Initial tack and viscoelastic properties of MF/PVAc hybrid resins used as adhesives for composite flooring materials

Sumin Kim & Hyun-Joong Kim

Initial tack and viscoelastic properties of MF/PVAc hybrid resins used as adhesives for composite flooring materials

SUMIN KIM and HYUN-JOONG KIM *

*Lab. of Adhesion & Bio-Composites, Major in Environmental Materials Science,
Seoul National University, Seoul 151-921, South Korea*

Abstract—The initial tack and viscoelastic properties of blends of melamine–formaldehyde (MF) resin and poly(vinyl acetate) (PVAc) emulsion on decorative veneer and plywood surfaces were investigated using a texture analyzer and dynamic mechanical thermal analysis (DMTA) at room temperature with respect to the 'open time', the time delay between applying an adhesive to a surface and contacting that surface with the other material. We determined and compared the effects of PVAc content, at 0, 30, 50, 70 and 100 wt%, in blends with MF resin. As PVAc is curable at room temperature, PVAc markedly affected the initial tack, as well as DMTA results. The degree of 'tack' was determined quantitatively based on the probe tack data. As the adhesion in an engineered flooring should be achieved in 2–3 min, the acceptable tack range is between 100 and 200 g. From the DMTA results, i.e., the $\tan \delta_{\max}$ values, the maximum loss modulus (E'') and the rigidity ($\triangle E$) of MF/PVAc blends at room temperature, it was found that $\tan \delta$ and loss modulus (E'') increased with increasing MF resin content. Moreover, the rigidities of the 70 : 30 and 50 : 50 MF/PVAc blends were higher than those of the other blends, especially in comparison with the pure 100% PVAc and 100% MF. We conclude that the initial tack correlates with the MF/PVAc blend ratio during the adhesion process at room temperature.

Keywords: Initial tack; viscoelastic property; melamine–formaldehyde resin; poly(vinyl acetate); decorative veneer; engineered flooring.

1. INTRODUCTION

Poly(vinyl acetate) (PVAc) adhesive is commonly known as an emulsion resin or simply as 'white glue'. It is manufactured by polymerizing vinyl acetate monomer and stabilizers with other monomers to form copolymers. It is supplied in a liquid form with viscosity ranging from 2000 to 3000 cP at 21°C. PVAc is an odorless, non-flammable adhesive. It can be used in cold temperatures and it solidifies

---

*To whom correspondence should be addressed. Tel.: (82-2)880-4784. Fax: (82-2) 873-2318.
E-mail: hjokim@snu.ac.kr

UV coating layer

Decorative veneer (0.5 mm)
Plywood (7.2 mm)
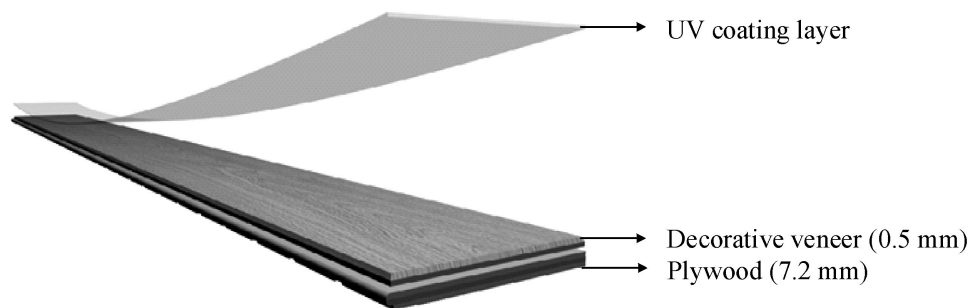
**Figure 1.** Structure of an engineered wood flooring.

quickly. Its application is straightforward and it does not damage cutting tools. However, its mechanical resistance decreases with increasing temperature, and it rapidly loses its ability to bond at $> 70°C$ [1–3].

   Generally, there are three types of wood floorings: laminate, engineered, and solid wood. Laminate floorings have high-density fiberboard (HDF) as the core material, whereas an engineered flooring consists of plywood with a thin decorative veneer bonded onto the face of the plywood with urea–formaldehyde (UF) and melamine–formaldehyde (MF) hot-press adhesive resins. The structure of an engineered flooring is shown in Fig. 1. To reduce formaldehyde emission from flooring, PVAc is added to UF resin or MF resin. Furthermore, as PVAc can also improve the initial tack of the decorative veneer, production productivity of an engineered flooring is increased [1, 4, 5]. However, as Creton and Leibler [6] indicated, those who manufacture an engineered flooring use the touch 'tack' to assess the initial cure. Simply, some time after spreading the adhesive on the plywood, the operator touches the freshly adhesive-covered surface and by removing his finger assesses the tack, i.e., the adhesion he feels on removing his finger. The question then is how to quantify this feeling of 'tackiness', and, in particular, what test can be used to reproducibly measure this effect? Clearly two process stages have to be distinguished: bonding (applying the finger) and debonding (removing the finger).

   The tack, or 'instantaneous adhesion', is one of the most important properties of a pressure-sensitive adhesive, and is a reflection of the adhesive's ability to form bonds with a substrate at low pressure and in a short contact time. The tack is measured using two methods: the probe tack test and the rolling ball tack test [7].

   The tack has been studied intensively and the probe tack test is a simple test whereby a cylindrical probe is brought into contact with a thin film of adhesive (thickness typically 50–300 μm) for a short time (a few seconds), after which it is pulled away at a constant velocity V ranging between 0.001 and 100 μm/s. Although this tack test is rather simple, it is governed by a range of parameters [8, 9]:

– Adhesive viscosity, mechanical properties and the degree of cross-linking.

– Adhesive film thickness (e) and cross-sectioned area (A_0).
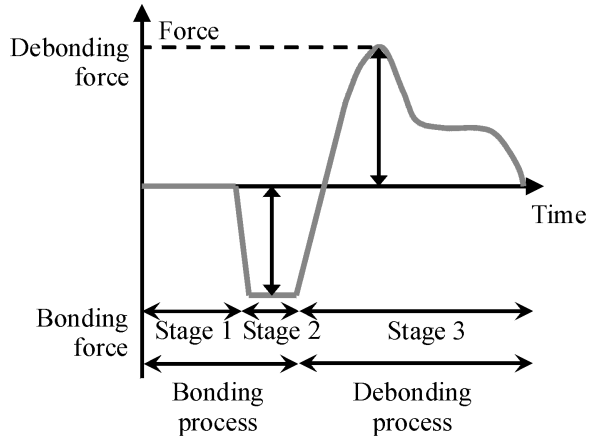
Figure 2. Force–time curve from a typical probe tack test.

– Probe radius.
– Probe velocity (V) and applied force [$F(t)$].
– Contact time (t_c) and applied pressure (P).
– Temperature (T) and relative humidity (RH).
– Surface treatment and surface roughness (of both substrate and probe).

A typical probe tack test can be divided into three stages (Fig. 2). In the first stage, a flat, stainless-steel probe approaches the adhesive layer applied to a microscope glass slide at a constant velocity. When the contact pressure (CP) reaches the set pressure, the probe stops (stage 2) for a contact time (t_c) of 1 s. The probe is then removed during stage 3 at a constant debonding velocity (V_{deb}) [10].

Thermal analysis is a powerful technique for studying the kinetics of physico-chemical processes, making time–temperature predictions and optimizing process variables. Another popular technique, which is based on heat evolution during the course of a reaction, is the adiabatic reactor technique. This requires a highly reactive polymerizing mixture at a set initial temperature [11].

The dynamic mechanical technique, which involves application of a sinusoidally oscillating stress to a material and determines the resultant strain, 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 temperature probe measurements alone. The complex viscous and time-dependent behaviors of polymers make the dynamic mechanical testing such a useful means of characterizing. One of the most common uses of dynamic mechanical testing is for the determination of the glass transition temperature (T_g), and an important application area for dynamic mechanical thermal analysis (DMTA) is in monitoring the resin curing. DMTA is highly dependent on the curing process and isothermal experiments enable optimal curing schedule to be developed [12].

In this study, we focused on investigating the effect of adding PVAc to enhance the initial tack using the probe tack test and by measuring the viscoelastic properties of MF and PVAc blends. The initial tack of blends was studied by determining the probe tack strength and the viscoelastic properties were measured by DMTA at room temperature. In addition, we investigated correlations between the initial tack and the viscoelastic properties at room temperature.

2. EXPERIMENTAL

2.1. Materials

The MF resin was synthesized in the laboratory. Briefly, the resin was prepared at an F/M molar ratio of 1.75, with a solid content of 49 wt%. 37% formalin from Duck San (South Korea) was used. The pH was adjusted to 9.0 by adding 1 M NaOH solution (because methylated intermediates of the reaction rapidly condense under acidic conditions) and then melamine was added. It was synthesized at 80°C. As a hardener, 10% NH_4Cl solution was used. The viscosity as measured using a Brookfield Viscometer Model DV-II+ was 140 cP (spindle No. 6 at 21°C). PVAc in the liquid form was used with the following characteristics: density, 1.1 g/cm^3; viscosity, 700 000 cP at 21°C; pH, 5; and solid content, 65 wt%. PVAc adhesive was supplied by Tae Yang (Incheon, South Korea).

2.2. Blend preparation

Blends with various MF resin/PVAc ratios were prepared. To determine and compare the effect of PVAc content, compositions containing 0, 30, 50, 70 and 100 wt% of MF resin were used. Blends were stirred together by a mechanical stirrer and in all there were 5 blend systems; containing MF 100, MF 70 : PVAc 30, MF 50 : PVAc 50, MF 30 : PVAc 70 and PVAc 100 wt%.

2.3. Probe tack test for initial tack

Each blend (*ca.* 1.2 g) was coated onto a stainless steel plate, MDF and engineered flooring plywood of dimensions 5 cm (width) × 15 cm (length). Tack tests for initial tack were conducted using a Texture Analyzer (TA-XT2i, Stable Micro Systems, UK) with a polished stainless steel cylindrical probe of diameter 5 mm, which was designed to measure force (F) *versus* time required to break the adhesive bond at controlled rates of separation, temperature, contact pressure and contact time. Measurements were conducted at four different blend open times, i.e., the delay time after applying the blend to the substrate (1, 3, 5 or 10 min) and bringing in contact with the probe, at three different probe contact times (0.5, 1 or 2 s), and at three different contact pressures (70, 100 or 120 g/cm^2). The blends were coated on stainless steel, MDF and decorative veneer with a bar coater (no. 22). The probe approached the blend layer at a constant velocity (V_{app} = 10 mm/s). When the

contact pressure reached 70, 100 or 120 g/cm^2, the probe was stopped for a contact time of 0.5, 1 or 2 s. The probe was removed at a constant debonding velocity (V_{deb}) of 0.5 mm/s. The tack test was conducted in a constant temperature/humidity room, at 20°C and 50% RH. The probe used in this test was a polished, stainless steel probe with an average roughness of $R_a = 10$ nm, as measured with an optical profilometer. The probe was cleaned with acetone after each test. Because these adhesives are typically insensitive to small amounts of contamination from organic materials, this cleaning procedure was considered adequate to obtain accurate and reproducible results.

2.4. Contact-angle measurements

To determine the wettability of the three substrates, stainless steel, decorative veneer and MDF, static contact angles were measured using a surface measurement system, video contact angle analyzer (VCA) (Phoenix 600, SEO, South Korea) 10 min after depositing the drop. The VCA was used to register angles on both sides of the drop. Contact angles were recorded with MF resin, by averaging the measurements of five 10-μl drops on all three substrate specimens. Because of high viscosity of blends and PVAc, contact angles were measured only with MF resin.

2.5. Dynamic mechanical thermal analysis (DMTA)

The viscoelastic properties of all samples were determined at room temperature using a dynamic mechanical thermal analyzer (DMTA; Rheometric Scientific DMTA mark IV). As the initial tack is used to determine tack at room temperature before hot pressing, we examined the viscoelastic properties of the blends using DMTA at room temperature for 8000 s (40 000 s in the case of 100% MF resin). As the blends were viscous materials, the DMTA samples were prepared by sandwiching the blends between two layers of beech wood veneer, each 0.6 mm thick, as shown in Fig. 3, and a three-point bending mode was applied [13]. The blend 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 at a strain of 0.05.
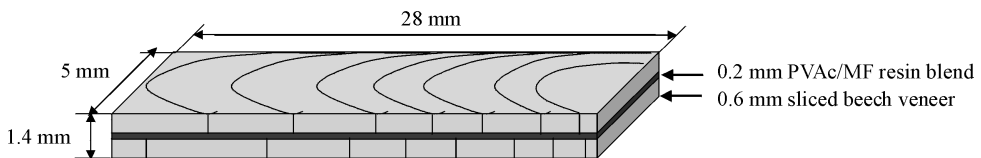
**Figure 3.** Sample configuration for DMTA (three-point bending mode) test.

3. RESULTS AND DISCUSSION

3.1. Initial tack

Although the end-use of the MF/PVAc blends was on decorative veneer and plywood surfaces, we applied them to stainless steel, medium density fiberboard (MDF) and decorative veneer because the surface of the plywood that is normally used for an engineered flooring is too rough for an accurate tack measurement. During flooring manufacturing process, the adhesive is spread for 1–2 min before the surfaces are contacted together. During this process, the adhesive must develop an optimum tack, to ensure that the two surfaces do not move relative to each other during subsequent processing, i.e., during cutting operations.

Figure 4 shows typical experimental curves of probe tack force as a function of time for an 50:50 MF/PVAc blend on a stainless steel plate with different open assembly times ($V_{deb} = 0.5$ mm/s). Increasing the open assembly time clearly increased the maximum probe tack force, decreased the strain and increased the blend viscosity as the water was evaporated. The curves did not show a plateau before complete debonding, and the debonding occurred suddenly, especially at the longest open assembly time.

Figure 5 shows the maximum initial tack for an 50:50 MF/PVAc blend on stainless steel. Generally, with increasing contact time of the probe with the blend prior to release, the tack increased, which is similar to the behavior of pressure-sensitive adhesives (PSAs) reported by Zosel [8]. With increasing open assembly
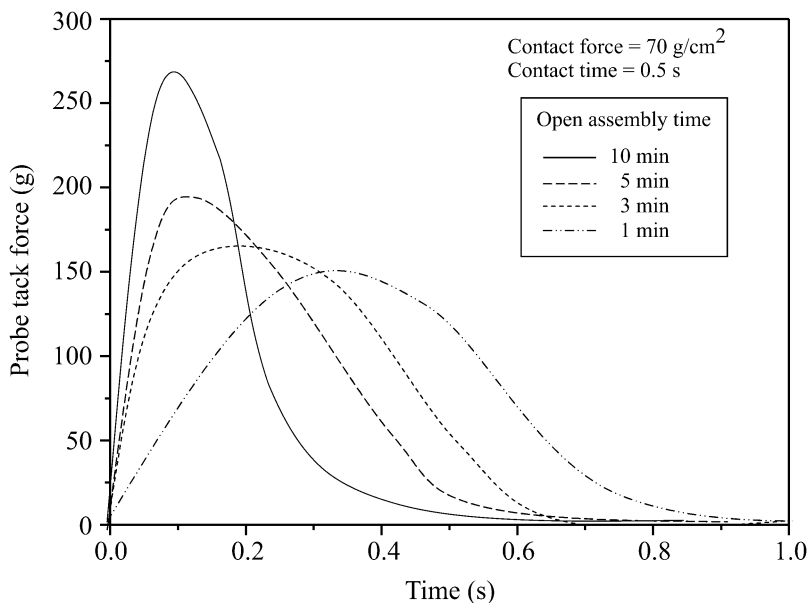

Figure 4. Typical experimental curves obtained in the probe tack test on an 50:50 MF:PVAc blend at various open assembly times.

time, the contact force slightly increased at 10 min, but for most cases of stainless steel it did not change. As time passed, the adhesive became stickier because the volatiles, such as solvent and water, evaporated. Furthermore, because 10 min are inadequate to allow the water to evaporate and there is no interaction between the liquid thermosetting resin and the stainless steel, we did not expect the tack on stainless steel to increase with open time. However, the results in Figs 6 and 7 for the maximum initial tack on MDF and decorative veneer differ. The tack was low at 1 min, especially in the case of MDF. As MDF is manufactured from wood fibers
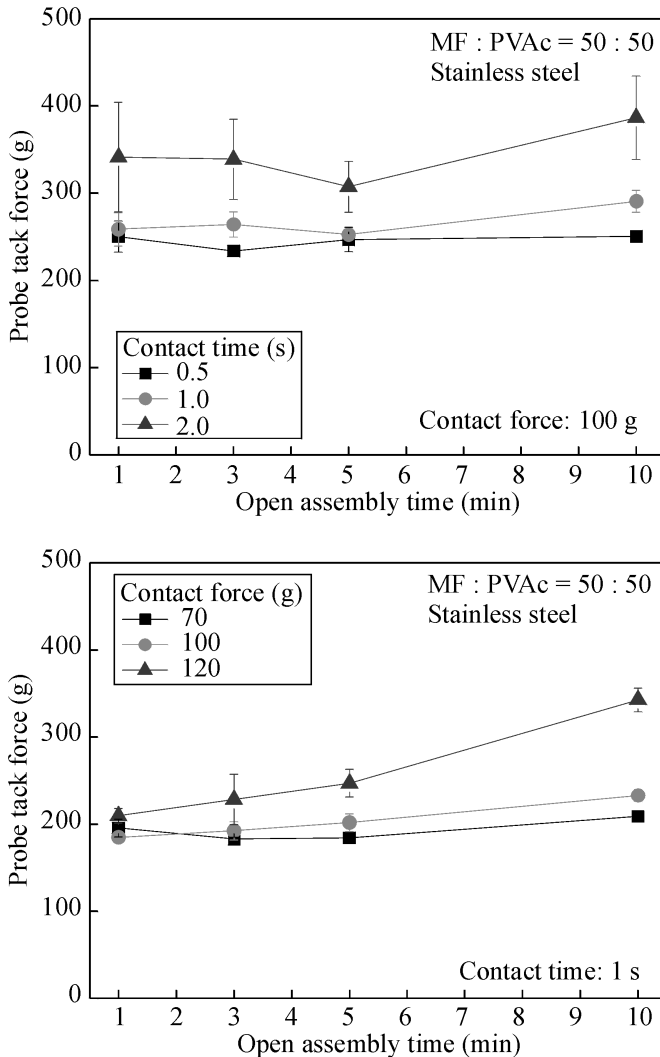
Figure 5. Probe tack force of 50 : 50 MF/PVAc blend on stainless steel as a function of open assembly time.
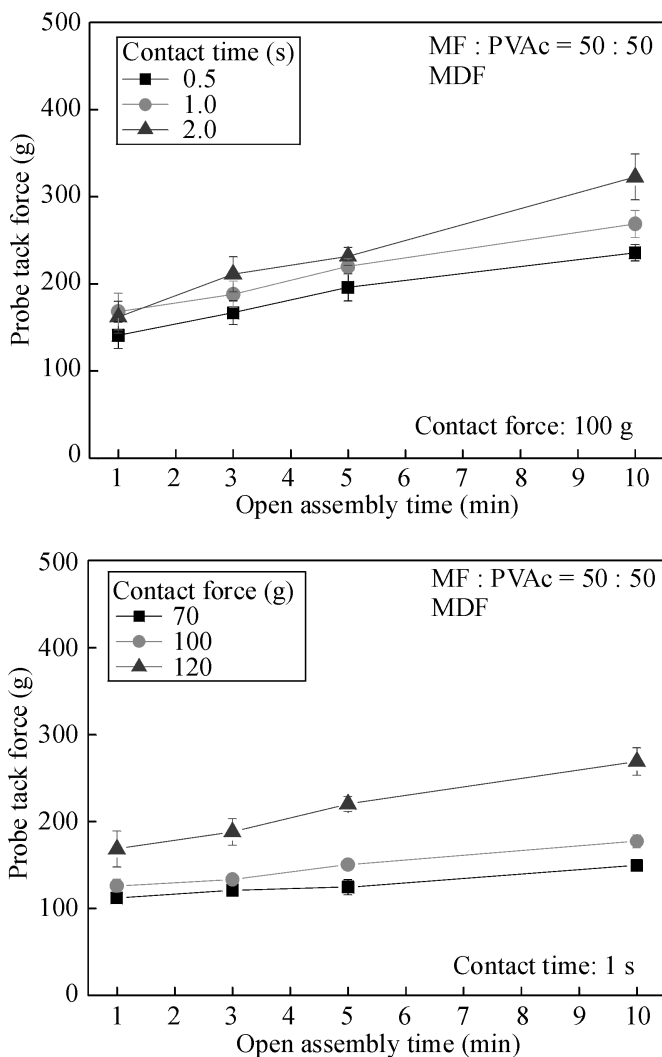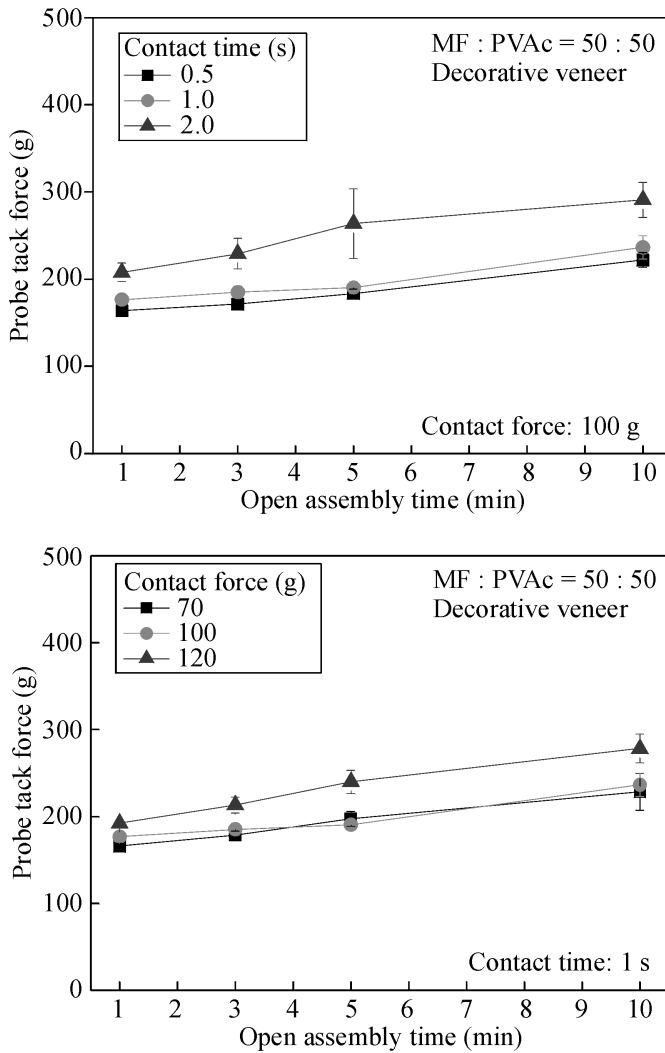
Figure 6. Probe tack force of 50 : 50 MF/PVAc blend on MDF as a function of open assembly time.

which are absorbing so the adhesive solvents are absorbed rapidly by MDF, and the adhesive wets the substrate rapidly due to hydrogen bonding between the wood fiber and water. The wettability of plywood was lower than that of MDF.
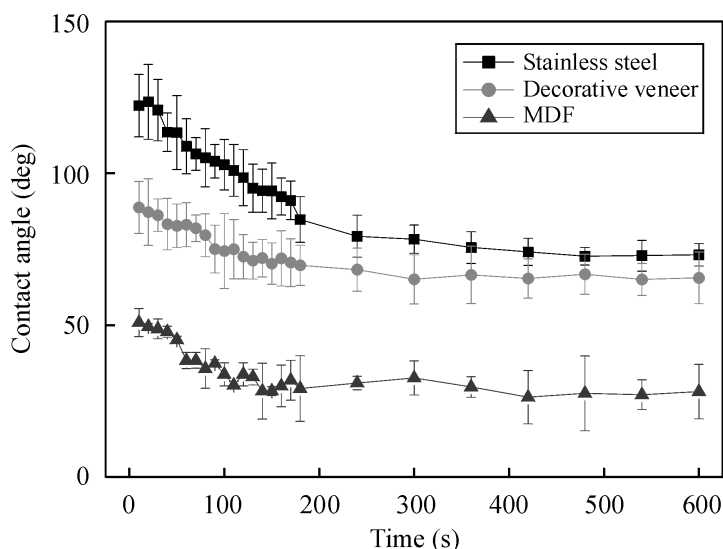
MF resin contact angles on the three substrates versus time are shown in Fig. 8. Contact-angle analysis is widely used to study the wetting characteristics of solid materials [14]. A goniometer equipped with a video camera was used to obtain the contact angles of MF resin on stainless steel, decorative veneer, and MDF. As can be seen from Fig. 8, contact-angle values on decorative veneer were higher than those on MDF. The tack results at 1 min were higher on decorative veneer than on MDF. As the contact force, we obtained a higher tack at 120 g pressure, although the

Figure 7. Probe tack force of 50 : 50 MF/PVAc blend on decorative veneer as a function of open assembly time.

results at 70 and 100 g were very similar. This tendency for maximum initial tack to vary with changes in substrate, contact time, contact force and open assembly time was also demonstrated with other blend ratios.

Figure 9 lists the initial tack of all blend ratios and experimental conditions such as substrates, contact times, contact forces and open assembly times. The tack of the 100% MF resin was the lowest because it is a thermosetting resin. Thus, the addition of PVAc increased the initial tack of MF resin dramatically, especially for MDF and decorative veneer. The highest tack by the 50 : 50 MF/PVAc blend and the lowest by the 100% MF resin indicates that the optimal initial tack must be in this

Figure 8. MF resin contact angles on the three substrates *versus* time.

blend range and contact pressure between 100 and 200 g. These values are much lower than those of over 500 g for general SIS-based hotmelt PSA and water-borne acrylic PSA [15]. The blends we tested were not designed for optimal adhesion between decorative veneer and plywood, like PSAs. The process of adhesion for an engineered flooring should be accomplished within 2–3 min and a tack with a range between 100 and 200 g is acceptable. Figure 10 shows the tack property versus open assembly time for all blend ratios. Up to an open assembly time of 5 min, most tack data were within the optimal initial tack range, whereas at 10 min most results were out of this range. However, at an open assembly time of 10 min, the tack results were higher than the acceptable tack range. This acceptable tack range can replace the thumb test in the process of manufacturing an engineered flooring because the thumb test does not characterize the performance of adhesives for engineered floorings.

### 3.2. Dynamic mechanical thermal analysis (DMTA)

Dynamic mechanical thermal test methods have been widely used to investigate the structure and viscoelastic properties of thermosetting adhesives [13, 16]. However, we used DMTA to investigate the curing behavior and solidification of all MF/PVAc blends at room temperature, because we focused on the performance of adhesives spread on plywood before hot pressing. Kim and co-workers reported on the curing behavior of thermosetting resins using the DMTA method of increasing temperature [13, 17, 18]. Thermosetting resins are in a liquid state at room temperature and become solid at high temperature after curing has taken place. DMTA is able
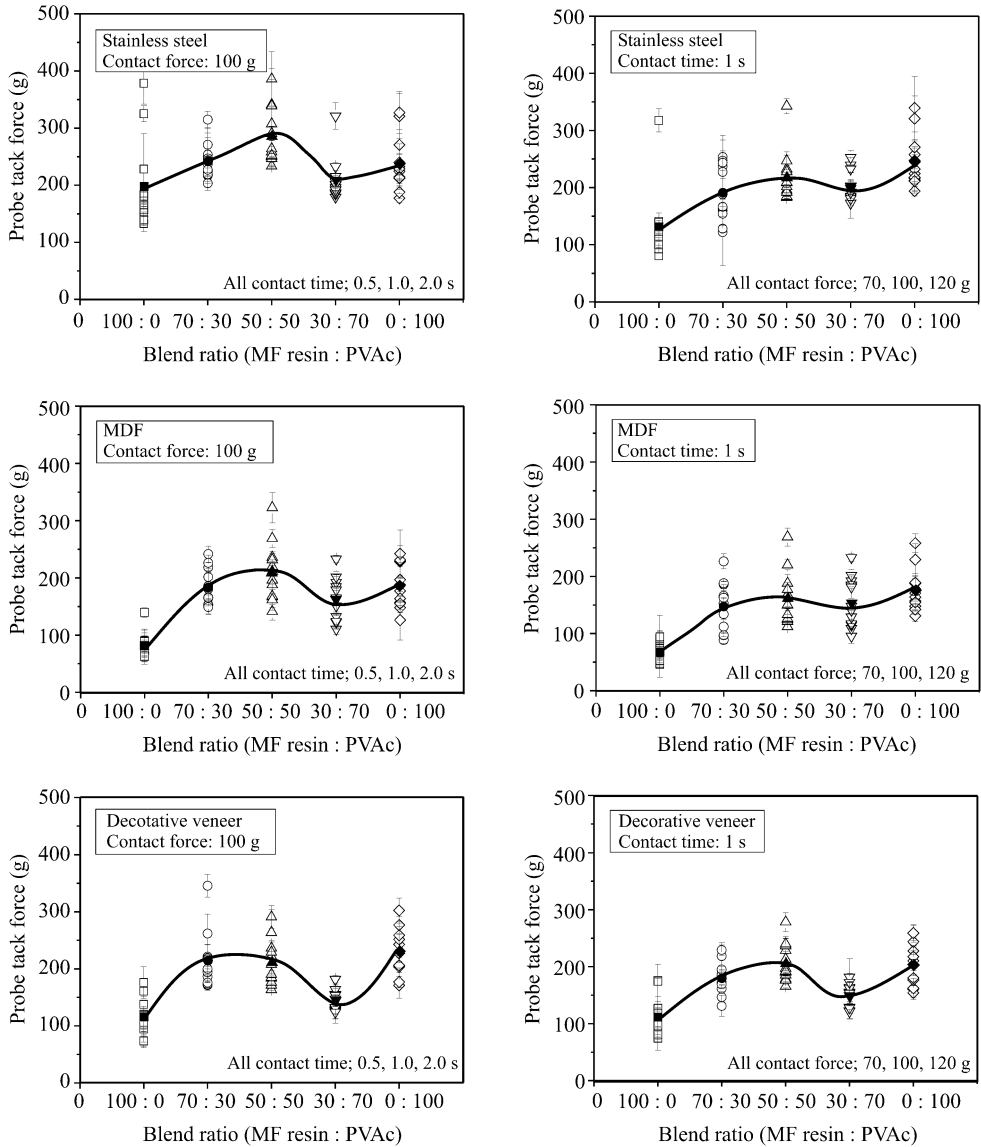
Figure 9. Probe tack force of all blends on stainless steel, MDF and decorative veneer.

to detect certain 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 ($\tan\delta$) of each blend system were obtained by DMTA. From the DMTA thermograms, we checked the viscoelastic properties of all blends in the liquid state by using wood veneer. Figure 11 shows DMTA thermograms under isothermal conditions for 100% PVAc and a 50:50 MF/PVAc blend at room temperature and
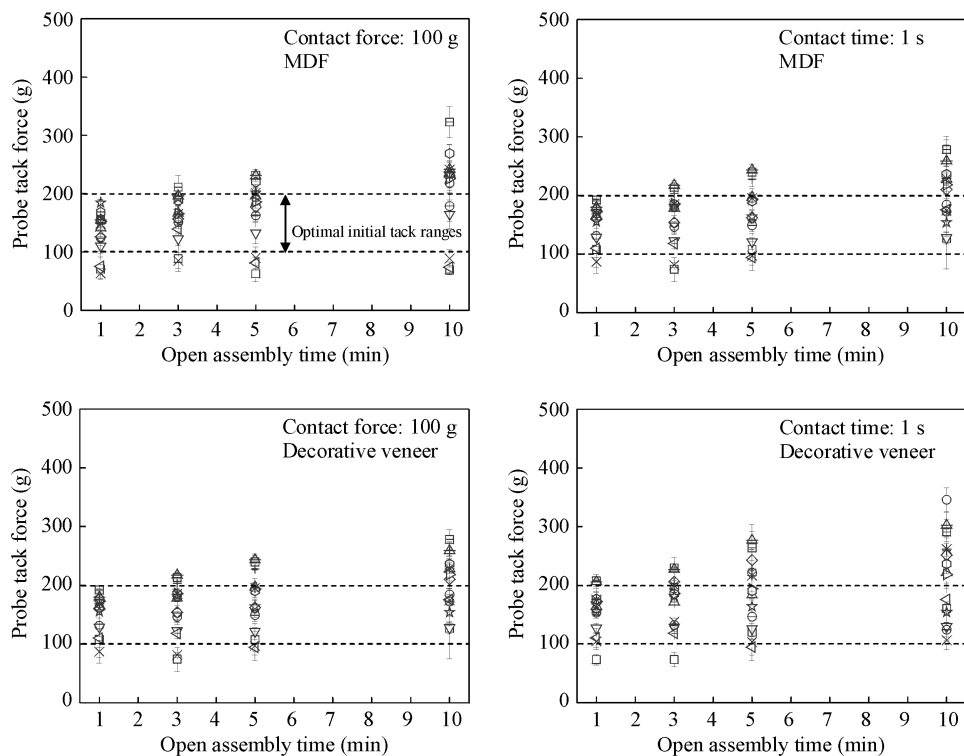
Figure 10. Optimal initial tack range by probe tack of all blends on MDF and decorative veneer as a function test on open assembly time.

over a period of 4000 s. The peak indicating the curing point, maximum $\tan \delta$, and increasing rigidity from storage modulus (E') are clearly evident. With passing time, i.e., increasing open assembly time, PVAc becomes solid as solidification and curing occur. 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 lower, as shown in Fig. 11. The test time of 4000 s was too short to show the solidification of MF resin. MF resin cannot be cured at room temperature. Thus, we tested it for 40 000 s, almost 12 h, as shown in Fig. 12. A maximum $\tan \delta$ was shown but the curing degree from storage modulus (E') remained low.

The results of $\tan \delta$ for all blends are shown in Fig. 13. From the $\tan \delta$ results, the $t_{\tan \delta_{max}}$ values were 1548 s for 100% PVAc, 1978 s for the 30 : 70 MF/PVAc blend, 3015 s for the 50 : 50 blend, 4203 s for the 70 : 30 blend and 6969 s for 100% MF resin. With increasing MF resin content, $t_{\tan \delta_{max}}$ was shifted toward a longer time. In their investigation involving frequency sweeps at different temperatures, Roos *et al.* [10] reported that the shift of the $\tan \delta$ peak in frequency could be clearly seen because of the phase behavior of the polymer blend. However, in this case, as there
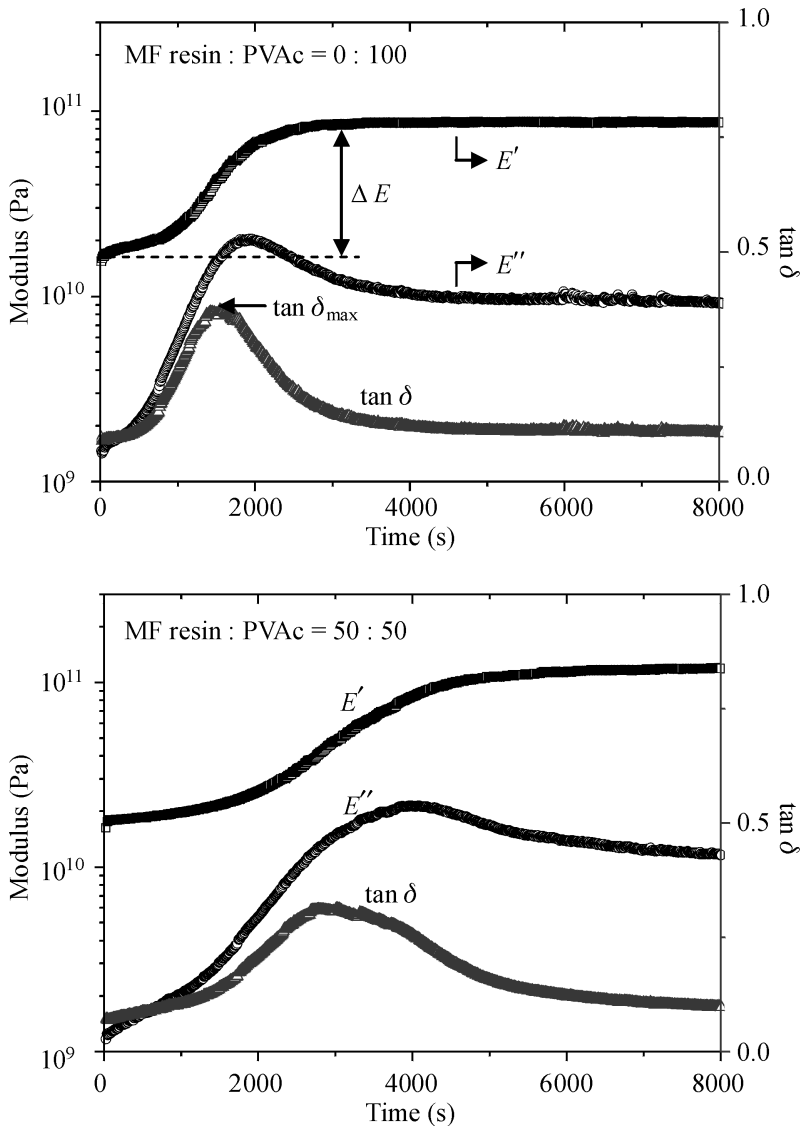
Figure 11. DMTA thermograms from isothermal tests on 100% PVAc and 50 : 50 MF/PVAc blends at room temperature.

was no heating, the high content of thermosetting MF resin caused the shift of $t_{\tan\delta}$ toward a longer time. We can suppose that $t_{\tan\delta}$ will be shifted toward a shorter time at temperatures higher than the room temperature, as shown by Novikov *et al.* [19] in their dynamic mechanical results on poly(N-vinyl pyrrolidone)–poly(ethylene glycol) blends which were highly shifted in temperature.

The heights of the $\tan\delta$ peaks were also different. The highest peaks were observed for resins with a high MF ratio, and the $\tan\delta$ peak increased with the
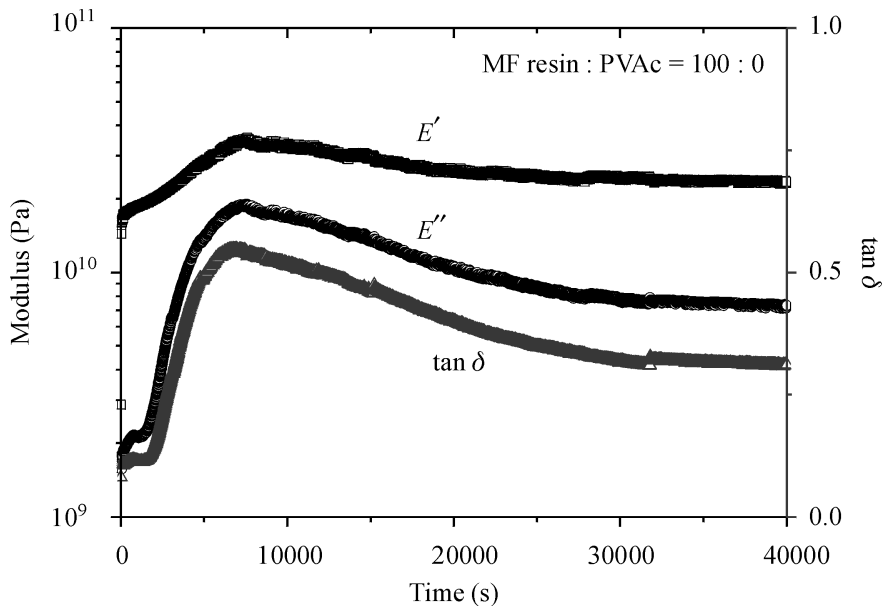
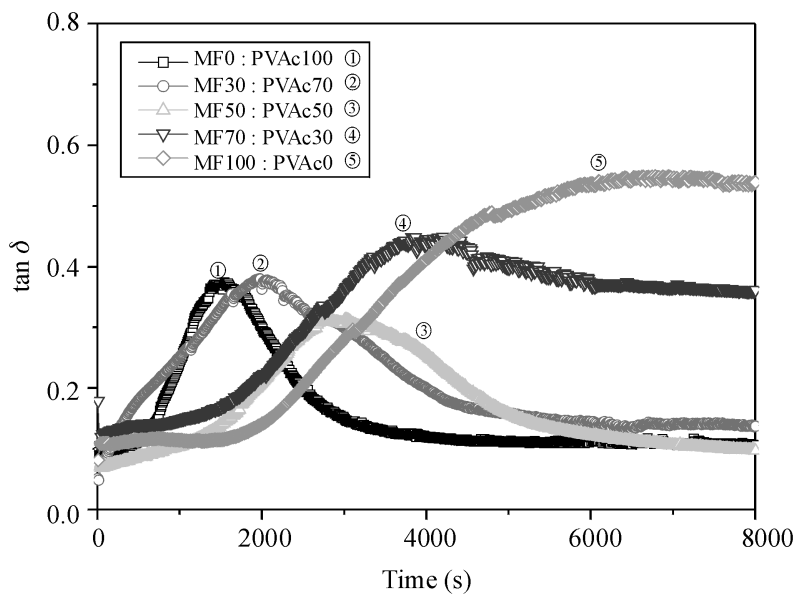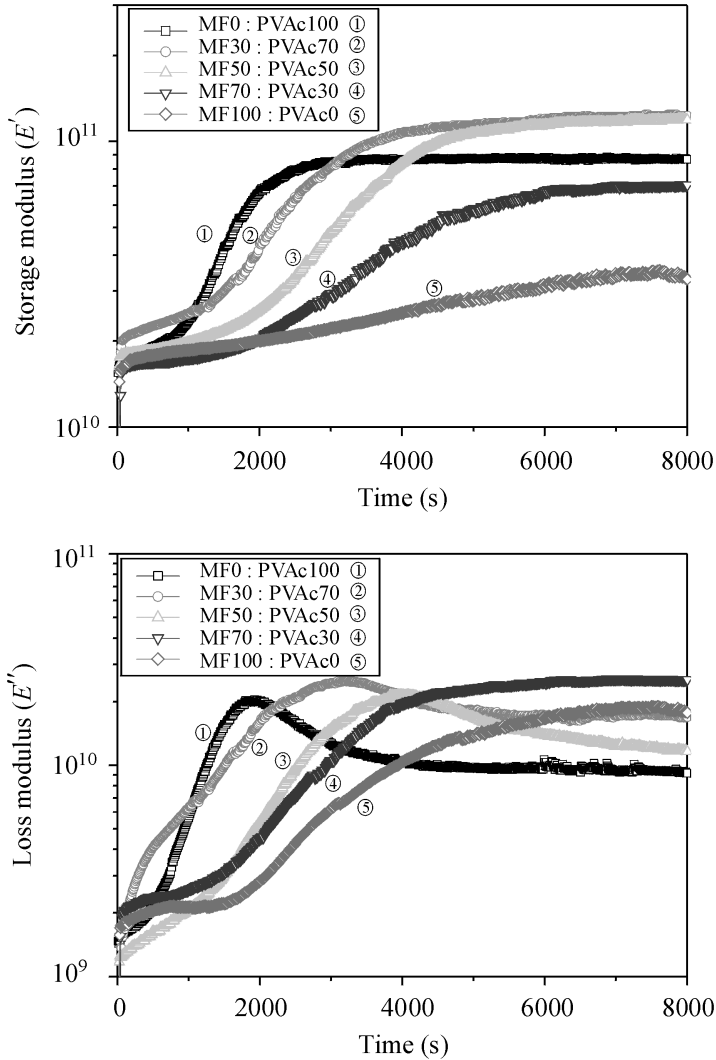**Figure 12.** DMTA thermograms from isothermal tests on 100% MF resin at room temperature.

Figure 13. Loss factor ($\tan\delta$) of PVAc, MF resin and MF/PVAc blends at room temperature as determined by the isothermal method.

Figure 14. Storage modulus (E') and loss modulus (E'') of PVAc, MF resin and MF/PVAc blends at room temperature as determined by the isothermal method.

addition of MF resin, but there was only a little difference between this result and that for 50 : 50 MF/PVAc blend. The storage modulus (E') and loss modulus (E'') of MF/PVAc blends at room temperature are shown in Fig. 14. The storage modulus (E') increased with increasing PVAc content. All blends were initially in a liquid state and then solidified. With increasing MF content, degree of cure and rigidity ($\triangle E$) remained unchanged. However, at higher MF contents of 70% and 100%, the cure rate was too low due to their thermosetting nature. Rigidity ($\triangle E$) increased as the MF content increased to 50%, but then decreased. A high MF level in the
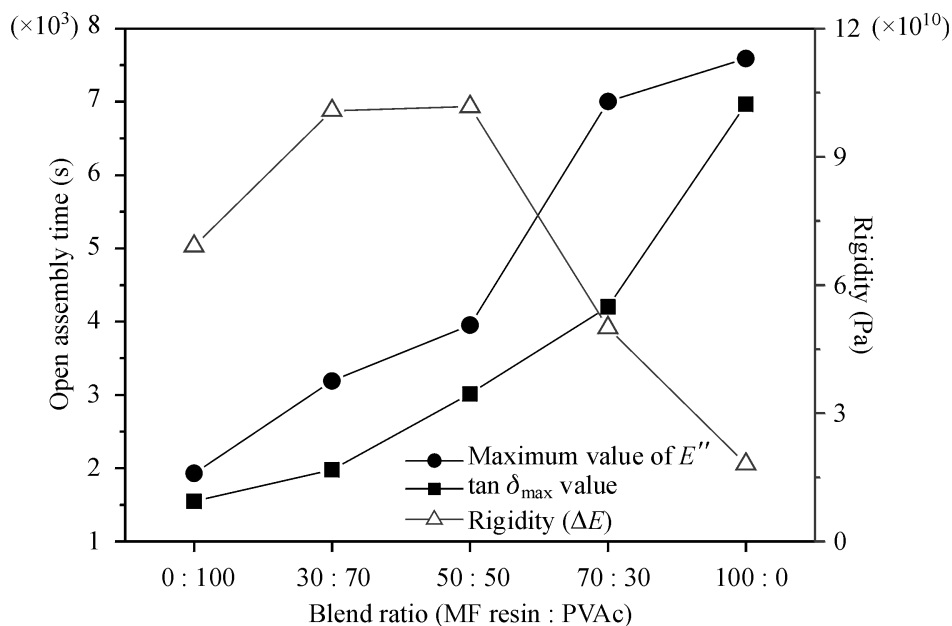
Figure 15. $\tan \delta_{max}$ values, maximum value of loss modulus (E'') and rigidity ($\triangle E$) of MF resin/PVAc blends at room temperature as a function of open assembly time.

blend caused a loss of PVAc properties at room temperature and, consequently, these blends tended to behave more like thermosetting adhesives.

Figure 15 shows the $\tan \delta_{max}$ values, maximum values of loss modulus (E'') and rigidity ($\triangle E$) of MF resin/PVAc blends at room temperature as functions of open assembly time. The $\tan \delta_{max}$ values and the values of maximum loss modulus (E'') increased with increasing MF content. However, the rigidities of 70 : 30 and 50 : 50 MF/PVAc blends were higher than those of other blends, especially when compared to 100% PVAc and 100% MF. These results indicated that high miscibility between MF and PVAc led to a high degree of cure. This miscibility between MF and PVAc caused the maximum storage modulus and $\tan \delta_{max}$ curves to merge into one, as shown in Fig. 15. 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 behind the miscibility of some thermosetting polymer blends [20].

By comparing DMTA results with initial tack results, with a maximum adhesion time between the decorative veneer and plywood surfaces of 5 min, the viscoelastic properties of blends containing more than 50% MF were unchanged, whereas those for 100% PVAc and 30 : 70 MF/PVAc were increased in value. The initial tack properties and viscoelastic properties of blends for an engineered flooring were found to be related to the MF/PVAc blend ratios, as shown in Fig. 16. Although the
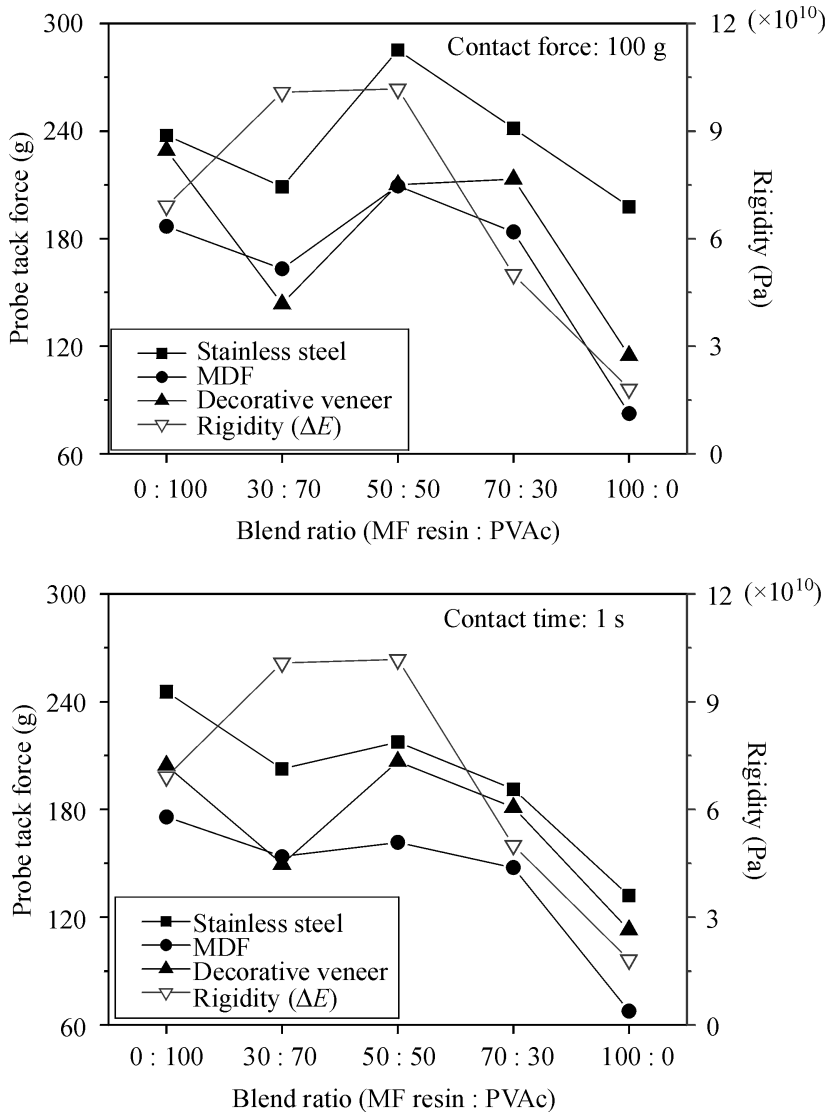
Figure 16. The relation between rigidity ($\triangle E$) and probe tack force of all MF resin/PVAc blends on stainless steel, MDF, and decorative veneer at room temperature as a function of MF/PVAc blend ratio.

rigidity at PVAc content above 70% decreased and the initial tack increased, both the rigidity and initial tack dramatically reduced with increasing MF resin content. These results clearly demonstrate the effect of thermosetting MF resin on the viscoelastic properties and initial tack of MF/PVAc blends to an engineered flooring.

4. CONCLUSIONS

From the initial tack obtained from five MF/PVAc blends, at ratios of $100:0$, $70:30$, $50:50$, $30:70$ and $0:100$, in terms of probe tack force between the decorative veneer and plywood for the manufactured engineered flooring, we were able to obtain quantitative tack results, as opposed to merely subjective 'thumb tack' results. As the process of adhesion in an engineered flooring should be completed in 2–3 min, the acceptable tack range is between 100 and 200 g. Changes to room temperature-curable PVAc, by adding MF resin into the blend, were investigated with DMTA. With time, rigidity ($\triangle E$) increased at room temperature, though this was prominent for PVAc only. During the initial 5 min, the initial tack and viscoelastic properties of the blends were essentially unchanged. We conclude that initial tack property, as measured in terms of probe tack strength, is correlated with the viscoelastic properties during the adhesion process at room temperature.

REFERENCES

1. S. Kim and H.-J. Kim, *Int. J. Adhesion Adhesives* **25**, 456–461 (2005).
2. D. Tuncer and H. Salim, *Building Environ.* **39**, 1199–1205 (2004).
3. Ö. Yalçin, A. Musa and Ö. Ayhan, *J. Appl. Polym. Sci.* **76**, 1472–1479 (2000).
4. S. K. Brown, in: *Organic Indoor Air Pollutants: Occurrence, Measurement, Evaluation*. p. 171. Wiley-VCH, Weinheim (1999).
5. P. Wolkoff, P. A. Clausen, P. A. Nielsen and L. M∅lhave, *Indoor Air* **4**, 478–490 (1991).
6. C. Creton and L. Leibler, *J. Polym. Sci. Polym. Phys.* **34**, 545–554 (1996).
7. H. Mizumachi, *J. Appl. Polym. Sci.* **30**, 2675–2686 (1985).
8. A. Zosel, *Int. J. Adhesion Adhesive* **18**, 265–271 (1998).
9. C. Verdier and J.-M. Piau, *J. Polym. Sci. Polym. Phys.* **41**, 2149–3139 (2003).
10. A. Roos, C. Creton, M. B. Novikov and M. M. Feldstein, *J. Polym. Sci. Polym. Phys.* **40**, 2395–2409 (2002).
11. J. Dupuy, E. Leroy and A. Maazouz, *J. Appl. Polym. Sci.* **78**, 2262–2271 (2000).
12. R. Wetton, R. Marsh and J. V. Velde, *Thermochim. Acta* **175**, 1–11 (1991).
13. S. Kim and H.-J. Kim, *J. Adhesion. Sci. Technol.* **17**, 1369–1383 (2003).
14. D.-H. Lim, S.-E. Kim, B.-J. Kim, H.-S. Do and H.-J. Kim, *J. Adhesion Interface* **4**(4), 7–14 (2003) (in Korean).
15. I. Aydin, *Appl. Surface Sci.* **233**, 268–274 (2004).
16. L. Onic, V. Bucur, M. P. Ansell, A. Pizzi, X. Deglise and A. Merlin, *Int. J. Adhesion Adhesives* **18**, 89–94 (1998).
17. S. Kim, H.-J. Kim, H.-S. Kim, Y. K. Lee and H.-S. Yang, *J. Adhesion. Sci. Technol.* **20** (2006) (in press).
18. S. Kim and H.-J. Kim, *Thermochim. Acta* **444** (2), 134–140 (2006).
19. M. B. Novikov, A. Roos, C. Creton and M. M. Feldstein, *Polymer* **44**, 3561–3578 (2003).
20. H. Lü and S. Zheng, *Polymer* **44**, 4689–4698 (2003).