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Abstract—The objective of this research was to investigate the miscibility behavior of melamine-formaldehyde (MF) resin and poly(vinyl acetate) (PVAc) blends for their use as adhesives for bonding fancy veneer and plywood in engineered flooring, by differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) and Fourier transform infrared spectroscopy (FT-IR). Blends of various compositions of MF resin/PVAc were prepared. To determine and compare the effect of PVAc content, blends with PVAc to MF resin weight ratios of 0, 30, 50, 70 and 100% were prepared. These blends displayed a single cure temperature over the entire range of compositions indicating that this blend system was miscible in the amorphous phase due to the formation of hydrogen bonding between the amine groups of the MF resin and the carbonyl groups of PVAc.

Keywords: Miscibility; melamine-formaldehyde resin; poly(vinyl acetate); blend.

1. INTRODUCTION

Recently, concern about human health as well as the environment has been increasing. Poly(vinyl chloride) flooring which has been used in most Korean houses is currently being replaced by wood flooring materials, especially in new apartments [1]. Engineered flooring, one of the flooring materials, 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. In the case of engineered flooring, fancy veneer of 0.5 mm thickness consisting of wood such as birch, oak, beach, cherry, or maple is glued onto the plywood of 7.2 mm thickness and pressed at about 160°C. An ultra-violet

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(UV) curable coating is applied to this fancy veneer [2]. 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 conflicts with the prevailing environmental awareness and concern [3]. Interest in poly(vinyl acetate) (PVAc)-based materials having higher bond strength and better film properties has grown considerably in the past two decades in the adhesive, paint, paper and the textile industries [4]. The 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 or co-polymers. It comes in a liquid form with viscosity ranging from 2000 to 3000 cP at 21°C. The PVAc is an odorless, nonflammable adhesive. It can be used in cold climates and it 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 its bonding capacity above 70°C [5, 6]. When the PVAc was added to the MF resin and the blend used to bond plywood and fancy veneer in engineered flooring, the formaldehyde emission was dramatically reduced [1].

Huang *et al*. studied the miscibility of thermo-setting resins and PVAc blends. It was found that the phenolic/PVAc blends were miscible in the amorphous phase over the entire composition range. The results obtained by differential scanning calorimetry (DSC), Fourier transform infrared (FT-IR) and high-resolution solid-state ^{13}C-NMR revealed strong inter-association hydrogen bonds between the hydroxyl groups of the phenolic and the carbonyl groups of the PVAc [7]. In the case of blends of phenolic resin with polymers such as poly(ethylene vinyl acetate) and aliphatic polyester, it was reported that hydrogen bond formation was critical in enhancing the miscibility of the various phenolic blends with modifiers containing ether, carbonyl, or hydroxyl functional groups [8, 9]. Considerable effort has been made to study the miscibility and phase behavior of different polymer blends [10]. Intermolecular interactions are usually considered to be the driving force for miscibility, and their important role in the miscibility of polymer blends has been clearly demonstrated [11].

FT-IR spectroscopy is a rapidly expanding technique in polymer miscibility determination and has provided much information over the years on molecular vibrations. The rapid development of FT-IR has revolutionized the applications of infrared spectroscopy and recently it has been used to elucidate the interactions occurring in blends, from which the blend miscibility has been deduced [12]. DSC is a classical method for the determination of miscibility. The phase structure of a blend is assessed by the number of glass transition temperatures (T_g) observed in the thermograms, with two transitions being a clear indication of phase separation. A single glass transition located at a temperature intermediate between those of the pure components indicates miscibility [13].

In this study, we have used a variety of techniques, including FT-IR, DSC and thermogravimetric analysis (TGA), to determine the miscibility behavior of

MF resin/PVAc blends for use as adhesives in engineered flooring to reduce formaldehyde emission level.

2. EXPERIMENTAL

2.1. Materials

The MF resin was synthesized in the laboratory. The resin was prepared at an F/M molar ratio of 1.75, with a solid content of 49 wt%. After the addition of water to the formalin, i.e., 38.5% by weight of formaldehyde in water, the pH was adjusted to 9.0 by adding a 1 M NaOH solution (because the methylolated intermediates of the reaction rapidly condense under acidic conditions) and the melamine was added. As hardener, 10% NH_4Cl solution was used. The viscosity as measured using a Brookfield Viscometer Model DV-II+ was 140 cP by spindle No. 6 at 21°C. PVAc in the liquid form with the following characteristics was used: density, 1.1 g/cm^3; viscosity, 3000 cP at 21°C, pH 5; solid content, 65 wt%. PVAc adhesive was supplied by Tae Yang Chemical (Incheon, Korea).

2.2. Blend preparation

Blends with various MF resin/PVAc content ratios were prepared. To determine and compare the effect of PVAc content, blends with 0, 30, 50, 70 and 100% by weight of MF resin were used. The blends were mixed together and all 5 blend systems were investigated.

2.3. Differential scanning calorimetry (DSC)

DSC analysis with a TA Instruments Q-1000 system (NICEM, Seoul National University) equipped with a Thermal Analysis Data Station enabled the curing exotherms of the MF, PVAc and MF/PVAc blends 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°C and 300°C.

2.4. Thermogravimetric analysis (TGA)

All 5 blend samples of MF resin and PVAc 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 Yalçin *et al*. [6] and by Kim and Kim [1] to maintain the adhesive layer of PVAc between the fancy veneer and the surface of plywood. The adhesive layer of PVAc was decomposed at temperatures higher than 60°C. Ten milligrams of each cured sample were placed on a balance located in the furnace which was heated 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 the 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.

2.5. FT-IR–ATR spectroscopy

FT-IR–ATR spectra were recorded on a Nicolet Magna 550 Series II spectrometer at a resolution of 4 cm^{-1}, in the mid-infrared range from 4000 to 600 cm^{-1} in the absorbance mode for resin characterization during the curing process. To enhance the signal-to-noise ratio, each of the reference and sample spectra represents the average of 40 scans recorded at 4 cm^{-1} resolution. The spectra were obtained using attenuated total reflectance (ATR). The temperature and relative humidity measured were $23 \pm 1°C$ and 60%, respectively. As samples for FT-IR spectroscopy analysis, all blend systems were used in a liquid state. The surfaces of the samples analyzed were in contact with a ZnSe crystal with a 45° angle of incidence. Net peak heights were determined by subtracting the height of the baseline immediately before the peak from the total peak height. The carbonyl and secondary amine indexes were calculated using the following equations:

$$\text{Carbonyl Index} = (I_{1733}/I_{3345}) \times 100, \tag{1}$$
$$\text{Secondary Amine Index} = (I_{1550}/I_{3345}) \times 100, \tag{2}$$

where I represents the peak intensity. The peak intensities were normalized using the peak at 3345 cm^{-1}, which corresponds to the hydroxyl group. This peak was chosen as the reference peak because it changed the least with variation in blend composition.

3. RESULTS AND DISCUSSION

3.1. Thermal analysis

Thermal characterization of polymer blends is a well-known method for determining the miscibility of polymer blends. Miscibility between any two polymers in the amorphous state is evidenced by the presence of a single T_g [7, 13]. The DSC cure curves for the MF resin as a function of PVAc addition are shown in Fig. 1. It can be seen that all blends display a single cure peak temperature (T_c), intermediate between those of the two pure components and it varies with the blend composition. The curing reaction then began and gave rise to the exothermic peak. The exothermic peak in the curing process is evident. All blends presented exotherms in the temperature range 81–106°C (Table 1), which is situated between the T_c values of PVAc (81.8°C) and MF resin (106.5°C). These T_c values correspond to the cross-linking reactions. In Fig. 1, the cure exotherms of the MF resin with added
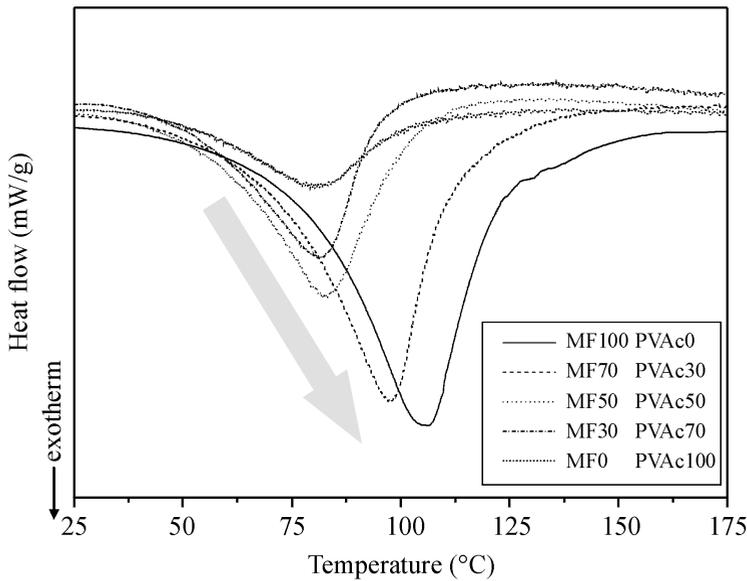
**Figure 1.** DSC thermograms of MF resin/PVAc blends.

Table 1.

Curing temperature and ΔH of MF resin/PVAc blends

| Blend	T_c (°C)	ΔH (J/g)
MF100 : PVAc0	106.5	1217
MF70 : PVAc30	97.6	1116
MF50 : PVAc50	81.2	830
MF30 : PVAc70	82.2	735
MF0 : PVAc100	81.8	315

MF resin/PVAc wt. ratio = 100 : 0, 75 : 25, 50 : 50, 25 : 75 and 0 : 100.

PVAc blends are shifted to higher temperatures than that for the 100% MF resin. It can, thus, be concluded that the MF resin/PVAc blends are completely miscible in the amorphous state. From Table 1, with increasing addition of PVAc to the MF resin, a shift of the ΔH to a lower temperature was observed. As the amino group in the melamine can accept 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 [14].

Figure 2 shows the weight loss of the cured blends of MF resin/PVAc in a temperature range from 30 to 800°C as measured under a nitrogen atmosphere. All the cured blends showed thermal stability up to 200°C. All MF resin/PVAc blends had a higher thermal stability than pure MF resin. For all the blends the eliminated products during the reaction vaporized continuously. Above 200°C
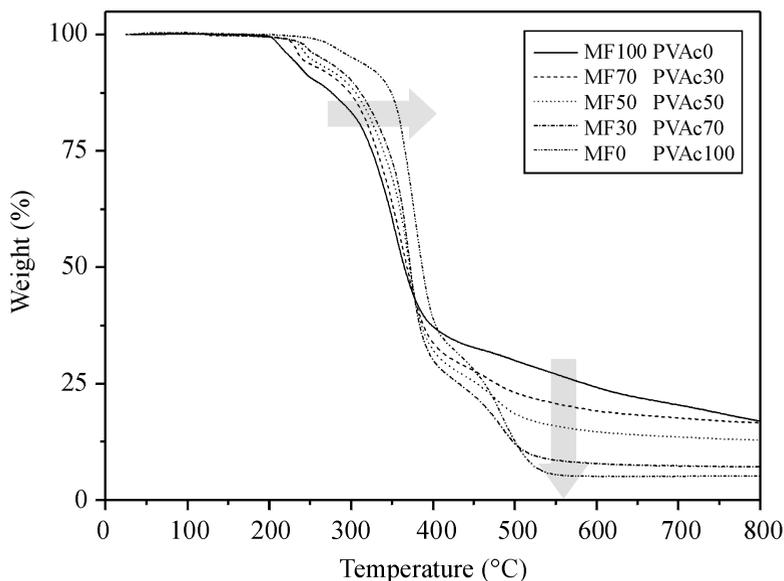
Figure 2. Weight loss curves of cured MF resin/PVAc blends.
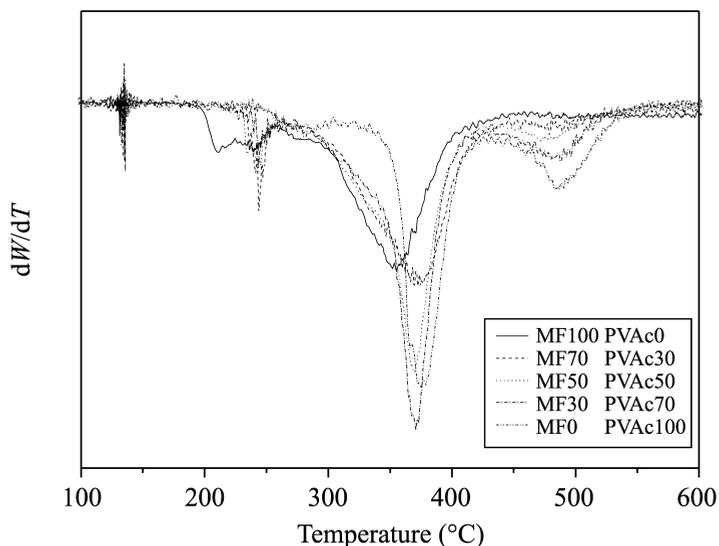
Figure 3. DTG curves of cured MF resin/PVAc blends.

the weight loss increased markedly. This can be clearly seen in the TGA curves (Fig. 2) and their first derivatives shown in Fig. 3. The thermograms of all blends show two steps. In general, the major weight loss was observed over the range of 200 to 400°C for the MF resin/PVAc blends, which corresponds to the structural decomposition of the polymers. Evidently, the thermal decomposition temperature of these PVAc materials shifted slightly toward a higher temperature range than that

(1) MF resin cross-linked network

(2) MF resin/PVAc cross-linked network
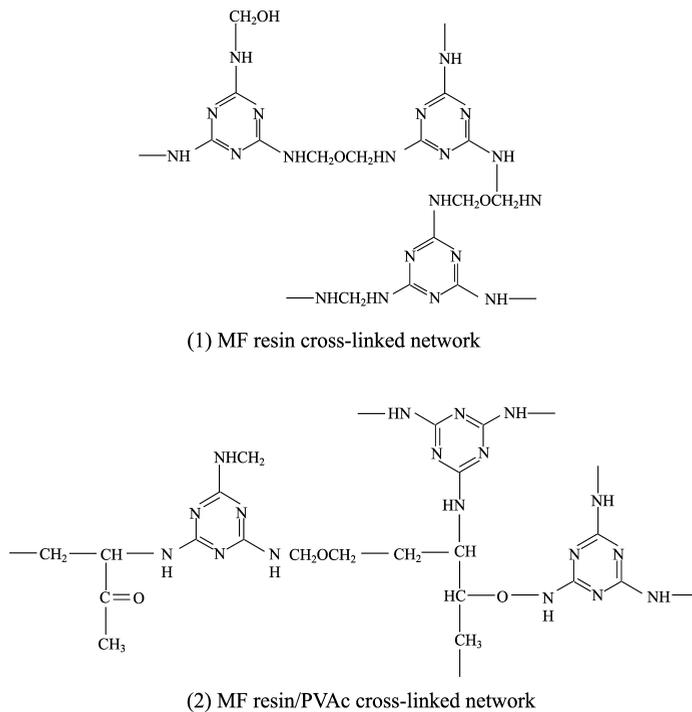
Figure 4. Cross-linked networks of MF resin, and MF resin/PVAc blends.

of MF resin in the first step, which confirms the enhancement of thermal stability of the intercalated polymer [15]. According to one report [1], although the adhesive layer of PVAc decomposed at temperatures above 60°C when it was used between the fancy veneer and the surface of plywood in engineered flooring, the high thermal stability of PVAc in the first step corresponds to the strength of hydrogen bonding in the cross-linked blends of MF resin/PVAc. The cross-linked network structures of MF resin and MF resin/PVAc are shown in Fig. 4. The second step of the thermal decomposition above 400°C is caused by the high molecular weight of the MF resin and PVAc.

In fact, most of the thermosetting polymer blends studied so far are found to be 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 [16]. However, the thermal stability of the blends varied systematically and thus showed the effect of hydrogen bonding between the MF resin and PVAc.

3.2. FT-IR analysis

FT-IR is a particularly suitable method to determinate the presence of specific interactions between various groups in polymer blends from the force constants,
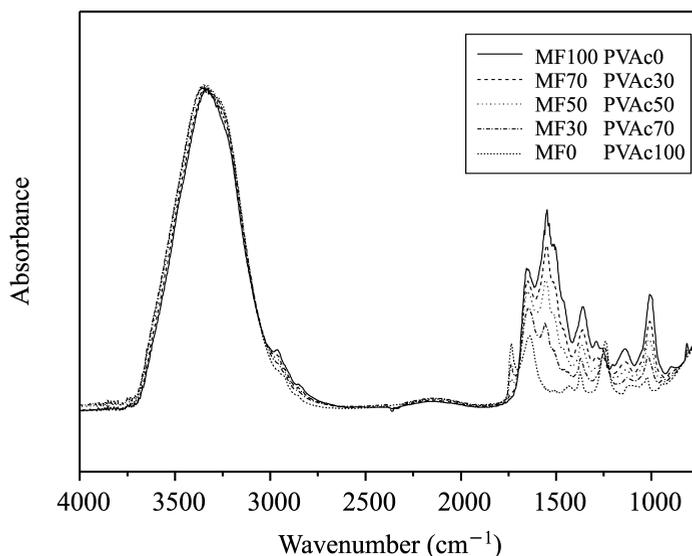
Figure 5. FT-IR spectra recorded at 25°C for MF resin/PVAc blends (liquid state).

and it is sensitive to both inter- and intra-molecular interactions [7]. FT-IR spectra of all blends are shown in Fig. 5. The broad peak in the region 3000–3700 cm^{-1} is characteristic of the −OH stretching of the water molecules in the blend solutions. It is expected that a large portion of these 'free' OH groups is consumed in the formation of inter-association hydrogen bonds between the PVAc and MF resin. This phenomenon reveals that a new pattern of hydrogen bonding formation results from the competition between amine–amine and amine–carbonyl interactions. Therefore, the amine group of the MF resin and the carbonyl group of PVAc have strong hydrogen bonding. The small peaks in the region 2700–2800 cm^{-1} are associated with the −CH stretching of the MF resin and PVAc, the methylene (−CH$_2$−) and dimethylene ether (−CH$_2$OCH$_2$−) bridges of the MF resin, and the methylene unit (−CH$_2$−) of the reaction with formaldehyde. It has been demonstrated that a large number of methylene ether bridges (−CH$_2$OCH$_2$−) occur, which rearrange themselves with relative ease to form methylene (−CH$_2$−) bridges with liberation of formaldehyde [17]. However, the N−H wagging peak in the 700–750 cm^{-1} range could not be recognized and the N−H stretch peak in the 3280–3320 cm^{-1} range overlapped with the −OH peak in the range 3000–3700 cm^{-1}.

To analyze the functional group change in the blends, Fig. 6 shows the scale-expanded infrared spectra in the functional group region with various compositions of MF resin/PVAc blends at room temperature. The signal at 1733 cm^{-1} is characteristic of the carbonyl (C=O) stretching of the PVAc. This peak increased with increasing PVAc addition ratio. The carbonyl absorption peak was located at
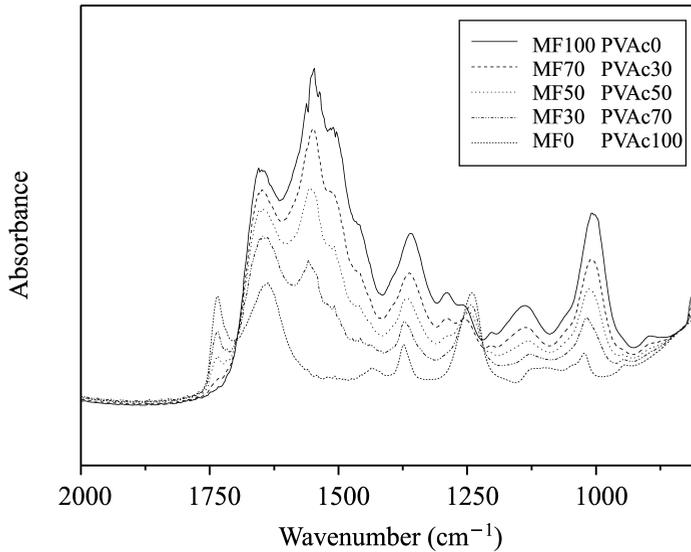
Figure 6. FT-IR spectra recorded at 25°C in the 600–2000 cm^{-1} region for MF resin/PVAc blends (liquid state).

approximately 1733 cm^{-1} for all compositions and the peak shift was negligible. The lack of peak shifting suggests that a relatively low level of specific interactions, if any, was present between the two molecules. Additionally, the carbonyl group of PVAc might not have interacted specifically with any specific sites of the MF resin molecule. The deformation the peak for the MF resin, which can be conveniently compared, gave absorption bands in the 1546–1558 cm^{-1} range, the 1635–1648 cm^{-1} range and the 1006–1022 cm^{-1} range. The 1546–1558 cm^{-1} range is for the secondary amine (aromatic band), while the 1635–1648 cm^{-1} range is for NH$_2$ scissoring vibration. These absorption peaks increased with increasing MF resin content in the blends.

The increase in carbonyl group concentration (calculated from equation (1)) *versus* the PVAc addition ratio is plotted in Fig. 7. With increasing ratio of PVAc in the blends, the carbonyl index increased at approximately the same rate as the carbonyl stretching. Also evident was the significant decrease in the secondary amine concentration, based on the peak in the 1635–1648 cm^{-1} range, with increasing ratio of PVAc in the blends.

The experimental FT-IR results in this study indicated that interactions between functional groups in the MF resin and PVAc were likely to be low or non-specific. In general, the FT-IR results for the PVAc/MF resin blends suggest that intermolecular interactions between the pairs are likely to be non-specific and, at best, only comparable with, rather than exceeding, those among the homopolymer molecules.
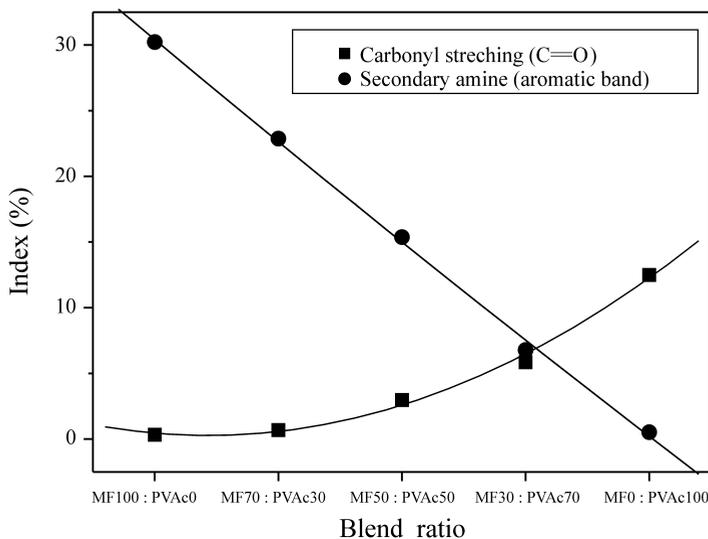
Figure 7. Carbonyl group and amine group indices as a function of blend ratio for MF resin/PVAc blends.

4. CONCLUSIONS

To reduce the formaldehyde emission from the adhesives used in engineered flooring, PVAc was added to MF resin at varying ratios. We investigated the miscibility behavior between the MF resin and PVAc for optimum adhesion. Thermal analysis showed that all blends displayed a single cure peak temperature (T_c), intermediate between those of the two pure components and varied with the blend composition. FT-IR results showed that the characteristic peaks of the MF resin (amine) and PVAc (carboxyl) regularly changed over the range of blend ratios from 0% to 100%. The MF resin/PVAc blends were miscible in the amorphous phase over the entire range of compositions. The results from DSC, TGA and FT-IR analyses revealed strong inter-association hydrogen bonds between the amine groups of the MF resin and the carbonyl groups of PVAc.

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