Effects of Hot Water Absorption and Desorption on Solid Particle Erosion of Poly(Ethylene Terephthalate)-Based Composites [*]

Bing Liu [a], Peng Zhu [a], Li-Min Bao [b,*]

[a]*Department of Bioscience and Textile Technology, Interdisciplinary Graduate School of Science and Technology, 3-15-1 Tokida, Ueda, Nagano 386-8567, Japan*

[b]*Faculty of Textile Science and Technology, Shinshu University, 3-15-1 Tokida, Ueda, Nagano 386-8567, Japan*

Abstract

Water aging is one of the causes of fiber-reinforced thermoplastic (FRTP) degradation during long-term service. It affects not only the mechanical properties of FRTPs, but also their erosion by solid particles. However, little research has been done on the effects of water aging on the erosion of FRTPs. The aim of this research was to study the effects of hot water absorption and desorption on the solid particle erosion of carbon-fiber-reinforced poly(ethylene terephthalate) (PET) composites. It was found that the PET-based composite erosion rate increased with increasing immersion time and decreased after redrying, whereas, the PET resin erosion rate decreased after hot water treatment. These effects depended on changes in the resin/fiber interfacial strength. Changes in the interfacial strength were investigated using short beam shear tests and dynamic mechanical analysis. It can be found that the interlaminar shear strength of the composite decreased sharply after hot water treatment based on the results of short beam shear tests and the storage modulus and glass-transition temperature decreased after hot water treatment according to the results of dynamic mechanical analysis.

Keywords: Solid particle erosion; Water absorption; Water desorption; Water Aging

1 Introduction

Fiber-reinforced plastic (FRP) composites have been used as alternatives to steel, metal, and wood in various applications over the last few decades. This is because of their high specific tensile strengths, modulus-to-weight ratios, and corrosion resistance. More recently, interest has shifted from thermosetting to thermoplastic matrices. This has extended the composite field in terms of thermoformability and improved recyclability because the thermoplastic matrix can be

---

[*]Corresponding author.
Email address: baolimin@shinshu-u.ac.jp (Li-Min Bao).

molten multiple times [1]. Because of its characteristic high tensile strength and modulus, light weight, solvent resistance, and relatively low cost, semi-crystalline poly(ethylene terephthalate) (PET) is a promising thermoplastic matrix for many applications [2]. However, the melt viscosities of thermoplastic matrices (500-5000 Pa s) are considerably higher than those of thermosetting resins (typically <100 Pa s) [3, 4], which makes it more difficult for the resin to impregnate a fabric. In our previous work, to solve this problem, we developed a solution impregnation method, which deceases the polymer viscosity, and used it to manufacture fiber-reinforced thermoplastics (FRTPs) with excellent mechanical properties [5].

In practical situations, materials degrade during long-term service. For example, the majority of wind turbines are installed near the seaside, where humidity is high. The effects on these materials of long-term exposure to a high-humidity environment are similar to those of water [6]. The tensile strength and elastic modulus of a composite decrease significantly with increasing water absorption [7] because the absorbed moisture or water can cause swelling and plasticization of the polymer matrix and debonding at the fiber/matrix interface.

Another concern in many energy applications is the wear and damage of composite surfaces caused by solid particles in the air [8], which can lead to lengthy maintenance periods, security risks, and other serious problems. PET, the common thermoplastic matrix used in the present work, is hygroscopic, i.e., it absorbs water from its surroundings (at equilibrium about 0.3% in 24 h), therefore the interface between the reinforcing material and PET is weakened by water absorption. It has been reported that the erosion resistance of composites depends on the fiber/matrix interface [9], therefore for composites operating in high-humidity environments for lengthy periods, it is important to investigate not only the erosion behavior of dry composites, but also the erosion behavior of the composites after water absorption. Most research has focused on the effects of various factors (e.g., impact angle, impact velocity, and amount of fibers) on solid particle erosion of FRTPs under dry conditions [10, 11]. However, less research has been performed on the effects of moisture/water aging on the erosion of FRTPs. It is therefore important to clarify the solid particle erosion behavior of FRTPs degraded by water aging.

The objective of this research was to clarify the effects of water absorption and water desorption on the solid particle erosion of carbon-fiber-reinforced PET thermoplastics. Higher temperature can accelerate the rate of water absorption, which can greatly shorten experimental time, therefore the kinetics of water absorption by carbon fiber/PET and PET resin at high temperatures were investigated. Short beam shear tests were used to determine the effects of water absorption and desorption on the interlaminar shear strengths (ILSSs) of carbon fiber/PET specimens. Scanning electron microscopy (SEM) was used to examine the eroded surfaces to study the effects of water absorption at the microstructural level. Changes in the viscoelastic behaviors of aged and unaged materials were examined using dynamic mechanical analysis (DMA).

2   Experimental Details

2.1   Materials

Carbon fibers are widely used as reinforcing materials because of their superior properties such as high mechanical strength and modulus of elasticity, low density, and good flame resistance [12].

The thermoplastic matrix used in this study was semi-crystalline PET supplied by the Toyobo

Co. It has no established melting point, but has a softening point at 185 °C, and a high melt viscosity of 7000 dPa s at 250 °C. The PET solvent was *N*-methyl-2-pyrrolidone (Kanto Chemical, Tokyo, Japan).

2.2 Manufacture of Composite Materials

A solution impregnation method [5] was used for composite manufacture. PET resin was dissolved in *N*-methyl-2-pyrrolidone to obtain a 20 wt% resin solution. A hand lay-up method was used for pre-impregnation of the reinforcing fabric with the resin solution. The fabric impregnated with resin solution was placed in a vacuum oven for adequate solvent evaporation. Prepregs with a smooth surface were obtained by thermal treatment of sheets using a hot-press machine (table-type test press, SA-302, Tester Sangyo Co., Ltd., Tokyo, Japan). Each prepreg sheet was cut to fit a metallic mold, placed in the mold, and pressed at 3.74 MPa for 30 min at 200 °C.

2.3 Water Absorption and Desorption

Each five specimens were dried in an oven for 24 h at 60 °C. The weights of the dried specimens were measured to a precision of 0.001 g. The specimens were then immersed in deionized water and kept at 70 °C. The specimen weights were measured at different time intervals during long-term immersion after removal from the water. The water absorption percentages were calculated using the following equation

$$W_R(t) = \frac{W(t) - W_0}{W_0} \times 100\% \tag{1}$$

where $W_R(t)$ is the weight increase rate (%) at time t, W_0 is the oven-dried weight, and $W(t)$ is the weight of the specimen at a given immersion time t.

The redrying treatment was performed in a vacuum oven at 70 °C for 24 h. Adequate evaporation of the moisture present in the specimen was confirmed by comparing the initial weight of the specimen (W_0) and the weight of the hot-water-treated specimen after redrying. The results show that there was almost no residual water in the redried specimen.

2.4 Erosion Behavior

Solid particles were held in a hopper and fed into an air stream by a micro feeder at a constant feed rate. To save energy and reduce the experimental time, the average feed rate of the erodent particles was set at 2.1 g/min. The solid particles used in the erosion tests were angular alumina solid particles of average diameter 11.5 ± 21.5 μm. Erosion tests were conducted at an impact velocity of 122.8 m/s, controlled using an air compressor (Sulesanll AS4PD-6, Kobe Steel Ltd., Kobe, Japan). A nozzle of inner diameter 5.35 mm was used, and the distance between the nozzle and the surface of the test specimen was set at 40 mm. At least five specimens were assessed per sample and the average value was reported.

2.5   Short Beam Shear Tests

The short beam shear strengths of virgin, hot-water-treated, and redried hot-water-treated PET-based composites were tested according to JIS K 7078. At least five specimens were prepared for short beam shear tests to enable assessment of statistical effects. The average specimen size was 20 mm × 10 mm × 2 mm, the test span was 10 mm, and the test speed was 1 mm/min.

2.6   SEM

The fracture surfaces of the virgin, hot-water-treated, and redried PET-based composites after the solid particle erosion tests were examined using SEM (JSM-6010LA In Touch Scope, EOL Co., Ltd., Tokyo, Japan). The samples were sputtered with Au in an Ar atmosphere to reduce surface charging.

2.7   DMA

The impact of hot water immersion on the viscoelastic behavior of the materials was investigated by thermal and frequency scanning using a DVA-200 instrument (IPROS Co., Ltd., Tokyo, Japan). Rectangular PET resin and PET-based composite specimens of dimensions 45 mm × 5 mm × 1 mm were used. To improve the accuracy of the experimental data, a heating rate and test frequency of 5 °C/min and 10 Hz, respectively, were used.

3   Results and Discussion

3.1   Water Absorption by PET and PET-based Composite

The effects of immersion time on the percentage mass changes of the PET and carbon- fiber/PET composite are shown in Fig. 1. The immersion times shown in Fig. 1 were normalized to the specimen thickness to correct for the small thickness difference between PET and the carbon fiber/PET composite. The profiles of the water absorption curves for PET resin and the carbon fiber/PET composite are different. For the PET resin, the water absorption curve increased rapidly on immersion in hot water, and the PET resin mass reached a maximum at 200 $s^{1/2}$/mm, indicating saturation with water. However, the carbon fiber/PET composite did not reach an
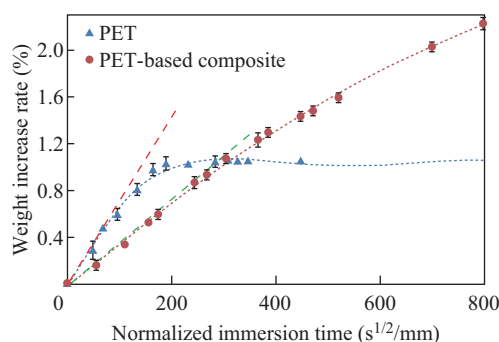

Fig. 1: Water absorption curves for PET resin and PET-based

equilibrium water content, even after immersion in hot water for 800 s$^{1/2}$/mm. Water absorption by PET resin follows Fick's law of diffusion. However, mechanisms such as capillarity or transport in microcracks operate when composites are immersed in water, resulting in non-Fickian behavior, i.e., a stable equilibrium water content is not attained, as was observed in the present study. A similar phenomenon has previously been reported [13]. Fig. 1 also shows that during the initial exposure period, the water absorption rate for the resin was higher than that for the PET-based composite. This is because the incorporation of fibers into the resin led to a reduction in the water absorption rate [14].

3.2   Erosion Behavior

The erosion rates of sized and desized PET and PET-based composites subjected to water immersion were investigated; the results are shown in Fig. 2. In the figure, PET(0) denotes the data for the virgin PET resin and PET(100) denotes the data for the PET resin degraded for a normalized immersion time of 100 s$^{1/2}$/mm. The erosion rates of the PET resins at three different impact angles decreased with increasing hot water immersion time. This could be because water absorption by the PET resin results in swelling and softening of the matrix [15], and the swollen and softened resin can absorb part of the energy from impacting particles, and this protects the resin from damage.

Although some physical changes such as swelling and softening of composites occur during water
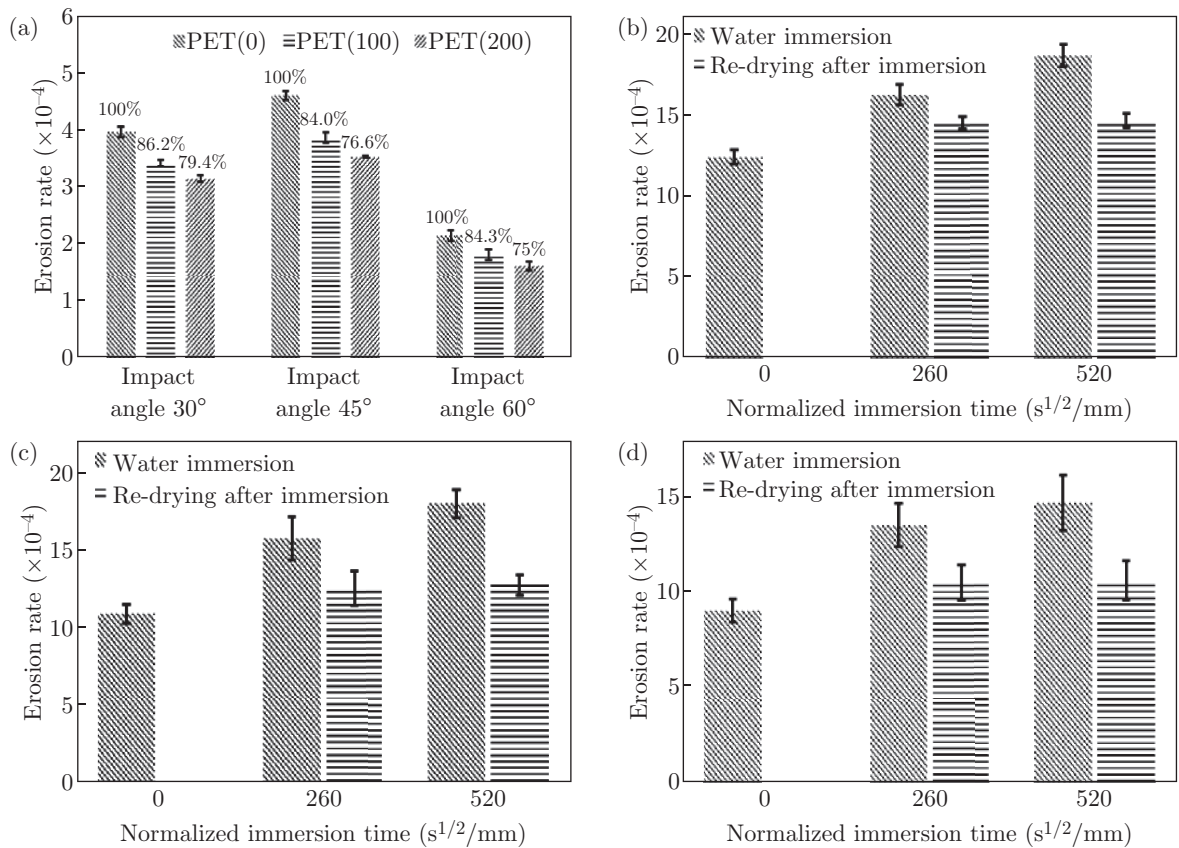

Fig. 2: Erosion behavior of (a) PET resin, and PET-based composites at (b) impact angle of 45°, (c) impact angle of 60°, and (d) impact angle of 75°

absorption, which can result in energy absorption and a reduction in solid particle erosion damage [16], this differs from resin matrix swelling and softening. In the case of a FRP, the resin absorbs water easily, which leads to volume expansion. Carbon fibers have good hydrolytic stability and do not absorb water [17], therefore resin swelling generates stress and can cause interfacial debonding [18]. Previous studies [19] have shown that poor fiber/matrix adhesion clearly decreases resistance to solid particle erosion. The erosion rates of all the studied composites therefore increased after hot water immersion.

It was also observed that regardless of the composite immersion time, the erosion rates of the composites after redrying treatment were similar. The PET-based composites recovered from erosion after redrying, but their erosion rates still differed from that of the virgin sample, showing incomplete recovery. These results indicate that hot water immersion irreversibly changed the PET-based composite.

3.3   Short Beam Shear Tests

A short beam shear test is used to evaluate the ILSS, and is therefore an effective experimental tool for assessment of the effects of various factors at the interface level on composite durability [20]. The ILSS values for virgin, hot-water-treated, and redried PET-based composites are shown in Fig. 3.
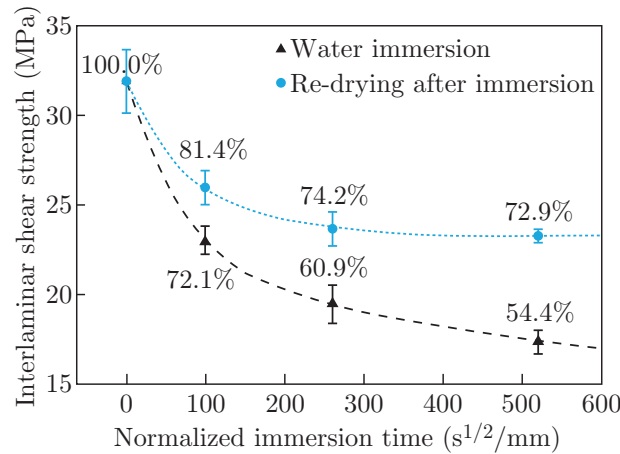

Fig. 3: Variations in interlaminar shear strength with normalized immersion time

The ILSS decreased rapidly during the initial stage of immersion, followed by a relatively gradual decrease. The ILSS reflects the interfacial strength between the matrix resin and the fibers. As mentioned in introduction section, the erosion of FRPs by solid particles depends closely on the interfacial strength. The erosion rates of the treated PET-based composites therefore increased sharply compared with that of the virgin PET-based composite for a normalized immersion time of 260 $s^{1/2}$/mm, followed by a relatively slow increase in the erosion rate up to a normalized immersion time of 520 $s^{1/2}$/mm (Fig. 2). The reduction in the ILSS may be caused by interfacial degradation (either debonding or osmotic damage) [21].

The reversibility of the changes in the ILSS values of PET-based composites caused by hot water immersion was also assessed. Fig. 3 shows the percentage recoveries of the ILSS values after redrying at 70 °C in a vacuum oven for 24 h. The results show that the ILSS values for

the dried specimens were higher than those of wet specimens subjected to the same aging. This is because of partial recovery of network relaxation after redrying [16]. PET-based composites exposed to hot water at 70 °C for 100, 260, and 520 $s^{1/2}$/mm showed ILSS recoveries of 81.4%, 74.2%, and 72.9%, respectively, after redrying. This indicates that removal of water contained in the composites resulted in incomplete recovery of the ILSS values. This is why the erosion rates of PET-based composites did not fully recover to that of the virgin composite. Fig. 3 also shows that after 200 $s^{1/2}$/mm the ILSS curve of the redried composite reached a plateau, and any damage caused by further hygrothermal aging was reversed to a similar level after redrying. Because of this, the erosion rates of redried PET-based composites exposed to hot water for 260 and 520 $s^{1/2}$/mm were similar.

3.4 Dynamic Mechanical Analysis

DMA is used to evaluate the failure behavior and fiber/matrix interface characteristics of materials. It has attracted much attention recently because of it is highly sensitive and enables non-destructive examination of interfacial regions [22].

Typical DMA curves for the virgin PET-based composite, hot-water-treated PET-based composites, and redried hot-water-treated PET-based composites are shown in Fig. 4. Fig. 4(a) shows the storage moduli (E') for five different types of PET-based composite plotted against temperature. In this figure, CFRTP(0) denotes data for the virgin PET-based composite, CFRTP(260) denotes data for the PET-based composite degraded for a normalized immersion time of 260 $s^{1/2}$/mm, and R-CFRTP(260) denotes data for the redried PET-based composite degraded for a normalized immersion time of 260 $s^{1/2}$/mm.

The DMA curves show that the E' values of the composites were lower after hot water treatment. The decrease in the storage modulus of the PET-based composite increased with increasing normalized immersion time. For example, at 35 °C, the E' of CFRTP(0) was about 410 GPa, and the E' values of CFRTP(260) and CFRTP(520) were 330 and 260 GPa, respectively. Based on the report by Aziz et al. [23] that greater interfacial adhesion and bonding strength between the resin and fibers increased the E' value of a treated kenaf–polyester composite, it can be concluded from the results of our study that the compatibility of the carbon fibers with the PET resin in the virgin PET-based composite was higher than those in the hot-water-treated composites. Fig. 4(a) also shows that the E' values of the treated composites after redrying were higher than those of the hot-water-treated composites. This indicates that the interfacial adhesion and bonding strength between the PET resin and carbon fibers improved after redrying. The figure also shows that the storage modulus curves of R-CFRTP(260) and R-CFRTP(520) basically coincide, which means that they have similar interfacial strengths and bonding strengths between the PET resin and carbon fibers. This is why the ILSS curve for the redried composite reached a plateau after 200 $s^{1/2}$/mm.

Fig. 4(c) shows that the peak $\tan\delta$ (the ratio of the loss modulus to the storage modulus) values of the hot-water-treated composites shifted sharply to lower values compared with that of the virgin PET-based composite. The peak of the $\tan\delta$ curve corresponds to the value for the glass-transition temperature (T_g) or usage temperature (T_u) [24]. Hot water treatment therefore decreased the T_g of the PET-based composite, and the reduction became more severe with increasing normalized time. The T_g of the virgin PET-based composite was about 10 °C higher than that of the PET-based composite treated with hot water for 520 $s^{1/2}$/mm. The reduction in
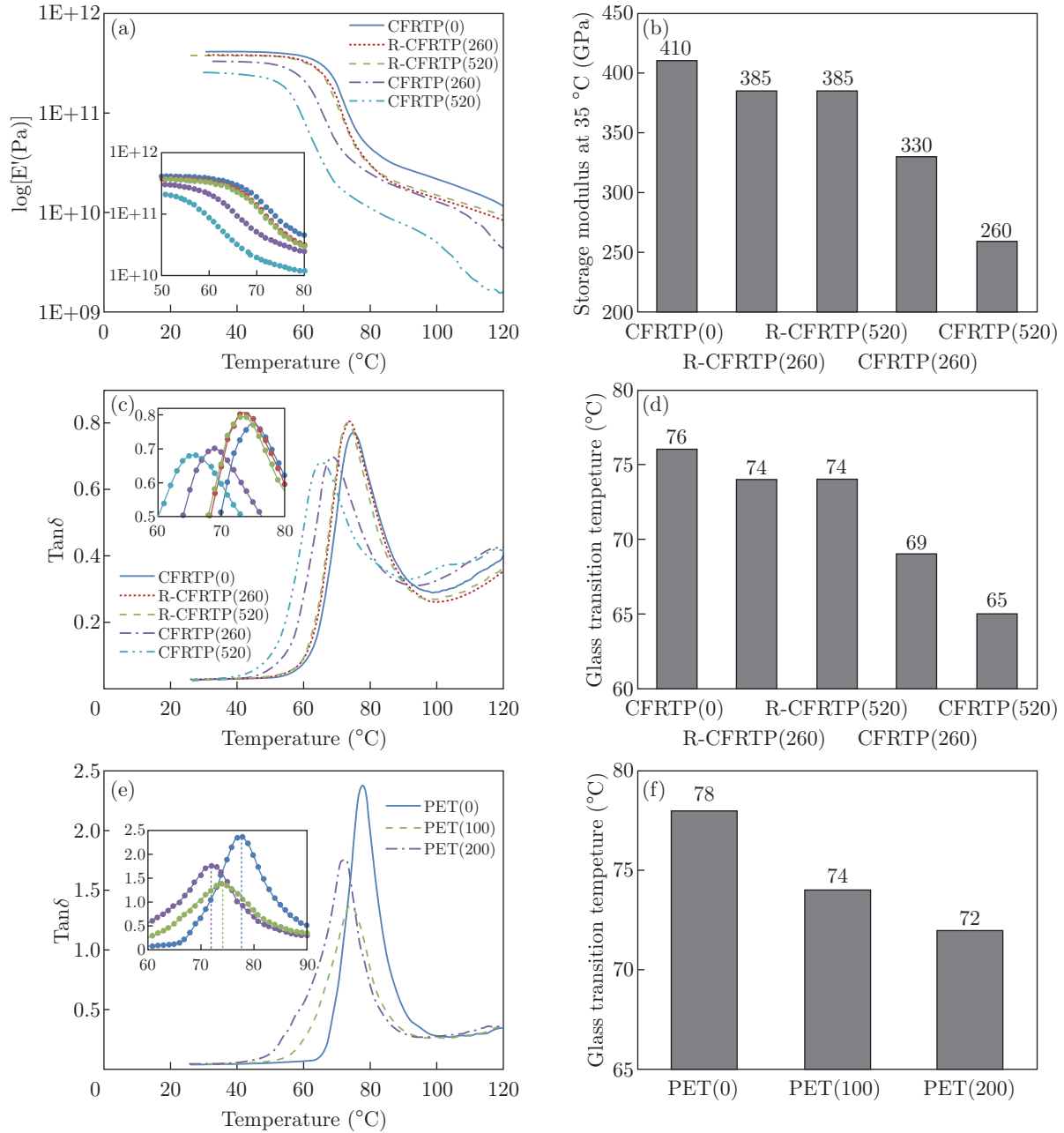
Fig. 4: (a) Storage modulus curves of PET-based composites, (b) storage moduli of PET-based composites at 35 °C, (c) tan δ curves of PET-based composites, (d) T_{g} values of PET-based composites, (e) tan δ curves of PET resins, and (f) T_{g} values of PET resins

T_{g} caused by hot water treatment is probably the result of chain scission, which increases chain mobility. The T_{g} of the PET resin therefore decreased as a result of hot water treatment, as shown in Fig. 4(e) and 4(f). Another possible reason for the reduction in the T_{g} of the hot-water-treated composite is debonding of the fibers from the matrix by water or moisture in the composite. Similar trends in the storage modulus curves were observed; the T_{g} values of the hot-water-treated composites increased after redrying, and the tan δ curves of R-CFRTP(260) and R-CFRTP(520) almost coincided.

3.5   Examination of Eroded Surfaces of Test Specimens

The eroded surfaces of the test specimens were examined using SEM. Fig. 5(a) and 5(c) show SEM micrographs of the eroded surfaces of the virgin PET-based composite and 520 $s^{1/2}$/mm hot-water-treated composite, respectively. Fig. 5(b) is a higher-magnification version of Fig. 5(a), and enables better examination of the damaged fibers. The exposed fibers on the damaged surface are covered with matrix resin (blue arrows), and more broken fibers remain in the matrix resin. This verifies that the natural dry specimen has good resin/fiber interfacial strength, and supports the results shown in Figs. 3 and 4. Good bonding between the carbon fibers and PET resin improves the erosion resistance because neither the fibers nor the resin can be removed easily, or their fragments can remain longer on the eroded surface. However, many grooves (red arrows) are created by local carbon fiber removal, as observed in Fig. 5(c) and 5(d). Moreover, many fibers with smooth surfaces are exposed on the damaged surface (green arrows); this may indicate debonding between the fibers and matrix resin. These phenomena explain why the erosion rate after hot water treatment increased significantly compared with that of the natural dry specimen. After redrying, because of the improved interfacial strength between the fibers and the resin, the resin cannot be easily removed from the fiber surface when the composite is damaged; the fibers with the clear profile shown in Fig. 5(d) cannot be found in Fig. 5(e) and 5(f). The fibers are covered with PET resin (blue arrows), which can protect the carbon fibers from damage, therefore the erosion rate of the redried hot-water-treated composites decreased. Although the ILSS of the redried composite clearly increased, it differed from that of the virgin composite, indicating poor interfacial strength in some places, local carbon fiber removal, and some groove formation (red arrows). This is why the erosion rate of the redried hot-water-treated composite was higher than that of the virgin PET-based composite.
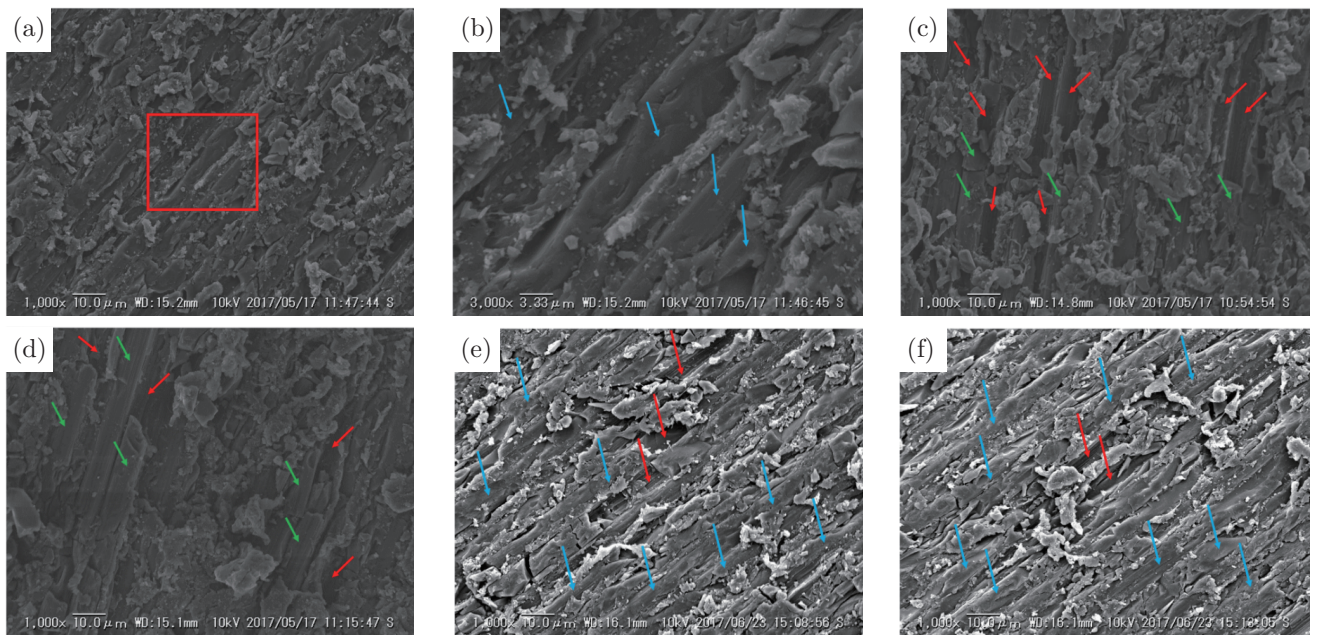

Fig. 5: SEM micrographs showing damage to virgin PET-based composite (a) at low magnification and (b) at high magnification, (c) and (d) hot-water-treated PET-based composite, and (e) and (f) redried hot-water-treated PET-based composite

4   Conclusions

The present study focused on the moisture absorption kinetics of PET resins and PET-based composites, and the effects of water absorption and water desorption on the erosion resistant properties, ILSS, and dynamic mechanical properties. The following conclusions can be drawn from the results.

The water content of the PET resin increased linearly with normalized immersion time and a water-saturated sample was obtained. However, the PET-based composite did not reach an equilibrium water content. Capillarity or transport in microcracks occurred when the composite was immersed in hot water, resulting in non-Fickian behavior.

The PET resin erosion rate decreased after hot water treatment because the swollen and softened resin can absorb part of the energy from impacting particles. The composite erosion rate increased after hot water treatment, but the increase in the erosion rate of the treated composite was reversed after redrying.

The ILSS of the composite decreased sharply after hot water treatment. The ILSS value of the redried composite was higher than that of the hot-water-treated composite subjected to the same aging.

Because the water content affects the interfacial adhesion and bonding strength between the resin and fibers, the storage modulus and glass-transition temperature decreased after hot water treatment; both recovered after redrying.

Acknowledgement

References

[1]   Prambauer M, Paulik C, Burgstaller C. Evaluation of the interfacial properties of polypropylene composite laminates, reinforced with paper sheets. Compos Part A — Appl Sci 2016; 88: 59-66.

[2]   Sombatdee S, Amornsakchai T, Saikrasun S. Reinforcing performance of recycled PET microfibrils in comparison with liquid crystalline polymer for polypropylene based composite fibers. J Polym Res 2012; 19: 9843-9855.

[3]   Svensson N, Shishoo R, Gilchrist M. Manufacturing of thermoplastic composites from commingled yarns — A review. J Thermoplast Compos Mater 1998; 11: 22-56.

[4]   Chang IY, Lees JK. Recent development in thermoplastic composites: a review of matrix systems and processing methods. J Thermoplast Compos Mater 1998; 1: 277-296.

[5]   Liu B, Xu AC, Bao LM. Preparation of carbon fiber-reinforced thermoplastics with high fiber volume fraction and high heat-resistant properties. J Thermoplast Compos Mater 2017; 30: 724-737.

[6] Huang G, Sun HX. Effect of water absorption on the mechanical properties of glass/polyester composites. Mater Des 2007; 28: 1647-1650.

[7] Mortazavian S, Fatemi A. Effect of water absorption on tensile and fatigue behavior of two short glass fiber reinforced thermoplastics. SAE Int J Mater Manuf 2015; 8: 435-443.

[8] Qian DN, Bao LM, Takatera M, Kemmochi K, Yamanaka A. Fiber-reinforced polymer composite materials with high specific strength and excellent solid particle erosion resistance. Wear 2010; 268: 637-642.

[9] Patnaik A, Satapathy A, Chand N, Barkoula NM, Biswas S. Solid particle erosion wear characteristics of fiber and particulate filled polymer composites: A review. Wear 2010; 268: 249-263.

[10] Rattan R, Bijwe J. Influence of impingement angle on solid particle erosion of carbon fabric reinforced polyetherimide composite. Wear 2007; 262: 568-574.

[11] Arjula S, Harsha AP, Ghosh MK. Erosive wear of unidirectional carbon fiber reinforced polyetherimide composite. Mater Lett 2008; 62: 3246-3249.

[12] Subagia IDG, Kim YJ, Tijing LD, Kim CS, Shon HK. Effect pf stacking sequence on the flexural properties of hybrid composites reinforced with carbon and basalt fibers. Compos Part B — Eng 2014; 58: 251-258.

[13] Pegoretti A, Penati A. Effect of hygrothermal aging on the molar mass and thermal properties of recycled poly(ethylene terephthalate) and its short glass fibre composites. Polym Degrad Stabil 2004; 86: 233-243.

[14] Mohd Ishak ZA, Tengku Mansor TSA, Yow BN, Ishiaku US, Karger-Kocsis J. Short glass fibre reinforced poly(butylene terephthalate) Part 1— Microstructural characterization and kinetics of moisture absorption. Plast Rubber Compos 2000; 29: 263-270.

[15] Bismarck A, Hofmeier M, Dorner G. Effect of hot water immersion on the performance of carbon reinforced unidirectional poly(ether ether ketone) (PEEK) composites: Stress rupture under end-loaded bending. Compos Part A — Appl Sci 2007; 38: 407-426.

[16] Sun P, Zhao Y, Luo YF, Sun L. Effect of temperature and cyclic hygrothermal aging on the interlaminar shear strength of carbon fiber/bismaleimide (BMI) composite. Mater Des 2011; 32: 4341-4347.

[17] Park JM, Shin PS, Wang ZJ, Kwon DJ, Choi JY, Lee SI, DeVries KL. The change in mechanical and interfacial properties of GF and CF reinforced epoxy composites after aging in NaCl solution. Compos Sci Technol 2016; 122: 59-66.

[18] Wang Y, Hahn TH. AFM characterization of the interfacial properties of carbon fiber reinforced polymer composites subjected hygrothermal treatments. Compos Sci Technol 2007; 67: 92-101.

[19] Barkoula NM, Karger-Kocsis J. Solid particle erosion of unidirectional GF reinforced EP composites with different fiber/matrix adhesion. J Reinf Plast Compos 2009; 19: 1-12.

[20] Kafodya I, Xian GJ, Li H. Durability study of pultruded CFRP plates immersed in water and seawater under sustained bending: Water uptake and effects on the mechanical properties. Compos Part B — Eng 2015; 70: 138-148.

[21] Gautier L, Mortaigne B, Bellenger V. Interface damage study of hydrothermally aged glass fiber-reinforced polyester composites. Compos Sci Technol 1999; 59: 2329-2337.

[22] Lisaka K, Shibayama K. Mechanical alpha-dispersion and interaction in filled polystyrene and polymethylmethacrylate. J Appl Polym Sci 1978; 22: 3135-3143.

[23] Aziz SH, Ansell MP. The effect of alkalization and fiber alignment on the mechanical and thermal properties of kenaf and hemp bast fiber composites: Part 1 — polyester resin matrix. Compos Sci Technol 2004; 64: 1219-1230.

[24] Berry NG, d'Almeida JRM, Barcia FL, Soares BG. Effect of water absorption on the thermal-mechanical properties of HTPB modified DGEBA-based epoxy systems. Polym Test 2007; 26: 262-267.