Urea–Formaldehyde-Resin Gel Time As Affected by the pH Value, Solid Content, and Catalyst

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ABSTRACT: An experiment was conducted to investigate the effects of the resin solid content, catalyst content, and pH value obtained by the addition of two kinds of catalysts on the gel time of a urea–formaldehyde (UF) resin. Upon the addition of ammonium chloride, the pH value of the resin mixture decreased to 7 but not significantly further because of the limited free formaldehyde in the system. The pH values of the critical points, at which the resin-curing rate dramatically increased and the gel time was reduced, were above 7 for both catalysts. To achieve the same gel time, the required pH value of the UF resin adjusted with ammonium chloride was higher than that of the resin modified by hydrochloric acid. This indicated that the main effects of ammonium chloride on the UF-resin cure included both the release of hydrochloric acid and the catalysis of the reactants in the UF-resin system. The gel time of the UF resin obviously decreased with increasing catalyst and resin solid contents and with decreasing pH. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 1566–1569, 2007

Key words: adhesives; catalysts; gelation; resins; thermosets

INTRODUCTION

The pH value, solid content, and catalysts of urea–formaldehyde (UF) resins play very important roles in providing (or generating) a combined pH environment at the interphase between wood and UF resins. To obtain the optimum bond strength, the press time and temperature must be adjusted for the pH environment. If this correction is not precise, the glue line will be uncured or overcured, and this will result in poor bond strength. Thus, an investigation of the effects of the pH value, solid content, and catalysts of UF resins on the gel time of UF resins is essential to the establishment of effective processing parameters for applying these polymers in wood-based-composite manufacturing. Some researchers have shown that wood extractives,[1,2] wood pH values, and buffering capacities[3–6] strongly affect the gel time of UF resins. Medved and Resnik[7] suggested that reducing the wood particle size could reduce the gel time of UF resins. Park et al.[8] revealed that the fiber acidity strongly affected the internal bond strength of medium-density fiberboard panels bonded with a UF resin. Xing et al.[9] also reported that the pH value and buffering capacities of refined fibers affect some properties of medium-density fiberboard panels. The type and content of the catalyst directly affect UF-resin curing and the performances of final products. Poblete and Pinto[10] reported that increasing the level of the catalyst reduces the pH and gel time of UF resins. Myers[11] suggested that the desirability of neutralizing an acidic cure catalyst after wood bonding reduced formaldehyde liberation and increased the durability of bonded products. The results of Elbert[12] show that formaldehyde emissions from UF resins and particleboards are affected by the type and content of the catalyst. However, Lee et al.[13] suggested that the amount of the hardener, which in their case varied from 0.8 to 3.2% (based on a resin with 66% solids), had practically no influence on the release of volatile acids from particleboards. Pinto and Poblete[14] showed that increasing the amount of the catalyst caused a reduction in the thickness swelling and water absorption and an improvement in the mechanical properties of particleboards. However, the addition of an acid catalyst could increase the degradation of a cured UF resin in particleboards.[15] Xing et al.[16] indicated that an optimal range of catalyst contents exists for the curing of UF resins. Evidence exists for the idea that a higher catalyst content accelerates not only the rate of cure of UF resins but also their rate of hydrolysis after resin curing.[17–22] The optimal catalyst content should generate an acceptable cure rate with the addition of less cata-

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lyst. Ammonium chloride (NH_4Cl) is a common and effective hardener used for accelerating UF-resin curing. Some references suggest that the effect of NH_4Cl on UF-resin curing involves the release of hydrochloric acid (HCl), which brings the pH to very low values and speeds up the cure rate.[19,23] In this case, a higher molar ratio (1 : 1.6–1 : 2) of the UF resin plays a role in supplying enough free formaldehyde to the system to react with NH_4Cl and release HCl. However, the UF resins currently used in the wood product industry are all lower molar ratio resins (normally 1 : 1.05 to 1 : 1.1). The limited free formaldehyde in the system limits the release of HCl by reacting with added NH_4Cl.

In previous research, the effects of a small amount of NH_4Cl on the pH and gel time of lower molar ratio UF resins are still unclear. Little is available concerning the influence of the solid content of UF resins on the gel time. Therefore, the purpose of this investigation was to determine how catalysts affect the pH of UF resins and how the effects of the pH and solid content of the resins influence the gel time of the resins.

EXPERIMENTAL

Raw materials

The UF resin used in this study was TL-200, which was supplied by Hexion (Levis QC, Canada). The solid content of the resin was 66% as measured by a solid pan technique.[24] The pH value of the resin was 7.88. The catalysts were a 10% NH_4Cl solution and 6*N* HCl.

Preparation of the samples

Five UF samples with different solid contents (45, 50, 55, 60, and 66%) were produced by dilution with distilled water. Eight UF samples with different pH values were obtained by the mixing of small drops of HCl into the UF resin. Fifteen UF samples with different catalyst contents ranging from 0 to 0.8% were prepared by the addition of an NH_4Cl solution.

Measurements of the pH and gel time

The pH values were measured with a Corning Pinnacle 530 pH meter (Corning Inc., Corning, NY). Before each measurement, the pH meter was calibrated with standardized buffer solutions at pHs of 4 and 7. After calibration, 200 g of a UF sample was pipetted into a 250-mL beaker, and the initial pH values of the resin and the solution, adjusted by the gradual addition of 10% NH_4Cl from 0 to 0.8% (solid based on solid) or HCl, were recorded after 5 min of magnetic agitation per step at 20°C. All gel-time measurements were made with a Sunshine gel-time meter (Davis Inotek Instruments, Baltimore, MD) through the addition of 5 g of the prepared samples to a test tube ($15 \times 150\ mm^2$) and heating in a 100°C glycerin solution. Two replicate measurements for each sample were made.

RESULTS AND DISCUSSION

Effect of the NH_4Cl content on the pH and gel time of the UF resin

The pH value of the UF adhesive obviously decreased with increasing NH_4Cl content, as shown in Figure 1. The decrease in the pH value was initially very quick. However, the changes in the pH value became very limited with increases in the catalyst content after the pH value reached 7. This seems to contradict the previous findings.[19,23] Both of the previous publications suggested that the pH decreased with NH_4Cl very quickly from the initial value (ca. 8) to 5 in the beginning (ca. 3 min) and then gradually decreased to very low values (2–4) with time. However, this did not occur in our study within 80 min. This could be because the resins that they studied were for plywood with higher molar ratios. The content of free formaldehyde in the resin system was much higher than that of the resin that we studied. Another factor could be that the amounts of NH_4Cl added were different. It is well known that the effect of NH_4Cl on UF-resin curing is to release H^+ by reacting with free formaldehyde, and then H^+ reacts with HO^- and forms water. For higher molar ratio UFs, the more NH_4Cl is added, the more HCl is released. With an increasing HCl concentration in the system, the rate of HCl release is retarded. Thus, the pH decreases very quickly in the beginning and then slowly. The chemical reactions include two steps in

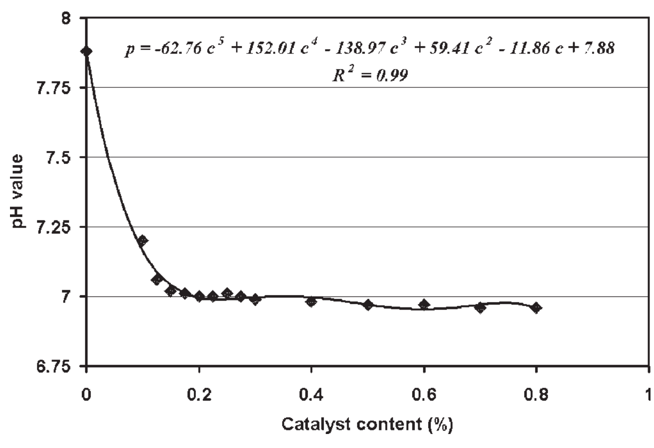

Figure 1 pH value of the UF resin (*p*) versus the catalyst (NH_4Cl) content (*c*).

the case of enough NH_4Cl and HCHO existing in the system:

$$\text{Fast step}: 4NH_4Cl + 6HCHO + 4NaOH \rightarrow 4NaCl + (CH_2)_6N_4 + 10H_2O \quad (1)$$

$$\text{Slow step}: 4NH_4Cl + 6HCHO \rightarrow 4HCl + (CH_2)_6N_4 + 6H_2O \quad (2)$$

For a lower molar ratio UF, there is very limited free formaldehyde in the system. If a small amount of NH_4CI is added, the effect of time on the pH will become very limited. When enough NH_4Cl is not added, the amount of HCl released by NH_4CI reacting with formaldehyde is not enough to equalize the amount of NaOH in the system. This will accelerate the reaction of NH_4CI with formaldehyde. Thus, the pH change is very fast when the pH value of the system is higher than 7. However, with increasing NH_4Cl content, at a certain point, no more H^+ can be released because there is no available free formaldehyde to react with NH_4Cl. This is why the decrease in the pH value was fast at lower levels of the catalyst (< 0.2%) and became very limited to nonexistent with the further addition of the catalyst. For a lower molar ratio UF resin, the chemical reactions can be expressed as follows:

$$xNH_4Cl + aHCHO + bNaOH \rightarrow xNaCl + (x/4)(CH_2)_6N_4 + 2.5xH_2O + (a - 1.5x)HCHO + (b - x)NaOH \quad (3)$$

For a given resin system, a and b are constants. The pH change of the system depends on the value of x, the NH_4Cl content ($x < \frac{2}{3}a$ and $x < b$, pH > 7; $x = b = \frac{2}{3}a$, pH = 7; $x > \frac{2}{3}a$ and $x > b$, pH < 7). When x is greater than b, the pH can be brought down to 7. However, the decrease in the pH is very limited

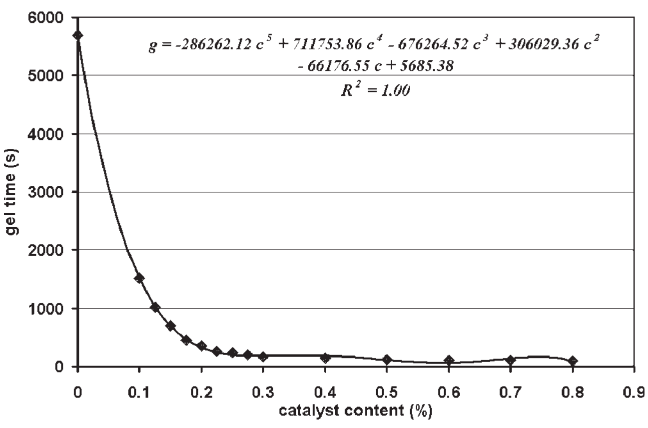

Figure 2 Gel time of the UF resin (g) versus the catalyst (NH_4Cl) content (c).

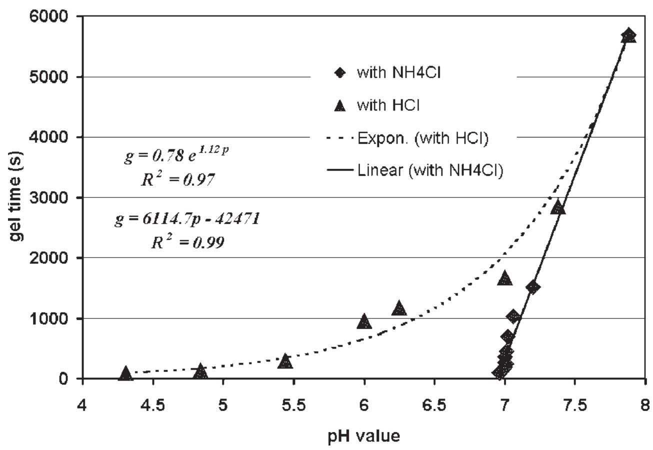

Figure 3 Effect of the pH value (p) on the gel time (g) with respect to the catalyst type.

because the release of HCl is limited by the following reaction:

$$NH_4Cl + H_2O \leftrightarrow HCl + NH_4OH \quad (4)$$

The results of a statistical analysis have provided a polynomial relationship between the pH values of the UF resin and the NH_4Cl content. The polynomial portion is highly significant at a probability level of 0.01, as shown in Figure 1.

The gel time of the UF resin was dramatically reduced from 5700 to 260 s as the catalyst content increased to 0.25%. With further increases in the catalyst content (> 0.25%), the changes in the gel time were not substantial, as shown in Figure 2. A statistically significant nonlinear model was fitted to the gel time of the UF resin with respect to the catalyst content, as presented in Figure 2. The UF-resin gel time could be predicted by the NH_4Cl content being inputted into the equation; nevertheless, the equation applied only to the UF resin studied or might apply to UF resins with similar molar ratios and free formaldehyde contents within the range of NH_4Cl contents used for this study.

Gel time of the UF resin as affected by the pH value of the system

As is well known, a UF resin is an acid-catalyzed curing resin. To determine the critical pH at which the resin-curing rate begins to dramatically increase, gel times were measured with decreasing UF-resin pH values. For samples adjusted with NH_4Cl solutions, the gel time decreased from around 5700 to 1500 s at pH 7.2. When the pH value of the resin reached 7, the gel time dramatically decreased to 350 s. This indicated that the pH value of the critical point was above 7. When HCl was used as a catalyst, the gel time decreased from 5700 to 2000 s at

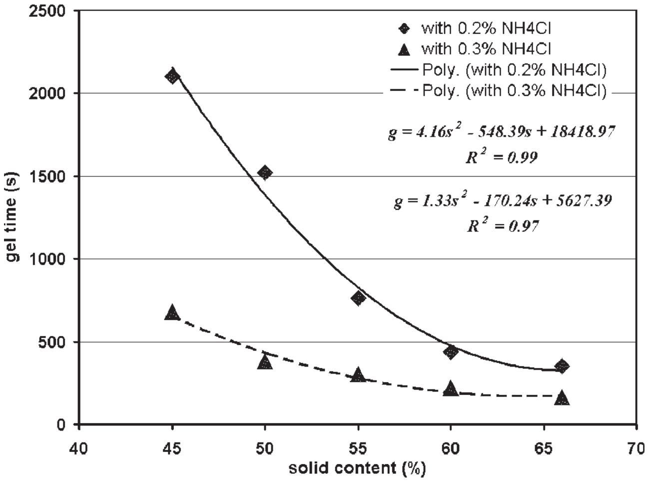

Figure 4 Effect of the solid content (*s*) on the gel time of the UF resin (*g*) with respect to the catalyst content.

pH 7. To achieve a gel time of 350 s, the pH value of the UF resin had to be reduced to around pH 5.5, as shown in Figure 3. Together, these results indicate that the pH values of the critical points of both catalysts were higher than 7. This also indicates that the effect of NH_4Cl on UF-resin curing is not just the release of HCl. It also has a strong catalyzing effect on UF resins by reducing the activation energy of the reactants in UF-resin systems.[16] The relationship between the pH value caused by the NH_4Cl solution and the gel time could be described as a linear regression model. On the other hand, the relationship of the pH value caused by HCl and the gel time generated an exponential regression model, as shown in Figure 3. This further proves that NH_4Cl has a strong catalyzing effect on reactants in UF-resin systems.

Effect of the UF-resin solid content on the gel time

The gel time of the UF resin was strongly affected by its solid content, as shown in Figure 4. This indicates that the gel time of the UF resin decreased with increasing resin solid content. The concentration of the reactants decreased with decreasing solid content. More water in the system diluted the curing reactions and acted as an energy barrier to resin curing. Therefore, the cure rate decreased, and this resulted in a longer gel time. Thus, it is important to control the moisture content of raw materials in the manufacture of wood-composite products. Figure 4 also indicates that the effect of the catalyst content on the gel time is more efficient for resins of lower solid contents than those of higher solid contents.

CONCLUSIONS

This study shows that the free formaldehyde content in resin system plays a role in pH changes by reacting with NH_4Cl. The pH of UF resins decreases with increasing NH_4Cl content, but this effect becomes limited to nonexistent with further NH_4Cl addition as most of the free formaldehyde reacts with NH_4Cl. The main effect of NH_4Cl on UF-resin curing is catalyzing the reactants in UF-resin systems, in addition to releasing HCl. The gel time of UF resins decreases with increasing catalyst and resin solid contents and decreasing pH.

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