Differential Scanning Calorimetry of Urea–Formaldehyde Adhesive Resins, Synthesized under Different pH Conditions

Byung-Dae Park, Eun-Chang Kang, Jong Young Park

Department of Forest Products, Korea Forest Research Institute (KFRI), Seoul 130–712, Republic of Korea

ABSTRACT: The purpose of this study was to investigate the effects of reaction pH conditions on thermal behavior of urea–formaldehyde (UF) resins, for the possible reduction of formaldehyde emission of particleboard bonded with them. Thermal curing properties of UF resins, synthesized at three different reaction pH conditions, such as alkaline (pH 7.5), weak acid (pH 4.5), and strong acid (pH 1.0), were characterized with multiheating rate method of differential scanning calorimetry. As heating rate increased, the onset and peak temperatures increased for all three UF resins. By contrast, the heat of reaction (ΔH) was not much changed with increasing heating rates. The activation energy (E_a) increased as the reaction pH decreased from alkaline to strong acid condition. The formaldehyde emission of particleboard was the lowest for the UF resins prepared under strong acid, whereas it showed the poorest bond strength. These results indicated that thermal curing behavior was related to chemical species, affecting the formaldehyde emission, while the poor bond strength was believed to be related to the molecular mobility of the resin used. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 422–427, 2006

Key words: adhesives; differential scanning calorimetry; thermal properties; thermosets

INTRODUCTION

To a large extent, amino resins include urea–formaldehyde (UF) resin, melamine–formaldehyde (MF) resin, melamine–urea–formaldehyde (MUF) resin, melamine-fortified UF resin, and melamine–urea–phenol–formaldehyde cocondensation resin. The world wide production of UF resins in 1998 was estimated to be ~6 billion tons per year, based on 66% resin solids, by mass.[1] Wood-based composite panel industry is a major consumer of amino resins. For example, the proportion of amino resin, including UF resins, MF resins, and MUF resins in North America was about 59% of wood-based adhesives in 1997.[2] Among these amino resins, UF resin, a polymeric condensation product of the chemical reaction of formaldehyde with urea, is the most important type of adhesive in wood-based panel industry, such as particleboard (PB), medium density fiberboard, partly oriented strandboard, plywood, and some other boards.

Compared to other wood adhesives, such as phenol–formaldehyde (PF) resins and diphenylmethane diisocyanate, UF resin possesses some advantages, such as fast curing, good performance in the panel,

water solubility, and lower price. Disadvantages of using the UF resin are lower resistance to water and formaldehyde emission from the panels. Lower resistance to water limits UF resin-bonded panels to interior applications. Formaldehyde emission was one of the important aspects of UF resin in the last few decades.[3–8] The reversibility of the aminomethylene link and susceptibility to hydrolysis explains formaldehyde emission.[9] Thus, the use of UF resin-bonded wood-based composite panels is limited only to nonstructural applications, because of the lack of water resistance.

Much attention has been paid to reduce or control the formaldehyde emission from UF resin-bonded panels. The presence of free formaldehyde in the UF resins prepared is one of the reasons for formaldehyde emission.[10] One of the approaches of reducing formaldehyde emission was to lower F/U molar ratio of the synthesized resin.[11] In addition, the number of urea additions during resin synthesis also influences the properties of prepared UF resin.[12] However, lower F/U molar ratio reduced formaldehyde emission at the expense of poor mechanical properties, such as internal bond (IB) strength and modulus of rupture.[11] To overcome this problem, many attempts have been made to modify the resin synthesis methods, hardener types, additives, etc.[9]

Until the midsixties, most UF resins were synthesized by the two-step reaction procedure: i.e., meth-

Correspondence to: B.-D. Park (byungdae@foa.go.kr).

ylolation under alkaline condition and condensation under acidic condition.[13] This synthesis method was widely employed for UF resin preparations for a long time. In the early seventies, however, this method faced the serious problem of formaldehyde emission. Lower F/U molar ratios from 1.1 to 1.2 started to be used in preparing UF resin. Obviously, these lower F/U molar ratio resins produced poor IB strength of the panel.[11]

In addition to lowering the F/U molar ratio, a number of studies have focused on modifying UF resin properties by manipulating resin synthesis parameters, such as reaction pH condition,[13–15] introduction of second urea addition,[16] and the use of additives.[17,18] In particular, Hse et al.[13] and a Japanese group[14–16] have studied the change of chemical structure of UF resins, prepared under different reaction pH conditions, using ^{13}C NMR technique. One of the common findings of these studies was the detection of uronic structures in the UF resin, prepared under a strong acid condition. Furthermore, Hse et al.[13] suggested weak acid reaction pH condition as a compromise between lower formaldehyde emission and poor mechanical properties of panel.

Even though many authors investigated the properties of UF resins prepared under different reaction pH conditions, studies on thermal curing behavior of UF resin using differential scanning calorimetry (DSC) have been limited. Therefore, this study was conducted to investigate the influence of reaction pH conditions on the thermal curing behavior of the UF resins, using DSC, for a possible reduction of formaldehyde emission.

Chemical reactions in UF resin

The use of different conditions of reaction and preparation could produce a broad variety of UF resins. Basically, the reaction of urea and formaldehyde is a two-step process: usually alkaline methylolation, followed by an acid condensation. The combination of these two chemicals results in linear and branched, as well as tridimensional, network in the cured resin. This is due to the functionality of 4 in urea (because of the four replaceable hydrogen atoms), and that of 2 in formaldehyde. The most important factors determining the properties of the reaction products are (1) the relative molar proportion of urea and formaldehyde, (2) the reaction temperature and time, and (3) the various pH values at which condensation takes place.[10]

The produced molecular species from the methylolation include mono-, di-, and trimethylolureas. It was known that tetramethylolurea had never been isolated.[10] Low temperature and weak acidic pH condition favor the formation of methylene ether bridges ($—CH_2—O—CH_2—$) over methylolation.[18]

Each methylolation step has its own rate constant (k), with different k values for the forward and backward reactions. The reversibility of this reaction is one of the most important aspects of UF resins. This feature is responsible for both the low resistance against hydrolysis and the subsequent formaldehyde emission. An acid condition for UF resin synthesis was known to produce varieties of uronic derivatives.[18] Many other studies detected the presence of some of these species.[14–16,19] The condensation reaction in acid condition refers to the reaction of methylolated ureas into methylene ureas, with water as byproducts.

EXPERIMENTAL

Resin preparation

All UF resins used for this study were prepared in the laboratory. Three different procedures were used, according to three reaction pH conditions, i.e., alkaline, weak acid, and strong acid conditions. For the alkaline reaction, UF resins were synthesized according to traditional two-step procedure. Formaldehyde (37%) was placed in the reactor and heated to 60°C, and then the reaction was adjusted to pH 7.5 with sodium hydroxide (20% wt). Subsequently, urea was added in equal parts at 1-min intervals, and the mixture was heated to 90°C for 1 h. Then, the reaction pH was adjusted to 4.5, with formic acid (20% wt), for the condensation. The second urea was again placed in the reactor at 40°C, before the reaction was terminated by rapid cooling to 25°C. For weak acid condition, the initial reaction pH was adjusted to 4.5 with formic acid. The mixture was heated to 70°C and followed by the addition of the second urea into the reactor at 40°C. For the strong acid condition, the initial pH was adjusted to 1.0 with concentrated sulfuric acid. The reaction was kept at 70°C for 1 h, and kept until the end reaction point. The initial F/U molar ratios were 2.2 for alkali–acid and weak acid condition while the strong acid condition was 3.0. For all resins prepared, both final F/U molar ratio and final pH were adjusted to 1.15 and 8.0, respectively.

Gel time measurement

To compare reactivity of UF resins synthesized, the gel time of the resins were measured, with 3% ammonium chloride (NH_4Cl, 20% wt) as a hardener, at 100°C. An average of three replications was reported.

Free formaldehyde determination

Free formaldehyde in the prepared UF resins was determined by a slightly modified sodium sulfite method.[20] The solution of $1M$ sodium sulfite (25 mL)

Parameters	Conditions
Board size	$12 \times 300 \times 300$ mm^3
Target board density	750 kg/m^3
Wax content	1%
Resin content	10% of oven dry weight of particle
Total hot-pressing time	5 min
Hot-pressing temperature	180°C
Board pressure	3.43 MPa

mixed with 10 mL HCl was added to 2–3 g of UF resin sample, dissolved in 100 mL distilled water. The mixed solution, containing about 10 drops of 0.1% thymol phthalein, was neutralized with 1N sodium hydroxide. The percent of free formaldehyde was determined by the equivalent of the amount of the consumed sodium hydroxide in titration.

DSC measurement

A DSC (TA Q10, TA Instrument, USA.), with high-pressure cells, was used to evaluate the curing behaviors of UF resins synthesized with different heating rates (5, 10, 15, and 20°C/min.). The UF resins of 3–5 mg, including 3% ammonium chloride (based on the resin solids), was weighed in the high-pressure cell prior to scanning, with at least two replications per heating rate and UF resin pH levels. For each heating rate, the onset temperature, peak temperature, and heat of reaction were recorded, and an average value, with at least two replications, was represented. This multiheating rate method was employed to determine the reaction activation energy (E_a) of the UF resins, using the Kissinger equation,[21] which is expressed as follows:

$$-\ln\left(\frac{\beta}{T_p^2}\right) = \frac{E}{RT_P} - \ln\left(\frac{ZR}{E}\right) \qquad (1)$$

where β is the heating rate (°C/min) and T_p is the peak temperature. The aforementioned equation provides a straight line between $-\ln(\beta/T_p{}^2)$ and $1/T_p$. From a fitted straight line, the activation energy (E_a) can be

calculated from the slope. It was reported that this multiheating rate scanning technique produced better results than a single dynamic scanning technique for PF resin.[22] However, it does not give any information on reaction order.

PB manufacture and determination of properties

Softwood particles, obtained from raw materials of a PB mill, were dried to 3% initial moisture content, before resin blending. Particles were blended in a drum blender, using the prepared UF resins at 10 wt % resin content, based on oven dry weight of the particles. Ammonium chloride (3%; based on the resin solids) was added into the resin, just prior to its blending. After blending, forming was done using the blended particles in a deckle box. Particle mat prepared was hot-pressed, and then conditioned for 7 days at 20°C and 65% RH. Other parameters for making PB are shown in Table I.

The formaldehyde emission of PB prepared was determined using 24-h desiccator method. Test specimens, with 50×150 mm^2 dimensions, were placed in a glass desiccator, containing 300 mL distilled water, for 24 h at 20°C and 65% RH. The concentration of formaldehyde emission in the water was determined using the acetyl–acetone method, with an UV spectrophotometer at the wavelength of 412 nm, following the procedure specified in the Korea Standard.[23] IB strength of PB was determined, following the procedure of the same standard.[23]

RESULTS AND DISCUSSION

The properties of UF resins prepared under three different reaction conditions are summarized in Table II. The resin prepared under weak acid condition showed relatively greater viscosity and higher free formaldehyde compared with other two resins prepared. The nonvolatile solid contents of UF resins prepared under three different reaction conditions were about 50% by weight.

The results of gel time measurements of the UF resins prepared under three different reaction conditions are shown in Figure 1. For all pH levels, the gel time of all UF resins rapidly decreased, with increasing ammonium chloride levels from 0 to 3%. How-

TABLE II
Properties of UF Resins Synthesized at Different pH Levels

Reaction pH	Nonvolatile solids content (%)	Initial F/U molar ratio	Final F/U molar ratio	Viscosity (cps)	Free HCHO (%)	Final pH
7.5	48.5	2.2	1.15	58	0.45	8.0
4.5	52.1	2.2	1.15	135	0.69	8.0
1.0	49.8	3.0	1.15	66	0.55	8.0
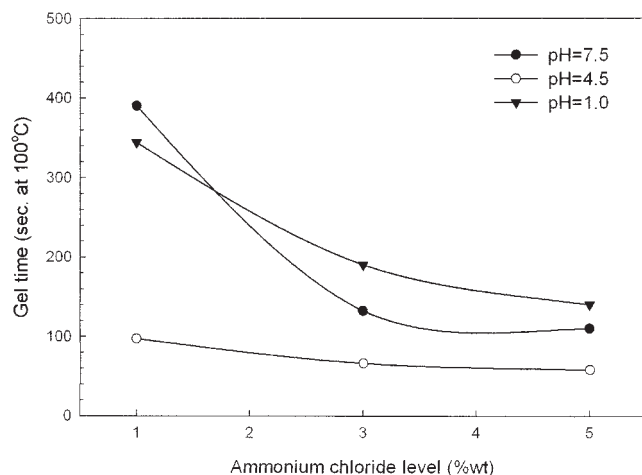
Figure 1 Gel time of UF resin synthesized under different reaction pH levels, at 100°C.

ever, the gel time did not proportionately decrease when the hardener level increased from 3 to 5%. The UF resins synthesized under strong acid condition showed longer gel time at 5% hardener level. The gel time of UF resins synthesized under weak acid condition was much shorter than those of the resins prepared under both alkaline and strong acid conditions, at all hardener levels. This result suggested that the weak acid reaction condition provides fast cure with UF resin, compared with other reaction conditions.

Figure 2 shows a typical DSC curve of UF resin

prepared under weak acid condition, showing onset temperature, heat of reaction (ΔH), and peak temperature (T_p). The onset point is defined as the extrapolated beginning point of any transition or phase change, determined from data analysis. Thus, the onset temperature (arrowed) may be expressed as an extrapolated and starting temperature of curing of the UF resin. The onset temperature of a UF resin, for each heating rate, was obtained from an average of three dynamic scans.

As shown in Figure 3, the onset temperature generally increases with increasing heating rates. The highest onset temperature, regardless of heating rates, was found at the UF resin synthesized under weak acid condition, followed by the one prepared under the alkaline condition, and then the one prepared under the strong acid condition. These results indicate that the UF resin synthesized under strong acid condition provides lower onset temperature, which makes cure fast in the early stage of UF resin cure.

Figure 4 shows the change of reaction heat (ΔH) of UF resins during their curing. The ΔH is the amount of energy required to complete the cure of a resin, which is the area under an exothermic DSC curve. Although there were variations, differences between the ΔH values of the UF resin, prepared under strong acid condition, were small for different heating rates. The ΔH of the strong acid UF resin was the lowest, compared with those of the others. It was expected that a longer gel time of the UF resin, prepared under strong acid
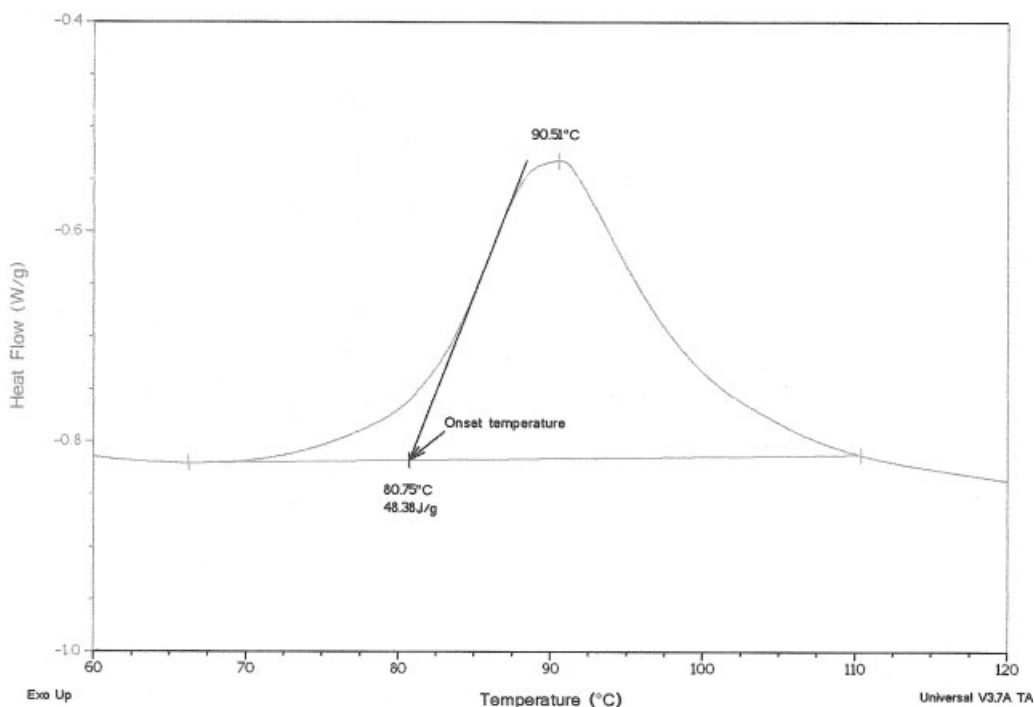
Figure 2 A typical DSC curve of UF resin, prepared under weak acid condition, showing the onset temperature and heat of reaction (ΔH), at a heating rate of 5°C/min.
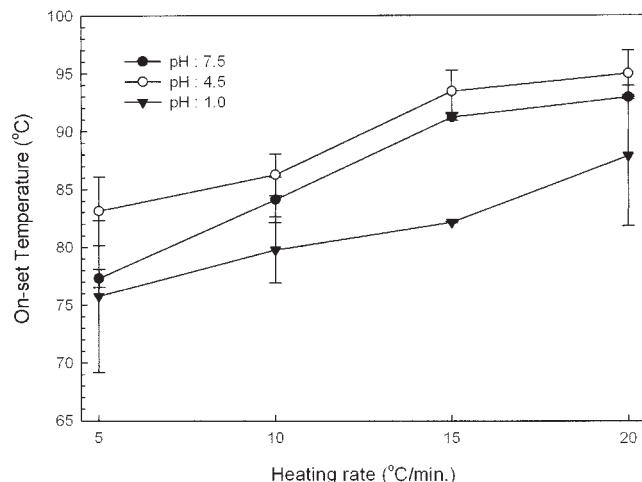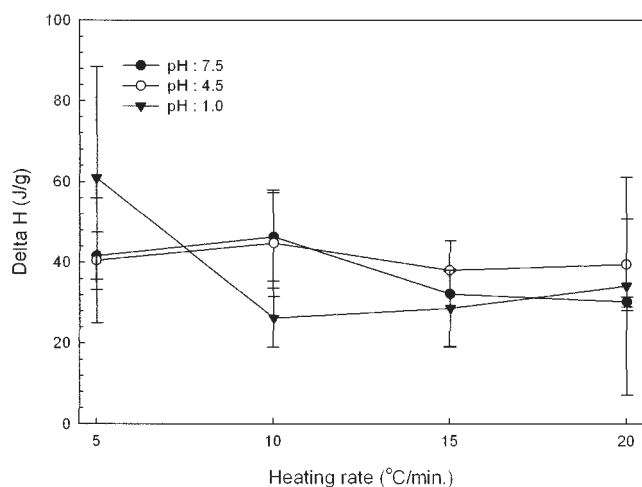
Figure 3 Changes of the onset temperatures of UF resins depending on heating rates.

Figure 5 Changes of peak temperatures of UF resins depending on heating rates.
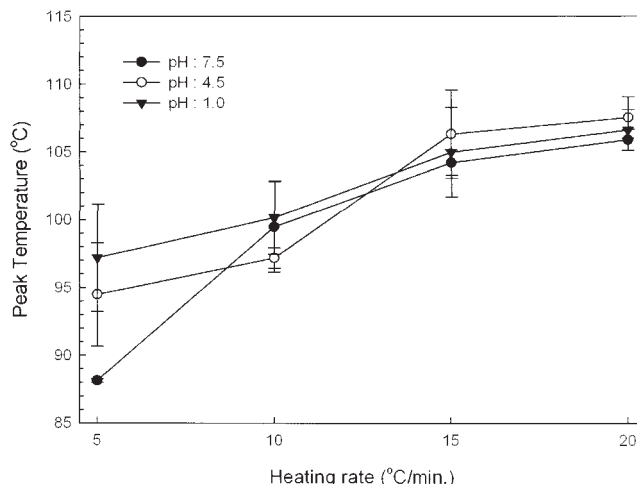
condition, could give a greater ΔH value. But this was not the case.

Even though the onset temperature is an indicator of UF resin cure or reactivity, the peak temperature is an important parameter of comparing the reactivity of UF resin.[24] The peak temperature is a temperature where the rate of cure reaches the maximum during a dynamic scan of the reaction. In general, the peak temperatures of UF resins increased, with increasing heating rate (Fig. 5). This result might be due to the thermal lag that occurred in transferring heat from the capsule to the sample resin inside the capsule. The peak temperatures of UF resins were quite close for all heating rates.

The peak temperatures of UF resins at different heating rates were used to build a linear relationship between $\ln(\beta/T_p^2)$ and $1/T_p$, as defined by eq. (1). The

slope of the linear regression line was used to calculate the activation energy. As shown in Figure 6, the activation energies (E_a) of UF resins, prepared under alkaline, weak acid, and strong acid conditions, were about 78, 94.8, and 152.2 kJ/mol, respectively. These E_a values were greater than the reported one.[25] In general, E_a increased, as the pH levels decreased from alkaline to strong acid condition. This result suggests that the UF resin synthesized under strong acid condition requires more energy to start its curing process than those of the other UF resins, prepared under weak acid and alkaline conditions.

The previous article reported that the strong acid reaction pH condition produced uronic structures in UF resin, using both FT-IR and ^{13}C NMR spectroscopies.[24] Also, the authors reported that the proton spin–lattice rotating frame relaxation times ($T_{1\rho H}$) value of

Figure 4 Changes of heat of reaction (ΔH) of UF resins depending on heating rates.
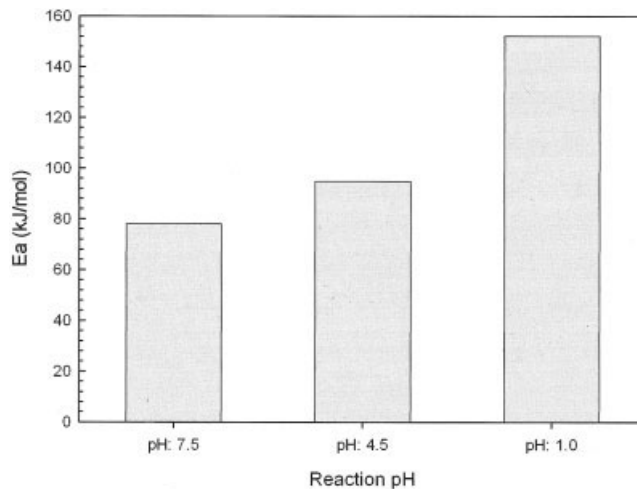
Figure 6 Activation energies of UF resins depending on synthesized pH conditions.

Reaction pH	Formaldehyde emission (mg/L)	Internal bond strength (MPa)
7.5	1.83	0.61
4.5	2.15	0.55
1.0	0.78	0.04

the peak at 46 ppm assigned to methylene linkages decreased with decreasing the reaction pH for UF resin synthesis, indicating that molecular mobility of UF resin increased with decreasing the reaction pH used during its synthesis.

It was known that more branched polymers were formed in methylolation reaction, while methylene linkages were formed in condensation reaction.[18] In other words, alkaline condition would produce short and sterically hindered polymers, while acid condition would produce less crosslinked and pliable polymers. Thus, a smaller relaxation time of the UF resin, synthesized under strong acid condition, indicated a greater mobility of the chemical structure. It was believed that a greater activation energy of UF resin resulted in a greater molecular mobility.

Formaldehyde emissions of PBs bonded with UF resins were shown in Table III. PBs bonded with UF resins, prepared under strong acid condition, showed the least formaldehyde emissions, followed by alkaline and weak acid condition. This result is related to the amount of free formaldehyde present in the resin. Thus, strong acid condition for UF resin synthesis would be an option to reduce formaldehyde emission of UF resin. However, the IB strength of PB showed quite contrasting results: PB prepared with UF resin, prepared under strong acid condition, showed the poorest strength followed by weak acid and alkaline conditions.

The poor bond strength of UF resin, synthesized under strong acid condition, could be explained by the fact that the $T_{1\rho H}$ values of UF resins decreased with decreasing reaction pH.[24] In other words, a decreased $T_{1\rho H}$ value of UF resin provided a greater flexibility (i.e., less rigidity) of molecular network, which could cause weak cohesive bond strength, which consequently resulted in poor bond strength, even though the strong acid condition resulted in more branched chemical species like uronic species. However, future studies are required to relate bond strength of UF resin in PB to its molecular mobility.

CONCLUSIONS

This study was conducted to investigate the effects of reaction pH conditions for the synthesis of UF resins on their thermal curing behaviors, using multiheating rate method of DSC. The conclusions drawn from this study were summarized as follows:

The gel time was the largest for the strong acid UF resin, followed by alkaline and then weak acid conditions. Both the onset temperature and ΔH of UF resin were the lowest for the one synthesized under the strong acid condition. The activation energy (E_a), obtained with a linear relationship between peak temperature and heating rate, increased as the pH level during UF resin synthesis decreased.

The formaldehyde emission of PB was the least for the UF resins prepared under strong acid, whereas it showed the poorest bond strength, which could be related to the molecular mobility of a cured network of UF resin.

References

1. Dunky, M. In Proceedings of the 2nd European Wood-Based Panel Symposium, Hanover, Germany, 1999; p 1.
2. Sellers, T., Jr. In Proceedings of the International Contributions to Wood Adhesion Research; Christiansen, A. W., Pilato L., Eds.; Forest Products Society: Madison, WI, 1999; p 31.
3. Myers, G. E. Forest Prod J 1983, 33, 49.
4. Myers, G. E. Forest Prod J 1984, 34, 35.
5. Myers, G. E.; Koutsky, K. A. Forest Prod J 1987, 37, 56.
6. Myers, G. E. Holzforschung 1990, 44, 117.
7. Myers, G. E. In Formaldehyde Release from Wood Products; Meyer, B.; Andrews, B. A. K.; Reinhardt, R. M., Eds., American Chem Society:Washington, DC, 1986; p 8.
8. Pizzi, A.; Lipschitz, L.; Valenzuela, J. Holzforschung 1994, 48, 254.
9. Dunky, M. Int J Adhesion and Adhesives 1998, 18, 95.
10. Pizzi, A. Wood Adhesives: Chemistry and Technology; Marcel Dekker: New York, 1983; p 59.
11. Marutzky, R. In Wood Adhesives: Chemistry and Technology; Pizzi, A., Ed.; Marcel Dekker: New York, 1986; Vol. 2, p 307.
12. Steiner, P. R. Forest Prod J 1973, 23, 32.
13. Hse, C. Y.; Xia, Z. Y.; Tomita, B. Holzforschung 1994, 48, 527.
14. Gu, J. Y.; Higuchi, M.; Morita, M.; Hse C. Y. Mokuzai Gakkaishi 1995, 41, 1115.
15. Tohmura, S.; Hse, C. Y.; Higuchi, M. J Wood Sci 2000, 46, 303.
16. Tomita, B.; Hatono, S. J Appl Polym Sci 1978, 16, 2509.
17. Dutkiewicz, J. J Appl Polym Sci 1984, 29, 45.
18. Pizzi, A. Advanced Wood Adhesives Technology; Marcel Dekker: New York, 1994; p 19.
19. Soulard, C.; Kamoun, C.; Pizzi, A. J Appl Polym Sci 1999, 72, 277.
20. McCaffery, M. Laboratory Preparations for Macromolecular Chemistry; McGraw Hill: New York, USA, 1970; p 61.
21. Kissinger, H. E. Anal Chem 1957, 29, 1702.
22. Park, B.-D.; Riedl, B.; Bae, H.-J.; Kim, Y. S. J Wood Chem Tech 1999, 19, 265.
23. KS F3104 2001 (Korea Industrial Standard). Particleboards; Korea Standards Association: Seoul, Republic of Korea.
24. Park, B.-D.; Kim, Y. S.; Sing, A. P.; Lim, K. P. J Appl Polym Sci 2003, 88, 2677.
25. Pizzi, A.; Panamgama, L. A. J Appl Polym Sci 1995, 58, 109.