

# Crosslinked and Entanglement Networks in Thermomechanical Analysis of Polycondensation Resins

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**ABSTRACT:** Thermomechanical analysis (TMA) tests on joints bonded with synthetic phenol–formaldehyde (PF) resins have shown that, frequently, the joint increase in modulus does not proceed in a single step but in 2 steps, yielding an increase of the modulus first-derivate curve presenting 2 peaks rather than a single peak. This behavior has been found to be due to the initial growth of the polycondensation polymer, leading first to linear polymers of critical length for the formation of entanglement networks. Two modulus steps and 2 first-derivate peaks then occur, with the first due to the formation of linear polymers entanglement networks, and the second due to covalent crosslinked networks. The faster the reaction of phenolic monomers with formaldehyde, or the higher the reactivity of a PF resin, the earlier and at lower temperature the entanglement network occurs; more important is its modulus value in relation to the final, crosslinked resin modulus. The accepted methods of calculating the gel point and gel temperature of a polycondensation resin or from the single peak of the first derivate of the modulus increase curve or from the start of the uprise of the modulus increase curve is still acceptable in resins in which the entanglement effect is small or it is not present. In resin systems in which the entanglement effect, instead, is of importance, the question of what is the gel point in such systems had to be addressed, and gel temperature and gel point must be obtained from the modulus and its first-derivate curve in a different manner, which is presented. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 70: 1111–1119, 1998

## INTRODUCTION

It is accepted wisdom in TMA experiments on polycondensation resins that the upstart of the modulus increase curve or the flex point in the increase of the modulus curve as a function of temperature, hence, in the second case, the temperature of its first-derivate peak, is the gel point of the resin.<sup>1–3</sup> Recent work on the polycondensation reaction with formaldehyde and other hardeners of polyflavonoid tannins, however, casts some doubts on this approach.<sup>4</sup> This is the consequence of the multistep modulus increase curves,

which were observed in the polycondensation of polyflavonoid tannins.<sup>4</sup> The original concept that the temperature of the modulus curve start of uprise or even its first-derivate peak are the gel point of the resin appeared to loose significance in these systems. This was so because, from the results obtained for these polycondensation polymers, the growth of which yielded, initially and for sometime only, linear polymers, noticeable increases in the modulus of the joint bonded with them to a first plateau was noticeable well before the increase of modulus to its stable final value due to crosslinking of the resin. The first noticeable increase in modulus was found to be due to the formation of linear polymers entanglement networks. The question had then to be addressed of where is the real gel point: at the flex point of

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the increase in modulus caused by the polymer reaching a critical, temperature- and concentration-dependent length sufficient to yield an entanglement network? Or rather at the flex point of the increase in modulus caused by the onset of tridimensional covalent crosslinking, especially when this might depend from the occurrence of the former? The increase in synthetic resins modulus curves is generally smoothed to eliminate this first entanglement shoulder, in resins which might present it, to yield a single flex point,<sup>1,2</sup> which is then considered as the "gel" point (an approach nonetheless conceptually incorrect, as this would represent, in a single-step curve, the start of vitrification<sup>1</sup> and not the gel point). This approach might still be technically acceptable, although conceptually open to debate, in cases in which the initial increase in modulus due to entanglement is small. Taking as the gel point the start of the uprise in the modulus increase curve is instead conceptually correct in the cases in which the initial increase in modulus due to entanglement is small and the modulus increase curve presents only one increase step.<sup>1</sup> Their use, however, is not correct in resins in which the initial entanglement-due modulus increase is important. In this case then, all the modulus increases should be taken into consideration.

This article addresses, then, this peculiar aspect of thermomechanical analysis (TMA)-derived parameters of polycondensation resins and, in particular, for synthetic phenol-formaldehyde (PF) resins.

## EXPERIMENTAL

### TMA Determination of Average Number of Degrees Freedom of Networks

Recently, work on the formation of polymer networks by photopolymerizable and polyester surface finishes on wood and of polycondensation resins used as wood adhesives has yielded a mathematical relationship<sup>5,6</sup> 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 2 crosslinking nodes, the coefficient of branching  $\alpha$  (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.<sup>5,6</sup> Regression equations<sup>6</sup> correlating directly  $m$  with  $E$  and  $m$  with  $f$  have been derived for hardened PF, resorcinol-formaldehyde (RF), melamine-formaldehyde (MF), and tannin-formaldehyde (TF) resins. These relationships have been used to calculate  $m$  for a commercial PF resin of the molar ratio of phenol-to-formaldehyde equal to 1 : 2.5, prepared by a multistep reaction procedure, at the delivered resin solids content of 48%, and diluted progressively with water to 46, 44, 42, and 40% resin solids content. They have also been used for the same purpose for the reaction of phenolic monomers of different reactivity, namely, phloroglucinol (1,3,5-trihydroxy benzene), resorcinol (1,3-dihydroxy benzene), phenol itself, and catechol (1,2-dihydroxy benzene) with formaldehyde (paraformaldehyde fine powder 96% was used) in the molar ratio of phenol-to-formaldehyde of 1 : 2 and with the phenol prepared at 40% concentration in water. They were finally used for the same purpose for water solutions of carboxymethyl cellulose and starch, also at 40% concentration in water. The low condensation and low level of polymerization PF resin, to which 7.2% on resin solids of glycerol triacetate accelerator was added, were prepared according to procedures already reported.<sup>7</sup>

To this purpose, the resins and models above were tested dynamically by TMA on a Mettler apparatus. Triplicate samples of beech wood alone and of two beech wood plys each 0.6 mm thick, bonded with each system, for total sample dimensions of  $21 \times 6 \times 1.4$  mm, were tested in nonisothermic mode between 40 and 220°C at a heating rate of 10°C/min with a Mettler 40 TMA apparatus in 3 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 (6s/6s). The classical mechanics relation between force and deflection  $E = [L^3/(4bh^3)][\Delta F/(\Delta f)]$  allows the calculation of the Young's modulus  $E$  for each case tested. As the deflections  $\Delta f$  obtained were proven to be constant and reproducible,<sup>5,6</sup> the values of  $m$  for the resins were calculated.

### <sup>13</sup>C Nuclear Magnetic Resonance

The liquid <sup>13</sup>C nuclear magnetic resonance (<sup>13</sup>C-NMR) spectrum of the PF resin used were obtained on a Brüker MSL 300 Fourier transform (FT)-NMR spectrometer. Chemical shifts were calculated relative to (CH<sub>3</sub>)<sub>3</sub>Si(CH<sub>2</sub>)<sub>3</sub>SO<sub>3</sub>Na dissolved in D<sub>2</sub>O for NMR shifts control.<sup>8</sup> The spec-

tra were done at 62.90 MHz for a number of transients of approximately 1000. All the spectra were run with a relaxation delay of 5 s, and chemical shifts were accurate to 1 ppm.

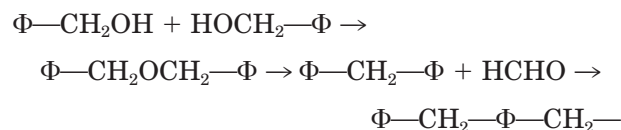
## DISCUSSION

The results in Table I indicate that the modulus of a joint bonded with a commercial phenolic resin increases first to a value of between 20 and 40% of the final value of the modulus after complete curing of the resin due to the effect of the formation of entanglement networks. The mechanism of formation of these entanglement networks depends from the relative balance between the linear increase in polymer length in the initial stages of the polycondensation; hence, it is polycondensation-dependent, and from the concentration of the linear polymers formed. Thus, as the linear length of the polymer increases, the water is also progressively removed from the growing polymer both by absorption by the substrate as well as by evaporation as the temperature increases during the test. Once a certain critical value of the length of the polymer is reached and a certain critical value of concentration is reached too, then entanglement networks will form.

The appearance of the modulus step due to entanglement networks is not determined by the polymer having to reach a fixed value of the average length of the polymer. Such a critical length varies: the higher the concentration of the polymer is at any moment (the greater the amount of water lost), the lower the critical length of the polymer needed to form entanglement networks is, and the earlier in the polycondensation reaction the entanglement networks appear. As a consequence, a PF resin such as that in Table I will show within a limited range of water contents, at parity with all other conditions, a variation in the extent of formation of entanglement networks, a variation in the number of degrees of freedom  $m$  (hence, of the length of the polymer segments between entanglement nodes), and an increase in the minimum temperature of formation of the network as the initial concentration of the resin decreases; this is indeed what is observed for the PF resin in Table I. From Table I, it is also clear that a tighter or less-tight entanglement network is the consequence of the combination of these contrastant effects; in short, there will be an optimum condition in which all the effects will combine to give the tightest network possible, hence,

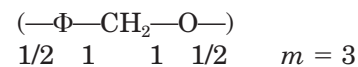
a network of minimum  $m$ . Under the limited range of conditions used in Table I, this occurs at a 46% solids content of the PF resin. The conditions for the formation of an optimal entanglement network do not correspond, and there is no reason why they should, to the conditions needed to obtain an optimal, final, hardened, covalently crosslinked network (which, in Table I, occurs at a 42% resin solids content). At least in the limited range of concentrations investigated, the appearance or not of an initial entanglement network does not appear to have any bearing on the final strength performance of the resin; it will definitely have some bearing, however, on other resin properties, such as resin flow and rheology during application, which also have a determining effect on the final performance or handling of the resin.

It must be pointed out that the correct interpretation of the values of the number of degrees of freedom  $m$  reported in Table I, obtained according to procedures already reported,<sup>5,6</sup> is different for the entanglement and for the final crosslinked networks. The PF resin chosen is a particularly fast one and is obtained by reaction of phenol and formaldehyde in such a manner that no free ortho or para sites exist on the phenolic nuclei. The <sup>13</sup>C-NMR in Figure 1 shows this as no peaks at 115 and 120 ppm are present (free ortho and para sites). It can only polymerize then, at first linearly by the formation of methylene ether bridges through the mechanism,

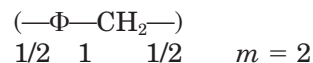


in which the first step forces the oligomers formed to be linear. The entanglement networks form at a stage in the reaction, in which mostly this type of methylene ether ( $-\text{CH}_2\text{OCH}_2-$ ) bridges occurs. In the final hardened network, instead, mostly methylene bridges ( $-\text{CH}_2-$ ) occur. The value of  $m$  given in Table I for the 2 types of network, according to what was reported previously,<sup>6</sup> can be interpreted as follows.

Entanglement networks:



Crosslinked networks:



**Table I Parameters of Entanglement and Crosslinked Networks Obtained by Thermomechanical Analysis**

	Entanglement						Crosslinked					
	Flex Point			Relative Modulus			Flex Point			Relative Modulus		
	Temperature (°C)	Relative Intensity	Temperature (°C)	Value	<i>f</i> (μm)	<i>m</i>	Temperature (°C)	Relative Intensity	Temperature (°C)	Value	<i>f</i> (μm)	<i>m</i>
<b>Resins</b>												
PF 48%	95-119	16	125	0.26	57.2	25.7	126-141	33	180	1.0	16.1	6.8
PF 46%	99-115	18	103	0.44	48.9	21.9	111-141	33	148	1.09	14.8	6.2
PF 44%	99-114	15	112	0.24	56.8	25.5	124-146	34	166	1.11	14.5	6.1
PF 42%	102-116	22	108	0.25	59.0	26.5	114-132	34	164	1.14	14.1	5.9
PF 40%	101	14	106	0.21	60.5	27.2	124-139	40	166	1.04	15.5	6.5
PF, low condensation	142	13	144	—	—	—	159	63	162	—	16.1	6.8
<b>Phenolic monomers</b>												
Phloroglucinol-formaldehyde	96	34	102	0.63	30.5	13.4	106	32	118	0.79	20.3	8.7
Resorcinol-formaldehyde	100	18	103	0.51	37.9	16.8	110	40	114	0.78	20.5	8.8
Phenol-formaldehyde	108	14	112	—	—	—	122	43	135	—	43.2	19.3
Catechol-formaldehyde	115	5	—	0.40	48.6	21.8	141	50	173	0.42	47.7	21.3
<b>Noncrosslinkable</b>												
CMC	112	35	150	1.09	18.7	16.6						
Starch	109	31	120	0.39	52.4	47.6						

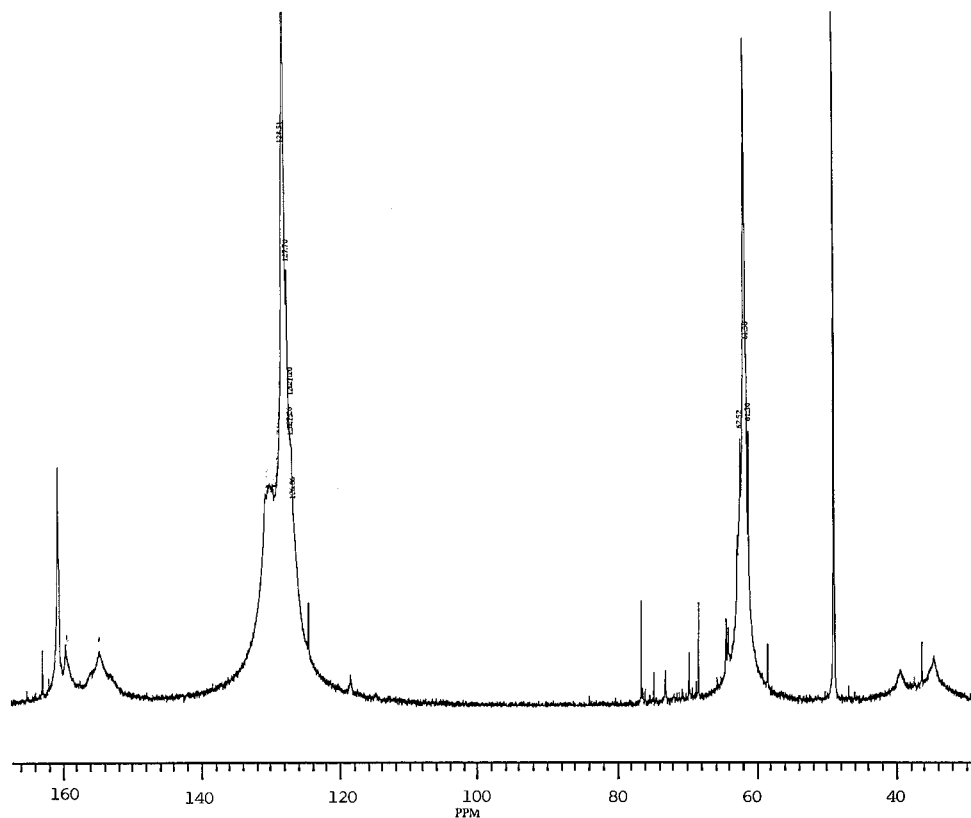


Figure 1  $^{13}\text{C}$ -NMR spectrum of the liquid 48% PF resin used.

This means that for the first case in Table I (PF at 48% resin solids content), for instance, the entanglement network  $m$  of 25.7 translates in an average of  $25.7/3 = 8.6$  repeating units between entanglement nodes, while for the final crosslinked network, there are, on average, the equivalent of  $6.8/2 = 3.4$  repeating units between covalent crosslinking nodes.

In Figure 2 are reported the curve of modulus increase as a function of temperature and its first-derivate curve. The first-derivate peak corresponding to the formation of the entanglement plateau of the modulus curve is clearly visible in this example and appears at  $119^\circ\text{C}$  with the plateau starting at  $125^\circ\text{C}$ . This pattern of an entanglement peak followed by the peak due to gelling is repeated in all the examples reported in Table I. The first-derivate peak is not always as clear as for the case shown in Figure 2, with the entanglement plateau of the modulus curve and the peak of its first derivate sometimes appearing just as shoulders of the main peak and plateau. The position of the entanglement peak and plateau tend to vary, although within a fairly narrow interval (Table I). This variability indicates that

the polycondensation-dependent entanglement process is a fairly random one; entanglement always occurs, but its extent is, within limits, rather variable.

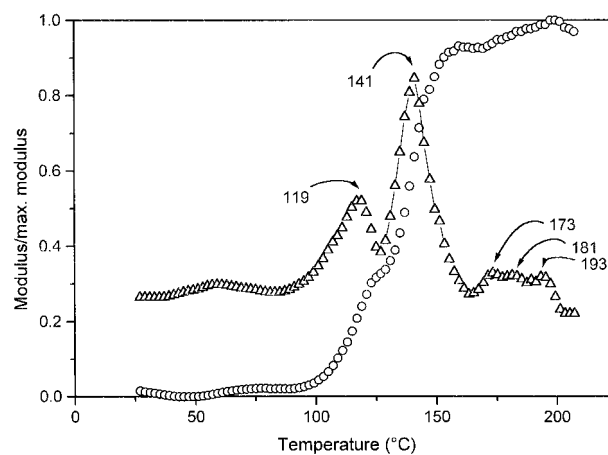
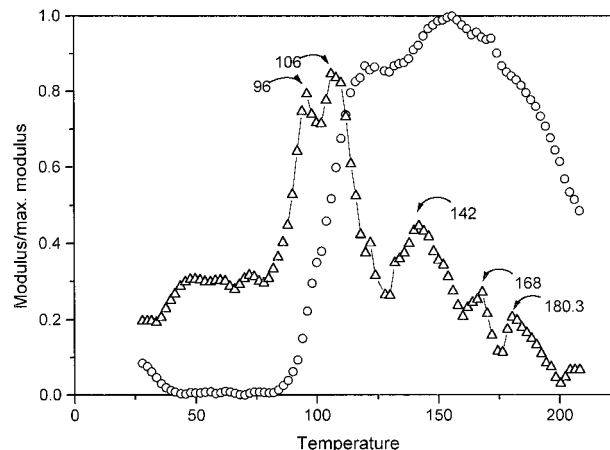


Figure 2 Curve of the variation of the modulus-to-max modulus ratio (O) as a function of temperature and curve of its first derivate ( $\Delta$ ) of a joint bonded with a PF resin of 48% resin solids content and a molar ratio of 1 : 2.5.



In the modulus curve in Figure 2, the small first-derivate peaks observable at 173, 181, and 193°C are due to the internal rearrangement of the network methylene ether bridges to methylene bridges and the further reaction of the formaldehyde liberated as a consequence to form further methylene crosslinks. In the case shown in Figure 2, the corresponding increases in modulus due to this reason are rather small as few free sites on phenolic nuclei exist for further reaction of the formaldehyde liberated in the PF resin used, which has a high formaldehyde-to-phenol molar ratio. Where such a molar ratio is lower, the further increase in modulus is more marked.

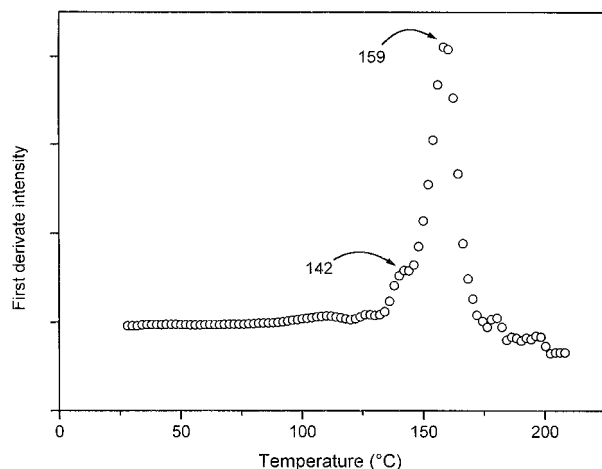
The results obtained for the reaction of formaldehyde with simple phenols at molar ratios of phenol-to-formaldehyde equal to 1 : 2, thus starting from a phenol monomer rather than from a premanufactured resin, also show some interesting trends (Table I). As could be foreseen from the dependence of the linear growth leading to entanglement from the polycondensation, the faster the reaction of the phenol with formaldehyde, the earlier the entanglement network appears. Thus, the first-derivate entanglement peak and the modulus curve entanglement plateau appear earlier (at a lower temperature) for phloroglucinol, followed by resorcinol, than for phenol, and later (at a higher temperature) for the less-reactive catechol, in line with the relative reactivity with formaldehyde of these 4 phenols.<sup>9,10</sup> Of interest is also that the proportional extent of the entanglement in the final modulus curve is more marked the more reactive the phenol is. Thus, from Table I, the proportion of entanglement to crosslinking passes from 34 : 32 for the very reactive phloroglucinol, to 18 : 40 for resorcinol, to 14 : 40 for phenol, and to only 5 : 50 for the less-reactive catechol. The case of phloroglucinol-formaldehyde is illustrated in Figure 3. This result infers also that the more reactive, for whatever reason (such as higher pH, for example) the PF resins are, the more noticeable the initial entanglement effect will be. An example of this is shown in Figure 4(a) and (b), showing the first-derivate peaks of a less-polymerized PF resin (and of lower molar ratio of P : F = 1 : 1.8) by itself and on addition of an accelerator, such as glycerol triacetate.<sup>7</sup> The entanglement and crosslinking peaks occur later for the less-polymerized PF resin alone (Table I) than in the case of the more advanced PF resins discussed above. The low level of polymerization PF resin to which the accelerator has been added develops the entanglement



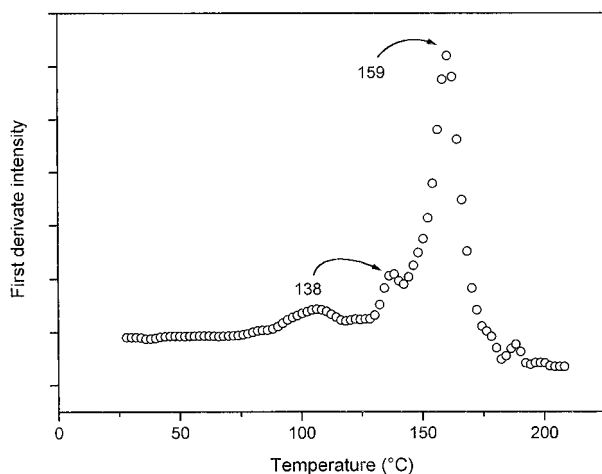
**Figure 3** Curve of the variation of the modulus-to-max modulus ratio (○) as a function of temperature and curve of its first derivate (△) of a joint bonded with phloroglucinol monomer-paraformaldehyde at pH 4.5 and at a phloroglucinol-to-formaldehyde molar ratio of 1 : 2.

peak (but not the crosslinking peak) at a slightly lower temperature than the same resin without accelerator. Comparing Figure 2 with Figure 4(a) and (b), and from Table I, it is also evident that in the less-polymerized resins, the extent of entanglement is much less (13 : 63) than in the more polymerized PF resin.

The effects outlined above would be expected, as entanglement networks are formed by the interaction of polymer chains when the product of polymer concentration ( $C$ ) and its molecular weight ( $M$ ) becomes greater than some critical molecular weight  $M_c$ .<sup>11-13</sup> In the initial stages of the polycondensations at hand, the  $C$  of polymer increases (as the polycondensation proceeds and as the solvent is also lost) and  $M$  increases. As a consequence,  $C \times M > M_c$  quite rapidly, and the more rapid this relationship is reached, hence, the higher the reactivity of the phenol or the more reactive the PF resin used is, the lower the temperature at which the modulus plateau starts to appear is, as shown in Table I and Figures 2-4. For the noncrosslinkable polymers of fixed average molecular weight (Table I and Figs. 5 and 6), the same applies with the reaching of the  $C \times M > M_c$  condition just relying on the increase of concentration due to the loss of solvent as the temperature increases. Both types of polymer than exhibit pseudogel behavior<sup>11-13</sup> at applied higher frequencies (hence, at higher temperatures and shorter time scales) than the lifetime of entanglements, as the lifetime (relaxation) of



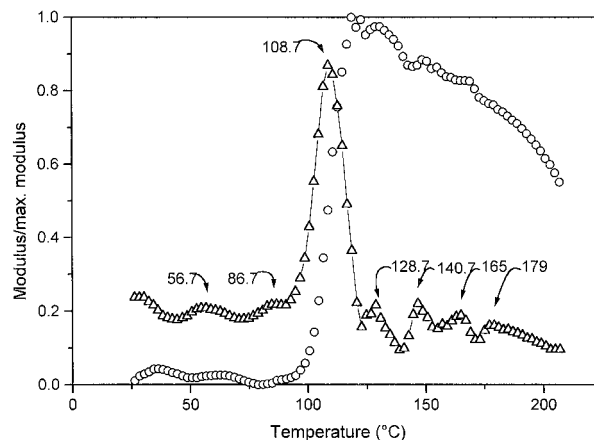
(a)



(b)

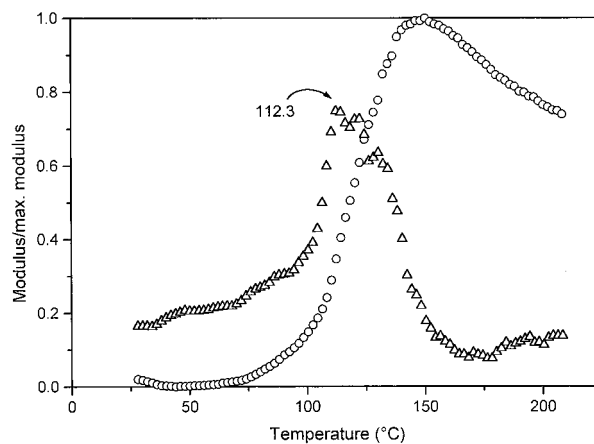
**Figure 4** Curve of the first derivate of the variation of modulus-to-max modulus ( $\circ$ ) as a function of the temperature of a joint bonded with (a) a low level of condensation PF resin and (b) the same low level of condensation PF resin with 7.2% glycerol triacetate accelerator added.

entanglements has been shown<sup>11,12</sup> to be directly proportional to  $M^3$ . Thus, the more rapidly the polycondensation proceeds, hence, the more rapid the increase of  $M$ , the earlier the pseudogel plateau of the modulus curve is reached. In the formation of pseudogels, the slopes of the curves of the elastic modulus  $G'$  and of the loss modulus  $G''$  are different, with  $G'$  having a sharper slope but initially with  $G''$  having a greater contribution to the total modulus (a higher curve as a function of the temperature) until a point of crossover of the 2 modulus curves, with this crossover point being defined often as the gel point.<sup>14</sup> The appearance of

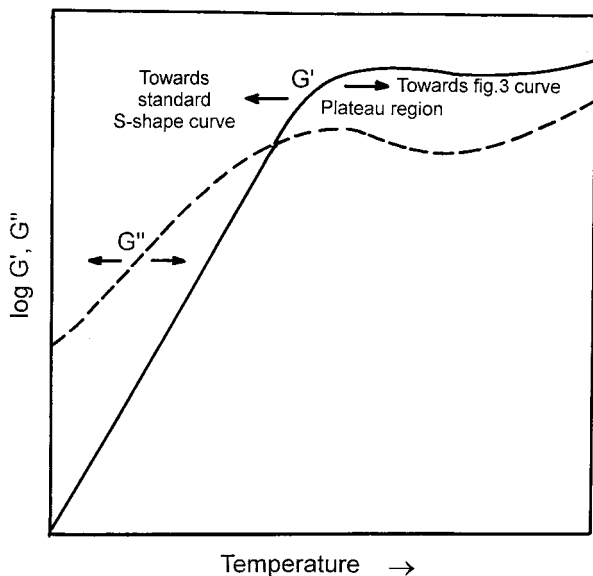


**Figure 5** Curve of the variation of the modulus-to-max modulus ratio ( $\circ$ ) as a function of temperature and curve of its first derivate ( $\triangle$ ) of a joint bonded with a linear noncrosslinked polymer (starch).

the total modulus curve then depends on where this crossover point is; hence, in Figure 7, it can be seen that when the crossover point is already in the pseudogel plateau region of  $G''$ , the modulus curve will appear as that of the PF resin shown in Figure 2; if the crossover point occurs before the  $G''$  plateau, this being a frequent case, then the appearance of the curve will be that of a simple S-shaped curve (Fig. 7); if, lastly the crossover point occurs well into the region of the  $G''$  plateau, then the modulus curve will have the same appearance as the modulus curve in Figure



**Figure 6** Curve of the variation of the modulus-to-max modulus ratio ( $\circ$ ) as a function of temperature and curve of its first derivate ( $\triangle$ ) of a joint bonded with a linear noncrosslinked polymer (carboxymethyl cellulose).



**Figure 7** Expected behavior of elastic modulus ( $G'$ ) and loss modulus ( $G''$ ) as a function of a variable, applied oscillatory strain frequency, or variable temperature at fixed standard frequency. The position of the crossover point of the  $G'$  and  $G''$  curves will determine the apparent shape of the total modulus curve.

3 for the phloroglucinol monomer–formaldehyde reaction.

The question of which is the gelling temperature of a polycondensation resin, when hardening and gelling are observed by TMA, then becomes topical, especially if one wants to relate what happens at the molecular level with what is observable at the macroscopic level. If the curve in Figure 2 is smoothed, as it is normal practice, then the single first-derivate peak corresponding to the gel temperature would appear at 132°C. This practice is equivalent to define the gel point as the temperature at which the reaction rate of crosslinking of the polycondensation is maximal (at the flex of the modulus curve). This is, by definition, an approximation. Equally defining the gel point as the start of the uprise of the smoothed curve gives a gel point of 105°C. Leaving instead, the curve as obtained experimentally (as in Fig. 2), shifts to 141°C the gel temperature, according to the first-derivate peak concept. It can also be argued that the first-derivate peak at 119°C, corresponding to the flex point of the modulus curve leading to the entanglement plateau, could also be the gel point. The latter, however, can be discounted because the results in Table I and in Figures 5 and 6 for linear, noncrosslinkable polymers, such as carboxymethyl cellulose

and starch, show only 1 plateau and 1 first-derivate peak, the ones given by entanglement of the linear polymers; and this cannot be considered as a gel point, but only the pseudogel point, as explained above. It is simply the results of the entanglement of the fixed length linear chains of these polymers at a certain concentration once evaporation of water allows the system to reach the critical concentration needed. Equally, the gel point by start of the modulus curve uprise at 105°C, if this is taken as the gel point, is nothing else than a pseudogel point caused by the start of the formation of the entanglement network.

The correct connection between what occurs at the molecular level with the macroscopically observed gel point then appears to depend on how the definition of gel point is expressed. If the gel point is just a physical phenomenon observable at the macroscopic level, which indicates partial immobilization of the polymer by whatsoever means, then a linear polymer tested strictly under the nonisothermal TMA conditions used also presents a gel point due to this entanglement network formed, once evaporation of water allows the system to reach the critical concentration needed (Figs. 5 and 6). In this case, the gel point temperature would be represented by the first-derivate peak at 119°C in Figure 2.

However, if the gel point is defined as the instant at which any tridimensional crosslinking starts or as the crossover point of the  $G'$  and  $G''$  contributions, both of which are the more accepted view,<sup>14,15</sup> then in Figure 2 this corresponds to the start of the second step in modulus increase; hence, it corresponds to the inverse peak of the first derivate curve at 126°C. This is very close to the values of 132 and 105°C obtained by the traditional way of smoothing the modulus curve, but it is conceptually more correct. In cases in which the inverse peak of the first derivate is not visible, hence when the crossover point of the  $G'$  and  $G''$  contributions occur before the  $G''$  plateau is reached, and such cases occur fairly frequently, even for the same resins discussed here, then smoothing the modulus curve, although conceptually incorrect, would still yield an approximate result, which might be acceptable in most cases. This value is also close to the values of gel points observed at the macroscopic level. In both cases described, however, the gel point never corresponds to the traditional flex point of the smoothed modulus increase curve.

It is also interesting to note that the application of the expression<sup>5,6</sup>  $f = -km/(\alpha E)$  to en-



tanglement networks formed during polycondensation reactions also allows to treat entanglement networks as equally well as what is shown for covalently crosslinked networks,<sup>5,6</sup> again indicating the validity of such an equation for all types of networks.

## CONCLUSION

TMA tests on joints bonded with synthetic PF resins have shown that, frequently, the joint increase in modulus does not proceed in a single step but in 2 steps, yielding an increase of modulus first-derivate curve presenting 2 rather than a single peak. This behavior has been found to be due to the initial growth of the polycondensation polymer leading first to linear polymers of critical length for the formation of entanglement networks. Two modulus steps and 2 first-derivate peaks then occur, with the first due to the formation of linear polymers entanglement networks, and the second due to covalent crosslinked networks. The faster the reaction of phenolic monomers with formaldehyde, or the higher the reactivity of a PF resin, the earlier and at lower temperature the entanglement network occurs, and more important is its modulus value in relation to the final, crosslinked resin modulus. Thus, the explanation of the formation of a multistep modulus increase curve for a phenolic resin can be ascribed to a series of different related and unrelated causes, namely, (1) the  $-\text{CH}_2\text{OCH}_2-$   $\rightarrow$   $-\text{CH}_2-$  rearrangement; (2) the important linear growth of the polymer before the start of tridimensional crosslinking, leading to the initial formation of entanglement networks; and (3) the relationship between the storage and viscous components  $G'$  and  $G''$  of the modulus as a function of temperature, time, and reaction advancement, which is related to the first 2 causes outlined. The accepted methods of calculating the gel point and gel temperature of a polycondensation resin or from (1) the single peak of the first derivate of the modulus increase curve (an approach nonetheless conceptually incorrect, as this would represent in a single step curve the start of vitrification<sup>1</sup> and not the gel point); or from (2) the start of the uprise of the modulus increase curve

are incorrect (the former), and the second still acceptable in resins in which the entanglement effect is small or it is not present. In resin systems in which the entanglement effect is, instead, of importance and multisteps modulus increase curves are obtained, the question of what is the gel point in such systems had to be addressed. In these cases, gel temperature and gel point must be obtained from the modulus and its first-derivate curve in a different manner, namely, from the inverse peak of the first derivate of the modulus increase curve, hence, from the start of the second uprise (the start of the real crosslinking phase) of the modulus increase curve, after the entanglement plateau is reached, thus, from the start of the crosslinking, leading to the covalent tridimensional network.

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