

Effect of Acrylate-styrene-acrylonitrile on the Aging Properties of Eucalyptus/PVC Wood-plastic Composites

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With the widespread use of wood-plastic composites, they are inevitably affected by aging during transportation and outdoor use. In this research, in order to improve the aging resistance of WPC, acrylate-styrene-acrylonitrile (ASA) was used as modifier (10 parts, 15 parts, and 20 parts). The effects of the ASA modification on the aging behavior of eucalyptus/polyvinyl chloride (PVC) composites was studied with simulated xenon lamp artificial aging conditions. Artificial aging caused the physical and mechanical properties of the composites to deteriorate. After 960 h of aging, the aging resistance of the ASA-modified WPC was better than unmodified WPC and the sample with 15% ASA added had the best performance.

Keywords: Xenon lamp artificial aging; Wood-plastic composites; ASA; Physical and mechanical properties

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INTRODUCTION

Wood-plastic composite (WPC) is an environmentally friendly material (Dou *et al.* 2015). Because of its good physical properties, it is widely used in the furniture, construction, and automotive industries (Koohestani *et al.* 2017). Light, oxygen, heat, rain, microorganisms, and other environmental factors or human effects during processing, transportation, and use will cause WPC to age. This phenomenon is manifested as fading, weight loss, surface roughness, and mechanical property loss, which shorten the service time. There have been studies to combat the effects of aging on WPCs. For example, Muasher and Sain (2006) the addition of a UV absorber, which produces free radicals after UV irradiation to alleviate WPC surface color changes. Chaochanchaikul and Sombatsompop (2011) studied the aging properties of three different UV absorber-modified wood / polyvinyl chloride (PVC) composites and found that UV stabilizers can reduce the photodegradability of WPC, but it seems that there was no significant improvement in mechanical properties. Stark and Matuana (2003) artificially accelerated the aging of WPC containing pigment, showing that both inorganic and organic pigments can inhibit the polymer matrix photodegradation in WPC. Hou *et al.* (2015) added anti-aging agents to study the artificial accelerated ultraviolet aging of wheat straw / polypropylene (PP) wood-plastic composites. The results showed that anti-aging agents can effectively improve the performance of wheat straw / PP wood-plastic composites, in the mechanical, thermal, and anti-aging of WPC (Hou *et al.* 2013). Although anti-aging agents or pigments can delay the aging process of materials, these additives will migrate with an increase in aging time, so the long-term protection effect is not satisfactory. ASA has excellent weather resistance and can be compatible with PVC, acrylate, and

acrylonitrile units, which could change the aging decomposition process of PVC and plant fiber, thereby improving WPC anti-aging performance.

Acrylate-styrene-acrylonitrile (ASA) resin is a terpolymer composed of acrylonitrile-styrene-butyl acrylate. Poly-ASA has a unique core-shell structure, and the poly(butyl acrylate) (PBA) and poly(styrene-acrylonitrile) (SAN) serve as the rubber core and graft shell, respectively. It has excellent mechanical properties, aging resistance, environmental stress resistance, crack resistance to many detergents such as alcohol, and is very compatible with PVC.

Styrene makes ASA have excellent processing fluidity, which can effectively improve the processing properties of PVC (Du *et al.* 2012), and the acrylonitrile phase imparts corrosion and chemical resistance to ASA (Chao *et al.* 2015). Butyl acrylate is a saturated structure, that is, there is no C=C double bond, so it is not easily oxidized, cross-linked, degraded in terms of mechanical properties, and is resistant to color changes caused by oxygen, ultraviolet radiation, and heat (Han *et al.* 2009).

In this paper, ASA was selected as the modifier to improve the anti-aging performance of eucalyptus/PVC wood-plastic composite, and a xenon lamp accelerated aging test was adopted to study the aging properties of ASA / eucalyptus / PVC composite material with different contents (Sun *et al.* 2014; Zhang *et al.* 2016; Song *et al.* 2016). The ASA-modified eucalyptus/PVC WPC composites were characterized by mechanical properties, surface color changes, characteristic functional group changes, and tensile fracture surfaces analysis. Advantages and disadvantages of this method were comprehensively evaluated.

EXPERIMENTAL

Materials

SG-5 PVC power was purchased from Xinjiang Tianye Group Co., Ltd., Urumchi, China. Eucalyptus fiber powder, H-108 PE wax, and non-toxic 603 Ca/Zn composite stabilizers were purchased from Shanghai Wenhua Chemical Pigment Co., Ltd., Shanghai, China. Maleic anhydride grafted polyvinyl chloride was purchased from Dongguan Lok Wah Plastic Chemical Co., Ltd, Dongguan, China.

Sample Preparation

Eucalyptus fiber powder was initially crushed and subsequently ground to pass through a 100-mesh screen, and then dried at 90 °C for 12 h in a DHG-9140A electro-thermostatic drum-wind drying oven (Nanjing Dongmai Scientific Instrument Co., Ltd., Nanjing, China).

The maleic anhydride grafted PVC, eucalyptus powder, ASA, calcium-zinc stabilizer were uniformly mixed, stirred, and dried at 105 °C for 4 h, mixed with a certain proportion of PVC, and then used. A pulverizer was used to break the mixture into powder, extrude it, and cut it into a 100 mm × 10 mm × 7 mm sample. The sample was placed in a xenon lamp accelerated aging test chamber.

Table 1. Sample Composition

Sample ID	1	2	3	4
PVC	50	50	50	50
Eucalyptus fiber powder	50	50	50	50
ASA	0	10	15	20
Stabilizer	8	8	8	8
PE wax	5	5	5	5
Maleic anhydride (PVC)	3	3	3	3

Note: 8 wt% of the stabilizer, 5 wt% of the PE wax, and 3 wt% of the maleic anhydride grafted PVC were added with respect to the total PVC.

Characterization

Microscopic structure of composites

Analysis of the internal structure of the composites was carried out using a S-4800 scanning electron microscopy (SEM, Hitachi, Tokyo, Japan). Prior to the SEM analysis, the surfaces of the PVC composites were sprayed with gold using an E-1010 ion sputter coater.

A Nicolet iS10 Fourier-transform infrared (FTIR) spectrometer (Thermo Fisher Scientific Co., Ltd., Beijing, China) was used to observe the transformation of chemical structures in the ternary composites. The equipment was operated in the range of 400 to 4000 cm^{-1} with a resolution of 4 cm^{-1} , and each spectrum was gathered using 16 scans in absorbance mode. There were three operational steps to the procedure. The WPC degradation was studied by carbonyl index and lignin index, which was calculated using Eqs. 1 and 2,

$$\text{carbonyl index} = I_c/I_R \quad (1)$$

$$\text{lignin index} = I_l/I_R \quad (2)$$

where I_c and I_l are the intensity of the carbonyl and lignin absorption band (1700 to 1800 cm^{-1} ; 1593 to 1597 cm^{-1}), and I_R is the intensity of the reference band (2900 to 2950 cm^{-1}). The reference band was not affected by UV irradiation.

Physical and mechanical properties

The mechanical properties of composites were measured using a CMT6104 electronic universal testing machine (MTS Industrial Systems Co., Ltd, China). The tensile and flexural strength of ternary composites were measured respectively according to GB/T 1040.1 (2006) and GB/T 9341 (2008) (determination of plastic water absorption). First, samples were dried at 90 °C for 12 h to eliminate water, and weighed with an electronic balance. The samples were immersed in distilled water at 23 ± 1 °C for 24 h. The samples were removed, the surfaces were wiped using blotting paper, and the samples were weighed again.

Color change

The color of the samples was characterized using an HP-200 precise color meter (Shanghai Chinaspec Optoelectronics Technology Co., Ltd., Shanghai, China), which reported color coordinates in the CIE 1976 color space ($L^*a^*b^*$),

$$\Delta E = (\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2})^{\frac{1}{2}} \quad (3)$$

where ΔE , ΔL , Δa , and Δb represent the difference in color (E), color lightness (L^*), red to green (a^*), and yellow to blue (b^*). Five characterization measurements per sample were made and the average value was reported. Measurements were made at room temperature (25 ± 1 °C).

Accelerated xenon lamp artificial aging

The artificial weathering test was performed according to GB/T 16422.3 (2014) to evaluate the durability of the studied WPC. An Atlas Ci3000+ xenon lamp was used, which simulated the severe conditions for climatic aging. The light source used was a 4500 W water-cooled xenon lamp, which provided radiation at wavelengths of 290 to 800 nm. One cycle was conducted every 2 h, with 102 min of illumination time and 18 min of rain time without illumination. The relative humidity of the light period was 60 ± 5 %, and the rain period was 50 ± 5 %. The radiant intensity and total aging time of the sample were 550 W and 960 h respectively. After the samples were exposed to radiation, they were taken out to investigate the mechanical properties, surface morphology, and chemical composition.

RESULTS AND DISCUSSION

Physical and Mechanical Properties of Composites

The mechanical properties of the composites are shown in Fig. 1. The tensile strength, flexural strength, and impact strength show an obvious initial increase and then lower with increasing ASA content before aging. The tensile strength increased by 80.5%, 89.1%, and 85.2%, respectively. The flexural strength increased by 45.5%, 46.0%, and 57.3%, respectively. It was found that the addition of ASA was generally beneficial to enhance the mechanical properties of sample. This is because there are polar groups (ester bonds, cyano groups) in the molecular structure of ASA, and there is an electronic transition between ASA and PVC which can make ASA and PVC more compatible and making the force transfer better (Cherian *et al.* 2013; Jiang *et al.* 2017). Additionally, the core phase of the core/shell structure ASA are PBA (polybutyl acrylate) particles, which create a toughening effect (Krishnaiah *et al.* 2017; Oushabi *et al.* 2017), and the shell phase is a SAN copolymer grafted on the surface of the PBA latex, which helps with compatibility (Zhang *et al.* 2016). In conclusion, the addition of ASA enhances the mechanical properties of WPC.

After aging for 960 h, the mechanical properties of all materials decreased and the WPC retention rate after modification was higher than that of the control group. The flexural strength and the tensile strength retention rates of sample 1, 2, 3, and 4 were 81.9%, 86.8%, 93.2%, 88.9%, and 75.6%, 88.7%, 89.4%, and 84.0%, respectively. The results show that the addition of ASA can effectively enhance the anti-aging performance of eucalyptus / PVC wood-plastic composites. This is because ASA wraps PVC and eucalyptus fibers well, thereby reducing material degradation and aging. However, too much ASA may not be compatible with eucalyptus fiber, resulting in decreased mechanical properties.

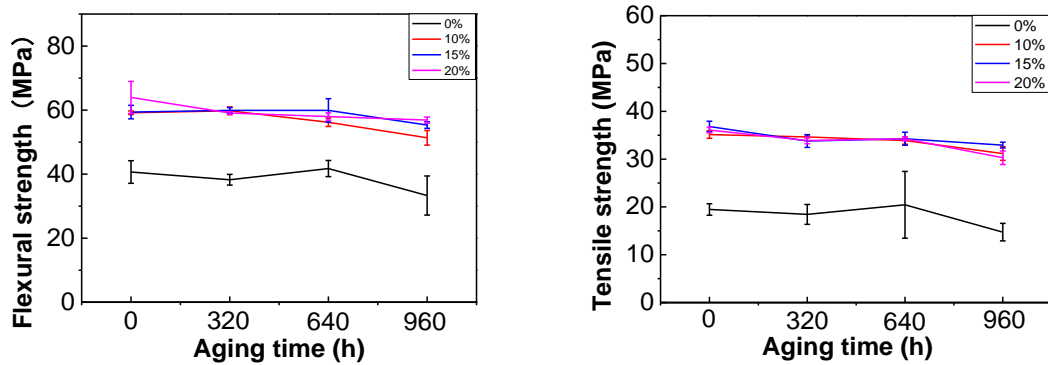


Fig. 1. Pre- and post-aging mechanical properties of eucalyptus/PVC wood/plastic composites with different content of ASA

Color change

The discoloration of the composites during the accelerated xenon aging experiments is shown in Fig. 2. The addition of ASA can reduce the chromatic aberration before and after aging of materials in different degrees under the action of strong light, and the chromatic aberration is reduced as the amount of ASA added increases (Hyvärinen *et al.* 2013).

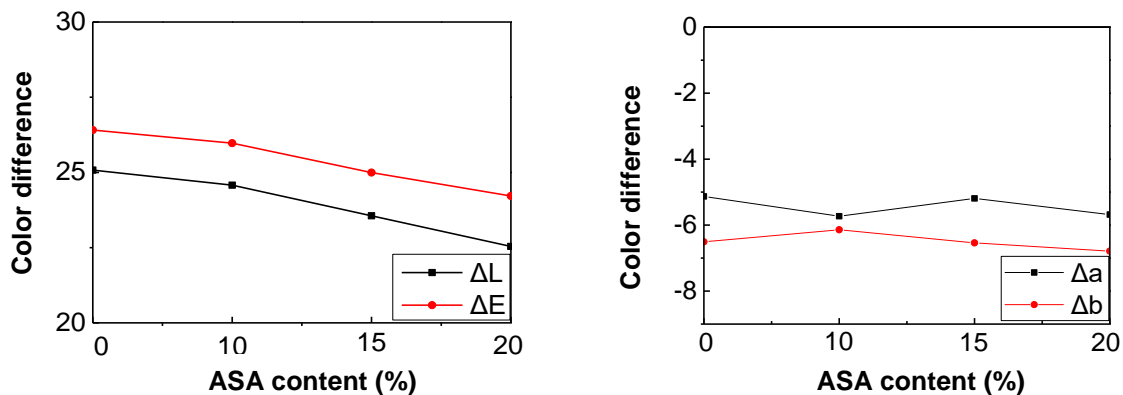


Fig. 2. Color change of WPC with different contents of ASA

Among the four samples, the ΔE value of Sample 2 was 19.5. Compared with Sample 1, the color difference ΔE and ΔL of Sample 2 decreased by 31.0% and 26.2%, respectively. In addition, Δa and Δb were greatly improved, and their absolute values were reduced by 15.6% and 25.1%, respectively. The color change of the sample surface is mainly caused by the photodegradation of lignin in the eucalyptus fiber. Photooxidation of lignin produces a p-benzoquinone chromophore group, and the p-benzoquinone structure produces hydroquinone, which has the ability of photobleach. However, ASA has compatibility with PVC, coating and protecting the eucalyptus fiber, thus inhibiting the damage of light to lignin and reducing the generation of hair color group, effectively slowing down the fading of WPC.

Fourier Transform Infrared (FTIR)

FTIR was used to further investigate the changes in the chemical functional groups (Fig. 3), which represented the composite sample before and after aging with different contents of ASA. As shown in Fig. 3, the stretching vibration peak of the carbonyl group is characterized by a wavenumber segment of 1700 to 1735 cm^{-1} . After aging, the peak was enhanced for three reasons. Firstly, the dehydrochlorination of PVC subsequently forms a carbonyl group, and secondly, the lignin contains an aromatic structure and a chromophoric group that absorb ultraviolet light and undergoes photodegradation to form a product containing a carboxyl group and a carbonyl group. Finally, a cellulose macromolecule reacts with oxygen to form cellulose peroxide and hydroperoxide, which decompose to form a ketone group and enhance the carbonyl peak (Vartanian *et al.* 2015). Therefore, the increase in the content of the carbonyl group reflects the degree of degradation of the wood-plastic composite material (Stark and Matuana 2007). The non-conjugated carbonyl group (1734 cm^{-1}) and the conjugated carbonyl group (1637 cm^{-1}) on the surface of the eucalyptus fiber increased. The lignin was destroyed (1508 cm^{-1} , 1462 cm^{-1}), on the guaiac wood-based aromatic ring. Partial C-O-H bond cleavage occurred (1240 cm^{-1}), cellulose C-H band (1425 cm^{-1}), C-O-C oxidative cross-linking vibration peak (1024 cm^{-1}) caused by bridging cross-linking of free radicals and oxygen after aging, and PVC C-H bending vibration (970 cm^{-1}), all indicating PVC degradation (Rosu *et al.* 2010).

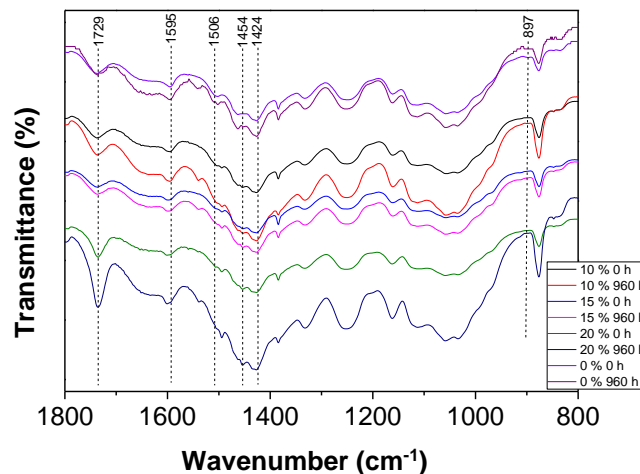


Fig. 3. FTIR of WPC with different ASA contents

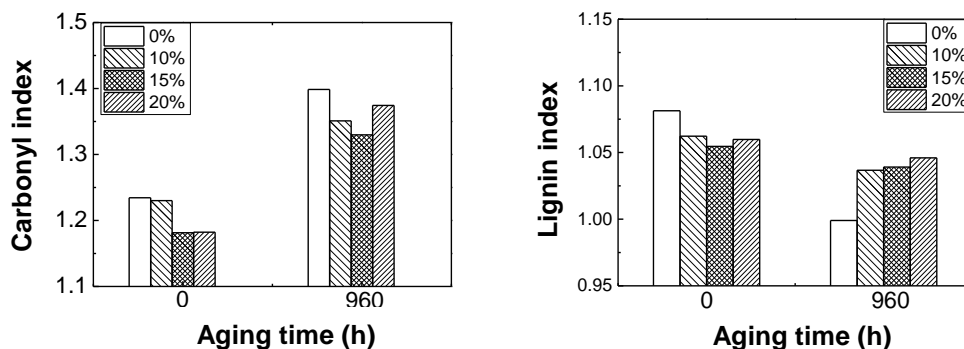


Fig. 4. Carbonyl index and lignin index of WPC with different ASA contents

Because the carbonyl and lignin content can reflect the degree of aging on the surface of the material, the carbonyl and lignin index of all samples were calculated. As shown in Fig. 4, the carbonyl index of the ASA wood-plastic composite was significantly increased after aging. Samples 1, 2, and the carbonyl indices of 3 and 4 increased by 13.29%, 6.22%, 3.86%, and 9.80%, respectively. The lignin index decreased by 7.61%, 2.46%, 1.07%, and 2.41%. The anti-aging performance of wood-plastic composites with ASA was improved, and the anti-aging performance of sample 3 with 10% ASA added was the best. This may be because the ASA is best wrapped in WPC in this sample, preventing oxidative decomposition of PVC and eucalyptus fibers.

Tensile Fracture Surfaces Analysis of Composites

Figure 5 shows that as the ASA content was changed, the tensile section became rough, and this was accompanied by a network structure, and the fiber is pulled out partially. On the one hand, the addition of PVC increases the plasticity of ASA and increases the strength of ASA. On the other hand, the addition of ASA exhibits a toughening effect, which causes the rubber particles in ASA to withstand stress and produce silver grain extension. The energy required for the fracture is increased, which is manifested by an increase in tensile strength and flexural strength (Vartanian *et al.* 2015).

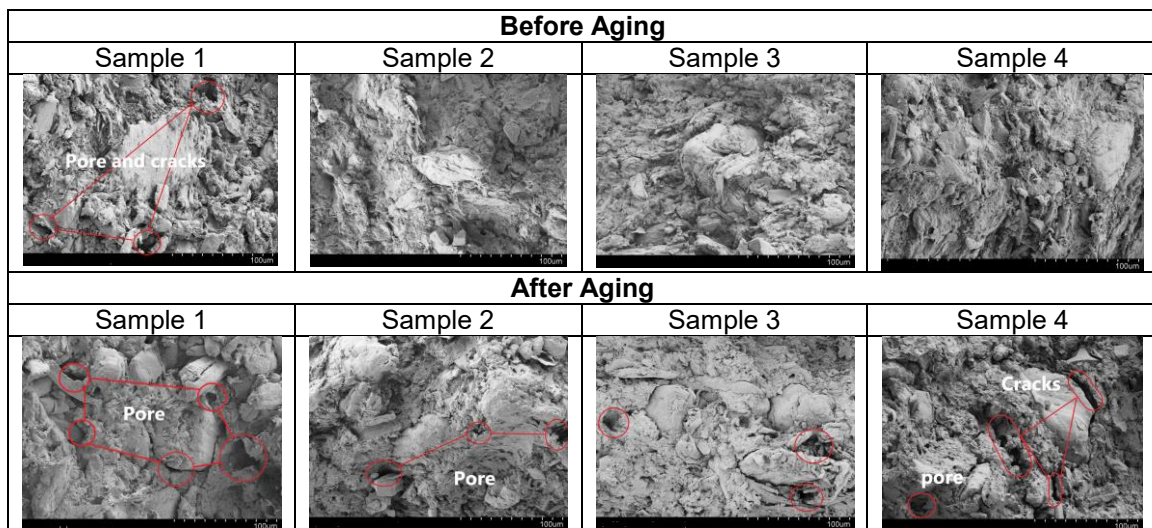


Fig. 5. Scanning electron micrograph of sample tensile section with different ASA contents

As shown in Fig. 5, in samples 2, 3, and 4 after aging there was only a small gap between the eucalyptus fiber and the matrix, the combination was relatively tight. Occasionally the fiber was pulled out without large holes. These observations show that ASA had certain influence on the internal bonding of composite materials after aging, and its anti-aging performance was excellent.

CONCLUSIONS

1. The physical and mechanical properties of the composites deteriorated when the PVC composite samples were subjected to 960 h of xenon lamp artificial aging time.
2. The ASA modified WPC exhibited a higher positive effect on the composite's physical and mechanical properties than unmodified WPC.
3. After 960 h of xenon lamp artificial aging, the aging resistance of the ASA modified WPC was better than unmodified WPC, and the sample with 15% ASA added had the best performance.
4. ASA modified WPC could not help to protect lignin and PVC degradation during long-term aging.

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