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THE EFFECTS OF EXPOXIDIZED SOYBEAN OIL ON THE MECHANICAL, WATER ABSORPTION THERMAL STABILITY AND MELTING PROCESSING PROPERTIES OF WOOD PLASTIC COMPOSITES

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ABSTRACT

To promote the environmentally friendly properties of wood plastic composites (WPC) fabricated via a polyvinyl chloride resin matrix, the effects of different amounts (0, 5, 15, 25, and 35 phr) of expoxidized soybean oil (ESO) on mechanical strengths, thermal stability, melting processing properties, and water absorption of the composite samples were studied. The results show that the tensile strength of WPC decreased. However, the elongation at break, water absorption and thickness swelling rates increased, especially for ESO addition amounts beyond 15 phr. The flexural strength and modulus of WPC followed an upward trend initially (at 5 phr ESO), then switching to a downward trend. The initial thermal stability at the first thermal decomposition stage and the melting processing temperature of the composites ewere effectively improved with the increase of ESO level. Compared to the samples without added ESO, the maximum thermal decomposition temperature (T_{max1} and T_{max2}) values of the composites increased by 31°C and 8°C, respectively, while the melting processing temperature of the composites significantly decreased by 24°C corresponding to an added level of 35 phr. In summary, the WPC samples with 5-15 phr ESO addition not only effectively retained their the mechanical strengths and water absorption stability, but also improved their the thermal stability and melting processing properties.

KEYWORDS: Epoxidized soybean oil, mechanical strength, thermal stability, melting processing temperature, water absorption.

INTRODUCTION

Currently novel sustainable products from renewable resources are desirable due to the ever growing concerns of global resource depletion and environmental pollution (Moshiul Alam et al. 2012, Azwa et al. 2013, Gurunathan et al. 2015). More attention has been focused on have been the development of natural fiber/thermoplastic biocomposites to reduce both the negative environmental impact of non-degradable synthetic plastics and the strong dependence on petroleum- based products (Sommerhuber et al. 2016, Zhou et al. 2016). As a member of the family of natural biocomposites, wood plastic composites (WPC) combine the advantages of wood and thermoplastics and have been rapidly developed, assuming an increasing global market share during recent years. WPC are extensively employed in interior and exterior applications, such as for decking, fencing, paneling, building, house wares, automobile components, and packaging (Zini and Scandola 2011, Xue et al. 2014).

In contrast to polyolefins based WPC, such as polyethylene (PE) and polypropylene (PP), polyvinylchloride (PVC) based WPC has a remarkable increase from 2002 to 2010 with the growth rate of 200 % due to its unique decoration, durability, and natural flame retardant properties (Jiang and Kamdem 2004, Muller et al. 2013, Xu et al. 2013). This suggests that PVC-based WPC is playing a more important role within the whole family of WPC. However, the existence of a repetitive vinyl chloride unit of head-to-tail arrangement with the various amounts of chain-branching and the low degree of crystallinity in PVC molecular chains leads to the strong secondary valence forces, which limit the mobility of molecular chains (Matuana 1997). This results in a pronounced macroscopic brittleness of PVC.

The most common plasticized polymer is PVC, its processing consumption is over 80 % of plasticizer production (Vieira et al. 2011, Vieira et al. 2014). In order to effectively improve the flexibility of PVC molecular chains and the flowing property in heat processing, plasticizers are usually incorporated into the formulation of PVC. Generally the dioctyl phthalate (DOP) and diisononyl phthalate (DINP) are widely used in PVC products. However, strict limitations have been triggered due to their high toxicity to human health and potential carcinogenicity (Chiellini et al. 2011, Lithner et al. 2011, Hines et al. 2012, Foghmoes et al. 2016). Furthermore, petroleum shortages and environmental pollution have encouraged extensive researches to develop the new chemical products based on renewable resources (Peng et al. 2014, Chen et al. 2016). As a result, some bio-based "green" plasticizers have already been reported to have a similar function as chemically synthesized plasticizers, such as soybean oil (Dong et al. 2014), linseed oil (Fernandez et al. 2015), sunflower oil (Chavan and Gogate 2014), fatty acid esters (Fenollar et al. 2009), glycerol esters (Lavorgna et al. 2010), polyol ester and polyester (Demertzis et al. 1990, Jia et al. 2015).

Soybean is a renewable resources with huge availability in China. Epoxidized soybean oil (ESO), as a vegetable oil), has been used as bio-plasticizer in the polymer and rubber industries and shows significant plasticizing effects due to the inherent advantages of low cost, biodegradation, and non-toxicity (Bueno-Ferrer et al. 2010, Yang et al. 2014, Zhang et al. 2010). Furthermore it has also been reported that ESO could effectively enhance the thermal stability of PVC products, involving a reaction between the epoxide ring of ESO with hydrogen chloride, generated during PVC degradation, thus restoring the labile chlorine atoms back into polymer chains. Until now, here no information has been published about the effects of ESO as bio-plasticizer on the mechanical, melting processing properties, thermal stability and water absorption capacity of the compound systems of ESO, wood flour, and PVC.

In the present study, we investigated the effects of ESO on the mechanical, thermal, and melting processing properties of PVC- based WPC using an electronic universal mechanical test instrument, thermogravimetric analysis (TG), differential scanning calorimetry (DSC), and water absorption testing.

MATERIALS AND METHODS

Materials

PVC resins (DG-800) with an average degree of polymerization of 800 and a density of 1.35 $g \cdot cm^{-3}$ were obtained from Tianjin Dagu Co. Ltd., China. Wood flour (WF) with a particle distribution of 80 to 100 mesh was obtained from Xishuangbanna Huakun Biological Technology Co., Ltd, China. ESO was purchased from Guangzhou Wen Jia Chemical Co., Ltd, China, It had an epoxy value above 6.0, and an iodine value below 5.

Preparation of composites

The wood flour (WF) particles were dried in an oven prior to use. Firstly the WF, PVC resin, ESO and other additives were blended at 110 °C and 1600 rpm for 15 min in a high-speed mixer (SHR-10A, Zhangjiagang, China). The main formulation of the composites is listed in Tab. 1. Then the mixture was extruded in the shape of a rod via a co-rotating twin-screw extruder (JIEENTE SHJ-20, Nanjing, China) with a temperature range of 145-175°C and an average rotation speed of 40 rpm. Subsequently, the granules were transferred to a conical twin-screw extruder (JINWEI SJZ-65, Suzhou, China) to produce sheet samples of 5 mm thickness. The processing temperature during extrusion was set at the range of 110-170°C from hopper to die zone. The rotation speeds of the twin screw and single screw were 20 rpm and 8 rpm, respectively.

Tab. 1: The main formulation of the WPC with various addition amounts of ESO.

Groups	PVC (phr)	WF (phr)	ESO (phr)	Other additives (phr)
WF/PVC/ESO-0	100	40	0	6
WF/PVC/ESO-5	100	40	5	6
WF/PVC/ESO-15	100	40	15	6
WF/PVC/ESO-25	100	40	25	6
WF/PVC/ESO-35	100	40	35	6

Mechanical properties testing

The flexural and tensile properties of composites with untreated and modified WF/CS were tested with a mechanical instrument (CMT5504, Shenzhen, China) corresponding to ASTM D 790-2010 and ASTM D 638-2010. The former involved a three-point bending test with a crosshead speed and a span length of 2 $mm \cdot min^{-1}$ and 80 mm, respectively. The latter was conducted at a tensile speed of 2 $mm \cdot min^{-1}$. Both tests were performed in five replicates to obtain an average value, calculating each standard deviation.

Thermogravimetry (TG) analysis

The thermal stability of the composites was analyzed with a thermogravimetric instrument (TG 209-F1, Netzsch, Germany) to obtain data about weight loss during heating. About 10 mg specimens were heated from 30 to 800°C under nitrogen atmosphere at a heating rate of $10°C \cdot min^{-1}$.

Differential scanning calorimetry (DSC) analysis

DSC measurements were conducted on a differential scanning calorimetry instrument (DSC 204-F1, Netzsch, Germany) to analyze the melting temperature of composites. Approximately 10 mg samples were sealed in an aluminum pan and placed in a heating chamber under a blowing and sweeping nitrogen atmosphere (25 ml·min^{-1}). To erase the thermal history, the samples were heated from 40°C to 300°C at 20°C·min^{-1}, then cooled to 40°C at 10°C·min^{-1} and reheated to 300°C at 5 °C·min^{-1}.

Water absorption test

The water absorption behavior of HDPE/RSS composites was investigated referring to ASTM D570-1995. Specimens with dimensions of 20 × 20 × 5 mm (length × width × thickness) were completely immersed into distilled water at 25 ± 2°C for 23 days. The weights of samples were measured every two days. Each sample was slightly wiped using filter paper to remove excess water before weighing, then immediately weighed and immersed in water again. Based on the weight percentage changes of samples, the water absorption rates of samples were calculated according to Eq. 1, the final thickness swelling rates of samples were calculated using Eq. 2.

$$WA = \frac{m_t - m_0}{m_0} \times 100\% \quad (1)$$

where: WA - water absorption rate (%),
m_0 - weight of the samples before testing (g),
m_t - weight of the samples at certain time (g).

$$TS = \frac{h_t - h_0}{h_0} \times 100\% \quad (2)$$

where: TS - final thickness swelling rate (%),
h_0 - thickness of the samples before testing (mm),
h_t - thickness of the samples after testing (mm).

RESULTS AND DISCUSSION

Mechanical properties analysis

The mechanical properties of composite samples are very important for their practical applications and are highly depended on the miscibility and compatibility between components. The tensile and flexural properties of PVC-based WPC with various addition amounts of ESO are shown in Fig. 1.

As for the tensile properties, it can be seen from Fig. 1a that the tensile strength values of the samples were lower after ESO addition; However, higher elongations at break were observed than the control group (WF/PVC/ESO-0). The variation trend became more pronounced when the addition level of ESO was beyond 15 phr. The tensile strengths of WF/PVC/ESO-25 and WF/PVC/ESO-35 groups decreased to 15.61 MPa and 11.28 MPa from 31.13 MPa of the control group, respectively. On the other hand, the elongation at break of the WF/PVC/ESO-35 group featured a maximum increase of 43.72%. The results can be ascribed to the fact that the molecular of the plasticizer could partly be inserted in the middle of the polymer molecular chains with increasing, intermolecular distance, thus resulting in easier mobility between the molecular chains. Therefore the flexibility of the samples was improved in their macro-performance.

Furthermore, the excess ESO may form an interference layer to affect the interfacial bonding between wood flour and PVC resin, resulting in a significant decrease of tensile strength.

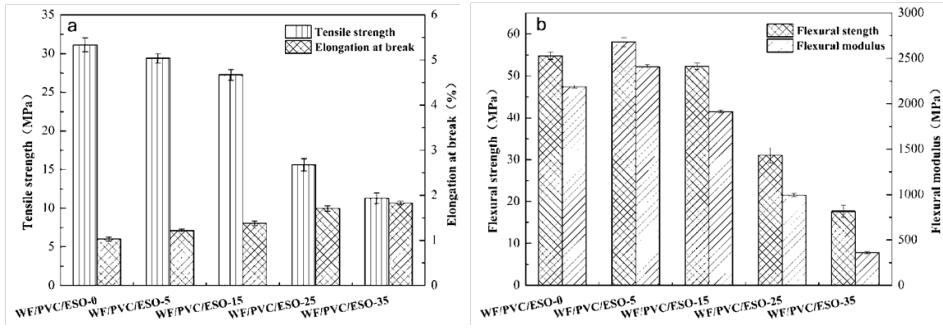

Fig. 1: Mechanical properties of PVC- based WPC with various addition amounts of ESO: (a) flexural strength and modulus, (b) tensile strength and elongation at break.

Fig. 1b shows the flexural properties of PVC- based WPC with various addition amounts of ESO.The flexural strength and modulus initially increased to 58.08 and 2409 MPa from 54.77 and 2187 MPa, respectively, in response to increasing additional ESO amounts from 0 to 5 phr. After the added level reached at 15 phr, both specific flexural indexes showed decreasing trends. Specifically, the flexural strength and modulus of the composites decreased by 4.51, 43.34, 67.73 % and 12.53, 54.60 and 83.54 %, respectively, corresponding to an ESO addition of 15, 25 and 35 phr. When a small amount of plasticizer was added into the compound system, the activity of the macromolecule chain of the PVC resin was strengthened, leading to the production of a microcrystal effect, thus slightly increasing the strength value of the composite material. In summary, an additional amount of ESO ranging from 5-15 phr could effectively maintain the mechanical strengths of PVC-based WPC.

TG-DTG analysis

Fig. 2a shows thermogravimetric graphs of PVC- based WPC with various addition amounts of ESO. It can be observed from Fig. 2a and Tab. 2 that two major thermal decomposition stages corresponded to a temperature range of 220-400°C and 400-500°C for all specimens.

Major pyrolysis of semi-cellulose, cellulose as well and partial decomposition of lignin as well as the volatilization of hydrogen chloride (HCl) occurred during the first stage. Specifically, the amorphous structures of branches were removed from the main hemicelluloses chains. Long chains of glucose units were broken, and aromatic ring within lignin appeared to be cross-linked. The second stage mainly involved thermal cracking of carbonaceous conjugated polyene sequences in PVC (Levchik and Weil 2005).

Fig. 2a and the data of Tab. 2 shows that the weight loss rate (52.51 %) of the composite samples without ESO were lower than the samples added 5, 15, 25 and 35 phr ESO, corresponding to the weight loss rates of 52.68, 53.51, 54.77 and 56.13 %, respectively, at the first stage of thermal decomposition. This demonstrated that the ESO was mainly decomposed at this stage. Moreover, it is observed from Fig. 2b and Tab. 3 that the T_{max1} and T_{max2} (maximum decomposition temperature (T_{max}), i.e. the temperature that corresponds to the maximum mass loss rate) of the composite samples gradually increased with increasing ESO addition, especially for T_{max1}. The specific temperature value increased by 9, 19, 28 and 31 °C corresponding to an ESO addition of 5, 15, 25 and 35 phr, compared the specific temperature obtained without ESO

addition. This indicates that a reaction between the epoxide ring from ESO and the hydrogen chloride that was generated during PVC degradation, restored the labile chlorine atoms back into the polymer chains, which slowed the continuous decomposition of PVC.

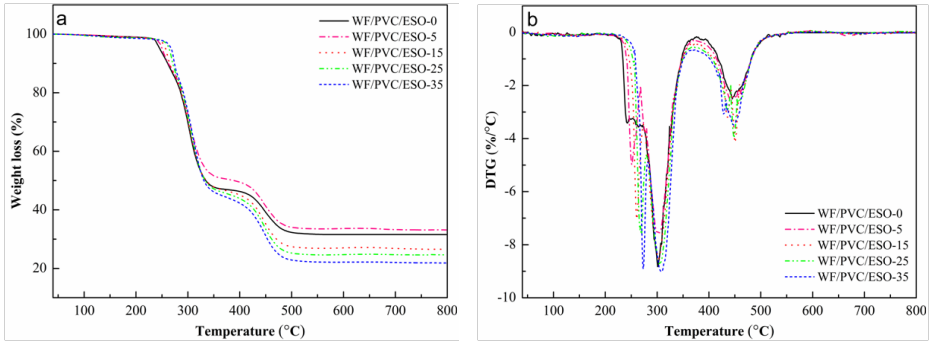

Fig. 2: TG and DTG curves of PVC- based WPC with various addition amounts of ESO.

During the second main thermal decomposition stage, opposite trends were found for the weight loss rate and the maximum decomposition temperature (T_{max3} and T_{max4}) of composites with various ESO addition amounts due to the occurrence of thermal decomposition of ESO at the first stage. Furthermore, the T_{max4} could also be observed in Fig. 2b and Tab. 3 when the added amount of ESO was beyond 15 phr; however, T_{max4} followed a decreasing trend as the added amount of ESO increased that incorporating the ESO into the formulation can effectively promote the thermal stability of PVC- based WPC during the first main thermal decomposition process.

Tab. 2: Thermal degradation data of PVC- based WPC with various addition amounts of ESO.

Groups	First stage of thermal decomposition (220-400°C)	First stage of thermal decomposition (400-550°C)	Residues (%)
WF/PVC/ESO-0	52.51	14.65	31.55
WF/PVC/ESO-5	52.68	16.48	30.84
WF/PVC/ESO-15	53.51	18.23	26.54
WF/PVC/ESO-25	54.77	19.24	24.65
WF/PVC/ESO-35	56.13	20.12	21.85

Tab. 3: The maximum decomposition temperature values of PVC- based WPC with various addition amounts of ESO.

Groups	T_{max1}	T_{max2}	T_{max3}	T_{max4}
WF/PVC/ESO-0	242	301	445	—
WF/PVC/ESO-5	251	301	442	—
WF/PVC/ESO-15	261	302	436	450
WF/PVC/ESO-25	270	305	435	448
WF/PVC/ESO-35	273	309	428	447

DSC analysis

The DSC curves of PVC-based WPC with various addition amounts of ESO are illustrated in Fig. 3. As seen in the Fig. 3, the different group composite samples produced similar graphs. Two marked endothermic peaks were observed for all samples with an increasing temperature from 40 to 300°C. It was found that the first endothermic peak could shift to the lower value when the addition amount of ESO increased from 0 to 35 phr. The variation of the first endothermic peak was not apparent when the addition amount of ESO was at 5 or 15 phr. But the endothermic peak temperature significantly decreased when the addition level of ESO reached at 25 or 35 phr, specifically the first endothermic peak temperature decreased to 206°C and 201°C from 225°C, respectively.

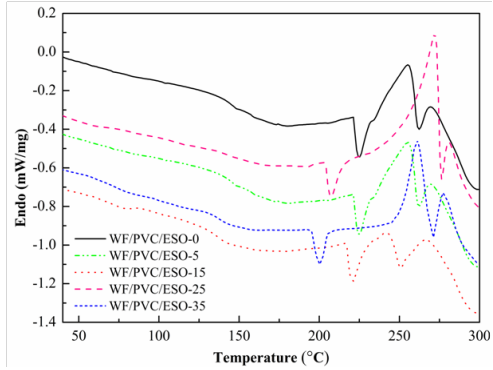

Fig. 3: DSC curves of PVC -based WPC with various addition amounts of ESO.

In addition, it can be noticed that the distance between two endothermic peaks of the samples added by 5 or 15 phr was almost the identical or even shorter than the sample without ESO. It can be concluded that ESO effectively promoted the flexibility and melting processing property of the entire compound system. Furthermore the ESO even possibly enhanced the interfacial bonding at the suitable addition range of 5-15 phr, which was consistent with the presented analysis.

Water absorption analysis

The water absorption and thickness swelling rates of the different WPC groups are plotted in Fig. 4. As can be seen in Fig. 4a , the water absorption rates of all the WPC groups with various addition amounts of ESO generally showed a rapid ascending tendency in the initial stage (within five days), increasing from 0 to 1.18, 1.61, 1.40, 3.55 and 4.05 %, corresponding to an addition amount of ESO of 0, 5, 15, 25 and 35 phr, respectively. The maximum water absorption rates of the specimens with added 25 phr and 35 phr ESO (6.13 and 7.71 %) were much higher than these samples with 0, 5 phr and 15 phr ESO (2.49, 2.90, and 3.31 %), respectively. Additionally both curves of the ESO-5 and ESO-15 groups crossed each other, which is likely due to the result of interface improvement of WPC at a suitable addition level of ESO. However the excess ESO led to the decrease of water resistance of WPC. These results matched the analyses of mechanical and melting processing properties mentioned above.

A similar variation trend was found for the thickness swelling rates of the WPC as illustrated in Fig. 4b. A higher added ESO amount led to a higher value of thickness swelling rate. The average maximum thickness swelling rate for the samples of the ESO-35 group was increased by 149 % compared to the control group (WF/PVC/ESO-0).

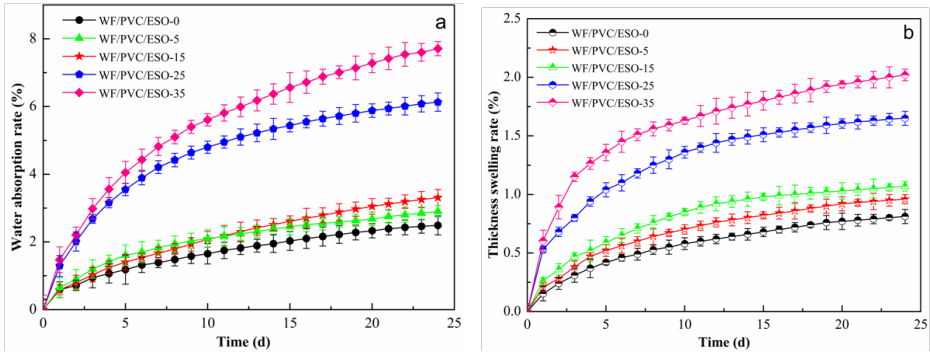

Fig. 4: Water absorption and thickness swelling rates of PVC- based WPC with various addition amounts of ESO.

The comparison discussion of results

Bueno-Ferrer et al. (2010) indicated that the initial degradation temperature value ($T_{95\%}$) increased with the addition of higher amounts of ESO to pure PVC resin, which was particularly pronounced for plastisol with 50 wt% ESO, where $T_{95\%}$ showed an increase of 9°C when compared to the 40 wt% counterpart. Our results demonstrated that T_{max1} and T_{max2} (maximum decomposition temperature (T_{max}), which is the temperature that corresponds to the maximum mass loss rate) of WPC samples gradually increased with increasing additional amount of ESO. This was particularly true for T_{max1}, where the specific temperature value increased by 31°C corresponding to an additional ESO amount of 35 phr and compared to the sample without any additional ESO. This confirmed the presence of ESO plasticizer to result in an increase in the thermal stability of PVC-based composites.

In addition, Zhang et al. (2010) found that the combination of plasticization and crosslinking effects derived from ESO resulted in good retention in mechanical strength for the plasticized composite materials as compared to those without 10 wt % of ESO additives. Using ESO additives in the materials also significantly increased the hydrophobicity of the composite films (Zhang et al. 2010). Our results show that the flexural strength and modulus of WPC increased at an additional level of 5 phr ESO; however, the hydrophobicity of WPC samples markedly decreased with higher water absorption and thickness swelling rates when the additional amount of ESO was above 15 phr. This suggests that ESO could exert a positive effect on the improvement of mechanical strengths of materials at the optimum additional level; however, hydrophobicity results remain inconclusive.

CONCLUSIONS

ESO with the advantages of low cost, biodegradation, non-toxicity could be considered as an available bio-plasticizer for the production of PVC-based WPC. The tensile strength of WPC decreased but the elongation at break, water absorption and thickness swelling rates of WPC all increased, especially when the addition amount of ESO was above 15 phr. The flexural strength and modulus of WPC followed an initially upward trend (at 5 phr ESO), followed by a downward trend. The thermal stability at the first main thermal decomposition stage and the melting processing temperature of composites were effectively promoted with the increase of

the addition level of ESO. Compared to samples without adding ESO, the maximum thermal decomposition temperature (T_{max1} and T_{max2}) values of the composites increased by 31°C and 8°C, respectively; the melting processing temperature of the composites significantly decreased by 24°C corresponding to the addition level of 35 phr. In summary, the WPC samples that received an additional 5-15 phr ESO could not only effectively maintain their mechanical strength and water absorption stability, but the addition also improved their thermal stability and melting processing property. Furthermore, the cost of production and equipment wear could be reduced.

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