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Analysis of Curing Process and Thermal Properties of Phenol-Urea-Formaldehyde Cocondensed Resins[*1]

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フェノール・ユリア共縮合樹脂の硬化過程と熱的性質の解析[*]

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フェノール・ユリア共縮合樹脂の硬化過程を，レゾール，ユリア樹脂，レゾールとユリア樹脂の機械的混合物，ならびに，トリメチロールフェノールとユリアの混合物と比較検討した。また，これらの樹脂の硬化後の熱的性質についても比較した。

結果は次のようにまとめられる。

(1)　機械的ブレンド系を酸性下で硬化する場合は，ユリア樹脂の硬化が初期反応を支配し，レゾールの硬化が不十分になる。塩基性下で硬化するとレゾールと同様の硬化過程をたどるが，硬化にはレゾールより高温を要する。また，一般に，ブレンド物の硬化後の熱安定性は劣った。

(2)　トリメチロールフェノールとユリアの混合系の硬化反応は2段階に分れて進行する。低温域の反応は，反応性の高いp-メチロール基の反応に，また，高温域の反応はo-メチロール基の反応に由来すると推定された。この混合物は，硬化後に高い熱安定性を示した。

(3)　共縮合樹脂も(2)と同様に，2段階の硬化過程を示した。また，共縮合樹脂は，酸性より塩基性で硬化させた場合に高い熱安定性を示すことが判明した。

The curing processes of resols, urea-formaldehyde (UF) resins, their mechanical blends, and phenol-urea cocondensed resins, as well as the reaction of 2,4,6-trimethylolphenol with urea, were investigated with the torsional braid analysis method. The thermal stabilities of these resins after curing also were compared.

The results were as follows:

(1) In the curing process of the mechanical blends under acidic conditions, it was found that the self-condensation of UF resins dominates in the initial stages, and that the curing of phenolic resin is apt to be incomplete. In alkaline curing, the blended resins require higher curing temperatures than resol, and their heat-resistances after curing generally were poor.

(2) It was found that the reaction of trimethylolphenol with urea involved two stages. It was suggested that the first stage at lower temperatures is attributed to the reaction of p-methylol groups with urea residue, and that the second stage at higher temperatures is due to the reaction of o-methylol groups and urea residue. This mixture gave a resin having a great heat-resistance after

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completion of the reaction.

(3) The curing process of the cocondensed resins also involved two stages. It was concluded that alkaline curing is better than acidic curing for these resins, and also that the heat-resistances of the cocondensed resins are superior to those of the mechanical blended resins.

Keywords: cocondensation, phenol-urea-formaldehyde, curing process, thermal stability.

INTRODUCTION

In the preceding papers,[1,2] we reported our success in finding an effective method of producing cocondensation between phenol and urea through a reaction with formaldehyde, and the synthesis of an alternating copolymer from 2,4,6-trimethylolphenol and urea as well as several kinds of cocondensates which included the self-condensation of phenol to some extent. It also has been found that the chemical structures of the cocondensed resins are greatly dependent on the reactivities of methylol groups. The reactivities of p-methylol groups to urea were greater than those of o-methylol groups to urea in the reaction of 2,4,6-trimethylolphenol with urea.

Apart from these works on the synthesis of cocondensed resins, investigations on their thermal properties during and after curing were considered to be of importance in developing their practical applications. In this paper, we report that the thermal properties of the cocondensates have been investigated by the torsional braid analysis method (TBA), where the temperature dependence of relative rigidity and logarithmic decrement can be followed. The curing processes of the cocondensed resins, which will be considered to relate to chemical kinetics on the reactivity of o- and p-methylol groups, have been compared with those of resol or mechanical blended resins of resol and urea-formaldehyde (UF) resin. The reactions of a mixture of trimethylolphenol and urea also have been analyzed with the TBA method.

2. EXPERIMENT

2.1 Synthesis of resol and UF resins

Industrial grade phenol, urea, and 37% formalin were used in all experiments. Resols were synthesized with two molar ratios of formaldehyde to urea (F/U = 1.5 and 3.0) using a NaOH catalyst by heating at 80°C. Final pHs of both resols were 10.0.

A UF resin was synthesized with the molar ratio of formaldehyde to urea (F/U = 1.5) by two steps: (1) methylolation at an initial pH of 8.0 (NaOH) without pH adjustment during the reaction for 15 min; (2) condensation at pH 5.0 (HCl) for one hour. The reaction mixtures then were cooled to room temperature and neutralized with NaOH solutions.

A blended resin was prepared by mechanically mixing the same amounts of resol (F/P = 3.0) and UF resin (F/U = 1.5). A mixture of resol (F/P = 3.0) and urea itself was also prepared, and its final molar ratio was F/P/U = 3/1/1.

2.2 Preparation of mixtures of 2,4,6-trimethylolphenol and urea

Sodium 2,4,6-trimethylolphenate, which was prepared according to Freeman,[3] was dissolved in water (20-30%, w/w), and acidified to pH 5.0 by 50% H_2SO_4. After adding an equimolar of urea, the pHs of the solutions were adjusted to 3.5, 9.8 and 11.2. The final molar ratios of the mixtures were F/P/U = 3/1/1.

2.3 Preparation of phenol/urea/formaldehyde cocondensed resin

A solution of sodium 2,4,6-trimethylolphenate also was acidified to pH 5.0 and added by a calculated amount of urea. The mixture was adjusted to pH 2.5 and reacted at 90°C. As the reaction proceeded, the mixture became cloudy. Finally oily precipitates separated from the water layer. These were washed with water several times, and dried in vacuum. Four kinds of cocondensed resin were prepared with molar ratios of F/P/U = 3/1/1, 3/1/2, 3/1/3, and 3/1/6. These dried resins were soluble in dimethylformamide (DMF). Their ^{13}C-NMR (carbon 13 magnetic resonance) spectra were analyzed as reported in the previous papers.[1,2] Table 1 shows the ratios of urea incorporated with the cocondensed resins, which are represented as molar ratios of urea to phenol (U/P).

2.4 Torsional braid analyses of curing processes of resins

Torsional braid analyses was made with a free torsional pendulum apparatus (RESCA Co. Ltd.). The liquid samples, such as resols, UF resin, blended resin of resol and UF resin, a mixture of resol and urea, and a mixture of 2,4,6-trimethylolphenol and urea, were brushed onto glass braids after adding a curing agent or adjusting the pHs to target levels. The TBA samples of the cocondensed resin of the initial condensation stage also were prepared after adjusting pHs to 3.5 and 9.5. The amounts of all dried resins on braid generally were 60-90 mg. TBA measurements were started immediately after placing resins onto glass braids. The rate of elevation of temperature was 3°C/min. Results were plotted in terms of logarithmic decrement, α_T, and relative rigidity, $Gt/Go=(Po/Pt)^2$, where Po is the frequency interval at the start of measurements (about 20°C) and Pt is that at a temperature of t°C. Curing conditions for dynamic mechanical measurements are cited in the figures.

2.5 Torsional braid analyses of thermal properties of cured resins

A commercial resol was cured on a glass braid at 150°C for 30 min, and a commercial UF resin was cured on it at 115°C for 30 min after adding ammonium chloride (5%). The dried cocondensed resins were dissolved in DMF. After adding p-touenesulfonic acid (PTS) or NaOH, the solutions were cured on a grass braid at 150°C for 30 min. The amounts of resins on glass braids were also 60-90 mg in dry weight. The measurements were performed under the same conditions as stated in the previous section, and curing conditions are shown in the figures.

3. RESULTS AND DISCUSSION

3.1 Curing processes of resol, UF resin, and their mechanical blended resins

Figures 1-(1) and 1-(2) show the changes of dynamic mechanical properties during the curing processes of two kinds of resols different in synthetic molar ratios of F/P. Curing processes involving the removal of water are well demonstrated by remarkable increases of relative rigidities. A great difference during the curing processes could not be observed between the two samples. The maximum peak of logarithmic decrement appeared between 130°C and 150°C, which was suggested to be necessary to attain complete curing of the resol at pH 10.0. A great heat-resistance was recognized because relative rigidity did not drop at above 200°C. On the other hand, the curing of urea-formaldehyde resin was completed between 110°C and 120°C as shown in Fig. 2-(1). However, relative rigidity began to drop remarkably from about 200°C together with the appearance of a large

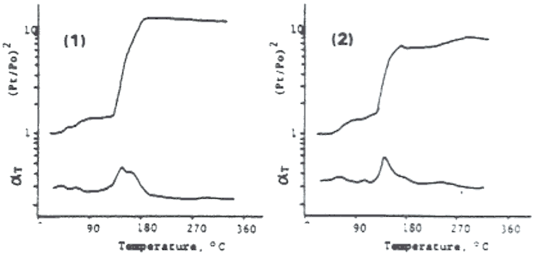

Fig. 1. Torsional braid analyses on curing processes of resols different in synthetic molar ratios at pH 10.0.
Legend: (1) Synthetic molar ratio is F/P=1.5, (2) Synthetic molar ratio is F/P=3.0.

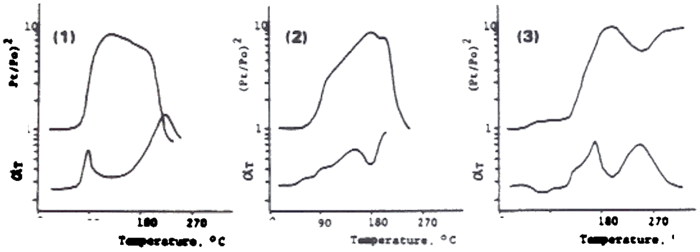

Fig. 2. Torsional braid analyses on curing processes of urea-formaldehyde resin and mechanical blended resin of resol and urea-formaldehyde resins.
Legend: (1) UF resin cured with NH_4Cl (1%), (2) Mechanical blended resin of resol (F/P=3.0) and UF resin (F/U) cured at pH 5.0, (3) The same resin as (2) cured at pH 9.5.

peak of logarithmic decrement.

The curing processes of mechanical blends of resol and UF resin were compared between acidic (pH 5.0) and alkaline (pH 9.5) conditions with the TBA method as shown in Figs. 2-(2) and 2-(3). Because the relative rigidity in acidic curing had a bending point at about 100°C in Fig. 2-(2), the self-condensation of UF resin was considered to proceed in a temperature region below this point. Afterwards the self-condensation of phenolic resin seemed to take place. However, the curing of phenolic resin seemed to be incomplete, because the heat-resistance after completion of curing was quite similar to that of UF resin itself. In alkaline curing as shown in Fig. 2-(3), on the other hand, the blended resin followed almost the same curing process as did resol. However, the temperature to reach the maximum relative rigidity in the blended resin was about 200°C, which was higher than that of resol (180°C). Furthermore, this resin did not have a good heat-resistance after completion of curing. Therefore, it was concluded that mechanical blending was not so effective in obtaining a cocondensation between phenolic and UF resins.

3.2 Reactions of 2,4,6-trimethylolphenol (TMP) with urea

The reactions of 2,4,6-trimethylolphenol with urea were investigated at three pH levels as shown in Figs. 3-(1), 3-(2), and 3-(3). In every reaction, it was shown that the curing process involved two stages. The sharp peaks of logarithmic decrements were observed in the lower temperature regions between 60°C and 70°C in Figs. 3-(1) and 3-(2), and simultaneously relative rigidities increased abruptly in these regions. Because these phenomena could not be observed in the cases of the curing processes of resol, UF resin, and their blended resin, it was suggested that methylol groups of trimethylolphenol would react with urea to produce cocondensed methylene linkages. Furthermore, the self-condensation of producing methylene linkages between phenolic rings was denied by using 2,4,6-trimethylolphenol, in which the reactive sites of ortho- and para-positions were occupied already by methylol groups. In the preceding paper, it was found that the reactivity of the p-methylol group with urea is much more than that of the o-methylol group with urea. From these considerations it was suggested strongly that the phenomena in the lower temperature region were attributable to the cocondensation between the p-methylol group of trimethylolphenol and urea residue. It should be noted that this first stage involves the removal of water from the sample. Furthermore, it was suggested that the second stage of the curing process above 150°C was due to the cocondensation of o-methylol

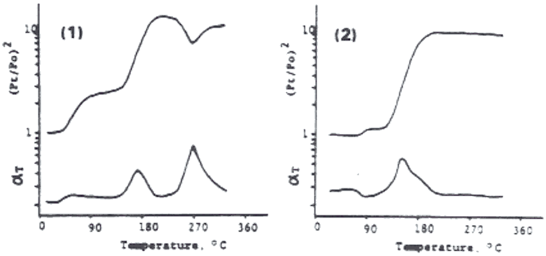

Fig. 4.　Torsional braid analyses on curing processes of mixtures of resol and urea at different pHs.
Legend: (1) pH 3.5, (2) pH 9.8
Notes: Molar ratios of all mixtures are F/P/U=3/1/1.

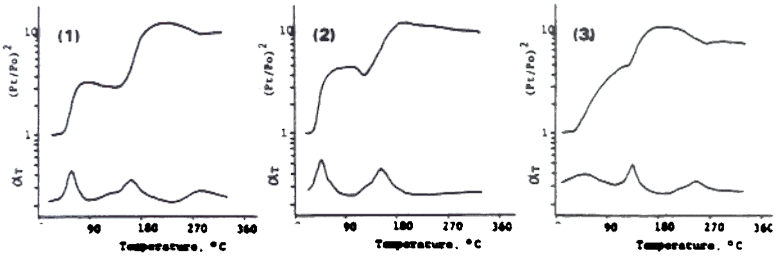

Fig. 3.　Torsional braid analyses on the reaction processes of mixtures of trimethylolphenol and urea at various pHs.
Legend: (1) pH 3.5, (2) pH 9.8, (3) pH 11.2
Notes: Molar ratios of all mixtures are F/P/U=3/1/1.

groups with urea residue. Finally, the resins having great heat-resistances were considered to be obtained by these cocondensations because relative rigidities were quite stable after completion of curings. Figures 4-(1) and 4-(2) show the results of TBA analyses the during curing process of the mixture of resol and urea itself. In acidic conditions (Fig. 4-(1)), the curing process also involved two stages. Under alkaline conditions (Fig. 4-(2)), however, the first stage was not obvious. Although this phenomenon can not be explained at this time, it might be due to the decrease of p-methylol groups during the storage of resol sample or to the formation of dimethylene ether groups which are well known to decompose to methylene linkages and formaldehyde at more than 140°C.

3.3 *Curing processes of phenol-urea-formaldehyde cocondensed resins*

The TBA analyses of curing processes of the cocondensed resins are shown in Fig. 5-(1) and 5-(2), which resemble Figs. 3-(1) and 3-(2), respectively. The ratio of the amount of urea incorporated into this cocondensate was U/P=0.65 as shown in Table 1. In both figures, it is obvious that the curing process involved two stages. Here it also was suggested that the cocondensation between p-methylol groups and urea residues dominates the first stage. The second stage may be due to the cocondensation between o-methylol groups and urea residues and also to self-condensation between phenolic rings. Judging from the decrease of relative rigidity and the behavior of logarithmic decrement after completion of curing reaction, the alkaline curing was superior to the acidic curing in obtaining a great heat-resistance, partly because phenolic methylol groups are apt to introduce self-condensations between phenolic rings as well as cocondensations.

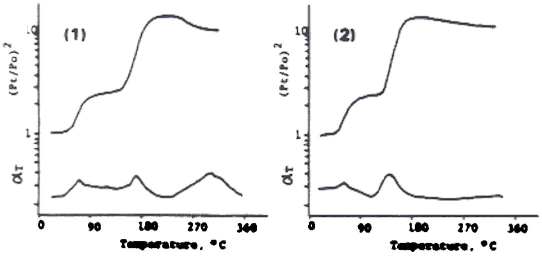

Fig. 5. Torsional braid analyses on curing processes of phenol-urea cocondensed resin at different pHs.
Legend: (1) pH 3.5, (2) pH 9.5
Notes: Synthetic molar ratio of the resin was F/P/U=3/1/1.

3.4 *Thermal properties of cured resins*

In Fig. 6. temperature dependence of dynamic mechanical properties after curing are compared between a commercial resol for plywood use and a UF resin for wood working use. The resol displayed a great heat-resistance within measuring temperatures. The relative rigidity of the UF resin began to gradually decrease from about 200°C and abruptly decrease over 250°C.

Four kinds of cocondensed resins, different in synthetic molar ratios were cured at 150°C with p-

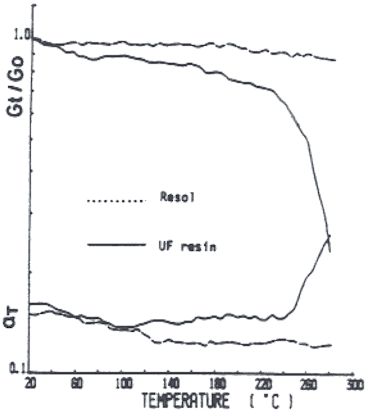

Fig. 6. Comparison of the thermal stabilities between cured resol and urea-formaldehyde resin with torsional braid analyses.

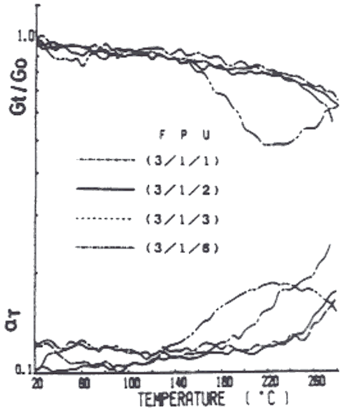

Fig. 7. Comparison of thermal stabilities of cured phenol-urea cocondensed resins synthesized at various molar ratios.
Notes: All resins were cured under acidic condition.

Table Ratios of urea residues to phenolic rings in cocondensed phenol-urea-formaldehyde cocondesed resins.

Synthetic molar ratio F/P/U	Incorporated molar ratio U/P
	0.65
	0.80
	1.0
	1.4

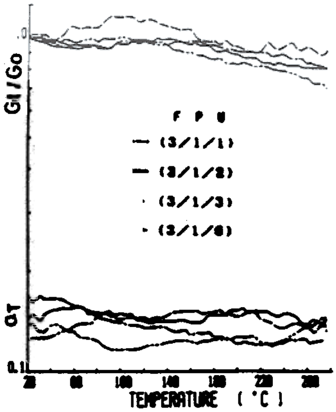

Fig. 8. Comparison of thermal stabilities of cured phenol-urea cocondensed resins synthesized at various molar ratios.

Notes All resins were cured under alkaline condition.

toluenesulfonic acid. Their thermal stabilities are compared in Fig. 7. The ratios of urea incorporated into the cocondensed resins were different according to the synthetic molar ratio of F/P/U as shown in Table 1. A drop of relative rigidity is observed from about 150°C for the resin of F/P/U=3/1/6. This will be derived from a low crosslinking density. Because an excessive amount of urea will react and consume methylol groups of methylolphenols when synthesizing the resin, it only has a small number of methylol groups before curing. On the other hand, the resin synthesized with the molar ratio of F/P/U=3/1/3 has good heat-resistance after curing. The ratio of urea incorporated into the resin will give a good stoichiometric balance between the number of methylol groups and urea residues.

The results of these cocondensed resins cured under alkaline conditions are summarized in Fig. 8. It is clear that the alkaline curing brings better heat-resistance than the acidic curing in every cocondensed resin. Furthermore, the poor heat-resistance of UF resin itself, as observed in Fig. 6, was not reflected in the cocondensed resins. It also should be noted that the heat-resistance of the cocondensed resins are superior to that of the mechanical blended resins of phenolic resin and UF resin, when compared with Fig. 2-(3).

4. CONCLUSION

It can be concluded that the mechanical blending of resol and UF resin is not effective in attaining great thermal stability as well as in introducing cocondensation between phenolic and UF resins. The heat-resistances of the cocondensed resins were indicated to be superior to those of the mechanical blended resins. Furthermore, the alkaline curing is better than the acidic curing in attaining great heat-resistance from the cocondensed resins.

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