Research on EP reinforced by nanoSiO$_2$/Al$_2$O$_3$/ZrO$_2$ and its mechanism

Xu Xuefeng, Cai Yuebo
Nanjing Hydraulic Research Institute, Nanjing, Jiangsu, 210029, China

Abstract: Epoxy resin is modified by nanoSiO$_2$, nanoAl$_2$O$_3$ and nanoZrO$_2$ dispersed by dispersing agent by combining the means of high-speed mechanical stirring and ultrasonic cavitation. It aims at studying the influences of different nanometer-particles types and its dosages on the properties of composite. Research results show that the optimum dosages of nanoSiO$_2$, nanoAl$_2$O$_3$ and nanoZrO$_2$ are 1%, 3% and 5% separately. The tensile strengths of three kinds of composites are similar when it is added by its optimum dosages. The mechanisms of reinforcing epoxy resin caused by nanometer-particles are investigated by combining the SEM.

1. Introduction

It has been proved effective to modify epoxy resin making use of nanometer particles[1][2]. However, different researchers draw different conclusions about the optimum dosages of nanometer particles and its subsequent improvement ranges of mechanical property by using different methods; sometimes, its difference can be very large. Liu Xidong solidifies nanoAl$_2$O$_3$/EP at the temperature of 120℃ for 5 hours; compared with pure EP, its tensile strength has been increased by 12%, impact strength increased by 16%, friction coefficient decreased by 7%. Liu Jingchao concludes that the optimum dosages of nanoAl$_2$O$_3$ is 5% and the tensile strength can be improved by 30%. Hamad[3] studies the mechanical properties of TiO$_2$/EP with different diameters and the result shows that different diameters have their own optimum dosages: to the one of small diameter, its optimum dosage is 3% and the tensile strength can be improved by 14%; to that of large diameter, its optimum dosage is 5% and the tensile strength can be improved by 13%. Li Chaoyang adds 15% nanoSiO$_2$ to epoxy resin and obtains the composite material, nanoSiO$_2$/EP, whose breaking stress is larger than that of yield stress, which shows ductile fracture. In the article, nanoSiO$_2$, nanoAl$_2$O$_3$ and nanoZrO$_2$ are chosen as modified particles separately in the same experimental condition. It aims at studying the epoxy resin’s heightened effect and mechanism brought about by adding different nano particles and its dosage.

2. Test

2.1. Test material

Nano particles used in tests are shown is Table1; E44 epoxy resin: industrial products, Wuxi Lanxing Petrochemical Engineering Co. Ltd.; acetone: industrial products, Beijing Yanshan Petrochemical Engineering Co. Ltd.; 650 polyamide (curing agent, macromolecule prepolymer type): industrial products, Wuxi Lanxing Petrochemical Engineering Co. Ltd.; dispersing agent (coupling reagent) industrial products, Nanjing.
| Crystal form | Particle diameter (Primary particle) | Appearance and color | Producing area |
|--------------|---------------------------------------|----------------------|---------------|
| nano SiO$_2$ sphere | 20 | White, fluffy | Nanjing |
| nano Al$_2$O$_3$ appearance | 40 | White, powder | Nanjing |
| nano ZrO$_2$ Monoclinic | 60 | White, powder | Nanjing |

2.2. Test method
Add nano particles to acetone solution with dispersing agents, disperse it at high speed for 60 minutes and do ultrasonic cavitation for 30 minutes. After that, add certain quantities of epoxy resin, disperse it at high speed for 40 minutes and then add curing agent. Pour it into mould made by us, take it out after 24 hours and cut it into dumbbell-shaped test block (shown as in Figure 1) using special cutter. At normal temperature solidify it for 7 days and solidify it at 60℃for 5 hours. After it has been completely solidified, carry out tensile tests using a tensile machine, as is shown in Figure 2. Its rate of extension is 10mm/min.

3. Test result
In normal condition, to casting body of pure epoxy resin, its tensile strength should be about 45 MPa. In the test, after being codified, its tensile strength is 35.6MPa, a little lower than that of the casting body. It may be caused by the fact that in the test, solvent is not specially removed, but volatilizes naturally and the volatilization might not be complete. As all the tests are carried out in the same condition, it does not affect the research on the tensile strength of epoxy resin by adding nano particles. As is shown in drawing 3-20 after adding three types of nano particles, its tensile strength has been improved. With the increase of nano particles, its tensile strength is increased first, and then decreased, which is the same tendency. To the three types of nano epoxy resin, its maximum tensile strength is similar, 57.8 MPa, 57.5 MPa and 58.2MPa separately and its improved range is 62.4%, 61.5% and 63.5%. However, when it reaches maximum tensile strength, the quantity of nano particles is different. nanoSiO$_2$ can reach its maximum when its mixing amount is 1%, whereas Al$_2$O$_3$ and nanoZrO$_2$ can reach its maximum when its mixing amount is 3% and 5% separately. After reaching its maximum, if continuously add nano particles, its tensile property decreases. When nano particles accounts for 7%, the tensile strength of nanoSiO$_2$/EP and nanoAl$_2$O$_3$/EP is lower than that of pure epoxy resin; the tensile strength of nanoZrO$_2$/EP is similar to that of pure epoxy resin.
4. Mechanism of improving EP by adding nano particles

Mechanism of improving EP by adding nano particles mainly includes two aspects: crazing effect and interfacial effect[4][5][6].

After being intensified by nano particles, when it is hit by outside force, a lot of crazing can be produced between nano particles and epoxy resin, which is also called microcrack. When outside force continuously increases, crazing can absorb a large amount of energy to prevent microcrack from enlarging and its tensile strength can be increased accordingly. A in drawing 4 is the scanning electron micrograph of pure epoxy resin’s stretching section. Its fracture surface is smooth and shows typical brittle rupture, which proves the fragile property of pure epoxy resin in microcosmic way. B in drawing 4 is the scanning electron micrograph of 3% nanoAl₂O₃/EP’s stretching section. Its surface has a lot of crazing and its fracture surface has many deep or shallow grooves. These crazing and grooves can absorb a large amount of energy to enhance its intensity.

Another reason of intensifying epoxy resin by adding nano particles is that a section with special function is produced between epoxy resin and nano particles. Because of nano particle’s own small dimension and surface activity, the interface region can be tightly cohered by nano particles and epoxy resin. When the composite is hit by outside force, the interface region will become a good carrier to transmit force, which can enhance the whole system’s capacity of standing load and be beneficial to improve tensile strength.

The precondition of nano particles’ ability to improve epoxy resin is that nano particles must be evenly dispersed in epoxy resin so as to create enough crazing and effective interface. With the increase of nano particles, crazing also increases and effective interface region enlarges accordingly, reaching an optimal value in the end. At this time, it absorbs external force to its largest capacity and manifests its strongest tensile strength. As is shown in Drawing 4C, crazing caused by nano particles is well distributed in epoxy resin with a smooth interface and good cementation. If continuously add nano particles, due to effect of VDW among nano particles, it leads to the fact that agglomeration of nano particles plays a leading role, which results in the phenomenon that nano particles agglomerate without homodisperse and the number of crazing decreases. Consequently, its strength decreases, as is shown in Drawing 3. In Drawing 4, D is the stretched fracture surface, shown by SEM, of modified epoxy resin with 5% nanoSiO₂. Agglomerated nanoSiO₂ is visible. When the quantity of reach a special value, crazing is not generated, whereas crack occurs. It is shown in Drawing 3 that tensile strength drops drastically, even lower than that of pure epoxy resin. On the other hand, when the quantity of nano particles is higher than that of optimal value and the composite is hit by outside force, carrier of force gradually shifts from the interface region of nano particles and epoxy resin to the action zone of nano particles, which leads to the strength reduction of the composite. In Drawing 4E, when the proportion of nanoSiO₂ is increased to 7%, cracks occur in the interface. F is the enlarged cracks of E.
Different nano particles have different optimal mixed quantities, which may be caused by different diameters of the three nano particles. The optimal mixed quantities of nano particles have connection to the diameters of nano particles; the smaller the diameter is, the larger the surface effect is and the easier it is to cluster together by overcoming steric hindrance from dispersing agents. Consequently, the smaller the diameter, the less the optimal mixed quantities.
5. Conclusion
(1) nanoSiO$_2$, nanoAl$_2$O$_3$ and nanoZrO$_2$ can improve epoxy resin. In the same test condition, the maximum tensile strength of three composite is similar. However, when it reaches its maximum, the content of nano particle is not the same and the optimal content of nanoSiO$_2$, nanoAl$_2$O$_3$ and nanoZrO$_2$ is 1%, 3% and 5% separately.

(2) The mechanism that nano particles can enhance epoxy resin is the effect of crazing and interface. The precondition that nano particles can enhance epoxy resin is due to the face that nano particles can be evenly dispersed in the body of epoxy resin.

Acknowledgement
This work is financially supported by the National Key R&D Program of China (No.2018YFC0406702)

References
[1] Nakamura Y, Yamaguchi M, Okubo M, et al. Effect of particle size on the fracture toughness of epoxy resin filled with spherical silica. Polymer, 1992, 33: 3415–3426.
[2] Kinloch AJ, Mohammed R, Taylor A, et al. The effect of silica nano-particles and rubber particles on the toughness of multiphase thermosetting epoxy polymers. J Mater Sci, 2005, 40: 5083–5086.
[3] Hamad A. Effect of nano TiO$_2$ particle size on mechanical properties of cured epoxy resin. Progress in Organic Coatings, 2010, 69: 241-246.
[4] West R D, Malhotra V M. Rupture of nanoparticle agglomerates, formulation of Al$_2$O$_3$-epoxy nanocomposites using ultrasonic cavitation approach: effects on the structural and mechanical properties. Polymer Engineering and Science, 2006, 46(4): 426-430.
[5] Mahfuz H, Uddin M F, Rangari V K, et al. High strain rate response of sandwich composites with nanophased cores. Applied Composite Materials. 2005, 12(3-4): 193-211.
[6] Sauter C, Emin M A, Schuchmann H P et al. Influence of hydrostatic pressure and sound amplitude on the ultrasound induced dispersion and deagglomeration of nanoparticles. Ultrasonics Sonochemistry, 2008, 15(4): 517-523.