



Study on Toughening Mechanism of Epoxy Adhesive Modified by Nano-SiO₂

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Epoxy resin adhesives are widely used in various sectors, particularly in the aerospace and automotive industries. However, the solidification of the three-dimensional network structure of pure epoxy resin, which causes greater density and brittleness, results in poor system resilience. With the ultimate goal of improving the resilience of epoxy resin, nano-sized SiO₂ particles were introduced to improve the adhesion strength of both modified and unmodified epoxy adhesive. The results indicated increases of shearing strength from 16.66-Mpa to 18.01 -Mpa, impact strength from 15.4 -kJ/m² to 33.68- kJ/m² and flexural strength from 70.5 -Mpa to 80.94 Mpa.

Key Words: Nano-SiO₂, Epoxy resin, Modified.

INTRODUCTION

Epoxy resin is one of the important type of thermosetting resins, which has a wide range of excellent physical and chemical properties, essential for the current technologies and for the development of new technologies, such as increased chemical activity and physical properties^{1,2}. In many industries, epoxy-based adhesives are employed extensively to bond different substrate materials because of their strong adhesion to various treated or untreated metal surfaces³⁻⁵. Polymer composite materials are the most widely used matrix resin. Epoxy resin possesses excellent adhesion, wear resistance, mechanical properties, electrical insulation, chemical stability, resistance to high and low temperature, as well low shrinkage. Nano-composites, with high stiffness and dimensional stabilities can also be used as flame retardant materials⁶⁻⁸.

EXPERIMENTAL

The main laboratory reagents in the present study are the following: Epoxy resin E-44 (DGEBA), nano-SiO₂ [Style: SS1, spherical particles, particle size (30 ± 5) nm, specific surface area (160 ± 20) m²/g, bulk density 0.11 g/cm³, w(hydroxy) = 19 %, UV reflectivity 75 %] and MeTHPA.

A certain percentage of dispersant nano-SiO₂ mixed with the melt mixed, was added to the suspension and stirred. The temperature increase is lower than that solvent mixing. The epoxy adhesive continued to strengthen and stabilized the dispersion of nano-particles after 0.5 h of heating to a higher temperature and then cooled to room temperature after dispersion by the emulsifying machine. As the nano-SiO₂

dispersed into the epoxy adhesive, stirring and heating continued until 80 °C-85 °C, Nano-SiO₂/epoxy adhesive was obtained from the suspension after a 2 h reaction. The uncured nano-SiO₂/epoxy adhesive suspension was mixed in certain proportion with MeTHPA.

RESULTS AND DISCUSSION

One of the important parameters in the molding process is the adhesive forming temperature. The development of curing temperature can be based on DSC curve. However, the simple curve makes it difficult to determine the use of a heat-curing temperature because the heating rate will be different for each curing temperature, whereas the use of T-β approximation can be obtained by extrapolation of the curing temperature⁹. Fig. 1 shows the DSC curves under different heating rates. Furthermore, Table-1 shows the corresponding characteristic temperature.

T-β fit straight lines, representing the three linear extrapolation to β = 0, can be deduced from the data in Table-1 (Fig. 2). The gel temperature (T_{gel}), curing temperature (T_{cure}) and post-processing temperature (T_{post}) are 86, 132 and 179 °C, respectively. The temperatures of 100 °C and 150 °C were selected as basis for the temperature-curing step.

Changes in mechanical properties of epoxy adhesive were examined by changing the m (nano-SiO₂) i.e., m (Toughening) ratio: Table-2 shows that, the addition of nano-SiO₂ improved the epoxy adhesive bending shear and impact strengths. Epoxy adhesive intensity increased with the approaching accession toughening phase, indicating the positive toughening effect of nano-particles.

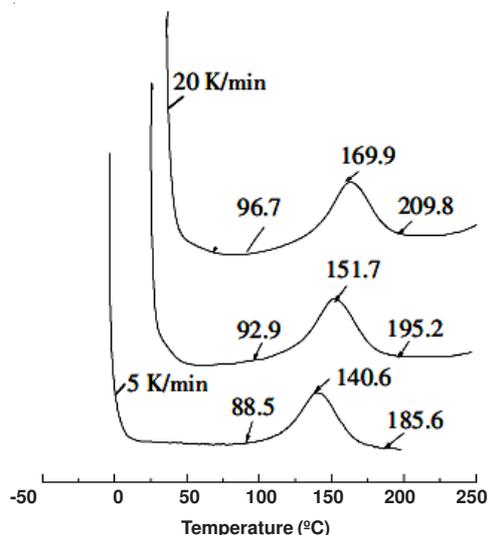


Fig. 1. DSC curves of adhesives at different heating speeds

Heating rate (K min ⁻¹)	T _i (°C)	T _p (°C)	T _f (°C)
5	88.6	140.5	186.6
10	92.8	151.7	196.2
20	96.6	169.9	209.7

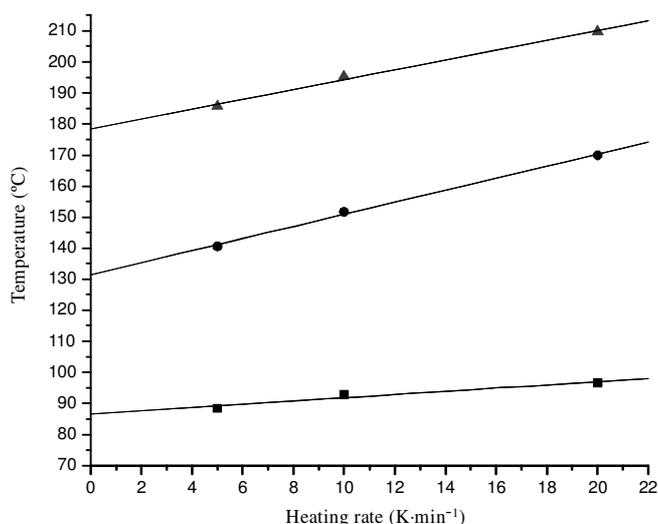


Fig. 2. Fitting beelines between temperatures-heating speeds

m (Nano-SiO ₂): m (toughening)	Shear strength (MPa)	Impact strength (kJ·m ⁻²)	Bending strength (MPa)
0:0	16.66	15.4	70.5
0:15	18.01	18.42	-
3:0	17.15	23.38	78.58
3:15	-	33.68	85.94

Fig. 3 shows the epoxy adhesive adhesive after curing the FT-IR curving. The characteristic absorption peak of epoxy adhesive has almost disappeared, indicating the completed reaction of cured epoxy adhesive.

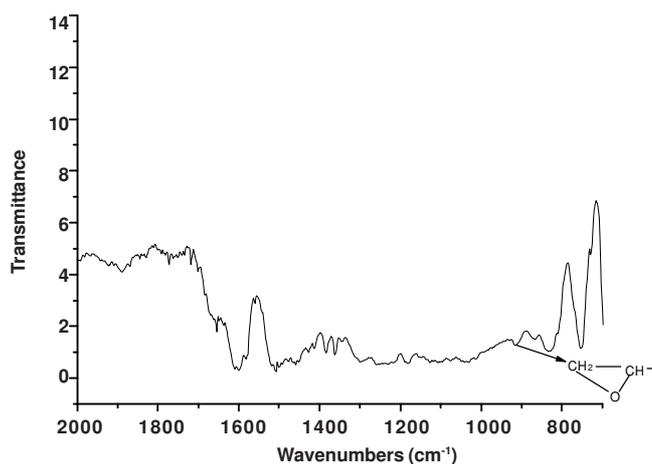


Fig. 3. FT-IR curves of cured epoxy adhesive adhesives

In the traditional model of crazing, two key factors affecting the results, the generation of crazes and the timely suspension of crazing, prevent macro-cracking. When the nano-particle/polymer matrix composites are subjected to external shocks, the small size of nano-particles leads to more silver patterns that can absorb large amounts of impact energy (higher surface activity of nano-particles, with the force between the matrix resin) and more importantly, prevent the silver nano-particles with a grain cracking function (Fig. 4).

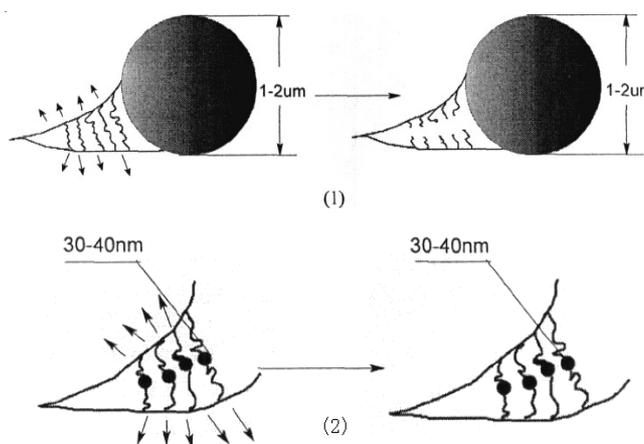


Fig. 4. Action mechanism of epoxy adhesive toughened by nano-particle

The width of the crazing in ordinary rigid particles/polymer composites is usually between 50 nm to 500 nm (Fig. 4). The silver grain is produced on the particle surface and the absorbed impact energy is mainly use to pull off the silver pattern and fill the polymer-based micro-fiber. The nano-particles/polymer composites in the silver nano-particles exist in the pattern when the nano-particles size is less than 100 nm and the high activity of nano-particles is due to surface crazing and is connected on both sides of the function.

The cross-section SEM images of impact specimens are shown in Fig. 5. The cross section of pure epoxy adhesive is relatively smooth upon impact. With the addition of nano-SiO₂, the impact fracture increased significantly at the torn edge and a number of degumming particles can be observed. The nano-SiO₂/epoxy adhesive fracture system is larger than the

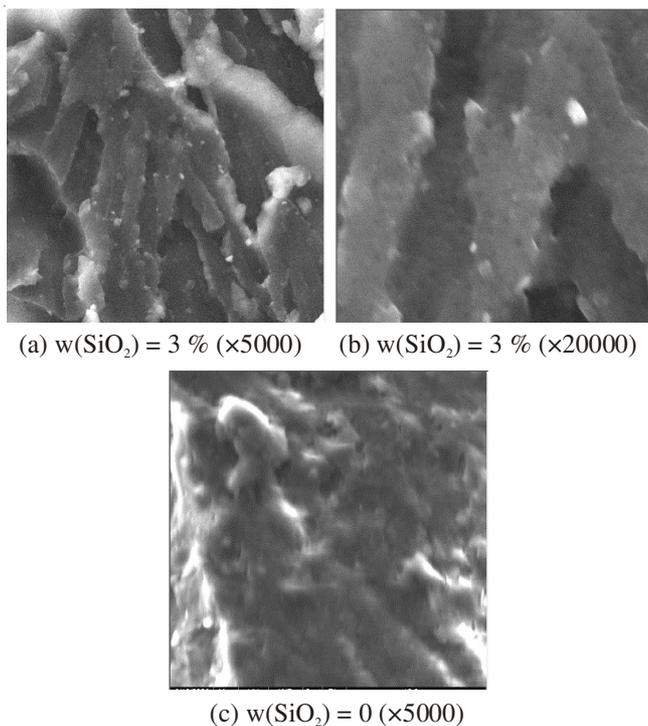


Fig. 5. SEM photos of nano-SiO₂/epoxy adhesive adhesives

pure epoxy adhesive system and the cross section at a larger relief. When $w(\text{nano-SiO}_2)=3\%$, the impact occurring at these tiny holes are embossed.

Conclusion

The epoxy adhesive matrix resin mixed with nano-SiO₂ achieves both the physical keys and chemical bonds to enhance

epoxy adhesive toughness. The dispersion of nano-particles further resulted in process improvements, where nano-particles can be dispersed in the epoxy adhesive matrix resin and be expected to further improve the nano-SiO₂/epoxy adhesive matrix composite mechanical properties. The carboxyl group, which was utilized to improve the adhesion of a commonly used epoxy adhesive coating¹⁰, showed the highest interaction with metal compared with other functional groups^{11,12}. The mechanisms responsible for adhesion were highly complex because they depended upon the simultaneous action of different factors. In the present study, one of the most important factors for adhesion improvement was new polar functional group.

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