Viscoelastic Properties of MF/PVAc Hybrid Resins as Adhesive for Engineered Flooring by Dynamic Mechanical Thermal Analysis[*1]

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ABSTRACT

The viscoelastic properties of blends of melamine-formaldehyde (MF) resin and poly(vinyl acetate) (PVAc) for engineered flooring used on the Korean traditional ONDOL house floor heating system were investigated by dynamic mechanical thermal analysis (DMTA). Because MF resin is a thermosetting adhesive, the effect of MF rein was shown across all thermal behaviors. The addition of PVAc reduced the curing temperature. The DMTA thermogram of MF resin showed that the storage modulus (E') increased as the temperature was further increased as a result of the cross-linking induced by the curing reaction of the resin. The storage modulus (E') of MF resin increased both as a function of increasing temperature and with increasing heating rate. From isothermal DMTA results, peak $T_{\tan \delta}$ values, maximum value of loss modulus (E") and the rigidities (ΔE) of MF/PVAc blends at room temperature as a function of open time, peak $T_{\tan \delta}$ and maximum loss modulus (E") values were found to increase with blend MF content. Moreover, the rigidities of the 70:30 and 50:50 MF/PVAc blends were higher than those of the other blends, especially of 100% PVAc or MF. We concluded that blends the MF/PVAc blend ratios correlate during the adhesion process.

Keywords : DMTA, viscoelastic properties, thermoset, MF resin, PVAc, engineered flooring

1. INTRODUCTION

There are three types of wood flooring: laminate flooring, engineered flooring and solid wood flooring. In the case of engineered flooring, fancy veneer of 0.5 mm thickness consisting of a wood such as birch, oak, beach, cherry, or maple is glued on plywood of 7.2 mm thickness and pressed at about 160°C. An ultra-violet (UV) curable coating is coated on this fancy veneer (Kim and Kim 2005a). However, the toxicity of wood-based panels bonded with these formaldehyde-based resins could act as an obstacle to their acceptance by the public, due to the formaldehyde emission and the associated possible health hazard which conflict with the

prevailing climate of environmental awareness and concern (Kim and Kim 2005b). Interest in PVAc-based adhesives having higher binding strength and better film properties has grown considerably in the past two decades because of their wide use in adhesives, paints, paper and the textile industries (Verma and Bisarya 1986). PVAc adhesive is commonly known as resin emulsifier or simply as "white glue". It is manu-factured by polymerizing vinyl acetate monomer and stabilizers with other polymers to copolymers. It comes in liquid form with viscosity ranging from 2000 to 3000 cPs at 21°C. PVAc is an odorless, nonflammable adhesive. It can be used in cold temperatures and solidifies quickly. Its application is very easy and it does not damage the tools during the cutting process. However, the mechanical resistance of PVAc adhesive decreases with increasing temperature and it loses bonding resistance capacity at over 70°C (Tuncer and Salim 2004; Yalcin et al., 2000). When PVAc was added to MF resin for the adhesion between plywood and fancy veneer in engineered flooring, the formaldehyde emission was dramatically reduced (Kim and Kim 2005c).

The ONDOL floor heating system has been used conventionally in Korea. At the floor surface, heat is radiated to warm the air tem-perature, thus warming the human body. The finishing materials of the flooring material should therefore be thermo-physiologically com-fortable (Song 2005). Various researchers have endeavored to study the physiological response of the human body to the surface of various flooring finishing materials. The recommended floor surface temperature is in the range of 19 ~26°C. Nonetheless, to sufficiently heat the entire room volume floor heating systems can set with a floor surface temperature as high as 29°C (Kim and Mizumachi 1995; Banhidi 1991). Although such previous research yielded significant benefits, it suffered from the limitation

of not considering the Korean peoples' habit of sitting on the floor. Consequently, a number of Korean researchers explored various flooring finishing materials and determined the ideal floor surface temperature for a person in a sitting position to be 22.0 to 38.8°C (Yoon et al., 1991; Kang et al., 2003; Kong and Sohn 1998; Lee and Rhee 1992).

Thermal analysis (TA) consists of analytical experimental techniques which measure the ther-mal behavior of thermosetting adhesives as a function of temperature (Kim et al., 2005). Dynamic mechanical thermal analysis (DMTA) has been widely used as a technique for inves-tigating the structures and viscoelastic behavior of composite materials for determining their storage modulus (E'), loss modulus (E") and loss factor (tan δ) (Kim and Kim 2003; Son et al., 2005). It is the viscous or time-dependent behavior of polymers that makes dynamic me-chanical testing such a useful characterization technique. One of the most common uses of dynamic mechanical testing is the determination of the glass transition temperature (T_g) of a sample. Another important application area for DMTA is in monitoring the curing of resins. DMTA is very sensitive to the curing process and isothermal experiments enable the develop-ment of an ideal curing schedule (Wetton et al., 1991).

The dynamic mechanical technique involves the application of a sinusoidally oscillating stress to a material and determining the resultant strain and is widely used as a polymer characterization technique. It has far greater sensitivity for both macroscopic and molecular relaxation processes than thermal analysis techniques based on tem-perature probe measurements alone. The complex viscous and time-dependent behaviors of poly-mers make the dynamic mechanical testing such a useful means of characterizing.

The purpose of this study was to investigate

the viscoelastic properties of the blends of MF resin and PVAc for adhesion in engineered flooring for application to the ONDOL system. The viscoelastic behavior was the blends were examined by ramp and isothermal methods of DMTA.

2. EXPERIMENTAL

2.1. Materials

Resin was prepared at a formaldehyde/melamine molar ratio of 1.75, with a solid content of 60%. After the addition of water to the formalin to give a formaldehyde content by weight of 38.5%, the pH was adjusted to 9.0 by the addition of 1 M NaOH solution (because the methylolated intermediates of the reaction rapidly condense under acidic conditions) and melamine was added. As hardener, 10% ammonium chloride solution was used. The viscosity as measured using a Brookfield Viscometer Model DV-II+ was 75cPs at 21°C. Liquid form PVAc was used with a density of 1.1 g/cm^3, viscosity of 2000 cPs at 21°C, pH value of 5% and ash ratio of 3%. PVAc adhesive was supplied from Tae Yang Chemical Co. Ltd (Incheon, Korea).

The fancy veneers were 0.6 mm thickness, made of birch (5.0% MC), and the plywoods manufactured in Indonesia were supplied from Dongwha Enterprise Co. Ltd.

2.2. Blend Preparations

Blends with various compositions of MF resin/PVAc content ratios were prepared. To determine and compare the effect of PVAc content, compositions of 0, 30, 50, 70 and 100%, by weight of MF resin, were used. The blends were merely stirred together physically and all were 5-blending systems.

2.3. Dynamic Mechanical Thermal Analysis (DMTA)

The viscoelastic properties of each sample were measured from 30°C to 200°C at a heating rate of 10°C/min (ramp method) and at room temperature for 8000 sec (isothermal method), 40,000 sec in case of 100% MF resin, using a dynamic mechanical thermal analyzer (DMTA; Rheometric Scientific DMTA MARK IV). As the resins were in a viscous liquid state, the DMTA samples were prepared by sandwiching the resins between two layers of birch, each 0.6mm thickness, and a three-point bending mode was applied (Kim and Kim 2003). The adhesive thickness was 0.2 mm and the sample dimensions were $28 \times 5 \times 1.4$ (mm). During the DMTA experiments, the static force was kept at 20% of the dynamic force and the frequency was maintained at 1 Hz with a strain of 0.05.

3. RESULTS and DISCUSSION

3.1. Ramp Method of DMTA

It is important to understand the thermal properties of MF resin, because, as thermosetting adhesives, they are both strongly affected by, and indeed cured by, heating. These resins are in the liquid state at room temperature and become solid at high temperature after curing has taken place. DMTA is able to detect some of the transitions that occur, such as gelation and vitrification, by measuring the change in the mechanical properties. In this study, E', E" and tan δ of each adhesive system were obtained by DMTA. Fig. 1 shows E', E" and tan δ of the MF resin. By using the DMTA thermogram, we checked the viscoelastic properties of a thermosetting resin that is in the liquid state by using wood veneer.
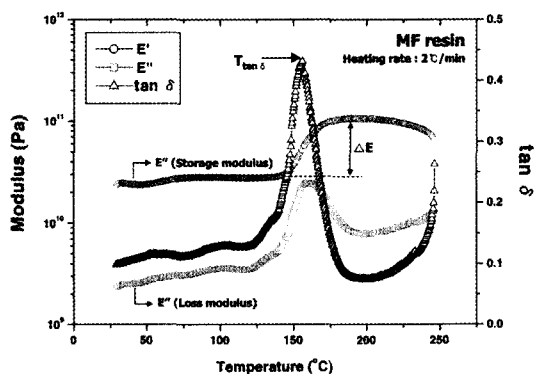
The DMTA thermogram in Fig. 1 shows that

Fig. 1. DMTA thermogram during heating ramp of MF resin at a heating rate of 2°C/min.

E' increased as the temperature was further increased due to the cross-linking induced by the curing reaction of the resin. E' reached a maximum when the curing reaction was completed. The increase in E' from the flat area of the curve following the evaporation of the water to this maximum value was the result of the consolidation of the resin network. This difference (ΔE) was used to evaluate the rigidity of the cured resin. As the temperature increased, E' increased and the resin was cured at about 155°C. The curing temperature and T_g of the resin were obtained from the tan δ peak. The tan δ value increased sharply up to its maximum value, due

to the increase in viscosity, and then decreased as the temperature was further increased. Finally, the tan δ value slightly increased again after the curing reaction was completed. The temperature of the active curing reaction can be determined from the maximum value of the tan δ value in this temperature range.

E', E" and tan δ results for the MF resins are shown in Fig. 2. E' increased both as a function of increasing temperature and with increasing heating rate. MF resin was in the liquid state at room temperature and became solid at high temperature, as a typical thermosetting resin, after curing had taken place. As the heating rate increased, the curing degree (ΔE) did not differ much. However, the hardening point temperature was increased as the heating rate increased. It should be noted that E' increased rapidly at around 150~180°C. The temperature of the active curing reaction can be determined from the maximum value of E" in this temperature range. The temperatures corresponding to the maximum values of E" were 160.4°C at a heating rate of 2°C/min, 190.8°C at 5°C/min and 212.9 at 10°C/min. These results showed that the heating rate affected the curing behavior of the thermosetting resin. In tan δ data in Fig. 2, this tendency is shown in detail.
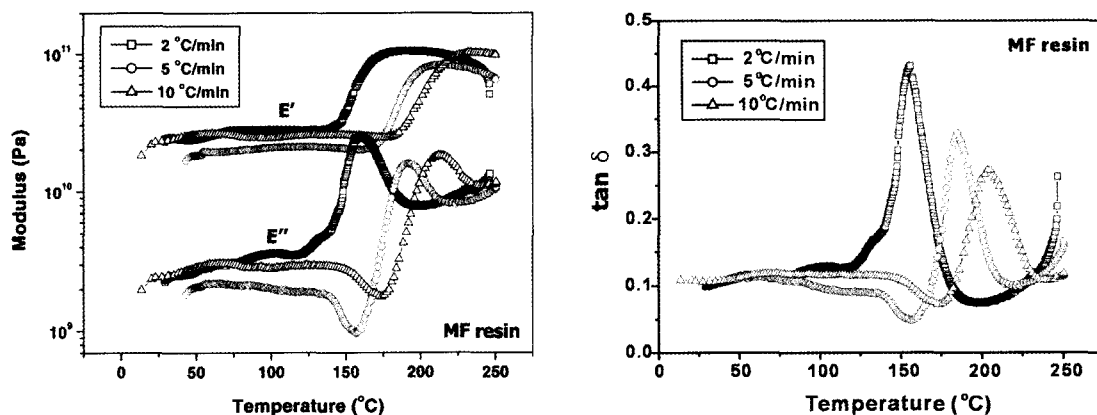

Fig. 2. Storage modulus (E'), loss modulus (E") and Loss factor (tan δ) of MF resin at different heating rates: 2, 5 and 10°C/min.
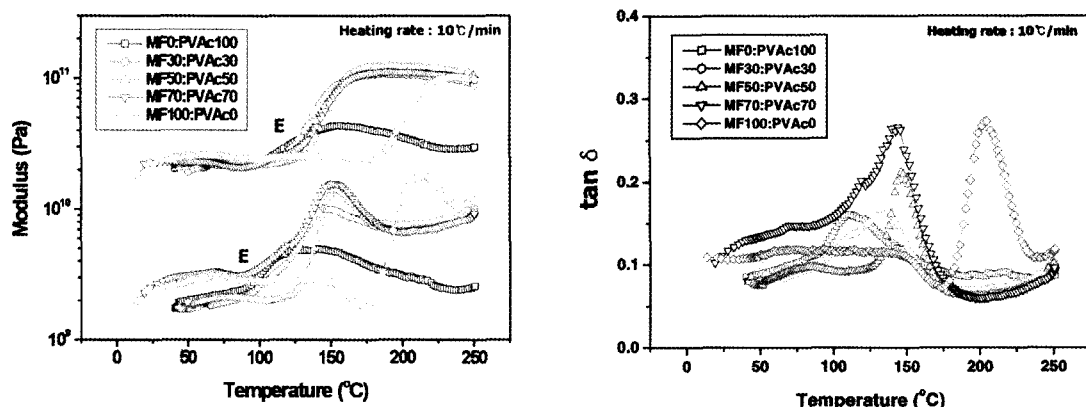
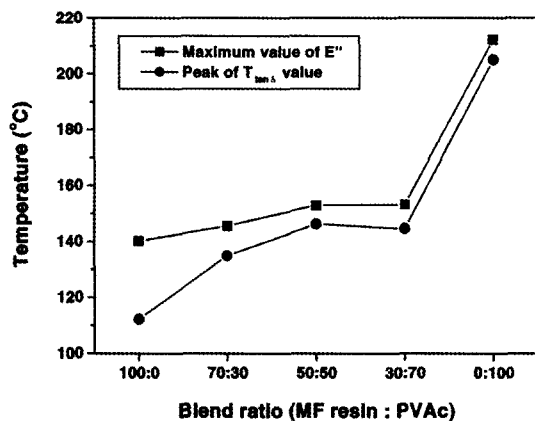Fig. 3. Storage modulus (E'), loss modulus (E") and Loss factor (tan δ) of MF resin/PVAc blends at a heating rate of 10°C/min.

Fig. 4. $T_{\tan \delta}$ peak values and maximum value of loss modulus (E") of MF resin/PVAc blends at a heating rate of 10°C/min.

The temperatures corresponding to the maximum values of tan δ were in the order of the heating rate. From the tan δ results, the peak of the $T_{\tan \delta}$ values were 155.7°C at a heating rate of 2°C/min, 190.8°C at 5°C/min and 205.0°C at 10°C/min. The heights of the tan δ peaks were also different. The highest peak was observed also for a heating rate of 10°C/min, with the tan δ peaks being in the order 2°C/min > 5°C/min > 10°C/min.

In Fig. 3, E, E" and tan δ of MF resin/PVAc

blends at a heating rate of 10°C/min are shown. As in the above result, even though the MF resin sample showed the behavior of a typical thermosetting resin in terms of the DMTA result, that of PVAc was quite different. From E', we can check that PVAc showed behavior of a water soluble adhesive. The peak was much broader than that of the others, and it showed the peak that was caused by water dried from 100°C. Because this PVAc is not a thermosetting adhesive, we could not find the viscoelastic properties with a temperature condition of DMTA. However, the blends of MF resin and PVAc showed the behavior of typical thermosetting adhesives. Only existence of pure MF resin, the peak showed typical thermosetting adhesive. With increasing MF resin content, the maximum E" was increased. There was little difference between the MF contents of 30, 50 and 70%. The rigidities (ΔE) increased with increasing MF content. The tan δ data in Fig. 3 illustrates this tendency of rigidities changes. With increasing MF resin content, the peak height of $T_{\tan \delta}$ values is high, indicating that E' is high and the change of state from liquid to solid is high. It was also possible to check if the peak of $T_{\tan \delta}$ values increased with increas-
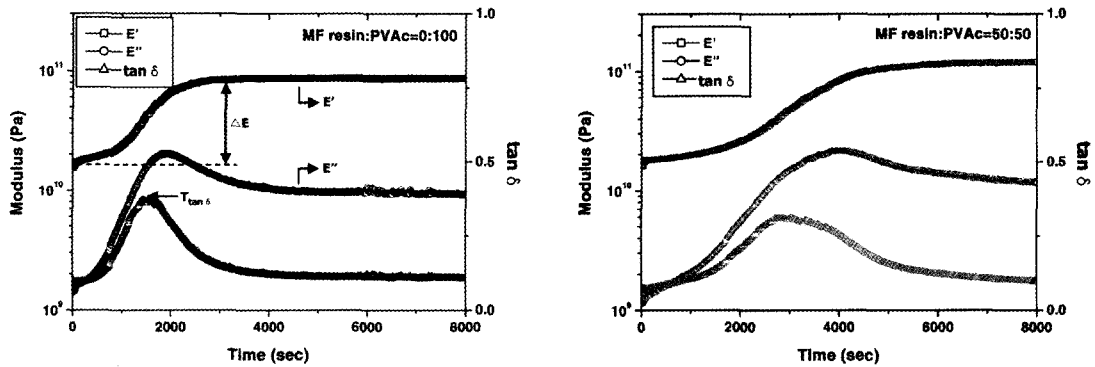
Fig. 5. DMTA thermograms of isothermal test of PVAc 100% and 50:50 MF/PVAc blends at room temperature.

ing MF resin content. The $T_{\tan \delta}$ peak values and the maximum value of E" of MF resin/PVAc blends are shown in Fig. 4.

From this different behavior between thermosetting and water soluble resin (cured at room temperature), the E' peak and tan δ were evident in just one data set. In fact, most of the thermosetting polymer blends found hitherto are immiscible except in the presence of favorable intermolecular specific interactions (e.g. hydrogen bonding) and these intermolecular specific interactions have been taken as the driving force for miscibility in some thermosetting polymer blends (Lü and Zheng 2003).

3.2. Isothermal Method of DMTA

Dynamic thermal mechanical test methods have been widely used for investigating the structures and viscoelastic properties of thermosetting adhesives (Kim and Kim 2003; Onic et al., 1998). However, we used DMTA to investigate the curing behavior and solidification of all MF/PVAc blends at room temperature, because we focused on performance of adhesives spread on plywood before hot pressing. Kim et al., reported on the curing behavior of thermosetting resins using DMTA method of increasing temperature (Kim and Kim 2003; Kim et al., in press). Thermosetting resins are in the liquid

state at room temperature and become solid at high temperature after curing has taken place. DMTA is able to detect some of the transitions that occur during this process, such as, gelation and vitrification, by measuring changes in mechanical properties.

In the present study, the storage modulus (E'), loss modulus (E") and loss factor (tan δ) of each adhesive system was obtained by DMTA. By using the DMTA thermogram, we can check the viscoelastic properties of all blends in the liquid state by using wood veneer. Fig. 5 shows DMTA thermograms of isothermal test of PVAc 100% and of a 50:50 MF/PVAc blend at room temperature over 4,000 sec. We can find the peak which shows the curing point, maximum peak of tan δ, and increasing rigidity from storage modulus (E'). As time passes, which means increasing open assembly time, PVAc is becomes solid. Solidification and curing are being processed. The normal temperature curing process of PVAc was successfully tested by DMTA. When we added MF resin (a thermosetting resin) to PVAc, the peak moved towards a lower. The test time, 4,000 sec, was too short to show the solidification of MF resin. MF resin cannot be cured at room temperature. Thus, we tested it for 80,000 sec, for almost 1 day, as shown in Fig. 6. A maximum tan δ peak is shown but the curing degree from
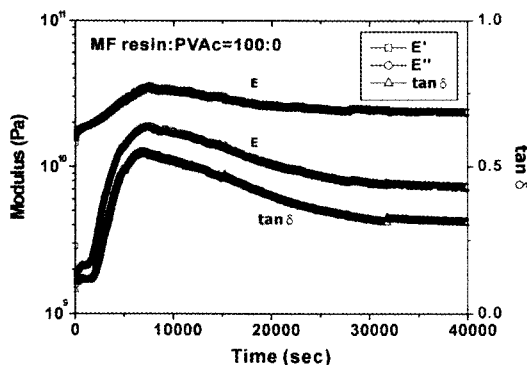
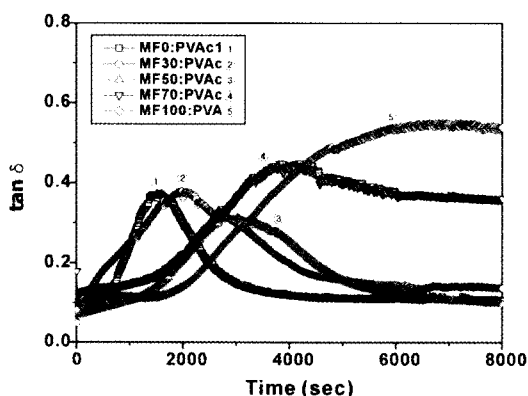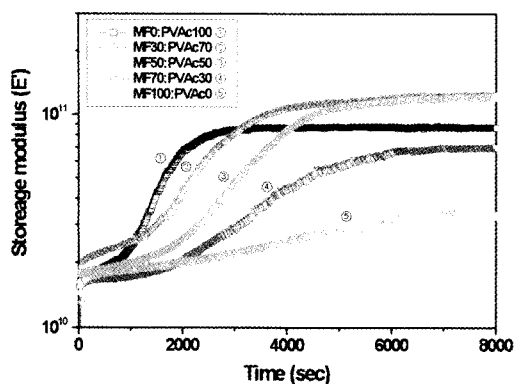Fig. 6. DMTA thermograms of isothermal test of MF resin at room temperature.

Fig. 7. Loss factor (tan δ) of PVAc and MF/PVAc blends at room temperature as determined by the isothermal method.

storage modulus (E') is low.

The results of tan δ for all blends are shown in Fig. 7. From the tan δ results, the $T_{\tan \delta}$ values were 1,548 sec for PVAc only, 1,978 sec for blend of MF/PVAc=30:70, 3,015 sec for MF/PVAc=50:50, 4,203 sec for MF/PVAc=70:30 and 6,969 sec of MF resin only. As increasing MF resin content, $T_{\tan \delta}$ shifted toward the long time. In the result from Roos et al., from the frequency sweeps at different temperatures, the shift of the tan δ peak in frequency can be clearly seen because of phase behavior of the polymer blend. However, in this case, because there was no heating condition, high content of thermosetting MF resin caused shift of $T_{\tan \delta}$ toward the long time. We can suppose that shifting of $T_{\tan \delta}$ toward the shot time if there is higher temperature than room temperature. Novikov et al. showed it in their dynamic mechanical result of PVP-PEG blends. These were highly shifted in temperature.

The heights of the tan δ peaks were also different. Highest peaks were observed for resins with a high MF ratio, and tan δ peaks increased on adding MF resin, but there was little difference between result and 50:50 MF/PVAc blend. The storage modulus (E') and loss modulus (E") of MF/PVAc blends at room temperature
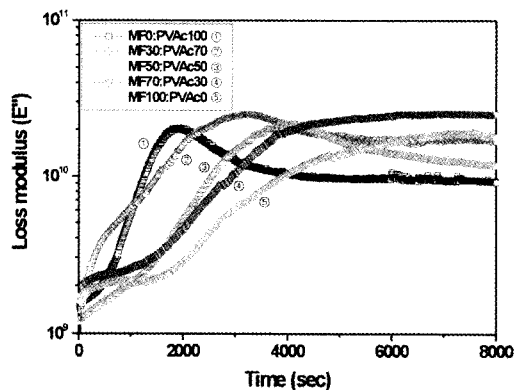

Fig. 8. Storage modulus (E') and loss modulus (E") of PVAc and MF resin/PVAc blends at room temperature by the isothermal method.
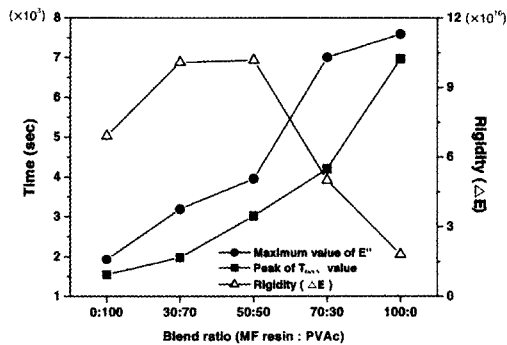
Fig. 9. Peak $T_{\tan \delta}$ values, maximum value of loss modulus (E") and the rigidities (ΔE) of MF resin/PVAc blends at room temperature as a function of open assembly time.

are shown in Fig. 8. The storage modulus (E') increased on increasing the PVAc content. All blends were in a liquid state at the beginning and then solidified. On increasing MF content, curing degree and rigidity (ΔE) remained unchanged. However, at higher MF contents, i.e., the 70% MF blend and 100% MF, the curing rate was too low, due to its thermosetting nature. Rigidities (ΔE) increased as the MF content increased to 50%, and then decreased. A high MF level in the blend caused a loss of PVAc room temperature properties, and these blends tended to behave more like thermosetting adhesives. From these results, thermosetting MF resin effect to viscoelastic properties on MF/PVAc blends for adhesion on engineered flooring. In Fig. 9, as explained above, peak $T_{\tan \delta}$ values, maximum value of loss modulus (E") and the rigidities (ΔE) of MF resin/PVAc blends at room temperature as functions of open time are shown. The peak $T_{\tan \delta}$ values and the maximum value of loss modulus (E") increased with increasing MF content. However, the rigidities of blends of 70:30 and 50:50 MF/PVAc were higher than those of other blends, especially of 100% PVAc and 100% MF. From these results, we found that high miscibility between MF and PVAc led to a high curing degree. This miscibility between MF and PVAc the peak of storage modulus and loss factor were shown in data was just one. In fact, most of the thermosetting polymer blends found to date are immiscible except in the presence of favorable intermolecular specific interactions (e.g. hydrogen bonding) and these intermolecular specific interactions are believed to be the driving force behinds the miscibility of some thermosetting polymer blends (Lü and Zheng 2003).

4. CONCLUSION

E' increased both as a function of increasing temperature and with increasing heating rate. MF resin was in the liquid state at room temperature and, as with typical thermosetting resins, became solid at high temperature after curing has taken place. The heating rate affected the curing behavior of the thermosetting resin. Room temperature curable PVAc was followed by DMTA and it was changed by introducing MF resin into the blend. With time after rigidities (ΔE) increased at room temperature, though this was prominent for PVAc only. For 5 min at the beginning, the initial tack properties and viscoelastic properties of adhesives were substantially unchanged. We conclude that these two properties are correlated during the adhesion process.

ACKNOWLEDGEMENT

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