Rheological Behaviors of Polymer Impregnated Maple Veneer

Chunfeng Li,^a Qingwen Wang,^b Mingli Liu,^{a,*} and Haigang Wang^b

The objective of this study was to determine rheological behaviors of maple veneer plastic composite (MVPC) prepared by full cell preparation technology through the use of a rotational rheometer. The results showed that at 25 to 105 °C, the storage modulus *G*' and loss modulus *G*'' of the MVPC were apparently higher than that of the control. In the range 105 to 210 °C, the storage modulus *G*' of the MVPC was basically the same as that of the control, and the loss modulus G'' was slightly higher than that of the control. At 105 °C, the Tan δ curve of the MVPC had an obvious peak, which indicated that the glass transition temperature (*T*g) of the MVPC was about 105 °C. The rheological behavior of the MVPC with different impregnation weight gain rates showed that the MVPC with a 55% impregnation weight gain rate had higher *G*', *G*'', and Tan δ .

Keywords: Veneer polymer composites; Glass transition temperature; Styrene; Methyl methacrylate; Rheological properties

Contact information: a: Jilin Provincial Key Laboratory of Wooden Materials Science and Engineering (Beihua University), Jilin, 132013, People's Republic of China; b: Northeast Forestry University, Harbin, 150038, People's Republic of China; *Corresponding author: liumingli17@163.com

INTRODUCTION

Wood is a natural polymer composite material that is characterized by its viscoelastic property, a mechanical property affected by time, temperature, and frequency. From a macro perspective, wood recovery from deformation by external forces mainly shows the elastic and creep recovery. From a micro perspective, the micro-Brownian motion of a wood molecular chain is constrained by its internal molecular connections, which also has an impact on the macroscopic properties of wood (Zhou 2003). Through dynamic mechanical properties testing, changes in wood orientation, glass transition, and other structural changes are shown, and these changes reflect the macro molecular motion. Polymers are typical viscoelastic materials, and also have the glass transition, crystallization, cross-linking, and orientation, as well as structural changes under the action of cyclic loading. Dynamic mechanical properties are affected by time and frequency, and are related to the mechanical state of the material (*i.e.*, glass, high elastic state, and viscosity) (Ferry 1980).

Wood plastic composite is composed of wood, monomers that are impregnated into the wood, and polymerized internal wood (forming polymer). Some studies were performed on wood impregnation modification. Poplar wood through MMA impregnation greatly improved its surface properties; PMMA is contained mainly in the void spaces of the wood (Ding *et al.* 2012; Koubaa *et al.* 2012). Through two different chemistry routes, the methacryl groups were inserted into wood cell walls, allowing them to be used as the anchoring points for grafting; various polymers can be inserted into the

wood structure (Keplinger *et al.* 2015). A novel two-step combined treatment in which MAN was dissolved in acetone made it possible to swell the cell wall and create chemical bonds to the cell wall components. Then a solution of mixed GMA/MMA or GMA/St was impregnated into wood cell lumens for graft polymerization. The results showed that MAN is partly chemically bonded to the cell wall *via* reaction with hydroxyl groups (Li *et al.* 2012, 2013). Polymers (monomer) are introduced into wood and affect wood dynamic viscoelastic mechanical properties.

Rheological measurement is a small amplitude dynamic rheological test, relying on rotary motion to produce simple shear flow. It is being used to quickly determine the viscosity and elasticity of various rheological properties of the material (Barnes et al. 1989). This rheological test method does not damage the internal structures of the composite material and can also help interpret the relationship between structure and rheological properties of biomass composites. The properties of materials can be characterized by their structure and molecular motion state (Xu et al. 2008). Therefore, the mechanical behavior of a polymer material is linked with temperature and frequency. It reflects the variation of elastic modulus (G'), loss modulus (G'), and tangent of the phase angle delta (fan δ) for composites with temperature under forced vibration, so presumably fatigue life, impact elasticity, heat and cold resistance, and aging resistance have been widely used in performance characterization of materials. Not only are the mechanical properties tested, but the polymer glass transition, low-temperature transformation, and the secondary relaxation process are also tested. Such work has important guiding significance for science and engineer research of polymer materials for evaluating the mechanical behavior of materials, heat and cold resistance, miscibility of polymer blends, interfacial properties of composites, and molecular motion mechanisms.

This study determines the dynamic mechanical properties of maple veneer plastic composite (MVPC) with the use of a rotary rheometer. We researched the relationship between the wood and its properties, as well as the relationship between the polymer molecular chains and the wood. The properties of MVPC and the effect of the impregnated polymer system on the plastic glass transition temperature of the MVPC were evaluated. The interaction between polymer and wood (interface) was analyzed, and the effects from the influence of different polymer weight rates on the basic movement of wood elements investigated. From this, the microstructure, molecular motion, and other important information on MVPC were obtained, which provided the basic data for MVPC.

EXPERIMENTAL

Materials

The materials considered in this experiment were maple (*Acer saccharum*) veneer (length \times width \times thickness: 1250 mm \times 130 mm \times 2.2 mm), styrene (St), methyl methacrylate (MMA), azobisisobutyronitrile (AIBN), and maleic anhydride (MAH).

Methods

Preparation technology of MVPC

The flow chart illustrating the preparation of the MVPC is shown in Fig. 1 (Wang *et al.* 2007). The impregnation liquid was prepared according to the design formula (with the ratio of MMA:St:MAH:AIBN being 400:80:20:1), and completed under a fume hood.

The dried maple veneers were weighed (M_0) and placed in a specialized rack in which the veneers were separated by a rack bar to provide spacing between the veneers. The veneer frame boards were placed in a treatment tank and exposed to a -0.1 MPa vacuum for a certain amount of time (10 to 30 min). The impregnation solution was then siphoned into the tank under vacuum to a level 5 mm above the veneers. The tank volume, veneer volume, frame volume, and weight rate of veneers were used to calculate the level of the impregnation solution. In case the vacuum was not high enough or the air purged from the wood was not up to the requirement, the vacuum may be increased. The tank was then pressurized with nitrogen to value (0.8 to 1.2 MPa), and the veneer impregnated for a prescribed time (30 to 60 min). At the end of the impregnation period, the tank was depressurized and the processing solution drained to a storage barrel. The solution was weighed, and the quantity of solution retained by the veneers was calculated.

The pressure in the tank was adjusted to 0.8 to 1.0 MPa, and it was heated with steam to a range from 60 to 65 °C. The heat source was then adjusted according to the numbers of samples. This procedure resulted in the temperature range (70 to 90 $^{\circ}$ C) needed for the experiment. Using the intermittent heat-cure process, discharged impregnation solution from the veneers was returned to the storage tank, where it merged with residual liquid. When no solution was discharged, the tank was heated (70 to 90 °C for 30 to 60 min) to cure the veneers. The tank was cooled with water until it reached room temperature. Most of the vaporized monomers were condensed on the inner surface of the tank, and were weighed and recycled. According to the various steps of recycled solution quality and total solution quality, the total polymerization rate of weight gain and the discharge rate of solution during heat-cure were calculated in addition to the solution monomer vaporization rate and its recycle rate. The pressure in the tank was purged, and the veneers were placed under a vacuum above -0.09 MPa for 10 min to remove any monomer adsorption. When the tank reached atmospheric pressure, the veneer racks were removed. Each veneer was measured (M_1) , and the polymerization rate of weight gain (polymer loading, PL) was calculated. The PL was calculated according to Eq. 1.



 $PL = \frac{M1 - M0}{M0} \times 100\%$

Fig. 1. Flow chart of the MVPC preparation

Specimens

According to the requirements of the experiment, the MVPC materials were cut into 53 mm \times 10 mm \times 2.2 mm (longitudinal \times tangential \times radial) specimens. Three specimens were prepared for each kind of test material.



Fig. 2. Schematic diagram of torsion fixture

Specification of parameters

Under alternating stress in Fig. 2, the polymer chain segments of MVPC were subject to internal friction during movement. When the force changed, the chain segment movement did not keep up with the changes of stress, so strain lagged behind stress, which is the phase angle (δ). For the ideal elastic material, δ is equal to 0. Work was done whenever deformation was generated by force and was deposited as potential energy. That potential energy was transformed into kinetic energy and then released. For an ideal viscous substance, $\delta = \pi/2$. This work was performed by external force, and was converted into heat and then lost. For polymers with viscous and elastic properties, $0 < \delta < \pi/2$. For this, work performed by external forces was stored; the remaining portion was converted into heat.

When the polymer materials were subjected to alternating stress, which is shown by the $\sigma = \sigma_0 \sin \omega t$ function, the strain lagged behind stress (represented by phase angle δ), and the strain is represented as $\varepsilon = \varepsilon_0 \sin (\omega t \cdot \delta)$. This can be expanded as Eq. (2):

$$\varepsilon = \varepsilon_0 \sin \omega t \cos \delta - \varepsilon_0 \cos \omega t \sin \delta \tag{2}$$

From Eq. 2, it can be observed that a part of the polymer strain is associated with elastic deformation as it is synchronized with the stress. On the other hand, the other part of the polymer is associated with viscous deformation, and its phase difference with stress is $\pi/2$. In addition, the polymer strain can also be controlled so the polymer stress change can be investigated. In the condition of $\varepsilon = \varepsilon o \sin \omega T$, because the stress lagged behind strain for a phase angle δ , $\sigma = \sigma o \sin(\omega t + \delta)$. This can be expanded as shown in Eq. 3.

$$\sigma = \sigma_0 \sin \omega t \cos \delta + \sigma_0 \cos \omega t \sin \delta \tag{3}$$

It is thus clear that stress is composed of two parts. One part of stress is the same as the phase for strain, which is represented by $\sigma_0 \sin\omega t \cos\delta$. This is the driving force of the elastic deformation. The second part of stress is a phase difference of $\pi/2$ for strain, which is represented by $\sigma_0 \cos\omega t \sin\delta$. The deformation corresponded to the viscous deformation was lost to overcome the frictional force. If *G*' is defined as the ratio of the same phase stress (σ_0) and strain amplitude (γ_0) in Eq. 4, *G*'' is the ratio of a phase angle (σ_0) of $\pi/2$ stress and strain amplitude (γ_0) in Eq. 5.

$$G' = \frac{\sigma_0}{\gamma_0} \cos \delta \tag{4}$$

$$G'' = \frac{\sigma_0}{\gamma_0} \sin \delta \tag{5}$$

For Eqs. 4 and 5, G' is the storage modulus, and it is proportional to the maximum elastic energy storage of the sample in each period; G' reflects storage energy for the material elastic deformation and characterizes stiffness of the material. In the equations, G" is the loss modulus and is proportional to the sample in the form of heat energy consumed in each period; G'' reflects the loss energy for the material deformation in the form of loss of heat energy, as well as characterizes the damping of the material. Also, δ is the mechanical loss angle, and tan δ is called the tangent of the phase angle delta. Tan δ is associated with the viscous dissipation, and its peak in the frequency-scanning curve is called the internal friction peak. Its position and shape have "fingerprint" characteristics and is closely related to polymer molecular chain segment movement (Nakano *et al.* 1990).

Rheological analysis

A dynamic mechanical test is usually carried out in wood composites with small strain that has mainly no impact or damage on the microstructure of its materials. Besides this, the test needs to be considered an effective method for the characterization of filling the filler dispersion state within a polymer system. The material is applied to torsional strain or stress to measure its responsive stress or strain, viscosity, and modulus.

In the dynamic test, the rotational rheometer can adjust the torsional vibration frequency, vibration amplitude, test temperature, and test time. In a typical test, two of the listed conditions will be fixed. Moreover, systematic variation is the third condition. This study adopts the temperature and frequency-scanning tests.

The dynamic temperature-scanning mode is based on the strain amplitude and frequency, and applies sinusoidal deformation under different temperatures, which is tested at each temperature. An increase or decrease in temperature can be linear or logarithmic, or can produce a series of discrete temperatures. Dynamic temperature scanning can be used to analyze the time-dependent behavior of the material.

The dynamic frequency-scanning mode is based on certain strain amplitude and temperature, and applies sinusoidal deformation at different frequencies, which is tested at each frequency. An increase or decrease in frequency can be linear or logarithmic, or produce a series of discrete frequencies. In the frequency scan, the parameters need to be identified: strain amplitude, frequency scan mode, and experimental temperature. The dynamic frequency scan can be used to analyze the time-dependent behavior of the material.

Test methods and conditions

Figure 2 shows the fixture configuration of an AR2000ex rotational rheometer (TA Instruments, USA). The lower fixture is the stator, and the upper fixture is the rotor. The specimen is vertically fixed between the two fixtures, and the rotation of the upper fixture provides sinusoidal alternating stress.

The specimens were clamped between the test fixtures, as shown in the Fig. 2. The shim thickness was adjusted, which made the center of the specimen align with the center of the clamp. Adjusting the gap value to 40000 provided a testing of the specimen at a distance of 40 mm. The specimen was clamped, and the furnace door was closed. The temperature was set to 25 $^{\circ}$ C, and when the set value was reached, the door was opened, the specimen was clamped again, and the nuts were tightened. The furnace door was then closed, the temperature adjusted to 25 $^{\circ}$ C, and the specimen was kept inside for 10 min. After this, testing began.

For the temperature scanning, the tested temperature range was 25 to 250 °C, the frequency was 1 Hz, the ascent rate of temperature was 5 °C per min, and the strain was 0.5%. For the frequency scanning, the tested frequency was 0.1 to 10 Hz (1 Hz = 6.28 rad, s⁻¹) (Di *et al.* 2007), since it is beneficial to supervise the relaxation properties of the motor units of the polymer's molecular structure.

RESULTS AND DISCUSSION

Linear Viscoelastic Region

When the viscoelastic materials were subjected to alternating stress and deformation, the elastic component was able to store energy (strain energy), and the viscous component of the material responded in the form of a flow process. A small amount of energy was also dissipated as heat. The viscoelastic material was divided into linear and nonlinear categories.

The storage modulus (G') is also known as the elastic modulus, as it accounted for the elastic (reversible) deformation of the materials. It reflected the materials' magnitude of elasticity. It expressed the performance index of the materials based on their stiffness, as well as the relationship between stress and strain within the scope of the linear viscoelastic region. There was a linear viscoelastic region for all the viscoelastic materials considered. Within the linear region, the structural changes of the material were reversible. The viscoelastic experiment data had good repeatability, such that it was easy to apply the mathematical equations. The explanation for the experimental phenomena can also be greatly simplified: When the external force makes the material deformation exceed a linear viscoelastic region, it can cause irreversible structure changes in the material. Therefore, the pattern of stress/strain response will become complicated, as in the sense of damage mechanics (Mano 2002).

The viscoelastic spectrometer and some classical viscoelastic models with linear viscoelastic regions were used as the theoretical basis for the materials. Therefore, in the study of the viscoelastic properties of the materials, it was necessary to ensure that the material viscoelastic tests were performed in the linear viscoelastic regions. In order to

determine the linear viscous regions, dynamic strain scan samples determined the modulus dependent strains (Nakano *et al.* 1990).

Figure 3 shows G' values of the MVPC and control under different frequencies as a function of strain. From Fig. 3, it can be observed that when the strain amplitude was smaller than 1%, abiding to the conditions of frequency scanning, G' of the MVPC had nothing to do with the strain amplitude. In this experiment, the 0.05% strain guaranteed that the viscoelastic tests of the materials (MVPC and control) were performed in the linear viscoelastic region.



Fig. 3. G' of MVPC and control under different frequencies as a function of strain

Rheological Properties of MVPC

Storage modulus (G'), loss modulus (G''), and tangent of the phase angle delta (Tan δ) as a function of temperature

Figure 4 shows G' of the MVPC and control as a function of temperature. From Fig. 4, one can observe that G' values of the MVPC and control in the initial stage were at their maximum, and then decreased with the increase of temperature.



Fig. 4. G' of MVPC and control as a function of temperature

The behavior shown in Fig. 4 can be attributed to the kinetic energy within the wood and filled polymer molecules. Under the condition of low temperatures, this was very low. Also, under the action of an external force, only some small size units (such as various functional side groups and branched chains, as well as individual links) happened to move (Giyama and Norimoto 1996). With the increase of temperature, thermal motion energy to the wood and filled polymer molecules increased, and the chain segments or certain portions of the chain segments began more intense movement, so that *G*' decreased. The *G*' value of the MVPC and control appeared to plateau at 100 to 200 °C; therefore, this temperature range was called the glass transition region. The storage modulus decreased rapidly at 200 °C. From the combination of *G*' of the materials (Fig. 4) with the tan δ of the materials (Fig. 6), the glass transition temperature of hemicellulose was determined as 200 °C, and lignin had a glass transition temperature range of 160 to 200 °C. Therefore, there was an obvious change in storage modulus.

The loss modulus (G'') is also known as a viscous modulus. It accounted for the elastic (reversible) deformation of materials, and reflected the materials' viscosity magnitude and toughness. Figure 5 shows G'' of the MVPC and control as a function of temperature. From Fig. 5, in the temperature range of 25 to 215 °C, one can observe that G'' of the control was apparently lower than that of the MVPC. Thus, the toughness of MVPC was apparently higher than that of the control. This is because the polymers filled into wood were frozen; there was no relative migration between the chain segments, so loading did not have the need to overcome the friction between chain segments. When the temperature was over 215 °C, G'' of MVPC and control were similar. This is because the polymers that filled the wood had undergone viscous flow, so the G'' of MVPC reflects that of the control.



Fig. 5. G" of MVPC and control as a function of temperature

Figure 5 can also show that the control materials appeared to have two relaxation processes; the first was at 65 °C and the second at 215 °C. Research has shown that in the material, the first relaxation process of the control is a chemical component of wood to approximate the glass transition (Giyama *et al.* 1998). Generally, in the condition of an absolutely dried state, the thermal softening points of lignin, hemicellulose, and cellulose are 130 to 205 °C, 200 to 250 °C, and 200 to 250 °C, respectively. The temperature of thermal degradation and destruction of cellulose crystalline is 250 to 400 °C; therefore,

the second relaxation process was caused by thermo-softening of the polymers in the wood cell walls, and by the micro-Brownian motion of the polymer molecules under thermogenesis (Back and Salmen 1982). The G'' temperature spectra of the MVPC can be observed by two relaxation processes. The first relaxation process of the MVPC occurred at 105 °C, which was caused by motion of the main chain segments and side group motion of the polymers. The second relaxation process of the MVPC occurred at about 215 °C, which was caused by the thermal degradation of the main chemical components of the wood (cellulose and hemicellulose). The ratio of the loss modulus to the storage modulus is known as the tangent of the phase angle delta, which reflects the viscous elastic ratios of the materials.

Figure 6 shows $\tan \delta$ of the materials as a function of temperature. Tan δ indicates the relative magnitude of loss of energy. In the same system, the peak of $\tan \delta$ was greater, as the internal friction caused by the segment relaxation movement of molecules and the relative loss of capacity was bigger. The peak of $\tan \delta$ exhibited a series of peaks; each peak corresponded with a particular relaxation process. A peak with corresponding temperature shows a series of transition temperatures. Among them, the glass transition temperature (T_g) is the characteristic temperature of the polymer chain segment movement, as well as an important characteristic parameter for the properties of the polymers. At the glass transition, many properties of materials will change dramatically, especially the mechanical properties (Chow and Pickeles 1971). Below T_g , the polymers were in a glassy state; above T_g the amorphous polymers were in a rubbery state. Also, G'' and T_g reached their maximum values in this transition region (Di *et al.* 2007).



Fig. 6. Tan δ of MVPC and control as a function of temperature

Figure 6 shows that compared with that of the control, $\tan \delta$ curves of the MVPC increased apparently at 25 to 215 °C. This indicated that the main chain segment movement was in a "frozen" state, but some molecular units smaller than the segments still had the ability to move. Therefore with external force, the molecular units can undergo deformation and absorb energy. Moreover, the peak of the $\tan \delta$ curve was higher than that of the control. This indicated that at 25 to 215 °C, the impact resistance of the MVPC was better than that of the control. At about 215 °C, the T_g peak became higher as the segmental relaxation transition was more difficult and needed more energy. The T_g

peak became wider, which reflected a large dispersion of the chain segment movement (mainly molecular weight distribution of the polymers filled in the wood was wide), and indicated the long segmental relaxation process. The combination of the *G*' mutations (Fig. 4) with the tan δ transition peak (Fig. 6) indicated that the glass transition temperature was about 105 °C.

Influence of weight gain rate on rheological properties of MVPC

The factors that influence the rheological properties of the wood plastic composite are the weight gain rate of the wood plastic composite, impregnation solution types, polymer molecular weights, and the preparation method of the wood plastic composite. This is due to the results of intermolecular force. The polymer molecular activity near the wood and polymer phase interface decreased; thereby the G' and G'' curves of the wood plastic composites concerning temperature were different from the corresponding values of the bulk polymers.



Fig. 7. G' of MVPC with different weight gain rates as a function of temperature

Figure 7 shows G' of the MVPC with different weight gain rates as a function of temperature. From Fig. 7, one can observe that with the increase of weight gain rate, G' of the MVPC increased first, and then decreased. The G' of the MVPC with a weight gain rate of 55% appeared to peak when compared to other MVPC with different weight gain rates. This is because with the increase in the weight gain rate, the density of the MVPC increased since the cell walls of the wood bonded with polymers. When the weight gain rate of the MVPC was less than 55%, the main part of the MVPC was wood; however, when the weight gain rate of the MVPC was a synthetic polymer.

Figure 8 shows the relationship curves between temperature and G'' of the MVPC with different weight gain rates. From Fig. 8, one can observe that the MVPC of different weight gain rates appeared to have a relaxation process at 215 °C. However, with the increasing weight rate of polymerization, the MVPC appeared to have a relaxation process at about 100 °C, increased height of relaxation peak, and a more obvious peak shape. This is because as the weight gain rate increased, the main part of the MVPC

transitioned from wood to polymer. Therefore, polymer chain relaxation was reflected in the rheological results.



Fig. 8. G" of MVPC with different weight gain rates as a function of temperature



Fig. 9. Tan δ of MVPC with different weight gain rates as a function of temperature

Figure 9 shows the relationship between temperature and $\tan \delta$ of the MVPC with different weight gain rates. From Fig. 9, it can be observed that the $\tan \delta$ -temperature curve of the MVPC prepared by different weight gain rates was the same as the *G*'-temperature curve. With the increase in the weight gain rate of the MVPC, the loss of the peak appeared at about 100 °C. The peak was higher and the peak shape became more obvious.

PEER-REVIEWED ARTICLE

Influence of frequency on rheological properties of MVPC

The frequency range was 0.1 to 10 Hz (1 Hz = 6.28 rad, s⁻¹). These frequencies are beneficial in monitoring the relaxation properties of movement in the polymer molecular structure.



Fig. 10. G 'of MVPC and control as a function of frequency

Figure 10 shows that frequency had little effect on G' of the test specimens. The G' of the MVPC was higher than that of the control at 25 °C. At 100 °C, G' of the MVPC was comparable to that of the control. The observed results were the same as those shown in Fig. 4. This indicated that, in the condition of room temperature, the stiffness of the MVPC was higher than that of control. As temperature increased, the stiffness of the MVPC and control decreased.



Fig. 11. G" of MVPC and control as a function of frequency

Figure 11 shows that G'' of the MVPC and control increased with the increase in temperature. The value of G'' of the MVPC was greater than that of control under the same temperature. The observed results were the same with those of Fig. 5. This indicated that compared to control, the MVPC tends to be a more viscous material.



Fig. 12. Tan δ of MVPC and control as a function of frequency

Figure 12 shows that in the condition of the same temperature, $\tan \delta$ of the MVPC was greater than that of the control. At 25 °C, $\tan \delta$ of both the MVPC and control first increased as frequency increased until it reached a certain value. This can be mainly attributed to movement of side group segments or segments with only low molecular weight polymers. With the increase of frequency, the molecular chain segment movement could not keep up with changes in stress; the moving polymer chain segments were subject to increase the internal friction role; the generated friction force was limited because the amount of movement of the segments was limited. Therefore, the energy loss reached a certain value. At 100 °C, with the increase of frequency, $\tan \delta$ of the control was reduced. Additionally, $\tan \delta$ of the MVPC increased, and then it decreased until it reached a certain value. This is because, at 100 °C, polymers molecular in the MVPC came to move, so the energy loss was greater. Moreover, with the increase of frequency, the energy loss reached a certain value.

Practical Implication

In this work a type of WPC was prepared through a modification treatment, under the conditions of maintaining the excellent performance of maple. The main mechanical properties of this maple were improved, especially hardness, abrasion resistance, bending strength, and impact strength. The corresponding parameters increased by about 130%, 50%, 31%, and 100%, respectively. The impregnated-veneers were used as surface layer of floor and furniture, which can improve the hardness and the dimensional stability of floor, and therefore increase the service life of the floor. This product was applied to Fine Furniture (Shanghai) Ltd. in China.

CONCLUSIONS

- 1. At 25 to 215 °C, G' of the MVPC was higher than that of the control, which indicated that the stiffness of the MVPC was greater.
- 2. Compared with the control, *G*["] of the MVPC increased and had two relaxation peaks. They occurred at about 105 °C and 215 °C. The glass transition peaks of the MVPC were at 105 °C.
- 3. With the increase in the weight gain rate, G' of the MVPC increased, and then decreased. When the weight gain rate was 55%, G' appeared to be an extreme maximum value.
- 4. With the increase of frequency, at both 25 °C and 100 °C, $\tan \delta$ first increased, and then it decreased until it reached a constant value.

ACKNOWLEDGMENTS

The authors are grateful for the financial support from the National Natural Science Foundation of China (Grant No. 31300477 and 31400503).

REFERENCES CITED

- Back, E. L., and Salmen, N. L. (1982). "Glass transition of wood components hold implications for molding and pulping processes," *TAPPI Journal* 65(7), 107-110.
- Barnes, H. A., Hutton, J. F., and Walters, K. (1989). *An Introduction to Rheology*, Elsevier, Amsterdam.
- Chow, S. Z., and Pickeles, K. J. (1971). "Thermal softening and degradation of wood and bark," *Wood and Fiber Science* 3(2), 166-178.
- Di, H. Y., Wu, S. Z., Yang, Z. X., Dai, P. J., and Gao, G. M. (2007). "Analysis of factors influencing the result of dynamic mechanical analysis," *Polymer Materials Science* and Engineering 23(4), 188-191.
- Ding, W. D., Koubaa, A., and Chaala, A. (2012). "Dimensional stability of methyl methacrylate hardened hybrid poplar wood," *BioResources* 7(1), 504-520.
- Ferry, J. D. (1980). Viscoelastic Properties of Polymers, 3rd edition, Wiley, New York.
- Giyama, M., and Norimoto, M. (1996). "Temperature dependence of dynamic viscoelasticities of chemically treated woods," *Mokuzai Gakkaishi* 42(11), 1049-1056.
- Giyama, M., Obataya E., and Norimoto, M. (1998). "Viscoelastic properties of the matrix substance of chemically treated wood," *Journal of Material Science* 33(14), 3505-3510. DOI: 10.1023/A:1004678506822
- Keplinger, T., Cabane, E., Chanana, M., Hass, P., Merk, V., Gierlinger, N., and Burgert, I. (2015). "A versatile strategy for grafting polymers to wood cell walls," *Acta Biomaterialia* 11, 256-263.
- Koubaa, A., Ding, W. D., Chaala, A., and Bouafif, H. (2012). "Surface properties of methyl methacrylate hardened hybrid poplar wood," J. Appl. Polym. Sci. 123(3), 1428-1436.

- Li, Y. F., Dong, X. Y., Lu, Z. G., Jia, W. D., and Liu, X. Y. (2013). "Effect of polymer in situ synthesized from methyl methacrylate and styrene on the morphology, thermal behavior, and durability of wood," *J. Appl. Polym. Sci.* 128(1), 13-20.
- Li, Y. F., Wu, Q., Li, J., Liu, Y., Wang, X. M., and Liu, Z. (2012). "Improvement of dimensional stability of wood via combination treatment: Swelling with maleic anhydride and grafting with glycidyl methacrylate and methyl methacrylate," *Holzforschung* 66(1), 59-66.
- Mano, F. (2002). "The viscoelastic properties of cork," *Journal of Material Science* 37(2), 257-263. DOI: 10.1023/A:1013635809035
- Nakano, T., Honma, S., and Matsumoto, A. (1990). "Physical properties of chemically modified wood containing metal I: Effects of metals on dynamic mechanical properties of half-esterified wood," *Mokuzai Gakkaishi* 36(12), 1063-1068.
- Wang, Q. W., Zhou, J. H., Sui, S. J., Wang, W. H., Song, Y, M., and Liao, H. (2007).
 "Method for preparing wood vinyl monomer plastics composites," *Chinese Patent Number* ZL200710072699.2.
- Wang, Y. B., Huang, Z. X., and Zhang, L. M. (2004). "Application of DMA in the research of polymer materials," *Technology of Foreign Building Materials* 25(2), 25-26.
- Xu, J. Z., and Xu, C. (2008). "Viscoelasticity of polymer materials analyzed with DTMA," *Chemical Engineering and Equipment* (6), 22-26.
- Zhou, C. X. (2003). *Experiment and Application of Polymer Rheology*, Shanghai Jiao Tong University Press, Shanghai.

Article submitted: November 6, 2014; Peer review completed: March 17, 2015; Revisions received and accepted: April 30, 2015; Published: July 14, 2015. DOI: 10.15376/biores.10.3.5278-5292