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Effects of Water-Heat Water Aging on Epoxy Composites Containing Nano-Particles of ZnO

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***Abstract*—In this work, different weight percentages of Nano-ZnO were added to epoxy resin to enhance its strength and the water aging property. Meanwhile, the wear testing was using to evaluate the adhesive strength between the Nano-ZnO and epoxy resin. The composites were placed in a water bath at 80 ℃ for more than 100 days to accelerate the aging process. Using the strength reduction of the composite to characterize the aging properties. The results showed that the suitable addition of Nano-ZnO may effectively improve the strength of the composites, and reduce the strength loss of the composites caused by wet and heat aging. Under the water-heat environment, besides the strength of the epoxy resin, the interface bonding strength between the Nano-ZnO and the matrix resin was also reduced.**

Keywords-nanoparticles; epoxy resin; water absorption; wear

I. INTRODUCTION

Epoxy resin plays a very important role in the the coating, adhesive, and composite material industries, because of its high strength, high modulus, and advantages of excellent dimensional stability and corrosion resistance[1-4]. However, epoxy resin has some disadvantages, such as poor wear resistance and low weather fastness et al., which were limited its further application[5-10]. Epoxy resins can easily absorb water from their surroundings due to the three-dimensional network structure, resulting in decreased performance[11-16].

This work aims to discuss the effects of water aging on epoxy composites containing nano-particles of ZnO. The specimens were placed in 80 ℃ water for more than 100 days to accelerate the aging process. The loss of strength of the composite, as calculated from the tensile strength before and after water-heat aging, was used to characterize the aging degree of the composite. By comparing the worn surface morphology of the composites before and after aging, the influence of water aging on the adhesion between the Nano-ZnO and the resin was analyzed. This work provides a reference for further experimental research and application.

II. MATERIALS AND METHODS

A. *Materials and sample preparation*

The epoxy resin, produced by Wuxi Resin Co., Ltd, Wuxi, China, which epoxide equivalent is 0.44. The hardener used in this work was diethylenetriamine (H2NCH2CH2NHCH2CH2NH2), which also supplied from Wuxi resin Co., Ltd, China. The resin and hardener were mixed at a volume ratio of 100:8. Nano-ZnO particles were supplied by McLean biochemical technology co., LTD (Shanghai, China) and had a particle size of 30±10 nm. Epoxy resin was placed in a vacuum drying chamber to remove any air bubbles at room temperature. Nano-ZnO particles were dried in an oven at 80 ℃ to remove the absorbed water. Then, the dry Nano-ZnO particles were dispersed in isopropanol using a ball-milling technique.

The Nano-ZnO/isopropanol dispersion was added slowly to the bubble-free epoxy resin. The mixture was stirred slowly using a magnetic stirrer to avoid the formation of air bubbles within the sample. Subsequently, the mixture was placed in a vacuum drying chamber to remove the isopropanol until it was fully volatilized. Then, the different weight percentages (5 wt. %, 10 wt. %, 15 wt. %, and 20 wt. %) of Nano-ZnO/epoxy resin mixtures were obtained. The hardener was added to the mixture and slowly stirred until no layering occurred. Finally, the mixture with Nano-ZnO particles was injected into the mold. The composite was cured for 24 h at room temperature and post-cured at 80 ℃ for 4 h.

B. *Characterization*

1) *Water absorption*

The specimens were placed in a water bath at 80 ℃ for 105 days. An electronic balance with 0.1 mg accuracy was used to measure the weight of the composites. Before weighting, the specimen should be dried with filter papers. The equation used to calculate the absorption rate (Mt) is as follows:

$$M_t = \frac{W_t - W_0}{W_0} \times 100\% \qquad (1)$$

where W_0 is the initial weight, W_t is the weight of the sample after an immersion time *t*.

2) *Tensile strength*

A universal mechanical testing machine was used to test the tensile strength of the composite before and after aging at room temperature, with 0.5 mm/min displacement rate. The average value of the tensile strength was obtained by measuring three different specimens for each group. The strength loss rate was calculated using the following equation:

$$\eta = \frac{\sigma - \sigma_0}{\sigma_0} \times 100\% \quad (2)$$

where σ0 is the strength of the unaged sample, σ is the strength of the aged sample and η% is the strength loss rate.

Wear test

Friction tests were carried out using a high-temperature scratch testing machine against a steel bearing ball with a radius of 5 mm and a hardness level of HRC62. The applied load was 14 N, the rotation speed of the ball was 200 rpm, and the sliding radius was 9 mm. The specific wear rate was calculated using the following equation:

$$I = \frac{V}{t \times F} \quad (3)$$

where V is the wear volume (cm3), t is the wear time (min), F is the applied load (N), and I is the specific wear rate (cm3/min·N). By comparing the worn surface morphology and specific wear rate of the composites before and after aging, the adhesion between the Nano-ZnO and matrix resin was analyzed.

III. RESULTS AND DISCUSSION

A. *Water absorption*

Water absorption treatment was carried out by placing specimens with different weight percentages of Nano-ZnO in a water bath at 80 ℃ for more than 100 days. Figure 1 is the curve of water absorption for composites with different weight percentages of Nano-ZnO.

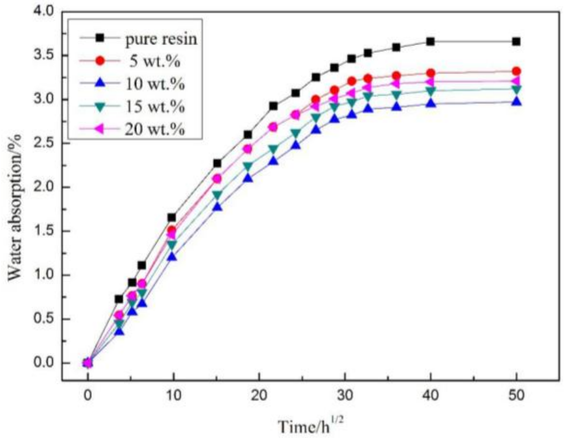


Figure 1. The water absorption curve of composites with different weight percentages of Nano-ZnO.

Figure 1 shows a linear relationship between the water absorption of all composites and the square root of the immersion time ($\sqrt{h}$) when $\sqrt{h} \leq 30$. This stage belongs to the Fickian domain. The dates of this stage can be used to calculate the diffusion coefficient (D). When $\sqrt{h}$ was longer than 32.7, the absorption rate of all specimens basically remained constant over time. This stage is called the non-Fickian domain.

At the Fickian domain, the composites with different weight percentages exhibited a similar trend. Using a simplified Fickian diffusion equation, as shown below, the diffusion coefficients of the specimens were obtained.

$$I\phi \ \frac{m_t}{m_\infty} \leq 0.6 \ , \ \frac{m_t}{m_\infty} = \frac{4}{e}\sqrt{\frac{Dt}{\pi}} \quad (4)$$

where mt is the absorbed mass at time t; m∞ is the mass uptake at saturation, e is the thickness of the specimen, and D is the diffusion coefficient. Diffusion coefficients were calculated for each water absorption curve and are shown in Table 1.

TABLE I. THE DIFFUSION COEFFICIENT AND THE SATURATED ABSORPTION RATE OF THE COMPOSITE WITH DIFFERENT WEIGHT PERCENTAGES NANO-ZNO

Content	Pure resin	5 wt.%	10 wt.%	15 wt.%	20 wt.%
Diffusion coefficient *D* (×10^{-6} mm^2/s)	4.2	3.3	2.4	2.9	3.5
Saturated absorption rate (%)	3.7	3.3	2.9	3.1	3.2

Table 1 shows that the diffusion coefficient and saturated absorption rate of specimens with Nano-ZnO were all less than those of pure resin. Moreover, as the Nano-ZnO content increased, the diffusion coefficient initially decreased to a minimum value of 2.4×10-6 mm2/s at the content of 10 wt. %, after which it increased. The saturated absorption rate of the composite exhibited the same variable trend with the increase of Nano-ZnO content. When the Nano-ZnO content was 10 wt. %, the saturated absorption reaches the minimum value 2.9%. This result indicates that the addition of Nano-ZnO can effectively decrease both the diffusion rate and the saturated absorption rate of the epoxy resin composite.

Compared with the pure resin, the saturated absorption rate of the composite with 5 wt. %, 10 wt. %, 15 wt. %, and 20 wt. % content was decreased by 11%, 18%, 15%, and 14%, respectively. For the specimens with 5 wt. % and 10 wt. % contents, the percent reduction of saturated water absorption was larger than its volume of addition. It is generally known that Nano-ZnO has a larger specific surface. There are more uncoordinated atoms and misshapen chemical bonds on its specific surface. These give the Nano particles a higher chemical reactivity compared to the micron particles. When Nano-ZnO is well dispersed in epoxy resin, it can generate hydrogen bonds with more polar groups in the resin, thereby reducing the concentration of active polar groups in the epoxy resin. Thus, the diffusion coefficient and saturated absorption rate of the composite were effectively reduced. Moreover, when Nano-ZnO was added to the epoxy resin, the water could diffuse through the interface between the particles and resin but not through the particles directly. The more tortuous pathway created for water molecules to diffuse into the resin effectively reduces the diffusion coefficient. When the addition of Nano-ZnO was increased to more than 15 wt. %, the particles were prone to aggregate, thus enhancing the saturated absorption rate and diffusion coefficient of the composites.

B. Tensile strength

Figure 2 shows the tensile strength of the composite before and after water-heat aging. The strength loss rate was calculated according to equation 2, as shown in Figure 2. The aged specimens had been placed in distilled water at 80 ℃ for 105 days to ensure that they were saturated.

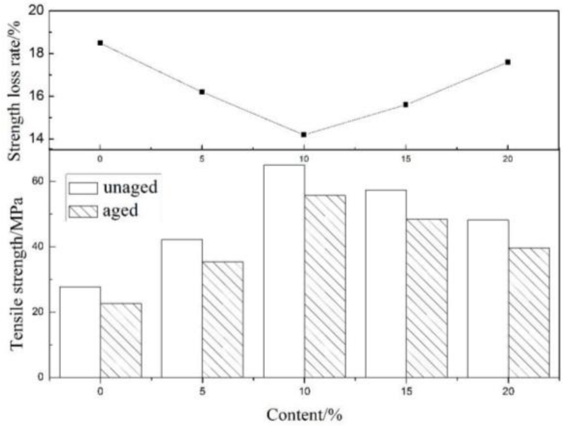


Figure 2. The tensile strength and strength loss rate of the composite with different weight percentage of Nano-ZnO.

For the unaged composite, when Nano-ZnO was less than 10 wt. %, the tensile strength increased with the increase in Nano-ZnO. The tensile strength reached its maximum of 65.0 MPa at the weight content of 10 wt. %, which was 135 % higher than that of the pure resin (27.7 MPa). Thereafter, with the Nano-ZnO content increasing to more than 10 wt. %, the tensile strength began to decrease but was still higher than that of the pure resin. Therefore, when the additive amount was small (≤ 10 wt. %), the strength of the composite was increased because the Nano-ZnO was evenly dispersed in the epoxy resin (particle-reinforced). When the additive amount was more than 10 wt. %, the Nano-ZnO particles easily agglomerated in the resin. Under external force, the agglomerate became the stress concentrative point, causing it to easily separate from the matrix resin, which decreased the strength of the composite.

After water-heat aging, the tensile strength of the composite was significantly lower than that of the unaged composite. With increasing Nano-ZnO content, the strength loss rate decreased initially and then increased, reaching its minimum, 14.2 %, at the addition of 10 wt. % Nano-ZnO. In a wet and hot environment, water molecules penetrated from the surface and gradually diffused into the interior of the sample, causing local swelling in the resin, thereby destroying the hydrogen bonding between the long-chain molecules. By this mechanism, the internal structure of the composite was changed, and the strength of the composite was reduced. The addition of Nano-ZnO could effectively slow the diffusion rate of water molecules into the composite and reduce its saturated water absorption, thus decreasing the effects that the water molecules had on the material structure. Therefore, Nano-ZnO enhances the strength of the composite material and reduces the rate of aging.

C. The wear resistance

A high-temperature scratch testing machine was used to test the wear resistance of the composite before and after aging. The aged specimens were placed in distilled water at 80℃ for 105 days to ensure that the specimens were saturated. Figure 3 and Table 2 show the friction coefficient as a function of time for the composite and average friction coefficients, respectively.

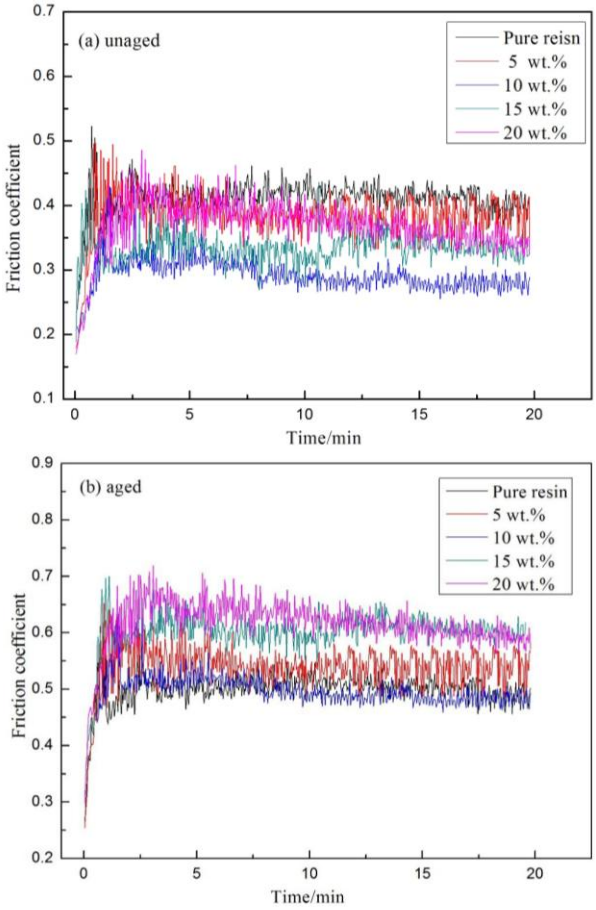


Figure 3. The friction coefficient curve of composites with different weight percentages of Nano-ZnO.

TABLE II. THE AVERAGE FRICTION COEFFICIENT OF COMPOSITES WITH DIFFERENT WEIGHT PERCENTAGES OF NANO-ZNO

Content (wt.%)	Average friction coefficient	
	unaged	aged
Pure resin	0.415	0.504
5wt.%	0.378	0.533
10wt.%	0.283	0.538
15wt.%	0.334	0.556
20wt.%	0.345	0.592

For the unaged composite, the friction coefficient of the composite first decreased and then increased with increasing Nano-ZnO content. After water-heat aging, the friction coefficient increased significantly compared to the unaged composite. Additionally, the friction coefficient of unaged composite was increased with Nano-ZnO content.

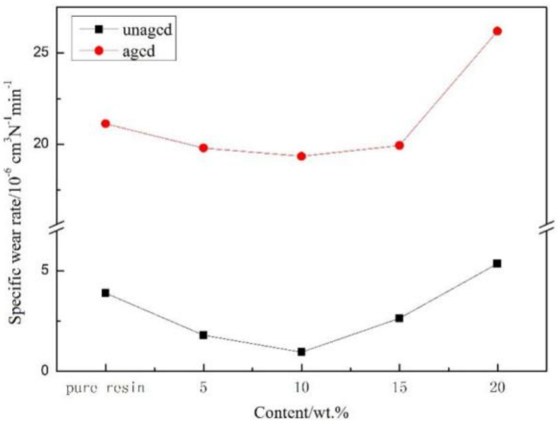
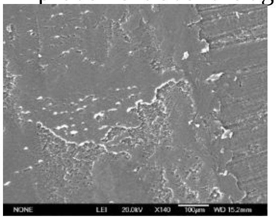
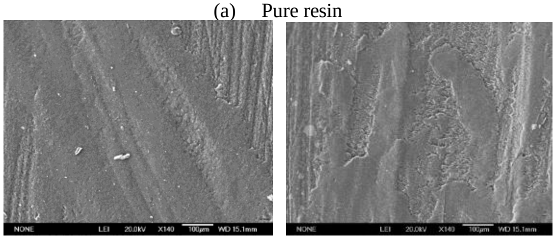


Figure 4. The specific wear rate of the composite with different weight percentage of Nano-ZnO.

Figure 4 shows the specific wear rate of the composite. The specific wear rate of the unaged composite first decreased and then increased with the content of Nano-ZnO. The specific wear rate reduced to its minimum value, 1×10-6 cm3/(N·min), when the Nano-ZnO content was 10 wt. %. With the Nano-ZnO amount increasing to 15 wt. %, the specific wear began to increase. Meanwhile, the specific wear of the composite with 20 wt. % Nano-ZnO was substantially higher than that of the pure resin. After water-heat aging, the specific wear of the composite was substantially increased. The specific wear of the aged composite was stable at approximately 2×10-5 cm3/(N·min) when the addition was 5~15 wt.%, which was slightly smaller than that of the aged pure resin. When the addition of Nano-ZnO increased to 20 wt. %, the specific wear of the aged composite rapidly increased to 2.6×10-5 cm3/(N·min), which was a 24 % improvement over the aged pure resin.



(a) Pure resin

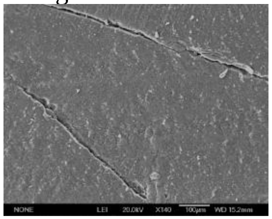


(b) 5wt. %; (c) 15wt. %

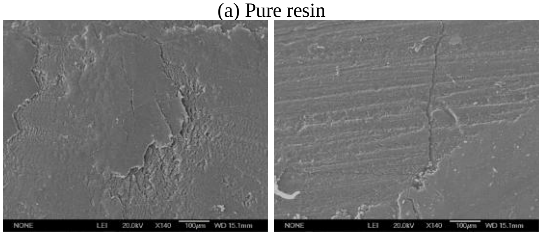
Figure 5. Micrographs of wear tracks on the composite before aging.

Figures 5 and 6 present the micrographs of wear tracks on the composite before and after aging. There were a lot of scratches and delamination on the unaged pure resin (Figure 5 a). Compared with pure epoxy resin, adding 5 wt. % Nano-ZnO made the wear tracks appear relatively smooth. There were no large-area spalling phenomena, except for small amounts of shallow furrows (Figure 5 b). With the Nano-ZnO amount increasing to 20 wt. %, there were some deep gullies on the surface. The surface damage was serious (Figure 5 c).

The above analysis shows that when the Nano-ZnO was added in low level, at the beginning of the sliding friction, the Nano-ZnO particles were gradually exposed to the surface along with the ongoing sliding friction. As an inorganic non-metallic material, the hardness and strength of Nano-ZnO are higher than those of the epoxy resin. Nano-ZnO has played the role of bearing loads in composite materials and protecting the wear surface effectively. That is the reason that adding Nano-ZnO can reduce the sliding shear forces during sliding, protect the substrate material, reduce the wear surface damage and delamination, and effectively enhance both the resistance to friction and wear properties of epoxy resins. When the Nano-ZnO content is high, the ZnO aggregates become first stress concentration points, causing it to be easily stripped out of the resin. The loose particles are abrasive and have a higher hardness than do epoxy resins, leading to an increase in the wear rate.



(a) Pure resin



(b) 5wt. % (c) 15wt.%

Figure 6. Micrographs of wear tracks on the composite after aging.

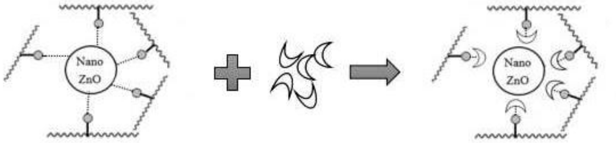


Figure 7. Destruction of secondary links between Nano-ZnO and matrix resin by water molecule diffusion.

After long periods of immersion, deep and wide cracks were easily observed on the wear track of pure resin (Figure 6 a). These occurred because the strength of epoxy resin dropped after water-heat aging. Under the action of shear force, cracks were easily formed in the aged resin, and the energy needed for crack propagation of aged resin was lower than that of the unaged resin. For the composite with Nano-ZnO in low level, after a long aging time, there also have many small cracks and furrows on the wear track. This is due to the water, which were diffusion to the juncture between the nano particles and matrix resin from, destruct the secondary links between Nano-ZnO and matrix resin, reducing the interface bonding strength. Thus, the Nano particles were easy to striping off from the resin, failing to enhance the strength of epoxy resin. Above knowable, under the water-heat environment, besides the strength of the epoxy resin, the interface bonding strength between the Nano-ZnO and the matrix resin was also reduced.

IV. CONCLUSIONS

In this work, Nano-ZnO particles were added to epoxy resin. The water absorption, strength and wear resistance before and after water-heat aging were tested and researched. The results show the following:

The diffusion coefficient of the composite first decreased and then increased with the addition of Nano-ZnO composite. It reached its minimum value at 2.4×10-6 mm2/s when the Nano-ZnO content was 10 wt. %. For unaged composite, when Nano-ZnO ≤ 10 wt. %, the tensile strength increased with the increase of Nano-ZnO. Then, the tensile strength reached the maximum 65.0 MPa at a weight content of 10 wt. %. With the Nano-ZnO content increasing to more than 10 wt. %, the tensile strength began to decrease. After water-heat aging, the tensile strength loss rate first decreased and then increased with the increasing Nano-ZnO content.

The specific wear rate and friction coefficient of the unaged composite first decreased and then increased with the increasing Nano-ZnO content. The specific wear rate and friction coefficient reached their minimum values, 1×10-6 cm3/(N·min) and 0.335, respectively, when the Nano-ZnO content was 10 wt. %. After water-heat aging, the specific wear of the composite was substantially increased. Adding Nano-ZnO can effectively prevent long perfoliate cracks from forming and propagating. In addition, the interface bonding strength between the Nano-ZnO and the matrix resin was also reduced by the water.

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