Properties of *Abutilon theophrasti* Fiber-reinforced High-density Polyethylene Composites

Xianquan Zhang, Chenxi Zhang, and Weihong Wang*

Chinese *Abutilon theophrasti* fiber (AF) ranks first in the world for yield; however, its application in the textile field is limited due to its characteristics. In this study, AF was used to reinforce high-density polyethylene (HDPE). Mechanical property tests, observations of the internal combination, creep behavior, and resistance to accelerate ultraviolet (UV) aging were conducted on these composites with different mass ratios. The results showed that the addition of the fiber could improve the impact resistance of the AF/HDPE composites. However, when the additive fiber content was > 60%, the flexural properties and resistance to creep deformation of the composites significantly decreased. Under the same conditions, the hygroscopic properties of the composites increased. After exposure to accelerated UV aging, the flexural strength of the composites decreased, but their impact resistance slightly improved. Infrared analysis demonstrated that lignin and other botanical compositions induced oxidative degradation in the composites. When the fiber-to-HDPE mass ratio was 60:40, the properties of the material were optimal.

INTRODUCTION

China is a large, agricultural nation with more than 100 kinds of bast fiber plants. *Cannabis sativa* grows in the east, *Apocynum venetum* grows in the west, sisal hemp grows in the south, flax and *Abutilon theophrasti* grows in the north, and ramie grows in the central plain. Ambary and jute are planted in most areas (Qu 2002). Of these, the *Abutilon theophrasti* fiber (AF) ranks first in the world for yield. *Abutilon theophrasti* can be planted in both wild and cultivated areas, as its bast fiber possesses outstanding water and salt tolerance. However, the lignin content in the fiber is typically about 16.4%, which limits the development potential of AF in the textile field (Guan *et al.* 2003). Applications for this fiber primarily consist of the production of ropes, jute bags, and other forms of packaging.

Fibrilia fiber in general is recyclable, highly biodegradable, and has relatively high specific strength and modulus properties. It has a high length-to-diameter ratio, which makes it suitable for use as reinforcement in composite materials (Liu and Huang 2005a; Velde and Kiekens 2001). Meanwhile, thermoplastic resin possesses good linear molecule structure, and its toughness can be 10 times of that of thermosetting resin. This resin also possesses low hygroscopicity, good impact resistance, low storage condition requirements, and a relatively long preservation time. The production of thermoplastic-based composites is fast and produces little pollution. Therefore, the selection of

thermoplastic resin as a matrix material is an advisable direction for studies and applications.

The processing method for these composites is relatively simple, and its production cost is low (Xiao *et al.* 2000). Since the late 1980s, researchers in India, Europe, the United States, and Japan have conducted considerable research on long fiber-reinforced plastic composites. The properties of the fibrilia-plastic composites mainly depend on the variety, content, property, and structure of the fibers, as well as on the matrix properties and on the interface bonding condition. The German BASF Company made thermoplastics composites using jute, sisal hemp linen fiber, and polypropylene (PP). The prepared natural fiber-reinforced thermoplastics were 17% lighter than the glass fiber-reinforced thermoplastics. Wambua *et al.* (2003) employed the hot-press approach for the reinforcement of PP using jute, ambary, sisal hemp, *C. sativa*, and coconut fiber. They found that the fiber-reinforced composite was capable of being produced with mechanical properties comparable to those of the glass fiber-reinforced PP composite. Gassan *et al.* (1999a; 1999b; 2000; 2002) systematically studied variations (*e.g.*, flax, ramie) of the fiber-reinforced resin matrix composite, considering the effects on the composite of such factors as the variety, properties, and content of the fibers; textile structure; modifications by NaOH and silane; and other aspects. Bos (2006) felted the linen fiber, which efficiently improved the strength and rigidity of the PP composites. They also proved that the complex structure of the reinforced fiber had the greatest influence on the mechanical properties of the composite. Both Bledzki *et al.* (1997) and Doan *et al.* (2006) utilized a maleic anhydride solution to modify the PP matrix. They found that compared with the unprocessed composite material, the interface property and strength of the modified material was significantly improved.

As a country with many fiber plants, Chinese researchers also have studied fibrilia in terms of multi-aspect development and utilization. Liu (2005b; 2007) twisted PP and fiberflax into yarn, forming the yarn texture of flex with a PP covering. The weaving method was used for pre-forming, and the hot pressing was used for modeling. This method improved the mixing uniformity of the two phases. Xi and Chen (2007) found that the pretreatment to flax yarn had significant improvement effects on the mechanical properties of the composite materials. Lei and Zhang (2008) used a twin-screw extruder to extrude granulation and then conducted hot-press molding. They studied the influences of the mass fractions of coupling agents, ramie fabric structure, and the molding pressure on the board property. Cui *et al.* (2010) explored the influence of the mass ratio of PP on the composite tensile property. They concluded that when the mass ratio of PP was 50%, the tensile property of the composite was best. This conclusion was similar to the results found by Liu (2005b). Chen *et al.* (2002) studied the plant fiber/PP composite and explored the uniformity of fiber dispersion in the matrix, the wettability of interface, and the twisting conditions of the fiber/PP composite.

With the widespread use of bio-fiber/plastic composites, the problem of outdoor aging has received increasing attention (Wang *et al.* 2008a). The aging resistance of these materials is considered to be an important indicator of material quality. A large number of studies have demonstrated that in the case of outdoor use, wood/plastic composites will suffer significant fading of color, diminished physical and mechanical properties, and changes in the carbonyl concentration wood component (Yuan 2011).

In contrast to studies on wood fiber/polymer composites, the aging resistance of fibrilia-reinforced thermoplastic composite has not been fully explored. The present study aimed to analyze the physical and mechanical properties of AF-reinforced high-density

polyethylene (HDPE) composites, focusing on its degree of deterioration in the condition of accelerated aging. This study will provide helpful information for the use and preparation of fibrilia-reinforced composites.

EXPERIMENTAL

Materials
Raw materials

An HDPE film was cut into fibers, each with a width of 0.3 to 0.8 cm and a length of 3 to 5 cm. AF fiber was in the form of knitted cloth, whose major component is cellulose. An orthogonal 2-D woven fabric consists of two sets of yarns interlaced at 90° to each other.

Preparation of Abutilon theophrasti fiber/HDPE composites

After the AF cloths were dried to moisture content less than 3%, they were felted into mats layer by layer in ratios of 50:50, 55:45, 60:40, 65:35, 70:30, and 75:25 AF to HDPE fiber, respectively. The HDPE fibers were placed on the mat surfaces and between each layer of the AF. The mats were pre-pressed for 30 min at 1 MPa and then preheated in an oven to lift the temperature of the cores to over 130 °C. Each preheated mat was immediately placed into a hot press and pressed for 12 min at 180 °C. The mats were removed from the hot press and cooled under pressure. Each board measured 160 mm × 160 mm × 6 mm and its density was 0.83 g/cm^3.

Methods
Ultraviolet (UV)-accelerated aging

This study utilized a UV aging machine (QUV/SPRAY, America Q-Panel Company) to apply UV-accelerated aging treatment to the composites. In accordance with the American Standard ASTM G154, each aging cycle was set for 12 h. The first 8 h of the cycle consisted of UV irradiation, and the remaining 4 h of the cycle consisted of condensation. After aging for 500, 1,000, and 2,000 h, mechanical property testing and infrared spectroscopic analysis were conducted. The property retention of the composite was calculated in accordance with Eq. 1.

Property retention = (property value after aging/property value before aging) × 100%   (1)

Mechanical properties

In accordance with ASTM D790-03, a sample of size $120 \times 24 \times 6$ mm^3, test span 96 mm, and compression speed 2.56 mm/min was prepared for the bending test.

In accordance with the GB/T 16420 1996 Chinese national impact strength test standard, a sample of size of $80 \times 10 \times 6$ mm^3, test span 60 mm, pounding speed 2.9 m/s, and pendulum bob energy 5 J was prepared.

At least six samples were utilized for each test item.

Water absorption

In accordance with the GB/T 17657-1999, which outlines the test methods for evaluating the properties of wood-based panels and surface-decorated wood-based panels, the samples were sawn into pieces of 50 mm × 50 mm × 6 mm for the water

bioresources.com

absorption test. At least six samples were utilized for each group. The pH value of the water bath was 7 at 20 °C. After 24 h, the sample was collected, the floating water on the surface was removed, and the thickness measurement was completed in 30 min.

The thickness swelling of the samples was calculated according to the following equation:

$$TS = (h_2 - h_1) / h_1 \times 100, \tag{2}$$

where TS (in %) represents the thickness swelling caused by water absorption; h_1 (in mm) represents the sample thickness before immersion; and h_2 (in mm) represents the sample thickness after immersion.

Short-term creep

The short-term creep performance was tested by dynamic mechanical analysis (Q 800, America TA Company). A three-point bending mode was selected, with a temperature of 25 °C, a loading stress of 3.5 MPa, and a sample size of 50 mm × 10 mm × 6 mm.

Scanning electron microscope (SEM) analysis

The internal structure of the AF/HDPE composite sample was observed using SEM (FEI Quanta200, Netherlands). The sample was placed in liquid nitrogen so that it would freeze completely and then was rapidly fractured. A cross section was cut, and the broken surface was coated with gold in a sputter coater. The section morphology of the sample was observed at an accelerating voltage of 12.5 kV.

Fourier transform infrared (FTIR) spectroscopy analysis

FTIR spectroscopy (Magna-IR 560, America Nicolet Company) was conducted to analyze the surface of the composite without aging and after 2000 h. A small quantity of powder was scraped from the surface of the AF/HDPE composite sample. The potassium bromide tablet compressing method was used to prepare the sample for analyzing. The resolution ratio was 4 cm^{-1}, and the scan rate was 40 times/min.
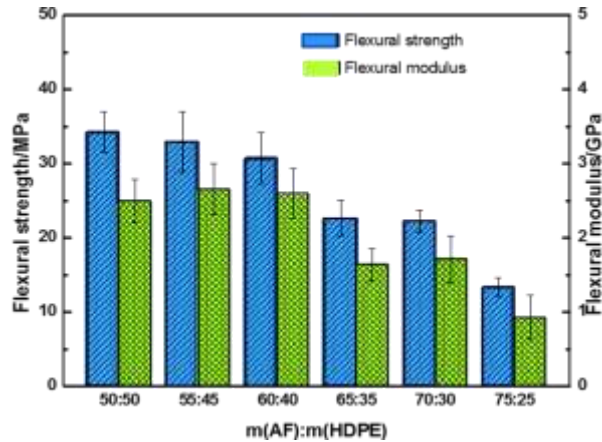
Statistics

Significance differences was determined using Analysis of Variance at p=0.05, testing the data for significant differences.
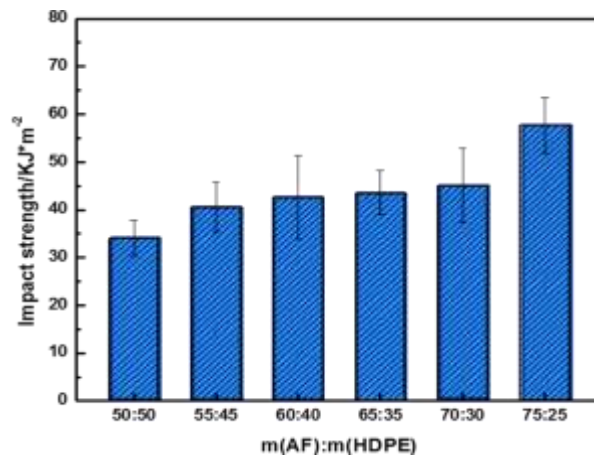
RESULTS AND DISCUSSION

Physical and Mechanical Properties of AF/HDPE Composites

Flexural strength of HDPE was determined to be 21.9 MPa, and the flexural modulus was 0.89 GPa. For the AF-reinforced HDPE, the highest flexural strength and modulus values were 35 MPa and 2.66 GPa, respectively (Fig. 1). This indicates that the introduction of AF, within 70% content, was able to provide HDPE with a higher flexural property. The HDPE content in composite decreased with increasing amounts of AF fiber, which decreased the wetting and permeation of HDPE onto the fiber surfaces. Thus, when the AF content was too high, the clustering fibers could not be bonded with a sufficient amount of HDPE.

When the mass ratio of AF to HDPE increased, the impact strength of the boards increased (Fig. 1b). When the mass ratio of fiber to HDPE was 75:25, the impact strength was the highest, at 57.70 /kJ·m^{-2}. A higher fiber content indicates better toughness. Another study has also shown that within limits, poorer two-phase bonding indicates better impact energy absorption and increased impact strength (Han *et al.* 2003). More gaps occurred with increased AF content, as shown in Fig. 1. These gaps contributed to the energy absorption, thus increasing the impact strength of the composite. In this study, the AF used was in the form of knitted cloth. The mutual tangle of warp and weft fibers also prevented the composite boards from being easily destroyed by the impact.

(a)

(b)

Fig. 1. Mechanical properties of AF/HDPE composites: (a) flexural strength and modulus and (b) impact strength

Water Absorption of AF/HDPE Composites

As the AF content increased, the thickness-swelling rate caused by water absorption also increased. Because bio-fibers are hygroscopic, greater AF contents introduced into the HDPE resulted in more water being absorbed by the composite. When the AF content was greater than 60%, the thickness-swelling of the composite increased significantly (p=0.05) compared to AF content 50%. When the fiber-to-HDPE mass ratio was 75:25, the thickness-swelling rate of the composite reached its maximum, at 12.5%

(Fig. 2). However, in comparison to particleboard and medium-density fiberboard, this composite possessed better water resistance if AF fiber content was limited in 65%.
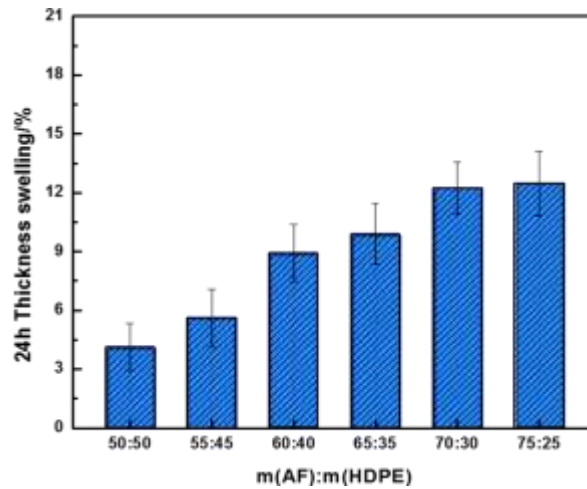

Fig. 2. Thickness-swelling of AF/HDPE composites at 24 h due to water absorption

Interface Bonding of AF/HDPE Composites

The broken surface of the AF/HDPE composites is shown in Fig. 3. When the mass ratios of AF to HDPE were 50:50 and 55:45, the fiber bundles had a relatively uniform dispersal in the HDPE matrix.
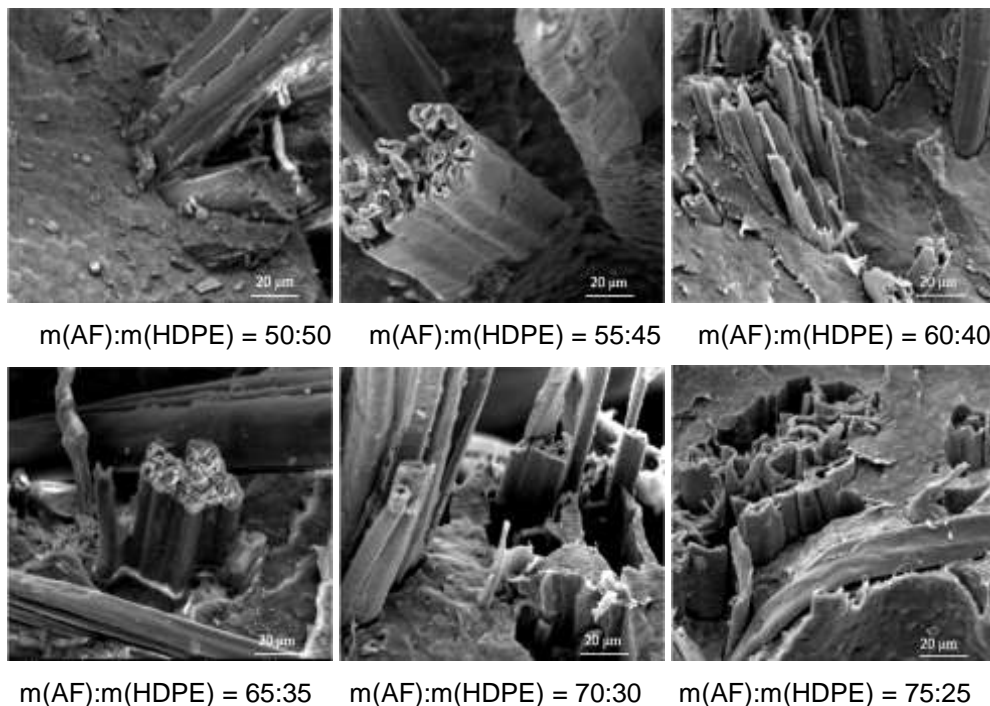

m(AF):m(HDPE) = 50:50   m(AF):m(HDPE) = 55:45   m(AF):m(HDPE) = 60:40

m(AF):m(HDPE) = 65:35   m(AF):m(HDPE) = 70:30   m(AF):m(HDPE) = 75:25

Fig. 3. SEM image of AF/HDPE composites (1000×)

The fibers were coated with a large quantity of HDPE matrix. In this case, the bonding of AF with HDPE was strong, and the gaps between them were less frequent. Thus, the pulling-out of the fiber was also less common. When the mass ratio of AF to HDPE was increased to 60:40 and 65:35, the fiber bundles agglomerated, and gaps between fibers and HDPE matrix were common. When the mass ratio of AF to HDPE was increased to 70:30 and 75:25, a large number of fiber bundle clusters were observed, while single-fiber bundles were less common. This indicates that it is difficult to uniformly disperse a large number of fibers within the HDPE matrix. In addition, less HDPE was available to bond with the AF. At this time, many pores and gaps from fiber pulling were observed. The degree of bonding between the matrix and the reinforced fiber as well as the presence of pores are factors that have a significant influence on the physical and mechanical properties of the composite, as shown earlier in this article.

Creep Properties of AF/HDPE Composite

Biofiber-reinforced plastic composites are widely utilized in environments that involve long-term loading, such as in furniture shelves. The evaluation of the creep behavior of the AF/HDPE composite is thus important.

Creep usually has three stages: decreasing speed, constant speed, and increasing speed to damage. In this study, the short-term creep curve progressed only through the first two stages, as shown in Fig. 4. The strain of the composite gradually increased with increasing AF content, which indicated that the creep resistance of the composites decreased with increasing fiber content.
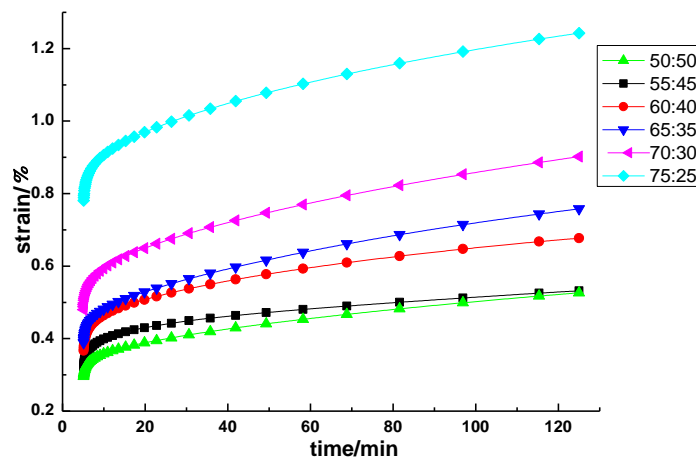

Fig. 4. Creep trends of AF/HDPE composites

When the AF content reached 60%, the strain of the composite was significantly (p=0.05) larger than that of the composite when the fiber content had been low. When the AF content was 75%, the fibers were only loosely connected with the HDPE. Under this condition, the resistance of this composite to creep deformation became extremely severe. The introduction of AF fibers, within limitations, improved the rigidity of the HDPE. However, increasing the fiber content means decreasing the content of the HDPE matrix, which contributes to weakened adhesion. When stress was applied to the boards, relative slippage and dislocation occurred between the fibers and the matrix, which finally resulted in the interface separation. Therefore, when the fiber content was too high,

AF were not able to provide HDPE with adequate resistance-to-deformation characteristics due to the poor bonding that occurs within the diminished HDPE matrix.

Resistance of AF/HDPE Composites to Aging

The aging properties of the HDPE-based composites depend to a large extent on the fiber wrapping quality by HDPE matrix. During the aging process, water induces the first signs of aging by making the bio-fiber swell and enlarging the molecular space. The swelling also leads to spreading cracks in the matrix, expanding the pores, and ultimately causing the fracture of this material. Published literature has shown that the damage caused to HDPE composites by water erosion is more serious than that caused by thermo-oxidative aging (Huang and Yu 2006). In UV aging, degradation leads to the chain scission of HDPE, which generates carbonyl and vinyl and crosslinks the short chains (Wang *et al.* 2008b).

The *Abutilon theophrasti* fibers used in this study consist of 51.92% cellulose, 16.85% hemicelluloses, 16.4% lignin, 8.76% pectin, and other extractives (Guan *et al.* 2003). Although each component in bio-fibers absorbs UV light and contributes to degradation to a certain degree (James *et al.* 2008), lignin is the major constituent that absorbs UV radiation. As shown in Fig. 5, unaged AFs were bonded into bundles by the cohesion of lignin and pectin. After being exposed to 2000 h of aging, the fiber bundles were separated into single fibers, although they did not show any signs of fracture or damage on the surface. The surface bonding substance dropped away and left gaps between the fibers. This has harmful effects on the flexural strength of the composite but may have favorable effects on its capacity to absorb impact energy.
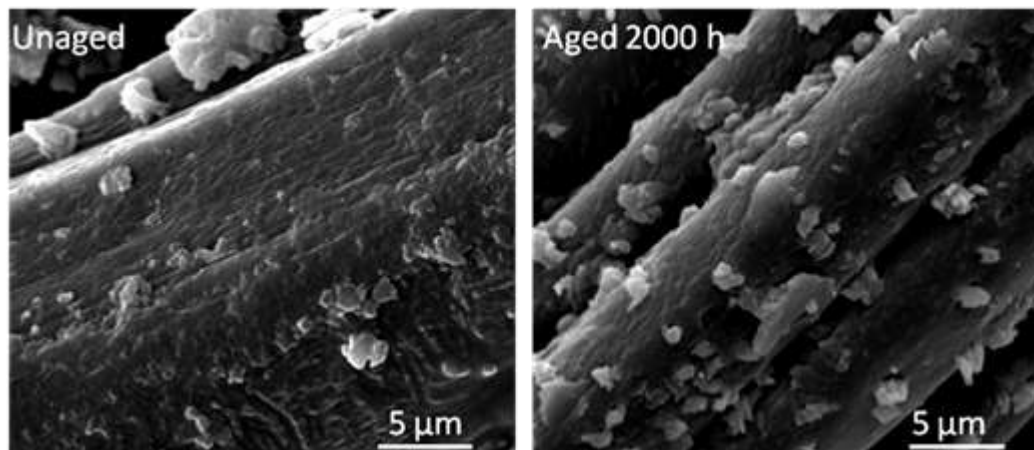

Fig. 5. SEM image of AF before (left) and after 2000 h of aging (right) (500×)

Mechanical Properties of Aged AF/HDPE Composite

In accordance with Eq. (1), the retention rates of the flexural strength, modulus, and impact strength of the AF/HDPE composites were calculated after 500, 1,000, and 2,000 h of aging. Figure 6 shows that with increasing aging time, the retention rates of the flexural strength and modulus decreased. That is, the flexural resistance of the composite became worse. After 2,000 h of aging, the retention rate of the flexural strength was 70%, while the modulus of elasticity decreased to 65%. Compared with the loss in flexural strength, the loss in modulus of elasticity was more serious.

During the process of UV-accelerated aging, the swelling of AF, the crosslinking and chain scission reaction of HDPE, and the aging degradation reaction of AF proceeded simultaneously. The swelling rates of AF were high in the first 500 h of aging, which led to cracks between the interfaces. Accordingly, the mechanical properties of the material were seriously degraded. The intermolecular crosslinking reaction that occurred in the early aging stage was not enough to offset the decline in mechanical properties. From 500 h to 1,000 h, it seems that the swelling did not reach saturation and that aging degradation continued. These phenomena were reflected in the continuous decrease in mechanical properties. After 1,000 h of aging, the damage caused by the swelling and crack diffusion tended to stabilize. The crosslinking and chain scission degradation aging also began to proceed more slowly. Thus, the decrease in the property of the AF/HDPE composite was considerably slower during this stage.

In the initial aging stage, the swelling of the constituents, the crosslinking reaction of the HDPE matrix, and the slight cracks all helped absorb impact energy. Therefore, before the composite had undergone 500 h of aging, the impact strength maintained an increasing trend. However, the intensifying chain scission and crack diffusion promised to ultimately result in damage to the composite. The damage gradually became severe enough to offset the positive effects on energy absorption, which led to a decrease in the impact strength after 500 h. After 1000 h, the impact strength tended to stabilize.
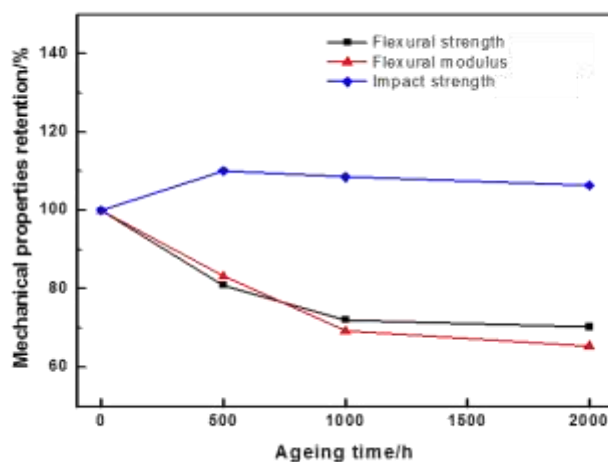

Fig. 6. Mechanical property retention of AF/HDPE composite (50:50) during aging

FTIR Spectroscopy Analysis

Figure 7 shows the FTIR spectra of AF/HDPE composites aged for 2000 h. At 2914 cm^{-1}, a stretching vibration characteristic peak of C–H was observed in –CH$_2$–; at 3310 cm^{-1}, a typical absorption peak of –OH occurred; and at 1037 cm^{-1}, a characteristic absorption peak relevant to cellulose and hemicelluloses was found. After 2000 h of aging, these characteristic peaks were weaker than they had been before aging. After aging, the characteristic peaks at 1594 cm^{-1} representing the lignin had nearly disappeared. This is consistent with the change shown in Fig. 5, where it is apparent that the surface bonding substance (lignin and pectin) dropped away and left gaps between the fibers. The changes in these characteristic peaks indicated that cellulose, hemicelluloses, and lignin underwent serious degradation. The strengthened C=O peak at 1712 cm^{-1} indicated that oxidation occurred at the surface of the composite.
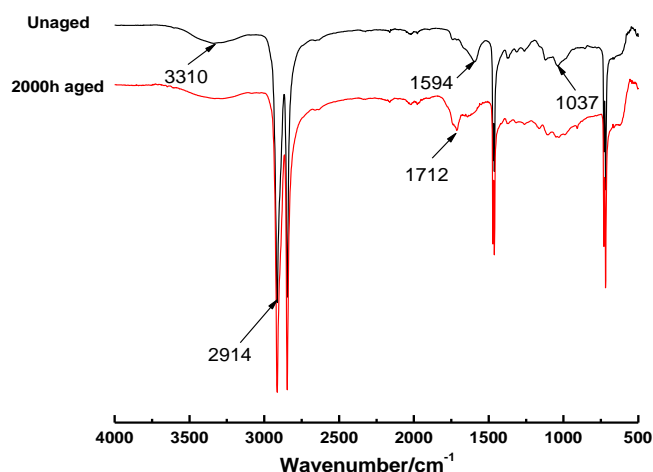
Fig. 7. FTIR spectra of original AF/HDPE composites (50:50) and composites aged for 2000 h

CONCLUSIONS

1. The water absorption of the *Abutilon theophrasti* fiber/ high density polyethylene (AF/HDPE) composite increased with increasing AF content, which helped improve the impact strength of the composite. However, when the AF-to-HDPE mass ratio was greater than 65:35, the flexural strength significantly decreased. Meanwhile, high AF contents tended to decrease the resistance of the composite to creep deformation.

2. During the process of UV-accelerated aging, oxidative degradation occurred at the surface of the AF/HDPE composite. The flexural properties of the composite declined significantly between 0 h and 1000 h of aging, and the impact properties improved insignificantly during the same stage.

3. AF can be used to reinforce thermoplastic polymers. Composites can be produced to possess good properties within certain limits of fiber usage, in this research which is 65%. When the mass ratio of AF to HDPE was 60:40, the properties of the composite were optimal.

ACKNOWLEDGMENTS

REFERENCES CITED

Bos, H. L., Müssig, J., and Oever, M. J.A. (2006). "Mechanical properties of short-flax-fibre reinforced compounds," *Composites Part A: Applied Science and Manufacturing* 37(10), 1591-1604.

Chen, Y. F., Chuai, C. Z., and Cui, Y. Y. (2002). "Behaviors of long length-to-width ratio vegetable fiber blended with polypropylene," *Polymer Materials Science and Engineering* 18(3), 132-135.

Cui, P., Chu, X., and Ai, H. L. (2010). "Studying of preparation processing and tensile properties of the flax/polypropylene composites," *Fiber Reinforced Plastics/Composites* (2), 41-43.

Doan, T. T. L. Gao, S. L., and Mader, E. (2006). "Jute/polypropylene composites I: Effect of matrix modification," *Composites Science and Technology* 66(7-8), 952-963.

Gassan, J., and Bledzki, A. K. (1997). "The influence of fibre-surface treatment on the mechanical properties of jute-polypropylene composites," *Composites Part A: Applied Science and Manufacturing* 28(12), 1001-1005.

Gassan, J. (1999a). "Alkali treatment of jute fibers: Relationship between structure and mechanical properties," *Journal of Applied Polymer Science* 71(4), 623-629.

Gassan, J., and Bledzki, A. K. (1999b). "Possibilities for improving the mechanical properties of jute/epoxy composites by alkali treatment of fibres," *Composites Science and Technology* 59(9), 1303-1309.

Gassan, J., Dietz, T., and Bledzki, A. K. (2000). "Effect of silicone interphase on the mechanical properties of flax-polyurethane composites," *Composite Interfaces* 7(13), 103-115.

Gassan, J. (2002). "A study of fibre and interface parameters affecting the fatigue behaviour of natural fibre composites," *Composites Part A: Applied Science and Manufacturing* 33(3), 369-374.

Guan, Y. T., Dong, Z. E., and Weng, G. Q. (2003). "A preliminary study of ATM Fiber degumming," *Journal of Textile Research* 24(6), 572-573.

Han, H. F., Cui, Y. D., and Cai, L. B. (2003). "Removing the resins of original hemp," *Journal of Cellulose Science and Technology* 1(3), 50-54.

Huang, C. R., and Yu, W. D. (2006). "The spinning capability of hemp fiber and the studying getting on," *Journal of Wuhan University of Science and Engineering* 19(1), 35-38.

composites weathering: Visual appearance and chemical changes," *Polymer Degradation and Stability* 93(8), 1405-1414.

Lei, W., and Zhang, C. S. (2008). "Mechanical properties of ramie cloth/polypropylene composites," *Acta Materiae Compositae Sinica* 25(1), 40-45.

Liu, L. Y., and Huang, G. (2005a). "Development of thermo-plastic resin composites reinforced with flax fibers," *Journal of Tianjin Polytechnic University* 24(4), 5-7.

Liu, L. Y., and Huang, G. (2005b). "Research and preparation of flax/PP woven sheet composite," *Fiber Reinforced Plastics/Composites* (5), 17-19.

Liu, L. Y., Huang, G., and Wang, R. (2007). "Impact resistance of flax reinforced polypropylene laminates," *Journal of Textile Research* 28(3), 38-41.

Qu, L. J. (2002). "Application for bast fibre in automobile upholstery materials," *Industrial Textile* 143(20), 36-39.

Velde, K. V. D., and Kiekens, P. (2001). "Thermoplastic pultrusion of natural fibre reinforced composites," *Composite Structures* 54(2-3), 355-360.

Wambua, P., Ivens, J., and Verpoest, I. (2003). "Natural fibres: Can they replace glass in fibre reinforced plastics," *Composites Science and Technology* 63(9), 1259-1264.

Wang, W. H., Wang, Q. W., and Zhang, Z. M. (2008a). "Natural weathering and accelerated UV weathering of rice-hull-polyethylene composite," *Forestry Science* 44(8), 90-94.

Wang, W. H., and Wang, Q. W., and Song, Y. M. (2008b). "Compatibility of wood fiber/plastic composite with environment," *Forestry Science* 44(5), 143-149.

Xi, Y., and Chen, N. L. (2007). "The influence of pretreatment on flax reinforced thermoplastic composite materials mechanics performance," *Fiber Composite* 24(4), 36-39.

Xiao, J. Y., Zeng, J. C., and Wang, C. Q. (2000). "Status of research and development for the natural high performance fiber reinforced composite and its product," *Fiber Reinforced Plastics/Composites* (2), 38-43.

Yuan, S. L. (2011). *Straw/Fibrous PE Composite Material Preparation Method of Hot Pressing*, Northeast Forestry University Press, Harbin.