used in this paper is a kind of amphiphilic block copolymer. The liquid precursor of epoxy resin is its selective solvent. One end of the toughening agent molecule is compatible with epoxy resin, and the other end is incompatible with each other to form micelles. It is self-assembled into nano particles in the system, which are fixed by curing cross-linking reaction, Finally, a micro phase separated epoxy resin curing
compound is formed at nanometer scale. As stress concentration, nano elastic particles induce multiple crack to propagate into shear band when the material is under tension. At the same time, the formation of holes and the obstruction of crack propagation are the toughening mechanism of plastic deformation in epoxy matrix. However, when the content of toughening agent increases too much, the island structure of nano particles in the curing system is destroyed, on the contrary, a large number of defects may be generated, which leads to the decrease of the strength and ductility of the material. The elastic modulus of nano elastic particles is lower than that of pure epoxy. When the content of nano elastic particles is lower, the particle size is smaller, so the decrease of elastic modulus is smaller. When the content of nano elastic particles is higher, it may become columnar or layered and other phase separation structures, resulting in a significant decrease of elastic modulus.

Although the cross-section of epoxy containing 3wt.% fumed silica is smooth, the microstructure of epoxy has dense and short irregular stripes and a large number of dimples, and there are small cavities formed by nano particle debonding. Due to its small size, rigid nanoparticles are not suitable for the crack anchor mechanism, which should be similar to the toughening mechanism of nano elastic particles. Rigid nanoparticles initiate and terminate multiple crazes, and the plastic hole growth caused by particle debonding and the shear band of matrix may be the toughening mechanism. The effect of rigid particles on crazing termination is more obvious, so the cross-section fringes are shorter. When the content of fumed silica is small, the silica particles are uniformly dispersed in the epoxy matrix with the original particle size, and the strengthening and toughening effect increases rapidly. When the content of fumed silica is greater than 1wt.%, agglomeration inevitably occurs. At this time, the particle size of nanoparticles increases and the number of nanoparticles increases slowly, so the performance growth slows down. When the content of fumed silica is too high, not only the mechanical defects are produced by agglomeration, but also the viscosity of epoxy mixture is greatly increased and the process performance is reduced.

![Figure 2. SEM micrographs of the tensile fracture surfaces of (a) pure epoxy resin (b) 4wt.% toughener (c) 3wt.% fumed silica](image)

Fig. 3 shows the relationship between the impact strength of epoxy system containing toughener or fumed silica and the filler content. In the range of filler content, the impact strength increases with increasing toughening agent and fumed silica content, and there is no general rule of tensile strength. The impact strength of 4wt.% toughener and 3wt.% fumed silica reached 13.36kJ/m² and 12.24kJ/m² respectively, which increased 33.85% and 22.62% respectively. The different rules of impact strength and tensile strength may be related to the loading mechanism of the two tests.

![Figure 3. Impact strength of toughener or fumed silica at different weight fractions.](image)
3.2 the influence of two-component filler blending on the comprehensive properties of epoxy casting system

It can be seen from the previous section that, the effect of toughening agent and fumed silica on the mechanical properties of epoxy resin is similar but different in quantity, because of the different toughening mechanism of elastic nanoparticles and rigid nanoparticles. In this section, the mechanical properties of epoxy resin are further improved by controlling the total amount of fillers and changing the ratio of two fillers. As shown in table 1, the mechanical properties of all formulations with a total filler content of 4wt.%.

| toughener/fumed silica/wt.% | Young's modulus./GPa | Tensile strength /MPa | elongation at break /% | Impact strength /kJ·m⁻² |
|----------------------------|----------------------|-----------------------|------------------------|------------------------|
| 4/0                        | 1.44                 | 62.07                 | 6.30                   | 13.36                  |
| 3/1                        | 1.56                 | 67.42                 | 6.03                   | 13.69                  |
| 2/2                        | 1.59                 | 56.54                 | 5.69                   | 11.22                  |
| 1/3                        | 1.67                 | 56.48                 | 4.95                   | 12.40                  |
| 0/4                        | 1.72                 | 57.64                 | 4.17                   | 12.16                  |

It can be seen from the table that the elastic modulus of the epoxy resin composite with double fillers increases gradually with the increase of fumed silica and the decrease of toughener, which is consistent with the law obtained in the previous section. The tensile strength of the composite with 3wt.% toughener and 1wt.% fumed silica reached the maximum, even larger than that of the composite with single filler, indicating that the reinforcement mechanism of the two fillers played a synergistic role. However, the tensile strength of the formula with large content of fumed silica decreases sharply, which indicates that the two fillers do not play a synergistic role, but there is a possibility of mutual exclusion in the mechanism when the content of fumed silica is large.

The elongation at break decreases with increasing fumed silica ratio, because the effect of inorganic rigid particles on ductility is not as good as that of toughener. The impact strength shows the same rule as the tensile strength, and it is also the largest when the toughener 3wt.% and fumed silica 1wt.%. A large number of literatures have shown that inorganic nanoparticles and elastomers play a synergistic role in toughening epoxy materials, elastomers have a significant role in improving the toughness and ductility of epoxy materials, while inorganic nanoparticles have a role in strengthening and toughening, while maintaining the heat resistance of the material. The results of S. Balakrishnan [10] show that inorganic nanoparticles are distributed along the interface of elastic particles / epoxy which can promote the deformation of elastic particles to generate internal holes, and play a role of absorbing fracture energy.

The results show that the mechanical properties of epoxy curing system are optimum when the amount of toughener and fumed silica is 3wt.% and 1wt.%.

4. Conclusion

In this paper, alicyclic epoxy resin was selected as basic resin, MeTHPA as curing agent, DBU as accelerator, toughening agent and fumed silica were added respectively to prepare epoxy resin nanocomposite insulation materials. The preparation process and mechanical properties were studied. The conclusions are as follows:

(1) The alicyclic nanocomposite insulating materials toughened by adding toughening agent and fumed silica were used. The tensile strength of the toughening agent and fumed silica reached 62.07mpa and 61.36mpa respectively at 4wt% and 3wt% respectively, which was 54.22% and 52.46% higher than that of pure epoxy. Among them, the elastic modulus of the flexible particles decreased,
while the inorganic rigid particles were the opposite, the impact strength increased monotonously, and reached 13.36kJ/m² and 12.24kJ/m² under the maximum tensile strength addition, which increased 33.85% and 22.62%.

(2) The results show that 3wt.% toughener and 1wt.% fumed silica have synergistic effect. By coordination toughening, the tensile strength and impact strength of the system reach 67.42MPa and 13.69kJ/m², respectively, which are 67.51% and 37.15% higher than those of pure epoxy.

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