

A Rheological Study of the Gelling of UF Polycondensates

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ABSTRACT: The gelling process of urea–formaldehyde resins has been investigated by rheological methods. The gel point values were determined by three methods, and compared with those obtained by low resolution impulsional ¹H-nuclear magnetic resonance. The activation energy of the curing process was determined and the effect of the molar ratio was investigated. In addition, the critical power exponents were calculated and the parameters of the relaxation modulus function were also determined. Equations describing the gel time as a function of degree of conversion and reactants molar ratio are presented. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 75: 1296–1302, 2000

Key words: urea–formaldehyde; polycondensation; rheology; gel point; gelling; curing; activation energy

INTRODUCTION

Urea-formaldehyde (UF) resins are currently the most extensively used resins for bonding interior wood products. The gelling process of wood adhesives is important from the point of view of strength of the adhesive bond. During the curing process, a network structure is formed and the adhesive passes through different physical and relaxation states from viscous to rubbery or even glassy states. The transition from a liquid to a solid state occurs at the gel point. Before the gel point, the liquid-like behavior can be characterized by the zero shear viscosity. This value is increasing as crosslinking is evolving, and theoretically becomes infinite at the gel point. In the neighborhood of the gel point, the zero shear viscosity obeys the power relationship:^{1,2}

$$\eta_0 \approx |\alpha_c - \alpha|^{-k} \quad \text{if } \alpha < \alpha_c \quad (1)$$

where α and α_c are respectively the degree of conversion before the gel point and the degree of conversion at the gel point, and k is a universal constant, the value of which is 0.80 ± 0.10 .

Beyond the gel point, the solid material and the degree of conversion are characterized by the equilibrium modulus, G_e , which is theoretically zero at the gel point. The equilibrium modulus shows a similar power relationship as the zero shear viscosity:

$$G_e \approx |\alpha - \alpha_c|^m \quad \text{if } \alpha > \alpha_c \quad (2)$$

where m is a universal constant, the value of which is 3.2 ± 0.5 .

Critical gels exhibit an unusually simple and regular relaxation behavior that can be described as a simple power law:^{3–9}

$$G(t) = St^{-n} \quad (3)$$

where S is commonly called the gel stiffness and n is the critical relaxation exponent. There is an interrelationship between the critical exponents⁸

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Table I Gel-Point Values for Urea-Formaldehyde Resin with Molar Ratio U/F = 1 : 1.3

Temperature (K)	Gel Point from $G' = G''$ (s)	Gel Point from $1/\eta_0$ (s)	Gel Point from $\tan \delta$ (s)
303	1532 ± 2	1456 ± 2	1480 ± 2
308	820 ± 2	792 ± 2	810 ± 2
315	330 ± 2	365 ± 2	290 ± 2
320	122 ± 2	226 ± 2	156 ± 2

$$n = \frac{m}{m + k} \quad (4)$$

In this work, the gel point, the values of these critical exponents, and the gel stiffness have been determined in the case of UF polycondensation systems.

EXPERIMENTAL

A series of commercial UF resins of predetermined known formaldehyde/urea molar ratios of 1.3 and 1.5 obtained respectively from Elf Atochem (France) and Sadepan (Italy) were used in the presence of 1% NH_4Cl used as hardener. The temperatures of measurements were: 303, 308, 310, 315, 320, 325, 330, and 335 K.

The complex viscosity and complex modulus of the systems were determined by a Rheometric dynamic stress rheometer (RS-500) under oscillatory dynamic mode. A parallel plate-measuring head was used with a 25-mm plate diameter and 0.2 mm gap. The measurements were performed with a small strain (below 5%) at five frequency values (3, 5, 7, 9, and 11 rad/s). The complex viscosity, the loss and storage moduli, and $\tan \delta$ vs frequency were continuously registered (the zero shear viscosity and equilibrium modulus

were determined by extrapolating to zero frequency the values of complex viscosity and relaxation modulus).

The gel point was determined by three methods:

1. Extrapolating the reciprocal of zero shear viscosity to zero value;
2. Determining the crossover value of storage and loss modulus curves;
3. Determining the intersection of $\tan \delta$ curves over the frequency window.

The scaling exponents were determined on the basis of eqs. (1), (2), and (4). In the case of eqs. (1) and (2), the time was used instead of the degree of conversion, which is an acceptable approximation within a narrow range around the gel point.

RESULTS AND DISCUSSION

Gel Points

The gel times obtained by the three methods outlined in Experimental are summarized in Tables I and II for formaldehyde/urea ratios of 1.3 and 1.5, respectively. It can be seen that with the increase of the F:U ratio, the gel time is increasing. If we

Table II Gel-Point Values for Urea-Formaldehyde Resin with Molar Ratio U/F = 1 : 1.5

Temperature (°C)	Gel Point from $G' = G''$ (s)	Gel Point from $1/\eta_0$ (s)	Gel Point from $\tan \delta$ (s)
42	1176 ± 2	1555 ± 2	1670 ± 2
47	983 ± 2	883 ± 2	1100 ± 2
52	630 ± 2	590 ± 2	601 ± 2
57	430 ± 2	410 ± 2	380 ± 2
62	257 ± 2	269 ± 2	220 ± 2

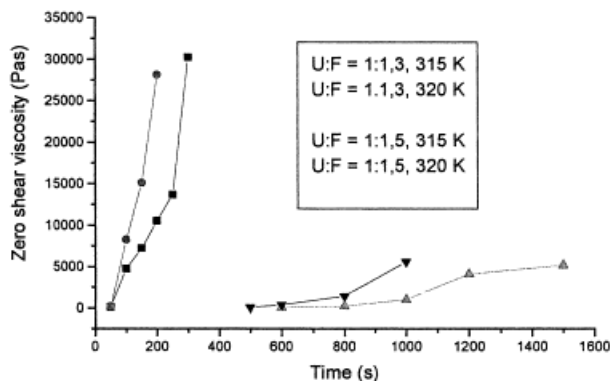


Figure 1 Zero shear modulus vs time for two UF glue mixes (●) U/F 1:1.3 at 320 K (□), U/F 1:1.5 at 320 K (▽), U/F 1:1.3 at 315 K (△), and U/F 1:1.5 at 315 K.

compare the results in Tables I and II with the results obtained by low resolution impulsional ^1H -nuclear magnetic resonance (NMR),¹⁰ the rheometrically determined gel times are shorter. In the case of UF resins, low resolution impulsional ^1H -NMR measurements are characterized by a long induction period, meaning that the real beginning of the curing process cannot be determined. Figure 1 shows the zero shear viscosity as a function of time for the two urea/formaldehyde molar ratios below the gel point. The higher amount of formaldehyde causes a slower curing rate. Figure 2 shows the equilibrium relaxation modulus as a function of time above the gel point. The behavior of the equilibrium modulus is similar to that of the zero shear viscosity. The Figures show that the reaction rate of the curing process is much slower in the case of a U/F molar ratio of 1:1.5 than in the case of a molar ratio of 1:1.3. This might be due not only to the molar ratio but also from the different advancement of the two resins, with the one of molar ratio 1.3 being more advanced (reacted longer) than the one of 1.5.

On the basis of gel time results obtained at different temperatures, the activation energy of gelation was determined. In the case of the U/F molar ratio 1:1.3, a value of 104.6 kJ/mol is obtained, whereas in the case of the U/F molar ratio 1:1.5, a value of 66.9 kJ/mol is obtained. The first value is the same as was found in the work by low resolution impulsional ^1H -NMR,¹⁰ and the last one is the same as was obtained previously by the condensation process.^{11,12} The differences in the value of activation energy show that the curing processes might be different and might depend on the molar ratio or on other factors (i.e., diffusion factors).

For the crosslinking of a multifunctional precursor as urea with a difunctional crosslinker as formaldehyde, the Flory-Stockmayer¹³ theory using the Durand and Bruneau formula^{14,15} predicts the critical extent of reaction at the gel point, α_g :

$$\alpha_g = \frac{1}{\sqrt{R(f_u - 1)}} \quad (5)$$

where R is the molar ratio between the reactive sites of urea and formaldehyde and f_u is the functionality of urea. The urea in principle is tetrafunctional with respect to formaldehyde (in practice it is only trifunctional as tetrasubstituted urea has never been observed).^{16,17} In the case of the U/F 1:1.5 molar ratio resin, the calculated critical degree of conversion at the gel point according to the Flory Stockmayer theory is 0.707, whereas in the case of the U/F 1:1.3 molar ratio resin, the calculated critical degree of conversion at the gel point is 0.759. More accurate formulas developed recently to predict the critical degree of conversion at the gel point^{18,19} indicate more exact values of 0.770 and 0.790 for the two molar ratios.

Activation Energy

If one considers the curing process in a range in which diffusion control is negligible, the rate of a kinetically controlled reaction can be expressed by an Arrhenius equation:

$$\frac{d\alpha}{dt} = kg(\alpha) = k_0 \exp\left(-\frac{E}{RT}\right)g(\alpha) \quad (6)$$

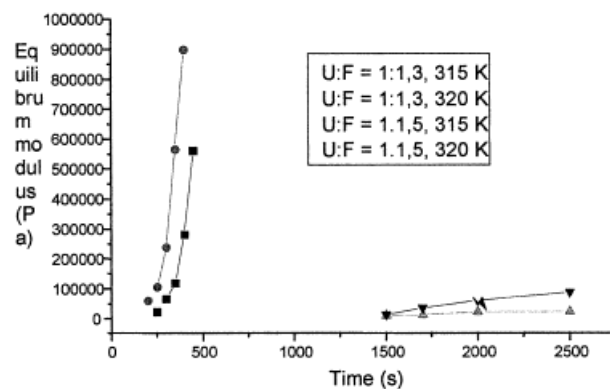


Figure 2 Equilibrium shear modulus vs time for two UF glue mixes (●) U/F 1:1.3 at 320 K (□), U/F 1:1.5 at 320 K (▽), U/F 1:1.3 at 315 K (△), and U/F 1:1.5 at 315 K.

Table III The Values of Scaling Exponents for Urea-Formaldehyde Resin with Molar Ratio U/F = 1 : 1.3

Temperature (°C)	k	m	n	p_-	p_+
30	0.65	1.61	0.71	2.24	2.27
35	0.71	1.52	0.70	2.37	2.17
42	0.69	1.72	0.73	2.55	2.36
47	0.72	1.63	0.70	2.40	2.33

where α is the degree of conversion, k is the reaction rate constant, k_0 is the Arrhenius preexponential factor, E is the activation energy, and $g(\alpha)$ is the conversion-dependence function. By rearranging and integrating eq. (6) for a curing time of $t = 0$, where $\alpha = 0$ at a time t with a degree of conversion α one obtains the following:

$$\ln t = \frac{E}{RT} + \left[\ln \int_0^\alpha \frac{d\alpha}{g(\alpha)} - \ln k_0 \right] \quad (7)$$

At a fixed degree of conversion, the terms within the square parenthesis are constant. Equation (7) can then be expressed as:

$$\ln t = A + \frac{E}{RT} \quad (8)$$

where constant A is only a function of α or of the zero shear viscosity below the gel point, or of the equilibrium modulus beyond the gel point, because these two rheological parameters are uniquely determined by the extent of the reaction, hence by the degree of conversion. By using the times belonging to the same zero shear viscosities below the gel point and the times belonging to the same equilibrium modulus above the gel point we get a series of activation energy values that show

how the reaction proceeds. In the case of the resin at molar ratio U/F = 1:1.3, the activation energy values are very near to the value of 104.6 kJ/mol determined experimentally, but at the early stages of reaction, the values are slightly higher. In the case of the resin at molar ratio U/F = 1:1.5, the activation energy values are very close to the value of 66.9 kJ/mol determined experimentally.

Power Exponents

For relaxation of a solid near the gel point, the critical gel may serve as a reference state. Equation (3) gives a relationship between the relaxation modulus and the time. On the basis of this equation, the longest relaxation time can be defined for the nearly critical gel as:

$$\lambda_{\max} = \left(\frac{G_e}{S} \right)^{-1/n} \quad (9)$$

The longest relaxation time can then be expressed from the dynamical scaling equations:

$$\lambda_{\max} \approx (\alpha_g - \alpha)^{-p_-} \quad \text{with} \quad p_- = \frac{k}{1-n} \quad \text{if} \quad \alpha \leq \alpha_g \quad (10)$$

Table IV The Values of Scaling Exponents for Urea-Formaldehyde Resin with Molar Ratio U/F = 1 : 1.5

Temperature (°C)	k	m	n	p_-	p_+
42	0.79	1.40	0.65	2.26	2.15
47	0.75	1.65	0.70	2.50	2.36
52	0.73	1.35	0.65	2.09	2.08
57	0.68	1.35	0.67	2.06	2.06
62	0.70	1.69	0.71	2.41	2.38

Table V The Values of Stiffness of Systems

Systems	Stiffness (Pas) Temperatures (°C)						
	30	35	42	47	52	57	62
Molar ratio U/F = 1 : 1.3	3814	25,143	37,770	48,500			
Molar ratio U/F = 1 : 1.5			15,253	28,000	34,363	42,850	43,292

and

$$\lambda_{\max} \approx (\alpha - \alpha_g)^{-p_+} \quad \text{with} \quad p_+ = \frac{m}{n} \quad \text{if} \quad \alpha > \alpha_g \quad (11)$$

where m is a modulus dependent exponent, k is a zero shear viscosity dependent exponent, n is the critical relaxation exponent correlating k and m according to eq. (4), and p_- and p_+ correlate respectively n and k , and m and k according to eqs. (10) and (11).

In Tables III and IV the values of the exponents k , m , n , p_- and p_+ have been summarized for the U/F 1:1.3 and 1:1.5 molar ratio resins. Table V presents the values of stiffness for the resins at the two molar ratios. The values of k are not far from the theoretically derived value of 0.7, but the values of m are smaller than the theoretical value. The relaxation exponents change slightly with the change of molar ratio. The stiffness values increase with the increase in curing temperature.

Relaxation Parameters

A relationship has been experimentally observed^{8,9} between the gel stiffness S , and the relaxation exponent, n

$$S = G_0 \lambda_0^n \quad (12)$$

where λ_0 is the crossover relaxation time, equal to the longest time of the precursors and G_0 is equal to the plateau modulus. $G_0 \lambda_0$ can be calculated

from the zero shear viscosity. From the values of gel stiffness summarized in Table V and the zero shear viscosities, the crossover relaxation times were calculated. Table VI shows the calculated crossover relaxation times. The values are almost independent of the curing temperature, and show a significant difference in the case of the resins at the two molar ratios. On the basis of the crossover relaxation times obtained, it appears, as already deduced early from the anomalous relative reaction rates of the two resins, that the oligomers in the UF 1.3 molar ratio resin have a greater average molecular mass (hence the resin is more advanced) than in the case of the higher molar ratio resin.

Curing Process

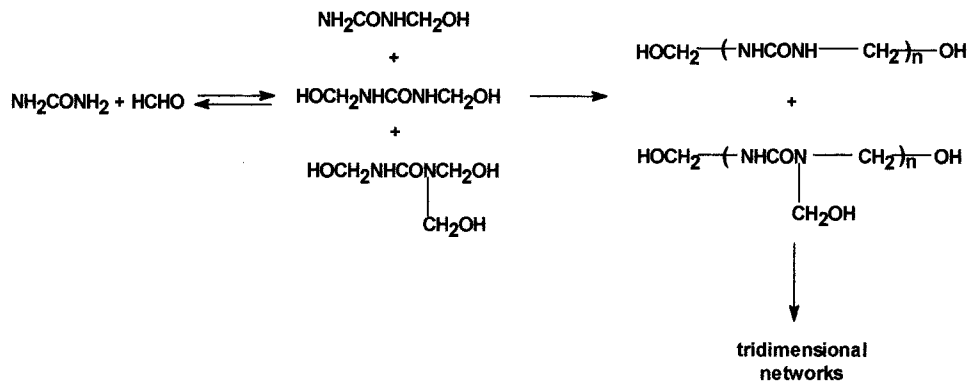
UF adhesives form and harden in three steps.^{1,12,16} In the first step, urea and formaldehyde react under weak basic conditions to form mono-, di-, and trimethylolureas, their relative proportions depending on the initial U/F molar ratio. In the second step, oligomers are formed from the mixture of methylolureas. The main reactions are the reaction of methylolureas with each other and with urea. In the third step, a tridimensional network of urea molecules connected by methylene and methylene ether bridges is formed, especially if the U/F ratio is smaller than 1.

The reaction system is complex but a general formula can nonetheless be used for the curing process, namely:

$$\frac{d\alpha}{dt} = k(1 - \alpha)^m (R - \alpha)^s \quad (13)$$

Table VI Crossover Relaxation Times

Systems	Relaxation Times (s) Temperatures (°C)						
	30	35	42	47	52	57	62
Molar ratio U/F = 1 : 1.3	0.70	0.69	0.68	0.65			
Molar ratio U/F = 1 : 1.5			0.53	0.53	0.50	0.49	0.47



Scheme 1

where $\alpha = (U_0 - U)/U_0$ is the degree of conversion, U is the urea concentration at time t , U_0 is the urea initial concentration (at time = 0), R is the ratio of the initial concentrations of formaldehyde and urea, and m and s are characteristic exponents. For the formation of monomethylolurea $m = 1$ and $s = 1$, whereas for the formation of dimethylolurea, $m = 1$ and $s = 2$. On the basis of the analysis of the activation energies obtained, because the activation energy remained constant during curing, the reaction can then be described by a reaction equation during the curing process. A difference can be observed between the two resins of different molar ratios. By solving eq. (12) between α and α_g for the two simpler cases ($m = 1, s = 1$ and $m = 1, s = 2$), the following equations are obtained:

$$t_g - t = \frac{1}{(R-1)k} \left[\ln \frac{1 - \alpha_g}{R - \alpha_g} - \ln \frac{1 - \alpha}{R - \alpha} \right] \quad (14)$$

and

$$t_g - t = \frac{1}{(R-1)k}$$

Table VII Reaction Rates for the Two Urea/Formaldehyde Ratios

Temperature (°C)	Reaction Rates for Reaction (14) 10^{-4} mol/s	Reaction Rates for Reaction (15) 10^{-4} mol/s
35	0.71	1.22
42	1.05	2.33
47	2.45	3.45
52	3.56	4.78
57	5.12	6.22

$$\times \left[\ln \frac{1 - \alpha_g}{R - \alpha_g} + \frac{R-1}{1 - \alpha_g} - \ln \frac{1 - \alpha}{R - \alpha} - \frac{R-1}{1 - \alpha} \right] \quad (15)$$

From these equations by preparing graphs of the gel time vs $\ln(1 - \alpha_g)/(R - \alpha_g)$ or $\ln[(1 - \alpha_g)/(R - \alpha_g)] - [(R - 1)/(1 - \alpha_g)]$, respectively for different molar ratios, the reaction rate coefficients can be obtained from the slope of the straight lines obtained.

Table VII shows the reaction rate coefficients for eqs. (14) and (15), respectively. In the case of eq. (15), the obtained reaction rates are very closely comparable to that reported in the literature.¹² The calculated activation energy value was of 82.3 kJ/mol, which is an average value of the two values previously calculated and presented. In this case the method that was used by others⁷ cannot be used because the mechanism of the curing process is changing with the change of molar ratio.

In conclusion, rheological methods can be used to good effect to determine the parameters defining the gelling of UF resins. They allowed the proposal of equations describing the gel time as a function of degree of conversion and of reactants molar ratio. The difference in molar ratio also appears to introduce different mechanisms or differences in the preponderance of different mechanisms in the curing of UF resins.

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