On the Correlation Equations of Liquid and Solid ^{13}C-NMR, Thermomechanical Analysis, T_g, and Network Strength in Polycondensation Resins

A. PIZZI

ENSTIB, University of Nancy 1, Epinal, France

ABSTRACT: Wide-scope mathematical relationships have been established between the ^{13}C-NMR of liquid polycondensation resins, such as urea–formaldehyde and phenol–formaldehyde resins, and the strength of the network formed by the same resin when hardened under well-defined conditions, the thermomechanical analysis deflection, the number average molecular mass and the number of degrees of freedom of the average polymer segment between crosslinking nodes in the hardened resin network, the resin network glass transition temperature, its solid-phase ^{13}C-NMR proton-rotating frame spin-lattice relaxation time, and the homogeneous and heterogeneous polymer segment/polymer segment interfacial interaction energy calculated by molecular mechanics. These mathematical relationships allow the calculation of any of these parameters from any of the techniques listed, provided that all of the systems are used under well-defined conditions. Under different conditions, the values of the numerical coefficients involved change; and, whereas the equations are still valid, a different set of coefficients needs to be recalculated. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 1703–1709, 1999

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INTRODUCTION

Recently correlation equations between different properties and techniques in polycondensation resins have been advanced. Thus, equations connecting the network strength and other properties of urea–formaldehyde (UF), melamine–formaldehyde, melamine–urea–formaldehyde, and phenol–formaldehyde (PF) polycondensation resins with their liquid phase ^{13}C nuclear magnetic resonance (NMR) spectra have been advanced.[1–6] Equally, equations correlating thermomechanical analysis (TMA) bending deflections during the same

resins curing with number of degrees of freedom (hence the number average mass) of polymer segments between crosslinking nodes and with molecular mechanics-derived energies of interaction at the interface between different polymers, as well as within the same polymer have also been presented.[7–11] Relations between polycondensation network strengths and TMA bending deflections,[12] as well as relations between solid-phase ^{13}C-NMR spin-lattice relaxation times, glass transition temperature (T_g), and number average mass of polymer segments between crosslinking nodes have also been derived.[13] All of these relationships then allow a deduction in the number of relationships of a much wider scope connecting the results of sev-

eral techniques of characterization for polycondensates.

This article deals with the development of correlation equations of a much wider scope connecting parameters defining different properties of polycondensates derived from the different techniques described previously, and with the experimental evidence supporting them.

EXPERIMENTAL

Resin Preparation

UF resins of final U : F molar ratios of, respectively, 1 : 0.9, 1 : 1.05, 1 : 1.15, 1 : 1.3, 1 : 1.5, 1 : 1.8, and 1 : 2.0 were prepared as follows: to a UF concentrate (formurea) containing 23% urea and 57% formaldehyde in water was added enough urea to reach an initial molar ratio of 1 : final molar proportion +0.4 and 22% NaOH to set the pH between 8.3–8.5. The temperature is raised in 50 min to 90°C maintaining the pH between 7.3–7.6 by small additions of 22% NaOH, and the mixture maintained at 90°C for $\sim$ 20 min. The pH then decreases by itself and is maintained not lower than 4.7–5.1 and the temperature increased to 98°C. The reaction is stopped when a water tolerance point of 170% is reached in the case of all resins by cooling down to 40°C, the second urea added to reach the final molar ratio wanted, the pH readjusted to 8.7 with NaOH, and the resin left to mature overnight at 40°C and then cooled at ambient temperature. All the resins were at resin solid contents in the range of 53.3–54.9%.

A series of PF resins of P : F molar ratios 1 : 1.1, 1 : 1.25, 1 : 1.45, 1 : 1.75, 1 : 2.0, 1 : 2.5, and 1 : 2.8 were prepared as follows: 94 g of phenol technical grade, the relative amount of paraformaldehyde technical grade to obtain the molar ratios indicated herein, and 40 g of 80/20 water/methanol were mixed and while mixing mechanically two amounts of 4 mL of 33% NaOH solution were added at 15-min intervals at ambient temperature. The reaction mixture was brought to reflux over a period of 30 min. During this period, two other amounts of 4 mL of 33% NaOH were added at 10-min. intervals to reach a pH of 11. The mixture was refluxed under mechanical stirring for 30 min, then cooled to ambient temperature in 10–15 min, and stored. Before application and testing, the resins were adjusted to the same resin solid content and their pH adjusted to 12.5 by the addition of 33% NaOH.

TMA

Recently, work on the formation of polymer networks by photopolymerizable and polyester surface finishes on wood and polycondensation resins used as wood adhesives has yielded a mathematical relationship[7,8] between the energy of interaction (E) at the synthetic polymer/wood interface calculated by molecular mechanics (work of adhesion), the number of degrees of freedom (m) of the segment of the synthetic polymer between two cross-linking nodes, the coefficient of branching α hence the functionality of the starting monomer and the relative deflection (f) obtained by TMA of wood specimens coated or bonded with the adhesive through the expression $f = km/\alpha E$, where k is a constant.[7,8] UF and PF resins herein were tested by TMA on a Mettler apparatus. Triplicate samples of beech wood alone, and of two beech wood plys, each 0.65 mm thick (bonded with each system for a total sample dimension of $21 \times 6 \times 1.4$ mm) were tested in nonisothermic mode between 40°C and 220°C at a heating rate of 10°C min^{-1} with a Mettler 40 TMA apparatus in three points bending on a span of 18 mm exercising a force cycle of 0.1/0.5N on the specimens with each force cycle of 12 s (6 s/6 s). The classical mechanics relation between force and deflection $E = [L^3/(4bh^3)][\Delta F/(\Delta f)]$ allows the calculation of Young's modulus E for each case tested. As the deflections Δf obtained were proven to be constant and reproducible,[7,8] the values of m for the resins were calculated.

^{13}C-NMR Spectra

The liquid ^{13}C-NMR spectrum of the UF and PF resins used were obtained on a Brüker AC 200 Fourier transform-NMR spectrometer. Chemical shifts were calculated relative to $(CH_3)_3Si(CH_2)_3$-SO_3Na dissolved in D_2O for NMR shift control.[14] Spectra were done at 50.3 MHz, with the sample spectra at 35 Hz. Acquisition time was 1.8 s, with the number of transients of $\sim$ 10,000. All of the spectra were run with a relaxation delay of 5 s, and chemical shifts were accurate to 1 ppm.

The result of solid-phase CP-MAS ^{13}C-NMR spectra were taken from the literature.[13] They were obtained on a Bruker 300 MSL Fourier transform-NMR at 75.47 MHz, with a spinning frequency of 4 kHz. Relaxation delay was 3.75 s, and number of transients were $\sim$ 600.

Table I   UF Liquid Resins, ^{13}C-NMR Peak Shift Assignments and Integrated Areas, and Panel IB Strength

Functional Group (ppm)	U : F Molar Ratio				
	1 : 1.8	1 : 1.5	1 : 1.3	1 : 1.15	1 : 0.9
Carbonyl group {C}					
NH$_2$—CO—NH$_2$ (165.4) {urea}	—	6.6	21.3	55.5	49.7
NH$_2$—CO—NH—CH$_2$— (163.6) {C1}	23.7	52.5	42.1	58.8	28.9
—CH$_2$—NH—CO—NH—CH$_2$— (162.0) {C2}	4.0	27.7	37.3	54.2	25.1
Methylene group {Me}					
—NH—CH$_2$—NH— (48.8) {A}	2.4	9.0	7.1	14.0	8.9
—N(CH$_2$—)CH$_2$—NH— (55.5) {C}	3.5	9.6	6.2	12.2	8.0
—N(CH$_2$—)CH$_2$—N(CH$_2$—)— (61.6) {E}	1.0	2.7	1.0	1.3	1.2
Methylol group {Mo}					
—NH—CH$_2$OH (66.6) {Mo1}	26.3	101.5	68.0	115.9	67.1
—N(CH$_2$—)CH$_2$OH (71.0) {Mo2}	5.3	18.4	12.2	21.3	11.9
HO—CH$_2$—OH, free HCHO (84.7)	7.9	9.4	2.4	3.3	—
IB strength (MPa)	0.733	0.756	0.724	0.629	0.305

Wood Particle Board Internal Bond (IB) Determination

Duplicate single-layer laboratory particle boards of dimensions 350 × 300 × 14 mm were bonded with the UF resins prepared herein using 2% ammonium chloride as hardener on total resin solids. Adhesive solids percentage on dry wood was 7%. Boards were pressed at 195°C and a maximum pressure of 30 kg cm^{-2}, and a pressing time of 180 s, namely of 12.8 s mm^{-1} panel thickness. Boards were tested for IB strength dry (V20) (DIN 68763).[15]

Duplicate single-layer laboratory particle board of dimensions 350 × 300 × 12 mm were bonded with the PF resins prepared herein. Adhesive solids percentage on dry wood was 8%. Boards were pressed at 190°C and a maximum pressure of 25 kg cm^{-2}, and a pressing time of 7.5 min. Boards were tested for IB strength dry (V20) (DIN 68763). Boards were left to stabilize for 2 weeks and then tested for IB strength dry (V20) (DIN 68763).[15] All boards were prepared at a density of 0.700 g cm^{-3}.

DISCUSSION

The absolute areas of ^{13}C-NMR peaks can never be taken as a measure of the abundance of a particular chemical group. They can be used in quantitative NMR, but then mathematical relationships correlating these few quantitative studies to the actual macroscopic strength and other properties of the network formed by the resin do not exist.[16,17] Furthermore, many university and industrial laboratories that have to use NMR extensively do not possess the necessary equipment and rely on routine, qualitative spectra delivered often under a set of standard conditions by NMR services located elsewhere. Under these conditions, it is more convenient to fix a set of standard, routine conditions under which the liquid resin spectrum is done and use a direct calibration method of the macroscopic property wanted with ratios of NMR peak areas. This has been done for several formaldehyde-based resins and always with reproducible results.[1-4] Arguments[16] well applicable to quantitative NMR, as regard the more or less suitable pulse interval for a certain resin, and hence on some groups having reached thermal equilibrium whereas others have not, become invalid if a much simpler calibration method is used. This is so because once the spectra are all done under identical pulse and other conditions, the delay on thermal equilibrium of certain groups is then always the same. This has been done for several formaldehyde-based resins, and always with reproducible results,[1-4] leading to valid mathematical relationships correlating ratios of NMR peak areas with macroscopic strength and other properties. It is just one of these calibration method[1] mathematical relationships that has been used to obtain the following relationship for a series of UF resins of

Table II   UF Liquid Resins, TMA Deflections in Bending, and Panel IB Strengths

	U : F Molar Ratio					
	1 : 2.0	1 : 1.8	1 : 1.5	1 : 1.3	1 : 1.15	1 : 1.05
IB strength (MPa)	0.765	0.754	0.750	0.730	0.600	0.442
TMA deflection f (μm)	20.80	21.10	21.60	22.45	27.65	36.00

molar ratio U : F 1 : 1.8, 1 : 1.5, 1 : 1.3, 1 : 1.15, and 1 : 0.9 from the data in Table I

$$IB = 0.4275[(C + 2E)/(A + C + E)]$$
$$- 0.3623[\text{urea}/(C1 + C2)]$$
$$+ 2.389(Me/Mo) \quad (1)$$

where A = —NHCH$_2$NH— (peak at 48.8 ppm); C = —N(CH$_2$—)CH$_2$NH— (peak at 55.5 ppm); E = —N(CH$_2$—)CH$_2$N(CH$_2$—)— (peak at 61.6 ppm); $C1$ = NH$_2$CONHCH$_2$— (peak at 163.0 ppm); $C2$ = —CH$_2$NHCONHCH$_2$— (peak at 162.0 ppm); urea = —CO— of unreacted urea; Me = total methylene groups (peaks from 45 to 60 ppm); Mo = total methylol groups (peaks from 65 to 72 ppm). In eq. (1) and all the equations that follow derived by it, the numerical coefficients reported are valid for the series of homologous UF resins used; they would change for UF resins prepared in a different manner.

In Tables I and II are reported the IB values of particle board made with the resins herein and with another series of UF resins prepared according to the same procedure and of U : F molar ratio 1 : 2.0, 1 : 1.8, 1 : 1.5, 1 : 1.3, 1 : 1.15, and 1 : 1.1.05. In Table II, the values of TMA deflection obtained under identical conditions for this same set of resins are also reported. TMA bending deflections and particle board IB made with the same resins are correlated with a coefficient of correlation, r = 0.996 according to the following expression

$$IB = d(1/f) + e \quad (2)$$

where d and e have values of 15.88 and 0.011, respectively, and where f is the minimum TMA bending deflection in μm obtained on curing the resin. Equating eqs. (1) and (2) with the appropriate coefficients, as the values of IB obtained are very similar, one then obtains

$$1/f = 0.0269[(C + 2E)/(A + C + E)]$$
$$- 0.0228[\text{urea}/(C1 + C2)]$$
$$+ 0.1504 (Me/Mo) + 0.011 \quad (3)$$

and as $f = -(km)/(\alpha E)$ (the negative sign is due to the numerical values of E being negative for attractive interactions, by convention), the equation already derived by TMA on polycondensation resins[7,8] one obtains

$$-(\alpha E)/(km) = 0.0269[(C + 2E)/(A + C + E)]$$
$$- 0.0228[\text{urea}/(C1 + C2)] + 0.1504 (Me/Mo)$$
$$+ 0.011 \quad (4)$$

as a consequence, the equations

$$-E = k(m/\alpha) \{a'[(C + 2E)/(A + C + E)]$$
$$+ b'[\text{urea}/(C1 + C2)] + c'(Me/Mo) + e' \quad (5)$$

and

$$1/m = (-k/\alpha E) \{a'[(C + 2E)/(A + C + E)]$$
$$+ b'[\text{urea}/(C1 + C2)] + c'(Me/Mo) + e' \quad (6)$$

where a', b', and c' are numerical coefficients that vary for each unique homologous series of UF resins.

As has been previously found,[8,18] $m = 2M/M_0$, where M and M_0 are, respectively, the number average mass of the average segment between crosslinking nodes of a hardened network and M_0 the mass of the polymer repeating unit, then

$$1/M = -2k/(\alpha EM_0) \{a'[(C + 2E)/(A+C+E)]$$
$$+ b'[\text{urea}/(C1 + C2)] + c'(Me/Mo) + e' \quad (7)$$

This indicates that there are definite mathematical relationships between the interaction energy calculated by molecular mechanics E, or the number average mass M, or equally the average number of degrees of freedom m of the average segment between crosslinking nodes of a hardened resin network and data obtained by ^{13}C-NMR of the same resin in liquid form before hardening takes place.

Table III   PF Liquid Resins, ^{13}C-NMR Peak Shift Assignments and Integrated Areas, and Panel IB Strength

Functional Group (ppm)	P : F Molar Ratio					
	1 : 2.5	1 : 2.0	1 : 1.75	1 : 1.45	1 : 1.25	1 : 1.1
Methylene bridges {*Me*} Ph—CH$_2$—Ph (29.21, 34.93, 39.67)	6.39	3.84	7.55	9.87	3.87	4.53
Methylol groups {*Mo*} *ortho*-Ph—CH$_2$OH (61.4–61.5) di-*ortho*-Ph—(CH$_2$OH)$_2$ (61.6–62.3) *para*-Ph—CH$_2$OH (65.52)	42.62	28.69	45.50	48.71	21.79	21.08
Ortho, para free sites {*A*} *ortho* free sites (115.4–116.0) *para* free sites (119.9–120.9)	2.33	9.74	18.17	91.11	62.37	84.35
Reacted and unreactive sites {*B + C*} *meta* free sites (127.4–132.9) {*B*} *ortho, para* reacted sites {127.6–133.9} {*C*}	101.40	87.28	102.58	257.60	121.60	130.06
IB strength (MPa)	0.79	0.54	0.29	0.13	0.11	0.07

The same appears to be valid for PF resins. Results in Tables III and IV are the corresponding experimental data. Results in Table III yield the following relationship

$$IB = -0.470\ A/(A + B + C)$$
$$+ 1.431\ Mo/(A + B + C)$$
$$+ 3.734\ Me/(A + B + C)\quad (8)$$

where A = sum of peak areas of *ortho*- and *para*-sites still free to react on phenolic nuclei (110–122 ppm), B = sum of peak areas of *meta*-site on phenolic nuclei (125–137 ppm), C = sum of peak areas of already reacted *ortho*- and *para*-sites on phenolic nuclei (125–137 ppm), Mo = sum of peak areas of methylol groups (59–66 ppm), and Me = sum of peak areas of methylene bridges (30–45 ppm).

Results in Table IV instead yield a relationship of the type[22]

$$IB = d(1/f) + e\quad (9)$$

where a = 30.96, b = −1.55, and coefficient of correlation r = 0.974.

From eqs. (8) and (9), the following relationship can then be obtained

$$1/f = [1/(A + B + C)][-0.015\ A$$
$$+ 0.046\ Mo + 0.121\ Me] + 0.050\quad (10)$$

and as $f = -(km)/(\alpha E)$, substituting in eq. (10)

$$1/m = [-k/(\alpha E)][1/(A + B + C)][-0.015\ A$$
$$+ 0.046\ Mo + 0.121\ Me] + 0.050\quad (11)$$

and as $m = 2M/M_0$

$$1/M = [-2k/(\alpha E M_0)][1/(A + B + C)][-0.015\ A$$
$$+ 0.046\ Mo + 0.121\ Me] + 0.050\quad (12)$$

Results in Table V have been taken from the literature[13]: whereas the values of the NMR's proton rotating frame spin-lattice relaxation time T_{1p}

Table IV   PF Liquid Resins, TMA Deflections in Bending, and Panel IB Strengths

	P : F Molar Ratio						
	1 : 2.8	1 : 2.5	1 : 2.0	1 : 1.75	1 : 1.45	1 : 1.25	1 : 1.1
IB strength dry (Mpa)	—	0.79	0.54	0.29	0.13	0.11	0.07
TMA deflection f (μm)	13.5	13.6	14.3	17.5	17.9	18.8	—

Table V   Proton T_{1p} Solid-Phase CP-MAS, ^{13}C-NMR Results, and Molecular Weight M Between Crosslinking Nodes Obtained by Swelling Studies of Hardened PF Resins[13]

T_{1p} (ms)	4.8	4.4	4.55	4.15	3.85	4.1	3.65
M (g mol^{-1})	19	28	31	49	55	69	77

are correct, the authors[13] also remarked that the values of M obtained are far too low, because they were obtained by swelling studies through the Flory–Rehner equation.[19,20] It is well known that the absolute values of M obtained by the Flory–Rehner equation have little practical significance, due to some of the assumptions implicit in the theory.[13,21] However, the relative values and trends derived by the Flory–Rehner swelling equation are valid. Data in Table VI yield a relationship between the NMR's proton rotating frame spin-lattice relaxation time T_{1p} and the number average mass M of the average segment between crosslinking nodes of a hardened resin network

$$1/M = 0.00327 \, T_{1p} - 0.111 \qquad (13)$$

of coefficient of correlation $r = 0.91$. Data in Table VI, also obtained from the literature,[13] also indicate a relationship between T_g and M of the type

$$1/M = 0.0011 \, T_g - 0.098 \qquad (14)$$

of coefficient of correlation $r = 0.95$. Substituting for M eq. (13) in eq. (12), one obtains

$$T_{1p} \sim \; [-2k/(\alpha EM_0)]\{[1/(A + B + C)][-0.464 \, A \\ + 1.413 \, Mo + 3.688 \, Me] - 1.53\} - 3.39 \quad (15)$$

while substituting for M eq. (14) in eq. (12), one obtains

$$T_g \sim \; [-2k/(\alpha EM_0)]\{[1/(A + B + C)][-13.8 \, A \\ + 42.0 \, Mo + 109.7 \, Me] - 45.5\} - 89.5 \quad (16)$$

Table VI   Isothermal TMA T_g, and Molecular Weight M Between Crosslinking Nodes Obtained by Swelling Studies of Hardened PF Resins[13]

T_g (°C)	108	115	132	137
M (g mol^{-1})	55	(43.7)	28	19

The symbol $\sim$ instead of $=$ needs to be used in eqs. (13) and (15) because the PF resins used for the left term of the equation and for the right term, while similar, were however not the same. Thus, a numerical corrective factor still needs to be introduced for the equations to be valid in $=$.

As a consequence of the above equations, the hardened resin network $T_{1p} \sim T_g \sim 1/E$, and $T_{1p} \sim T_g \sim 1/M \sim 1/m \sim 1/f \sim A, Mo, Me$ liquid resin NMR signals. This means that all the other parameters can be derived from the above equations once just one of the parameters values, just through one of the techniques only, is known. It must be pointed out again that the numerical values of the coefficients presented in all of the equations, for both UF and PF resins, are strictly and only valid for the standard type of resin formulations used and that the coefficient values will be different for different types of formulations. The same approach outlined herein for PF and UF resins is likely to be valid also for melamine–formaldehyde and melamine–urea–formaldehyde resins for which equations similar to eqs. (1) and (8) for a variety of formulations already exist.[2,3,5]

From the results in Table VI only as $M = mM_0/2$ and $m = -f\alpha E/k$, then $T_g \sim 2/(mM_0)$ and hence $T_g \sim -2k/(M_0 f\alpha E)$ and from eqs. (13) and (14) $T_g \sim a2k/(M_0 f\alpha E) + b \sim a2/(mM_0) + b$, where a and b are numerical coefficients depending on the type of resins used. As $T_g \sim T_{1p}$, then $T_{1p} \sim T_g \sim 1/M \sim 1/m \sim 1/f \sim 1/E$ again confirming what is shown in the equations above. Equally, $M \sim -f\alpha EM_0/(2k)$, but as a regression equation for polycondensation resin eliminating the need to obtain E for polycondensation and other resins under well-defined conditions has already been presented,[8] namely $m = 0.919\alpha f + 0.579$ of $r = 0.99$, one can then obtain

$$M \sim M_0 \, (0.460 \; \alpha f + 0.290) \qquad (17)$$

that is much easier to use. Considering that, in a PF resin $\alpha = 0.5$ and $M_0 = 107$, and

$$M \sim 24.61 \, f + 31.03 \qquad (18)$$

that can also be expressed as $f \sim (M - 31.03)/24.61$ that gives the absurd results that f is ≤ 0

for $M \leq 31.03$ and for the maximum value found for $M = 77$; hence, $f = 1.83$, the elastic modulus being equal to 19.3 GPa, whereas all previous experiences yield PF resins values between 2.2 and 3.3 GPa. Thus, as admitted by the authors,[13] the absolute values of M obtained by the Flory–Rehner swelling equation in Table VI are wrong, hence the need for the $\sim$ symbol in some of the above equations.

CONCLUSIONS

Wide-scope mathematical relationships have been established between the ^{13}C-NMR of a liquid polycondensation resin and the strength of the network formed by the same resin when hardened under well-defined conditions, the TMA deflection, the number average molecular mass, and the number of degrees of freedom of the average polymer segment between crosslinking nodes in the hardened resin network, the resin network glass transition temperature, its solid-phase ^{13}C-NMR proton rotating frame spin-lattice relaxation time, and the homogeneous and heterogeneous polymer segment/polymer segment interfacial interaction energy calculated by molecular mechanics. These mathematical relationships allow the calculation of any of these parameters from any of the techniques listed, provided that all of the systems are used under well-defined conditions. Under different conditions, the values of the numerical coefficients involved change; whereas the equations are still valid, a different set of coefficients needs to be recalculated.

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