**Summary:** The effects of bio-scavengers on the formaldehyde emission, bonding strength, curing behavior, and thermal decomposition properties of MF resins for engineered flooring and adhesion for wood were investigated. Four varieties of bio-scavengers, tannin powder, wheat flour, rice husk flour, and charcoal, were added to MF resin at 5 wt.-%. To determine formaldehyde emission and bonding strength, we manufactured engineered floorings. MF-charcoal was most effective in reducing formaldehyde emission because of its porous nature, but its bonding strength was decreased. Tannin powder and wheat flour, which contain more hydroxyl groups, showed higher bonding strength and curing degree than pure MF resin did. Although the hydroxyl groups of the bio-scavengers were effective in reducing formaldehyde emission and improve bonding strength and curing degree, rice husk flour and charcoal behaved like inorganic substances, thereby disturbing the adhesion between MF resin and wood and thus reducing the bonding strength. In thermogravimetric analysis, MF-tannin showed the highest thermal stability in the low-temperature range from 100 to 300 °C.
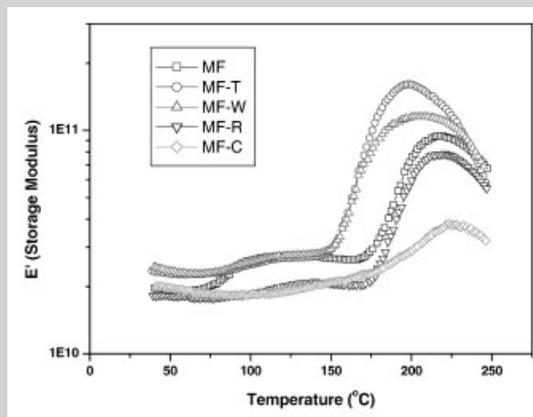
Storage modulus (E') of MF resin with various bio-scavengers at a heating rate of $10\,°C \cdot min^{-1}$.

Effect of Bio-Scavengers on the Curing Behavior and Bonding Properties of Melamine-Formaldehyde Resins

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Introduction

Recently, many countries have already imposed and some are about to impose regulations limiting the emission of formaldehyde during the manufacture of building materials and materials used for the manufacture of furniture and fitments. Formaldehyde emission from wood-based products can be reduced during the manufacturing process, by post-treatment of the wood-based products and by surface treatment. These techniques include the addition of wax scavengers of urea to the wood finish, treatment of the composite boards with ammonia gas or ammonia salts, and surface treatment of boards with paints, lacquers, veneers,

and papers. The surface treatment can be both a physical and a chemical minimization of formaldehyde diffusion. The most efficient route is the modification of the adhesives chosen. The use of phenolic and isocyanate or of urea-formaldehyde (UF) formulations with lower molar ratios is a powerful process to reduce the formaldehyde emission potential of wood products, and in some cases to nearly zero.[1] The molar ratio of formaldehyde to urea (F:U) is the most important factor affecting formaldehyde release in the production of boards. The combination of UF resins with formaldehyde-free adhesive systems may also be a way to reduce formaldehyde emission.[2,3]

Post-treatment methods to decrease and minimize formaldehyde release are based on compounds like ammonia, ammonium salts, or urea. Another effective way to reduce formaldehyde release is the addition of formaldehyde-binding substances, scavengers, to the resin or to the wood particles.[3,4] A conventional formaldehyde scavenger added to UF resins is urea, which is often used in combination with ammonium chloride (about 20:1). Urea also acts as a buffer by controlling the pH and improving the stability of UF resins. Ammonium chloride acts as an acid catalyst for the curing reaction and as a scavenger. The urea/ammonium chloride system apparently has no effect on resin curing and bonding properties if it is added up to 10% of the UF resin dry weight. Other approved formaldehyde scavengers are organic amines. Especially in Sweden, dispersion systems based on formaldehyde-binding paraffins were developed.[5,6] These wax systems are often added to the wood particles before drying. The amounts necessary to obtain perforator values below 10 mg depend on plant conditions and on the perforator value of the untreated board. The scavenger does not negatively influence the board strength and pressing time. The increase in cost is reported by the producer as varying between 1 and 5% of the total production cost. In one of the approaches, formaldehyde scavengers or acceptors have been used to reduce the free formaldehyde content of *N*-methylol cross-linking formulations and pad baths. Scavengers, such as ethyleneurea and urea, on addition to an *N*-methylol formulation, combine with some of the free formaldehyde in the solution. The odor of formaldehyde around the pad bath is reduced, but the reduced formaldehyde content in the pad bath can upset the chemical equilibrium and reduce the amount of the original cross-linking agent in the solution.[7]

Thermal analysis (TA) consists of analytical experimental techniques which measure the behavior of thermosetting adhesives as a function of temperature. 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 thermal dynamic conditions.[8–10] Dynamic mechanical TA (DMTA) has been widely used as a technique for investigating the structures and dynamic mechanical behavior of composite materials for determining their storage modulus (E'), loss modulus (E''), and loss factor (tan δ).[11] 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.[12]

In this study, melamine-formaldehyde (MF) resins were mixed with four types of bio-scavengers: tannin powder, wheat flour, rice husk flour, and charcoal, to reduce formaldehyde emission. We investigated the effect of bio-scavengers on the thermal stability and dynamic mechanical properties during the curing process of MF resin and compared the resulting adhesion properties.

Experimental Part

Materials

Plywood and Fancy Veneer

The plywood and fancy veneer used for manufacturing the test samples were donated by Easywood Co. Ltd., South Korea. The fancy veneers were of 0.5 mm thickness, the species was maple, and the plywoods were manufactured in China. The moisture contents of plywood and fancy veneer were 3.5 and 0.08%, respectively.

MF Resin

The resin was prepared at an F/M ratio of 1.75, with a solid content of 60%. After water was added 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 condenses 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 cP by spindle No. 6 at 21 °C.

Adhesive Preparation with Bio-Scavengers

Four materials, tannin powder, wheat flour, rice husk flour, and charcoal, were added as bio-scavengers at the level of 5 wt.-% of MF resin. The tannin powder from wattle (*Acacia mearnsii*, mimosa) was supplied by the Bondtite Co. Ltd., Australia. The particle sizes of rice husk flour and wheat flour were ≈150–200 mesh and supplied by SARON FILLER Co., South Korea. Charcoal is a black powder manufactured by the pyrolysis of wood or other carbonaceous materials, which is then oxidized at high temperature using steam or carbon dioxide to increase its adsorptive capacity through the formation of an internal trellis of pores with a surface area of $1\,000–2\,000\,\text{m}^2 \cdot \text{g}^{-1}$.[13,14] In this study, oak wood was used for charcoal and after grinding, a 200 mesh of charcoal was used. All bio-scavengers were of powder type of around 200 mesh with a moisture content of ≈5–6%. We prepared five adhesive systems: MF resin (MF), MF + tannin powder (MF-T), MF + wheat flour (MF-W), MF + rice husk flour (MF-R), and MF + charcoal (MF-C).

Methods

Manufacturing of Engineered Flooring Board

The engineered flooring boards, sized $400 \times 400\,\text{mm}^2$ (length × width), were manufactured using the MF resin and with four different bio-scavengers. We bonded fancy veneer and plywood for engineered flooring. The pressure schedule consisted of cold-pressing at 1 kgf · cm^{-2} for 2 min, in order to ensure the stability of the adhesive layer hot-pressing at 5 kgf · cm^{-2} and 120 °C for 160 s, followed finally by cold pressing at 1 kgf · cm^{-2} for 2 min.
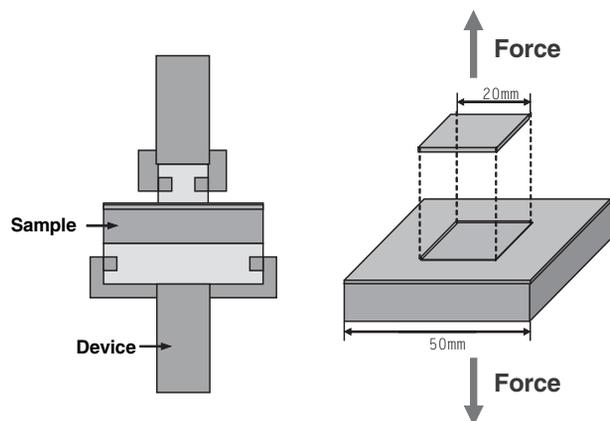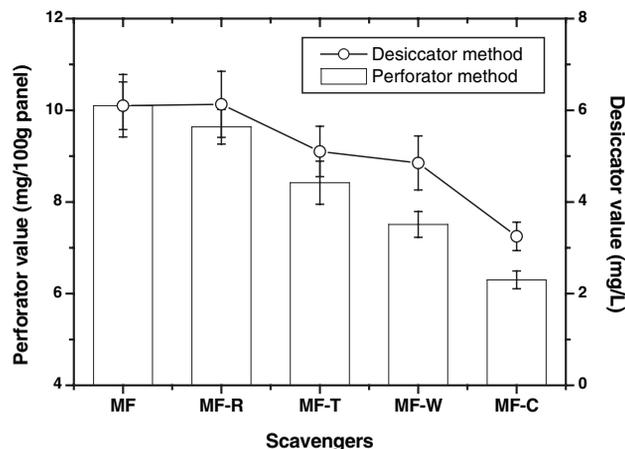
Figure 1.   Test of surface bonding strength.[13]

Figure 2.   Formaldehyde emission evaluated by desiccator and perforator method of MF resin with various bio-scavengers.

Formaldehyde Emission

Desiccator method: The Japanese Industrial Standard (JIS) and Korean Standard (KS) were used to determine the formaldehyde emission from engineered flooring. The 24 h desiccator method uses a common glass desiccator with a volume of 11 L. Ten test specimens, with dimensions of 50×150 mm^2, are positioned in the desiccator. The sample total surface area is 1 800 mm^2. The emission test lasts for 24 h in the covered desiccator at a temperature of 20 °C. The emitted formaldehyde is absorbed in a water-filled petri dish and analyzed using a UV spectrophotometer after treatment with acetyl acetone and acetyl acid ammonium.

Perforator method: This method is primarily used in Europe. The perforator value of formaldehyde emission was determined using the DIN EN 120 (European Committee For Standardization, 1991) method. For this method, a special perforator apparatus is necessary. Test pieces of approximately 110 g are weighed to an accuracy of 0.1 g and put in a round bottom flask, to which 600 mL of toluene is added. About 1 000 mL of distilled water is poured into the perforator attachment. Boiled toluene is passed through the distilled water for 2 h. In this process, the distilled water absorbs the formaldehyde and other volatile organic compounds stripped by the boiling toluene. Formaldehyde trapped by the water is then quantitatively determined using a UV spectrophotometer after
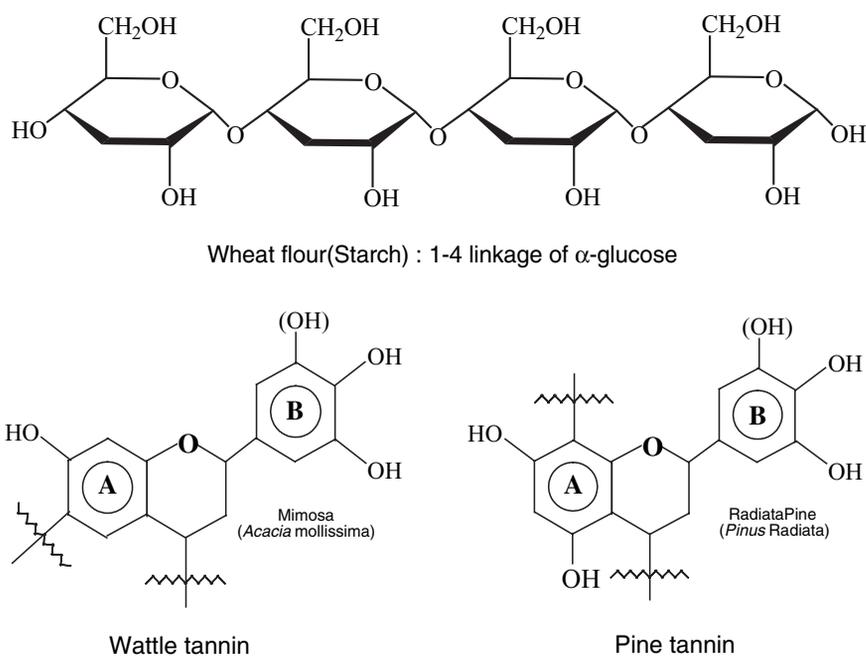

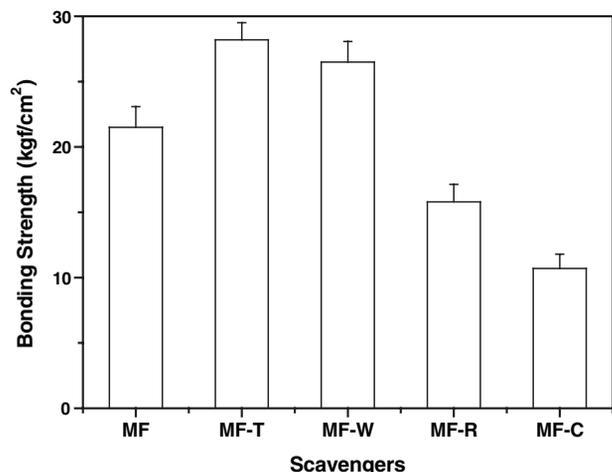Figure 3.   Chemical structure of wheat flour and tannins.

Figure 4. Bonding strength of MF resin systems with bio-scavengers.

treatment with acetyl acetone and acetyl acid ammonium. The perforator method provided by KS was used to evaluate the formaldehyde emission.

Bonding Strength

To determine the bonding strength between the fancy veneer and plywood, we tested with a Universal Testing Machine (UTM; Zwick Co.) in the tensile mode. Samples were cut at 5×5 cm^2 (length $\times$ width) and a knife mark of 2×2 cm^2 (length $\times$ width) was made on the surface (fancy veneer face) at a depth of 0.5 mm. We bonded the upper device of UTM and the knife mark of 2×2 cm^2 on the surface with hot-melt adhesive. Another face was bonded to the base of the device similar to the internal bonding strength test specimen. The tests were performed at a cross-head speed of 2 mm $\cdot$ min^{-1}, as shown in Figure 1.[15]

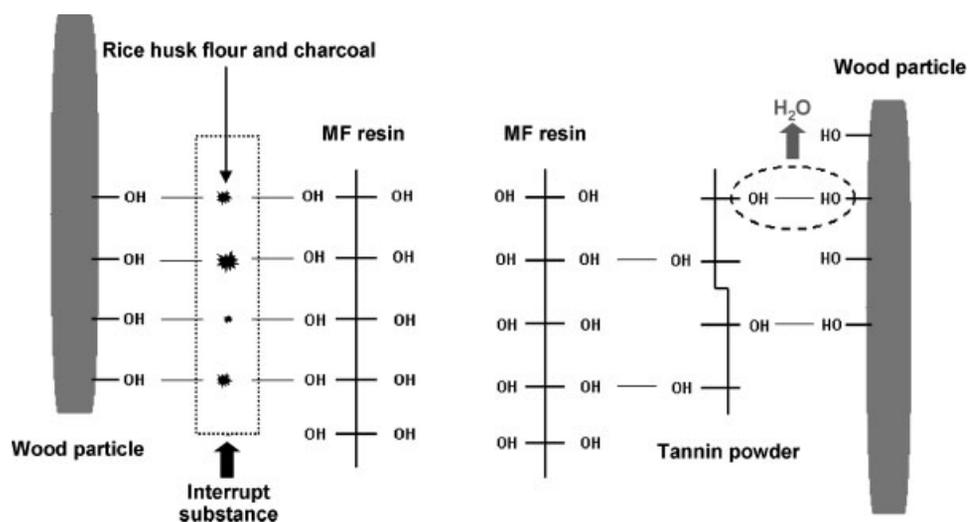### Thermogravimetric Analysis (TGA)

All MF resins with bio-scavengers were dried in an oven at 60 °C for 24 h and analyzed thermogravimetrically in nitrogen at a heating rate of 20 °C $\cdot$ min^{-1}. Ten milligrams of each cured sample was 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 (TA Q500, TA Instrument). 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 $\cdot$ min^{-1} from a point below the sample.

DMTA

The dynamic mechanical properties of each sample was measured from 40 to 250 °C at a heating rate of 10 °C $\cdot$ min^{-1} (ramp method) using a DMTA analyzer (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.[11] The adhesive thickness was 0.2 mm and the sample dimensions were $28 \times 5 \times 1.4$ mm^3. 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.

Results and Discussion

Formaldehyde Emission and Bonding Properties

MF resin gives excellent adhesive performance, good moisture resistance, and tends to give lower formaldehyde emission than UF resin.[16] However, in this study, the formaldehyde emissions from the products glued with MF resin were much higher than what we expected before surface coating: above 6 mg $\cdot$ L^{-1} and exceeding the E2 grade

Figure 5. Schematic diagrams of adhesion between rice husk, charcoal, and tannin with MF resin.

of formaldehyde emission level in the KS, as shown in Figure 2. The formaldehyde emission level was decreased with the addition of bio-scavengers to MF resin, except rice husk flour. Tannin powder and wheat flour, which contain many hydroxyl groups, as shown in Figure 3, reacted with free formaldehyde in MF resin. Because of this reason, agricultural byproducts containing hydroxyl groups, such as tannin powder and wheat flour, can be used as a scavenger for formaldehyde-based adhesive systems. However, rice husk flour did not reduce formaldehyde emission. The content of lignin and cellulose of rice husk flour was a little lower than that of other ligno-cellulosic materials such as wood flour. Ash content of rice husk flour, however, was much higher than that of wood flour because of silica (SiO_2) with 96% of ash.[17,18] This silica material disturbed the reaction between the hydroxyl group and free formaldehyde. On the other hand, charcoal remarkably reduced the formaldehyde emission compared to other bio-scavengers. This difference in the absorption properties of charcoal was caused by its porosity. The numerous minute holes of charcoal absorb molecular formaldehyde, enabling charcoal to act as an absorbent.[19] Generally, charcoal can be classified among the substances with the three-dispersed porous structure, and the investigation into the arrangement of the porous texture that has been conducted by a number of prestigious physical laboratories has elucidated the microporous character of the solid phase. Therefore, charcoal is a very suitable natural material for studying the adsorption and absorption phenomena, as well as for chemisorption and oxidation reactions.[14,20] According to present results, the four bio-scavengers effectively reduced formaldehyde emission in the increasing order of rice husk flour, tannin powder, wheat flour, and charcoal.

The results of the bonding properties are shown in Figure 4. For tannin powder and wheat flour, which contain more hydroxyl groups than the others, bonding strength was higher than that of the MF resin. Furthermore, rice husk flour and charcoal showed much lower bonding strength than tannin powder and wheat flour. The overall bonding strength of MF resin systems decreased in the order of
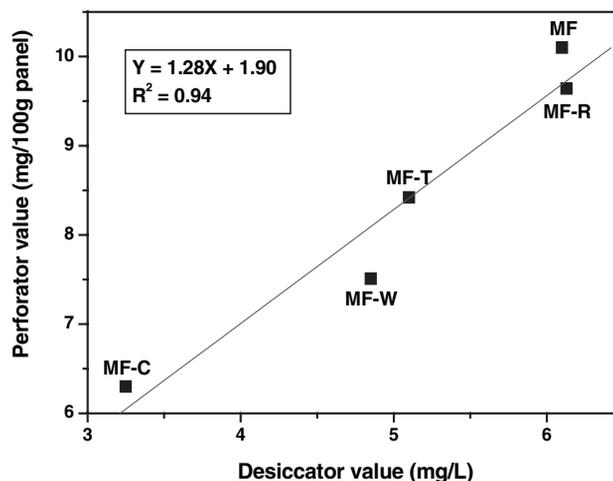

Figure 6. Correlation of formaldehyde emission results between perforator and desiccator.

tannin powder, wheat flour, rice husk flour, and charcoal. The present results of bonding strength were due to the MF resin. MF resin is a thermosetting adhesive, similar to phenol-formaldehyde and UF adhesives. At high press temperature, molecules of the MF prepolymer and functional group are cross-linked to each other and to hydroxyl groups of tannin powder and wheat flour. Rice husk flour, however, has components similar to the wood, as well as inorganic substances, while charcoal contains inorganic substances. These inorganic substances hamper the adhesive strength of the particle board (Figure 5).

Figure 6 compares the desiccator and perforator values. Although the perforator value was directly proportional to the desiccator, it increased less than the desiccator value. Whereas a precise amount (100 g) of wooden board was used in the perforator method, only the dimensions of the wooden board are taken into consideration in the desiccator method. In spite of the formaldehyde emission values from the same boards being slightly different because of the difference between the two sampling methods, these two methods produce proportionally equivalent results.
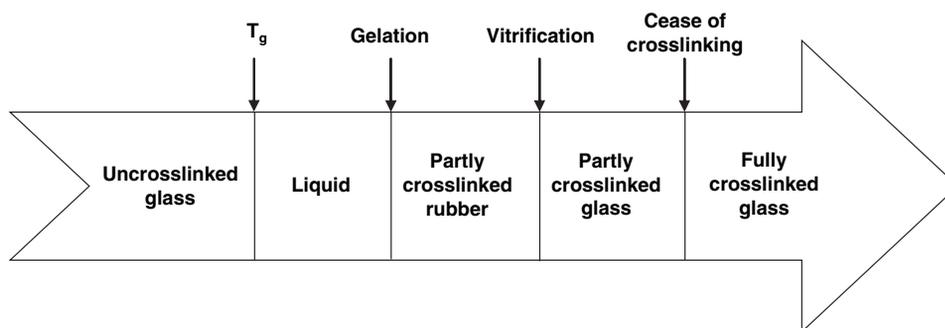

Figure 7. States and transition encountered during curing of MF. The times to gelation and vitrification are important processing parameters.[22]

DMTA

Dynamic thermal mechanical test methods have been widely used for investigating the structures and dynamic mechanical properties of thermosetting adhesives.[11,21] It is important to understand the thermal properties because MF resins are thermosetting adhesives. These resins are in the liquid state at room temperature become solidify at high temperatures 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. The time to reach gelation is an important processing parameter. Another crucial time limit is the point of vitrification ($T_g > T_{cure}$). This is illustrated in Figure 7. This is an example of a procedure that should take place before the material reaches the point of gelation, as shown in Figure 7.[22] In this study, E', E'', and tan δ of each adhesive system were obtained by DMTA, and those of the MF resin are shown in Figure 8. In the DMTA thermogram, the dynamic mechanical properties of the thermosetting resin, which was in the liquid state between wood veneers, were analyzed. The DMTA thermogram in Figure 8 shows that E' increased with increasing temperature, due to the cross-linking induced by the curing reaction of the resin, and 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 the maximum value was caused by 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 195 °C. Because of the high heating rate of $10\,°C \cdot min^{-1}$, the curing temperature of MF resin was higher than that reported in another study.[23] 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 increased again after the curing reaction was
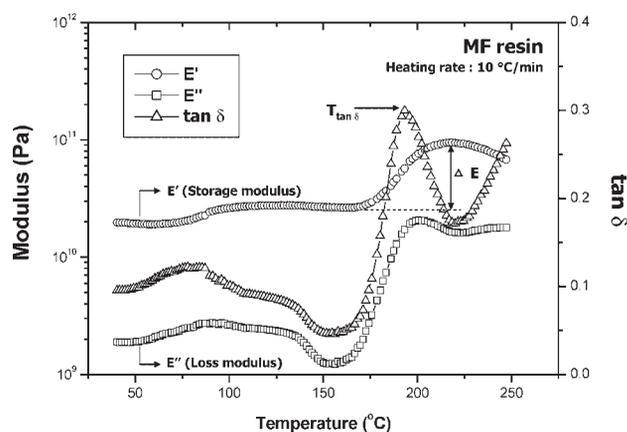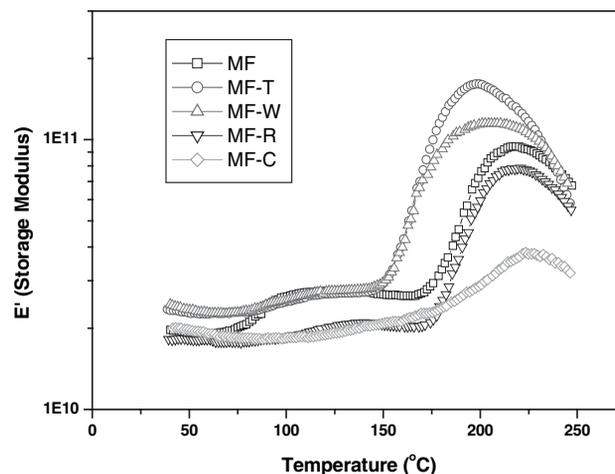

Figure 9. Storage modulus (E') of MF resin with various bio-scavengers at a heating rate of $10\,°C \cdot min^{-1}$.

completed. The temperature of the active curing reaction was determined from the maximum tan δ value in this temperature range.

Figure 9 shows E' of various bio-scavengers at a heating rate of $10\,°C \cdot min^{-1}$. E' increased with increasing temperature. MF resin was in the liquid state at room temperature and became a solid at high temperature, as a typical thermosetting resin, after curing had taken place. It should be noted that E' increased rapidly at around ≈150–190 °C. Especially, E' of MF resin with tannin powder and wheat flour began to increase from a lower temperature than pure MF resin did, and maximum values of E' were higher than those of pure MF resin. These results showed that the curing reaction presented a lower temperature for tannin powder and wheat flour, which contained more hydroxyl groups, than for pure MF resin. These hydroxyl groups contributed to the curing of MF resin during increasing temperatures. On the other hand, the maximum values of E' for rice husk flour and charcoal were much lower than those of the others.
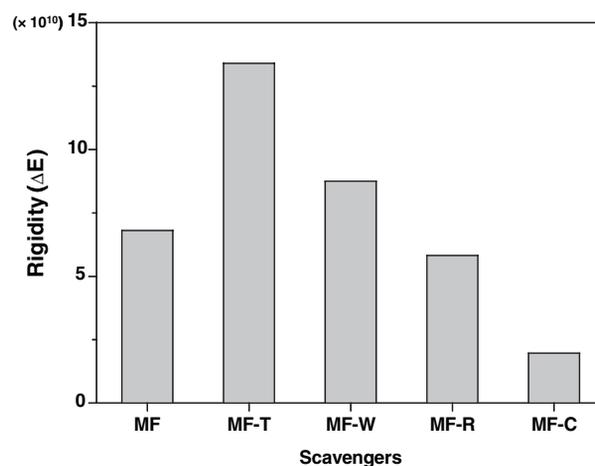

Figure 8. DMTA thermogram during heating ramp of MF resin at a heating rate of $10\,°C \cdot min^{-1}$.

Figure 10. Curing degree (ΔE) of MF resin with various bio-scavengers at a heating rate of $10\,°C \cdot min^{-1}$.

Based on these results, the rigidities (ΔE) of the resins are shown in Figure 10. The rigidity (ΔE) is another expression of curing degree where the change of state from liquid to solid is high.[24] The results were related to bonding strength. Greater curing showed higher bonding strength. Rice husk flour and charcoal disturbed the curing of MF resin. The tan δ data illustrate this tendency of changing rigidities. The results of E'' and tan δ presented in Figure 11 illustrate this behavior in detail. 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 200.6 °C for MF resin, 191.9 °C for MF-T, 182.4 °C for MF-W, 205.7 °C for MF-R, and 223.4 °C for MF-C. From the tan δ results, the peaks of the $T_{\tan \delta}$ value were obtained. The tendency of these two peaks was similar, as summarized in Figure 12. The temperatures corresponding to the
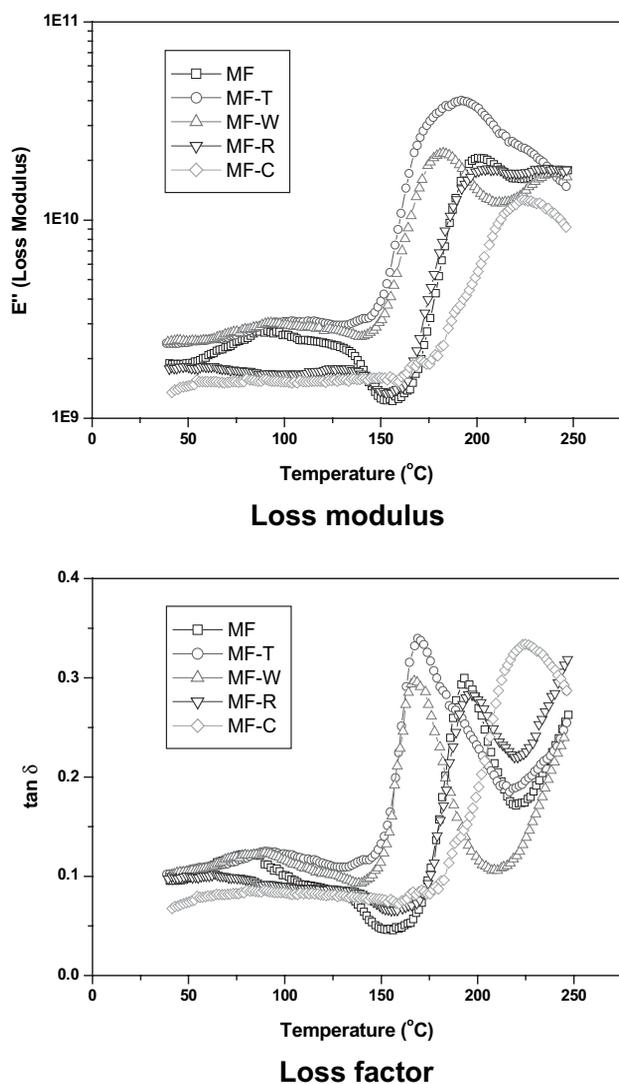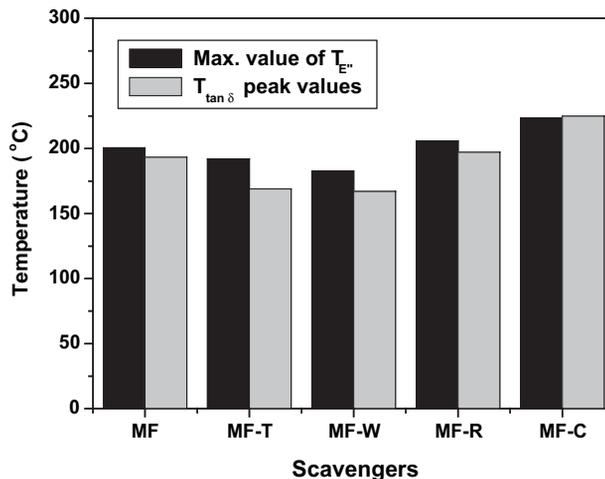

Figure 12. $T_{\tan \delta}$ peak values and maximum value of loss modulus (E'') of MF resin with various bio-scavengers at a heating rate of $10\,°C \cdot min^{-1}$.

Loss modulus

TGA thermogram

Loss factor

DTG curve

Figure 11. Loss modulus (E'') and loss factor (tan δ) of MF resin with various bio-scavengers at a heating rate of $10\,°C \cdot min^{-1}$.
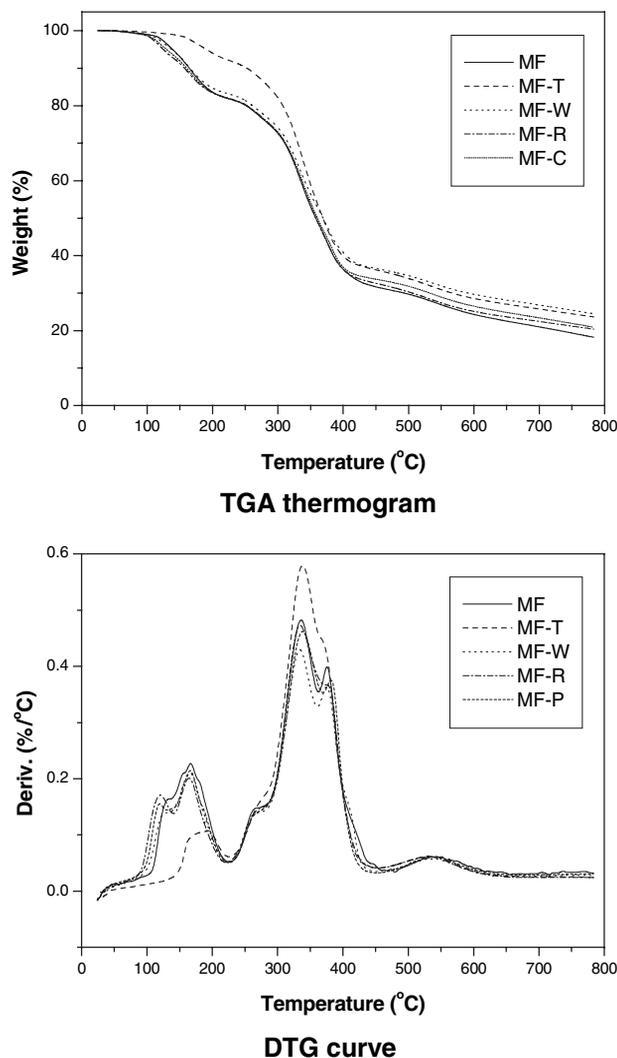
Figure 13. Weight loss and DTG curves of cured MF resin with various bio-scavengers.

maximum values of tan δ, differed as many hydroxyl groups contain bio-scavengers and other components. From the tan δ results, the peak of the $T_{\tan \delta}$ values were 193.3 °C for MF resin, 167.0 °C for MF-T, 167.1 °C for MF-W, 197.2 °C for MF-R and 224.9 °C for MF-C. These behaviors were also correlated with bonding strength and curing degree.

TGA

Using TGA, we checked the thermal decomposition and thermal stability of each dried adhesive. Figure 13 shows the weight loss of the dried MF resin with bio-scavenger and its first derivative over a temperature range of 30–800 °C, as measured under nitrogen atmosphere. All samples showed a two-step thermal decomposition behavior. The first step resulted from the moisture contained in each dried sample, while the second step was the main thermal decomposition step. Major weight losses were observed over the range of 200–400 °C for the MF resin with bio-scavengers, which may have corresponded to the structural decomposition of the polymers. In the first step, the thermal decomposition rate at 200 °C was 5% for MF-T and approximately 20% for the other samples. Because the hydroxyl groups of tannin powder reacted with MF resin, the moisture content was lower than that of the other adhesive systems of MF resin with bio-scavengers. However, in the second step, the thermal decomposition behavior of MF-T was dramatically reduced, eventually to the same level as that of the other adhesive systems of MF resin with bio-scavengers. The bio-scavengers affected the thermal decomposition behavior only in the low temperature range of 100–300 °C.

Conclusion

Bio-scavengers were added to reduce the level of formaldehyde emission from the adhesives used in engineered flooring and wooden interior materials. The formaldehyde emission level was decreased with the addition of bio-scavengers, except rice husk flour, up to 5 wt.-% in MF resin. The use of charcoal as bio-scavenger gave the lowest emission level. MF-C reduced the emission by up to 40% and MF-T and MF-W by about 20%. This difference in emission reduction arose from the absorption properties of charcoal caused by its high porosity. However, MF-T and MF-W showed higher bonding strength than pure MF resin, MF-R, and MF-C. The bonding strength of tannin powder and wheat flour, which contain more hydroxyl groups than the others, was higher than that of the others. In DMTA analysis, MF resin behaved as a typical thermosetting resin, being in a liquid state at room temperature and then becoming a solid at a higher temperature, after curing had occurred. The addition of various bio-scavengers affected the curing behavior of the thermosetting resin. The storage

modulus (E') increased in the case of MF-T and MF-W, which contain many hydroxyl groups, but decreased for MF-R and MF-C. These results were related to the bonding strength results. Due to variations in the chemical and phase structures, the effect of bio-scavengers on formaldehyde emission, bonding strength and curing were different even though all the four are lingo-cellulosic byproducts. Wheat flour was the most effective bio-scavenger among the four tested in this study.

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