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THE EFFECT OF COLORANTS ON THE DEGRADATION PERFORMANCE OF WOOD PLASTIC COMPOSITES

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ABSTRACT

The degradation performance of the colorful wood flour/poly (β-hydroxybutyrate valerate) composites (CWPHBVs) in natural outdoor landfill was investigated by some physical, analytical, and microscopic tests. The mass loss rate of the CWPHBVs within 80 days of degradation shows a growth trend and the mass loss rate decreases by more than 20%. With the increase of degradation time, the bending strength of the CWPHBVs continues to decline, the elastic modulus of the CWPHBVs shows a logarithmic decline trend. After 30 days, the bending strength of the CWPHBVs decreases over 50% and tend to be stable. The colorant has a certain inhibitory effect on the degradation. However, with the shedding of the colorant, the effect of the colorant on the degradation is gradually weakened. The addition of colorants reduces the decomposition rate of PHBV and improves the thermal stability of poplar fibers. However, after 20 days, this effect almost disappears.

KEYWORDS: Wood plastic composites, wood flour, poly (β-hydroxybutyrate valerate), colorants, degradation performance.

INTRODUCTION

Wood plastic composites (WPC) have performance advantages of both plastic and wood fiber materials: the natural and beautiful texture and the secondary processing of wood; the repeatable processing performance and superior durability of plastic (Lao et al. 2019 and Li et al. 2013). Therefore, the manufacturing technology of WPC is considered to be "green technology" by various countries (Turku and Karki 2014). With the abovementioned

properties, WPC can be applied in a wide range of fields, such as buildings, automobiles, packages, transportation, decorative materials, and daily living appliances (Gao et al. 2018 and Rimdusit et al. 2011). Nevertheless, WPC have simplex color and poor decorative effect. It cannot satisfy some consumers who have requirements for the color of product appearance. In order to solve this problem, WPC can be colored with different colorants to improve decorative performance and enrich color choices.Colorant is important auxiliaries in the molding process of the WPC, which has a significant influence on the comprehensive properties of WPC. In recent years, many experts and scholars (Zhang et al. 2010, Peng et al. 2013,Schirp et al. 2015, Xu et al. 2016, Kajaks et al. 2019 and Babatunde et al. 2021) have found that the WPCs can be colored with different colorants to improve their decorative performance and mechanical properties.

At the same time, in recent years, many scholars have also conducted a lot of research on the aging resistance of CWPC.Chi et al. (2016)investigated the natural aging properties of color woodplastic composites (CWPC) outdoors. The results showed that after aging test, the surface of CWPC is obviously faded and the mechanical strength is significantly reduced.The reason is that during the aging process of CWPC, on the one hand, it is photodegraded by ultraviolet light irradiation, on the other hand, it is washed away by rain for a long time, resulting in a large number of birch fibers and colorants peeling off the surface, thus reducing the interface bonding strength.Stark and Matuana (2006) studied the effect of adding UV absorbers and/or pigments to wood flour/HDPE composites. The results showed that both UV absorbers and pigments improved the weather resistance of the composites.Xu et al. (2015) studied the hygrothermal aging properties and bending properties of WPCs prepared by adding three different colorants. It was found that the colored WPCs had better hygrothermal aging properties, including lower water absorption, less total color change, and higher mechanical property retention rate.Butylina et al.(2015)examined the resistance of wood/polypropylene and wood/wollastonite/polypropylene composites containing pigments to natural weathering.The pigments used in this study reduced the color change of the composites exposed to outdoor weathering as compared with the uncolored composite. Moreover, the carbon black pigment was found to reduce the degradation of the surface layer of the composites, to have a positive effect on the dimensional stability of the composites.Only the combination of the carbon black pigment and wollastonite resulted in a composite which was capable to retain its Charpy impact strength both after one year of outdoor weathering and cyclic treatment.An et al.(2019) studied the changes of structure and mechanical properties of P34HB/wood flour biocomposites during natural degradation. The results showed that with the increase of degradation time, the mass loss of the composites increases, while the mechanical properties decrease.

As mentioned above, CWPC have been proven to have better decorative and mechanical properties. CWPC have been usually exposed to outdoor conditions (UV lights, rain, etc.) due to where they mostly maintain their service life (Durmaz and Zgen 2022). The main objective of this study was to investigate the effect of the colorants on the degradation performance of CWPHBV in natural outdoor landfill. The degradation of CWPHBVs during outdoor natural landfill was studied. The influence mechanism of colorants on the degradation performance was discussed by studying the surface morphology, mass loss, microstructure, mechanical properties and thermal properties.

MATERIAL AND METHODS

Materials

Poplar (*Populus tomentosa*Carr.) wood flour with a size passed 80 mesh sieve was provided by Lichang Wood Industry Co. LTD, China. Poly (3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV, with a density of 0.9 ($g \cdot cm^{-3}$) and a melt point of 176□) was purchased from Xinxing Plasticizer Co. LTD, China. Three different colorants, namely inorganic titanium dioxide (TiO_2, white colorant, titanium dioxide with inorganic or organic surface treatment, provided by Dongguan Shanyi Plastics Co. LTD, China), red wood thermochromotropic agent (a red colorant, prepared by microencapsulation of an electron transfer-type organic compound system with a discoloration temperature of 10□, provided by Shenzhen Dongfang Discoloration Technology Co. LTD, China) and organic permanent yellow ($C_{34}H_{28}Cl_4N_6O_4$, a yellow colorant, provided by YuyaoRanfeng Plastic Dyeing Co. LTD, China) were used.

Preparation of sample

The poplar flour was dried in an oven at 103°C for 24 h until the moisture content was less than 3%.Dried wood flour, PHBV, MAPP, and colorant were weighed and then mixed in a high-speed mixer with 1800 r/min for 3 min. Then, the mixture was oven-dried, distributed into the mold, and hot-pressed at 180°C and 7tons for 10 min by the hot press (Carver 3895, Mecono Technologies Co., Ltd.). After hot pressing, the formed panel (250×250×2 mm) was further pressed at 3 MPa for another 3 min at room temperature using a cold press (XLB, manufactured by China Yadong Machinery Group Co., Ltd.). Finally, the prepared panels were sawn into specified size specimens, which were sequentially dried to an oven-dry state. The resulting sample is shown in Fig.1.

ControlWhiteRed Yellow

Fig. 1:The colorful wood flour/Poly (β-hydroxybutyrate valerate) composites (CWPHBVs).

Characterization of composite specimens

The mass loss rate test

The prepared samples were processed into 40×10×2mm specimens, which were dried in a blower dryer for 12 h and weighed and recorded as m_0, and then the specimens were grouped into 10 groups, all buried in 10 cm deep soil. The spacing of each specimen is not less than 50 mm. A group was taken out every 10 days, washed with distilled water, dried in a blower dryer for 12 h, weighed and recorded as m, and then the mass loss rate (ISO 846: 2019) according to:

$$W\% = \frac{m_0 - m}{m_0} \times 100\% \quad (1)$$

where: $W\%$ represents the mass loss rate (%), m_0 (g) and m(g) denote the mass of the specimen before and after degradation, respectively.

Mechanical property test

The cut specimens of the CWPHBVs were installed on the universal testing machine (Instron 3369, made by Instron Corporation, USA) for testing. The load was applied evenly during the test, and the loading speed was set at 1 mm/min. The maximum load value was recorded. Finally, the modulus of rupture (MOR) and bending modulus of elasticity (MOE) were calculated according to the formula, the results were taken as the average of the five samples.

Scanning electron microscopy (SEM)

SEM experiments were performed with a JSM-IT300LV scanning electron microscopy (Electronics company, Japan) to observe the morphology of the dispersed phase. The scanning voltage was 10 kV, and the sample was coated with gold before the observation.

Fourier transforms infrared (FT-IR) microscopy

FT-IR spectra analysis was carried out taken on a ThermoFisher Scientific iS5 instrument (Thermo, USA). The resolution of each spectrum was 4cm^{-1}, obtained with 16 scans. The changes in the chemical structure of the CWPHBVs were analysed.

Thermogravimetric analysis (TGA)

The thermal stability of the samples was measured under 20ml/min N_2 flow atmosphere with a TGA-Q50 thermogravimetric analyzer (TA, USA).The heating process was conducted from room temperature to 600□ at a scanning rate of 10□/ min. The thermogravimetric curves (TGA) and differential thermogravimetric curves (DTG) were obtained.

RESULTS AND DISCUSSIONS

Mass loss rate of the CWPHBVs

The mass loss rate of the CWPHBVs within 80 days of degradation, as depicted in Fig. 2, shows a growth trend, and the mass loss rate decreases by more than 20%. PHBV is polymerized by two molecular monomers, 3HB and 3HV. The matrix contains a large amount of amorphous region structure, and the structure is relatively loose, so it began to hydrolyze first, and then is degraded, and finally degrades into H_2O and CO_2. Wood fibers also have active molecular chains which are hydrolyzed first, then degrade by microorganisms, and then decompose into H_2O and CO_2. However, after the colorant is added, it can be filled into the cracks and grooves of the CWPHBVs. It is more difficult for mold, water vapor and oxygen in the soil to enter it for corrosion degradation, but the colorant continues to fall off from the sample over time, which can eventually aggravate the degradation of CWPHBVs.

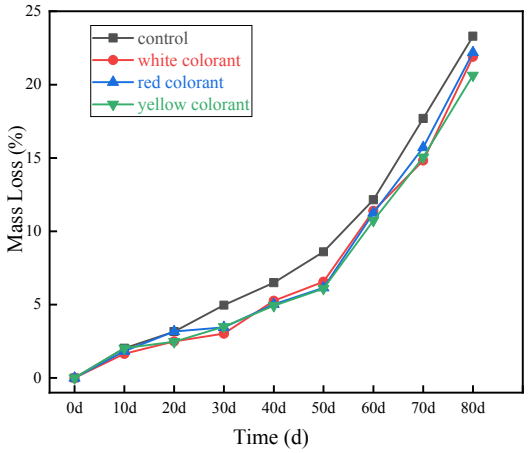


Fig.2: Mass loss rate of the naturally degradedCWPHBVs.

Mechanical property analysis

As shown in Fig. 3, with the increase of degradation time, the bending strength of the CWPHBVs continues to decline, the elastic modulus of the CWPHBVs shows a logarithmic decline trend. After 30 days, the bending strength of the CWPHBVs decrease over 50%. When the degradation time is 0 to 10 days, the elastic modulus of the CWPHBVs decreases greatly, and the decrease rate is over 50%. When the degradation time is 10~30 days, the elastic modulus of CWPHBVs is obviously reduced, and the reduction rate is over 70%. When the degradation time exceeds 30 days, the mechanical properties of the CWPHBVs tend to be stable.

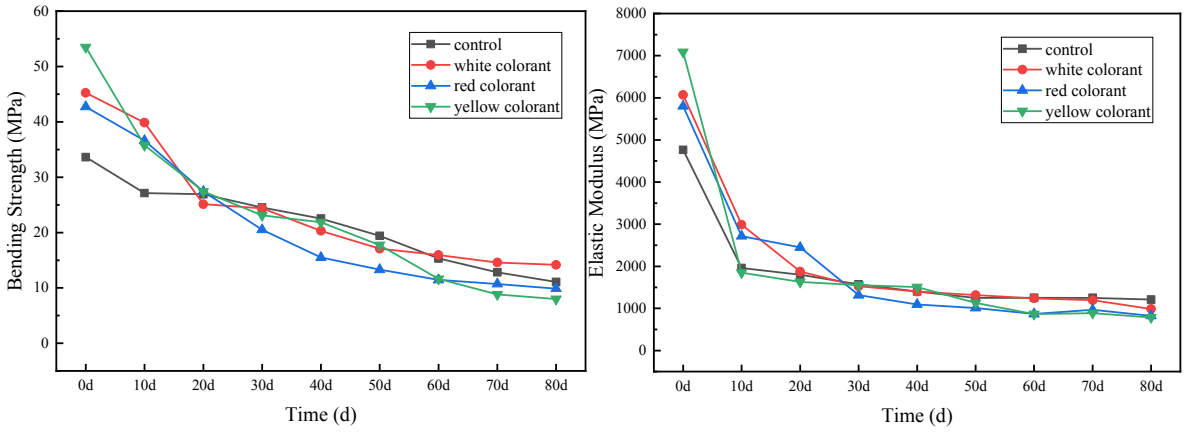


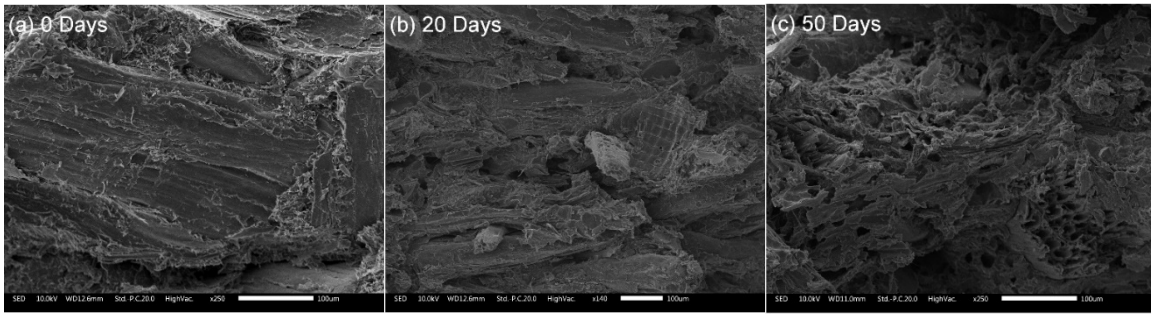
Fig. 3:Bending strengthand elasticmodulus of naturally degraded CWPHBVs.

In the early stage, because the colorant is filled into the cracks and grooves of the CWPHBVs, the interfacial compatibility and interfacial strength of the CWPHBVs are enhanced, and the mold, water vapor and oxygen in the soil are more difficult to enter for corrosion degradation (Nicole and Laurent 2006). Therefore, the colorant has a certain inhibitory effect on the degradation and hinders the decrease of strength. However, with the shedding of the colorant in the later stage, the effect of the colorant on the degradation is gradually weakened. The amorphous region of the PHBV matrix begin to degrade, and the wood flour fiber is exposed to the soil and begins to degrade. The integrity of CWPHBVs is destroyed, and the interface strength suddenly decreases, resulting in a significant decrease

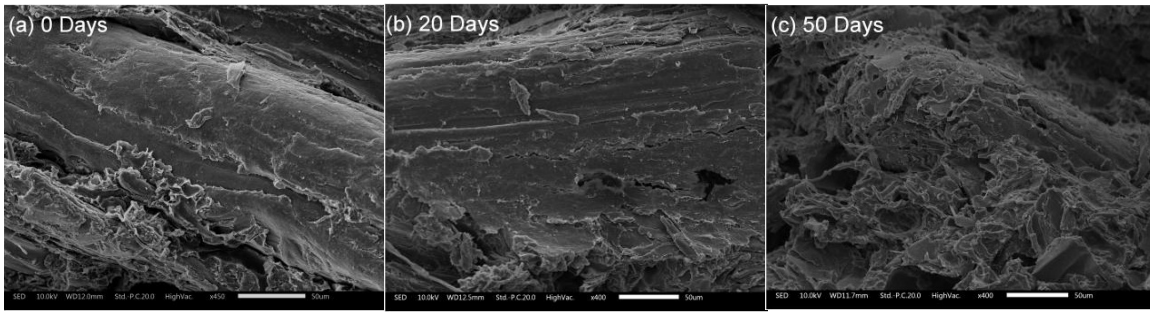
in flexural strength and elastic modulus (Li et al 2009). When the matrix is degraded to a certain extent, the interface bonding failed, the matrix is independent and separates from each other, and the bending strength and elastic modulus can't be reflected and remain stable (Xue 2012).

Scanning electron microscopy

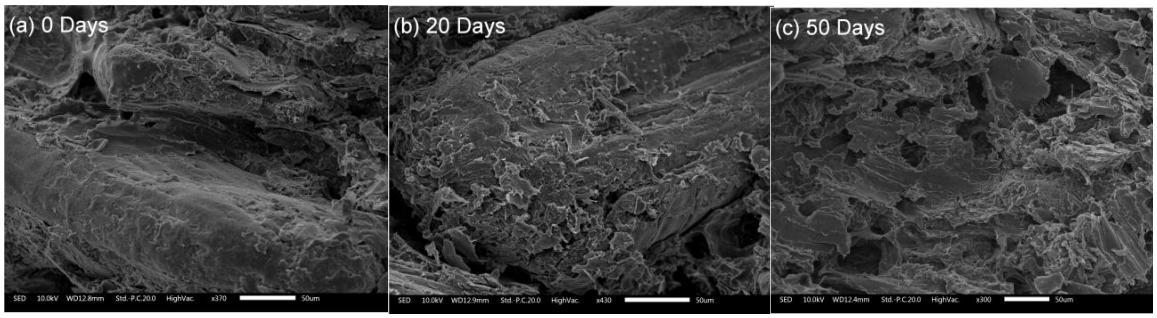
Fig. 4 is cross-sectional SEM images of CWPHBVs under natural degradation conditions for 0, 20 and 50 days. It can be found from the figures that the surface of the CWPHVBs is almost completely covered by PHBV and colorant, and almost no grooves and cracks at 0 days.



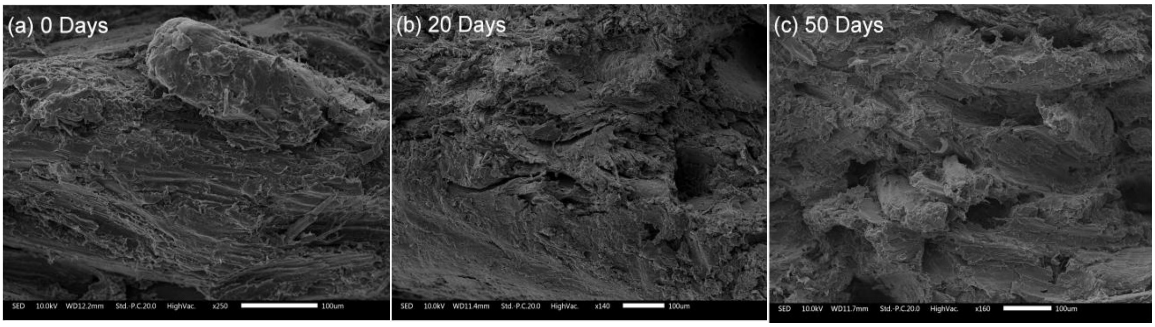
(a) WPHBVs with control



(b) WPHBVs with white colorant



(c) WPHBVs with red colorant



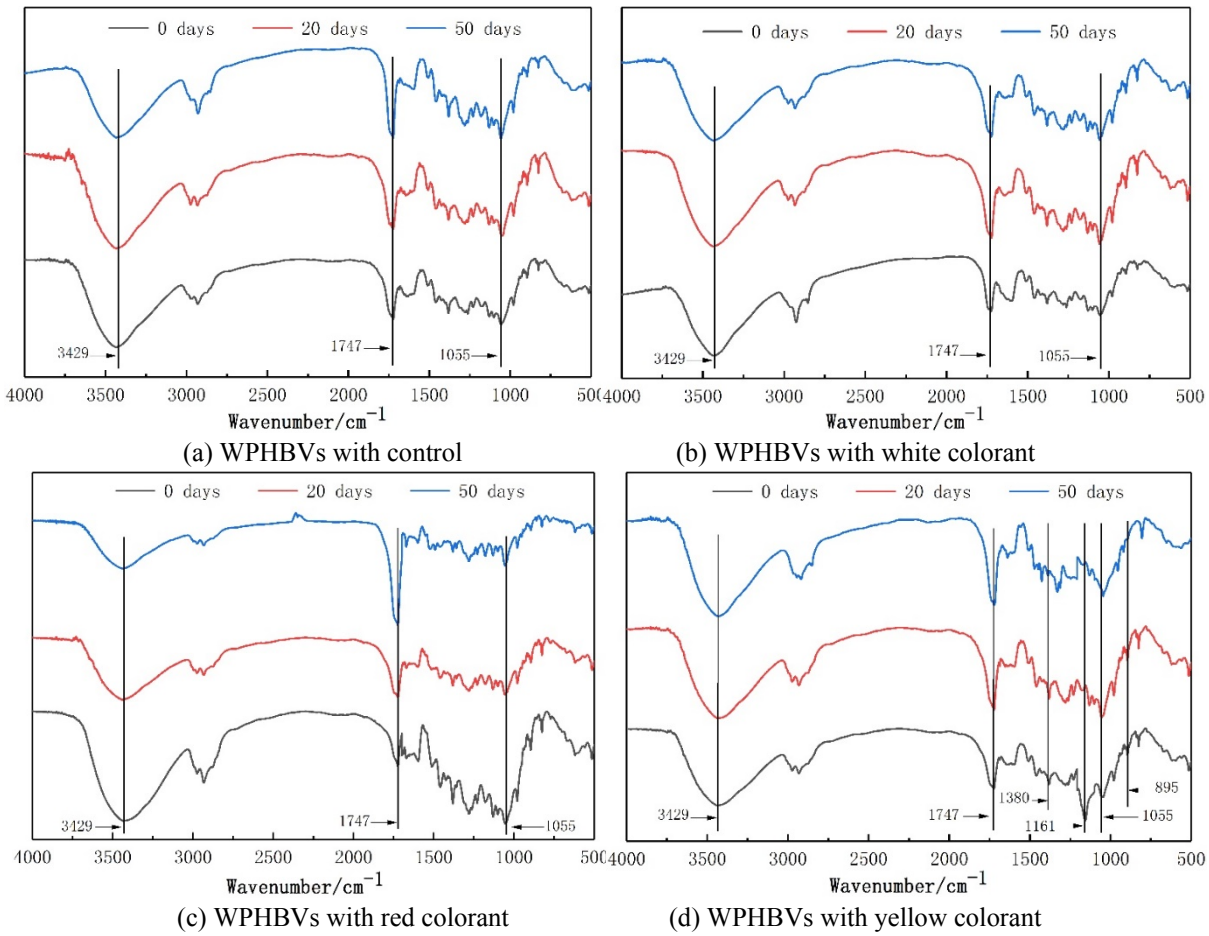
(d) WPHBVs with yellow colorant

Fig. 4:SEM images of cross section of naturally degraded CWPHBVs.

After 20 days, small cracks have begun to appear in the interface between poplar fiber and the PHBV matrix on the surface. The water and oxygen in the soil enter into the CWPHBVs and destroy the interface between the poplar fiber and the PHBV matrix. Therefore, the mechanical strength of CWPHBVs decreases. As the colorant beginning to fall off, the surface has begun to fade. After 50 days, most of the PHBV matrix degrade, and most of the colorants fall off, resulting in surface discoloration. The surface of CWPHBVs becomes rough due to corrosion and degradation. Most of the poplar fiber is exposed to the soil, and water molecules continue to enter the interior of the poplar fiber. Therefore, the interface of CWPHBVs is destroyed.

FT-IR analysis

It is proved in Fig.5 that three colorants can only enable wood flour to be fully mixed with PHBV and create a stronger interface among the WPHBVs because they do not easily undergo chemical changes with the substance to be dyed (Xie et al 2024).The peak at 1747 cm^{-1} can be observed from Fig.5, that is, the stretching vibration peak of carbonyl (C=O) increases significantly with the increase of degradation time.



(a) WPHBVs with control (b) WPHBVs with white colorant

(c) WPHBVs with red colorant (d) WPHBVs with yellow colorant

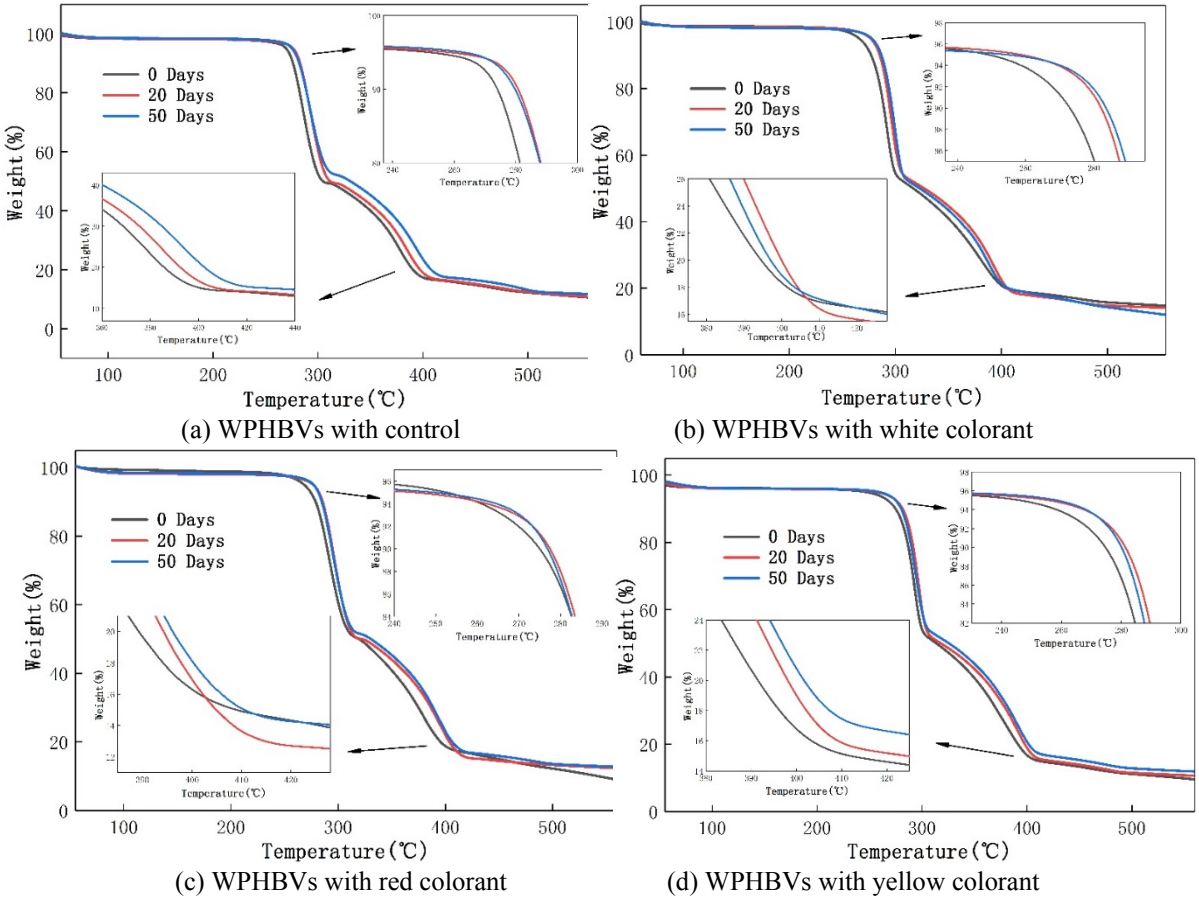
Fig. 5: Infrared spectra of naturally degraded the CWPHBVs.

The reason is that poplar flour is continuously degraded under the action of mold, water and oxygen, and the degradation products include carbonyl and carboxyl groups (Gao et al 2016). The peak value at 1055cm^{-1} increases with the increase of degradation time. This could

be due to the bridging crosslinking reaction between the free radicals in the composite and the oxygen in the soil during the degradation process, resulting in the enhancement of the vibration peak of C-O-C oxidative crosslinking. In addition, the O-H stretching vibration peak at 3429 cm^{-1} gradually decreases with the increase of the degradation time, because that under the action of water vapor and mold, part of the poplar fiber will peel off from the matrix, causing the O-H stretching vibration peak to continuously weaken (Stark and Matuana 2006). Since the yellow colorant is an organic colorant, its aging resistance is poor. Therefore, the yellow colorant on the surface of the CWPHBVs was peeled off, causing the peak at 1161cm^{-1} to continuously weaken in Fig. 5d (Zhou et al 2014).

Thermogravimetric analysis (TGA)

Fig. 6 shows the TGA curves of the CWPHBVs at different degradation times. It can be divided into three stages in total. The first stage is mainly the decomposition stage of PHBV and the main initial pyrolysis stage of poplar flour at 250°C-300°C, the second stage is the main decomposition stage of poplar flour at 300°C-400°C, and the third stage is the deep decomposition of residual fibers above 400°C until the stage of reaction.



(a) WPHBVs with control (b) WPHBVs with white colorant

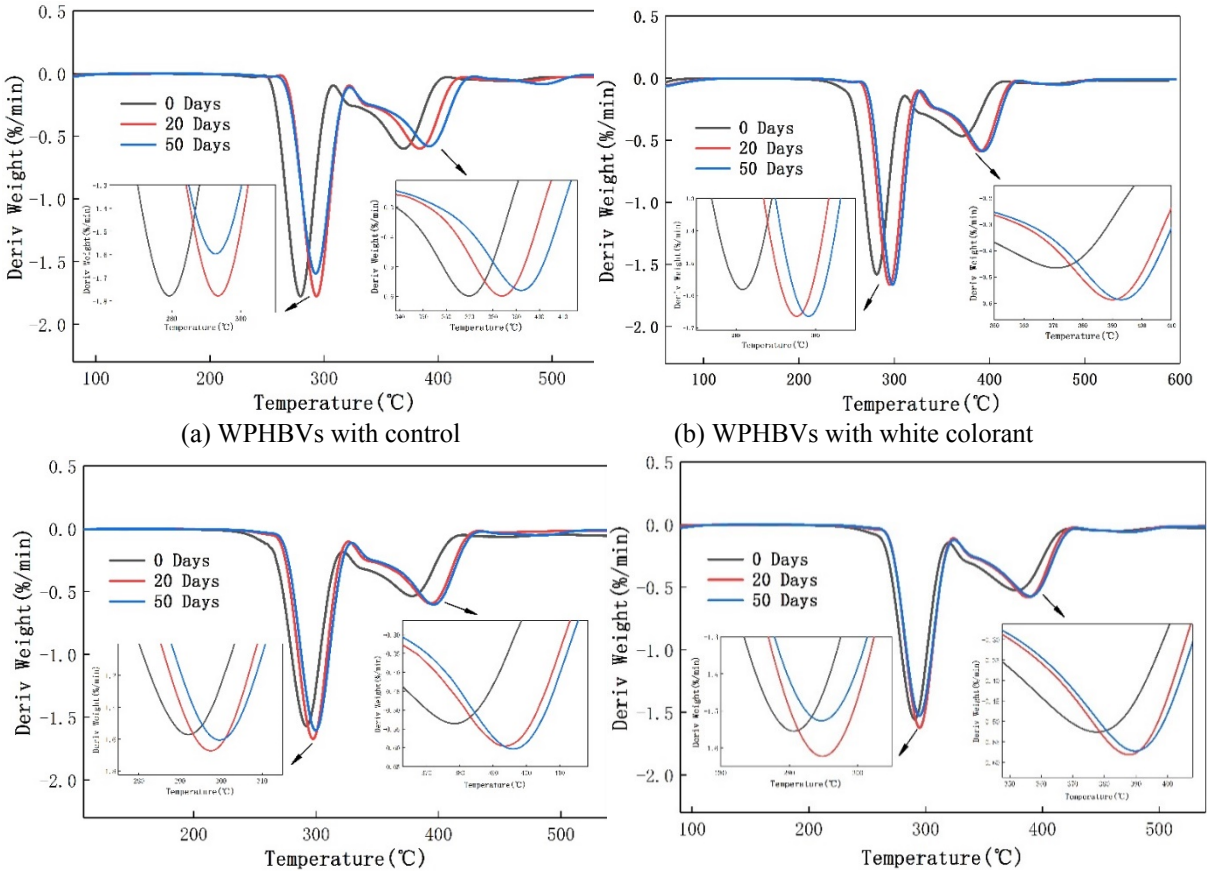
(c) WPHBVs with red colorant (d) WPHBVs with yellow colorant

Fig. 6:TGA curves of naturally degraded CWPHBVs.

From Fig. 6, with the increase of degradation time, the decomposition curves of the CWPHBVs gradually move to the right, indicating that because of the decomposition of PHBV, the thermal sensitivity of the CWPHBVs is reduced and the thermal stability is improved. In the second stage, with the increase of degradation time, the decomposition curve

also showed a tendency to shift to the right. When PHBV is completely decomposed, heat-resistant colorants can improve the thermal stability of poplar flour by filling the voids on the surface of wood fibers (Xie et al 2024).

In the DTG curve of the CWPHBVs (Fig. 7), two main weight loss peaks are the peak weight loss of PHBV closed to 290°C, and the peak weight loss of wood fiber occurs around 390°C. With the increase of degradation time, the weight loss peak at about 290°C moves to the right, the offset decreases first, and it is almost unchanged after 20 days. The intensity of the weight loss peak becomes stronger first, and it becomes weaker after 20 days. After adding the colorant, the offset is almost unchanged decreases and the intensity of the weight loss peak is almost constant. The weight loss peak at about 390°C also moves to the right. After adding the colorant, the offset is almost unchanged, and the strength of the weight loss peak is almost constant. These results indicate that the addition of colorants reduces the decomposition rate of PHBV and improves the thermal stability of poplar fibers. However, after 20 days, this effect almost disappears with the shedding of colorants.



(a) WPHBVs with control (b) WPHBVs with white colorant

(c) WPHBVs with red colorant (d) WPHBVs with yellow colorant

Fig. 7:DTG curves of naturally degraded CWPHBVs.

CONCLUSIONS

In this study, the effect of three colorants on the degradation performance of the CWPHBVs was investigated by some physical, analytical, and microscopic tests. The

mass loss rate of the CWPHBVs within 80 days of degradation shows a growth trend and the mass loss rate decreases by more than 20%. With the increase of degradation time, the bending strength of the CWPHBVs continues to decline, the elastic modulus of the CWPHBVs shows a logarithmic decline trend. After 30 days, the bending strength of the CWPHBVs decrease over 50%, the mechanical properties of the CWPHBVs tend to be stable. In the early stage of degradation, because the colorant is filled into the cracks and grooves of the CWPHBVs, the interfacial compatibility and interfacial strength of the CWPHBVs are enhanced, and the mold, water vapor and oxygen in the soil are more difficult to enter for corrosion degradation. Therefore, the colorant has a certain inhibitory effect on the degradation and hinders the decrease of strength. However, with the shedding of the colorant in the later stage of degradation, the effect of the colorant on the degradation is gradually weakened.After adding the colorant, three colorants can only enable wood flour to be fully mixed with PHBV and create a stronger interface among the WPHBVs.The addition of colorants reduces the decomposition rate of PHBV and improves the thermal stability of poplar fibers. However, after 20 days, this effect almost disappears with the shedding of colorants.

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