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Hydrothermal ageing mechanisms of unidirectional flax fabric reinforced epoxy composites

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ABSTRACT

Hydrothermal ageing of plant fiber reinforced composites could cause degradation of mechanical properties due to the synergic effect of moisture and temperature. This paper explored the degradation mechanisms of plant fiber reinforced composites in the hydrothermal environment. The ageing behaviors of each component, i.e. the fiber, matrix and interface were investigated. Water absorption, dimensional variation and mechanical properties of the materials were continuously measured and analyzed. Supplementary methods of Scanning Electronic Microscopy (SEM) and Fourier Transform Infrared Spectroscopy (FTIR) were also employed in this study. Results revealed that the deterioration of flax fibers is the crucial factor for the ageing of plant fiber reinforced composites which is very different with that of synthetic fiber reinforced composites, where resin was the dominate component. A recovery study on the mechanical properties showed consistent results with other experimental results and analysis. Additionally, a systematic hydrothermal ageing mechanism was proposed.

1. Introduction

Plant fiber reinforced composites are promisingly used in aerospace, civil engineering, automotive and many other industries due to their unique properties, such as environment friendly, relatively high specific strength and modulus, abundant availability, favorable sound absorption and heat insulation [1–4]. In order to respond to the environmental protection requirements and new ecological regulations, plant fibers are in great development in making fiber reinforced composite materials and structures [2–4]. However, their relatively poor mechanical performance and severe deterioration in hydrothermal conditions mainly limit their wide applications in making structural components [4]. For example, in the research conducted by Lefeuvre et al. about tensile properties of elementary fibers of flax and glass, they found that the stress at break of glass fibers varied between 1765 and 2319 MPa and Young's modulus between 70.3 and 77.8 GPa. However, flax fibers usually possess the high mechanical performance levels among bastose fibers, and their stress at break ranged between 970 and 1109 MPa and Young's modulus between 53.3 and 58.9 GPa which were tested in the same condition with the glass fibers [5].

Since the durability in aggressive environments, particularly in wet conditions undergoing a long time is considerably important for materials, hydrothermal ageing of composite materials has been extensively researched. A series of recognized ageing mechanisms of composites reinforced with synthetic fibers have been reported, including swelling, plasticizing, cracking and hydrolyzing of matrix along with the debonding of fiber–matrix interface [6–12]. While the synthetic fibers themselves, such as carbon and glass fibers, are generally considered no or less degradation during ageing which can be attributed to their hydrophobic characteristics [6,10,12].

However, plant fibers feature a high affinity to water, which is totally different with those synthetic fibers. Most literature reported this phenomenon was caused by their unique microstructures and various chemical components. Generally an elementary flax fiber (Fig. 1) was composed of a primary outer wall and a secondary wall made up by three different layers, i.e. S_1, S_2 and S_3 [3]. In the center, a cavity known as a lumen presented, making it a hollow structure which was quite different with synthetic fibers [13]. If consider it as a sink, it may play a major role in the water sorption of the material. The main layer- S_2, representing around 80% of the total section, was constituted of highly crystalline cellulose fibrils spirally wound in a matrix of amorphous hemicelluloses and pectins. The cellulose fibrils made a 10°angle with

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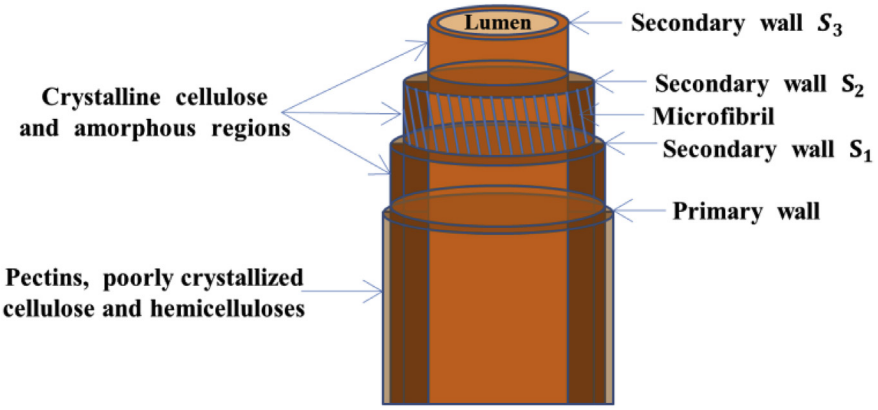

Fig. 1. Schematic diagram of an elementary flax fiber.

the axis of the fiber, which was called microfibrillar angle and had a significant effect on the mechanical properties of fibers [14]. Pectins, poorly crystallized cellulose, and xyloglucans as the main hemicelluloses moieties formed the main components of primary wall, shouldering the dominating responsibility for water absorption due to their amorphous structure and high majorities of available hydroxyl groups [3,14]. The multi-scale structure and hydrophilic constituents led composite materials reinforced with plant fibers more vulnerable to degradation. Most published studies showed that the exposure of plant fiber reinforced composites in a wet environment, particularly in water for a period of time resulted in a loss of the mechanical properties [13,15–28]. When water was absorbed into materials after 10-day immersion, the percentage reduction of tensile strength for flax fiber reinforced composites was three times larger than that of glass fiber reinforced composites [15]. A more significant reduction in Young's modulus was shown in the water-saturated plant fiber reinforced composites [16]. The apparent shear strength and frictional strength dropped quickly then stabilized with the increase of the immersion time [17]. Most researchers considered the weakening of matrix interface was the main damage mechanism for plant fiber reinforced composites during hydrothermal ageing.

Although hydrothermal ageing of plant fiber reinforced composites has been explored by many researchers [13,15–28], no systematic degradation mechanisms have been acquired especially from the plant fiber's point of views. Few researches have taken the multi-layer structure of plant fibers into consideration and finding out the transition from recoverable physical changes to unrecoverable damages of the composites has scarcely been involved in previous studies.

In order to have a better understanding of the degradation mechanisms of plant fiber reinforced composites, unidirectional flax fabric reinforced epoxy composite (FFRP) was manufactured and studied in this paper. Measurements of water absorption, dimensional variation, and mechanical properties were performed. An individual analysis of each component of the composites, containing epoxy matrix, fiber-matrix interface and flax fibers, was conducted to evaluate the changes of these components under hydrothermal environment, so that the degradation mechanisms of plant fiber reinforced composites could be revealed.

2. Experiment

2.1. Materials

The unidirectional flax fabric was purchased from Lineo, Belgium. The areal density and thickness were 200 g/m^2 and 0.36 mm, respectively. The matrix was an epoxy system consisting of an Araldite resin (NPEL-128), an amine curing agent (EH-6303) and an accelerator (EH-6412), at a weight ratio of 100:26:8, all of which were supplied by Shanghai Zongsi Company.

2.2. Fabrication

The unidirectional flax fabric reinforced epoxy laminates were manufactured by Vacuum Assisted Resin Transfer Molding (VARTM). The laminates were cured at room temperature for 24 h inside the vacuum bags and then post-cured at 60 °C for 8 h in an oven. 6 and 13 layers of unidirectional flax fabric were applied to make the laminates with different thicknesses, which were 2.5 mm and 5.5 mm, respectively. The fiber volume fractions were all kept at 37%. Meanwhile pure epoxy specimens and single flax yarns which were randomly removed and selected from the fabric were also prepared to study the durability of pure resin and reinforcing fibers.

2.3. Preparation of specimens

In order to ensure the quality of materials before being aged in the environment, firstly all the laminates and epoxy castings were scanned with the aid of an ultrasound C-scan instrument (NAUT21, JAPAN PROBE). Fig. 2 showed the equipment set up and C-scan image of the FFRP laminates. Then plates with few defects were selected and cut into specimens for water absorption and dimensional variation measurements and mechanical tests. Later all the specimens, including the composites, epoxy resin and flax yarns were pre-conditioned in a humidity chamber which was set at a constant relative humidity (RH) of 50% and a constant temperature of 23 °C for 28 days until the weight of each specimen became constant. Then all the specimens were numbered and immersed into the deionized water at 23 °C, 37.8 °C and 60 °C for further testing. For the purpose of investigating the reversibility of mechanical properties, another group of specimens were prepared at each testing point. The specimens were dried at 120 °C for 2 h before being tested.

2.4. Test

2.4.1. Water absorption

The water absorption measurement was conducted according to ASTM-D5229. At each ageing point, specimens were taken out from the bath, and their surfaces were meticulously dried with tissue papers, then weighed immediately with an analytical balance having precision of ±0.01 mg. The water uptake M_t was then

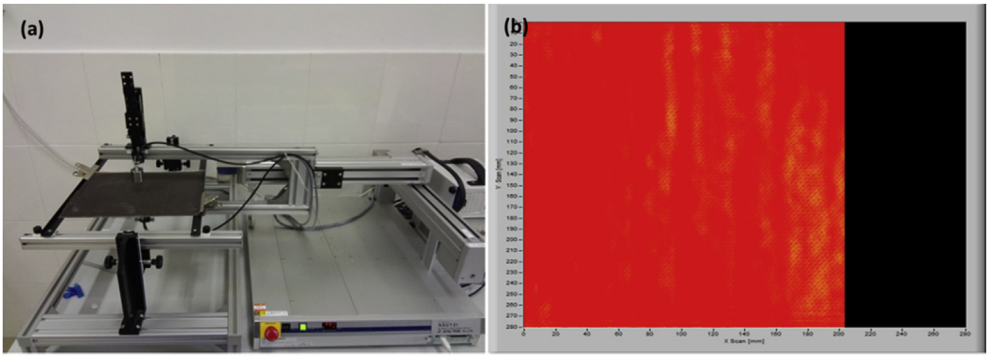

Fig. 2. (a) The C-scan equipment set up and (b) C-scan image of a FFRP laminate.

evaluated by equation (1).

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

where W_t is the weight of specimen at time t, and W_0 is the weight of dry specimen. Three specimens were measured for each group. Average value of M_t will be the final experimental data.

2.4.2. Dimensional variation

At each testing time, the width and thickness of each specimen were measured at three different positions by using a Vernier caliper. Three specimens were measured to obtain the average value for each measuring point.

2.4.3. Mechanical properties

Tensile and short beam shear tests of FFRP were performed using a Universal Testing Machine (Wance Co. Ltd., China) with a 20 KN load cell in accordance to ASTM-D3039 and ASTM-D2344, respectively. The nominal dimensions of tensile test specimens were 250 × 15 × 2.5 mm^3 and the test speed was 2 mm/min. An extensometer with a 50 mm gauge length was used to determine the strain. The dimensions of shear test specimens were 35 × 10 × 5 mm^3 and the speed of load cell was 1 mm/min with the span to thickness ratio of 4. Tensile properties of the epoxy resin were measured according to GB-T1040 standard. Specimens were made in dumbbell-shaped as the standard specified and the test speed was 1 mm/min, also using the extensometer to determine the strain of epoxy resin. Five specimens were tested for each group.

3. Results and discussions

3.1. Water absorption

Fig. 3(a) and (b) showed the water absorption of neat epoxy resin and FFRP at three different temperatures, as a function of square root of immersion time divided by the thickness of the specimen, for the reason of being convenient for later study of curve fitting of Fick's law. From the experimental data, it can be seen that the water uptake for all the materials at different temperatures basically showed two-step behaviors: a linear initial part followed by an equilibrium plateau.

In order to determine the model of water absorption, transmission kinetic equation was referred to, as equation (2).

$$\frac{M_t}{M_m} = \mathrm{k} \cdot t^n \quad (2)$$

where, M_t is the moisture uptake at time t, M_m is the maximum water absorption at saturation, and k, n are the diffusion kinetic parameters [15].

Fig. 4(a) and (b) presented the logarithmic fitting of the experimental data of water absorption based on equation (2). The diffusion kinetic parameters could then be obtained from the curve fitting and were summarized in Table 1. It could be discovered that the values of n were all close to 0.5, representing the water absorption of both epoxy resin and FFRP were approximate to Fickian behavior. Therefore, Fick's law can be applied to theoretically analyze the water absorption of these materials.

The theoretical equation of Fick's law was shown as equation (3):

$$\frac{M_t}{M_m} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left[-\left(\frac{D \times t}{h^2}\right)\pi^2 \times (2n+1)^2\right] \quad (3)$$

where, h is the thickness of specimens and D is the diffusivity, a key parameter of Fickian model. It can be determined from the linear initial part of the curve as it is usually dominated by this part. Equation (4) was usually employed to calculate the diffusivity [15].

$$\mathrm{D} = \frac{\pi}{(4M_m)^2} \times \left(\frac{M_t \times h}{\sqrt{t}}\right)^2 = \frac{\pi \cdot k'^2}{(4M_m)^2} \quad (4)$$

where, the coefficient k' is the slope of the linear part of the curve $M_t = \mathrm{f}(\sqrt{t}/\mathrm{h})$. Therefore, the maximum water absorption and diffusivity of both epoxy resin and FFRP were summarized in Table 2.

The results in Table 2 presented that at the same ageing conditions, maximum water absorption, M_m and diffusivity, D of FFRP were much larger than those of epoxy resin, which was quite different with carbon or glass fibers reinforced composites. Normally the difference of M_m and D between resin and composites reinforced with synthetic fibers was much less than that of the plant fiber composites since the reinforcing fibers did not absorb water at all [6–12]. It was suggested that besides resin, both the interface and flax fibers played an important role in the water absorption.

By comparing M_m and D of the same material aged at different conditions, it can be observed that temperature showed a significant effect on water absorption. Both the saturation level and diffusivity increased with the increasing of temperature. This is in agreement with other research results [15–17]. Arrhenius equation

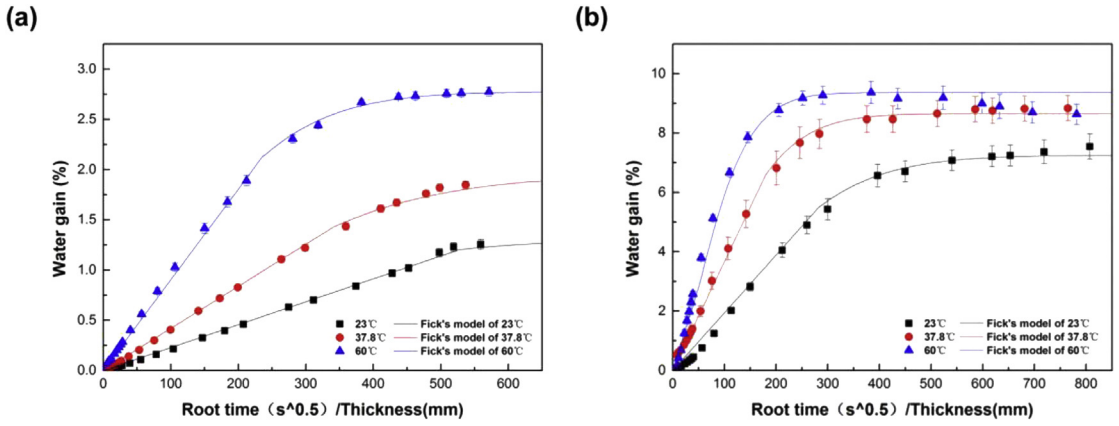

Fig. 3. Evolution of water uptake of (a) epoxy resin and (b) FFRP being aged at 23 °C, 37.8 °C and 60 °C.

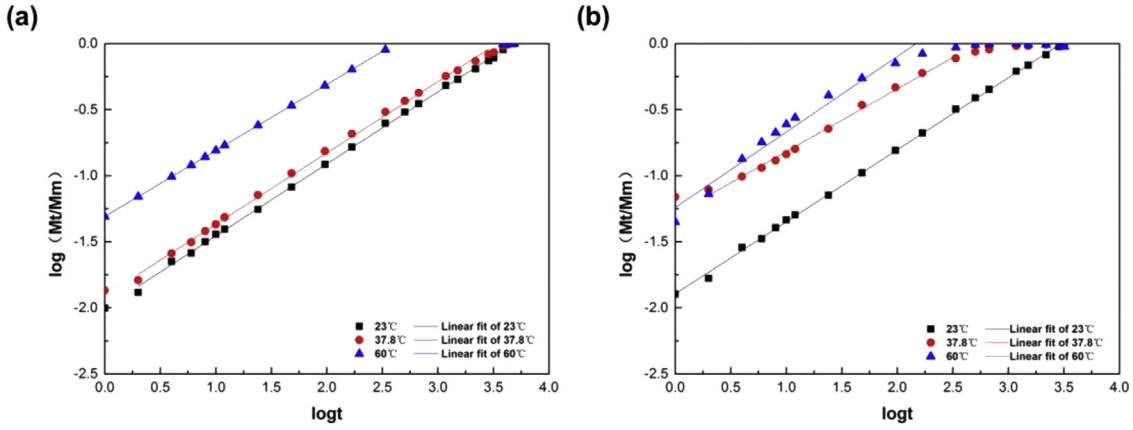

Fig. 4. Diffusion curve fitting plots of (a) epoxy resin and (b) FFRP being aged at 23 °C, 37.8 °C and 60 °C.

which stated temperature affected constants of reaction rate in the same manner was shown as equation (5).

$$D = D_0 \exp\left(-\frac{E_a}{RT}\right) \tag{5}$$

where, D_0 is the diffusivity constant, E_a is the active energy (J/mol), R is Universal gas constant (8.3144 J/mol) and T is temperature in Kelvin.

D_0 and E_a can be obtained from the logarithmic fitting of equation (5) by the experimental data. Fig. 5(a) and (b) showed the fitting results for both the epoxy resin and FFRP and the Arrhenius parameters acquired from the fitting were presented in Table 3. Thus, the diffusivity, D at any temperature can be calculated from the obtained equation (6) and equation (7).

Table 1
Diffusion kinetic parameters.

Ageing conditions	Epoxy resin			FFRP		
	n	k	R^2	n	k	R^2
23 °C	0.545	0.009996	0.9992	0.545	0.012794	0.9993
37.8 °C	0.54	0.012362	0.9984	0.475	0.051168	0.9945
60 °C	0.5	0.049147	1	0.571	0.057554	0.9679

Table 2
Maximum water absorption and diffusivity.

Ageing conditions	Epoxy resin		FFRP	
	M_m (%)	$D \times 10^{-6}$ (mm^2/s)	M_m (%)	$D \times 10^{-6}$ (mm^2/s)
23 °C	1.304	0.599	7.245	1.414
37.8 °C	1.947	0.909	8.652	3.525
60 °C	2.775	2.078	9.365	11.924

$$D_E = 4.5753 \times 10^{-8} \exp\left(-\frac{27776.21}{RT}\right) \tag{6}$$

$$D_C = 3.0437 \times 10^{-4} \exp\left(-\frac{47218.86}{RT}\right) \tag{7}$$

where, D_E is the diffusivity of epoxy and Dc is the diffusivity of FFRP.

Eventually taking the values of D back to equation (3), the theoretical water absorption curves predicted by Fick's law were plotted, as shown by the solid lines in Fig. 3(a) and (b). Compared to the experimental data, it was found that at the beginning of hydrothermal ageing, the behavior of water uptake of epoxy resin and FFRP obeyed Fick's law very well. However, at later stage of FFRP aged at 60 °C, the experimental data deviated from the Fick's law, which might indicate other mechanisms of water absorption occurred in materials rather than diffusion.

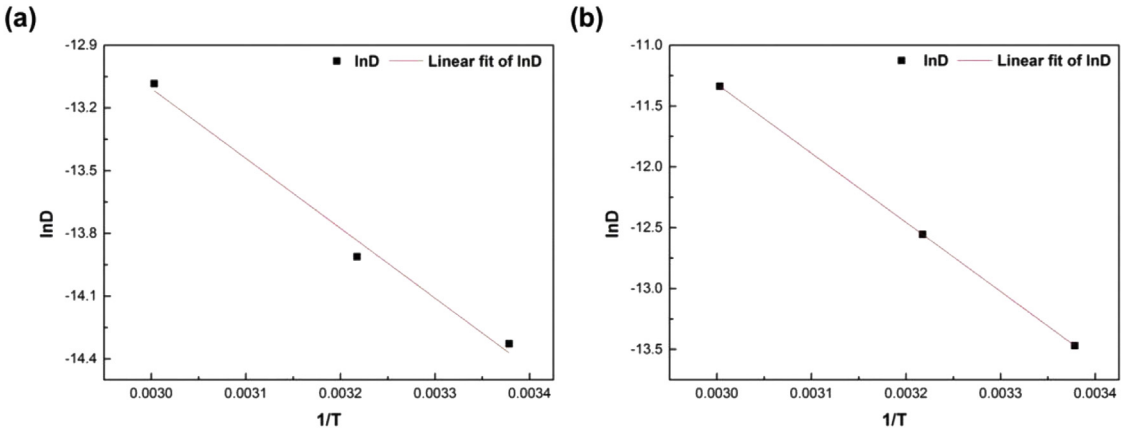

Fig. 5. Arrhenius fitting plots of (a) epoxy resin and (b) FFRP.

Table 3
Arrhenius parameters.

	E_a (J/mol)	D_0 (m^2/s)	R^2
Epoxy resin	27776.21	4.5753E-8	0.97747
FFRP composite	47218.86	3.0437E-4	1

3.2. Dimensional variation

Fig. 6 exhibited the changes of cross-sectional areas of FFRP in the hydrothermal conditions. It can be seen that the dimensions of the composites increased at the beginning of immersion, and then leveled off. Whereas for specimens aged at 60 °C, a little decrease of the cross-sectional area was observed. The changes of cross-sectional areas of the composites with the increase of moisture absorption were also plotted in Fig. 7. It can be discovered that the dimensional variation of FFRP was strongly correlated with the moisture uptake, and a linear relationship was observed between them.

In order to further study the influence of water absorption on the dimensions of FFRP, the diameters of flax yarns before and after being immersed into deionized water and dried after being aged for certain period of time were measured and compared in Fig. 8. It can be found that for flax yarns aged for 2 weeks, the diameters after being dried were the same to those of virgin ones, indicating that the water absorbed by flax fibers for the first 2 weeks only made them swelling physically, no deterioration occurred. However, for flax yarns aged for 17 weeks, the diameters were smaller after being dried compared to the values of the virgin ones, suggesting that chemical degradation caused by water uptake might happen.

Therefore, during the initial ageing period, due to the high water absorption rate, dimensional variation of FFRP was significant. The absorbed water caused flax fibers an apparent swelling largely as a result of the physical expansion of lumen and the combination of cellulose and water molecules, directly leading to an increase of fiber diameters. Meanwhile, water uptake by matrix might also result in an expansion of the specimens. As the water uptake reached saturation, the dimension became constant.

In order to verify the dissolution of flax fibers in FFRP after being immersed in water for 17 weeks, FTIR was employed to study the soaking solution and the spectra was shown in Fig. 9. Characteristic peaks were found at about 2966 cm^{-1}, 2929 cm^{-1}, associated to C–H stretching vibration attributed to methyl and methylene groups, respectively. Peaks at 1600–1650 cm^{-1} might correspond to non-esterified pectins and peaks at about 1735 cm^{-1} associated to carbonyl (C=O) stretching of acetyl groups of hemicellulose [29]. The 1430 cm^{-1} band was attributed to the CH_2 bending of cellulose. Peaks due to deformation of alcohol group of cellulose (OH) were characterized by the peaks located at 1370 cm^{-1} and 1340 cm^{-1}, while the peak at 1320 cm^{-1} corresponded to the CH_2 wagging of cellulose [30]. Peak at 900 cm^{-1} assigned to the out of phase ring stretching was characteristic of the cellulose backbone [31]. The symmetric glycosidic stretch C–O–C or a ring stretching mode at 1100 cm^{-1} and the C–OH stretching vibration of the cellulose backbone at 1060 cm^{-1} (C–O secondary alcohol) and 1035 cm^{-1} (C–O primary alcohol) arise from the polysaccharide components,

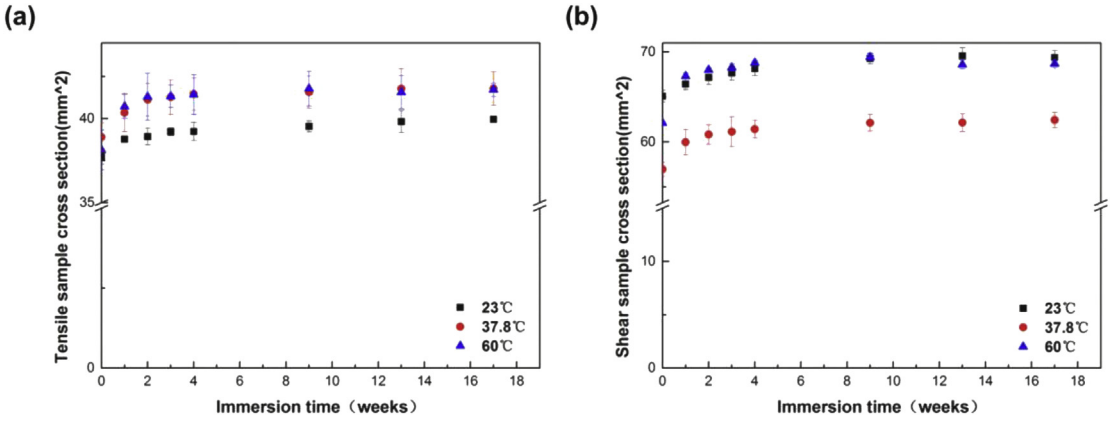

Fig. 6. Cross-sectional areas versus ageing time of FFRP (a) tensile specimens and (b) shear specimens at 23 °C, 37.8 °C and 60 °C.

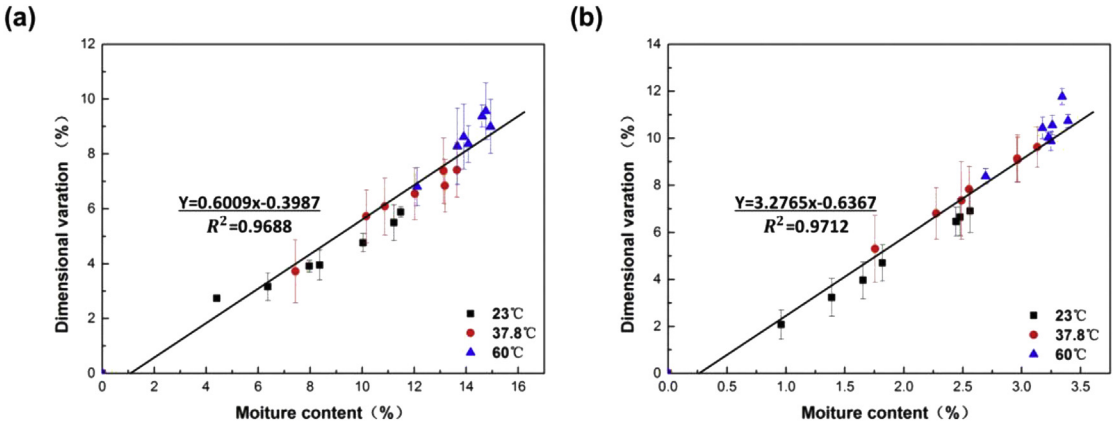

Fig. 7. Dimensional variation of FFRP versus moisture content of (a) tensile specimens and (b) shear specimens.

largely cellulose [32]. Thus, it could be inferred that pectins, hemicellulose and some poorly crystallized cellulose of the primary wall in flax fibers were dissolved into the solution. Therefore, the dissolution of the components of the flax fibers after being aged for certain period of time accounted for the reduction of fiber diameters.

3.3. Mechanical properties

3.3.1. Tensile properties of epoxy resin

Fig. 10 and Fig. 11 showed the changes of tensile strength and Young's modulus of epoxy resin with the increase of ageing time, respectively. The changes of moisture content were also plotted in the Figures to better show their effects on the mechanical properties of the composites. It can be seen that, tensile strength and Young's modulus firstly decreased then stabilized. Referring to the water absorption, it can be discovered that with the increase of the water uptake, both the tensile strength and Young's modulus showed a remarkable decline trend due to the plasticization of the epoxy. As the water absorption approached saturation, both strength and modulus also showed a tendency of stabilization.

Fig. 12(a) and (b) presented the failure mode of epoxy resin before and after being aged at 60 °C for 17 weeks. It can be seen that the fracture surfaces of the unaged specimens were neat and

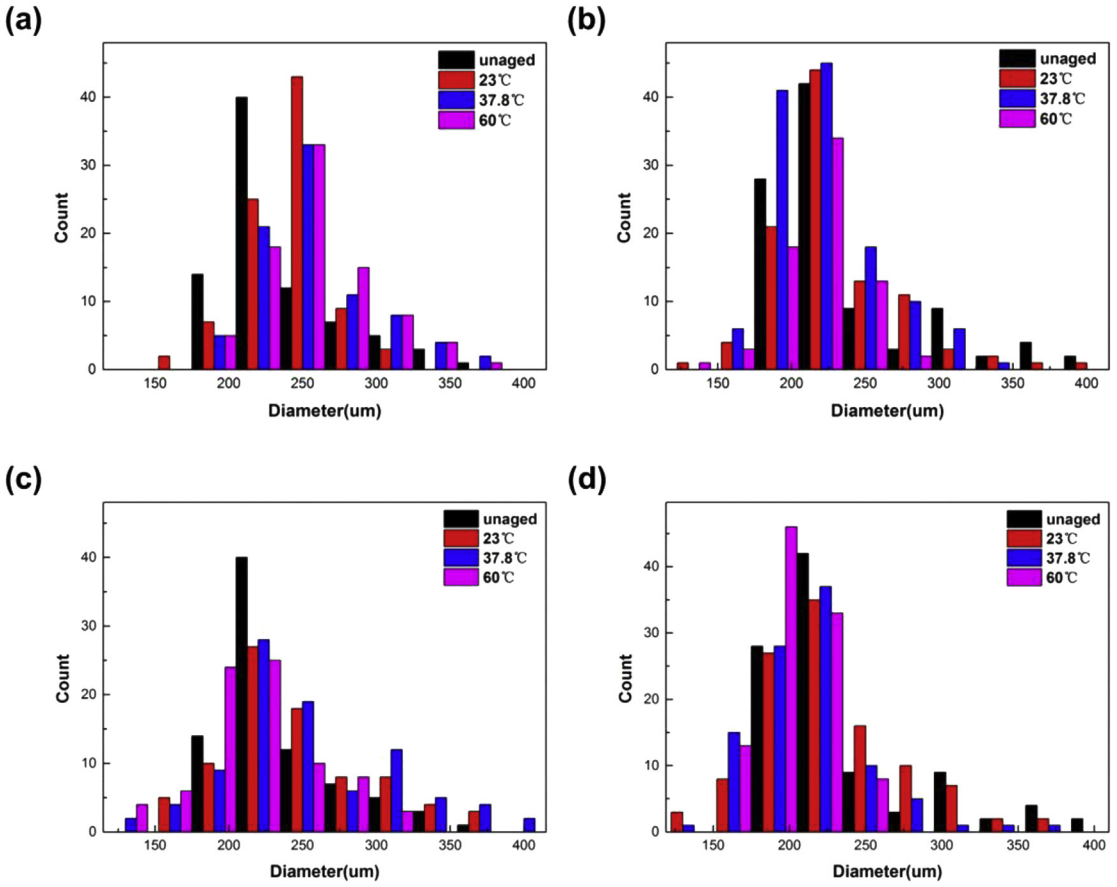

Fig. 8. Diameters of flax yarns immersed in water for (a) 2 weeks (b) 2 weeks and being dried (c) 17 weeks (d) 17 weeks and being dried.

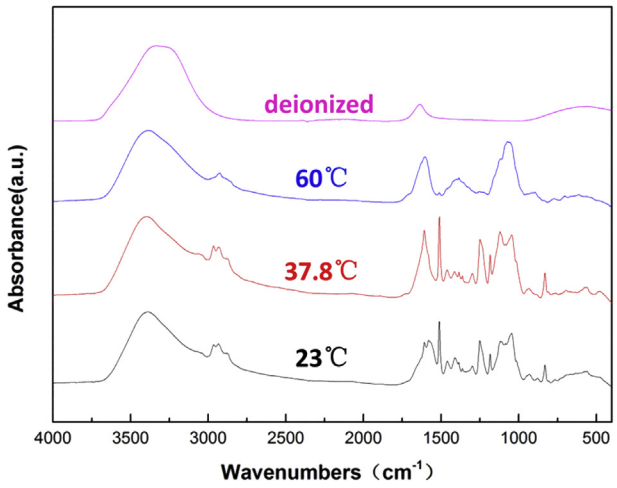

Fig. 9. FTIR spectra of soak solution before and after being aged for 17 weeks at 23 °C, 37.8 °C and 60 °C.

indicated a brittle failure (Fig. 12(a)); however, a shape of quicksand was observed for the specimens being aged for 17 weeks which represented a typical plastic failure mode (Fig. 12(b)). It was the plasticization effect of water which contributed to this failure mode transition.

3.3.2. *Tensile properties of FFRP*

Fig. 13 exhibited the changes of tensile strength of FFRP with the increase of ageing time. The changes of moisture content were also shown in the Figure. It can be seen that tensile strength showed a remarkable increase at the beginning of ageing then stabilized for the specimens being aged at 23 °C, slightly decreased for those aged at 37.8 °C and seriously decreased for those at 60 °C.

Firstly, water molecules permeated into composites at the initial ageing stage. Different absorption and combination occurred inside fibers due to their complex components and multi-stack structure. The microfibrillar angle would be modified when free hydrophilic groups in S_2 layer were attached onto water molecules [3]. Fig. 14 showed the typical tensile stress–strain curves of unaged FFRP and FFRP being aged for 17 weeks. The curve for the specimens being aged for 17 weeks and then dried was also shown in the Figure. It can be observed there was an alteration for the curves after being dried. Curves for the undried specimens showed a three linear phases, but only two linear phases was observed for the dried specimens including unaged and aged-dried specimens. Some researchers attributed this phenomenon to the collective reorientation of flax microfibrils stimulated by moisture absorption [17]. This would enhance the tensile strength of fibers to some extent, thus the increase of the tensile strength of the composites at the initial stage of the ageing, since it was the fibers which dominated the tensile strength of the unidirectional composites.

Secondly, as plenty of water being absorbed by FFRP, flax fibers swelled. Local swelling of each component and each cell-wall layer resulted in the overall swelling. As each component and each layer had different swelling behaviors as well as within the S_2 layer, swelling stresses induced the damages of the fibers. It can be obviously seen that the flax fibers before being aged was entirely intact, with rough surface as shown in Fig. 15(a). While after being immersed in water at 60 °C for 7 weeks, serious splitting can be observed from Fig. 15(b), accompanying cell-walls peeling from flax yarns (Fig. 15(c) and (d)). This was attributed to the multilayer structure of the fibers which induced delamination among different layers inside of flax fibers due to the interface modifications after being aged. The same phenomenon was also observed from the FFRP specimens aged for 7 weeks at 37.8 °C and 3 weeks at 60 °C which were fractured by tensile test (Fig. 15(e) and (f)). The structural damages of flax fibers led to the degradation of the tensile strength of FFRP, as indicated by the first decline trend in Fig. 13 for the specimens aged at 37.8 °C and 60 °C. Due to the relatively low water absorption for the specimens aged at 23 °C, no decrease trend of tensile strength was observed yet. Consistently, moisture content increased during this stage.

Thirdly, when the water absorption approached saturation, tensile strength also presented stabilization. Finally, as ageing time continued, tensile strength declined a second time for the specimens being aged at 60 °C. It was caused by the dissolution of pectins, hemicelluloses and some poorly crystallized celluloses of the primary wall in flax fibers, which has been proved by FTIR

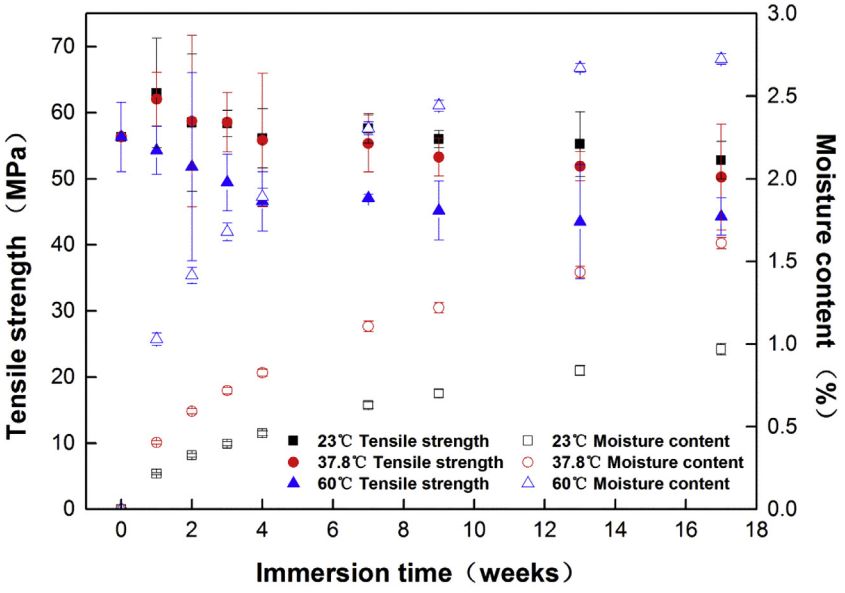

Fig. 10. Evolution of tensile strength and moisture content with immersion time of epoxy resin at 23 °C, 37.8 °C and 60 °C.

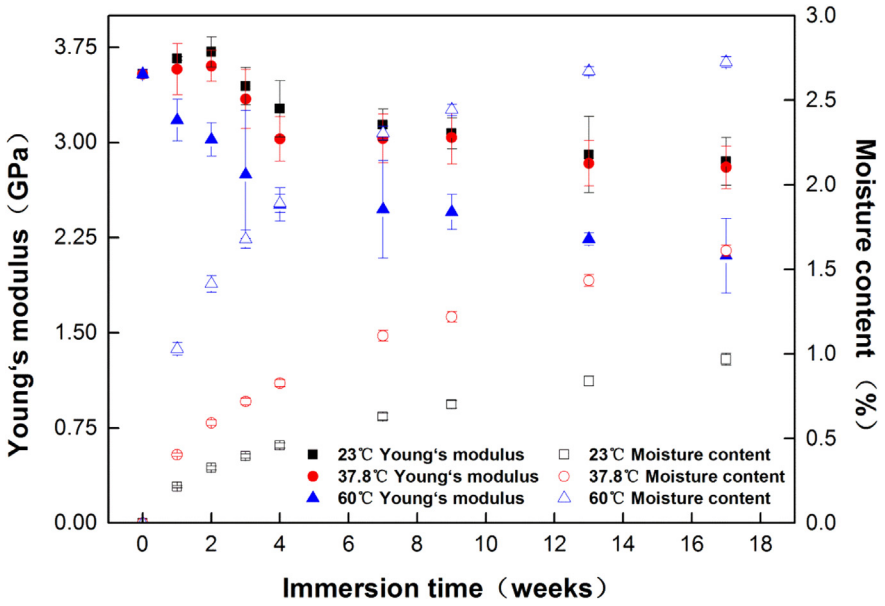

Fig. 11. Evolution of Young's modulus and moisture content with immersion time of epoxy resin at 23 °C, 37.8 °C and 60 °C.

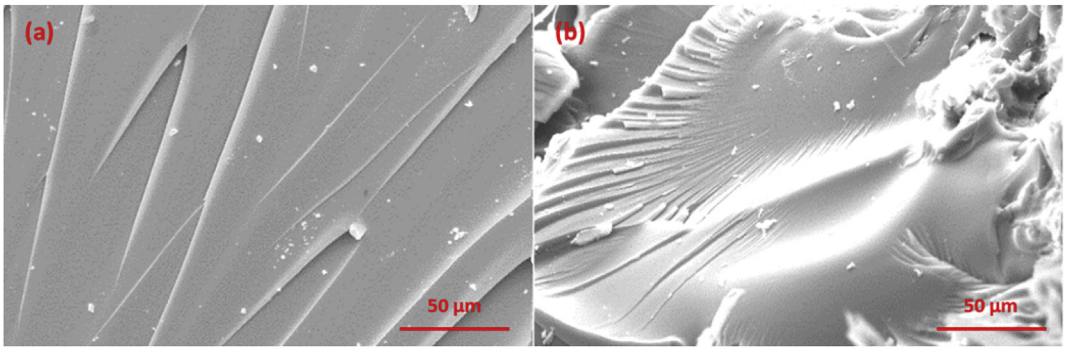

Fig. 12. SEM micrographs showing the fracture surfaces of epoxy resin: (a) unaged, (b) after being aged for 17 weeks at 60 °C.

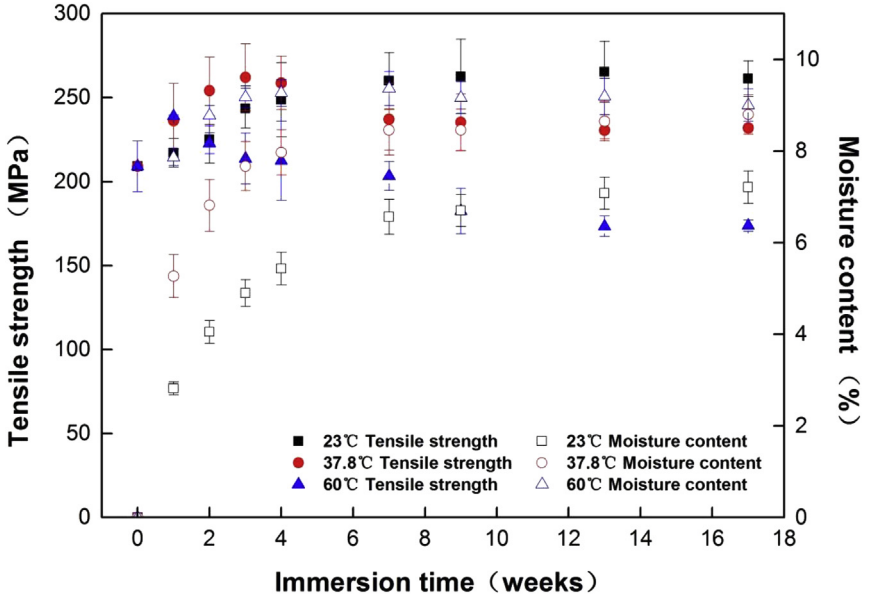

Fig. 13. Evolution of tensile strength and moisture content with immersion time of FFRP at 23 °C, 37.8 °C and 60 °C.

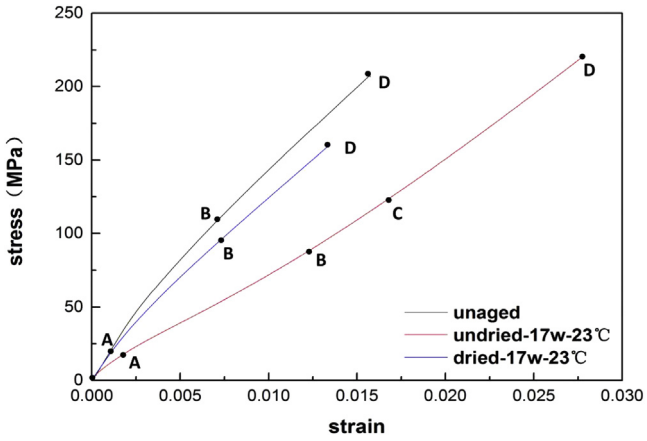

Fig. 14. Tensile stress-strain curves of FFRP.

aforementioned. As the amorphous hemicelluloses and pectins acting as a role of matrix in elementary flax fibers, when they were dissolved into soaking solution, stresses cannot efficiently transfer to the highly crystalline cellulose fibrils and led to the deterioration of the tensile strength [14]. During this stage, though the moisture content presented a constant value from the weight gain measurements, actually it was the result of the competition of weight gain and weight loss. The structure damages of the fibers provided more spaces for water absorption, while chemical degradation, i.e. the loss of pectins, hemicelluloses and some poorly crystallized celluloses, led to the decrease of the weight of the specimens. When the latter became dominant, water absorption showed a decline trend as seen in Fig. 3(b).

Fig. 16 presented the variation of tensile strength with ageing time for the specimens being aged and then dried before being tested. The changes of moisture content were also shown in the same Figure to help to reveal the ageing mechanisms. It can be seen that the tensile strength could be recovered for the specimens being aged at 23 °C and specimens being aged at 37.8 °C for 7 weeks, which indicated the non-permanent damage of the composites, especially the flax fibers since the dominate role of the fibers in this loading condition. During this ageing stage, physical effects of water absorption known as plasticization and swelling of flax fibers and polymer matrix were active and dominated the FFRP degradation mechanisms with a viscoelastic behavior. However, after fibers split and peeled, the tensile strength cannot be completely recovered and decreases were observed, suggesting that the absence of microstructural damage

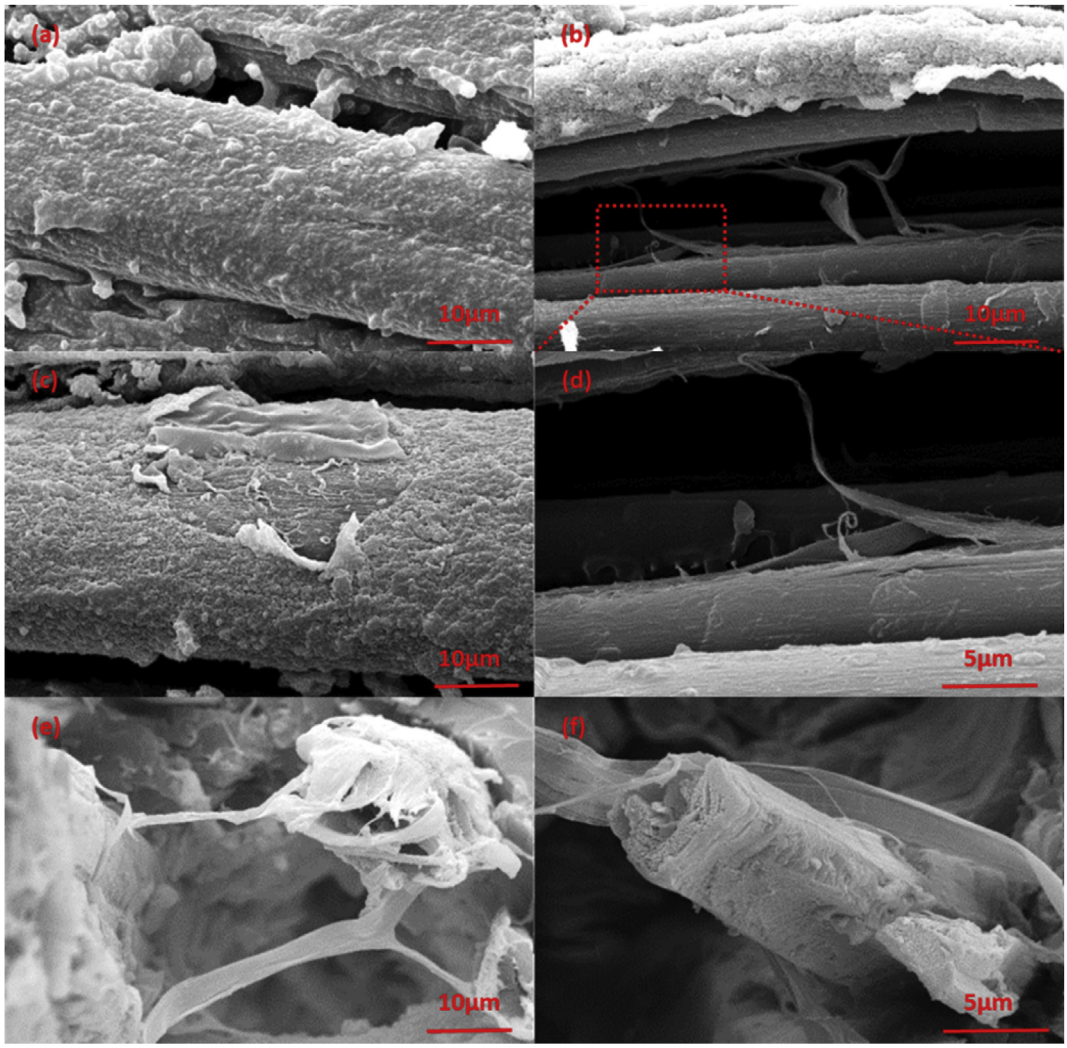

Fig. 15. SEM micrographs of flax yarns (a) unaged, (b-d) being aged at 60 °C for 7 weeks, and fracture surfaces of FFRP after tensile tests after being aged (e) at 37.8 °C for 7 weeks and (f) at 60 °C for 3 weeks.

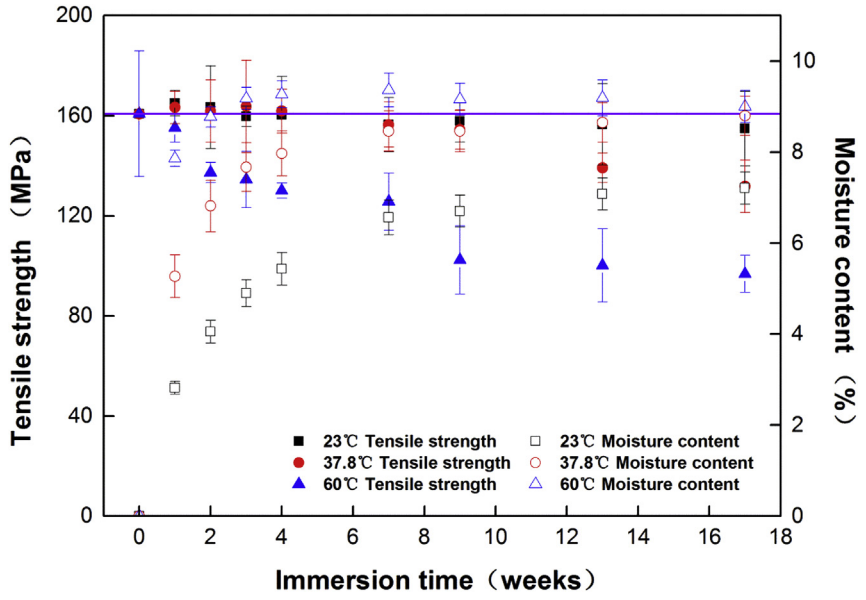

Fig. 16. Evolution of tensile strength of the specimens being aged and dried. The changes of moisture content with immersion time of FFRP at 23 °C, 37.8 °C and 60 °C were also shown.

was the dominant ageing mechanism. When the chemical degradation occurred, a further reduction of tensile strength was obtained as expected and the chemical effects which were verified as the hydrolysis and leaching of components in primary wall of flax fibers became active.

Fig. 17 showed the evolution of Young's modulus of FFRP specimens with the increase of the immersion time. It can be seen that Young's modulus decreased seriously with the increase of water absorption at the initial ageing stage. This was mainly due to the plasticization of the resin caused by the water. When water absorption approached saturation, Young's modulus stopped decreasing and became level off. Fig. 18 presented the Young's modulus of the aged and dried specimens. It can be seen that Young's modulus was completely recovered at the beginning of ageing. However, after the structural damage and chemical degradation emerged in materials, Young's modulus was not recovered any more but decreased continuously.

3.3.3. *Interlaminar shear strength of FFRP*

Fig. 19 showed the variation of interlaminar shear strength of FFRP with the increase of the immersion time. It can be seen that the shear strength had a moderate rise at beginning then descended gradually and stabilized eventually. Fig. 20(a) presented an unaged flax-epoxy interface and a good adherence between flax fiber and epoxy resin was observed. However, with water being absorbed by the materials, hygroscopic stresses were induced due to the different swelling behaviors of flax fibers and the matrix. It can be remarked that the expansion of flax fibers

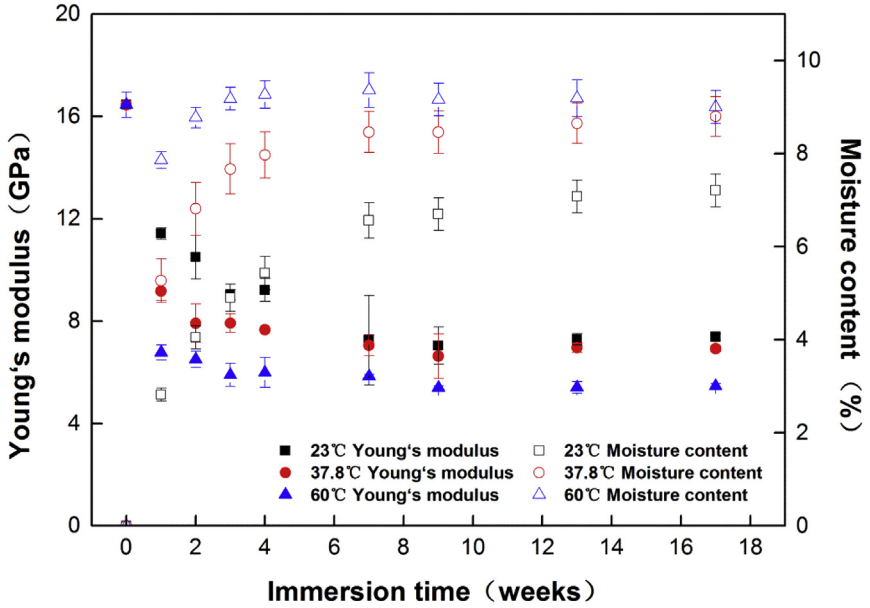

Fig. 17. Evolution of Young's modulus and moisture content with the increase of the immersion time of FFRP aged at 23 °C, 37.8 °C and 60 °C.

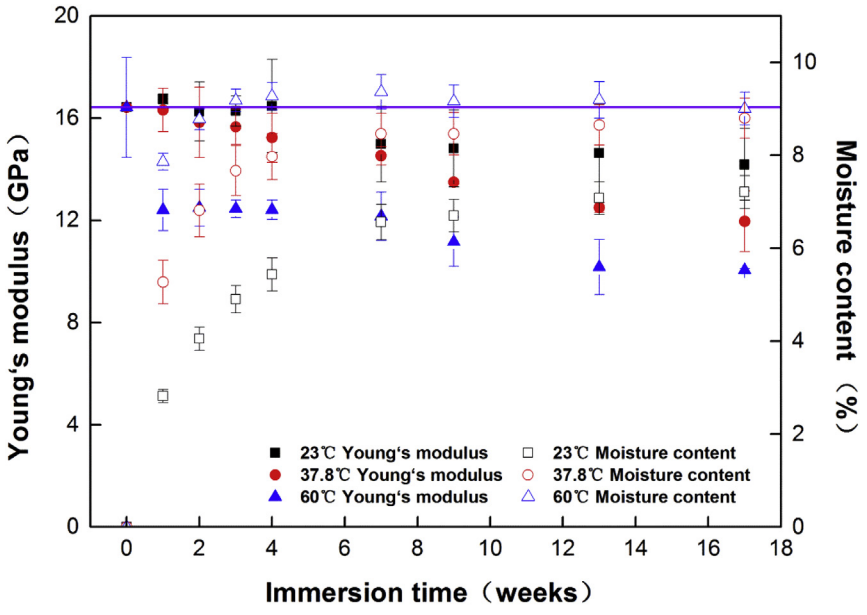

Fig. 18. Evolution of Young's modulus for the aged and dried specimens and moisture content with immersion time of FFRP at 23 °C, 37.8 °C and 60 °C.

was much larger than that of epoxy as indicated from the variations of the cross-sectional areas of the specimens shown in Table 4. Thus, swelling of fibers will exert a radial stress on the matrix. At the initial ageing stage at 23 °C, swelling of flax fibers was weak due to the less water absorption. This resulted in a smaller hygroscopic stress and enhanced the interfacial clamping and frictional stresses, which led to an increased interlaminar shear strength of FFRP.

As more water was absorbed by the specimens, swelling of flax fibers increased, resulting in a larger swelling stress. When it cannot be sustained by the epoxy resin, matrix cracked around the swollen fibers, which could be clearly seen from Fig. 20(b) for the composites being aged at 23 °C for 17 weeks. These cracks promoted the transport of water and in turn weakened the interfacial adherence. Therefore, the interlaminar shear strength decreased severely when the water was absorbed abundantly as shown in Fig. 19. When the moisture content approached saturation in materials, shear strength showed a stabilization. Moreover, at later ageing stage at 37.8 °C and 60 °C, as pectins, hemicelluloses and some poorly crystallized celluloses of flax fibers dissolved into water, interlaminar shear strength decreased a second time. Ultimate debonding of interface and gaps could be clearly observed from Fig. 20(c) and (d).

Fig. 21 showed the interlaminar shear strength of the aged and then dried specimens. It can be seen that when water uptake was slight at the initial ageing stage, the influence of fibers' swelling on shear strength was completely revisable, suggesting this was a physical mechanism. However, after epoxy matrix cracked, drying

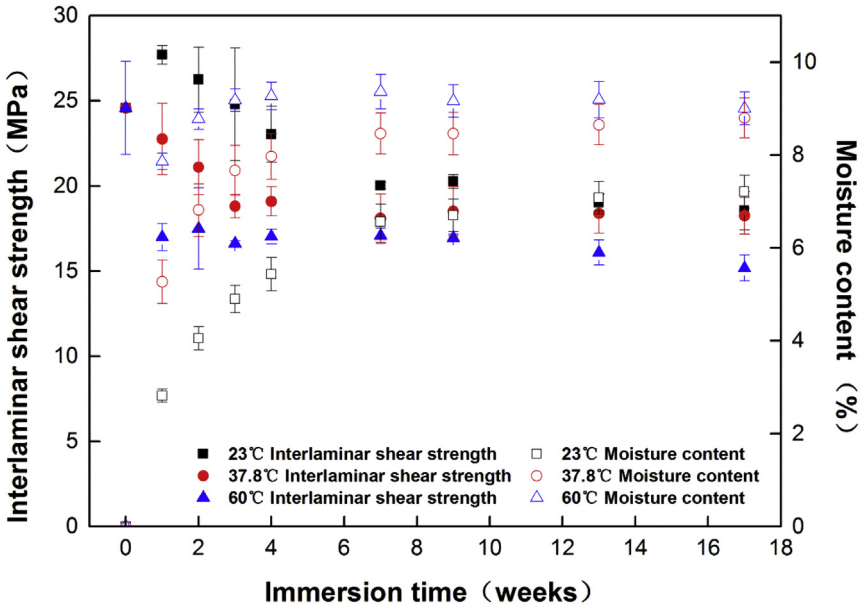

Fig. 19. Evolution of interlaminar shear strength and moisture content with the increase of immersion time of FFRP at 23 °C, 37.8 °C and 60 °C.

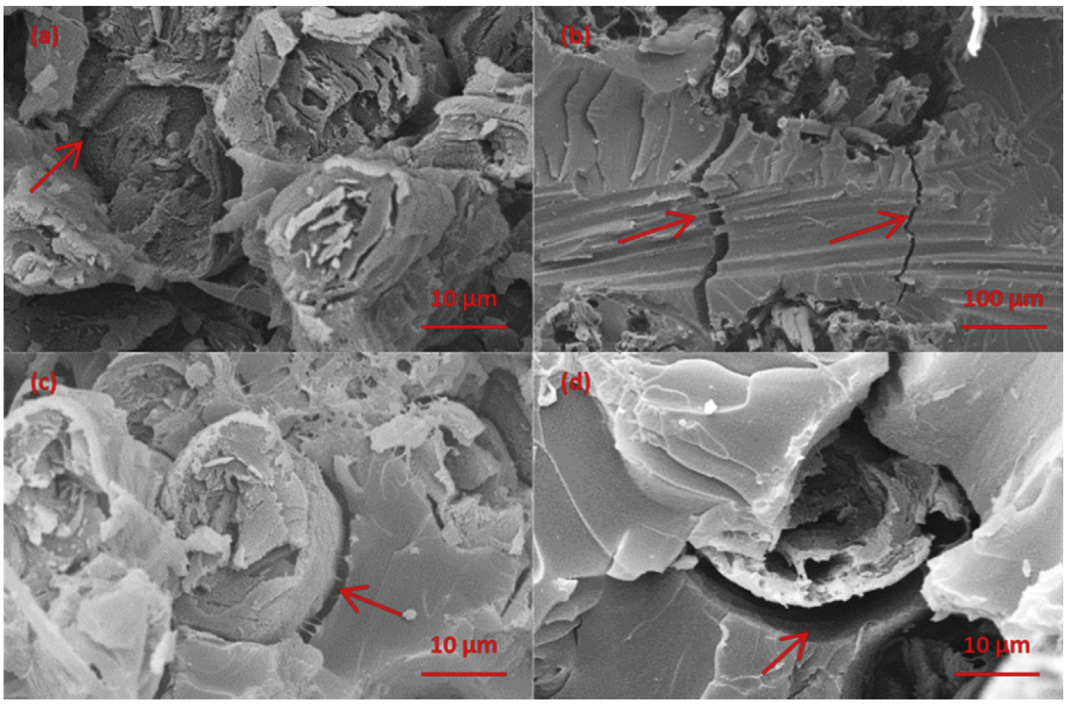

Fig. 20. SEM micrographs showing the fracture surfaces of FFRP: (a) unaged, after being aged for 17 weeks at (b) 23 °C (c) 37.8 °C and (d) 60 °C.

Table 4
Variation of cross-sectional areas of epoxy resin and FFRP after being aged for 17weeks.

Ageing conditions	Variation of cross-sectional areas (%)	
	Epoxy resin	FFRP
23 °C	0.341313	6.642531
37.8 °C	0.77298	9.625104
60 °C	3.207582	10.56236

allowed a partial recovery of the mechanical property and the irreversible behavior observed during this ageing stage was related to the microstructural damage. After the soluble substances inside flax fibers were washed out, only a little of the interlaminar shear strength could be recovered and chemical degradation became the underlying cause of the hydrothermal ageing. This again proved the mechanisms of the degradation of the interlaminar shear strength we proposed.

In fact, because of the degradability of flax fibers, clear peeling and debonding between different layers within flax fibers were also observed as shown in Fig. 22. Whether the debonding happened on

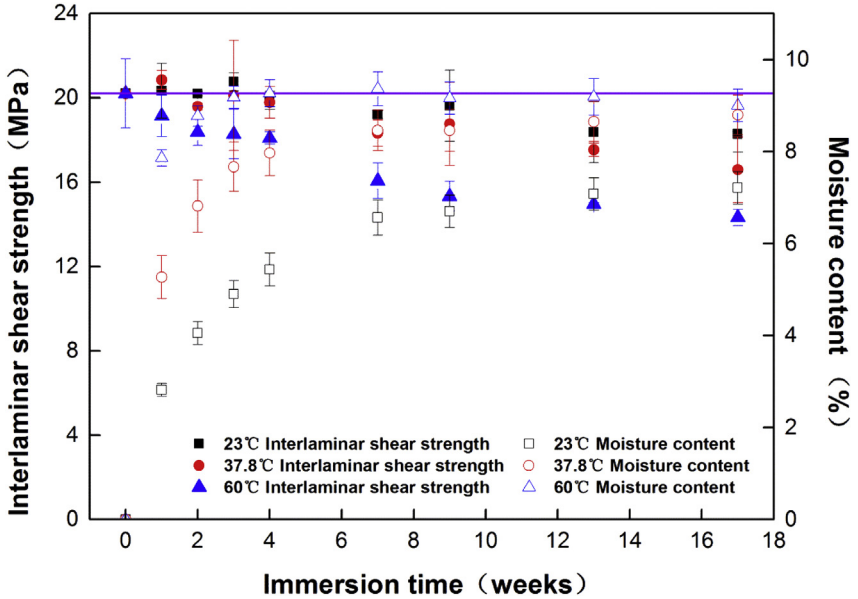

Fig. 21. Evolution of interlaminar shear strength of FFRP after being aged and dried with the increase of the immersion time at 23 °C, 37.8 °C and 60 °C. Variation of moisture content was also shown.

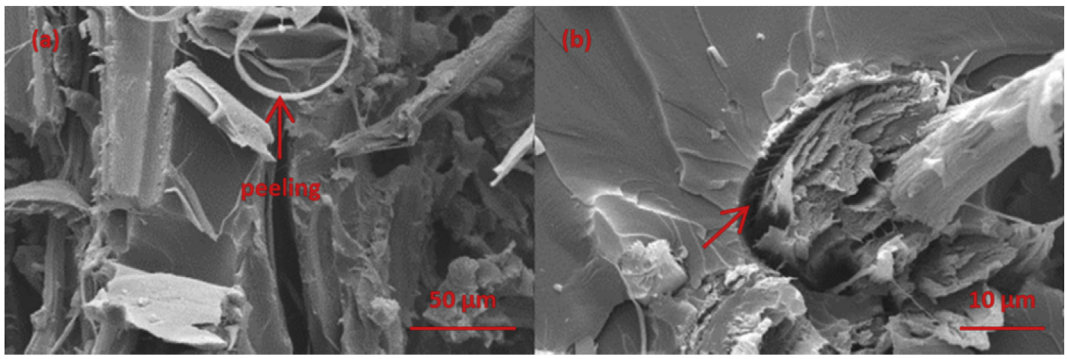

Fig. 22. SEM micrographs showing the fractured interface of the specimens aged at 60 °C for 17weeks being tested by short beam shear tests.

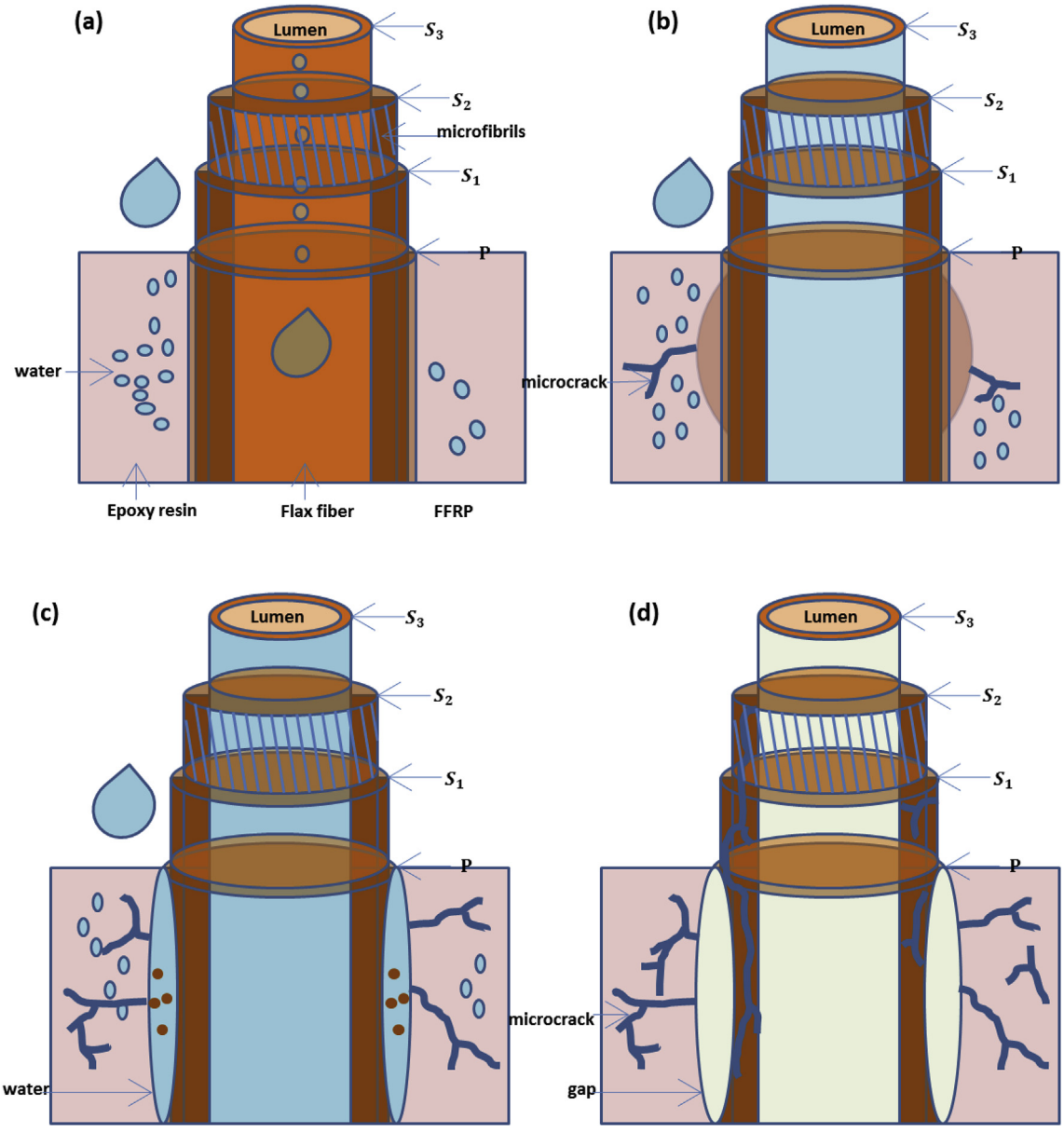

Fig. 23. Hydrothermal ageing mechanisms of FFRP.

the external interface between fibers and epoxy matrix or the internal interfaces between different cell-wall layers inside fibers is more essential for the deterioration of FFRP needs further more researches.

3.3.4. Hydrothermal ageing mechanisms of FFRP

The ageing mechanisms of FFRP in a hydrothermal environment can be summarized in Fig. 23. Firstly, water accesses composites through the diffusion into matrix, by the capillarity at fiber-matrix interface, with the absorption of hydrophilic components and transportation along lumens inside fibers, as described in Fig. 23(a). Then, due to the physical expansion of lumen and combination of cellulose with water molecules, flax fibers induced an apparent swelling. When it became big enough, matrix cracked around the swollen fibers. Meanwhile, due to the complex components and multi-stack structure of flax fibers, different absorption and combination mechanisms with water made the microfibrillar angle modified as shown in Fig. 23(b). Gradually, as ageing continued, pectins, hemicelluloses and some poorly crystallized celluloses inside flax fibers started leaching out, leading to an ultimate fiber-matrix interfacial delamination, as presented in Fig. 23(c). Finally, different swelling behaviors of each cell-wall layers induced the reinforcing fibers being split and peeled, as revealed in Fig. 23(d). The hydrothermal ageing mechanisms of FFRP can be summarized as three different stages: the first stage dominated by the physical mechanism including the plasticization and swelling of materials along with a reversible behavior. The second stage is the propagation of the microstructural damage of fibers and matrix in FFRP and can be determined as damage mechanism stage. While the chemical mechanism assured as the hydrolysis and leaching of components in primary wall of flax fibers became active during the third stage. Moreover, the ageing mechanisms of the second and third stages administer materials with irreversible mechanical properties.

4. Conclusion

This study aimed at investigating the hydrothermal ageing mechanisms of unidirectional flax fabric reinforced epoxy composites with the emphasis on the degradation of flax fibers due to their unique chemical composition and microstructure. The following conclusions can be drawn.

- Water absorption of both epoxy and FFRP were proved to follow Fickian's law, while disagreement appeared on FFRP after prolonged immersion due to the degradation of flax fibers.
- Different swelling among matrix, fibers and different cell-wall layers within fibers resulted in the evolution of the mechanical properties of FFRP.
- A serious of variations emerged inside flax fibers during hydrothermal ageing, including the alteration of microfibrillar angle, the dissolution of pectins, hemicelluloses and some poorly crystallized celluloses, the peeling and splitting of the fibers.
- Mechanical properties of FFRP could be recovered before structural damage and chemical degradation of flax fibers. If permanent damages have occurred inside the materials, the mechanical properties cannot be recovered.
- The hydrothermal ageing mechanisms of FFRP includes: plastifying of matrix, swelling of materials, structural damage of flax fibers and epoxy matrix, dissolving of flax fibers.

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