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Research Article

Mechanical Properties of the Epoxy Resin Composites Modified by Nanofiller under Different Aging Conditions

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The effects of aging conditions on the mechanical properties of epoxy resin (EP) with halloysite nanotube (HNT) were studied. The aging conditions include soaking in water at various temperatures, soaking in acid solution, soaking in alkali solution, thermal shock cycling (TSC), and soaking coupled with subsequent thermal shock cycling (i.e., composite aging conditions). Under aging conditions, the EP is degraded, plasticized, and swelled, resulting in different degrees of cracks and pores in EP. The tensile and bending properties of EP and HNT/EP nanocomposites decreased after aging, indicating that the durability of the EP decreased under aging conditions. The addition of HNT could improve the immersion aging resistance and delay the immersion aging behavior of EP. Under TSC conditions, the reduction in mechanical properties of HNT/EP nanocomposites with HNT is slightly more than that of the neat EP due to different thermal expansion coefficients between HNT and EP. The fracture morphology and chemical change were studied to reveal the aging degradation mechanisms in the presence of HNT addition.

1. Introduction

Epoxy resin (EP) is a typical cross-linked thermosetting polymer material, which has many outstanding advantages, such as good mechanical properties, strong stability and bonding ability, low shrinkage, excellent heat resistance, chemical resistance, and fire-retardant [1–5]. Therefore, it is widely used in the field of surface coating, adhesives, composite manufacturing, civil engineering, etc. [6–9]. However, the performance of EP is degraded in harsh environments, including humidity, high-temperature, hygrothermal, and radiation conditions, which decreases their lifetime and durability [10–13].

The hygrothermal aging condition has strongly deteriorated the mechanical performance of the EP [9–14]. Under the hygrothermal aging condition, EP will absorb water, leading to the deterioration in the physical and chemical properties of the resin because of hydrolysis, plasticization, and matrix swelling [2, 9–13]. To reduce the damage and deterioration of the resin in a hygrothermal environment, some nanofillers are used, such as carbon nanotube (CNT), graphene nanoplatelet (GNP), graphene oxide (mGO), nanoclay, and nano-silicon carbide (n-SiC) [11–14]. Nanoclay is one of the commonly used nanofillers to improve multiple properties of the EP because of its low cost, high aspect ratio, unique chemical properties, high mechanical properties, and thermal stability [15, 16]. Halloysite nanoclay is from silicate minerals and is also named halloysite nanotube (HNT) due to its hollow nanotube structure [17, 18]. Due to its excellent properties, HNT is widely used in the research of composite materials [19, 20]. Previous research work shows that the addition of HNTs into polymers can significantly enhance mechanical properties, which improves the tensile strength, flexural strength, and durability of EP, and delay the degradation behavior of the EP in a humid environment [21–24].

The aging behavior of resin composites is related to several variables, such as temperature, corrosion medium, additives, and aging time [22–27]. Uthaman et al. [14] considered the effects of water and acid solutions at different

temperatures on the properties of EP. The reduction in tensile strength of the resin is depending on the soaking time and temperature, and a long soaking time and high temperature accelerate the aging behavior. Shettar et al. [23] studied the effect of thermal shock cycling (TSC) on the properties of EP. Under the condition of TSC, the tensile strength of neat EP was reduced by 6%-11%, and the bending strength decreased by 8%-15%. The tensile strength and bending strength of EP added with nanoclay decreased by 7%-13% and 9%-17%, respectively. It can be attributed to stress formation at the nanoclay/epoxy interface due to the mismatch coefficient of thermal expansion, and therefore, the addition of nanoclay is not helpful to improve aging resistance under thermal shock cycling (TSC) conditions. Ulus et al. [26] investigated the effect of the addition of halloysite nanoclay on the properties of the resin in a saltwater environment. They found that after 6 months of aging, the tensile strength and flexural strength of neat EP decreased by about 37.4% and 41.9%, respectively, while the tensile strength and flexural strength of EP with halloysite nanoclay decreased by about 28% and 35.1%, respectively.

Although some studies have investigated the aging behavior of resin composites under hygrothermal and thermal shock cycle conditions, there is little research on coupled aging factors, e.g., a combination of soaking aging and thermal shock cycle; therefore, the effects of single condition aging and coupling aging on the mechanical properties of neat EP and HNT/EP nanocomposites were investigated. The accelerated aging conditions were set as water soaking (20°C, 40°C, and 60°C), thermal shock cycling (TSC), and soaking coupled with subsequent thermal shock cycling (composite aging). The degradation in mechanical properties under these conditions was studied to obtain a comprehensive understanding of the effects of the aging condition and nanofiller on EP in a variety of applications.

2. Materials and Methods

2.1. Preparation of Composites. The materials used were commercially available bisphenol-A EP (Yehao Co., Ltd. Wuxi, China), JD-230 curing agent (Qiwei Chemical Co., Ltd. China), and halloysite nanotubes (HNTs, Mingchuag Technology Co., Ltd. China).

For the preparation of neat EP and its composites, mix EP and curing agent and stir for about 30 minutes. Then, the mixture was made available for a vacuum drying oven to remove bubbles, and then, the resin composites were poured into the mold. Afterward, in the curing process, a two-step curing process was used for a total of 5 hours, and then, the composites were cooled to room temperature.

For the preparation of HNT/EP nanocomposites, HNTs were ultrasonically dispersed in 50 ml acetone, and the HNT acetone dispersion was added to that appropriate amount of EP to obtain 2 wt.% content in a beaker under stirred effect for 3 h. And then, the mixture was put into a vacuum drying oven to remove bubbles. Afterward, in the curing process, a two-step curing process was used for a total of 5 hours, and then, the nanocomposites were cooled to room temperature.

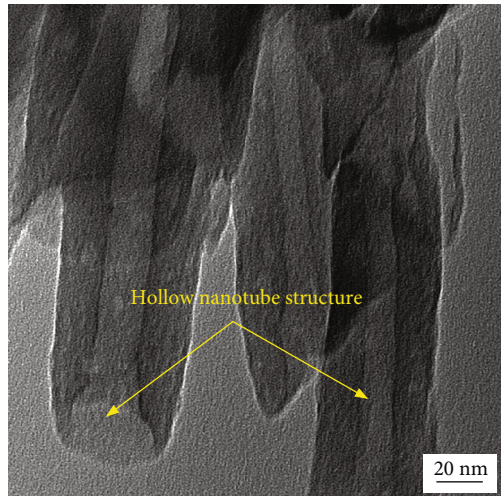

Figure 1: TEM image of halloysite nanotube (HNT).

2.2. Aging Tests. Neat EP and HNT/EP nanocomposites were soaked in deionized water at different temperatures (20°C, 40°C, and 60°C), HCl solution (5 wt.%) at 20°C, and NaOH solution (10 wt.%) at 20°C for 720 h. These conditions are generally applied in some aging tests reported in previous studies [14, 28].

Sudden temperature changes of neat EP and HNT/EP nanocomposites from the hot chamber (100°C) for about 7 min to the cold chamber (0°C) for about 3 min were applied, and the thermal shock cycling (TSC) was repeated 100 cycles, which is similar to TSC test reported in previous studies [29, 30].

Composite aging conditions were combined soaking condition with TSC condition. The samples are firstly soaked in deionized water, HCl solution, and NaOH solution at 20°C, and then, they are dried and employed in TSC for 100 repeated times.

2.3. Mechanical Test and Characterization. The tensile test is carried out by the universal material testing machine (MTS810, USA), and the test rate is 2 mm/min. Referring to GB/T2567-2008, the resin casting was machined in the appropriate size. To ensure the accuracy of the data, the experiment was repeated five times, and the calculated average value was used in this study.

The three-point bending test was carried out by the universal testing machine; the test speed is 2 mm/min. To ensure the accuracy of the experimental results, five parallel data for each experiment condition were calculated to obtain the average value in this study.

Fourier transform infrared spectroscopy (FTIR, Thermo Scientific, Waltham, MA, USA) was conducted to estimate the chemical structure change of neat EP and HNT/EP nanocomposites arranged from 500 to 3700 cm^{-1} with a resolution of 4 cm^{-1}. A Q2000 differential scanning calorimeter (DSC) was used to measure the glass transition temperature (Tg) of the sample at a rate of 10°C/min.

A scanning electron microscope (SEM, Evo-18 Zeiss, Oberkochen, Germany) was used to observe the fracture surface of the samples. The failure modes of EP and its

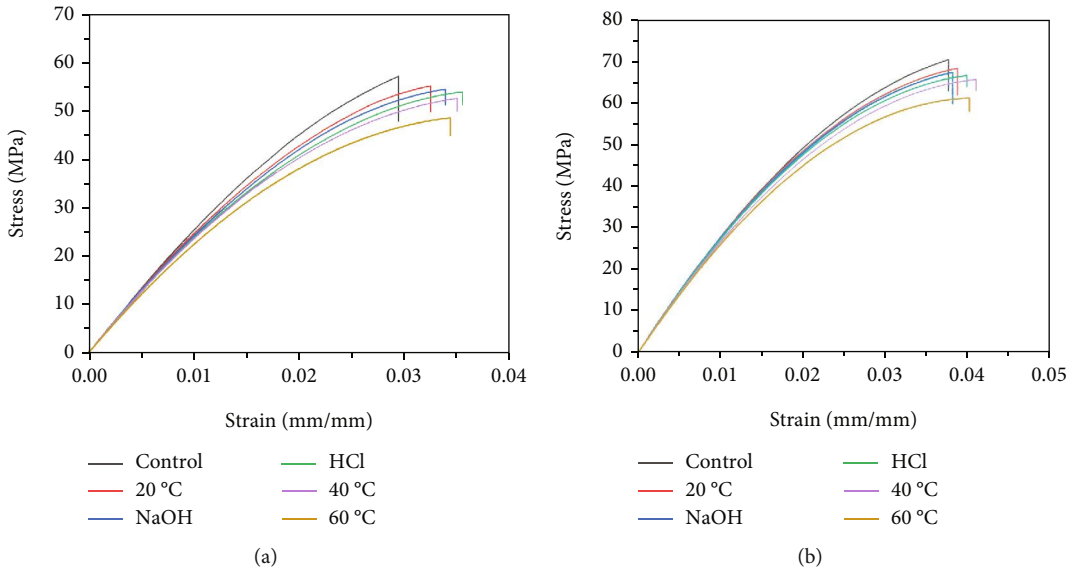

Figure 2: Tensile stress-strain curves of (a) neat EP and (b) HNT/EP nanocomposites under different immersion aging conditions.

Table 1: Tensile properties of EP under different soaking and aging conditions.

Sample	Mechanical properties	Control (dry condition)	Water soaking at 20°C	Water soaking at 40°C	Water soaking at 60°C	HCl soaking at 20°C	NaOH soaking at 20°C
Neat EP	Tensile strength (MPa)	57.23 ± 2.31	55.26 ± 1.37	52.71 ± 1.89	48.68 ± 2.24	54.04 ± 2.43	54.62 ± 1.98
	Tensile modulus (GPa)	2.69 ± 0.13	2.64 ± 0.10	2.57 ± 0.08	2.46 ± 0.09	2.61 ± 0.06	2.63 ± 0.07
EPs with nanoclay	Tensile strength (MPa)	70.61 ± 2.97	68.46 ± 2.39	65.78 ± 1.74	61.32 ± 2.11	66.74 ± 3.16	67.49 ± 2.55
	Tensile modulus (GPa)	3.07 ± 0.13	3.02 ± 0.15	2.94 ± 0.08	2.82 ± 0.11	2.99 ± 0.09	3.03 ± 0.05

Table 2: Tensile property reduction (%) of the sample under different immersion aging conditions.

Sample	Mechanical properties	Water immersion at 20°C	Water immersion at 40°C	Water immersion at 60°C	HCl immersion at 20°C	NaOH immersion at 20°C
Neat EP	Tensile strength	3.44	7.90	14.94	5.57	4.56
	Tensile modulus	1.86	4.46	8.55	2.97	2.23
EPs with HNT	Tensile strength	3.04	6.84	13.16	5.48	4.42
	Tensile modulus	1.63	4.23	8.14	2.61	1.30

composites can be analyzed by SEM image. A transmission electron microscope (TEM, TECNAI F20, Hillsboro, OR, USA) was used to observe the microstructure morphology of the halloysite nanotube (HNT).

3. Results and Discussion

3.1. Structure and Morphology of Halloysite Nanotube. Figure 1 shows the TEM image of the halloysite nanotube (HNT). HNT is a kind of clay mineral. It can be seen that the HNT is a hollow nanotube structure with an outer diameter of about 30-50 nm and an inner diameter of about 1-30 nm. Previous studies revealed that the addition of HNT can significantly improve the mechanical properties of EP, partly due to its high aspect ratio [18, 21, 22].

3.2. Tensile Properties under Immersion Aging Conditions. Figure 2 shows the tensile curves of neat EP and HNT/EP nanocomposites under different conditions. Tables 1 and 2, respectively, show the tensile properties and the reduction (%) of tensile properties of EP under different soaking and aging conditions. As shown in Figure 2(a), the tensile strength and tensile modulus of neat EP in the dry state were 57.23 MPa and 2.69 GPa, respectively. The tensile strength of

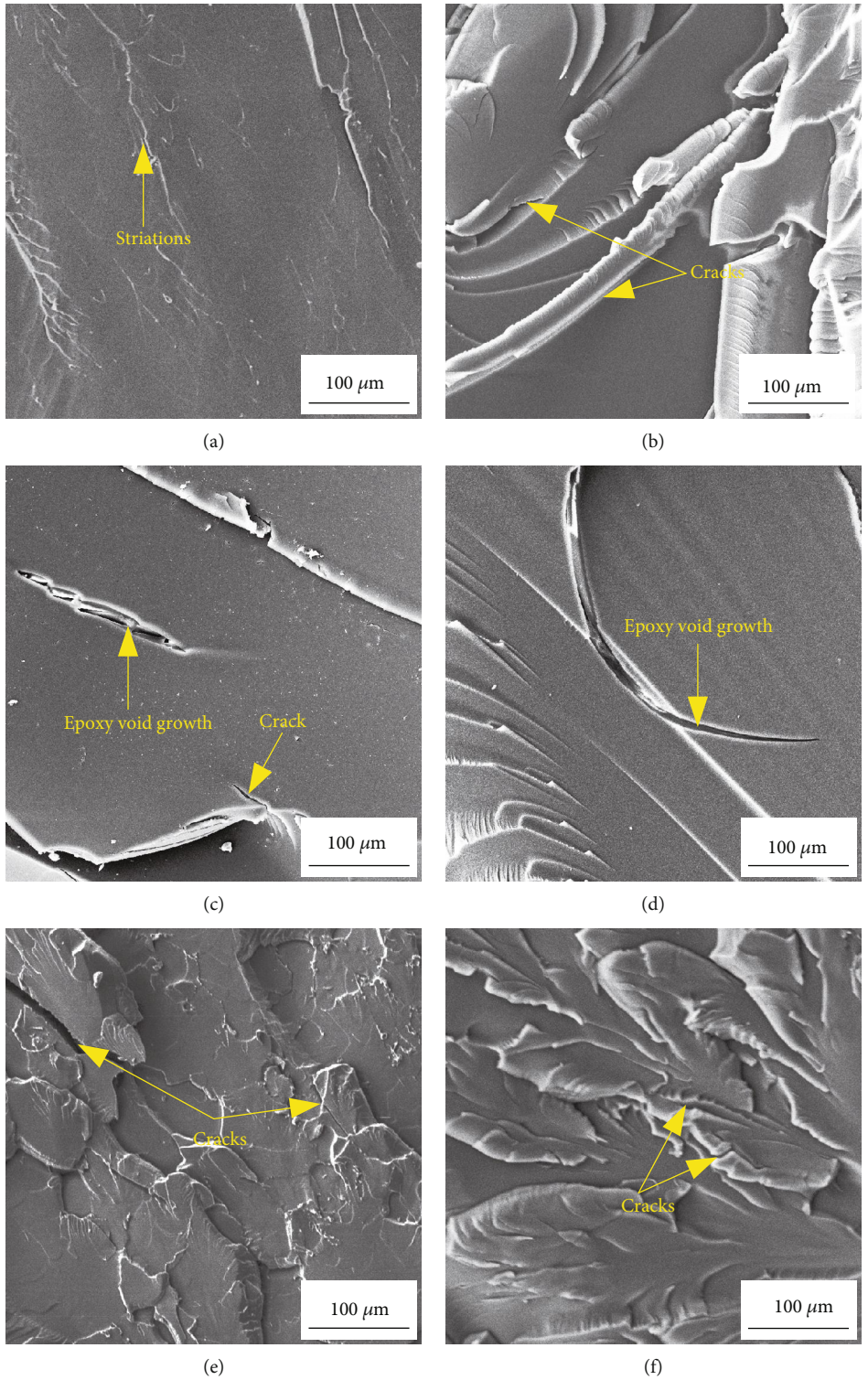

Figure 3: Fracture surface of neat EP: (a) dry state, (b) immersion in water at 20°C, (c) immersion in water at 40°C, (d) immersion in water at 60°C, (e) immersion in HCl solution, and (f) immersion in NaOH solution.

neat EP is depending on the immersion temperature in deionized water. When the resins were soaked in the water at 20°C, 40°C, and 60°C, the strength was decreased by 3.44%, 7.90%, and 14.94%, respectively. The immersion of water molecules will lead to degradation, plasticization, and swelling of the EP, which will degrade the mechanical properties [14, 31]. It also can be seen that the addition of HNT improves the strength of the resin, and this is due to the high mechanical properties of HNT with a large aspect ratio [22]. Figure 2(b) shows that the strength of HNT/EP

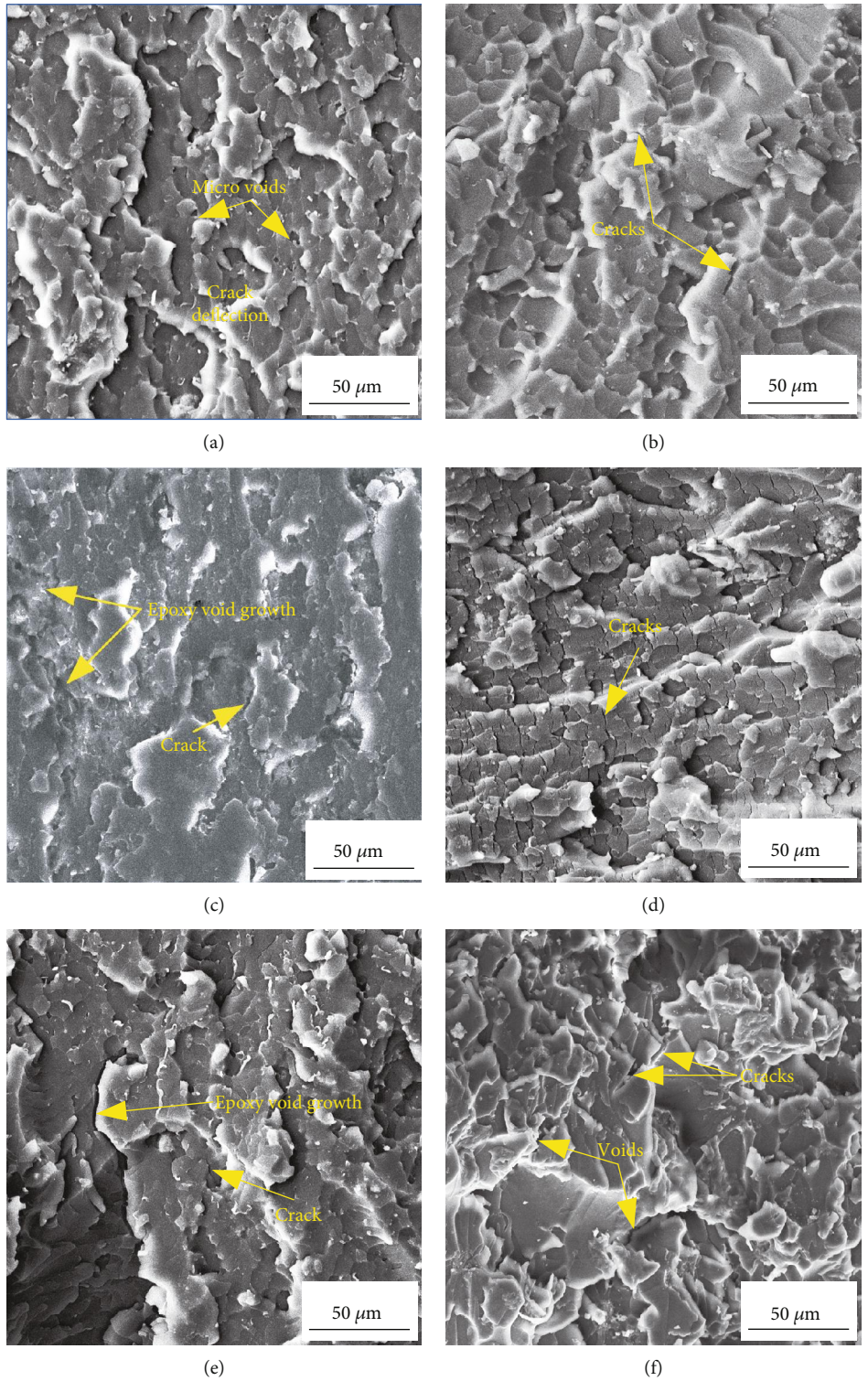

Figure 4: Fracture surface of HNT/EP nanocomposites: (a) dry state, (b) immersion in water at 20°C, (c) immersion in water at 40°C, (d) immersion in water at 60°C, (e) immersion in HCl solution, and (f) immersion in NaOH solution.

nanocomposites decreased under aging conditions. After soaking in water at 20°C, 40°C, and 60°C, the tensile strength was decreased by 3.04%, 6.84%, and 13.16%, respectively. It indicated that compared with the neat EP, HNT/EP nanocomposites are lower in strength reduction, mainly because the addition of HNT hinders the infiltration of water molecules as a "barrier" [13]. In addition to the soaking temperature, the corrosive medium also influences the aging behavior of the resin. It can be seen from Figure 2 and Table 2 that the HCl solution and NaOH solution degrade

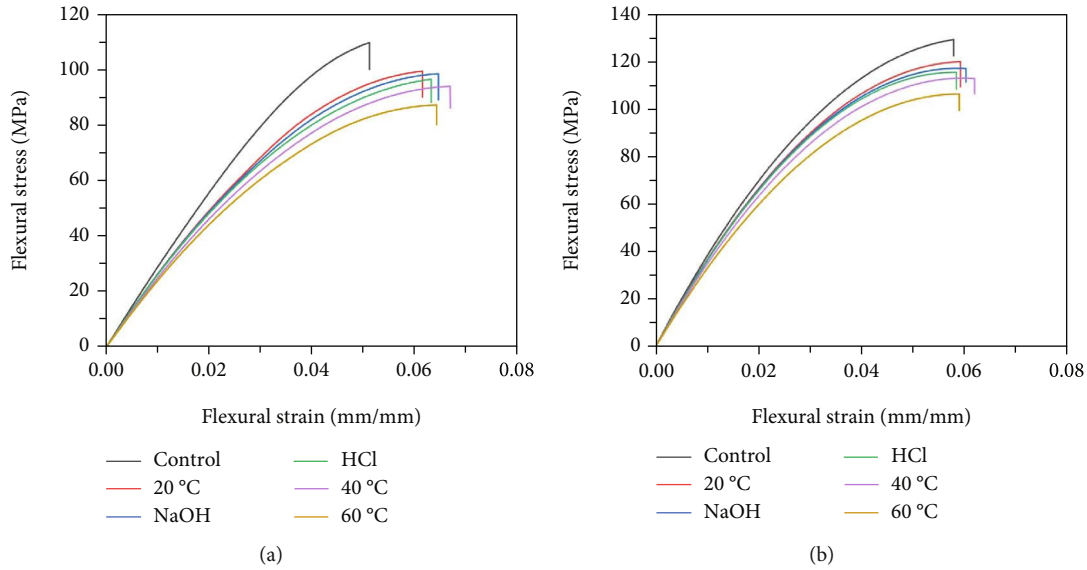

Figure 5: Flexural stress-strain curves of (a) neat EP and (b) HNT/EP nanocomposites under different conditions.

Table 3: Flexural properties of EP under different soaking and aging conditions.

Sample	Mechanical properties	Control (dry condition)	Water soaking at 20°C	Water soaking at 40°C	Water soaking at 60°C	HCl soaking at 20°C	NaOH soaking at 20°C
Neat EP	Flexural strength (MPa)	109.61 ± 5.41	99.28 ± 3.98	93.85 ± 4.14	87.10 ± 4.29	96.40 ± 3.58	98.37 ± 2.81
	Flexural modulus (GPa)	2.97 ± 0.13	2.77 ± 0.09	2.61 ± 0.10	2.51 ± 0.07	2.74 ± 0.11	2.75 ± 0.13
EPs with nanoclay	Flexural strength (MPa)	129.96 ± 4.59	120.55 ± 4.31	113.65 ± 2.66	106.93 ± 4.82	116.12 ± 2.27	117.84 ± 5.04
	Flexural modulus (GPa)	3.27 ± 0.12	3.10 ± 0.15	2.91 ± 0.11	2.78 ± 0.08	3.03 ± 0.10	3.06 ± 0.11

the mechanical properties more than deionized water. This is because the water absorption of EP in HCl and NaOH is higher than that in deionized water, which makes the deterioration of EP more serious [32, 33].

Figure 3 shows the fracture surface of neat EP under different conditions. Figure 3(a) displays that the fracture surface of the unaged EP is smooth and flat, and there is little crack deflection during the fracture process, indicating a characteristic of brittle fracture [25]. Figures 3(b)–3(f) show fracture surfaces of the neat EP under different aging conditions. As reported during dry condition, the aging condition brings resin more cracks and crack branches. Figures 3(b)–3(d) show the SEM images of the fracture surface of the sample after soaking in deionized water at different temperatures. With the increase in soaking temperature, the number of the crack increases. Figures 3(b), 3(e), and 3(f) display the SEM images of the sample which was soaked in different mediums at 20°C. There are more cracks in HCl solution and NaOH solution than in deionized water, indicating that the corrosion is more serious under acidic and alkaline conditions.

Figure 4 shows the fracture surface of HNT/EP nanocomposites under different conditions. It can be observed in Figure 4(a) that the fracture surface of the unaged sample is rough. In addition to some crack deflections, there are some traces left due to the pull-out of HNT [13]. Figures 4(b)–4(f) show the fracture surface of HNT/EP nanocomposites after immersion aging condition. It can be found that voids, cracks, and scarps have occurred under aging conditions, which reduce the strength of the sample. The effects of soaking temperature on the aging behavior of samples could be compared in Figures 4(b)–4(d). With the increase in soaking temperature, voids and cracks increased, resulting in a serious deterioration of samples. Figures 4(b), 4(e), and 4(f) show the fracture surface of aged samples in diverse mediums at 20°C. Compared with deionized water, NaOH solution and HCl solution increase the number of crack and void in the sample.

3.3. Flexural Properties under Immersion Aging Conditions. Figure 5(a) shows the flexural properties of neat EP under various conditions. Tables 3 and 4 show the flexural

Table 4: Flexural property reduction (%) of the sample under different immersion aging conditions.

Sample	Mechanical properties	Water soaking at 20°C	Water soaking at 40°C	Water soaking at 60°C	HCl soaking at 20°C	NaOH soaking at 20°C
Neat EP	Flexural strength	9.42	14.38	20.54	12.05	10.25
	Flexural modulus	6.73	12.12	15.49	7.74	7.41
EPs with HNT	Flexural strength	7.24	12.55	17.72	10.65	9.33
	Flexural modulus	5.20	11.01	14.98	7.34	6.42

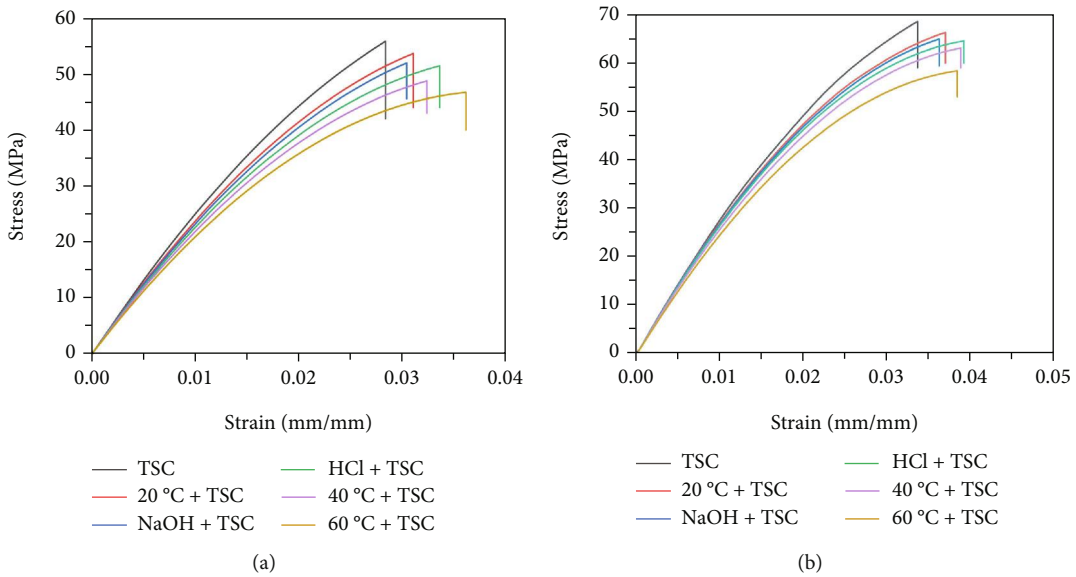

Figure 6: The tensile stress-strain curves of (a) neat EP and (b) HNT/EP nanocomposites under composite aging conditions.

Table 5: Tensile properties of EP under single thermal shock cycle (TSC) and different composite aging conditions.

Sample	Mechanical properties	Thermal shock cycling (TSC)	Water soaking at 20°C+ TSC	Water soaking at 40°C+ TSC	Water soaking at 60°C+ TSC	HCl soaking at 20°C+ TSC	NaOH soaking at 20°C+ TSC
Neat EP	Tensile strength (MPa)	55.89 ± 1.84	53.70 ± 1.33	48.79 ± 2.01	46.73 ± 2.22	51.49 ± 1.78	51.98 ± 2.58
	Tensile modulus (GPa)	2.66 ± 0.10	2.62 ± 0.13	2.49 ± 0.07	2.35 ± 0.08	2.57 ± 0.11	2.61 ± 0.12
EPs with nanoclay	Tensile strength (MPa)	68.58 ± 3.24	66.30 ± 2.83	63.07 ± 3.03	58.36 ± 1.66	64.54 ± 1.39	64.95 ± 2.37
	Tensile modulus (GPa)	3.03 ± 0.06	3.00 ± 0.13	2.88 ± 0.09	2.72 ± 0.11	2.95 ± 0.12	2.99 ± 0.08

Table 6: Reduction (%) of tensile properties of EP under single thermal shock cycle (TSC) and different composite aging.

Sample	Mechanical properties	Thermal shock cycling (TSC)	Water immersion at 20°C+TSC	Water immersion at 40°C+TSC	Water immersion at 60°C+TSC	HCl immersion at 20°CTSC	NaOH immersion at 20°C+TSC
Neat EP	Tensile strength	2.34	6.17	14.75	18.35	10.03	9.17
	Tensile modulus	1.12	2.60	7.43	12.64	4.46	2.97
EPs with HNT	Tensile strength	2.87	6.10	10.68	17.35	8.60	8.02
	Tensile modulus	1.30	2.28	6.19	11.40	3.91	2.61

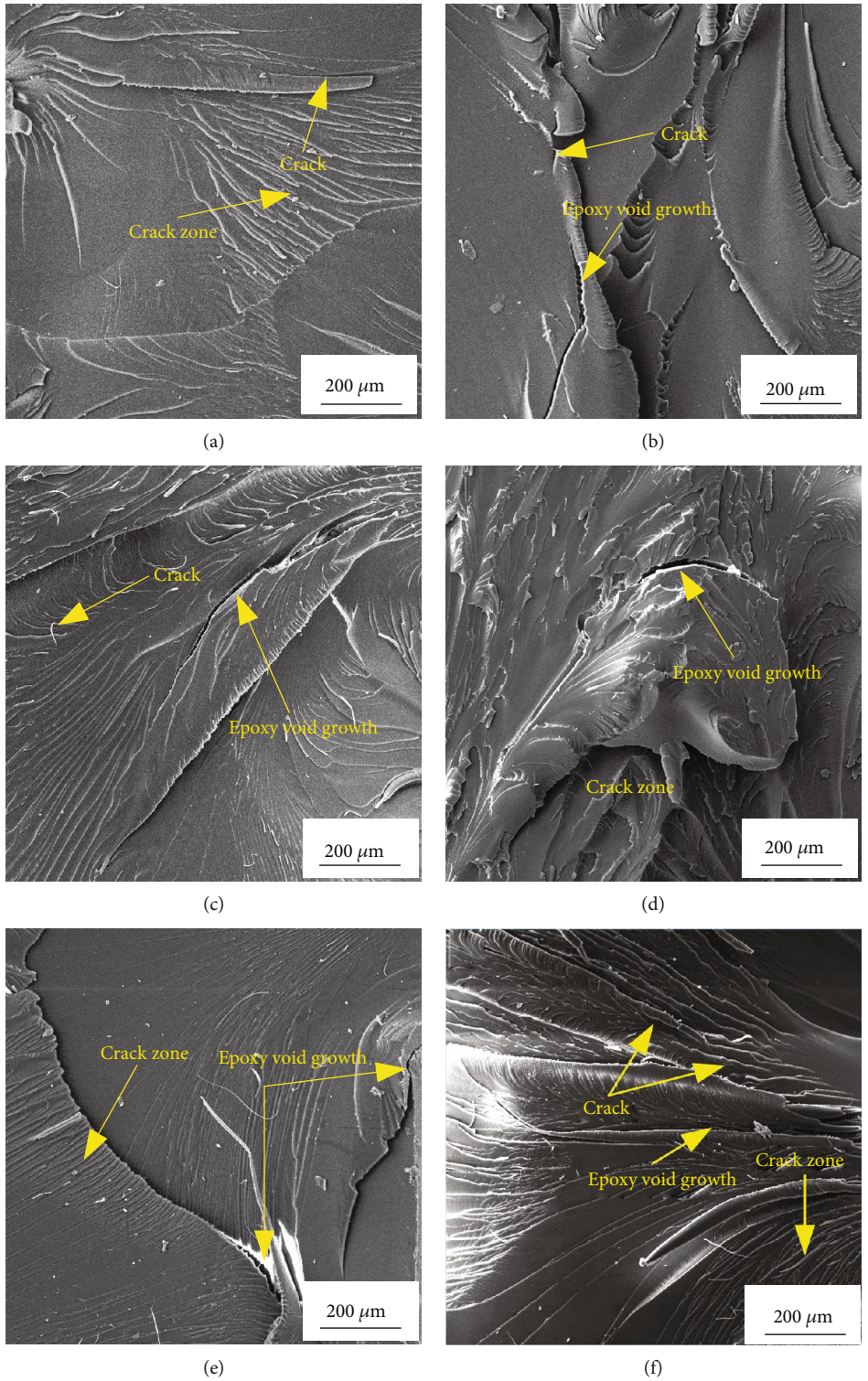

Figure 7: Fracture surface of neat EP under different aging conditions: (a) single TSC, (b) immersion in water at 20°C+TSC, (c) immersion in water at 40°C+TSC, (d) immersion in water at 60°C+TSC, (e) immersion in HCl solution+TSC, and (f) immersion in NaOH solution+TST.

properties and the reduction (%) of flexural properties of EP under different immersion conditions, respectively. The flexural strength of the EP decreased after soaking aging. This is further caused by the infiltration of water molecules into the resin [13, 34]. The addition of HNT improves the flexural properties of the resin under immersion aging conditions,

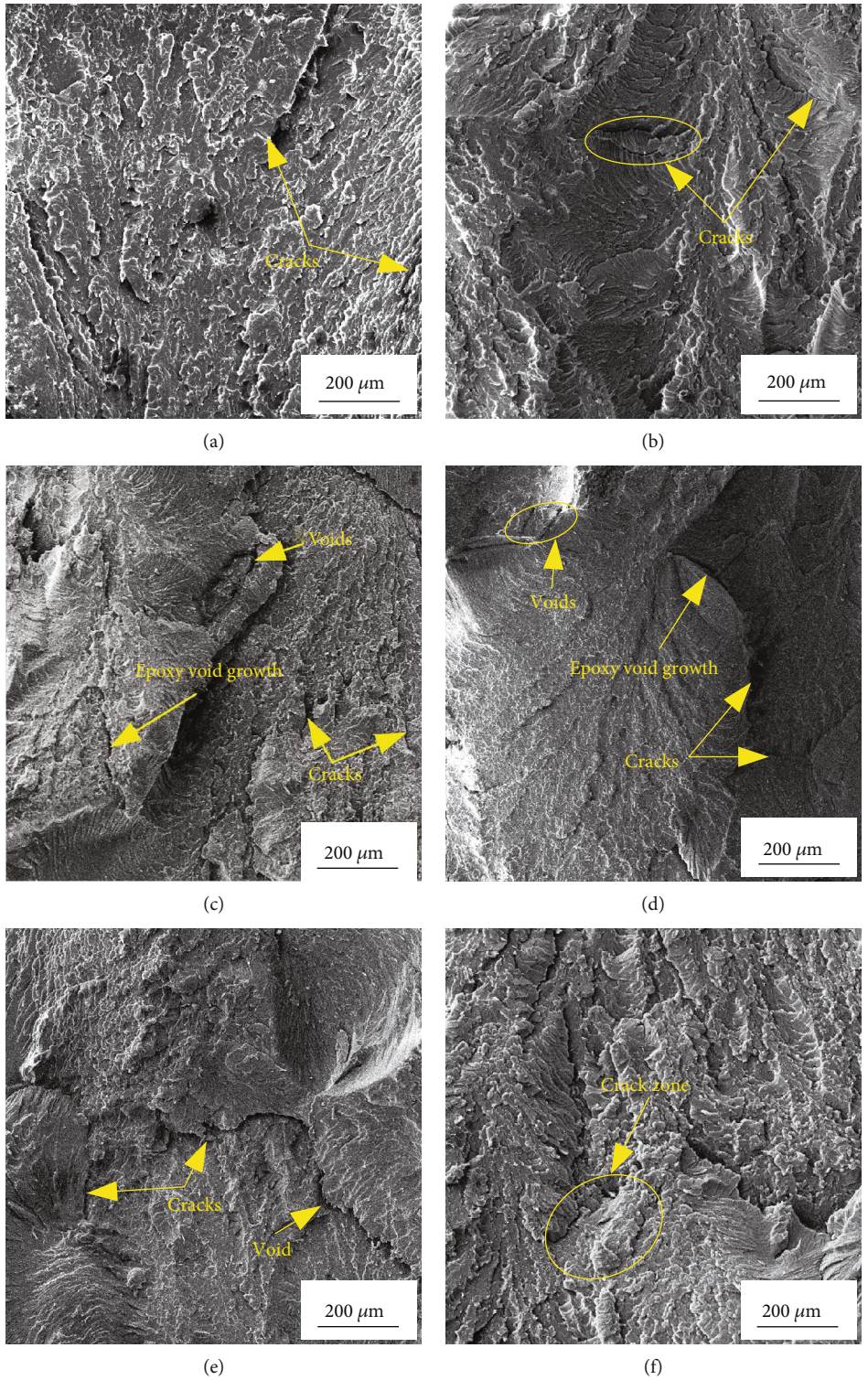

Figure 8: Fracture surface of HNT/EP nanocomposites under different aging conditions: (a) single TSC, (b) immersion in water at 20°C+TSC, (c) immersion in water at 40°C+TSC, (d) immersion in water at 60°C+TSC, (e) immersion in HCl solution+TSC, and (f) immersion in NaOH solution+TSC.

as shown in Figure 5(b). Under the same soaking conditions, the reduction in flexural strength of HNT/EP nanocomposites is slightly lower than that of neat EP.

3.4. Tensile Properties under Composite Aging Conditions. Figure 6 shows the tensile stress-strain curves of the EP under a single thermal shock cycle (TSC) and composite

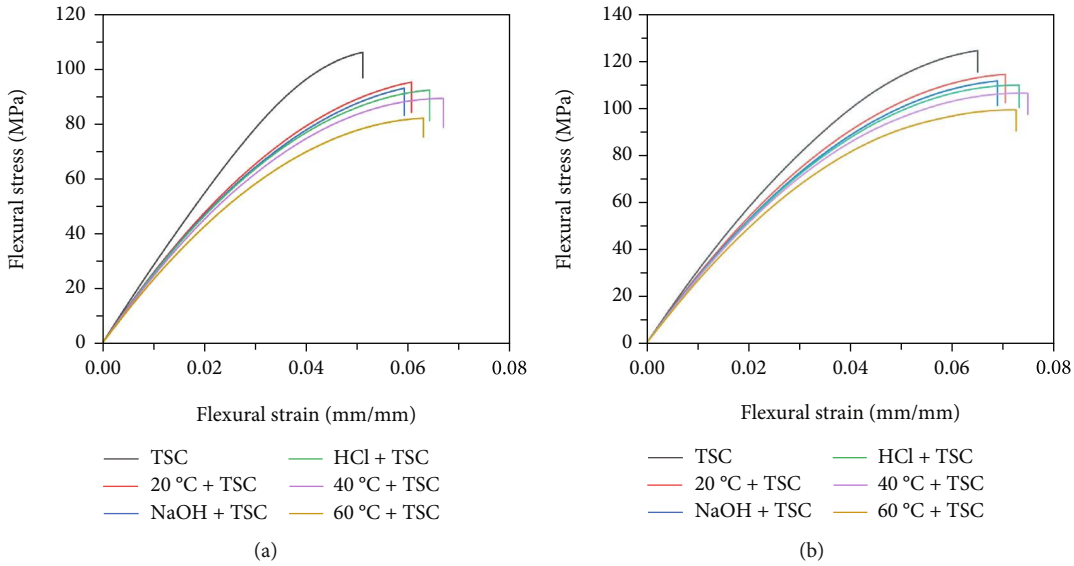

Figure 9: Flexural stress-strain curve of (a) neat EP and (b) HNT/EP nanocomposites under composite aging conditions.

aging conditions (immersion aging coupled with thermal shock cycle). Tables 5 and 6 show the tensile properties and the reduction (%) of tensile properties of the EP under a single thermal shock cycle (TSC) and different composite aging conditions, respectively. It can be seen from Figure 6(a) and Table 6 that the tensile strength of neat EP under a single TSC condition decreases by 2.34%. In addition, composite aging conditions made lower tensile strength of either EP or its composites more than a single TSC. It is reported that during the immersion aging process, the crack in EP has occurred due to the infiltration of water molecules [12]. Therefore, subsequent thermal shock makes the degradation of the resin matrix more serious.

Figure 6(b) shows the tensile stress-strain curves of HNT/EP nanocomposites under single thermal shock cycle and composite aging conditions. Under single thermal shock cycle conditions, the tensile strength falls by 2.87%. This indicates that the EP composites reduced higher value in strength than neat EP due to different thermal expansion coefficients between HNT and EP. In addition, under composite aging conditions, the tensile strength decreases sharply, mainly because the resin has more cracks and interface debonding between HNT and resin after stress mismatch.

Figure 7 shows the fracture surface of the neat EP after single thermal shock cycle and composite aging conditions. It can be seen from Figure 7(a) that microcracks and crack branches are generated in the EP under single thermal shock cycle condition, which is the result of thermal residual stress [23, 35]. Figures 7(b)–7(f) display the fracture surface of the neat EP after composite aging conditions. The crack increases, and the scarp is deep, indicating that the degradation of the sample under composite aging conditions is more serious than that of the sample under single thermal shock cycle conditions. Besides, high temperature will aggravate the damage to the EP, as shown in Figures 7(b)–7(d).

Figure 8 shows the fracture surface of HNT/EP nanocomposites after single thermal shock cycle and composite aging conditions. It can be seen from Figure 8(a) that some tiny cracks appear after the single thermal shock cycle, resulting in a decrease in strength. Figures 8(b)–8(f) show the SEM images of the fracture surface of the samples after composite aging conditions. Compared with the single thermal shock cycle condition, the composite aging condition makes the deterioration of the sample more serious. From Figures 8(b)–8(d), it can be seen that the cracks are more and the scarps are deeper with the increase in aging temperature, indicating that the deterioration degree of the sample increases.

3.5. Flexural Properties under Composite Aging Conditions. Figure 9 shows the flexural properties of EP and EP composites under different aging conditions. Tables 7 and 8 list the bending properties and the reduction (%) of bending properties of EP under single thermal shock cycle (TSC) and different composite aging conditions, respectively. Flexural strength of neat EP and HNT/EP nanocomposites decreased after single thermal shock cycle. But the addition of HNT scarcely improves the reduction rate in flexural properties. In addition, under composite aging conditions, the reduction rate in flexural strength of HNT/EP nanocomposites is slightly lower than that of neat EP, indicating that the HNT could delay the aging behavior of the resin because HNT with a high aspect ratio hinders the infiltration of water molecules during an immersion aging.

3.6. FTIR Analysis. FTIR experiments of the samples under different aging conditions were conducted, and the FTIR curves are presented in Figure 10. Changes in functional groups of the neat EP and HNT/EP nanocomposites were analyzed by specific wavenumbers. According to the previous studies, some peaks were applied to detect the chemical

Table 7: Flexural properties of EP under single thermal shock cycle (TSC) and different composite aging conditions.

Sample	Mechanical properties	Thermal shock cycling (TSC)	Water soaking at 20°C+TSC	Water soaking at 40°C+TSC	Water soaking at 60°C+TSC	HCl soaking at 20°C+TSC	NaOH soaking at 20°C+TSC
Neat EP	Flexural strength (MPa)	105.87 ± 2.77	95.02 ± 4.55	89.06 ± 3.80	81.87 ± 3.04	92.13 ± 4.14	92.81 ± 2.03
	Flexural modulus (GPa)	2.90 ± 0.14	2.67 ± 0.10	2.56 ± 0.12	2.41 ± 0.07	2.62 ± 0.09	2.64 ± 0.11
EPs with nanoclay	Flexural strength (MPa)	124.15 ± 3.66	114.03 ± 3.41	106.01 ± 2.01	98.89 ± 3.94	109.42 ± 4.83	111.22 ± 4.62
	Flexural modulus (GPa)	3.17 ± 0.12	2.99 ± 0.14	2.84 ± 0.11	2.73 ± 0.06	2.89 ± 0.08	2.93 ± 0.05

Table 8: Reduction (%) of flexural properties of EP under single thermal shock cycle (TSC) and different composite aging conditions.

Sample	Mechanical properties	Thermal shock cycling (TSC)	Water immersion at 20°C+TSC	Water immersion at 40°C+TSC	Water immersion at 60°C+TSC	HCl immersion at 20°C+TSC	NaOH immersion at 20°C+TSC
Neat EP	Flexural strength	3.41	13.31	18.75	25.31	15.95	15.33
	Flexural modulus	2.36	10.10	13.80	18.86	11.78	11.11
EPs with HNT	Flexural strength	4.47	12.26	18.43	23.91	15.80	14.42
	Flexural modulus	3.06	8.56	13.15	16.51	11.62	10.40

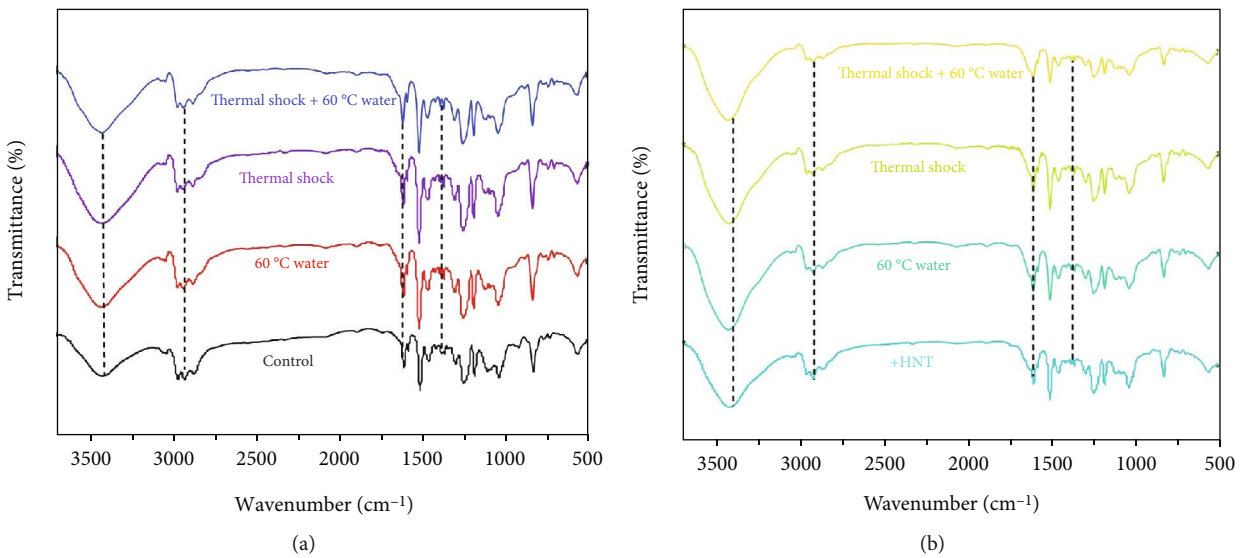

Figure 10: FTIR curve of (a) neat EP and (b) HNT/EP nanocomposites.

structure change of the EP (and its nanocomposites) or the EP suffered by aging conditions [36–40]. The peaks of all aged and nonaged samples at 3400 cm^{-1} belong to -OH groups. Compared with the spectra of nonaged samples, the peak displacement and depth of aged samples have some changes, which indicate that the samples have been oxidized during aging [33]. According to FTIR, the samples were aged in different conditions. It can be seen that the spectrum of neat EP is almost the same as that of HNT/EP nanocomposites, which indicates that no new chemical action occurs after adding HNT. As for the peaks ranging from 3290 cm^{-1} to 3350 cm^{-1}, all samples appeared in this region, which was the stretching vibration of hydroxyl single-bond -OH group [39]. Peaks at 1640cm^{-1} and 1380 cm^{-1} are related to the single-bond -OH bending vibration of the carbonyl (double bond CO) group and carboxyl COOH group, respectively. The -OH groups in HNT/EP nanocomposites are mostly the same as those in neat EP. The main reasons are that less water diffuses in HNT/EP nanocomposites and more serious hydrolysis of neat EP under hydrothermal aging conditions. The addition of HNT hindered the hydrothermal aging behavior of the EP.

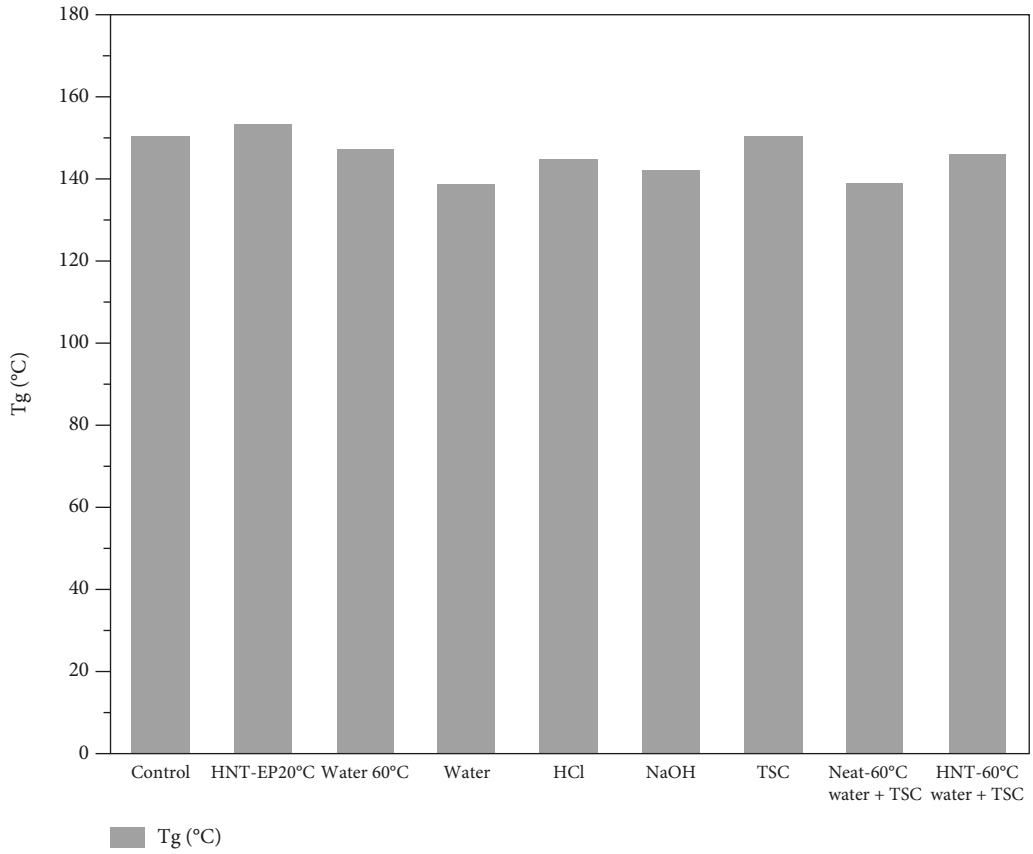

Figure 11: Tg of epoxy resin under different aging conditions.

3.7. DSC Analysis. Figure 11 shows the DSC tests of EP and HNT/EP nanocomposites. The Tg changes after aging under different conditions were studied. It can be seen that the Tg of neat EP is about 149.7°C, while the Tg of HNT/EP nanocomposites is about 153.5°C, indicating that the addition of HNT increases the Tg of EP composites. After aging in 20°C and 60°C deionized water, the Tg of EP is gradually reduced. After aging in HCl solution and NaOH solution, the Tg of EP is about 143.4°C and 142.3°C, respectively. It is concluded that the Tg decreases to varying degrees after aging under different soaking conditions. In addition, under TSC conditions, the Tg of EP is about 150.1°C. The main reason is that water molecules penetrate the EP to cause degradation. A high temperature of deionized water makes the Tg drop more [41]. However, high temperature may lead to the postcuring of EP [42].

4. Conclusions

(1) The tensile strength and flexural strength of neat EP decrease under soaking aging conditions. In deionized water, a high soaking temperature accelerated aging behavior, causing a decrease in mechanical properties. HCl and NaOH solutions lead to a higher degradation rate in tensile and flexural properties than deionized water

(2) The tensile strength and flexural strength of neat EP and HNT/EP nanocomposites decreased under immersion aging conditions, and HNT could slow down the aging behavior of the EP, mainly because the addition of HNT hinders the infiltration of water molecules into the EP matrix as a "barrier"

(3) Under TSC conditions, the HNT addition scarcely delays the reduction rate in mechanical properties of EP. Under composite aging conditions, the tensile strength and flexural strength of neat EP and HNT/EP decreased significantly due to microcrack in the resin during soaking aging

Data Availability

The data used to support the findings of this study are included within the article.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Authors' Contributions

S.J. Lu was responsible for writing the original draft and data curation; T. Yang was responsible for writing, editing, and investigation; X. Xiao was responsible for conceptualization

and validation; X.Y. Zhu was responsible for the methodology and resources; J. Wang was responsible for the methodology and investigation; P.Y. Zang was responsible for investigation and formal analysis; J.A. Liu was responsible for conceptualization and project administration. All authors have read and agreed to the published version of the manuscript.

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References

[1] N. Domun, H. Hadavinia, T. Zhang, T. Sainsbury, G. H. Liaghat, and S. Vahid, "Improving the fracture toughness and the strength of epoxy using nanomaterials – a review of the current status," *Nanoscale*, vol. 7, no. 23, pp. 10294–10329, 2015.

[2] S. Sugiman, I. K. P. Putra, and P. D. Setyawan, "Effects of the media and ageing condition on the tensile properties and fracture toughness of epoxy resin," *Polymer Degradation and Stability*, vol. 134, pp. 311–321, 2016.

[3] H. Alamri and I. M. Low, "Microstructural, mechanical, and thermal characteristics of recycled cellulose fiber-halloysite-epoxy hybrid nanocomposites," *Polymer Composites*, vol. 33, no. 4, pp. 589–600, 2012.

[4] S. Q. Huo, T. Sai, S. Ran et al., "A hyperbranched P/N/B-containing oligomer as multifunctional flame retardant for epoxy resins," *Composites Part B Engineering*, vol. 234, p. 109701, 2022.

[5] S. Q. Huo, Z. Zhou, J. Jiang et al., "Flame-retardant, transparent, mechanically-strong and tough epoxy resin enabled by high-efficiency multifunctional boron-based polyphosphonamide," *Chemical Engineering Journal*, vol. 427, p. 131578, 2022.

[6] A. Cerit, M. E. Marti, U. Soydal, S. Kocaman, and G. Ahmetli, "Effect of modification with various epoxide compounds on mechanical, thermal, and coating properties of epoxy resin," *International Journal of Polymer Science*, vol. 2016, Article ID 4968365, 13 pages, 2016.

[7] N. Saba, M. Jawaid, O. Y. Alothman, M. T. Paridah, and A. Hassan, "Recent advances in epoxy resin, natural fiber-reinforced epoxy composites and their applications," *Journal of Reinforced Plastics and Composites*, vol. 35, no. 6, pp. 447–470, 2016.

[8] H. Ku, S. Y. Fung, M. Islam, X. Li, and Y. P. Chong, "A pilot study on flexural properties of epoxy nanoclay reinforced composites," *Journal of Reinforced Plastics and Composites*, vol. 32, no. 2, pp. 96–104, 2013.

[9] C. X. Ji, H. W. He, and Y. K. Yang, "Moisture absorption process of epoxy resin and mechanical properties of its fiber composites," *Materials Testing*, vol. 61, no. 1, pp. 23–26, 2019.

[10] S. Madduri, W. Infantolino, and B. G. Sammakia, "An experimental and computational study on moisture induced epoxy swelling in non-hermetic optoelectronic packages," *Journal of Electronic Packaging*, vol. 134, no. 1, article 011007, 2012.

[11] P. Jojibabu, G. D. J. Ram, A. P. Deshpande, and S. R. Bakshi, "Effect of carbon nano-filler addition on the degradation of epoxy adhesive joints subjected to hygrothermal aging," *Polymer Degradation and Stability*, vol. 140, pp. 84–94, 2017.

[12] O. Starkova, S. Gaidukovs, O. Platnieks et al., "Water absorption and hydrothermal ageing of epoxy adhesives reinforced with amino-functionalized graphene oxide nanoparticles," *Polymer Degradation and Stability*, vol. 191, p. 109670, 2021.

[13] H. Alamri and I. M. Low, "Effect of water absorption on the mechanical properties of nano-filler reinforced epoxy nanocomposites," *Materials & Design*, vol. 42, pp. 214–222, 2012.

[14] A. Uthaman, G. Xian, S. Thomas, Y. Wang, Q. Zheng, and X. Liu, "Durability of an epoxy resin and its carbon Fiber-Reinforced polymer composite upon immersion in water, acidic, and alkaline solutions," *Polymers*, vol. 12, no. 3, p. 614, 2020.

[15] N. A. Siddiqui, R. S. C. Woo, J. K. Kim, C. C. K. Leung, and A. Munir, "Mode I interlaminar fracture behavior and mechanical properties of CFRPs with nanoclay-filled epoxy matrix," *Composites Part A Applied Science and Manufacturing*, vol. 38, no. 2, pp. 449–460, 2007.

[16] A. A. Azeez, K. Y. Rhee, S. J. Park, and D. Hui, "Epoxy clay nanocomposites – processing, properties and applications: a review," *Composites Part B-engineering*, vol. 45, no. 1, pp. 308–320, 2013.

[17] X. C. Yin, L. Wang, S. Li, G. J. He, and Z. T. Yang, "Effects of surface modification of halloysite nanotubes on the morphology and the thermal and rheological properties of polypropylene/halloysite composites," *Journal of Polymer Engineering*, vol. 38, no. 2, pp. 119–127, 2018.

[18] N. Y. Ning, Q. J. Yin, F. Luo, Q. Zhang, R. Du, and Q. Fu, "Crystallization behavior and mechanical properties of polypropylene/halloysite composites," *Polymer*, vol. 48, no. 25, pp. 7374–7384, 2007.

[19] J. Hong, T. Wu, H. Wu et al., "Nanohybrid silver nanoparticles@halloysite nanotubes coated with polyphosphazene for effectively enhancing the fire safety of epoxy resin," *Chemical Engineering Journal*, vol. 407, p. 127087, 2021.

[20] W. T. He, H. Xu, P. Song, Y. Xiang, and S. Qin, "P, N-decorated halloysite nanotubes for flame retardancy enhancement of polyamide 6/aluminum diethylphosphinate," *Polymer Degradation and Stability*, vol. 196, p. 109847, 2022.

[21] Y. P. Ye, H. B. Chen, J. S. Wu, and L. Ye, "High impact strength epoxy nanocomposites with natural nanotubes," *Polymer*, vol. 48, no. 21, pp. 6426–6433, 2007.

[22] S. Q. Deng, J. N. Zhang, L. Ye, and J. S. Wu, "Toughening epoxies with halloysite nanotubes," *Polymer*, vol. 49, no. 23, pp. 5119–5127, 2008.

[23] M. Shettar, U. A. Kini, S. Sharma, P. Hiremath, and M. C. Gowrishankar, "Study on the mechanical properties of nanoclay-epoxy composites under different hygrothermal aging conditions," *Materials Research Express*, vol. 6, no. 8, article 085333, 2019.

[24] G. Ravichandran, G. Rathnakar, N. Santhosh, R. Chennakeshava, and M. A. Hashmi, "Enhancement of mechanical properties of epoxy/halloysite nanotube (HNT) nanocomposites," *SN Applied Sciences*, vol. 1, no. 4, p. 296, 2019.

[25] M. Shettar, U. A. Kini, S. Sharma, P. Hiremath, and M. C. Gowrishankar, "Hygrothermal chamber aging effect on mechanical behavior and morphology of glass fiber-epoxy-nanoclay composites," *Materials Research Express*, vol. 7, no. 1, article 015318, 2020.

[26] H. Ulus, H. B. Kaybal, V. Eskizeybek, and A. Avci, "Enhanced salty water durability of halloysite nanotube reinforced epoxy/basalt fiber hybrid composites," *Fibers and Polymers*, vol. 20, no. 10, pp. 2184–2199, 2019.

[27] J. M. Tomasi, A. S. Krieg, N. J. Jensen, I. Miskioglu, J. A. King, and G. M. Odegard, "Accelerated hygrothermal aging of talc/cycloaliphatic epoxy composites," *Polymer Composites*, vol. 40, no. 7, pp. 2946–2953, 2019.

[28] Z. K. Wang, G. J. Xian, and X. L. Zhao, "Effects of hydrothermal aging on carbon fibre/epoxy composites with different interfacial bonding strength," *Construction and Building Materials*, vol. 161, pp. 634–648, 2018.

[29] M. Shettar, U. A. Kini, S. Sharma, P. Hiremath, and M. C. Gowrishankar, "Investigation and optimization of thermal shock effects on the properties and microstructure of nanoclay-glass fiber reinforced epoxy composites," *Materials Research Express*, vol. 6, no. 10, p. 105360, 2019.

[30] F. Azimpour-Shishevan, H. Akbulut, and M. A. Mohtadi-Bonab, "The effect of thermal shock cycling on low velocity impact behavior of carbon fiber reinforced epoxy composites," *Journal of Dynamic Behavior of Materials*, vol. 5, no. 2, pp. 161–169, 2019.

[31] S. G. Prolongo, M. R. Gude, and A. Urena, "Water uptake of epoxy composites reinforced with carbon nanofillers," *Composites Part A-applied Science and Manufacturing*, vol. 43, no. 12, pp. 2169–2175, 2012.

[32] Q. A. Yang, G. J. Xian, and V. M. Karbhari, "Hygrothermal ageing of an epoxy adhesive used in FRP strengthening of concrete," *Journal of Applied Polymer Science*, vol. 107, no. 4, pp. 2607–2617, 2008.

[33] A. Aslan, E. Salur, H. Duzcukoglu, O. S. Sahin, and M. Ekrem, "The effects of harsh aging environments on the properties of neat and MWCNT reinforced epoxy resins," *Construction and Building Materials*, vol. 272, p. 121929, 2021.

[34] S. U. Hamim and R. P. Singh, "Effect of hygrothermal aging on the mechanical properties of fluorinated and nonfluorinated clay-epoxy nanocomposites," *International Scholarly Research Notices*, vol. 2014, Article ID 489453, 13 pages, 2014.

[35] G. C. Papanicolaou, A. F. Koutsomitopoulou, and A. Sfakianakis, "Effect of thermal fatigue on the mechanical properties of epoxy matrix composites reinforced with olive pits powder," *Journal of Applied Polymer Science*, vol. 124, no. 1, pp. 67–76, 2012.

[36] W. Fan and J. L. Li, "Rapid evaluation of thermal aging of a carbon fiber laminated epoxy composite," *Polymer Composites*, vol. 35, no. 5, pp. 975–984, 2014.

[37] S. T. Cholake, M. R. Mada, R. K. S. Raman et al., "Quantitative analysis of curing mechanisms of epoxy resin by mid- and near- Fourier transform infra red spectroscopy," *Defence Science Journal*, vol. 64, no. 3, pp. 314–321, 2014.

[38] Y. Lin, X. Chen, H. Zhang, and Z. Wang, "Effects of hygrothermal aging on epoxy-based anisotropic conductive film," *Materials Letters*, vol. 60, no. 24, pp. 2958–2963, 2006.

[39] Y. Wang, Z. Meng, W. Zhu et al., "Hygrothermal aging behavior and aging mechanism of carbon nanofibers/epoxy composites," *Construction and Building Materials*, vol. 294, p. 123538, 2021.

[40] Y. Korkmaz and K. Gultekin, "Improvement of structural, thermal and mechanical properties of epoxy composites and bonded joints exposed to water environment by incorporating boron nanoparticles," *International Journal of Adhesion and Adhesives*, vol. 116, p. 103141, 2022.

[41] G. Bouvet, S. Cohendoz, X. Feaugas, S. Touzain, and S. Mallarino, "Microstructural reorganization in model epoxy network during cyclic hygrothermal ageing," *Polymer*, vol. 122, pp. 1–11, 2017.

[42] C. V. Lacombre, G. Bouvet, S. Cohendoz et al., "Influence of internal stresses on the physicochemical and mechanical properties evolution of pigmented epoxy systems during hygrothermal ageing," *Surface & Coatings Technology*, vol. 341, pp. 86–94, 2018.