

Influence of the Synthesis Conditions on the Curing Behavior of Phenol–Urea–Formaldehyde Resol Resins

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ABSTRACT: The curing behavior of synthesized phenol–urea–formaldehyde (PUF) resol resins with various formaldehyde/urea/phenol ratios was studied with differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA). The results indicated that the synthesis parameters, including the urea content, formaldehyde/phenol ratio, and pH value, had a combined effect on the curing behavior. The pH value played an important role in affecting the shape of the DSC curing curves, the activation energy, and the reaction rate constant. Depending on the pH value, one or two peaks could appear in the DSC curve. The activation energy was lower when pH was below 11. The reaction rate constant increased with an increase in the pH value at both low and high temperatures. The urea content and formaldehyde/phenol ratio had no significant influence on the activation energy and rate constant. DMA showed that both the gel point and $\tan \delta$ peak temperature ($T_{\tan\delta}$)

had the lowest values in the mid-pH range for the PUF resins. A different trend was observed for the phenol–formaldehyde resin without the urea component. Instead, the gel point and $T_{\tan\delta}$ decreased monotonically with an increase in the pH value. For the PUF resins, a high urea content or a low formaldehyde/phenol ratio resulted in a high gel point. The effect of the urea content on $T_{\tan\delta}$ was bigger than that on the gel point because of the reversible reaction associated with the urea component. Too much formaldehyde could lead to more reversible reactions and a higher $T_{\tan\delta}$ value. The effects of the synthesis conditions on the rigidity of the cured network were complex for the PUF resins. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 95: 1368–1375, 2005

Key words: curing of polymers; differential scanning calorimetry (DSC); resins; synthesis

INTRODUCTION

Phenol–formaldehyde (PF) resol resins have been widely used as wood adhesives for many years, especially in the manufacturing of plywood, particleboard, and oriented strandboard for exterior applications. Liquid and solid resins with very different formulations have been developed to meet the processing and property requirements of these wood products. Recently, urea has been successfully used to partially replace phenol in making a cocondensed phenol–urea–formaldehyde (PUF) resin.^{1–9} The addition of the urea component to the PF resin reduces the free formaldehyde content, cuts manufacturing costs, and increases the reactivity of the resin. This type of cocondensed PUF resin has become a very attractive wood adhesive in the manufacturing of forest products.

The cocondensed PUF resin was first synthesized through the reaction of methylolphenol with urea under acidic conditions^{2,3,10} because urea cannot condense to form a urea–formaldehyde (UF) resin under alkaline conditions,¹¹ even though phenolic resins may react under either acidic or alkaline conditions.¹² An analysis has shown that cocondensed methylene groups between the methylolphenol and urea are produced,³ and the reaction rate constant of cocondensation is much greater than that of self-condensation in the PUF resins under the acidic conditions.¹⁰ Resol cocondensed resins can be made by a simple alkaline treatment of the cocondensed resins, which were once prepared under acidic conditions. Resol PUF resins display almost the same curing behavior and heat resistance as a commercial PF resol, but it is quite different from that of a UF resin.⁶ Resol PUF resins can also be synthesized by direct cocondensation of phenol, urea, and formaldehyde under alkaline conditions.^{8,9} The cocondensed resin has a faster curing rate than pure PF resins. Research⁷ has also indicated that the urea component in PUF resins reduces the curing rate, internal bond strength, and water resistance of panels.

Although the curing behavior of PUF resins is very similar to that of PF resins, as determined by dynamic

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mechanical analysis (DMA),^{6,8} the curing reactions are much more complicated than those of PF resins. These reactions contain self-condensations of both the phenolic component and urea component and condensations between the phenolic and urea components. The kinetic parameters of PUF resins are also different from those of PF resins in curing.⁹

The purpose of this study was to investigate the influence of the synthesis conditions on the curing process of PUF resins. Understanding this influence will provide useful information for designing and developing appropriate formulas in the manufacturing of PUF resins. In this study, PUF resins were synthesized with various formaldehyde/urea/phenol (F/U/P) ratios. The curing processes of the synthesized PUF resins were analyzed with both differential scanning calorimetry (DSC) and DMA. The influence of the urea content, formaldehyde/phenol (F/P) ratios, and pH values on the curing kinetics and physical properties of the resins was investigated.

EXPERIMENTAL

Resin synthesis

For the synthesis of PUF resins, liquid phenol (90%), an aqueous formaldehyde solution (37%), solid urea, and an aqueous sodium hydroxide solution (50%) were used directly as raw materials without further purification. Phenol, formaldehyde, and urea were charged into the reaction vessel according to the calculated amounts; only two-thirds of the total amount of formaldehyde was charged at this time. An appropriate amount of distilled water was also added to the reaction system as needed. A calculated amount of the sodium hydroxide solution was dropped slowly into the vessel for 10–15 min with constant mechanical stirring at room temperature. After that, the reaction temperature was gradually raised to 90°C within 30 min and maintained at 90°C for 30 min more. Then, the second portion of formaldehyde was added to the reactor. The temperature was set back to 90°C and kept unchanged until the Gardner–Holdt viscosity of the reaction system was between B and C (65–85 mPa s). The temperature was kept at 90°C for another 10 min, and the system was cooled to 30°C with cold water. More of the sodium hydroxide solution was added to adjust the pH value to the target level. The final product was stored in a refrigerator for further tests. The solid content of all the synthesized resins was about 50% according to oven-drying measurements.

DSC measurements

All DSC measurements and analyses were made with a Q1000 DSC instrument and Universal analysis soft-

ware from TA Instruments (New Castle, DE). High-volume pans that could withstand vapor pressure up to 3.8 MPa were used to prevent components of the test samples from evaporating at high temperatures of up to 250°C. Dynamic scans were performed at heating rates of 2, 5, and 10°C/min, and the scanning temperature ranged from 25 to 250°C.

DMA measurements

DMA measurements were made with a Q800 DMA instrument and Universal analysis software from TA Instruments. A test sample was made through the bonding of two pieces of birch wood veneer to a PUF resin; the dimensions of each sample were 50 mm × 13 mm × 1.3 mm, and the dimensions of each piece of wood veneer were 50 mm × 13 mm × 0.65 mm. The amount of resin applied to each sample was about 140 mg. The grain direction of the wood veneer was parallel to the length and vertical to the loading force. Each sample was made right before the testing. All samples were tested in the dual-cantilever mode at a heating rate of 5°C/min, and the temperature ranged from room temperature to 220°C. The clamp torque for the sample installation was set at 0.9 N m. The frequency used for the test was 1 Hz, and the strain of the samples was controlled to within 0.01%. Four repetitions were performed for each sample.

RESULTS AND DISCUSSION

Nonisothermal DSC kinetic analysis

The DSC kinetics was analyzed with the multiple-heating-rate technique. The samples were tested at three or more different heating rates. The activation energy of the curing reaction was evaluated with the peak temperatures of the DSC curves at these heating rates. Ozawa¹³ and Flynn and Wall¹⁴ developed an equation for calculating kinetic parameters with the multiple-heating-rate technique. Another useful method was developed by Kissinger,¹⁵ from which an equation related to the heating rate (Φ) and temperature (T) was obtained as follows:

$$\ln(\Phi/T^2) = -E/(RT) + \ln(RA/E) \quad (1)$$

where E is the activation energy, A is the pre-exponential factor, and R is the gas constant. A plot of $\ln(\Phi/T^2)$ versus $1/T$ is a straight line, from which E and A can be obtained. The reaction rate constant (k) at a given temperature can be calculated with an Arrhenius equation:

$$k = A \exp[-E/(RT)] \quad (2)$$

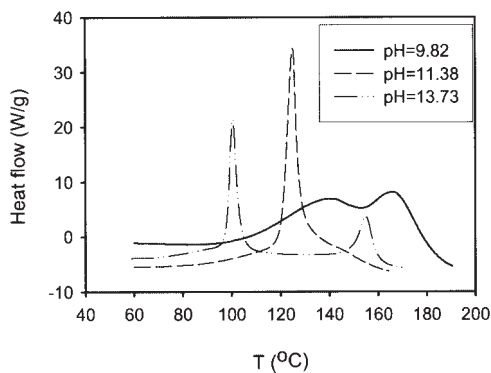


Figure 1 DSC curves for PUF samples at various pHs (heating rate = 5°C/min; F/U/P = 4.0/1.0/1.0).

Figure 1 shows typical DSC curves for the PUF resins at various pH values. The DSC curves display two peaks at the low and high pHs, whereas only one peak can be seen at the mid-pH value of 11.38. Previous research has shown that the DSC curves for phenolic resins can have two or multiple peaks under certain conditions, such as high formaldehyde residues in the curing systems¹⁶ and high NaOH/phenol molar ratios.¹⁷ The urea component in PUF resins may result in more reactions with different activation energies,^{8,9} which can possibly lead to separated peaks under particular conditions.

The pH value had the most significant influence on all the synthesized PUF resins. The number of peaks in the DSC curves was influenced by the pH, as shown in Figure 1, regardless of the F/P ratio and urea content. An exception was that, at the lower pH, only the resins with the higher F/P ratios had two peaks. This implied that various types of individual reactions in PUF resins might be accelerated or retarded by the pH. Furthermore, some new types of reactions may have occurred under certain pH conditions, such as the reaction of phenoxy with methylolphenol to form a methylene carbon structure (Ar—O—CH₂—Ar, where Ar represents a phenolic ring).¹⁸

The activation energy is an important kinetic parameter that describes the effect of the temperature on the curing reactions. Figures 2 and 3 show the variation of the activation energy with the formaldehyde/urea/phenol (F/U/P) ratio and pH. There were two activation energies at both the low and high pHs for some samples because there were two peaks in the DSC curves, which are marked p1 (peak at the lower temperature) and p2 (peak at the higher temperature) in the figures.

The pH value has the most significant influence on the activation energy. The activation energies obtained with p1 are divided into two groups according to the pH. Generally, the activation energy values ranged from 75 to 89 kJ/mol for pHs below 11, and this is consistent with results from previous research.⁹ The

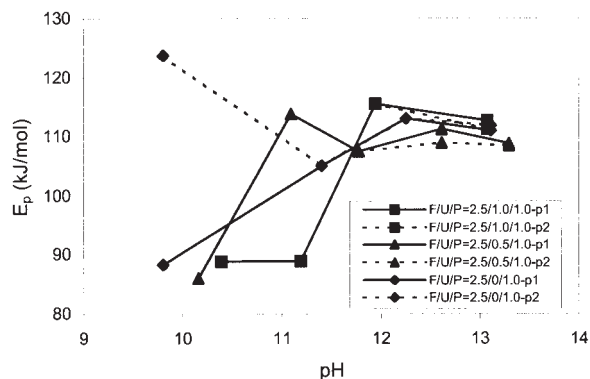


Figure 2 Effect of the urea content on the activation energy (E_p) for the curing of PUF resins.

activation energy increased sharply beyond 105 kJ/mol for pHs greater than 11. However, the activation energies were not very different and varied between 105 and 115 kJ/mol when the pH was between 11 and 13. The activation energies for the second peak were around 110 kJ/mol, being high at both the low and high pHs.

The effect of the urea content and F/P ratio on the activation energy was not clear. The activation energy for the PUF resin with F/U/P = 2.5/1.0/1.0 was almost unchanged when the pH was below 11.2; this was very different from the other formulas. This difference resulted from the asymmetric DSC peaks, which are discussed later.

The curing reaction rates of the PUF resins at the low temperature of 120°C are shown in Figures 4 and 5. The pH had the most influence on the rate constant. The rate constant generally increased with an increase in the pH for different urea contents and F/P ratios. In the lower pH range (pH < 11), the effect of the pH was smaller. This effect became bigger as the pH value increased. The rate constant increased sharply at the higher pH values. However, there was also a secondary peak with a low rate constant at the high pH

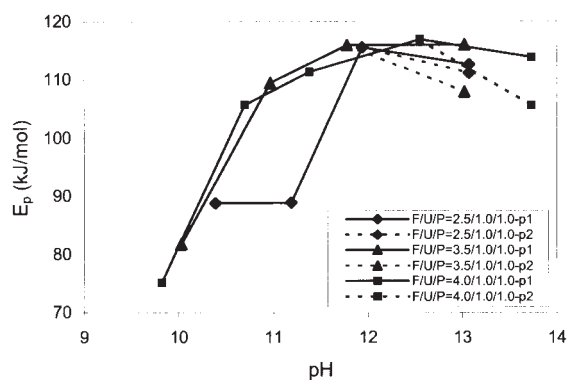


Figure 3 Effect of the F/P ratio on the activation energy (E_p) for the curing of PUF resins.

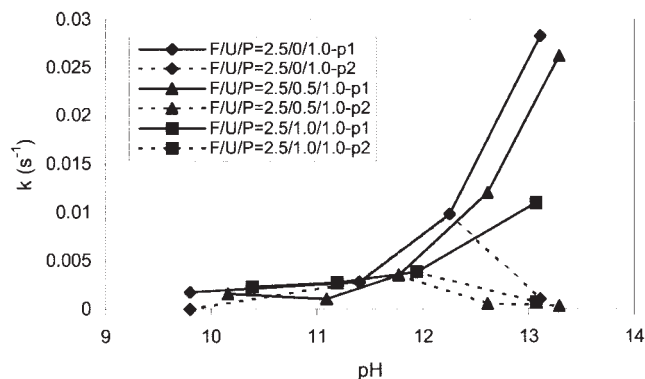


Figure 4 Effect of the urea content on the rate constant (k) at 120°C for the curing of PUF resins.

values. These figures also show that a lower urea content or a higher F/P ratio could enhance the influence of the pH on the rate constant. In the lower pH range, the rate constants were somewhat bigger when the urea content was high or the F/P ratio was low.

Figures 6 and 7 present the rate constant variation for PUF resins at the high temperature of 200°C. The curing reaction rates at 200°C were much faster than those at 120°C. The effects of the pH, urea content, and F/P ratio on the rate constant at high temperatures were similar to the effects at low temperatures.

The influence of temperature on the rate constant is further shown in Figure 8. The temperature had such a big effect that the rate constant increased by five orders of magnitudes when the temperature changed from 80 to 200°C because of the high activation energies. The resin with the lowest pH had the smallest change in the rate constant because it had the lowest activation energy of the resins. The higher the activation energy was, the bigger the change was in the rate constant.

The careful observation of Figures 4–7 shows that the rate constant decreased with an increase in the pH at 120°C when the pH ranged from 10.16 to 11.19 for

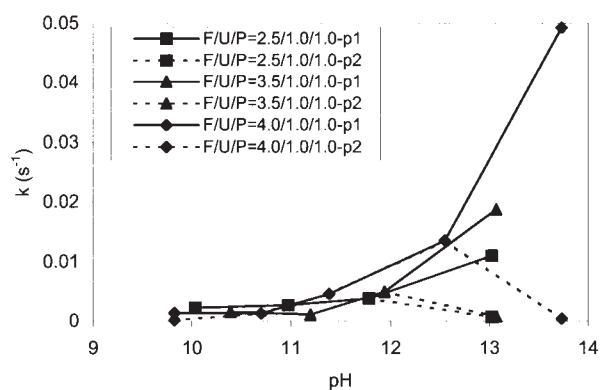


Figure 5 Effect of the F/P ratio on the rate constant (k) at 120°C for the curing of PUF resins.

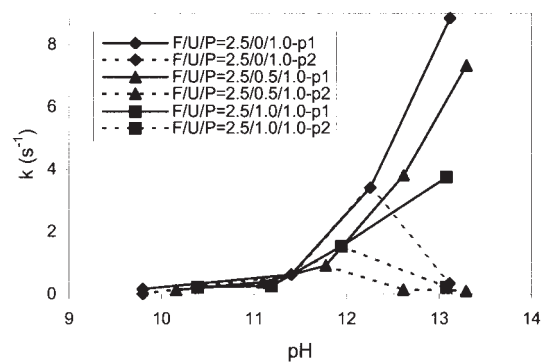


Figure 6 Effect of the urea content on the rate constant (k) at 200°C for the curing of PUF resins.

the resins with F/U/P = 3.5/1.0/1.0 and F/U/P = 2.5/0.5/1.0. This disagrees with the result for the other resins: the rate constant increased with an increase in the pH. This inconsistency resulted from the asymmetric peak in the DSC curves, as shown in Figure 9. One curve has an asymmetric peak with a left shoulder, which led to a higher peak temperature than the curve with a right shoulder, even though the former reaction was faster than the latter one. As a result, the calculation based on these peaks differed from the actual reaction rate. The asymmetric peaks also influenced the calculated activation energies discussed before. In fact, all the resins, except the resin with the F/U/P ratio of 2.5/1.0/1.0, showed asymmetric DSC peaks with left shoulders at the pH near 11 (the second points from the left in Figs. 2 and 3). The estimated activation energies based on these peaks may be higher than the actual values, which are closer to the calculated values based on the second peaks.

The aforementioned DSC kinetic analysis indicated that the pH value had the most significant influence on the curing reaction of the PUF resins under alkaline conditions. The influence was more stable at pH values below 11, in terms of the shape of the DSC curve,

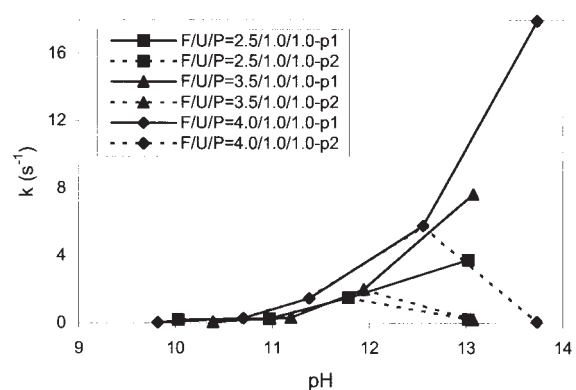


Figure 7 Effect of the F/P ratio on the rate constant (k) at 200°C for the curing of PUF resins.

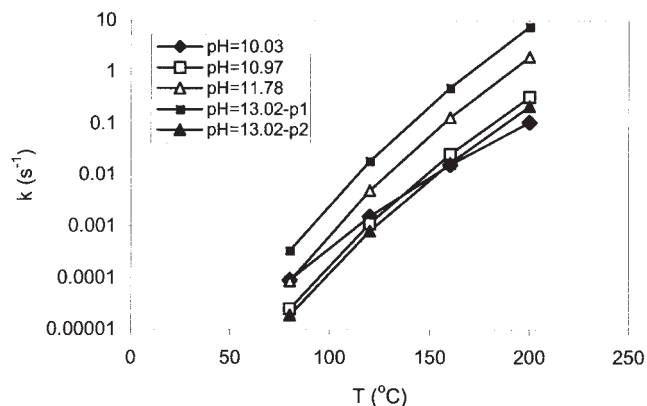


Figure 8 Effect of the temperature on the rate constant (k) for the curing of PUF resins.

the activation energy, and the rate constant, than at high pH values. The curing behavior changed significantly at high pH values, especially at pH values above 12.5. At pHs above 12.5, a much higher activation energy and rate constant and two completely separated peaks were obtained. The change in the kinetics suggested that too high a pH might lead to unstable reactions and more side reactions in addition to the normal addition and condensation reactions in the curing processes of the PUF resins.

DMA of the curing process

PUF resins, as thermosetting polymers, undergo significant changes in their physical properties during curing, such as gelation and vitrification. DMA is able to detect some of these transitions by measuring the changes in the mechanical properties.

Figure 10 presents DMA for the curing of a PUF resin, including the storage modulus (E') and $\tan \delta$ ($\tan \delta = E''/E'$, where E'' is the loss modulus, which is not displayed in Fig. 10). E' initially increased with an increase in the temperature as water evaporated in

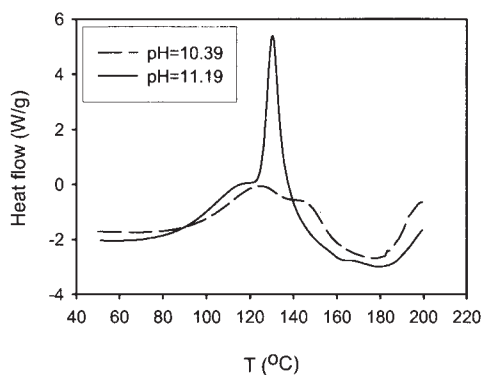


Figure 9 Different asymmetric peaks in DSC curves for PUF resins (F/U/P = 3.5/1.0/1.0).

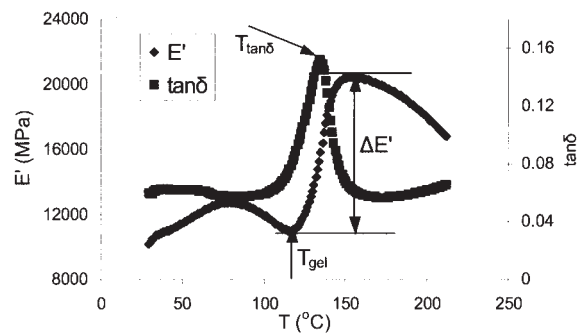


Figure 10 DMA curves for the curing of PUF resins.

this temperature range. After the water evaporated, E' decreased with a further increase in the temperature and reached a minimum, corresponding to the decrease in the viscosity of the resin with the increase in the temperature. E' then increased again with the increase in the temperature as the result of the crosslinking induced by the curing reaction of the resin. E' reached a maximum when the curing reaction was completed and decreased again as the temperature rose.

The minimum point in E' was treated as the starting point for the crosslinking in the curing of the resin. The temperature at this point was defined as the gel point (Fig. 10).^{19,20} The difference in E' from the gel point to the maximum value was the result of the consolidation of the resin network. This difference was used to evaluate the rigidity of the cured resin.

$\tan \delta$ had transitions similar to those of E' . However, the cause of the transitions in $\tan \delta$ was unclear before the gel point. After the gel point, $\tan \delta$ increased sharply to its maximum value because of the increase in the viscosity, and $\tan \delta$ decreased with a further increase in the temperature. Finally, $\tan \delta$ slightly increased again after the curing reaction was completed. The $\tan \delta$ peak temperature ($T_{\tan \delta}$) shown in Figure 10 was used to evaluate the curing progress.

Figures 11 and 12 present the gel point variation during curing for the various PUF resin formulas. Figure 11 shows that the gel point decreased with an increase in the pH across the whole pH range measured for the resin (PF) without a urea component, whereas the gel point decreased first to a minimum value at the pH between 11 and 12 and then increased with an increase in the pH value for the resins (PUF) with a urea component. All other PUF resins showed the same trend for the gel point, as shown in Figure 12.

Because the DSC kinetic analysis indicated that the rate constant of the curing reactions increased with an increase in the pH for both the PF and PUF resins, we expected the gel point to decrease with an increase in the pH. However, the gel point results for the PUF resins contradicted the results obtained by the DSC kinetic analysis. A probable explanation is that the

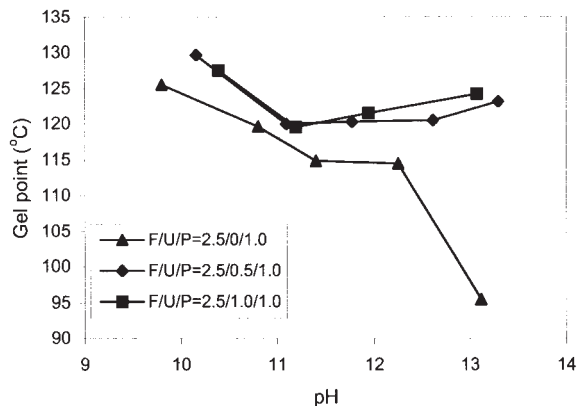


Figure 11 Effect of the urea content on the gel point for the curing of PUF resins.

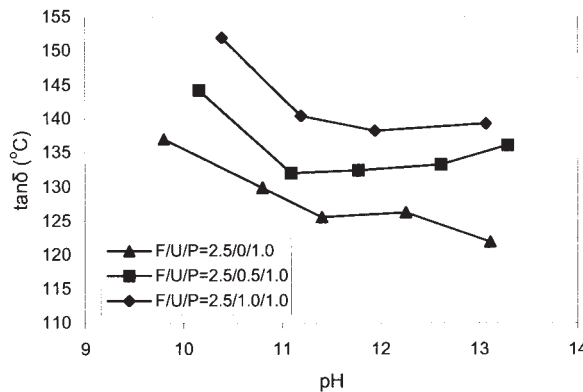


Figure 13 Effect of the urea content on $T_{\tan\delta}$ for the curing of PUF resins.

self-condensation and cocondensation reactions associated with the urea component under alkaline conditions are reversible reactions. These reversible reactions may shift toward the left considerably at high pHs and retard the formation of crosslinking networks. This shift may not have been reflected in the rate constant, but it affected the gel point because the gel point was closely related to the viscosity of the curing system.

Figure 11 also shows that the gel point increased when the urea content in the curing systems increased. This result seemed not to agree with the results from previous research,^{8,9} in which the urea content was found to accelerate the curing process. The trend in our study may have been caused by the fact that the addition of urea led to a shortage of formaldehyde in these PUF resins. Figure 12 shows that the gel point decreased substantially as the F/P ratio increased from 2.5/1.0 to 4.0/1.0. This implies that the appropriate formaldehyde content is important for optimizing the curing process for both the PF and PUF resins.

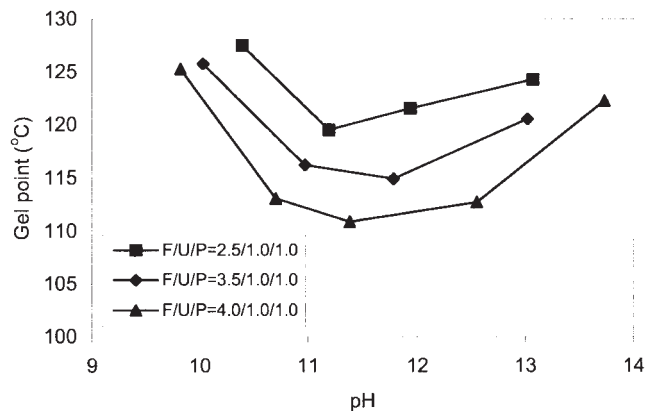


Figure 12 Effect of the F/P ratio on the gel point for the curing of PUF resins.

The variation of $T_{\tan\delta}$ with the urea content, F/P ratio, and pH is illustrated in Figures 13 and 14. The trend for $T_{\tan\delta}$ versus pH is similar to that of the gel point. However, the effect of the urea content on $T_{\tan\delta}$ was bigger than that on the gel point (cf. Figs. 11 and 13). This difference can be seen clearly in Figure 15: the PF resin without a urea component and the PUF resin with a urea component had almost the same gel point, but $T_{\tan\delta}$ for the PUF resin was higher. Also, the PUF resin reached the maximum E' value at a higher temperature and had a lower E' value than the PF resin. This could be due to the fact that $T_{\tan\delta}$ was closely related to the viscoelastic property of the resin network. Lower rigidity may have led to a higher $T_{\tan\delta}$ value in the curing process of the resin. Another reason may be that the reversible reactions associated with the urea component retarded the formation of the network and thus led to a higher value of $T_{\tan\delta}$.

On the contrary, the effect of the formaldehyde content on $T_{\tan\delta}$ was smaller than that on the gel point (cf. Figs. 12 and 14). The $T_{\tan\delta}$ values for the resins with the F/U/P ratio of 4.0/1.0/1.0 were even higher than those with the F/U/P ratio of 3.5/1.0/1.0, although

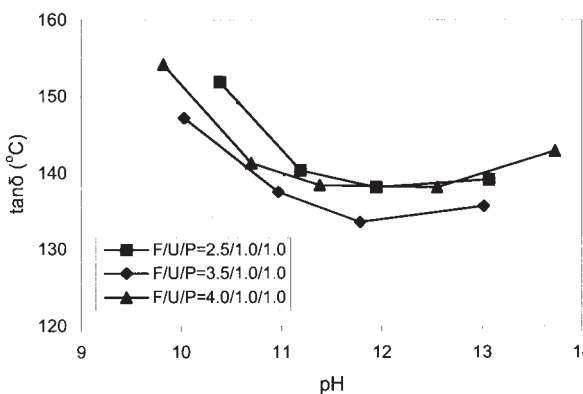


Figure 14 Effect of the F/P ratio on $T_{\tan\delta}$ for the curing of PUF resins.

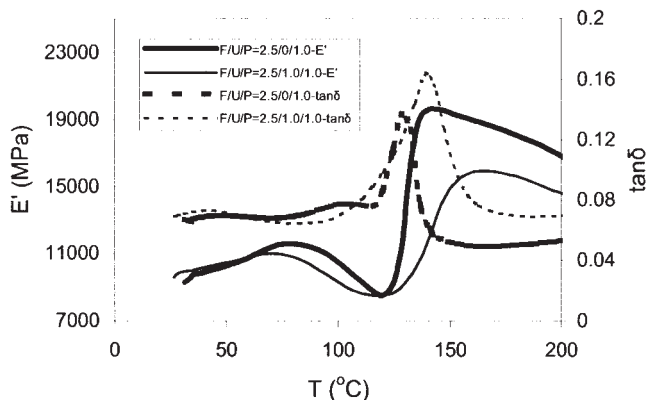


Figure 15 Comparison of the differences in the effect of the urea content on the gel point and $T_{\tan\delta}$.

the former resins had lower gel points than the latter ones. This suggests that too much formaldehyde in a PUF resin might be disadvantageous for the rigidity of the network and result in more reversible reactions in the curing process.

Figures 16 and 17 display the rigidity of the cured resin as a function of the urea content, F/P ratio, and pH. In general, the rigidity of the PF resin without a urea component was higher than that of the PUF resins with a urea component because of the reduced number of phenolic rings in the PUF resins.⁹ The rigidity decreased for the PF resin as the pH increased. This indicated that the faster curing rate possibly resulted in more defects in the structure of the network. However, the effects of the urea content, F/P ratio, and pH value on the rigidity for the PUF resins were not clear. More complex interactions may have taken place during the curing process and influenced the mechanical properties of the cured network of the PUF resins.

CONCLUSIONS

The effects of the synthesis parameters, including the urea content, F/P ratio, and pH, on the curing behav-

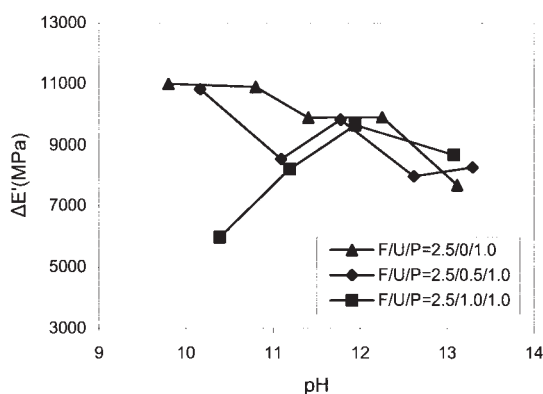


Figure 16 Effect of the urea content on the rigidity of cured PUF resins.

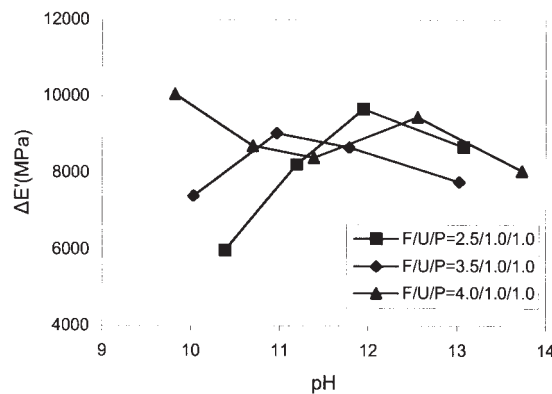


Figure 17 Effect of the F/P ratio on the rigidity of cured PUF resins.

ior of the PUF resins were studied with both DSC and DMA techniques. The shape of the DSC curve, activation energy, reaction rate constant, gel point, $T_{\tan\delta}$, and rigidity of the resin network for the PUF resins were dependent on these parameters. It is important to consider the combined effect of these parameters to optimize the curing of PUF resins.

The DSC curves displayed two peaks for both low and high pHs, whereas only one peak was found for the mid-pH values; this indicated that the pH played different roles in the individual reactions involved in the curing processes of the PUF resins. The pH value had a strong influence on the activation energy. The activation energy was lower when the pH value was below 11 and much higher when the pH was above 11. The reaction rate constant also became faster as the pH value increased at both low and high temperatures. The effects of the urea content and F/P ratio on the activation energy and rate constant were not obvious.

DMA indicated that the gel point had the lowest value in the mid-pH range (11–12) and was higher at both the lower and higher pHs for the PUF resins. This trend was different for the PF resin without the urea component. The gel point for the PF resins decreased monotonically with an increase in the pH value. The gel point was higher for the resins with a high urea content or a low F/P ratio. $T_{\tan\delta}$ showed a trend similar to that of the gel point as a function of pH. The difference was that the effect of the urea content on $T_{\tan\delta}$ was bigger than that on the gel point because of the reversible reaction associated with the urea component. Too much formaldehyde could lead to more reversible reactions and higher $T_{\tan\delta}$ values, even though the gel point was low for this resin. The effects of these synthesis parameters on the rigidity of the network were complex for the PUF resins.

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