Effects of Bio-based Plasticizers on Mechanical and Thermal Properties of PVC/Wood Flour Composites

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Poly(vinyl chloride)/wood flour (WPVC) composites with dioctyl phthalate (DOP), dibutyl phthalate (DBP), cardanol acetate (CA), or epoxy fatty acid methyl ester (EFAME) were prepared using twin-screw extrusion. The effects of plasticizers on the mechanical, dynamic mechanical, and melt rheological properties of composites and the thermal migration of plasticizers were characterized. The results demonstrated that WPVC/DBP and WPVC/EFAME composites had better elongation at break; however, composites with bio-based plasticizers exhibited significantly higher impact strength. The morphology indicated that the compatibility between CA and WPVC was poor, while the surface of the composites showed good plasticity with the addition of DBP or EFAME. The PVC matrix with a plasticizer of higher molecular weight exhibited a higher glass transition temperature (T_g). The dynamic rheological test showed that WPVC/EFAME composites had the lowest storage modulus, loss modulus, and complex viscosity, but EFAME migrated more easily from composites than other plasticizers.

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INTRODUCTION

Poly(vinyl chloride) (PVC) has among the highest market shares of polymeric material, and has been used extensively in industrial applications such as packaging materials, toys, and construction materials (Fenollar *et al.* 2009b). To improve its flexibility and processability, PVC is usually blended with plasticizers. The most common plasticizers used on the industrial scale are based on phthalates, such as dioctyl phthalate (DOP) and dibutyl phthalate (DBP) (Starnes and Ge 2004; Sejidov *et al.* 2005; Navarro *et al.* 2010). However, many traditional plasticizers show undesirable migration out of substrates, causing significant concerns about toxicity. Therefore, the use of these plasticizers in relation to the migration of phthalates has been questioned (Wang and Storm 2005). To solve this serious problem, alternative plasticizers with low migration and toxicity have been widely researched in recent decades. These alternative plasticizers could be useful for applications that are especially sensitive to migration and subsequent toxicity. Recently, there has been increasing interest in the use of bio-based plasticizers used in PVC. Cardanol and its derivatives are considered to be attractive precursors because they originate from renewable bio-resources (Tyman *et al.* 1984). Cardanol is obtained through the distillation of cashew nut shell liquid, a by-product of the cashew industry. Cardanol is a sustainable, inexpensive, and widely-available natural resource

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(Mohapatra and Nando 2013). The chemical and physical properties of cardanol are very similar to those of DOP. Typically, esterification of the hydroxyl group of cardanol is necessary in order to obtain a good miscibility between cardanol derivatives and the base PVC (Calò *et al.* 2011). Greco *et al.* (2010) obtained cardanol acetate by the esterification of the cardanol hydroxyl group and used it as a plasticizer for PVC. The modified PVC showed mechanical and thermal properties similar to those of soft PVC with diethylhexyl phthalate (DEHP) as a plasticizer. Other derivatives of cardanol have also been proven as efficient plasticizers for PVC (Neuse and Van Schalkwyk 1977; Varma *et al.* 1987). Epoxy fatty acid methyl ester is another promising new alternative plasticizer because of its low toxicity and partial biodegradability, and because it is mainly produced by modifying natural products (Fenollar *et al.* 2009a), such as rubber seed oil, soybean oil (Karmalm *et al.* 2009), and sunflower oil (Bouchareb and Benaniba 2008). Faria-Machado *et al.* (2013) synthesized epoxy-modified bio-based plasticizers *via* the esterification of rice fatty acids, and the plasticizers showed high plasticizing performance and incorporation into the PVC polymeric matrixes.

Wood plastic composites (WPCs) are manufactured by dispersing wood fibers or wood flour (WF) into molten plastics to form composite materials (Fang *et al.* 2013). There has been a considerable growth in demand (200% from 2002 to 2010) for PVC-based WPCs (WPVC) because of their inherent advantages, such as high stiffness, resistance to biological and solvent attacks, flame retardance and low cost, as well as favorable paintability (Khalil *et al.* 2013; Kositchaiyong *et al.* 2013). The WPVC are important in the family of WPCs and play an important role in various research fields, as well as in practical applications. The processability of WPVC is usually poor because of the use of high-content rigid wood flour and the limited flowability of PVC during processing. PVC is sensitive to thermal degradation during processing and use at high temperature, and hydrochloric acid is eliminated by a free radical reaction. A few strategies have been developed to solve processability problems, including the introduction of additives, such as plasticizers, lubricants, and paraffin. In order to obtain flexible products with good mechanical properties, adding plasticizers has been a common method in industrial production (Faria-Machado *et al.* 2013). Plasticized PVC and its composites are widely used in automobile parts and household materials because of their excellent physical properties.

In this study, in order to improve the processability of WPVC composites, two kinds of bio-based plasticizers, cardanol acetate (CA) and epoxy fatty acid methyl ester (EFAME), were used to plasticize PVC/wood flour (WPVC) composites. WPVC composites and composites with DOP or DBP were also prepared as references. Mechanical testing, scanning electron microscopy (SEM), dynamical mechanical analysis (DMA), dynamic rheological testing, and migration measurements were used to investigate the effect of bio-based plasticizers on properties of the composites.

EXPERIMENTAL

Materials

The PVC, SG-5 with a *K* (molecular weight of the polymer) value of 66 was provided by the Yibin Tianyuan Group Co., Ltd. (Yibin, China). Wood flour with a particle size of 0.13 to 0.34 mm and an aspect ratio of 3.01 to 10.94 was supplied by Jiajing Composite Materials Co., Ltd. (Nanjing, China). Calcium stearate was purchased

from Kemiou Chemical Reagent Co., Ltd. (Tianjin, China), DOP was obtained from Sinopharm Chemical Reagent Co., Ltd., and DBP was purchased from West Long Chemical Co., Ltd. (Gansu, China). CA was synthesized by esterificating cardanol with acetic anhydride. EFAME was prepared via epoxidating rubber seed oil by hydrogen peroxide. Both CA and EFAME were provided by our laboratory. The chemical structures of DOP and DBP, and the typical structures of CA and EFAME are shown in Fig. 1.
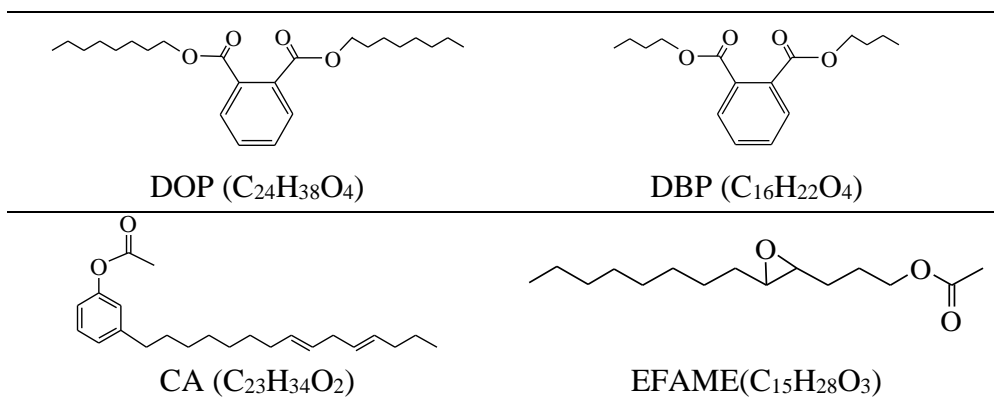
DOP ($C_{24}H_{38}O_4$)   DBP ($C_{16}H_{22}O_4$)

CA ($C_{23}H_{34}O_2$)   EFAME($C_{15}H_{28}O_3$)

Fig. 1. Chemical structures of the plasticizers

Methods

Composite preparation

        The WF and PVC were dried for 12 h at 80 °C before composite fabrication. A constant ratio of PVC: WF: plasticizers: calcium stearate (49:32:16:3 in weight) was maintained in each formulation. The PVC, plasticizers, and calcium stearate were first mixed in a SHENMA SHR-5A high-speed mixer (China) at 1500 rpm for 20 s, and then WF was added to blend for 5 min. After that, the mixture was introduced into a twin-screw extruder MiniLab II (HAKKE, Thermo Scientific; USA). Screw speed was maintained at 100 rpm and the temperature was 165 °C. The extrudates were cooled in air and granulated into particles. The un-plasticized composites (WPVC) were prepared as reference. Testing specimens were prepared by injection molding *via* MiniJet II (HAKKE, Thermo Scientific) with an injection temperature of 170 °C and an injection pressure of 550 bars.

Mechanical testing

        Tensile tests and flexural tests were performed on a universal testing machine (Newsans, China) according to GB/T 1040.1 (2006) and GB/T 9341 (2008), respectively. The tensile test samples were in dog-bone form according to the ASTM D638 (2007). The tensile testing region of a specimen was 3.18 mm thick, 3.18 mm wide, and 7.62 mm long. The flexural testing samples had an oblong form; the width was 10 mm, the thickness was 4 mm, and the length was 80 mm. Five replicates were tested for each sample. The crosshead speed was 10 mm/min, and the temperature was 25 °C.
        The izod impact tests were carried out on a XJJY-5 impact testing machine (Chende, China) according to GB/T1040.1 (2006). The dimensions of the samples were 80 mm ×10 mm ×4 mm. Five replicates were tested for each sample.

Scanning electron microscopy

The tensile fracture surfaces were coated with a thin gold layer using a high-vacuum gold sputter. Micrographs were recorded by an S-3400N scanning electron microscope (Hitachi, Japan) under conventional secondary electron imaging conditions at an accelerating voltage of 15 kV.

Dynamic mechanical analysis measurement

Dynamic mechanical properties were measured with a Q800 dynamic mechanical thermal analyzer (TA Instruments, USA) at a heating speed of 3 °C/min in a range of −100 to 120 °C. The dimensions of the samples were 80 mm×10 mm×4 mm. All samples were measured in the dual cantilever clamp mode, the frequency was 1 Hz and the amplitude was 15 μm.

Rheological test

The rheological behaviors of composites were investigated using a Mars II Rotational rheometer (HAKKE, Thermo Scientific). A 25-mm parallel plate arrangement was adopted with a temperature of 190 °C. The specimens were transformed into circular form with 25 mm diameter and 1.80 mm thickness by MiniJet II machine. A frequency range of 0.01 to 15 Hz and a strain of 3% were supplied during the measurement.

Plasticizer thermal migration test

Three pieces of samples were placed in an 85 °C oven for a specified time after being weighed; then, the samples (circular form with 25 mm diameter and 1.80 mm thickness) were taken out and cooled in a dryer to room-temperature. The samples were weighed after being scrubbed by ethanol and filter paper, and the weight loss was calculated according to Eq. 1,

$$M\ (\%) = \frac{M_0 - M_1}{M_0} \times 100\%$$ (1)

where M_0 is the initial weight of the samples (g), M_1 is the weight of samples after being exposed in the oven (g), and M is the weight loss rate (%).

RESULTS AND DISCUSSION

Mechanical Properties of Composites

The tensile strength and elongation at the break of composites are shown in Fig. 2. It can be seen that the tensile strength of plasticized composites was lower than that of unplasticized composites (WPVC), which was due to the plasticization. Composites with DOP or DBP had similar tensile strengths at 16.7 MPa; however, WPVC/CA and WPVC/EFAME composites had lower tensile strengths, *i.e.*, 12.6 MPa and 11 MPa, respectively. There was a long nonpolar alkyl chain ($-C_{15}H_{27}$) and carbon-carbon double bonds in the CA molecule, and accordingly the compatibility between CA and PVC/WF was probably poor, as PVC and WF are polar materials. Limited compatibility led to weak interfacial adhesion and low tensile strength, which was confirmed by SEM characterization. The EFAME plasticizer penetrated into the PVC matrix more easily during blending because of its smaller molecular dimension, and the inner lubrication reduced the tensile strength of the composites.
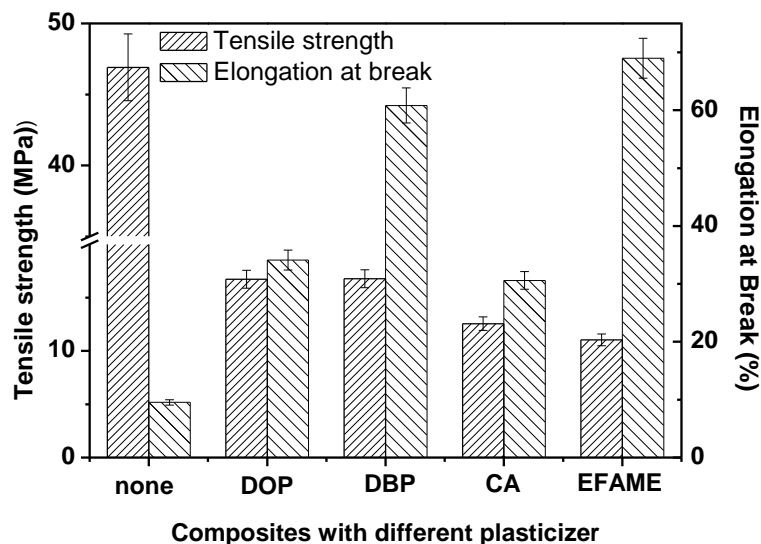
Fig. 2. Tensile properties of the composites, composites without plasticizer was signed as WPVC composites.

Composites with DBP or EFAME had higher elongation at break (61% and 69%, respectively), while WPVC/DOP and WPVC/CA composites had elongations of 34% and 31%, respectively. The elongation of plasticized composites was much higher than that of WPVC composites, which was 9.53%. The elongation at break was associated with the motion of the PVC matrix's molecular chain under tensile stress. The plasticizers with smaller molecular structures penetrated easier through the PVC matrix, resulting in a partial relaxation of the PVC chains. Therefore, the addition of DBP and EFAME plasticizers, whose molecular structures are smaller than DOP and CA, led to a considerable increase in elongation at the break.

Representative tensile stress-strain curves of the composites are shown in Fig. 3. WPVC composites showed the lowest stress, and it was associated with its brittle fracture.
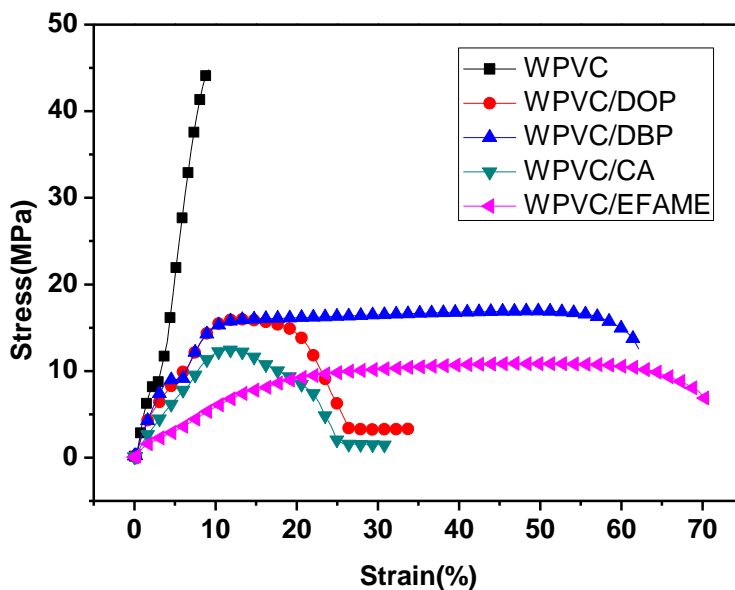

Fig. 3. Stress-strain curves of composites

Composites with CA exhibited low stress and strain, which resulted from the poor compatibility between CA and PVC/WF. The better elongation of WPVC/DBP and WPVC/EFAME composites discussed above can be seen in the stress-strain curves.

Figure 4 demonstrates the influence of plasticizers on the flexural strength and flexural modulus of composites. The flexural strength and modulus decreased with the addition of plasticizers, and the flexural strength and modulus of WPVC/DBP composites was close to that of WPVC/DOP composites. WPVC/EFAME composites showed the lowest flexural strength and modulus (12.39 MPa and 565 MPa, respectively). Reduced flexural strength could correspond to the inner lubrication brought by EFAME. The penetration of the plasticizer through the PVC matrix caused a partial relaxation of the PVC chains via the reduction of the intermolecular force of attraction (Yu *et al*. 2014). Limited compatibility between CA and PVC/WF, as well as phase separation, compromised stress transfer and resulted in stress concentration. Therefore, the flexural strength of composites plasticized with EFAME presented a low value.
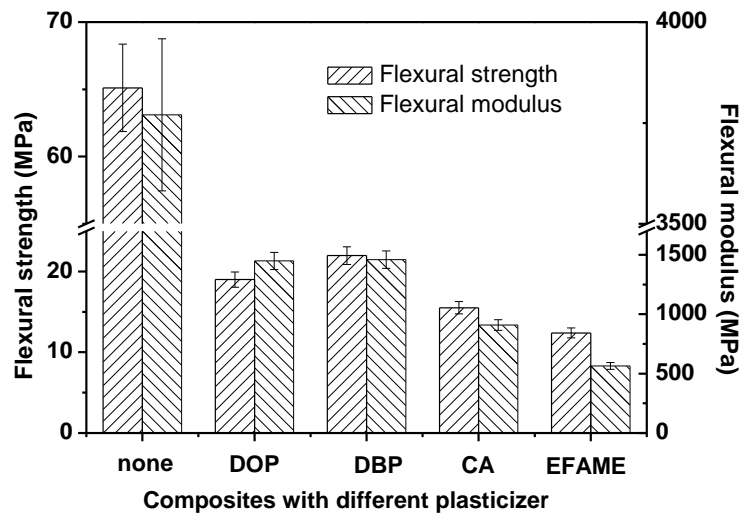

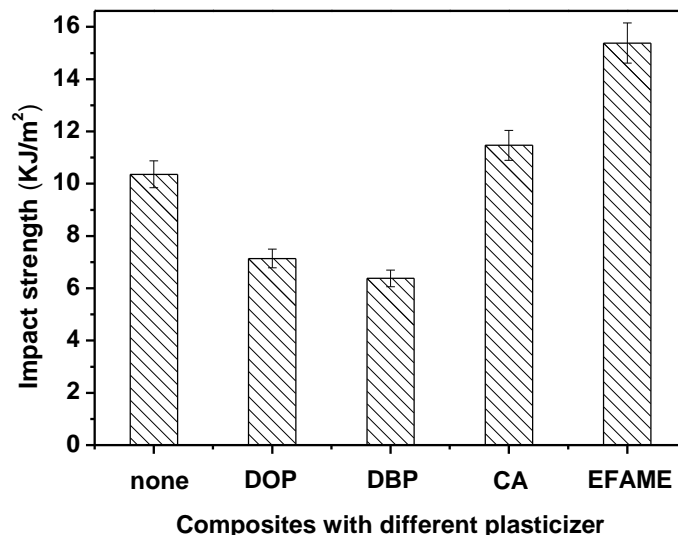**Fig. 4.** The flexural properties of composites

Fig. 5. The impact strength of composites

The effect of different plasticizers on impact strength is shown in Fig. 5. Composites with DOP and DBP had impact strengths of 7.1 kJ/m^2 and 6.4 kJ/m^2, which were lower than that of WPVC composites at 10.4 kJ/m^2. However, WPVC/CA and WPVC/EFAME composites had impact strengths of 11.5 kJ/m^2 and 15.4 kJ/m^2, respectively. The high impact strength of composites plasticized with CA was primarily attributable to carbon-carbon double bonds, as well as CA's long alkyl chain. Because of the easier relaxation and the lubrication of the PVC matrix in WPVC/EFAME composites, the impact energy could disperse more quickly into the composites, which led to a higher impact strength of than other composites.

Morphology

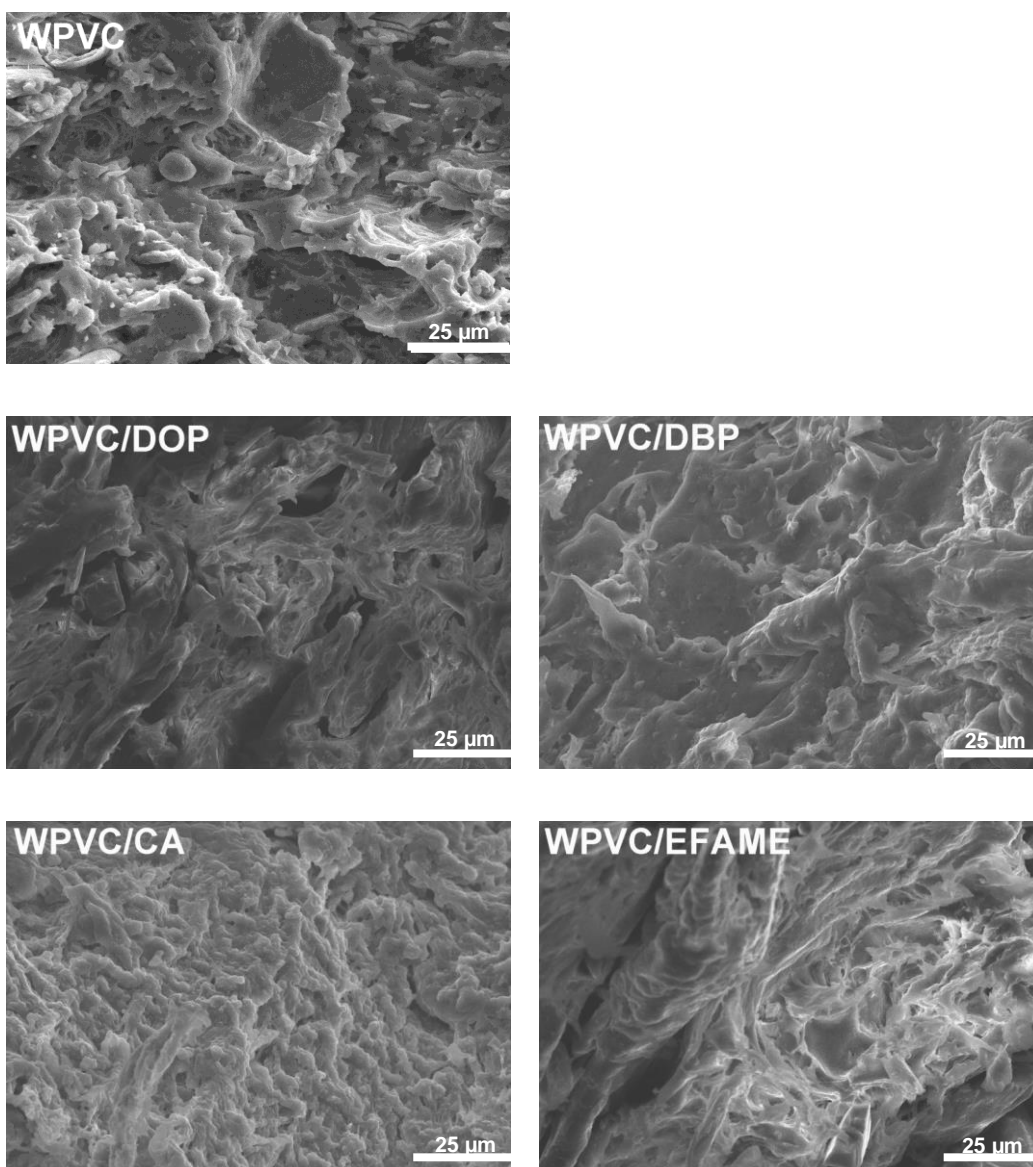Figure 6 shows SEM micrographs of the fractured surfaces of different composites.

Fig. 6. SEM micrographs of composites

There were gaps and cavities in all images of the fracture surface, which were associated with the pulling out of WF in the PVC matrix (Zhao *et al.* 2006). WPVC composites exhibited brittle failure behaviors as the fracture showed little sign of plastic deformation. The surface of WPVC/DBP composites was more homogeneous and showed a better plasticizing effect than those of WPVC/DOP composites, and resulted in higher elongation at the break. However, the surface of WPVC/CA composites showed a rough interface and poor plasticization, which were caused by poor compatibility between CA and WPVC composites. This incompatibility resulted in phase separation; thus the fracture surface exhibited lower toughness than that of composites with DBP or DOP. The surface of WPVC/DBP or WPVC/EFAME composites showed obvious signs of plastic fracture and tough characteristics, and this phenomenon was consistent with the improved elongation at break of the WPVC/DBP and WPVC/EFAME composites.

Dynamic Mechanical Properties of Composites

Dynamic mechanical analysis (DMA) was used to study the interactions and movements of molecules. Storage modulus and tan delta curves are shown in Fig. 7.
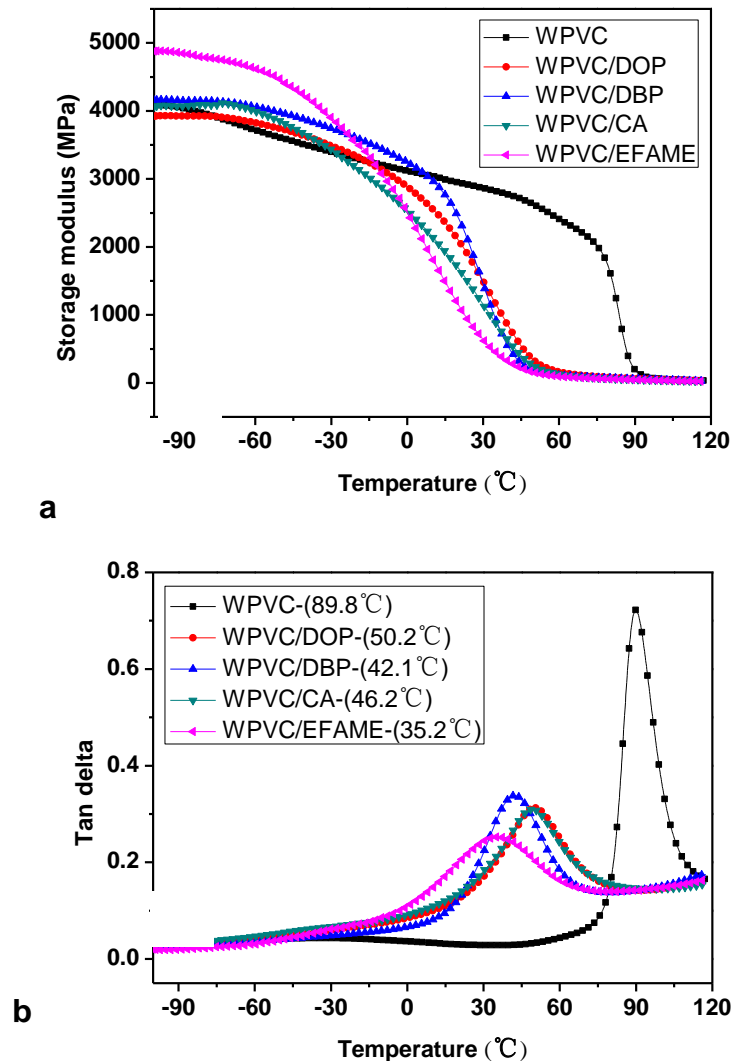

Fig. 7. DMA curves of composites: (a) storage modulus; (b) tan delta

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All composites displayed a similar trend: Storage modulus decreased from −100 to 120 °C, with a sharp transition in the curves (Fig. 7a). The storage modulus of the PVC matrix was maintained at a high level below −50 °C because of the frozen molecular chain. The frozen segmental structure began to relax gradually with increasing temperature (Sahoo *et al*. 2013), and the storage modulus decreased sharply after -30 °C. It could be seen that WPVC composites showed a higher heat distortion temperature (HDT), range from 70 to 90 °C, while the HDT of the plasticized composites located in the 0 to 45 °C region. The motion of the molecular chain became more flexibility because of the addition of plasticizers, and the lubrication reduced the force between the PVC molecules (Wilkes and Summers 2005). Above this temperature, the storage modulus of all composites decreased to zero, indicating the transformation of the composites to the liquid state.

The tan delta curves of the composites are depicted in Fig. 7b. Almost all plasticized composites displayed one peak in the curves, which was related to the T_g of the PVC matrix. However, the PVC matrix in WPVC composites showed the T_g at 89.8 °C, which was much higher than that of others. WPVC composites exhibited the highest intensity of tan delta, whereas that of the WPVC/EFAME composites was the lowest. The T_g of PVC matrix decreased with the addition of plasticizers, and the PVC matrix in composites with plasticizers of larger molecular weight had higher T_g. The T_g of the PVC matrix in WPVC/DOP composites was 50.2 °C, compared with that of WPVC/EFAME, at 35.2 °C, as shown in Fig. 7b. The lowest T_g suggested that the PVC chains slide more easily, and the interactions between the PVC molecules reduced because of the plasticizing effect provided by the smaller molecular plasticizer.

Rheology of Composites

Rheological tests are sensitive to differences in molecule chain entanglements or chain structure, such as small differences in chain length, branching, or networking. These factors can cause large variations in flow behavior (Lee *et al.* 2007). In polymer processing, a better understanding of the rheological properties of various polymers or polymer composites is important. Rheological behavior can provide information on the internal structure of materials for industrial applications (Li *et al.* 2003; Du *et al.* 2013). The dependence of storage modulus and loss modulus on frequency can measure the relative motion of molecules in the bulk and can also give important information about the flow behavior of melts (Okay and Oppermann 2007). Figures 8 and 9 show the plots of storage modulus (G') and loss modulus (G'') *versus* the frequency of composites. The G' and G'' both exhibited a monotonic change with frequency and increased with increasing frequency. WPVC composites showed the highest G' and G'' while WPVC/EFAME composites exhibited the lowest G' and G''. Because of the small molecular structure and formula, EFAME could fill the free volume between PVC chains and the gaps between PVC and WF more easily. On the other hand, the epoxy groups in EFAME could form hydrogen bonds with the hydroxyl on the surface of WF; therefore, the rigid WF could slip more easily into the PVC matrix. EFAME had a plasticizing effect and lubricated molecular movement, and the movement of PVC became easier than that of other composites. The improved movement of PVC molecular chains plasticized by DOP, DBP, and CA were not as obvious, and their G' and G'' were higher than WPVC/EFAME composites because their molecular weight was higher than that of EFAME.
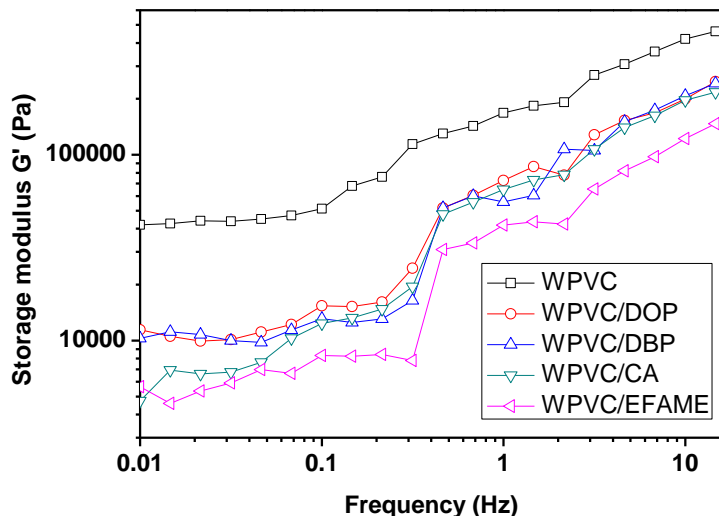
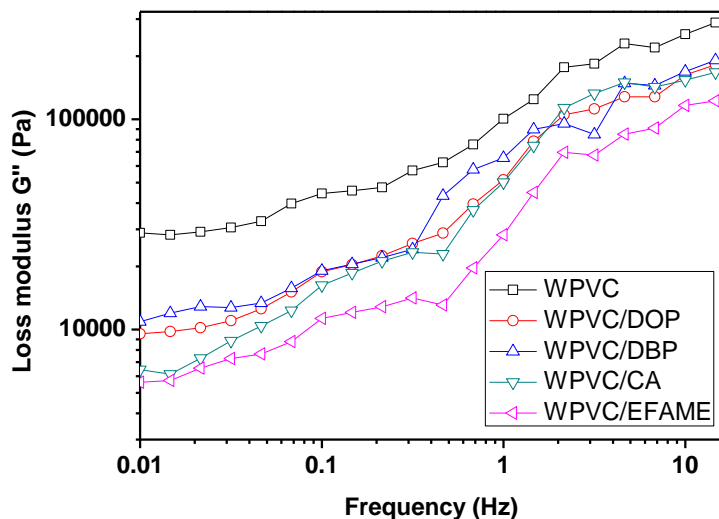**Fig. 8.** Relationship between storage modulus (G') and frequency

Fig. 9. Relationship between loss modulus (G'') and frequency

Figure 10 illustrates complex viscosity (η^*) curves as a function of frequency. The η^* of composites decreased with frequency and exhibited a shear thinning phenomenon, which suggested the melt of the composites was non-Newtonian fluid. WPVC composites showed the highest η^*, which was mainly corresponded to its poor processability. Composites with DOP, DBP, or CA exhibited a similar η^*; however, WPVC/EFAME composites showed the lowest η^* than other composites. This was similar to the changes in G' and G'' discussed earlier. This demonstrated that the lubricating effect between PVC and WF improved by EFAME was more significant than the other three plasticizers. The plasticizer molecules penetrated into PVC matrix during addition, and the lubrication reduced the friction between PVC and WF. Further, the epoxy might react with the charged hydrogen via hydrogen bonding, resulting better plasticization between EFAME and PVC. The lower complex viscosity of composites melt resulted in better processability, and it was benefit to the process and molding of the composites.
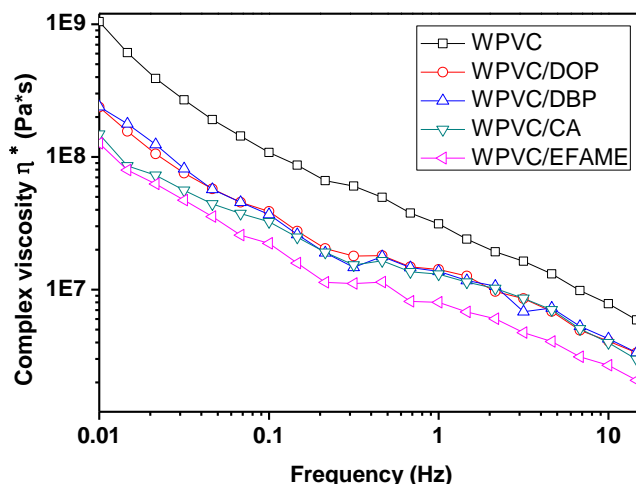
Fig. 10. Relationship between complex viscosity (η*) and frequency

Migration of Plasticizers

Figure 11 shows the thermal migration of plasticizers in composites at 85 °C. Weight loss increased with time, composites with EFAME showed the highest weight loss, and the weight loss of composites plasticized with DBP was slightly lower. However, composites plasticized with DOP and CA exhibited the lowest weight loss. After 1360 min, the weight loss of composites with EFAME was 2.95%, while that of composites plasticized with CA was 1.06%. The plasticizers in composites would migrate to the surface of the composites and volatilize into the air under heat, and it would be more difficult for plasticizers with a bigger molecular structure to migrate. An increase in plasticizer molecular weight tended to hinder migration (Coltro *et al.* 2014); therefore, the weight loss of composites with DBP or EFAME were higher than that of composites plasticized with DOP or CA. Marcilla *et al.* studied the migration of PVC plasticizers and found that plasticizers with the highest molecular weights tended to migrate more slowly than those of lower molecular weight (Marcilla *et al.* 2008).
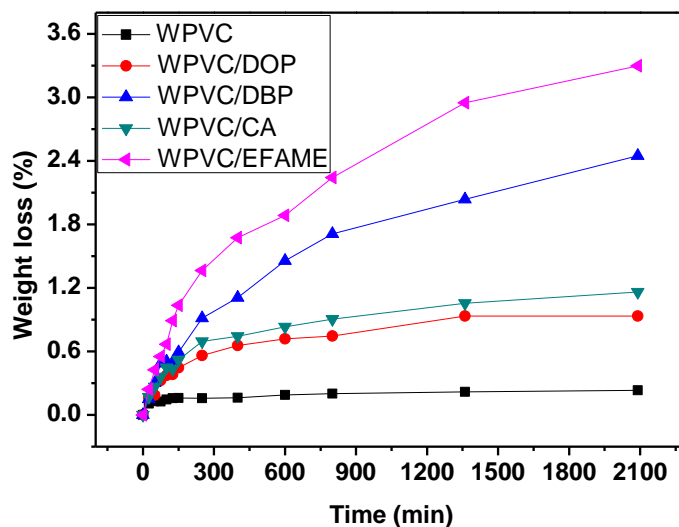

Fig. 11. Weight loss of composites at 85 °C

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CONCLUSIONS

1. The poly(vinyl chloride)/wood flour (WPVC) composites with dioctyl phthalate (WPVC/DOP) and with dibutyl phthalate (WPVC/DBP) exhibited better tensile strength, while composites plasticized with DBP or epoxy fatty acid methyl ester (EFAME) showed higher elongation at the break because of their lower molecular weight and smaller structure. However, composites with bio-based plasticizers exhibited better impact strength. The SEM results indicate the poor compatibility between cardanol acetate (CA) and WPVC composites, and the surface of composites plasticized with DBP or EFAME showed more signs of better fracture.

2. The plasticized composites showed much lower heat distorted temperature and T_g of PVC matrix than WPVC composites. However, the PVC matrix with plasticizers of higher molecular weight exhibited higher T_g. The dynamic rheological test revealed that all plasticized composites exhibited lower G', G'', and η^* than WPVC composites. Composites plasticized with EFAME showed the lowest G', G'', and η^*, which were associated with the better inner lubrication. The results indicated that the use of EFAME as same amount as DOP and DBP could provide better fluidity and improve the processability of WPVC composites.

3. The thermal migration of plasticizers demonstrated that the plasticizer with the highest molecular weight and larger structure had the most difficulty migrating under heat, and the smaller plasticizer migrated more readily from the composites.

ACKNOWLEDGEMENTS

REFERENCES CITED

ASTM D638. (2007). "Standard test method for tensile properties of plastics," *ASTM International*, West Conshohocken, PA.

Bouchareb, B., and Benaniba, M. T. (2008). "Effects of epoxidized sunflower oil on the mechanical and dynamical analysis of the plasticized poly (vinyl chloride)," *J. Appl. Polym. Sci*. 107(6), 3442-3450. DOI: 10.1002/app.27458

Calò, E., Greco, A., and Maffezzoli, A. (2011). "Effects of diffusion of a naturally-derived plasticizer from soft PVC," *Polym. Degrad. Stab*. 96(5), 784-789. DOI: 10.1016/j.polymdegradstab.2011.02.012

Coltro, L., Pitta, J. B., da Costa, P. A., Fávaro Perez, M. Â., de Araújo, V. A., and Rodrigues, R. (2014). "Migration of conventional and new plasticizers from PVC films into food simulants: A comparative study," *Food Control*. 44, 118-129. DOI: 10.1016/j.foodcont.2014.03.058

Du, Y., Gao, J., Yang, J., and Liu, X. (2013). "Dynamic rheological behavior and mechanical properties of PVC/CPE/MAP-POSS nanocomposites," *J. Appl. Polym. Sci*. 129(1), 174-180. DOI: 10.1002/app.38719

Fang, Y., Wang, Q., Guo, C., Song, Y., and Cooper, P. A. (2013). "Effect of zinc borate and wood flour on thermal degradation and fire retardancy of polyvinyl chloride (PVC) composites," *J. Anal. Appl. Pyrol*. 100, 230-236. DOI: 10.1016/j.jaap.2012.12.028

Faria-Machado, A. F., da Silva, M. A., Vieira, M. G. A., and Beppu, M. M. (2013). "Epoxidation of modified natural plasticizer obtained from rice fatty acids and application on polyvinylchloride films," *J. Appl. Polym. Sci*. 127(5), 3543-3549. DOI: 10.1002/app.37671

Fenollar, O., García, D., Sánchez, L., López, J., and Balart, R. (2009a). "Optimization of the curing conditions of PVC plastisols based on the use of an epoxidized fatty acid ester plasticizer," *Eur. Polym. J*. 45(9), 2674-2684. DOI: 10.1016/j.eurpolymj.2009.05.029

Fenollar, O., Sanchez-Nacher, L., Garcia-Sanoguera, D., López, J., and Balart, R. (2009b). "The effect of the curing time and temperature on final properties of flexible PVC with an epoxidized fatty acid ester as natural-based plasticizer," *J. Mater. Sci*. 44(14), 3702-3711. DOI: 10.1007/s10853-009-3495-7

GB/T 1040.1. (2006). "Plastics - Determination of tensile properties - Part 1: General principles," Chinese National Standardization Management Committee, China.

GB/T 9341. (2008). "Plastics - Determination of flexural properties," Chinese National Standardization Management Committee, China.

Greco, A., Brunetti, D., Renna, G., Mele, G., and Maffezzoli, A. (2010). "Plasticizer for poly (vinyl chloride) from cardanol as a renewable resource material," *Polym. Degrad. Stab*. 95(11), 2169-2174. DOI: 10.1016/j.polymdegradstab.2010.06.001

Karmalm, P., Hjertberg, T., Jansson, A., and Dahl, R. (2009). "Thermal stability of poly (vinyl chloride) with epoxidised soybean oil as primary plasticizer," *Polym. Degrad. Stab*. 94(12), 2275-2281. DOI: 10.1016/j.polymdegradstab.2009.07.019

Khalil, H. A., Tehrani, M., Davoudpour, Y., Bhat, A., Jawaid, M., and Hassan, A. (2013). "Natural fiber reinforced poly (vinyl chloride) composites: A review," *J. Reinf. Plast. Comp*. 32(5), 330-356. DOI: 10.1177/0731684412458553

Kositchaiyong, A., Rosarpitak, V., Prapagdee, B., and Sombatsompop, N. (2013). "Molecular characterizations, mechanical properties and anti-algal activities for PVC and wood/PVC composites containing urea-and triazine-based algaecides," *Compos. Part B-Eng*. 53, 25-35. DOI: 10.1016/j.compositesb.2013.04.036

Lee, S. H., Cho, E., Jeon, S. H., and Youn, J. R. (2007). "Rheological and electrical properties of polypropylene composites containing functionalized multi-walled carbon nanotubes and compatibilizers," *Carbon*. 45(14), 2810-2822. DOI: 10.1016/j.carbon.2007.08.042

Li, J., Zhou, C., Wang, G., and Zhao, D. (2003). "Study on rheological behavior of polypropylene/clay nanocomposites," *J. Appl. Polym. Sci*. 89(13), 3609-3617. DOI: 10.1002/app.12643

Marcilla, A., García, S., and Garcia-Quesada, J. (2008). "Migrability of PVC plasticizers," *Polym. Test*. 27(2), 221-233. DOI: 10.1016/j.polymertesting.2007.10.007

Mohapatra, S., and Nando, G. B. (2013). "Chemical modification of natural rubber in the latex stage by grafting cardanol, a waste from the cashew industry and a renewable resource," *Ind. Eng. Chem. Res.* 52(17), 5951-5957. DOI: 10.1021/ie400195v

Navarro, R., Pérez Perrino, M., Gómez Tardajos, M., and Reinecke, H. (2010). "Phthalate plasticizers covalently bound to PVC: Plasticization with suppressed migration," *Macromolecules* 43(5), 2377-2381. DOI: 10.1021/ma902740t

Neuse, E. W., and Van Schalkwyk, J. D. (1977). "Cardanol derivatives as PVC plasticizers. II. Plasticizer evaluation," *J. Appl. Polym. Sci.* 21(11), 3023-3033. DOI: 10.1002/app.1977.070211116

Okay, O., and Oppermann, W. (2007). "Polyacrylamide-clay nanocomposite hydrogels: Rheological and light scattering characterization," *Macromolecules.* 40(9), 3378-3387. DOI: 10.1021/ma062929v

Sahoo, S., Misra, M., and Mohanty, A. K. (2013). "Effect of compatibilizer and fillers on the properties of injection molded lignin-based hybrid green composites," *J. Appl. Polym. Sci.* 127(5), 4110-4121. DOI: 10.1002/app.37667

Sejidov, F. T., Mansoori, Y., and Goodarzi, N. (2005). "Esterification reaction using solid heterogeneous acid catalysts under solvent-less condition," *J. Mol. Catal. A-Chem.* 240(1), 186-190. DOI: 10.1016/j.molcata.2005.06.048

Starnes, W. H., and Ge, X. (2004). "Mechanism of autocatalysis in the thermal dehydrochlorination of poly(vinyl chloride)," *Macromolecules* 37(2), 352-359. DOI: 10.1021/ma0352835

Tyman, J., Tychopoulos, V., and Chan, P. (1984). "Long-chain phenols: XXV. Quantitative analysis of natural cashew nut-shell liquid (*Anacardium occidentale*) by high-performance liquid chromatography," *J. Chromatogr.* 303(1), 137-150. DOI: 10.1016/S0021-9673(01)96053-4

Varma, I., Dhara, S., Varma, M., and Biddapa, T. (1987). "Cashewnut shell liquid: Characterization and studies of PVC degradation in solution," *Angew. Makromol. Chem.* 154(1), 67-86. DOI: 10.1002/apmc.1987.051540105

Wang, Q., and Storm, B. K. (2005). "Separation and analysis of low molecular weight plasticizers in poly (vinyl chloride) tubes," *Polym. Test.* 24(3), 290-300. DOI: 10.1016/j.polymertesting.2004.12.002

Wilkes, C. E., and Summers, J. W. (2005). "PVC handbook," Munich: Hanser.

Yu, Z., Zhou, J., Zhang, J., Huang, K., Cao, Fei., and Wei, P. (2014). "Evaluating effects of biobased 2, 5-furandicarboxylate esters as plasticizers on the thermal and mechanical properties of poly (vinyl chloride)," *J. Appl. Polym. Sci.* 131(20), 40938-40947 DOI: 10.1002/app.40938

Zhao, Y., Wang, K., Zhu, F., Xue, P., and Jia, M. (2006). "Properties of poly (vinyl chloride)/wood flour/montmorillonite composites: Effects of coupling agents and layered silicate," *Polym. Degrad. Stab.* 91(12), 2874-2883. DOI: 10.1016/j.polymdegradstab.2006.09.001