Effect of Silica on Thermal and Mechanical Properties of Eucalyptus-PVC Wood-Polymer Composites

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Wood plastic composites (WPCs) were prepared by extrusion molding with eucalyptus powder, polyvinyl chloride (PVC), and silica as additives. The mechanical properties, creep behavior, thermal properties, and cross-section microstructure of the composites were analyzed by universal testing machine, thermogravimetric analyzer, and scanning electron microscope. The results show that with the increase of silica content, the tensile strength, bending strength, and impact strength of the WPCs first increased and then decreased. When the silica content was 3.0%, the tensile strength, bending strength, and impact strength of WPC reached the maximum values of 27.5 MPa, 48.8 MPa, and 4.18 KJ • m^{-2}, respectively, which represented increases of 12.6%, 9.4%, and 20.1%, respectively, compared with those without silica. When the stress was 13.4 MPa, the strain value of 3.0% SiO_2-eucalyptus/PVC wood plastic composite was 3.3 times that of 4.46 MPa and 1.7 times that of 8.92 MPa. The pyrolysis process of eucalyptus/PVC WPCs showed a similar trend with different silica content.

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INTRODUCTION

Wood plastic composites (WPCs) are environmentally friendly materials prepared by mixing wood fiber and plastic with different molding methods. The material has the workability of plastic and the durability of wood. The materials are mainly recycled wood and plastic; thus, their use can reduce pollution (Chen *et al.* 2018; Jiang *et al.* 2019; Wang *et al.* 2019; Shao *et al.* 2019; Wang *et al.* 2022). In this paper, eucalyptus wood powder was used as wood fiber and PVC was used as matrix material to prepare wood-plastic composites. Eucalyptus has the characteristics of high strength and fine texture, and it is abundant. China now has more than 4.5 million hectares of eucalyptus plantation, accounting for about 2.1 percent of the total forest area and 6.3 percent of the total artificial forest area, with an annual output of more than 30 million cubic meters of wood, which is more than 1/3 of the country's total wood production (Lu *et al.* 2022). PVC is an indispensable material in production and life, and it is also suitable for recycling. Song *et al*. (2013) made WPCs from polyvinyl chloride (PVC) resin and eucalyptus flour and concluded that the mechanical properties of wood plastic composites were the best when the grain size of wood flour was 70 to 80 mesh. Zhang *et al*. (2022) improved the storage modulus, loss modulus, and complex viscosity of the blend system by adding nano SiO_2

compatibilizer, which improved adhesion between wood fibers and plastic. Wang *et al*. (2011) showed that with the increase of the content of nano-SiO_2, its tensile strength was improved, and the waterproof performance of the film was also improved. Xu (2022) found that when the additional amount of silica was 6%, the mechanical properties of the composite were significantly improved. Thus, the filler played a role in toughening, and the water absorption was decreased. Zhang (2021) showed that the addition of silica not only improved the flame retardancy of wood plastic composites, but it also improved their mechanical properties. Zhao *et al*. (2006) elaborated the influence of different nanoparticles on the toughening effect of polypropylene, and they concluded that the interfacial effect and interfacial morphology are the technical keys to affect the performance of polymer/inorganic nanoparticle composites. In this paper, silica (SiO_2) was used as a toughening agent to improve the mechanical properties of wood plastic composites in order to improve the interfacial adhesion between reinforcement materials and matrix materials (Sun *et al.* 2021).

EXPERIMENTAL

Materials

Raw material parameters are shown in Table 1.

Table 1. Raw Material Parameter

Material	Parameter	Place of Origin
Polyvinyl chloride(PVC)	SG-5	Dongguan City, Guangdong Province
Eucalyptus powder	100 mesh	Huizhou City, Guangdong Province
Calcium zinc stabilizer	300II	Shenzhen Hai 'an Plastic Chemical Co. LTD
PE wax	0020P	Henan Huayue Chemical Products Co. LTD
Malay grafted polyethylene		Shenzhen Hai 'an Plastic Chemical Co. LTD
Silicon dioxide	Powder,2μm	Guangzhou Metal Metallurgy (Group) Co. LTD

Composites Preparation

First, 100 g of dried eucalyptus wood (less than 5% moisture) and 100 g of polyvinyl chloride (PVC) were added to 6 g of maleic grafted polyethylene, 16 g of calcium zinc stabilizer, 10 g of PE wax, and 0, 3, 6, or 9 g of silica (ultrasonic dispersion) and mixed for 5 min. The mixture was placed into a three-dimensional mixer to mix evenly. It was melted and extruded through a conical twin-screw extruder. The temperature of the conical twin-screw extruder was set to 150, 155, 160, and 165 °C in turn, and the motor speed was 20 rpm. After the preparation was completed, it was completely cooled and aged, and then the size required for relevant test performance was prepared through secondary machining.

Fourier Transform Infrared Spectroscopy

A total of 0.002 g of sample powder was placed in a mortar with 0.2 g of potassium bromide powder for full grinding and mixing. The mixture was placed evenly in the YP-2 tablet press for tableting and pressed into a disc with a diameter of 13 mm. The sample disc was examined using the Fourier transform spectrometer (Nicolet iS10 Thermo Fisher Technology (China) Co., LTD., Shanghai) with a resolution of 4 cm^{-1}, wavelength scanning setting range of 4000 to 400 cm^{-1}, and 16 scans.

Tensile and Bending Strength

The tensile strength and bending strength of eucalyptus/PVC composites were tested with an electronic universal testing machine (CMT6104, Metz Industrial Systems (China) Co., LTD., Shenzhen, Guangdong) at room temperature according to the national standards GB/T1040.4-2006 and GB/T9341-2008. The test speed was 2 mm/min. The average value of three tests was taken as the result.

Impact Strength

The XJJ-5 simply supported beam impact tester was used to test the impact strength of wood fiber/PVC composites at room temperature according to the national standard GB/T1043.1-2008. The average value of the three tests was taken.

Creep Property Test

The CMT6104 electronic universal testing machine was used to test the short-term creep of wood fiber/PVC composites. The stress and strain were tested at room temperature according to the national standard GB/T111546-2008, and the creep time was set as 4 h.

Scanning Electron Microscopy

The microstructure of cross sections of modified starch degradable composites was observed by LEXT OLS 4100 laser confocal microscopy (Olympus Ltd., China). The size of specimen was 10 mm*2 mm.

Thermal Performance Test

Using a synchronous thermal analyzer (to test the thermogravimetric curve (TG/DTG) of composite materials, the sample was raised from room temperature to 800 °C at the rate of 10 °C/min in air atmosphere, its thermal weight loss was investigated, and the TG curve was recorded.

RESULTS AND DISCUSSION

Effect of Silica Content on FT-IR Spectra of Eucalyptus/PVC Wood Plastic Composites

Figure 1 shows that the infrared spectra of eucalyptus/PVC wood plastic composites with different content of silica were basically the same, but the difference was the strength of the characteristic peaks. The -OH stretching vibration peak was at 3250 to 3500 cm^{-1} in each case.

At 2990 to 3000 cm^{-1}, 2840 cm^{-1}, 1755 cm^{-1}, and 1633 cm^{-1}, there were $-CH_3$, -CH, and C=O stretching vibrations from lignocellulose, ketone compounds, lignin, and hemicellulose, respectively. The absorbance peak at 1058.8 cm^{-1} is attributed to the asymmetric stretching vibration of Si-O bond of silicon dioxide molecule. The absorbance peak at 798.5 cm^{-1} is attributed to the symmetric stretching vibration of the Si-O bond of silicon dioxide (Yu *et al.* 2022).

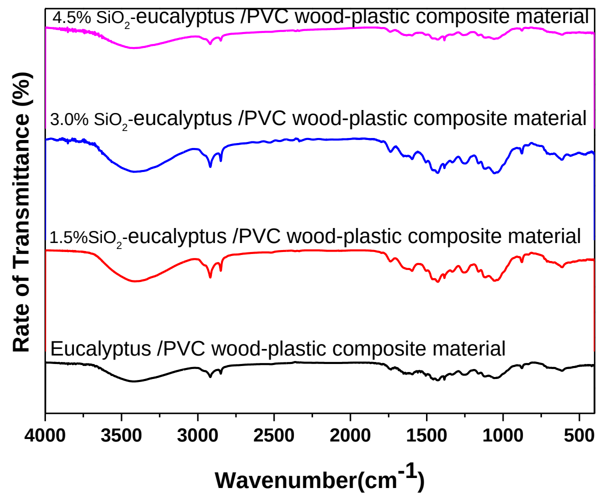


Fig. 1. FT-IR spectra of eucalyptus dioxide /PVC wood-plastic composites with different contents

Effect of Silica Content on Mechanical Properties of Eucalyptus/PVC Wood Plastic Composites

The tensile strength, bending strength, and impact strength of eucalyptus/PVC wood plastic composites with different silicon dioxide content were tested, as shown in Fig. 2.

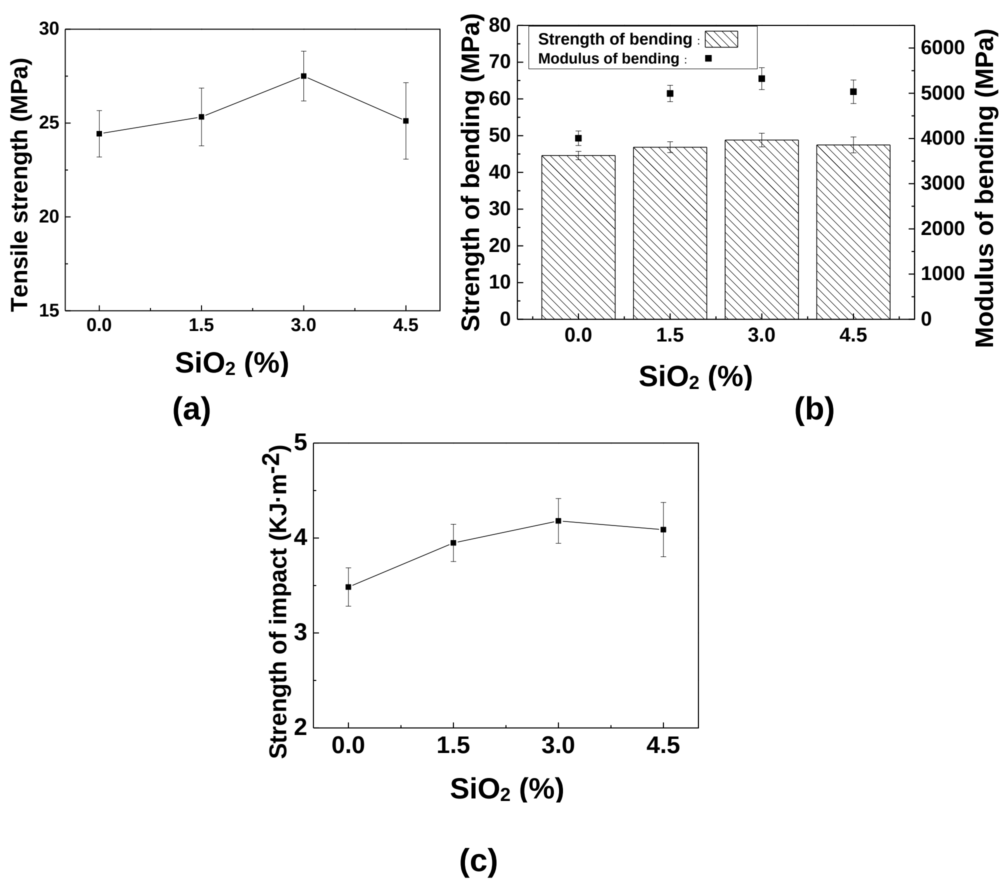
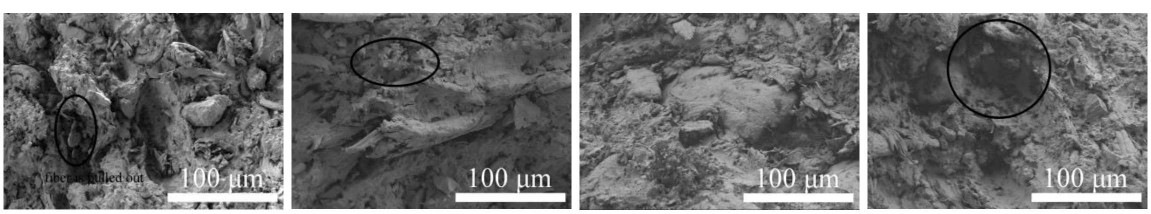


Fig. 2. Mechanical properties of eucalyptus /PVC wood-plastic composites (a)Tensile strength of eucalyptus /PVC wood-plastic composites,(b)Bending strength of eucalyptus /PVC wood-plastic composites,(c)Impact strength of eucalyptus /PVC wood-plastic composites

With the increase of silicon dioxide content, the mechanical properties showed a trend of increasing and then decreasing. When the silicon dioxide content was 3%, the mechanical properties reached the maximum values, which were 27.5 MPa, 48.8 MPa, and 4.18 kJ • m^{-2}, which represented increases by 12.6%, 9.4%, and 20.1%, respectively, compared with the corresponding specimens without silica. This was attributed to the fact that the addition of silicon dioxide increases the contact area of the two-phase interface, enhances the compatibility of the two-phase interface, effectively disperses the stress when subjected to external loads, delays and passivates the growth and extension of microcracks in the tensile process, and improves the tensile properties of the composite (Huang 2021). These effects further improve the toughness of the wood plastic composite, while the addition of excessive silicon dioxide will cause agglomeration and holes. The comprehensive mechanical properties of wood plastic composites were reduced at higher silica content.

Sectional Microstructure of Eucalyptus/PVC Wood Plastic Composites with Different Silica Content

Silica is the main factor affecting the two-phase bonding of wood plastic composites, and its section morphology was observed by scanning electron microscope, as shown in Fig. 3. The microstructure of the section of eucalyptus/PVC wood plastic composite without adding silica in Fig. 3(a) shows an obvious two-phase interface, and there were holes left after the wood fiber was pulled out on the section. This indicates that the compatibility of the two-phase interface was poor, and the two-phase interface adhesion was insufficient (Zhao *et al.* 2021). When the addition of silica was 1.5%, Fig. 3(b) shows that fiber pullout was still evident on the joint surface, but the porosity was significantly reduced. When the silica content was 3.0%, Fig. 3(c) shows that the two-phase interface was obviously better than that of the eucalyptus/PVC wood plastic composite without silica, and the joint surface was closely connected. When the additional amount of silicon dioxide was 4.5%, Fig. 3(d) shows that the silicon dioxide was agglomerated, and the interface between two phases was more easily damaged. Therefore, when the silica content was 3.0%, the mechanical properties of eucalyptus/PVC wood plastic composites were most greatly improved.

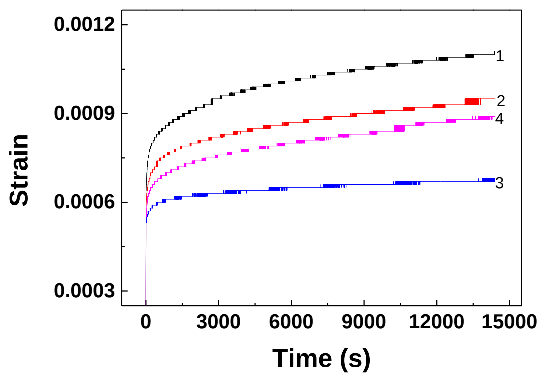


(a) (b) (c) (d)

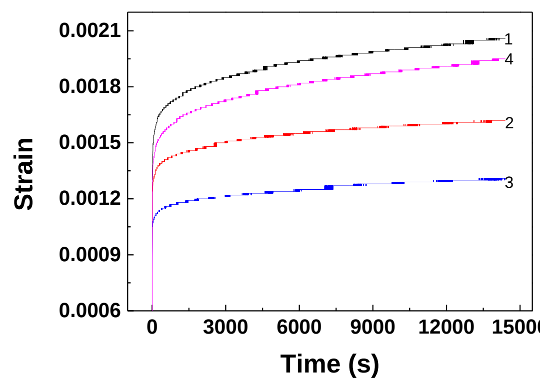
Fig. 3. Microstructure of cross section of eucalyptus/PVC wood-plastic composite: (a) Eucalyptus/PVC wood-plastic composite material, (b) 1.5%SiO_2-eucalyptus/PVC wood-plastic composite material, (c) 3.0%SiO_2-eucalyptus /PVC wood-plastic composite material, (d) 4.5%SiO_2-eucalyptus /PVC wood-plastic composite material

Effect of Silica Content on Creep Properties of Eucalyptus/PVC Wood Plastic Composites

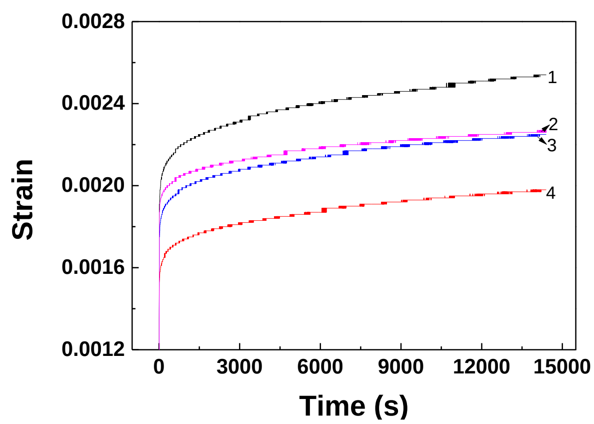
Figure 4 shows the influence of silicon dioxide content on creep performance under three stress conditions (4.46, 8.92, and 13.38 MPa), wherein the three stresses are 10%, 20%, and 30% of bending strength, respectively. The creep process underwent a transition from transient creep to constant creep. The strain value after adding silica was lower than that of the wood plastic composite without silica. The main reason was that the addition of silica improved the toughness of the wood plastic composite. Rigid silica can effectively inhibit the slippage and rearrangement of polymer chain segments, thus improving its creep resistance (Hao *et al.* 2021). With the increase of stress, the strain value of wood plastic composite with the same composition increased. Under the 30% stress level, the strain value of 3.0% SiO_2 eucalyptus/PVC wood plastic composite was 3.3 times that of the 10% stress level and 1.7 times that of the 20% stress level. These findings make it clear that stress affected the creep performance. A greater stress value resulted in a greater influence on creep (Du 2013).



(a) 4 h creep diagram of 10% stress



(b) 4 h creep diagram of 20% stress



(c) 4 h creep diagram of 30% stress

Fig. 4. Creep of eucalyptus dioxide /PVC wood-plastic composites with different contents under three stress states 1:Eucalyptus /PVC wood-plastic composite material,2:1.5%SiO_2-eucalyptus /PVC wood-plastic composite material,3:3.0%SiO_2-eucalyptus /PVC wood-plastic composite material,4:4.5%SiO_2-eucalyptus /PVC wood-plastic composite material

Effect of Silica Content on Thermal Properties of Eucalyptus/PVC Wood Plastic Composites

Thermal stability can effectively measure the degree of thermal degradation of wood-plastic composites. The pyrolysis curve of eucalyptus wood/PVC wood plastic composites with different silica content is shown Fig. 5. It can be seen from the figure that the pyrolysis process of eucalyptus wood/PVC wood plastic composites with different silica content had the same change trend: at the initial stage, about 5% weight loss was attributable to the evaporation of water in the wood plastic composites. The initial temperature of the first stage of pyrolysis was 260 to 270 °C, which is the decomposition of wood fiber in eucalyptus powder. The initial temperature of the second stage was 445 to 455 °C, which is the decomposition of PVC and the volatilization of hydrogen chloride. The addition of silicon dioxide increased the residual carbon amount of wood plastic composite, which can be attributed to the high thermal stability of silicon dioxide.

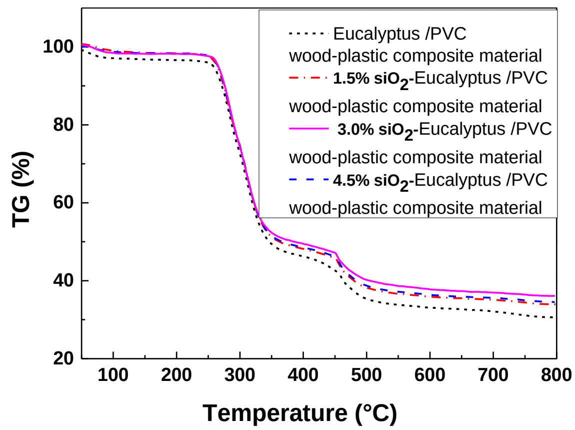


Fig. 5. Pyrolysis curve of eucalyptus /PVC wood-plastic composites

CONCLUSIONS

1. The peaks of Fourier transform infrared (FTIR) spectra were enhanced or weakened when SiO_2 was added to the composites. The FTIR spectra of composites showed both SiO_2 and base material peaks, which indicates that SiO_2 made a close bond between the wood fiber and plastic.
2. When the silicon dioxide content was 3.0%, the tensile strength, flexural strength, and impact strength of WPC reached the maximum values, which were 27.5 MPa, 48.8 MPa, and 4.18 kJ • m^{-2}, which represented increases by 12.6%, 9.4%, and 20.1%, respectively, compared with similar specimens prepared without silicon dioxide.
3. The addition of silica improved the interfacial bonding ability of eucalyptus /PVC wood-plastic composite material, and it reduced the phenomenon of holes left after the wood fiber was pulled out.
4. When the stress was 13.38 MPa, the strain value of 3.0% SiO_2 eucalyptus /PVC wood plastic composite was 3.3 times that of 4.46 MPa and 1.7 times that of 8.92 MPa，was 88.5% of the strain value without adding SiO_2. The pyrolysis process of eucalyptus/PVC wood plastic composites has a similar trend with different silica content.

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