Effects of Ultraviolet Aging on Properties of Wood Flour–Poly(Lactic Acid) 3D Printing Filaments

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An ultraviolet (UV) aging test chamber was used to analyze the aging behaviors of wood flour-poly (lactic acid) (PLA) 3D printing filaments under different temperatures. The materials were granulated using a twin-screw extruder, and the filaments were prepared using a single-screw extruder. The aging resistance was determined by comparing the color, tensile strength, scanning electron micrographs, and water absorption rate of the filaments before and after being processed. The aging behaviors tended to be stable when tested at 40 °C for 80 h, or 50 °C for 60 h, or 60 °C for 40 h. At this status, the tensile strength of the filaments was reduced by 44% compared to the originals; the internal structure of the filaments was severely damaged from the SEM images, and obvious porosities can be identified. The water absorption rate was greatly improved. The chromatic degradation (△E*) increased to 10.8 when tested at 40 °C, while this value increased to 10.9 at 50 °C and 10.8 at 60 °C. Therefore, the increase of aging temperature accelerated the UV aging process. It is recommended to add some ultraviolet absorbent into the filaments in order to improve the UV resistance of the materials.

Keywords: 3D printing; wood flour/PLA filaments; Ultraviolet aging; Tensile strength; Water absorption rate

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INTRODUCTION

With the growth of environmental awareness, wood-plastic composites (WPCs) occupy an increasing market share and play an important role in the sustainable socio-economic development. WPCs are capable of achieving a wide range of desirable characteristics such as design flexibility, lower material costs, corrosion resistance, lower petrochemical content, *etc*. (Shi 2012). Traditional WPCs are produced by air-forming and hot-pressing. They are usually processed at far lower temperatures than traditional plastics (Nourbakhsh and Ashori 2009). However, these processes usually result in dimensional failure issues.

As an innovative manufacturing technology, 3D printing can produce objects by adding material in layers that correspond to successive cross-sections of a 3D model. The method can be applied in architecture, construction, industrial design, automotive, and other fields. The use of 3D printing technology can overcome the shortcomings of traditional WPCs production by improving the manufacturing process (Garcia *et al.* 2012; Wang *et al.* 2015). Polylactic acid (PLA) is one of the two most commonly used materials in 3D printing.

Several studies have been conducted to analyze the performance of PLA filaments in terms of mechanical properties and dielectric properties. For example, Afrose *et al.*

(2016) investigated the fatigue behaviors of PLA parts processed by fused deposition modelling (FDM) additive manufacturing process and the effect of part build orientations (X, Y and 45°) on the tensile fatigue properties of PLA material during the melt-stacking process was analyzed.

Dichtl *et al*. (2017) studied the dielectric performance of 3D-printed PLA filaments and demonstrated that the conductivity of PLA filaments can be enhanced by mixing it with the ionic liquid trihexyl tetradecyl phosphonium decanoate. PLA can also be combined with other renewable resources (*e.g*., corn-starch, wood flour) to produce more eco-friendly filaments. For example, Daver *et al.* (2018) analyzed the preparation process and performance of cork–PLA biodegradable filaments via FDM. The biodegradable plasticiser, tributyl citrate (TBC), was used to improve the brittleness of PLA. The 3D printed composites were compared with compression-moulded composites, and the results showed that 3D printed composites had relatively lower elastic modulus and tensile yield strength, but higher elongation at break. Xie *et al.* (2017 and 2018) analyzed the impact of different plasticizers on wood flour/PLA composite 3D printing filaments to determine the optimal plasticizer type. The wood flour/PLA 3D printing filaments were optimized by using response surface methodology. The best processing parameters in the process of printing filaments were determined.

Similar to WPCs, wood flour/PLA 3D printing filaments will suffer from color change and a loss of mechanical properties during long-term applications. Some studies have been carried out to analyze the aging behaviors of WPCs and PLA filaments. For example, Stark *et al.* studied the performance changes of aging wood flour high density polyethylene (HDPE) composites using the arc lamp aging test chamber (Stark 2001; Stark and Matuana 2003; Stark and Rowlands 2003; Stark and Matuana 2004). The experimental results showed that different processing methods had different impacts on the surface chemistry of the composite, which then influences the properties of the composite after aging.

With regard to the composite materials based on PLA, Ho *et al.* (1999) compared two degradation tests, the natural degradation exposed to the soil *vs.* the UV-accelerated degradation in the laboratory. The authors found that an increase in temperature and relative humidity will enhance the degradation of PLA. Bi *et al.* (2017) analyzed the effect of ultraviolet absorber UV531 on the anti-aging properties of the PLA/wheat straw powder 3D printing filaments. The results showed that UV531 can effectively inhibit the UV aging of the filaments. It is noted that there has been no in-depth study on the aging behaviors of wood flour/PLA 3D printing filaments, which may restrict the application of such material in the field of 3D printing. Since UV irradiation can accelerate the degradation of PLA, increase the degradation rate (Ho and Pometto 1999), and finally determine the aging resistance of a filament, it is necessary to analyze the aging resistance of wood flour/PLA composite 3D printing filaments under different UV treatments in order to provide a reference for the stability of the filaments.

The objectives of the study were to: (1) Measure the chromatism, tensile strength, scanning electron micrographs, and water absorption rate of the wood flour/PLA 3D printing filaments before and after UV aging test; (2) compare the effects of different aging time and temperatures on the aging behaviors of wood flour/PLA 3D printing filaments; (3) identify the parameters for the wood flour/PLA 3D printing filaments to approach relatively stable aging status.

EXPERIMENTAL

Materials

Materials used were poplar wood flour (the wood flour was sieved into 140-mesh to 160-mesh size flour) and PLA. Experimental reagents used were tributyl citrate (TBC) (Shanghai Macklin Biochemical Co., Ltd., Shanghai, China), and distilled water (Xie *et al.* 2017).

Filament Preparation

A total of 42 g wood flour and 258 g PLA was prepared and the content of TBC used was 4% of the total material mass (Xie *et al.* 2018), thus 12 g TBC was needed. The materials were mixed with TBC and a twin-screw extruder (SHJ-20, Nanjing Giant Machinery, Nanjing, China) was used to granulate the mixtures into particles. Then, a desktop single-screw extruder (Kunshan Huan Xinyang Electric Equipment Co., Ltd., Kunshan, China) was used to extrude 3D printing filaments. The selected spray nozzle was 1.75 mm and the extrusion temperature was set up at 170 °C (Xie *et al.* 2017).

Filament UV Aging Experiment

The produced filament was cut off at intervals of 30 cm, and a total of 30 specimens were prepared, which were evenly divided into three groups. The filament UV aging experiment was conducted based on the standard practice for operating fluorescent light apparatus for UV exposure of nonmetallic materials (ASTM G154–06 2006). The first group (group 1) was placed in an ultraviolet (UV) aging test chamber (Changzhou National Test Equipment Research Institute) to conduct accelerated aging test at 40 °C. The second group (group 2) was placed in the UV aging test chamber at 50 °C. The third group (group 3) was placed in the UV aging test chamber at 60 °C (You *et al.* 2018). The properties of the filaments in each group after aging for 0 h, 20 h, 40 h, 60 h, and 80 h were tested for the three groups.

Methods

Mechanical properties

The tensile properties of the wood flour/PLA printing filaments before and after UV aging experiment were tested using a CMT-5504 Universal Mechanical Tester (Shenzhen Suns Technology Stock LLC., Shenzhen, China) according to the standard test method for tensile properties of plastics (ASTM D638-14 2014). Each filament specimen was tested 5 times and the average was applied.

Structure assessment

The cross section of the filaments was observed using a Quanta-200 SEM (FEI, Hillsboro, OR, USA). Each filament specimen was sprayed with metal powder and then tested with a magnification factor of 500.

Chromatic degradation test

The chromaticity values of wood flour/PLA 3D printing filaments under different aging time and temperatures were measured using a CM-2300d Spectrophotometer (Konica Minolta Holdings, Inc. Tokyo, Japan) according to the CIE $L^*a^*b^*$ coordinates. L^*, a^* and b^* were measured for six replicate samples, where L^* indicates lightness from black (0) to white (100), a^* is the red/green coordinate, and b^* is the yellow/blue coordinate.

An increase in L^* means that the sample is lighter and vice versa. Similarly, positive $\triangle a^*$ represents a color shift toward red and negative $\triangle a^*$ represents a shift toward green. Positive $\triangle b^*$ represents a color shift toward yellow and negative $\triangle b^*$ represents a shift toward blue. The total color change $\triangle E$ was calculated as follows (ASTM D2244 2016):

$$\Delta E = \sqrt{(\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2})} \tag{1}$$

Water absorption

According to the standard test method for water absorption of plastics (ASTM D570-98 1998), the filament samples was further cut into 25.4 mm length, and then vacuum-dried at 50 °C for 24 h, and subsequently weighed (recorded as m_1, g (gram)). The testing filaments were submerged into distilled water and soaked for 24 h. The filaments were then taken out of water, wiped by filter paper, and weighed again (recorded as m_2, g (gram)). The water absorption rate of each filament was calculated according to Eq. 2.

$$\text{Water absorption (\%)} = (m_2 - m_1) / m_1 \times 100 \tag{2}$$

RESULTS AND DISCUSSION

Tensile Strength Analysis

The tensile strength of wood flour/PLA 3D printing filaments under different UV aging time and temperatures is shown in Fig. 1. The tensile strength of the filaments before UV aging was 23.4 MPa, which was lower than the acrylonitrile butadiene styrene (ABS) filaments (34.0 MPa) and PLA filaments (46.8 MPa) (MakerBot 2019). The filaments in group 3 exhibited the fastest aging rate at 60 °C, and they tended to be stable at 40 h. At that time, the average tensile strength of the filaments had decreased by 44% compared to that before aging. At temperatures of 50 °C and 40 °C, the tensile strength of the wood flour/PLA 3D printing filaments became relatively stable after being treated for 60 h and 80 h, respectively. Therefore, the increase of aging temperature can accelerate the UV aging process. This can be explained by the fact that when the temperature in the aging chamber increases, the water vapor increases and the wood fiber gradually expands due to the hygrothermal effect, which leads to the significant decrease of the bonding force between the wood flour and the PLA. Meanwhile, the increase of water vapor promotes the UV photolysis of PLA within the wood flour/PLA matrix and decomposes the PLA into lactic acid (Joseph *et al*. 2002; Chen *et al*. 2007). This causes breakage of the joint surface between wood flour and PLA, which further induces filament aging. In addition, since the spraying device was used in this experiment to simulate the natural rainfall conditions, the wood fiber on the surface of the filament may be shed during the washing action by water, reducing the bonding strength between the wood flour and the PLA. This results in a large decrease in the tensile strength of the filaments. Since the effects of UV aging on different types of 3D printing filaments have not been documented, to the best of the authors' knowledge, it is hard to compare the UV resistance of these filaments. However, there is no doubt that there is various degree of aging for the filaments with different formulations. Bi *et al*. (2017) analyzed the anti-aging properties of PLA/wheat straw powder and found that by adding ultraviolet absorbent UV531 the mechanical properties of the composites were slightly reduced, but the mechanical strength retention rate can be improved. Therefore, it is recommended that some ultraviolet absorbent should be added into the wood flour/PLA 3D printing filaments in order to improve the anti-aging resistance of the materials.

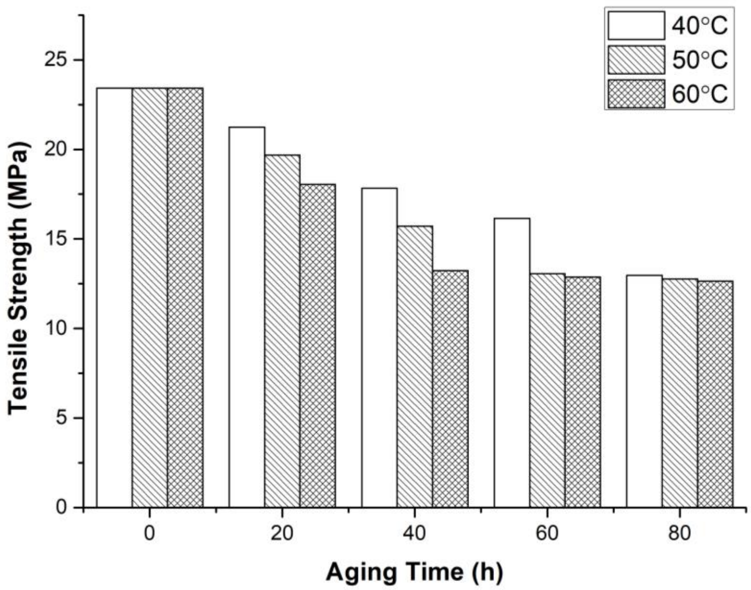
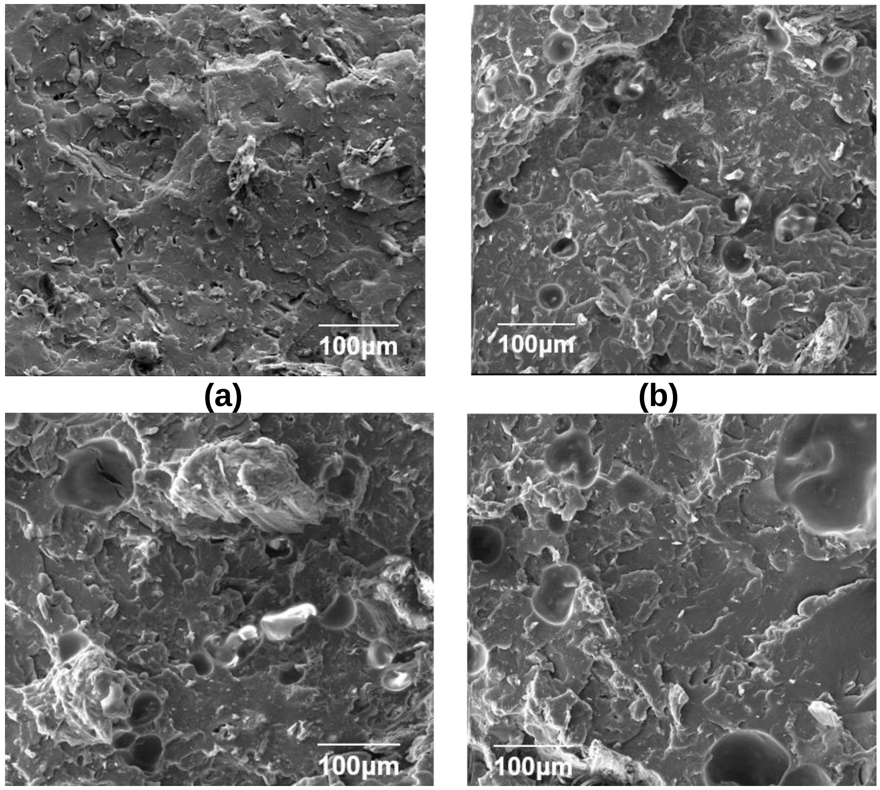


Fig. 1. Tensile strength of wood flour/PLA composite 3D printing filament under different aging conditions

Internal Structure Analysis

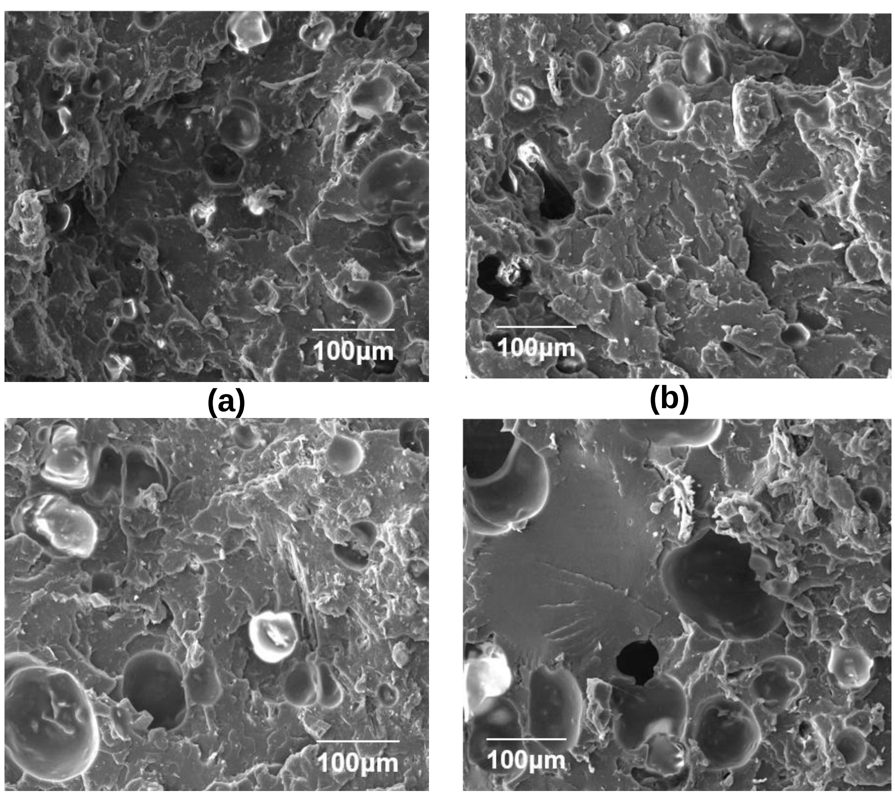
The SEM images of the wood flour/PLA 3D printing filaments after UV aging test under different aging time and temperatures are shown in Figs. 2, 3, and 4. The internal structure and aging degree of the filaments can be directly observed from the three groups of images. As the aging time increased, there were obvious porosities inside the filaments. At the initial aging stage, the porosities were small. However, as the aging time increased, the small pores gradually expanded, eventually forming large pores. Since the wood flour/PLA 3D printing filaments were translucent and thin, the UV light can penetrate the filaments. As time went on, the water vapor continuously penetrated the filaments, causing the wood flour and PLA in the filaments to be continuously degraded by UV light. The connection between the wood flour and PLA was destroyed, resulting in more free wood fiber and PLA with relatively lower mass.

When the aging time was kept constant, the aging temperature became a key factor affecting the degree of aging and the rate of aging. As the aging temperature increased, the aging rate of the filaments became faster. Pores began to appear inside the filaments after aging 20 h under different aging temperatures. The quantities and size of porosity increased with the increase of temperature, and the change rates of both also accelerated. Due to the combination effect of UV degradation and heat, the PLA inside the filaments was degraded into lactic acid, which is volatile, leading to the production of more pores inside the filaments and significant reduction of the compatibility of the filaments (Zuo *et al*. 2014). Therefore, the aging temperature promoted the aging of the filaments, which is consistent with the tensile strength analysis results.



(a) (b) (c) (d)

Fig. 2. SEM images for filaments (Magn 500x) at 40 °C: (a) 20 h; (b) 40 h; (c) 60 h and (d) 80 h



(a) (b) (c) (d)

Fig. 3. SEM images for filaments (Magn 500x) at 50 °C: (a) 20 h; (b) 40 h; (c) 60 h, and (d) 80 h

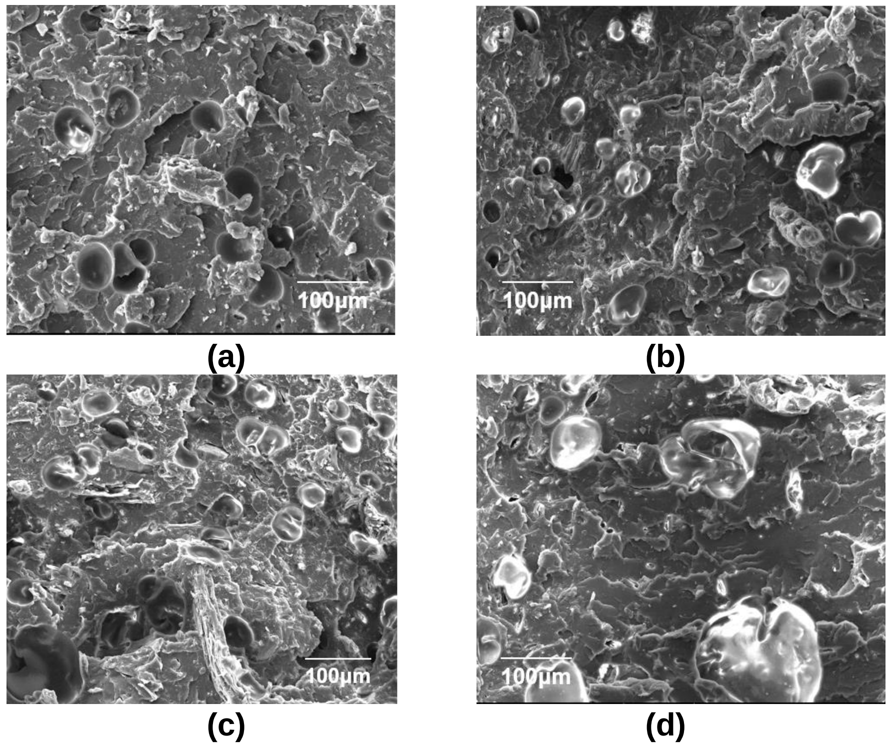


Fig. 4. SEM images for filaments (Magn 500x) at 60 °C: (a) 20 h; (b) 40 h; (c) 60 h and (d) 80 h

Chromatic Degradation Analysis

The chromatism and chromatic degradation of the wood flour/PLA 3D printing filaments under different UV aging time and temperatures are shown in Figs. 5 and 6. Figure 5(a) shows that $\triangle b^*$ and $\triangle L^*$ increased significantly with the increase of aging time at 40 °C, indicating that the surface color of the wood flour/PLA 3D printing filament became yellowish and whiter as aging time increased. Fig. 5(b) indicates that at 50 °C $\triangle b^*$ and $\triangle L^*$ increased from aging time 0 h to 60 h and then became stabilized as aging time continued to increase. Figure 5(c) shows that at 60 °C $\triangle b^*$ and $\triangle L^*$ increased from aging time 0 h to 40 h and after that $\triangle b^*$ increased slightly and $\triangle L^*$ tended to be stable. There was almost no change in $\triangle a^*$, indicating that the surface of the wood flour/PLA 3D printing filaments did not show obvious change in red-green hue value.

Figure 6 shows that the values of chromatic degradation ($\triangle E^*$) increased to varying degrees at different aging times and temperatures. $\triangle E^*$ increased significantly from aging time 20 h (2.7) to 80 h (10.8) at 40 °C, while this value tended to be stable after aging for 60 h (10.9) at 50 °C or after aging for 40 h (10.8) at 60 °C. Bi *et al*. (2017) reported that the chromatic degradation of PLA/wheat straw powder increased to 3.3 with UV aging time of 500 h. This indicates that compared to other materials the aging behavior of the wood flour/PLA 3D printing filaments was greatly affected as the aging time and aging temperature increased and less impacted when the aging time increased to the breaking points. The surface of the wood flour/PLA 3D printing filaments after aging changed from the original translucent wood color to whiter and yellowish. This was attributed to the photodegradation of PLA and wood fibers in wood flour/PLA 3D printing filaments. Since carbonyl groups are the main UV light absorbing species responsible for the photo-initiation reactions in wood/PLA composite and there are more carbonyl groups in lignin, the wood fiber within the wood flour/PLA 3D printing filaments can be more easily photodegraded (Wypych 2013). Meanwhile, with the prolongation of aging time, the structure of p-benzoquinone chromophore generated by lignin in wood fiber was converted into hydroquinone, which resulted in color change of the filaments (Stark and Matuana 2006). In addition, the aging temperature accelerated the process of chromatic degradation of the filaments. The analysis results on the chromatism and chromatic degradation are consistent with the above tensile properties and internal structural analysis results.

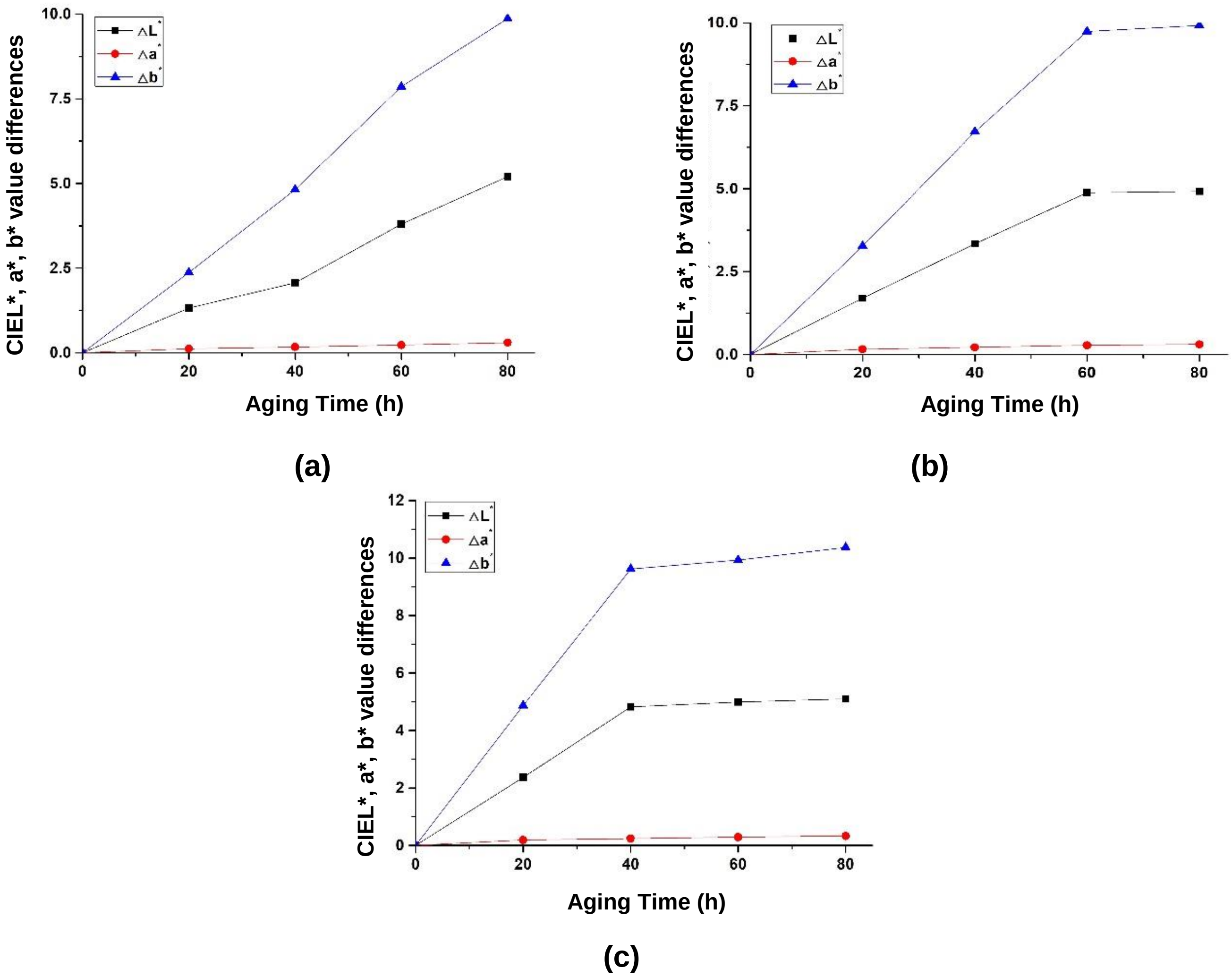


Fig. 5. Chromaticity curve at different temperatures: (a) 40 °C; (b) 50 °C, and (c) 60 °C

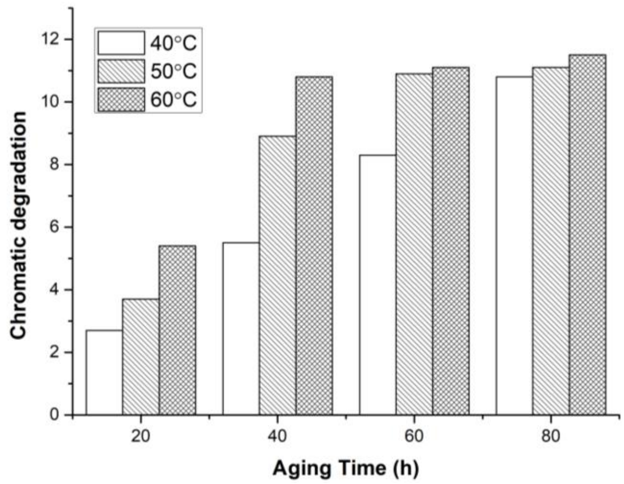


Fig. 6. Chromatic degradation curve at different temperatures

Water Absorption Analysis

The results of the water absorption rate of the wood flour/PLA 3D printing filaments as a function of different aging time and temperatures are shown in Fig. 7. The water absorption rate under different aging temperatures increased with the prolongation of aging time; however, the aging time for each group took to reach stable range was different. Group 1 (40 °C) was the slowest, which approximated the stable range after aging for 80 h; Group 3 (60 °C) was the fastest, which reached the stable range after aging for 40 h. The wood flour itself is hydrophilic, and the wood flour/PLA 3D printing filaments were destroyed by UV light, thereby destroying the joint surface of the wood flour and the PLA and releasing more wood fibers from the binding of PLA. The hydroxyl on the PLA molecular chain was simultaneously exposed to UV light, so that the water absorption rate of the aging filaments was greatly increased. Meanwhile, the temperature also promoted the increase of water absorption rate. The evaporation of lactic acid in the photodegradation of wood flour/PLA 3D printing filaments were greatly promoted, which increased the quantities and size of porosities in the filaments (Kamau-Devers *et al*. 2019).

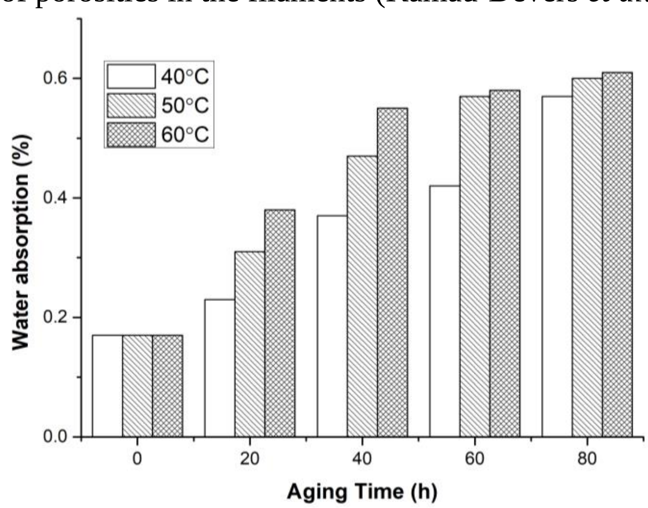


Fig. 7. Water absorption of wood flour/PLA composite 3D printing filament under different aging conditions

CONCLUSIONS

1. The tensile strength of wood flour/PLA 3D printing filaments gradually decreased with the extension of ultraviolet (UV) aging time. When the filaments were tested at 40 °C for 80 h, or at 50 °C for 60 h, or at 60 °C for 40 h, the tensile strength tended to be stable, decreasing by 44% compared to the originals. This result is similar to the average tensile strength loss for vectran fiber exposed to UV radiation (42.8%) (Liu *et al*. 2012).
2. With the extension of UV aging time, the internal structure of wood flour/PLA 3D printing filaments was changed from the original composite structure to the status of mutual separation of wood flour and PLA. The small molecular produced by photodegradation was hydrolyzed and evaporated, resulting in pores inside the filaments and further reduction of material compatibility.
3. The chromatic degradation and chromatism of wood flour/PLA 3D printing filaments changed greatly with the prolongation of UV aging time. Photodegradation led to decomposition of chromogenic groups in wood flour, and the color was changed from the original wood color to whiter and yellowish.
4. UV accelerated aging increased the water absorption rate of wood flour/PLA 3D printing filaments. The compatibility of the wood flour/PLA 3D printing filaments was reduced, and the wood fibers were no longer wrapped by the PLA, which greatly improved the contact surface of the wood fiber and the hydroxyl group with the water and thereby increased the water absorption rate of wood flour/PLA 3D printing filaments.
5. The combination effects of UV aging time and heating temperature showed that the increase of aging temperature accelerated the UV aging process and it is recommended to add some ultraviolet absorbent into the filaments in order to improve the UV resistance of the materials.

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