Thermal and Dynamic Mechanical Behavior of Poly(vinyl chloride)/Wood Flour Composites

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ABSTRACT: Thermal and dynamic mechanical behaviors of wood plastic composites made of poly vinyl chloride (PVC) and surface treated, untreated wood flour were characterized by using differential scanning calorimetry and dynamic mechanical analysis. Glass transition temperature (T_g) of PVC was slightly increased by the addition of wood flour and by wood flour surface treatments. Heat capacity differences (ΔC_p) of composites before and after glass transition were markedly reduced. PVC/wood composites exhibited smaller tan δ peaks than PVC alone, suggesting that less energy was dissipated for coordinated movements and disentanglements of PVC polymer chains in the composites.

The rubbery plateaus of storage modulus (E') curves almost disappeared for PVC/wood composites in contrast to a well defined plateau range for pure PVC. It is proposed that wood flour particles act as ''physical crosslinking points'' or ''pinning centers'' inside the PVC matrix, resulting in the absence of the rubbery plateau and high E' above T_g. The mobility of PVC chain segments were further retarded by the presence of surface modified wood flour. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 107: 951–957, 2008

Key words: thermal properties; dynamic mechanical analysis; poly(vinyl chloride); wood flour; composites

INTRODUCTION

Differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA) have been widely used to study the influence of the presence of wood fiber (flour) and natural fiber, compatibilizer on thermal behavior of various polymer matrices.[1–9] Espert and Karlsson studied thermal behavior of different natural fiber-filled polypropylene (PP) composites using DSC[8] and reported that crystallization and melting temperatures of PP decreased as the fiber content increased. Reduction in the crystallization temperature of PP was also observed on maleated polypropylene (MAPP) treated wood surfaces.[2] Wood flour particles acted as nucleating agents for PP.[10] Kinetics study found no differences in the crystal formation nucleated on the wood surface and in the bulk polymer PP.[11] The total degree of crystallinity of PP was decreased by the presence of untreated wood flour.[12] Selden et al. reported their DSC results on UV aged wood fiber-PP composites. The second DSC melting scan of degraded surface layers indicated a maximum of 33°C decrease in the melting temperature of PP due to the molecular chain scission and the formation of extraneous groups, such as carbonyls and hydroperoxides during UV aging.[13]

DMA studies on MAPP treated wood-PP composites showed that composite properties decreased when wood flour content was higher than 40 wt %.[10,14] MAPP had negligible effects on the main transitions of PP, the intensity and temperature of α-transition was almost proportional to fiber contents in composites.[15]

For wood–polyethylene (PE) composites, DSC has been used to evaluate the crystallinity of HDPE after aging.[16] Good correlations were detected between aging duration and the degree of crystallinity of PE as well as between melting enthalpy and wood fiber content. Silane coupling agent treated wood fiber had a higher loss of crystllinity of PE. A small reduction of the melting peak temperature was found as the aging time increased.[16] Increased crystallinity of PE was observed with increase in wood content up to 50%; the α-transition temperature and crystallization temperature of PE were shifted considerably in composites on DMA curves.[6]

Wang et al. studied boric acid-modified wood fiber–polystyrene (PS) composites by using DSC and DMA.[17] They reported that the addition of plasticizer lowered the glass transition temperature of PS, while the presence of boric acid showed insignificant effect.

Djidjelli et al. reported that wood fiber content had little influence on the glass transition temperature of plasticized PVC that appeared around 55°C on the DSC thermograms. They also found the inhibiting effect of wood fiber on PVC thermal decomposition.[18]

DMA and DSC studies of MAPP-treated wood veneer-PVC laminated composites showed that storage modulus of composites increased at low MAPP content and decreased at high MAPP content, but tan δ was independent of MAPP concentration.[7]

Thermal and dynamic mechanical behaviors studies in wood, natural fiber-plastic composites are far from adequate, especially the influence of the presence of wood particles on molecular chain movements of polymer matrix under increased temperatures. In this paper, wood composites made of PVC and surface treated, and untreated wood flour were examined by DSC and DMA to monitor the influence of the addition of wood flour and wood surface treatments on the thermal behavior. T_g, heat capacity, storage and loss modulus, tan δ, as well as the viscosity were measured. Results of these studies provide valuable information about high temperature performances of PVC/wood composites.

EXPERIMENTAL

Materials

PVC 190F was manufactured by Oxy Vinyls, and formulated with 3% tin stabilizer, MK-98 from Crompton (Hahnville, Louisiana) and 1.5% calcium stearate, extra density grade, provided by Crompton (Greenwich, Connecticut).

Red Oak (*Quercus rubra*) wood flour with an average diameter of 0.15 mm and an average length ranging from 74 to 590 μm was used as supplied by CertainTeed (Jackson, Michigan).

A copper ethanolamine solution (Cu-EA) was used for the wood flour treatment to reach a target copper concentration of 0.2 wt %. Copper ethanolamine treatment was selected to improve the biological performance of the resulting composite.[19]

Wood flour treatment

Wood flour was dip-treated by Cu-EA solution at a liquid to solid ratio of 1.5 : 1 at the room temperature and atmospheric pressure. Treated wood flour was oven dried at 60°C for 24 h, and then at 105°C for 24 h to reduce the moisture content to less than 1% before further processing.

The copper contents in the treated wood flour were analyzed by using atomic absorption spectroscopy according to the AWPA standard A11-93.

Sample preparation

Untreated and Cu-EA treated wood flour was mixed with PVC powder for 10 min in a 20-L high-intensity laboratory mixer. Sample compositions are listed in Table I. About 500 g of the mixture was poured in an

TABLE I
Compositions of PVC/Wood Flour Composite Samples with Different PVC, Treated and Untreated Wood Flour Contents, as well as Cu Concentrations in Treated Wood Flour

Sample ID	PVC (wt %)	Wood flour (wt %)	Cu content in wood flour (wt %)
PVC	100	0	0
PW64con	60	40	0
PW64Cu0.2	60	40	0.2
PW55con	50	50	0
PW55Cu0.2	50	50	0.2
PW46con	40	60	0
PW46Cu0.2	40	60	0.2

aluminum mold measuring $4 \times 280 \times 280$ mm^3 and the mold placed between two steel platens. A RHM Hydraulic oil heated press with a nominal maximum pressure level up to 6 MPa was used for the compression molding.

The press platens were maintained at 200°C. The press cycle consisted of two phases: the first phase involved the heating of the mold assembly to 200°C for 8 min. After the mold assembly reached the desired temperature, the press was slowly closed for 2 min. The goal of a slow closing of the press was to maintain contact with the mold assembly as the furnish began to melt to facilitate the flowing of the thermoplastic within the mold. This procedure reduces the probability of the formation of internal air voids in the panel during the release of gases that may cause undesirable defects.

The second phase was the closure of the press for 5 min. After the 15 min press cycle, the caul sheet assembly with the mold containing the molten wood plastic was removed from the hot press and placed in a cold press for 15 min to allow the composite to harden under pressure. PVC and composite boards were ground to 50 mesh (0.3 mm) particles for DSC analysis and cut into $1.2 \times 3.5 \times 15$ mm^3 specimens for DMA.

Differential scanning calorimetry (DSC) analysis

DSC temperature scans were carried out with a Perkin–Elmer Diamond DSC, and PYRIS™ Version 4.0 software were used for data acquisition and processing. The instrument was calibrated with a standard Indium sample before analyzing.

About 10 mg of each type of sample was sealed in an aluminum pan and placed in heating chamber and operated under N_2 atmosphere with a pressure of 150 kPa. Experiment was conducted in 3 steps. In step 1, the samples were heated from 25 to 160°C at a rate of 10°C/min, and cooled from 160 to 25°C at a rate of 10°C/min, to eliminate material heat history.
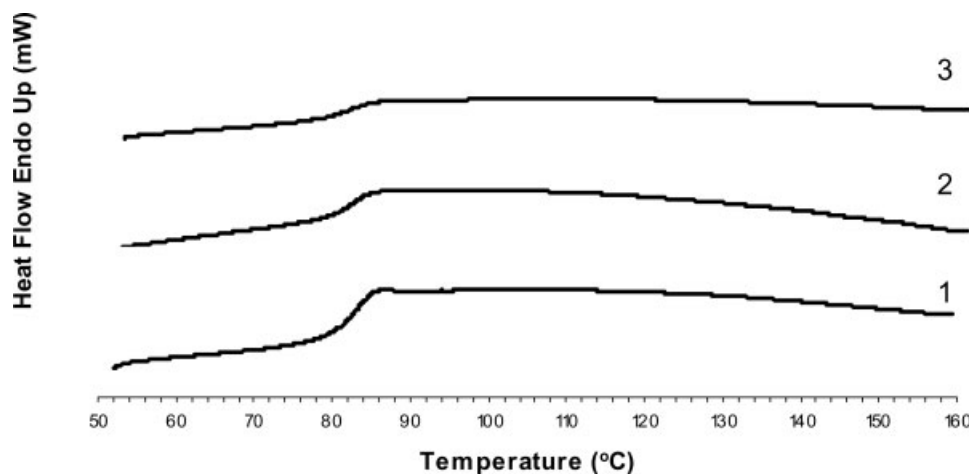
Figure 1 DSC diagrams of (1) pure PVC; (2) PW64con: composite made of PVC and untreated WF at a percentage PVC to wood ratio of 60 : 40; (3) PW64Cu0.2: composite made of PVC and treated WF containing 0.2% Cu at a percentage PVC to wood ratio of 60 : 40.

Finally they were reheated from 25 to 160°C at a rate of 10°C/min. The thermogram obtained in the reheating step was used for data processing and interpretation. Duplicate tests were conducted for each type of samples.

Dynamic mechanical analysis (DMA)

DMA was carried out by a Perkin–Elmer DMA7, and PYRIS Version 4.0 software was used for data acquisition and processing. A 3-point bending-rectangle device testing system was installed. A 110.0 mN static force and a 100.0 mN dynamic force were applied on the sample with an oscillating frequency of 1.0 Hz. Testing was conduct under helium atmosphere with a flow rate of 10.0 mL/min. The sample was heated from 25 to 160°C at a heating rate of 5°C/min. Five replicate specimens per type were scanned.

Data analysis

The glass transition temperature T_g, the heat capacity difference ΔC_p, the storage modulus E', the loss modulus E'', tan δ the ratio of the loss to storage modulus E''/E', and the viscosity η were calculated directly by PerkinElmer DMA Pyris software. T_g is the temperature point corresponding to the half of ΔC_p on the DSC diagram. The variation of C_p (ΔC_p) is the difference in heat capacity before and after glass transition (T_g). The loss of viscosity was obtained by using the following equation:

$$\eta'' = \frac{E''}{2\pi f} \qquad (1)$$

where η″ is the loss of viscosity and f is the frequency preset during DMA experiment.

RESULTS AND DISCUSSION

Table I contains the copper content in treated wood.

DSC glass transition temperature (T_g) and heat capacity differences (ΔC_p)

PVC generally has a T_g around 80 to 85°C. The T_g of cellulose is between 230 and 250°C, whereas lignin has a T_g of 130–190°C at dry state.[20] Figure 1 shows the DSC temperature scan diagrams of pure PVC, composite sample PW64con, and PW64Cu0.2. The glass transition step of PVC was evident in the DSC curve. After blending with wood flour, the α-transition step of PVC became weak, especially with Cu-treated wood. Pure PVC showed a T_g at 82°C. Glass transition temperatures of composites were around (84 ± 1)°C. Within 25–160°C temperature scan range, glass transition of lignin was not observed. Copper amine is a major component of copper based wood preservatives. Former studies indicate that mechanical properties and environmental stability of composites are improved by wood flour surface Cu-treatments.[19,21] The effect of wood flour contents and wood flour treatments on the glass transition temperatures of PVC was not considerable in DSC analysis.

Differences of heat capacity (ΔC_p) of PVC/wood flour composites were drastically reduced compared to that of pure PVC. ΔC_p and T_g of PVC, PVC-untreated wood flour composites, and Cu-treated composites with different Cu contents are given in Table II. Heat capacity of solid PVC is 1.2 kJ/kg K, almost similar to that of ovendry wood 1.2–1.3 kJ/kg K (17–27°C).[22] Below glass transition temperature of PVC, macromolecule chains of PVC are in the frozen state. When temperature reaches T_g, large segments of main chain of PVC start moving, leading to an increase of free volume. Chain segments movements

Sample ID	T_g (°C)	ΔC_p (mJ/g °C)
PVC	82	305
PW64con	83	157
PW64Cu0.2	84	132
PW55con	84	127
PW55Cu0.2	85	98
PW46con	83	96
PW46Cu0.2	84	70

absorb and consume heat so that more heat is needed to increase the material temperature by 1°C. Heat capacity (C_p) enlarges during glass transition in PVC polymer.[23] In PVC-wood flour composite, when PVC is experiencing its glass transition, the wood polymer chains are still in frozen state because the temperature is far below glass transition temperatures of lignin and cellulose. The presence of rigid wood polymer chains in PVC matrix may block the movement of adjacent PVC chain segments, prevent the expansion of free volume, and absorb less heat resulting in smaller C_p increases compared to that in pure PVC. After wood Cu-treatment, stronger adhesion between PVC and wood polymer chains is built up, and as a result, the movement of PVC chain segments can be further inhibited.

DMA storage modulus (E') and loss modulus (E'')

Figure 2 shows storage modulus (E') of PVC resin and PVC/wood flour composites in DMA temperature scans. It can be seen that composites had higher storage modulus than pure PVC through the whole

temperature scan range. As wood flour content enlarged from 40 to 50 wt %, storage modulus increased about 30% to 100 MPa, but when the wood content reached 60%, storage modulus decreased. This is consistent with the results reported in literature.[10,14] After a certain filling limit, PVC was insufficient to cover the large amount of wood flour, which resulted in poor adhesion and property deterioration of the composites. The rubbery plateau of PVC after glass transition was dramatically shortened by the presence of wood flour and almost disappeared when the wood content increased to 60 wt %. Composites can maintain higher storage modulus during a long temperature range above T_g of PVC, especially for composites containing 50 and 40 wt % wood flour. Their E' above T_g of PVC was even higher than the E' before T_g of the composite containing 40 wt % wood flour. Although the composite with 60 wt % wood had a lower E' before T_g than that of the composite containing 50 wt % wood flour, its E' above T_g was higher than that of 50 wt % wood contained composite in a certain temperature range.

Loss modulus (E'') showed similar trends to storage modulus. Loss modulus of PVC and PVC-wood flour composites are illustrated in Figure 3. Composites showed larger E'' than PVC, and E'' increased with enlarging wood flour content except for composites with 60 wt % or more wood. Above T_g, E'' of composites made of 60 wt % of wood was higher than those of composites containing 50 wt % wood flour until temperature increased to around 140°C. E' represents the elastic nature of material, while E'' is related to the energy lost to friction and internal motions reflecting viscous behavior.[24] The addition of wood flour leads to the increase in both elastic and viscous abilities of composites under the dynamic load.
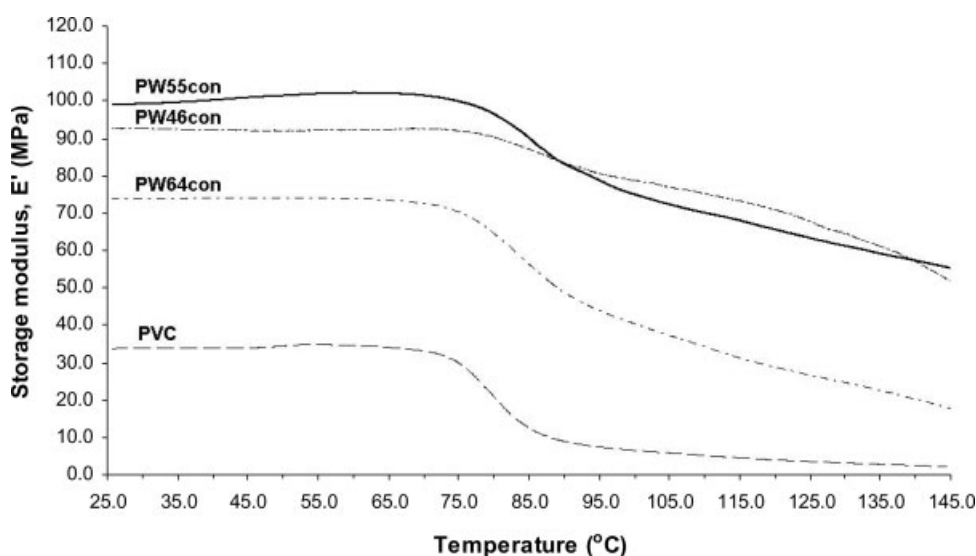

Figure 2 DMA temperature scans of storage modulus (E') of PVC resin and PVC/wood flour composites with increased WF content.
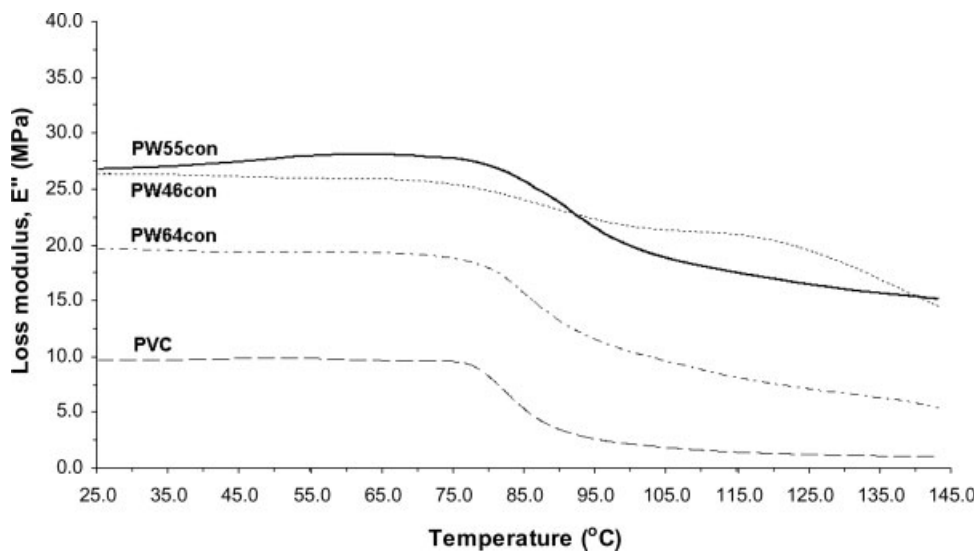
Figure 3 DMA temperature scans of loss modulus (E'') of PVC resin and PVC/WF composites with increased WF content.

Tan δ

Tan δ thermograms of PVC, composites made of PVC, and 40, 50, 60 wt % wood flour are presented in Figure 4. Pure PVC exhibited the largest tan δ peak with a peak temperature (T_g determined by DMA) of 85.8°C. Tan δ peaks were drastically weakened by the presence of wood flour, and disappeared when wood amount increased to 60 wt %. A slight increase in T_g (from 86.9 to 88.7°C) was observed when wood content enlarged from 40 wt % to 50 wt %. Tan δ reflects the mobility and movement capacity of molecule chain segments during glass transition. It is clear that the movements of PVC chain segments during glass transition were significantly limited and

obstructed by the presence of rigid wood molecule chains resulting in much smaller tan δ peaks in composite samples. This restricting effect became stronger as increasing wood flour contents. Wood flour particles acted as "physical crosslinking points" or "pinning centers" inside PVC matrix macromolecule chains and hindered their movements during glass transition.

Influence of wood surface treatment

E', E'', and tan δ of composites made of PVC-Cu treated and untreated wood flour are shown in Figure 5. Wood copper amine surface modification exhibited
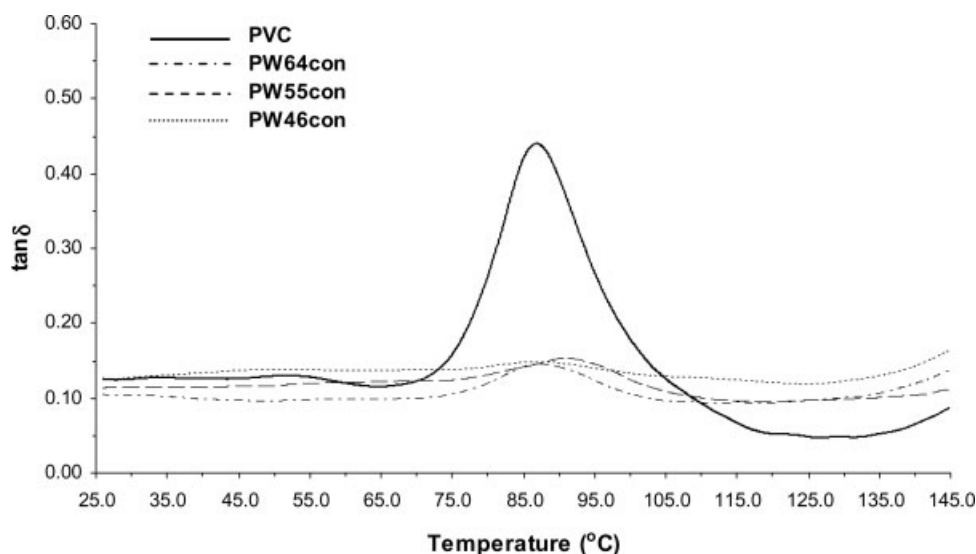

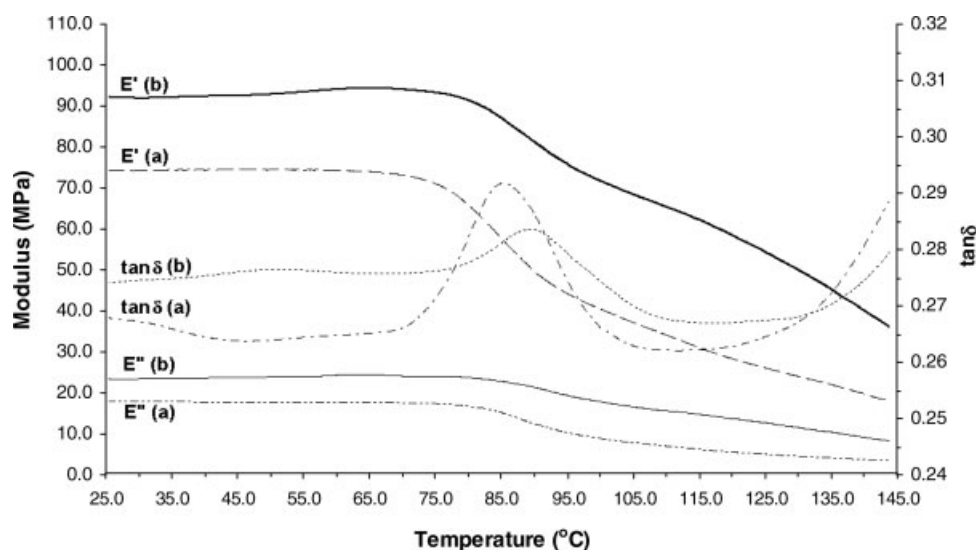**Figure 4** DMA tan δ thermograms of PVC resin and PVC/WF composites with increased WF content.

Figure 5 E', E'', and tan δ of (a) PW64con: PVC-untreated wood flour composites with a 40 wt % wood flour content, (b)PW64Cu0.2: PVC-Cu treated wood flour composite made of 40 wt % wood flour which had a 0.2 wt % Cu.

a similar effect to increasing wood content on E', E'', and tan δ of the composites. After using Cu-treated wood flour, E' and E'' increased and PVC rubbery plateau was further weakened, indicating the same "chain movement restricting" effect as increasing wood content in composites. This was also in correspondence with a smaller tan δ peak and slightly increased T_g of the Cu-treated composite. DMA analysis results of Cu-treated and untreated composites revealed that stronger adhesion and connection between PVC and wood polymer chains was built up by wood flour copper amine treatment. This may be attributed to the formation of stronger "physical crosslinking" between PVC and Cu-treated wood molecule chains. As a result, the movability of PVC

chain segments was further reduced by Cu-treated wood flour in the same wood content level.

Viscosity

The energy loss portion of viscosity of pure PVC and PVC/treated, untreated wood flour composites are presented in Figure 6. Composites showed higher viscosities than pure PVC, and viscosity increased with enlarging wood content in composites except for the composites containing 60 wt % wood flour. Compared to the composite containing 50 wt % untreated wood flour, composites made of 40 wt % PVC, and 60 wt % untreated wood flour exhibited lower viscosity before glass transition of PVC due to the poor
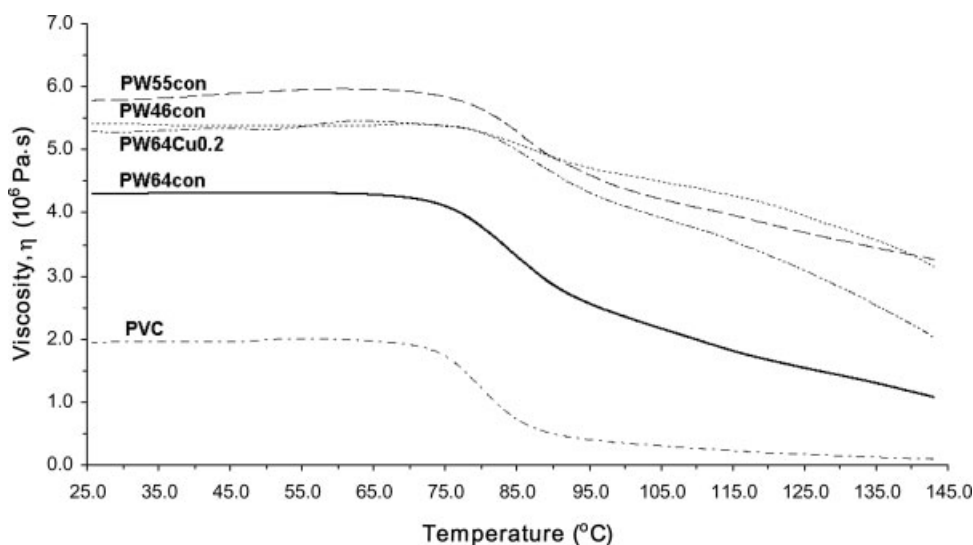

Figure 6 Loss viscosity of PVC and PVC-untreated wood flour composites with 40, 50, and 60 wt % wood flour content as well as PVC-0.2 wt % Cu containing wood flour composite with 40 wt % wood flour content.

interfacial adhesion, and higher viscosity after glass transition (from 88 to 140°C) because of a stronger physical crosslinking effect caused by the presence of larger amounts of wood flour particles. Composite containing 40 wt % Cu-treated wood flour demonstrated higher viscosities than corresponding composite made of untreated wood, suggesting the improved interfacial adhesion between PVC and Cu-treated wood flour.

CONCLUSIONS

DSC study showed slight increases in glass transition temperature (T_g) of PVC by the addition of untreated and Cu-treated wood flour, but this effect was not as significant as T_g determined from the peak temperature of tan δ by DMA. Heat capacity differences (ΔC_p) of composites before and after glass transition were dramatically reduced by the presence of wood flour and wood Cu-treatment.

Composites had increased E', E'', and viscosity, but had much smaller tan δ peaks than unfilled PVC. Enlarging wood flour content or using Cu-treated wood increased E', E'', and viscosity, but weakened tan δ.

DMA study revealed that the movement of PVC chain segments during glass transition was limited and obstructed by the presence of rigid wood polymer chains. This restriction effect became stronger as increasing wood flour content and by using Cu-treated wood flour. Wood flour particles acted as physical crosslinking points inside the PVC matrix, resulting in the absence of the rubbery plateau and higher E', E'', above T_g, and smaller tan δ peaks.

In comparison with the composites containing 50 wt % wood, 60 wt % wood content composites exhibited lower E', E'' and viscosity before glass transition due to the poor interfacial adhesion, but higher E', E'', and viscosity after glass transition because of a stronger physical crosslinking effect by increased amounts of wood flour particles.

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