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Thermal stability and viscoelastic properties of MF/PVAc hybrid resins on the adhesion for engineered flooring in under heating system; ONDOL

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Abstract

The thermal 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 thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) and dynamic mechanical thermal analysis (DMTA). The viscoelastic properties of the blends were also studied. 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 TGA results showed that the DTG_{max} temperature and thermal stability of the blends increased with increasing PVAc content. The blends were examined in non-isothermal DSC experiments at a heating rate of 10 °C/min. There was an exothermic peak in all the heating scanning curves, with each blend displaying a single curing peak temperature (T_p), intermediate between those of the two pure components and varying with the blend composition. 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. E' of MF resin increased both as a function of increasing temperature and with increasing heating rate.

Keywords: ONDOL; Engineered flooring; MF resin; PVAc; Hybrid resin thermal stability; Viscoelastic property; TGA; DSC; DMTA

1. Introduction

There are three types of wood flooring: laminate flooring, engineered flooring and solid wood flooring. The laminate flooring consists of HDF (high-density fiberboard) as the core material, while the engineered flooring consists of plywood with a thin fancy veneer bonded onto the face of the plywood using urea-formaldehyde (UF) and melamine-formaldehyde (MF) resins as hot-press adhesives. To reduce formaldehyde emission from flooring they add PVAc (poly(vinyl acetate)) to UF resin or MF resin. Furthermore, because PVAc also can improve the initial adhesion property of glue for fancy veneer, the productivity of flooring is increased [1–4].

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 [5]. 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 [6]. 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 [7]. PVAc adhesive is commonly known as resin emulsifier or simply as “white glue”. It is manufactured 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 [8,9]. When PVAc was added to MF resin for the adhesion between plywood

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and fancy veneer in engineered flooring, the formaldehyde emission was dramatically reduced [1].

The ONDOL floor heating system has been used conventionally in Korea since 400 BC [10]. For a short while, briquettes were used, but with Korea's rapidly increasing economic power since the 1970s, residential building has become dominated by the development of high-rise apartments featuring a modernized ONDOL system using a gas boiler instead of wood or briquettes. Hot water from a boiler is piped to the floor coil, which is an X-L pipe underneath the floor surface. The thermal storage mass consists of the cement mortar in place of the stone slab. Nevertheless, the principle of the ONDOL floor heating system has remained essentially the same, even as its form has changed. The finishing materials of the flooring material should therefore be thermo-physiologically comfortable [11,12]. 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 [13,14]. 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 22.0–38.8 °C [15–19].

Thermal analysis (TA) consists of analytical experimental techniques, which measure the thermal behavior of thermosetting adhesives as a function of temperature [20]. One of the most widely used techniques for cure kinetic studies of thermoset materials is differential scanning calorimetry (DSC) [21]. Thermogravimetric analysis (TGA) is one of the TA techniques used to measure the mass change, thermal decomposition and thermal stability of composite materials. Knowledge of the kinetic parameters associated with thermal degradation constitutes an important tool in estimating the thermal behavior of composites under dynamic conditions [22–24]. Dynamic mechanical thermal analysis (DMTA) has been widely used as a technique for investigating the structures and viscoelastic behavior of composite materials for determining their storage modulus (E'), loss modulus (E'') and loss factor ($\tan\delta$) [25]. 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 development of an ideal curing schedule [26].

The purpose of this study was to investigate the thermal properties of the blend of MF resin and PVAc for adhesion in engineered flooring for application to the ONDOL system. The thermal decomposition, thermal stability and $\mathrm{DTG_{max}}$ temperature of the blend was examined using TGA. The viscoelastic behavior, curing temperature and $\tan\delta_{max}$ of the blends were examined by DMTA and DSC.

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 75 cPs 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 molecular structures of MF resin and PVAc are shown in Fig. 1.

The fancy veneers were 0.5 mm thick, made of birch, 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. Thermogravimetric analysis (TGA)

All 5 MF resin and PVAc blends were cured in an oven at 60 °C for 1 h and analyzed thermogravimetrically in nitrogen at a heating rate of 20 °C/min. The cure temperature, 60 °C, was the temperature reported by YalçinÖ [9] and Kim [1] to maintain

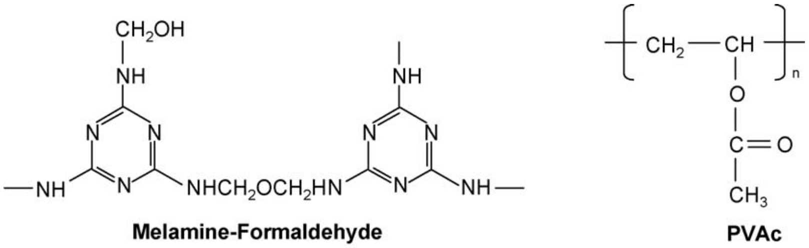

Fig. 1. Molecular structures of MF resin and PVAc.

the adhesion layer of PVAc. The adhesion layer of PVAc was delaminated at high temperature conditions over 60 °C. Ten milligrams of each cured sample were placed on a balance located in the furnace and heat was applied over the temperature range of room temperature to 800 °C using a thermogravimetric analyzer (Rheometric Scientific TGA 1000, NICEM, Seoul National University). High-purity nitrogen gas consisting of 99.5% N_2 and 0.5% O_2 was used as the inert purge gas to displace air in the pyrolysis zone in order to avoid unwanted oxidation of the sample. A constant flow was fed to the system at a rate of 20 ml/min from a point below the sample.

2.4. *Differential scanning calorimetry (DSC)*

DSC analysis with a TA Instrument Q-1000(NICEM, Seoul National University) equipped with a Thermal Analysis Data Station enabled the curing exotherms of the MF, PVAc and urea-MF resins to be determined. A sealed liquid type, aluminum capsule pan was used, under a nitrogen atmosphere, at a heating rate of 10 °C/min, between 25 and 300 °C.

2.5. *Dynamic mechanical thermal analysis (DMTA)*

The viscoelastic properties of each sample were measured from 30 to 200 °C at a heating rate of 10 °C/min 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 beech wood veneer, each 0.6 mm thick, and a three-point bending mode was applied [25]. The adhesive thickness was 0.2 mm and the sample dimensions were 28 mm × 5 mm × 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. *Thermogravimetric analysis (TGA)*

For the engineered flooring used in the ONDOL system, the adhesion layer in the engineered flooring must be able to bear up against heat. Using TGA, we can check the thermal decomposition and thermal stability of cured adhesive.

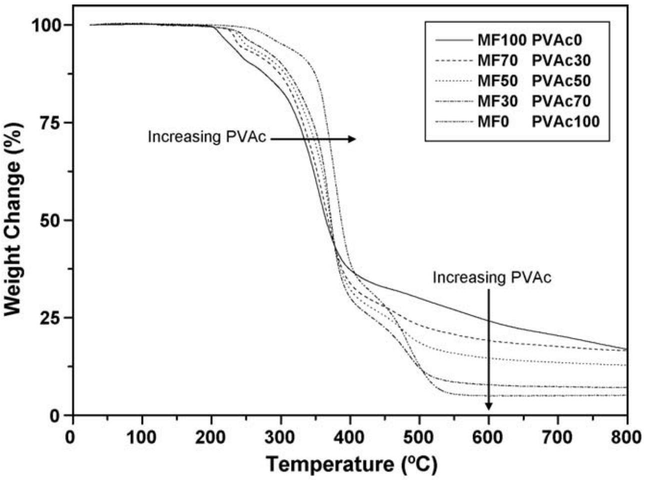

Fig. 2. Weight loss curves of cured MF resin/PVAc blends; MF resin/PVAc ratio = 100/0, 75/25, 50/50, 25/75, and 0/100 [27].

Fig. 2 shows the weight loss of the cured blends of MF resin/PVAc at a temperature range from 30 to 800 °C as measured under nitrogen atmosphere. All the cured blends showed thermal stability up to 200 °C. All MF resin/PVAc blends had a higher thermal stability. All the blends eliminated during the reaction vaporized continuously. Above 200 °C the weight loss increased markedly. This can be clearly seen in the 1st derivative of TGA curve shown in Fig. 3. The thermograms of all blends show two steps. In general, the major weight losses were observed over the range of 200–400 °C for the MF resin/PVAc blends, which may correspond to the structural decomposition of the polymers. Evidently, the thermal decomposition of these PVAc materials shifted slightly toward a higher temperature range than that of MF resin at the first step, which confirms the enhancement of thermal stability achieved with the intercalated polymer [28]. According to one report [1], although the PVAc adhesion layer was delaminated at high temperature conditions over 60 °C when PVAc is used for adhesion in engineered flooring, the high thermal stability of PVAc at the first step corresponds to the strength of hydrogen bonding in the cross-linked blends of PVAc and MF resin/PVAc. In the second step of the thermal decomposition above 400 °C, thermal stability is decreased as increasing PVAc ratio. This results are cleared from total weight loss of all MF resin/PVAc blends at 350 and 600 °C, which shown in Fig. 4. While total weight loss were decreased as PVAc contents were increased at 350 °C, total weight loss were increased as PVAc contents were decreased at 600 °C.

Fig. 5 shows the DTG_{max} temperature of MF resin/PVAc blends. All MF resin/PVAc blends were examined under the same method. Therefore, it is shown that the DTG_{max} temperature and thermal stability of the blends slightly increase with added PVAc. In fact, most of the thermosetting polymer blends found hitherto are immiscible except in the presence of favorable

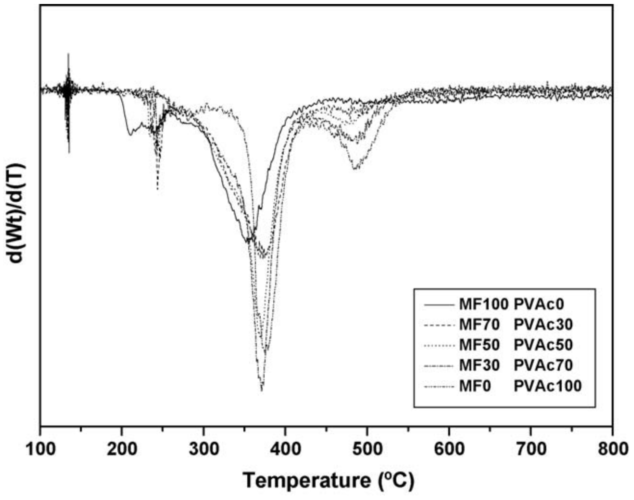

Fig. 3. DTG curves of cured MF resin/PVAc blends [27].

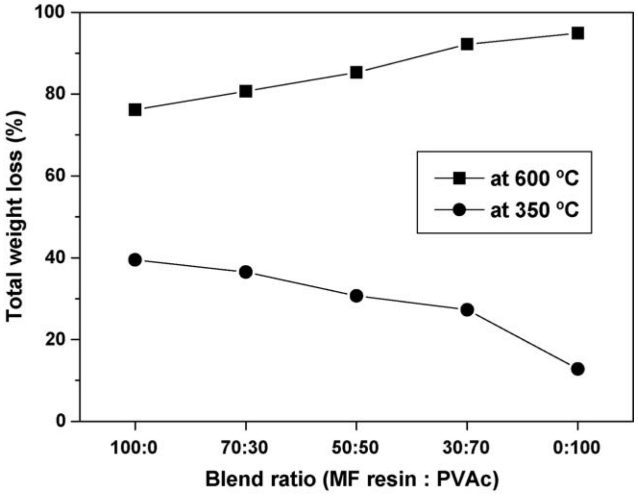

Fig. 4. Total weight loss of cured MF resin/PVAc blends at 350 and 600 °C.

intermolecular specific interactions (e.g., hydrogen bonding), which have been taken as the driving force for miscibility in some thermosetting polymer blends [29]. However, as a result the thermal stability of the blends was changed systematically and showed the effect of hydrogen bonding between MF resin and PVAc.

3.2. *Differential scanning calorimetry (DSC)*

Thermal characterization of polymer blends is a well-known method for determining their miscibility. The miscibility between any two polymers in the amorphous state is detected by the presence of a single T_g [7,13]. The effect of PVAc on the thermal properties of the blends was examined in non-isothermal DSC experiments at a heating rate of 10 °C/min. The DSC curing curves for MF resin as a function of PVAc addition are shown in Fig. 6. There is an exothermic peak in all the heating scanning curves, indicating that each blend displayed a single curing peak temperature (T_p), intermediate between those of the two pure components and varying with the blend composition. The curing reaction then began and gave rise to the exothermic peak.

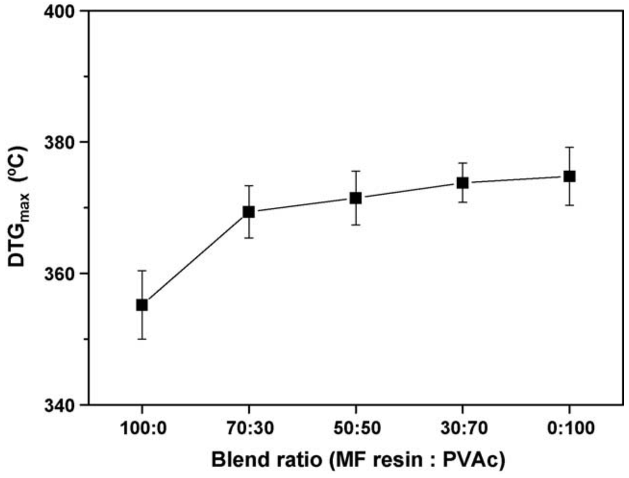

Fig. 5. DTG_{max} temperature of MF resin/PVAc blends.

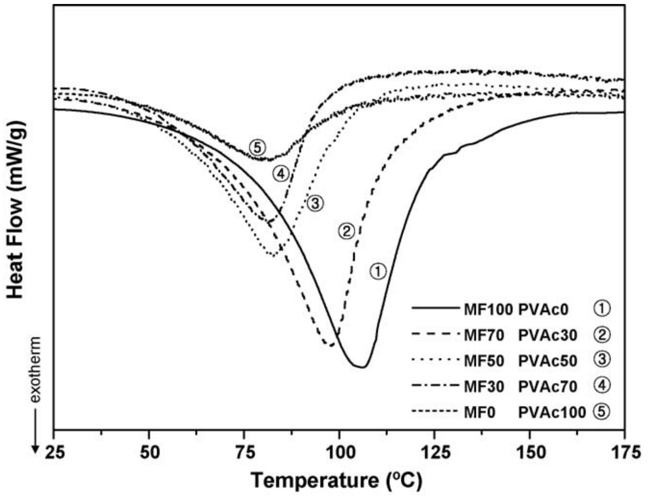

Fig. 6. DSC thermograms of MF resin/PVAc blends at a heating rate of 10 °C/min [27].

All blends are situated between the T_ps of PVAc (81 °C) and MF resin (106 °C). In the figure, the curing exotherms of the MF resins with added PVAc are shifted to a higher temperature than that for the 100% PVAc.

It can thus be concluded that the MF resin/PVAc blends are completely miscible in the amorphous state. From Fig. 7, with an increasing ratio of PVAc to the MF resin, ΔH was decreased to a higher temperature. The amino group in melamine accepts easily up to two molecules of formaldehyde. Thus, up to six molecules of formaldehyde can be attached to one molecule of melamine. This methylolation step leads to a series of methylol compounds with two to six methylol groups [30].

3.3. *Dynamic mechanical thermal analysis (DMTA)*

Dynamic thermal mechanical test methods have been widely used for investigating the structures and viscoelastic properties of thermosetting adhesives [25,31].

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

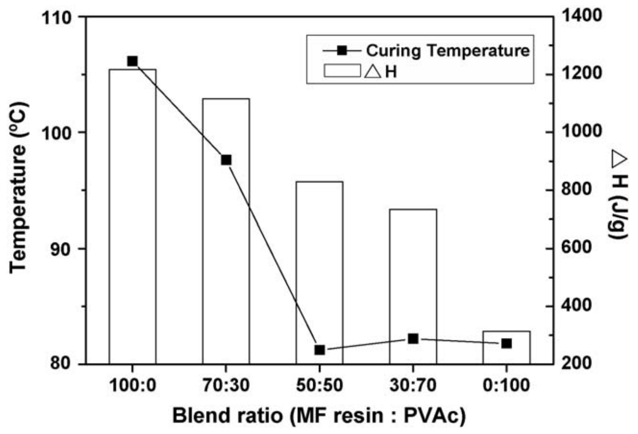

Fig. 7. Curing temperature and ΔH of MF resin/PVAc blends.

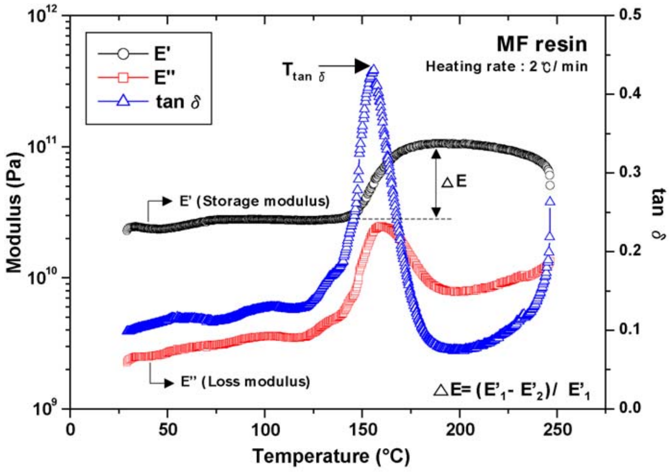

Fig. 8. DMTA thermogram during heating ramp of MF resin at a heating rate of 2 °C/min.

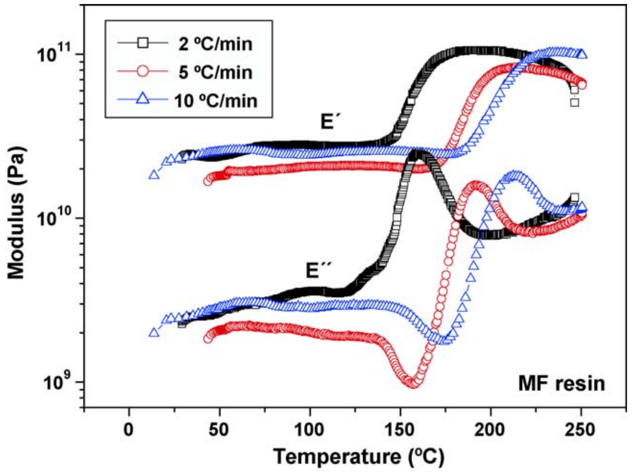

Fig. 9. Storage modulus (E') and loss modulus (E'') of MF resin at different heating rates: 2, 5 and 10 °C/min.

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 $\tan\delta$ of each adhesive system were obtained by DMTA. Fig. 8 shows E', E'' and $\tan\delta$ 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. 8 shows that 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 $\tan\delta$ peak. The $\tan\delta$ 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 $\tan\delta$ 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 $\tan\delta$ value in this temperature range.

E' and E'' results for the MF resins are shown in Fig. 9. 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 °C at a heating rate of 2 °C/min, 191 °C at 5 °C/min and 213 at 10 °C/min. These results showed that the heating rate affected the curing behavior of the thermosetting resin. Damping curve in Fig. 10, this tendency is shown in detail. The temperatures corresponding to the maximum values of $\tan\delta$ were in the order of the heating rate. From the $\tan\delta$ results, the peak of the $T_{\tan\delta}$ values were 156 °C at a heating rate of 2 °C/min, 191 °C at 5 °C/min and 205 °C at 10 °C/min. The heights of the $\tan\delta$ peaks were also different. The highest peak was observed also for a heating rate of 10 °C/min, with the $\tan\delta$ peaks being in the order 2 °C/min > 5 °C/min > 10 °C/min. These $T_{\tan\delta}$ peak values and maximum value of E'' of MF resin at different heating rate are shown in Fig. 11.

In Fig. 12, E' and E'' 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

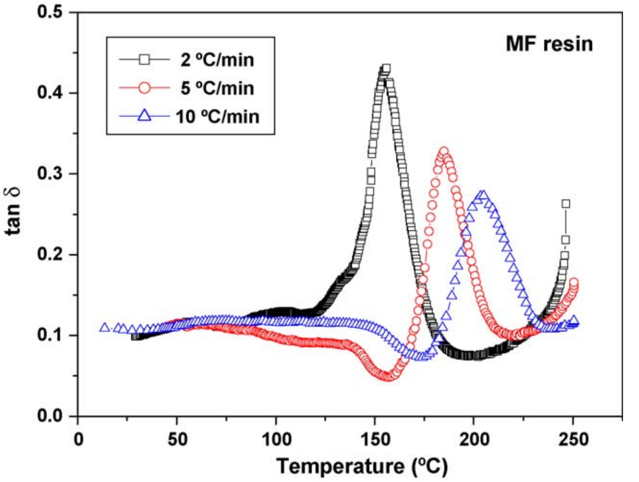

Fig. 10. Loss factor (tan δ) of MF resin at different heating rates: 2, 5 and 10 °C/min.

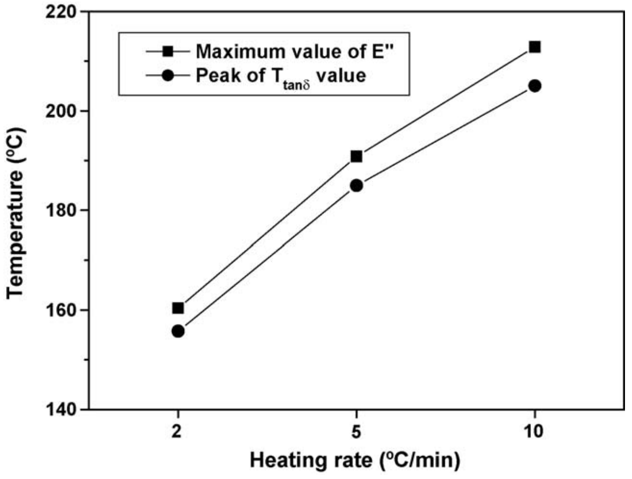

Fig. 11. $T_{\tan\delta}$ peak values and maximum value of loss modulus (E'') of MF resin at different heating rates: 2, 5 and 10 °C/min.

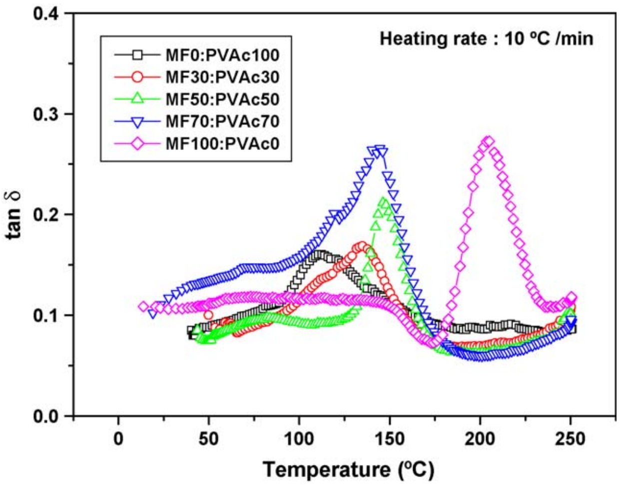

Fig. 13. Loss factor (tan δ) of MF resin/PVAc blends at a heating rate of 10 °C/min.

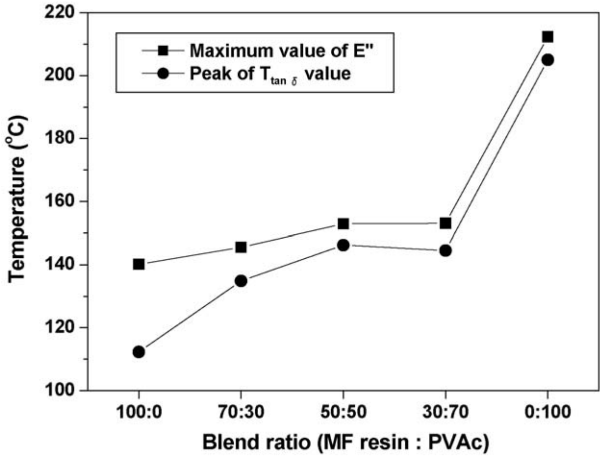

Fig. 14. $T_{\tan\delta}$ peak values and maximum value of loss modulus (E'') of MF resin/PVAc blends at a heating rate of 10 °C/min.

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. 13 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 increasing MF resin content. The $T_{\tan\delta}$ peak values and the maximum value of E'' of MF resin/PVAc blends are shown in Fig. 14.

From this different behavior between thermosetting and waster 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 [29].

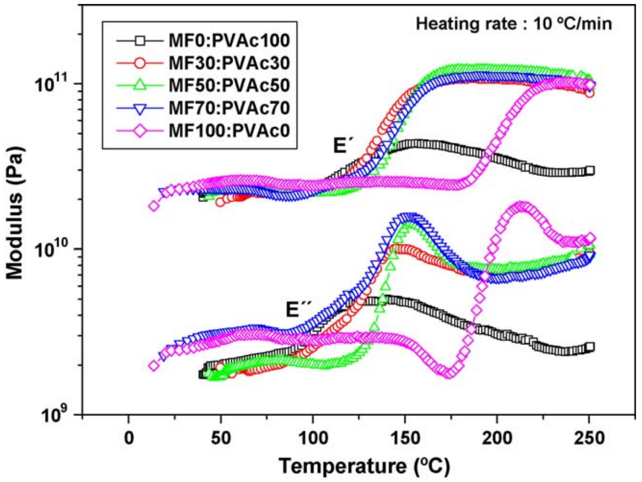

Fig. 12. Storage modulus (E') and loss modulus (E'') of MF resin/PVAc blends at a heating rate of 10 °C/min.

4. Conclusion

For use in the ONDOL floor heating system, the adhesives manufactured by blending MF resin and PVAc showed higher thermal stability as determined by TGA. All the cured blends, with PVAc weight content of 0, 30, 50, 70 and 100%, showed thermal stability up to 200 °C. Above 200 °C the weight loss increased markedly. The DTG$_{\max}$ temperature increased with increasing PVAc content. In addition, the mass loss of higher PVAc content sample began at a higher temperature than that of MF resin. The DSC results showed an exothermic peak in all the heating scanning curves, indicating that each blend displayed a single curing T_p, intermediate between those of the two pure components and varying with the blend composition. 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. The MF/PVAc hybrid resin system can be recommended using as adhesive in high temperature under heating system from these thermal behaviors.

Acknowledgement

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