

NOTE

Rheology Study of Gelling of Phenol-Formaldehyde Resins

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INTRODUCTION

Phenol-formaldehyde¹ (PF) resins are one of the most used (by volume) types of polycondensation resins. More than 60% of PF resins produced today in the world are used for thermosetting wood adhesives. During the curing process a network structure is formed and the adhesive passes through different physical and relaxation states from the viscous to the rubbery or even glassy state. The transition from the liquid to solid state occurs at the gel point. Before the gel point, the behavior of the liquid resin can be characterized by the zero shear viscosity. The value of this parameter increases as the polycondensation reaction proceeds, and at the gel point the weight average molecular mass becomes theoretically infinite. In the neighborhood of the gel point the zero shear viscosity obeys the scaling law^{1,2}

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

where α and α_g are the degree of conversion and the degree of conversion at the gel point, respectively, and k is a universal constant the value of which is 0.8 ± 1 . If t_g is the gel time and t the time for a given degree of conversion, eq. (1) can be written equally as a function of the reaction time³ (thus, t_g and t), rather than the degree of conversion α .

Beyond the gel point the solid material and the extent of reaction is characterized by the equilibrium modulus G_e , which is theoretically zero at the gel point.

The equilibrium modulus shows a scaling equation similar to the zero shear viscosity:

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

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

Equation (2), as in eq. (1), can be written as a function of time rather than as a function of the degree of conversion.

Critical gels exhibit an unusually simple and regular relaxation behavior that can be described by a simple power law⁴⁻⁹:

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

where S is commonly called the gel stiffness and n is the critical relaxation exponent. A relationship exists between the critical exponents⁹:

$$n = m/(k + m) \quad (4)$$

Recently, this approach was taken to determine the values of the relevant parameters for the even more common, but acid-setting, urea-formaldehyde (UF) resins.¹⁰ In this article we instead determined the gel point, the values of the critical exponents, and the gel stiffness of alkaline-setting PF resins.

EXPERIMENTAL

Materials

Two commercial PF resins (PR 141 and PR 240) produced by a South African wood processing company, one used for paper impregnation for high pressure lam-

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Table I Zero Shear Viscosity (η_0) and Equilibrium Shear Modulus (G_e) Values as Function of Reaction Time at Three Temperatures for PF Resins with 1 : 0.76 and 1 : 1.4 P : F Molar Ratios

Time (s)	1 : 0.76 η_0 (Pa s)			1 : 1.4 η_0 (Pa s)			1 : 0.76 G_e (kPa)			1 : 1.4 G_e (kPa)		
	393 K	403 K	413 K	393 K	403 K	413 K	393 K	403 K	413 K	393 K	403 K	413 K
0	0	0	0	0	0	0	0	0	0	0	0	0
100	0	0	0	—	—	—	—	—	—	—	—	—
200	0	0	100	—	—	—	—	—	—	0	0	2.5
250	0	0	1800	0	0	0	0	0	0	0	0	37.5
275	0	0	3300	—	—	—	—	—	—	0	0.5	71.2
300	0	0	5200	0	0	30	0	0	0	0	0.65	142.5
350	0	1100	—	0	0	100	0	0	0.1	0	1.5	—
400	0	6000	—	0	0	200	0	0	1.6	0	6.3	—
450	100	11600	—	0	0	420	0	0	10	0	22.5	—
500	100	—	—	0	—	3500	0	0.3	57	0	76.3	—
550	150	—	—	0	—	4750	0	—	—	—	—	—
600	200	—	—	0	100	—	0	2.1	—	0.1	—	—
700	850	—	—	0	160	—	0	12	—	2	—	—
800	3350	—	—	50	1300	—	0	—	—	13.8	—	—
900	—	—	—	100	4000	—	0	—	—	—	—	—
1000	—	—	—	150	4380	—	0	—	—	—	—	—
1500	—	—	—	500	5850	—	1	—	—	—	—	—
1750	—	—	—	1080	—	—	2.5	—	—	—	—	—
2000	—	—	—	2600	—	—	8.3	—	—	—	—	—

inates and the other as a plywood adhesive, were used in the experiments. PR 141 is a resin with a molar ratio of P : F of 1 : 1.4, a resin solids content of 60%, pH 12–13, a 110 Pa s viscosity at 25°C, and a density of 1.185–1.195 g/cm³.

PR 240 is a resin of molar ratio P : F = 1 : 0.76, solids content of 60%, pH 12–13, viscosity at 25°C is 100–150 Pa s, and density of 1.170–1.180 g/cm³.

Each resin was prepared with same percentage of sodium hydroxide (1.7% on resin solids) as the base catalyst.

Rheological Measurements

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 carried out with a small strain (below 5%) at five frequency values (2, 4, 6, 8, and 10 rad/s) and five temperatures (373, 383, 393, 403, and 413 K). The complex viscosity, the loss and storage moduli, and tan δ were continuously registered versus the frequency. The zero shear viscosity and equilibrium modulus were determined by extrapolating the values of the complex viscosity and relaxation modulus to zero frequency.

The gel point was determined by three methods: extrapolating the reciprocal of the zero shear viscosity

to zero value, determining the crossover value of the storage and loss modulus curves, and determining the intersection of the tan δ curves over the frequency window.

The scaling exponents were determined on the basis of eq. (1) expressed as a function of time rather than degree of conversion and eqs. (3) and (4).

Table I shows the zero shear viscosity and equilibrium modulus values as a function of time. At the same temperature the resin with a molar ratio of P : F of 1 : 1.4 showed much higher zero shear viscosity and equilibrium modulus values than the resin at a P : F ratio of 1 : 0.76.

RESULTS AND DISCUSSION

The experimental results obtained for the zero shear viscosity as a function of time, as well as for the equilibrium shear modulus (G_0) as a function of time, for the two 1 : 0.76 and 1 : 1.4 P : F resins are shown in Table I. Some of the results presented in subsequent tables can be derived from these.

The gel times obtained by our three methods are summarized in Tables II and III for the P : F ratios of 1 : 0.76 and 1 : 1.4, respectively. It can be seen that as the P : F ratio increases the gel time decreases. There was not much difference in the three methods.

On the basis of the gel times obtained at different temperatures, the activation energy of gelation was

Table II Gel Point Values for PF Resin with 1 : 0.76 P : F Molar Ratio

Temperature (°C)	Gel Point from G' = G'' (s)	Gel Point from $1/\eta_0$ (s)	Gel Point from $\tan \delta$ (s)
120	1850	1800	1780
130	780	830	750
140	360	390	370

determined. In the 1 : 0.76 P : F, we obtained a value of 86.7 kJ/mol, and in the P : F 1 : 1.4 a value of 97.5 kJ/mol was obtained. The activation energy was 85.2 kJ/mol in the reaction between P and F forming *o*- and *p*-methylphenol and a little bit lower activation energy in the reaction of an intermediate product (70–79 kJ/mol and in the network forming 96–106 kJ/mol).¹¹ On the basis of the activation energies it seems to us that before the gel point a linear or weakly branched structure was formed and beyond the gel point it started to form a network structure.

For the crosslinking of a multifunctional precursor as the P with a bifunctional crosslinker as the F, the Flory–Stockmayer theory predicts the critical extent of reaction at the gel point α_g through the formula

$$\alpha_g = \frac{1}{\sqrt{R(f_f - 1)}}$$

where R is the molar ratio of P : F and f_f is the functionality of P. Phenol is in principle trifunctional in regard to its reaction with F. In the P : F 1 : 0.76 the critical extent of reaction was 0.81 and in the P : F 1 : 1.4 the critical extent of reaction was 0.60.

On considering the curing process at times far from the diffusion control part of the process, the rate of a kinetically controlled reaction can be expressed by an Arrhenius law

$$\frac{d\alpha}{dt} = kg(\alpha) = k_0 \exp\left(-\frac{E}{RT}\right)g(\alpha) \quad (5)$$

where α is again 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. (5) for a curing time of $t = 0$ whereas $\alpha = 0$ for a time t with a degree of conversion α , we get

$$\ln t = \frac{E}{RT} + \left[\ln \int_0^\alpha \frac{d\alpha}{g(\alpha)} - \ln k_0 \right] \quad (6)$$

At a determined degree of conversion, the terms in the brackets are constant. Equation (6) can then be expressed as

$$\ln t = A + \frac{E}{RT} \quad (7)$$

where constant A is only a function of α , the zero shear viscosity below the gel point, or the equilibrium modulus beyond the gel point, because these two rheological parameters are uniquely determined by the degree of conversion. At the reaction times belonging to the same zero shear viscosities below the gel point and at the times belonging to the same equilibrium modulus above the gel point a series of activation energy values that show the evolution of reaction were obtained. In the PF 1 : 0.76 resins the activation energy values started at 85 kJ/mol, a value that decreases to 70 kJ/mol, while it increases to 95 kJ/mol value beyond the gel point. In the PF 1 : 1.4 resin a similar trend was observed but for an activation energy value of 103–105 kJ/mol beyond the gel point.

For relaxation of a solid near the gel point, the critical gel may serve as a reference state. Equation (2) when expressed as a function of time rather than as a function of degree of conversion relates the relaxation modulus and time. On the basis of this equation the longest relaxation time can be defined for the nearly critical gel as

$$\lambda_{\max} = \left(\frac{G_e}{S}\right)^{-1/n} \quad (8)$$

Table IV shows the values of the scaling exponents k , m , and n for both PF resins used. The values of n obtained are not far from the theoretically derived value of 0.7, but the values of k and m are smaller than what was foreseeable from theoretical values.

In regard to the relaxation parameters, a relationship was experimentally observed^{8,9} between the gel stiffness S and the relaxation exponent n ,

$$S = G_0 \lambda_0^n \quad (9)$$

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

Table III Gel Point Values for PF Resin with 1 : 1.4 P : F Molar Ratio

Temperature (°C)	Gel Point from G' = G'' (s)	Gel Point from $1/\eta_0$ (s)	Gel Point from $\tan \delta$ (s)
90	9535	8700	6800
100	3150	2900	3100
110	1410	1450	1330
120	730	830	750
130	378	420	360
140	245	290	230

Table IV Values of Scaling Exponents for PF Resins with 0.76 and 1.4 P : F Molar Ratios

Temperature (°C)	<i>k</i>		<i>m</i>		<i>n</i>	
	0.76	1.4	0.76	1.4	0.76	1.4
90		0.71		1.45		0.65
100		0.59		1.10		0.70
110		0.59		0.79		0.62
120	0.40	0.47	0.36	0.47	0.75	0.68
130	0.45	0.47	0.47	0.47	0.80	0.65
140	0.38	0.47	0.43	0.36	0.80	0.70

from the zero shear viscosity. Table V shows the calculated gel stiffness values and the crossover relaxation times. From the product of the equilibrium modulus and crossover relaxation time in eq. (4), the viscosity at the gel point was calculated. The crossover relaxation time decreased with the increase of temperature. As a consequence of these results it appears that as the temperature increases the proportion of shorter linear oligomers in the linear growth phase of the polycondensation¹² will be higher, and hence a lower level of entanglement will be expected. In reality it was not the proportion of shorter oligomers that was higher, but at higher temperature it was the value of the critical mass M_C needed for entanglement that increased; as a consequence, a lower level of entanglement was observed. There was good agreement between the values of the calculated and measured viscosities at the gel point.

In the curing process many similarities existed between the curing sequence of events occurring under alkaline conditions for the PF resin and that occurring in acid curing of UF resins.¹³ Thus, phenol condenses initially with F in the presence of either acid or alkali to form a methylphenol or phenolic alcohol and then dimethylolphenol.^{12,13} The initial attack may be at the 2, 4, or 6 position. The second stage of the reaction involves the condensation of the methylol groups with

phenol and the already formed methylolphenols, leading to the formation of linear polymers and oligomers. When continuing the reaction of polycondensation, from these linear PF oligomers the system proceeds to tridimensional networking by formation of methylene and methylene ether bridges.¹² Adopting the same general kinetic expression that was also used to describe the curing process of UF resins,¹⁰

$$\frac{d\alpha}{dt} = k(1 - \alpha)^m(R - \alpha)^s \quad (10)$$

where $\alpha = (P_0 - P)/P_0$ is the grade of conversion, P is the phenol concentration, P_0 is its initial concentration, R is the ratio of the P and F initial concentration, and m and s are the exponents. In the formation of monomethylolphenol $m = 1$ and $s = 1$, and in the formation of dimethylolphenol $m = 1$ and $s = 2$. If we solve eq. (10) between α and α_g for the two PF resins we get the following equations:

$$t_g - t = \frac{1}{(R - 1)k} \left[\ln \frac{1 - \alpha_g}{R - \alpha_g} - \ln \frac{1 - \alpha}{R - \alpha} \right] \quad (11)$$

and

$$t_g - t = \frac{1}{(R - 1)k} \left[\ln \frac{1 - \alpha_g}{R - \alpha_g} + \frac{R - 1}{1 - \alpha_g} - \ln \frac{1 - \alpha}{R - \alpha} - \frac{R - 1}{1 - \alpha} \right] \quad (12)$$

If one shows the resin gel time as a function of

$$\ln \frac{1 - \alpha_g}{R - \alpha_g} \quad \text{or} \quad \ln \frac{1 - \alpha_g}{R - \alpha_g} - \frac{R - 1}{1 - \alpha_g}$$

respectively, for the two different molar ratios, the reaction rate coefficients are obtained from the slope of the straight lines.

Table V Gel Stiffness Values and Relaxation Times for PF Resins with 0.76 and 1.4 P : F Molar Ratios at Different Temperatures

Temperatures (°C)	Stiffness (Pa s ⁿ)		Relaxation Time (s)		Calculated Viscosity (Pa s)		Measured Viscosity (Pa s)	
	0.76	1.4	0.76	1.4	0.76	1.4	0.76	1.4
90		9213		1.22		9788		9900
100		6157		0.91		5976		2976
110		3002		0.47		2391		2531
120	3561	1284	0.61	0.21	3224	806	3300	1150
130	548	922	0.11	0.15	350	520	560	620
140	347	729	0.08	0.13	213	397	397	420

Table VI Reaction Rates for Two P : F Ratios

Temperature (°C)	Reaction Rates for Reaction (11) (10 ⁻³ mol/s)	Reaction Rates for Reaction (12) (10 ⁻³ mol/s)
120	2.45	6.98
130	6.57	18.10
140	9.37	33.67

Table VI shows the reaction rate coefficients for eqs. (11) and (12). In eq. (12) the obtained reaction rates were similar to the values already reported in the literature.^{13,14} The calculated activation energy value was 92.6 kJ/mol, which is an average value of the previously calculated ones. From the experimental data it appears then that in the curing process first long, mainly linear polymers are formed in the initial part of the polycondensation reaction before the networking. While the chain length of these polymers appears to shorten at lower molar ratios, it is instead the critical value of the chain segment length that is necessary for entanglement to occur, which increases at lower temperatures. Finally, crosslinking leads these linear oligomers to form a network structure in which the crosslink density of the network is higher for higher molar ratio resins and at higher curing temperatures, this being valid only within the limited experimental conditions used. Such results are supported by thermo-mechanical analysis results already reported.^{12,14,15}

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