

Comparison of Formaldehyde Emission Rate and Formaldehyde Content from Rice Husk Flour Filled Particleboard Bonded with Urea-Formaldehyde Resin^{*1}

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ABSTRACT

The this study, the effect of rice husk flour (RHF) as scavenger on formaldehyde emission rate and formaldehyde content from urea-formaldehyde (UF) resin bonded RHF content wood particleboards (PB). Two type of particle size (30 μm and 300 μm) of RHF was premixed with the UF resin at 5% and 15% by weight. The performance of UF resins is greatly influenced by the curing characteristics in their curing processing. The curing behavior was monitored activation energy (E_a) by DSC and pH variation according to RHF contents. PB with dimensions of 27 cm \times 27 cm \times 0.7 cm was prepared at a specific gravity of 0.75 using E_1 and E_2 class UF resins. Formaldehyde emission and formaldehyde content from RHF filled PB bonded with UF resin was measured by 24 h desiccator and perforator method, respectively.

RHF causes an increased pH of UF resin. E_a of the modified UF resin decreased independently of RHF particle size. As the pH and the E_a variation of the UF resin containing RHF increased, the amount of formaldehyde content decreased. The formaldehyde emission and formaldehyde content levels of the PB bonded with 15 wt% of 30 μm RHF and E_2 type UF resin were low and satisfied grade E_1 , as measured by 24 h desiccator and perforator method. The result of a comparison between 24 h desiccator and perforator test using PB showed that the linear regression analyses show a good correlation between the results for the 24 h desiccator and the perforator tests. The linear regression of a correlation between the desiccator and the perforator was $Y=4.842X-0.064$ ($R^2=0.989$). RHF was effective at reducing formaldehyde emission and formaldehyde content in urea-formaldehyde adhesives when used as scavenger.

Keywords : rice husk flour, urea-formaldehyde resin, formaldehyde emission, formaldehyde content, desiccator method, perforator method, activation energy

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1. INTRODUCTION

Low cost and good performance has made urea-formaldehyde (UF) resin the most important wood adhesive for interior applications. However, the formaldehyde emission from UF resin bonded wood products has been recognized as a potential source of indoor air pollution, leading to inhabitant discomfort and health problems.

Beneficial steps have included reducing the formaldehyde to urea (F/U) mole ratio (Myers, 1984), synthesizing UF resin with acidic catalysts without first using an alkaline catalyst (Hse *et al.*, 1994), impregnating the wood furnish with a formaldehyde, and treating boards with formaldehyde scavengers and/or a barrier coating after manufacture (Myers, 1985). Also many materials have been shown to reduce formaldehyde emissions from UF resins, including powdered glass, inorganic salts, amines, and amine hydrochlorides as scavengers (Myers, 1986).

It is generally agreed that the hydrolysis of cured UF resins is responsible for the major portion of the formaldehyde emission. Thus, in principle, the board retains the potential to emit formaldehyde throughout its useful life, and the efforts to minimize its emission must be directed toward resin stabilization.

This study investigated effect of rice husk flour (RHF) as scavenger on formaldehyde emission and formaldehyde content from UF bonded particleboards (PB) according to the mixed RHF content.

Two types of particle size (30 μm and 300

μm) of RHF was premixed with the UF resin at 5% and 15% by weight. The performance of UF resins is greatly influenced by the curing characteristics.

To determine the scavenger characteristics of RHF to PB bonded with UF resins, experiments were conducted to assess, 1) the activation energy (E_a), as determined by differential scanning calorimeter (DSC), of two type particle size (30 and 300 μm) RHF modified and unmodified UF resins, 2) pH variation of modified UF resin, and 3) comparison of formaldehyde emission by 24 h desiccator and formaldehyde content by perforator method from the RHF filled particleboard used E_1 and E_2 class UF resins.

2. EXPERIMENTAL PROCEDURES

2.1. Materials

2.1.1. Urea - Formaldehyde Resin

Two kinds of UF resins (UF-1 and UF-2) were donated by PB manufacture company in South Korea. According to the degree of formaldehyde emission, the UF resins were belonged to either the E_1 class or the E_2 class. UF-1 is an E_1 type resin and UF-2 is an E_2 type resin (Table 1).

2.1.2. Rice Husk Flour (RHF)

Two types of RHF, were obtained from Saron Filler Ltd. in Ansong, Korea, and their particle sizes were as follows: A type (30 μm), and B type (300 μm) (Table 2).

Table 1. Type of urea-formaldehyde resin

	Formaldehyde emission class	Non-volatile content (%)	Viscosity (mPa · s)
UF-1	E_1	61.6	220 ± 25
UF-2	E_2	76.6	295 ± 20

2.1.3. Wood Particles

The wood particles used for manufacturing the particleboard were donated by PB manufacture company in South Korea, and the wood particles is used for face.

2.2. Methods

2.2.1. Formulation of Resins

Two types of UF resins were formulated by adding RHF with two different particle sizes (30 μm and 300 μm), which were premixed with the UF resin in the amounts of 5% and 15% by weight in proportion to the UF resin solids, respectively.

2.2.2. Activation Energy (E_a) Measurement by Differential Scanning Calorimeter (DSC)

E_a analysis with a TA Instrument DSC Q-1000 at NICEM, Seoul National Univ. equipped with a Thermal Analysis Data Station determined the exothermic curing of the unmodified UF resin, and the UF resin modified with 5 and 15 wt% RHF.

This study was done using a sealed liquid type aluminum capsule pan under a nitrogen atmosphere at 5 different heating rates of 2, 5, 10, 20, and 40°C/min between 25°C and 250°C.

2.2.3. pH Variation of Cured UF Resin

The pH of cured UF resins and the UF resins to which RHF was added were determined us-

ing the ASTM D 1583-01 (American Society for Testing and Materials, 2001) method. The film coating had a thickness of less than 0.51 mm. The films were placed on glass plates in a circulating air oven at $66 \pm 1^\circ\text{C}$ until most of the solvent was evaporated. This usually requires 4 hours. The temperature was then raised to $150 \pm 1^\circ\text{C}$ and the films on plates were heated continuously until they were cured. This process usually required less than 1 hr. The cured adhesive film was then ground to particle size of 425 μm . Immediately after grinding, the particles (2 g) were placed in a small glass vial that permitted adequate immersion of an electrode after 10 mL of distilled water was added. The suspension of ground particles was allowed to stand for 72 hours at room temperature. The solution was stirred and pH of solution was measured using a pH meter.

2.2.4. Manufacturing of Particleboard

Wood particles, RHF and the UF resin were blended with 10% NH_4Cl solution added as a hardener. Particleboards with dimension of $27 \times 27 \times 0.7$ (cm) were prepared at a specific gravity of 0.7 and RHF contents of 0, 5 and 15 wt.%, respectively. The mixture was then hot pressed to obtain a composite board at a peak pressure of 25 kg/cm^2 and a temperature of 140°C. The total press time was 6 min, including 0.5 min to reach full pressure and 2 min for a second step of pressure release. The PB was conditioned at 20°C and 65% RH for 2 weeks before testing.

Table 2. Chemical compositions of rice husk flour and wood particle (unit: %)

Code	Moisture	Lignin	Cellulose	Fat	Ash
Rice husk flour (30 μm)	5.8	16.9	58.7	0.3	18.3
Rice husk flour (300 μm)	6.0	21.0	60.0	0.2	12.8
Wood particle (163 μm)	10.3	26.2	62.5	0.6	0.4

2.2.5. Formaldehyde Emission by 24 h Desiccator Method

The formaldehyde emission value was determined using 24 h desiccator method (JIS A 1460). The interior volume of the desiccator was 11 liter and 5 × 15 cm specimens were used for desiccator test. The sample total surface area was 1,800 cm². The released formaldehyde was caught in the distilled water was analyzed using a UV spectrophotometer after treatment with acetyl acetone and acetyl acid ammonium.

2.2.6. Formaldehyde Content by Perforator Method

The perforator value of the formaldehyde content was determined using the DIN EN 120 (European Committee For Standardization, 1991) method. A sample (110 g) and 600 ml of toluene were placed into a flask, and then the perforator was filled with 1,000 ml of distilled water. The boiled toluene was passed through the distilled water for two hours. In this process, the distilled water absorbed the formaldehyde stripped by the boiling toluene. The formaldehyde trapped by the water was then quantitatively determined by using UV photometer after treatment with acetyl acetone and acetyl acid ammonium.

3. RESULTS and DISCUSSION

3.1. Activation Energy (E_a) by DSC Analysis

The E_a of the curing reaction of the unmodified UF, modified UF resin was calculated on the basis of the temperature variation of the maximum of each DSC scan exotherm as a function of the heating rate of the DSC scan, using the Kissinger equation. They can be expressed as follows. n-th order kinetics:

$$d\alpha/dt = k(1 - \alpha)^n \tag{1}$$

Where α , the extent of the curing reaction, is defined as $\alpha = \Delta H_t / \Delta H_{Total}$, and ΔH_t and ΔH_{Total} are the enthalpies of the curing reaction at time t and the end of the curing, respectively. These parameters can be determined from the DSC thermograms.

The rate constant can be expressed as:

$$k = Ae^{-E_a/RT} \tag{2}$$

where A is the frequency factor. Then,

$$\begin{aligned} \ln k &= \ln [(d\alpha/dt) / (1 - \alpha)^n] \\ &= \ln A - E_a/RT \end{aligned} \tag{3}$$

When the order of this reaction is properly assumed, a plot of $\ln k$ vs. $1/T$ allows one to predict A and E_a. Kissinger proposed:

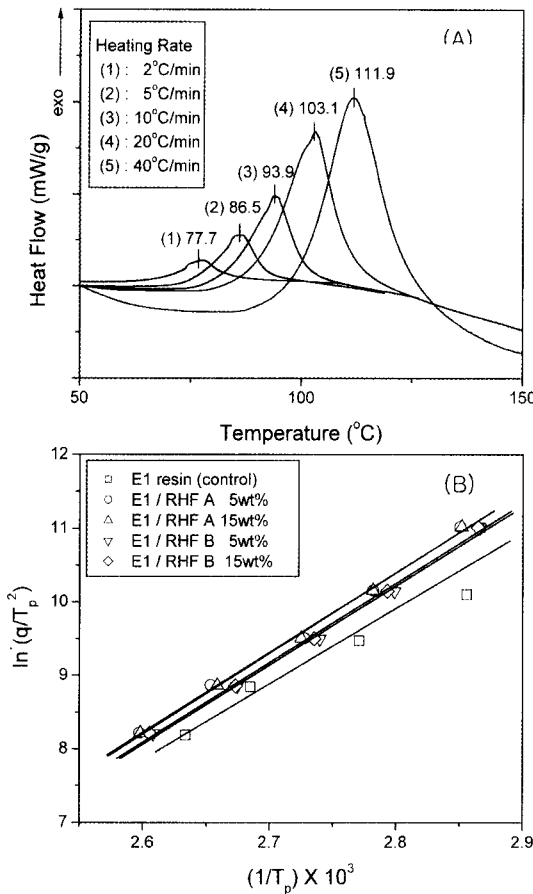
$$E_a \beta (RT_p^2) = Ae^{-E_a/RT_p} \tag{4}$$

Where, β is the heating rate and can be expressed as $\beta = dT/dt$. By taking the logarithm of eq. (4), the Kissinger equation is obtained as follows:

$$\begin{aligned} -\ln(\beta T_p^2) &= \\ -\ln(AR/E_a) + (1/T_p)(E_a/R) \end{aligned} \tag{5}$$

A and E_a can be obtained by plotting $-\ln(\beta T_p^2)$ vs. $1/T_p$.

The UF resins, with addition of 5 and 15 wt% RHF as a scavenger were analyzed by DSC to determine the effect of the amount of RHF on the curing reaction of the modified UF resins. In the DSC thermograms for the various UF-1 resin systems (Fig. 1-A), the curing peaks at the temperature range of 77~112°C correspond to the period of crosslinking reaction. The area of these peaks should be, therefore,



RHF A: 30 μm rice husk flour
 RHF B : 300 μm rice husk flour
 Fig. 1. DSC thermograms of UF-1 resin modified with 30 μm , 15 wt.% rice husk flour according to various heating rate (A), plot of $\ln(\beta/T_p^2)$ vs. T_p^{-1} for UF-1 resin and the contents of rice husk flour (B).

proportional to the frequency of $-\text{CH}_2\text{-O-CH}_2-$ linkages in the UF resin (Szesztay *et al.*, 1993).

The plots of $-\ln(\beta/T_p^2)$ against $1/T_p$ for unmodified UF resin and modified UF resin added with RHF are shown in Fig. 1(B). The curing kinetics with DSC at different heating rates, which were used to obtain the fundamental kinetic constants of E_a , were obtained from plotting $\ln(\beta/T_p^2)$ against $1/T_p$. Also, Fig. 2 and Table 3 present the E_a of the UF resins for the

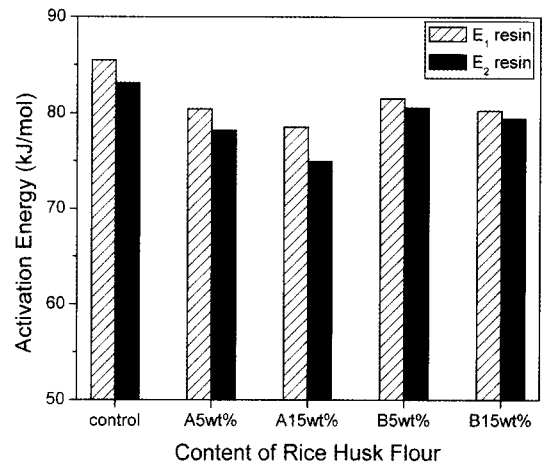


Fig. 2. The activation energy of the modified UF resins obtained by various heating rate.

curing process. The E_a is an important kinetic parameter describing the effect of temperature on the curing reactions.

The E_a of UF resin modified with RHF contented RHF was lower than the unmodified UF resin. The E_a of UF resin decreased with increasing RHF contents. In other words, the energy which UF resin must acquire before a curing process makes a difference with RHF content. Lower E_a of the modified UF resin resulted in faster curing than the high E_a of unmodified UF resins.

The E_a of UF resin unmodified with B type RHF was lower than A type. Since B type RHF with a larger particle size (lower surface area) had lower ash content.

3.2. pH Variation

The cured UF-1 resin with 5, 10 and 15 wt% of 30 μm and 300 μm RHF (Type A and Type B, respectively) were prepared. The pH of uncured UF-1 and UF-2 resins without addition of RHF was approximately 9.5. After the curing, the pH of both UF-1 and UF-2 sharply decreased to approximately pH 6.0 (Fig. 3 and

Table 3. Activation energies of UF resins calculated by the Kissinger equation

Resin type	Formulation of resins	$\ln(\beta/T_p^2)$ vs. T^{-1}	Activation Energy (kJ/mol)
E ₁ class	UF 1 resin (control)	$Y = 10.282X - 18.87$ $R^2 = 0.927$	85.5
	UF resin + 30 μm RHF 5 wt.%	$Y = 9.675X - 20.06$ $R^2 = 0.995$	80.4
	UF resin + 30 μm RHF 15 wt.%	$Y = 9.445X - 20.34$ $R^2 = 0.998$	78.5
	UF resin + 300 μm RHF 5 wt.%	$Y = 9.804X - 21.40$ $R^2 = 0.998$	81.5
	UF resin + 300 μm RHF 15 wt.%	$Y = 9.655X - 21.90$ $R^2 = 0.997$	80.2
E ₂ class	UF 2 resin (control)	$Y = 9.996X - 18.80$ $R^2 = 0.975$	83.1
	UF resin + 30 μm RHF 5 wt.%	$Y = 9.401X - 19.06$ $R^2 = 0.995$	78.2
	UF resin + 30 μm RHF 15 wt.%	$Y = 9.015X - 22.34$ $R^2 = 0.997$	74.9
	UF resin + 300 μm RHF 5 wt.%	$Y = 9.689X - 20.04$ $R^2 = 0.994$	80.5
	UF resin + 300 μm RHF 15 wt.%	$Y = 9.554X - 20.40$ $R^2 = 0.993$	79.4

4). The pH of the cured UF-1 and UF-2 resins of both type A and B slightly increased with increasing RHF content independent of particle size. However, the pH of the type A resins was

always slightly higher than the corresponding Type B resins. These results are in good agreement with those reported by Myers (1990), Koutsky and Myers (1987). In order to eluci-

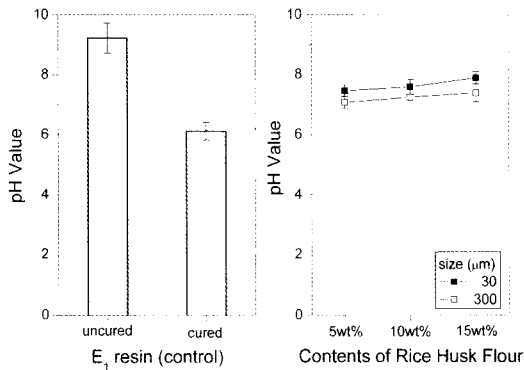


Fig. 3. The pH variation of cured UF-1 (E₁) resins to which rice husk flour was added.

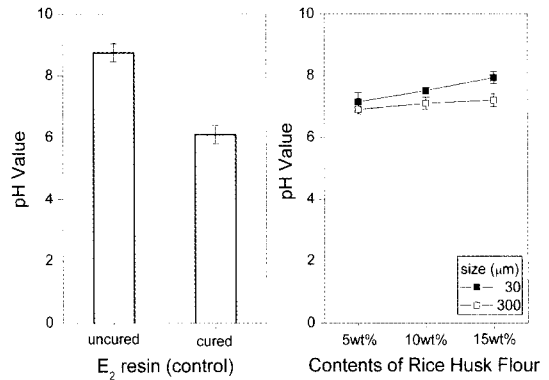


Fig. 4. The pH variation of cured UF-2 (E₂) resins to which rice husk flour was added.

date the effect of a scavenger, the UF resins were mixed with the following additives which are all water insoluble powders.

In this study, the pH of the modified UF resins increase more than unmodified UF resin in each case.

Hse and coworkers (1994) investigated the effect of reaction pH on properties and performance of UF resins, in which pH and F/U molar ratio were used as the variables. At the same reaction pH, the free-formaldehyde content increased with increasing F/U molar ratio. However, at the same F/U molar ratio, the free-formaldehyde content decreased with increasing reaction pH. Much evidence shows that low pH accelerates not only the rate of cure of UF resins but also their rate of hydrolysis after cure (Allan *et al.* 1980, Higuchi and Sakata 1979, Myers 1982).

Accordingly, the formaldehyde emission should decrease with increasing pH of cured resin. Thus, on the basis of these results, RHF plays an important role as scavenger in the rice husk flour filled PB.

3.3. Formaldehyde Emission by 24 h Desiccator Method

The formaldehyde emission of the control board and the rice husk flour-filled particle-boards show that the formaldehyde emission for the E₁ and E₂ class type UF resin decreased slightly with increasing RHF contents (Fig. 5).

The formaldehyde emission of E₂ type resin bonded PB was rapidly decreased with type A RHF of 15 wt% content. At RHF of 15 wt%, it reached 1.2 mg/ℓ. The formaldehyde emission from control PB (3.5 mg/ℓ) reduced about 65.7%. From the result of type A RHF of 15 wt% content, formaldehyde emission of PB decreased E₂ grade to E₁. The ash obtained from the combustion of raw rice husk flour at moderate temperature contains 87~97% of silica

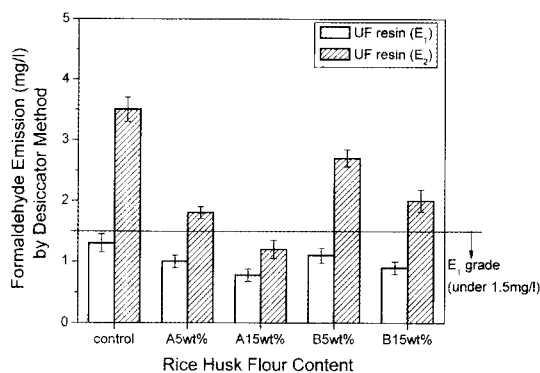


Fig. 5. Formaldehyde emission from PB by 24 h desiccator method with comparison of E₁ and E₂ resin.

in an amorphous form and some amount of metallic impurities.

The particle size of rice husk flour decreases with increasing silica content and surface area. Especially, the silica content is 25.8 wt% in the untreated rice husk and the silica content of the rice husk ash is 92.9 wt% (Della *et al.*, 2002; Kim & Eom 2001; Talcin & Sevinc, 2001). These inorganic compounds have an effect on the formaldehyde emission of the PB.

3.4. Formaldehyde Content by Perforator Method

The results comparing the formaldehyde content for the RHF with a particle size of 30 μm (type A) and that of the RHF with a particle size of 300 μm (type B) are presented in Fig. 6. The formaldehyde contents values of the PB made using type A were highly decreased.

This implies that RHF has a scavenger effect on the formaldehyde content in the PB. From the result of type A RHF of 15 wt% content, formaldehyde content of PB decreased from E₂ to E₁.

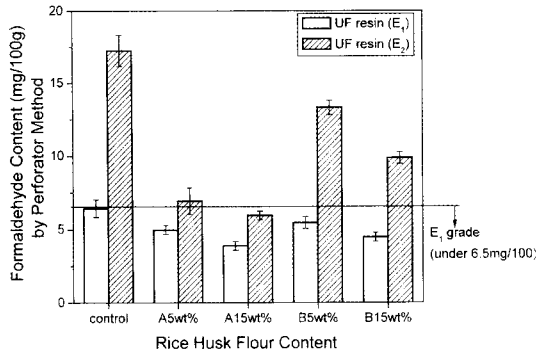


Fig. 6. Formaldehyde content from PB by perforator method with comparison of E₁ and E₂ resin.

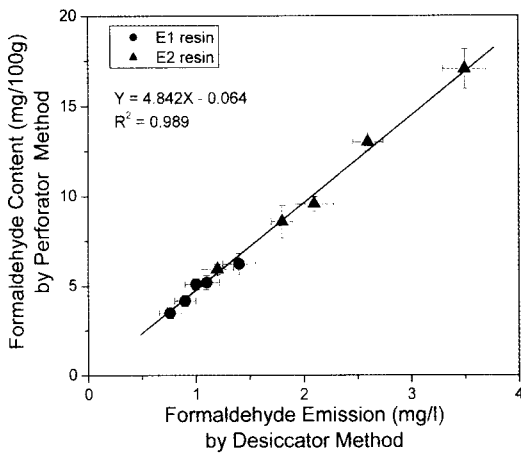


Fig. 7. Correlation between formaldehyde emission by 24 h desiccator method and formaldehyde content by perforator test.

3.5. Comparison between Formaldehyde Emission by 24 h Desiccator and Formaldehyde Content by Perforator Method

The result of a comparison between 24 h desiccator and perforator test using PB was shown in Fig. 7. The linear regression analyses show a good correlation between the results for the 24 h desiccator and the perforator tests. The linear regression of a correlation between the desiccator and the perforator was $Y=4.842X-$

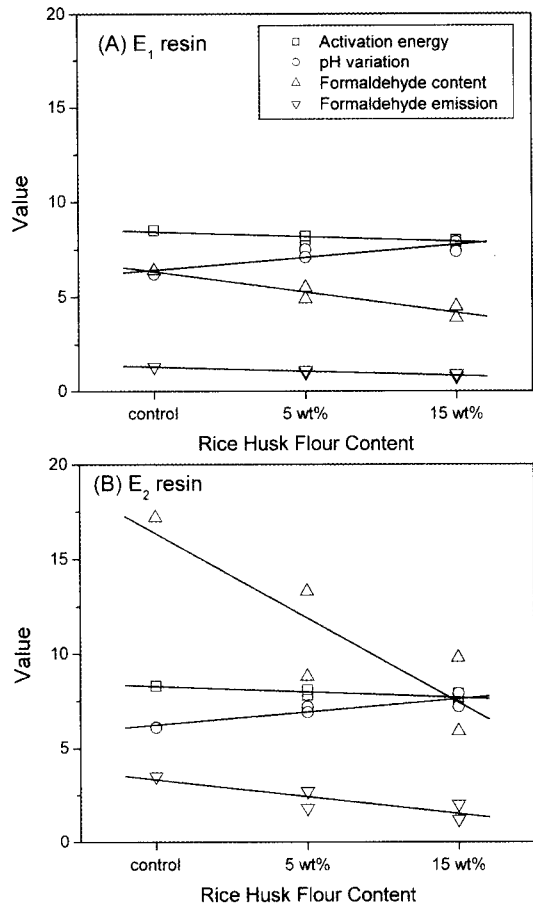


Fig. 8. Characteristics of UF resin and UF bonded PB as a function of the rice husk flour content.

0.064 ($R^2=0.989$).

The formaldehyde emission from a PB depends on its formaldehyde content therefore there is necessarily a correlation between the content and the emission rate. But, factor like the porosity or the density of the board, the properties of the surface materials and surface coatings and the size of the specimens influence the actual emission rate.

3.6. RHF as Scavenger

Fig. 8 show the amount of formaldehyde

content versus the E_a , pH variation, formaldehyde content by perforator method and formaldehyde emission by desiccator method. As the pH and E_a for the modified UF resin, the formaldehyde emission and content decreased. The formaldehyde emission and content behavior indicates that pH and E_a have a very strong influence, which is supplemented by the degree of curing and by the possible formaldehyde scavenging effect of the rice husk flour.

Because the most of the free formaldehyde that considerably influencing the emission disappears over time, then the presence of the $-CH_2-$ groups plays a role. Hence, increased resin crosslinking indicates a higher concentration of $-CH_2-$ groups, which may hydrolyze and emit formaldehyde slowly as time.

Thus on the basis of these results, RHF possibly plays an important role as scavenger in curing process of UF resin.

The RHF particle size decreased with an increase of silica content. This inorganic compound has an effect on the formaldehyde emission of the particleboard.

The formaldehyde content from the experiment result were evaluated to determine whether how formaldehyde content was related to the E_a and the RHF content of the modified resin. The high formaldehyde contents values for the unmodified UF resins compared with the low formaldehyde contents of the modified resins suggest that the addition of RHF to UF resins reduces formaldehyde content.

However, the resins with high formaldehyde content levels were generally those cured at low temperatures. As demonstrated previously by DSC data, the reactivity of UF resin containing RHF tends to increase with an increase in RHF content. Thus, those resins containing RHF with the lower formaldehyde contents were probably better cured.

Fig. 8 shows that the E_a of control UF resin is higher, and formaldehyde content is higher in

E_1 and E_2 resin. The control resin with the highest formaldehyde emission was probably not fully cured due to the fast curing reaction. Thus, the results suggest that the addition of RHF as a modifier to UF resin reduces formaldehyde content because of according slow curing reaction.

4. CONCLUSION

RHF shows only marginal cure interference but causes an increase in cured resin pH and lowers formaldehyde emission.

RHF causes an increase in cured resin pH. The pH of the modified UF resin slightly increased independently of particle size. The pH of the cured UF resin containing RHF of type A (30 μm in particle size) was higher than that of the cured UF resin containing RHF of type B (300 μm).

The curing peak temperature, due to the polymerization of the adhesives, decreased to a slightly lower temperature and E_a with the addition of RHF.

According to the pH and the E_a variation of the UF resin containing RHF, the amount of formaldehyde content were controlled. The formaldehyde emission and formaldehyde content levels of the PB bonded with 15 wt%, 30 μm RHF and E_2 class UF resin were satisfied E_1 grade, as measured by 24 h desiccator and perforator method.

The result of a comparison between 24 h desiccator and perforator test PB showed that the linear regression analyses have a good correlation between the results for the 24 h desiccator and the perforator tests.

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