

# polymer communications

## Viscoelastic properties of epoxy networks in the glass transition region

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What are the specificities of the thermomechanical behaviour of tridimensional polymers in glassy state or in the glass transition region? Despite the fact that it is often claimed that 'linear polymers are softer and tougher than tridimensional ones', detailed studies, for instance of elastic properties<sup>1</sup> indicate that these specificities, if they exist, are very scarce. A possible cause of systematic difference between both polymer families could be the crosslinking effect on relaxation spectrum. As a matter of fact, chain motions must be perturbed in immediate vicinity of crosslinks. Thus, if the width of the relaxation spectrum expresses the diversity of the situation of chain segments, it is expected to be higher in tridimensional than in linear polymers. The best way to obtain information on the relaxation spectra is dynamical testing and study of complex modulus  $E^*$  in the frequency domain from Cole–Cole plots. It seemed interesting to use this approach on a family of networks based on the same epoxide–amine pair: diglycidyl ether of bisphenol A (DGEBA)–diaminodiphenyl methane (DDM) with various amine/epoxide molar ratios. In such a family, it is possible to obtain large variations of the crosslink density with an almost constant chain stiffness. In non-stoichiometric samples, there is a great diversity of chain segment situations since certain ones are directly connected to the crosslinks whereas others are relatively far away. © 1997 Elsevier Science Ltd. All rights reserved.

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### Introduction

The cure conditions of the network synthesis were 2 h at 180°C plus 2 h at 200°C, which were chosen in order to obtain cure conversions close to unity and to avoid post-cure effects during viscoelastic measurements. Viscoelastic measurements were performed using a dynamic thermo-mechanical testing machine. DMTA (Polymer Laboratories) were used under the following conditions:  $\epsilon = 0.3\%$ ; temperature scanning rate, 0.5 K min<sup>-1</sup>; frequency range, 0.1–30 Hz; temperature range, 173–480 K. The modulus scale was calibrated from extensometric measurements made with an INSTRON 4502 tensile machine at 20°C, on the samples under study.

Some important characteristics of the samples under study are listed in Table 1.

The experimental curves  $E'$ ,  $\tan\delta$  and  $E''$  versus temperature for various frequencies and for various A/E are shown in Figures 1 and 2.

As expected,  $T_g$  is maximum and  $E''$  minimum at the stoichiometric point, which corresponds to the maximum crosslink density.

Cole–Cole plots are shown in Figure 3. A single curve is obtained in all cases except for A/E = 0.9 and 1.2 where some scatter is observed in the high modulus domain. The relaxed ( $E_0$ ) and unrelaxed ( $E_\infty$ ) moduli were then determined.  $E_0$  (Rubbery modulus) is graphically determined. Its values carry strong uncertainties but they have a negligible influence on the model parameters.  $E_\infty$  is determined by linear extrapolation from the glassy state points, using the best compromise between the broadness of the modulus range and the value of the correlation coefficient.

No trend appears in  $E_0$  values owing to their high scatter. They are expected to be maximum at the stoichiometric point.

$E_\infty$  values are minimum at the stoichiometric point as a result of an internal antiplasticization effect<sup>3–6</sup>.

Two empirical relation functions were used to represent the complex modulus variations: 'Havriliak–Negami (HN)':

$$E^* = E_\infty - \frac{E_\infty - E_0}{[1 + (i\omega\tau)^{1-a}]^\gamma} \quad (1)$$

In fact, equation (1) is a transportation of the original HN<sup>7</sup> function for complex permittivity, e.g. compliance to complex modulus. It contains a modification of the term  $(1 + i\omega\tau)$  in the signal relaxation time function for  $E^*(\omega)$  in the same sense as that of HN: i.e. it is replaced by

$$[1 + (i\omega\tau)^{1-a}]^\gamma$$

and Perez<sup>8</sup>

$$E^* = E_0 - \frac{E_\infty - E_0}{1 + (i\omega\tau)^{-\kappa} + Q(i\omega\tau)^{-\kappa'}} \quad (2)$$

Both models fit the experimental curves within experimental uncertainties. The corresponding parameters are given in Table 2. These results determine the following.

(a) It appears difficult to distinguish between the predictive values of both functions for the sample family under study. Both give excellent results. In this case, the function having the smallest number of parameters ('HN') should, in principle, be used. However, the choice of the Perez function can be justified by the fact that it derives from a physically consistent theory.

(b) In a first approach, it could be observed that the parameters of the functions, except  $E_0$  and  $E_\infty$ , are almost independent of the structure. For 'HN' function:  $\alpha = 0.440 \pm 0.035$ ;  $\gamma = 0.310 \pm 0.050$  and for Perez function:  $\kappa = 0.21 \pm 0.03$ ;  $\kappa' = 0.60 \pm 0.04$  and  $Q = 0.70 \pm 0.3$ .

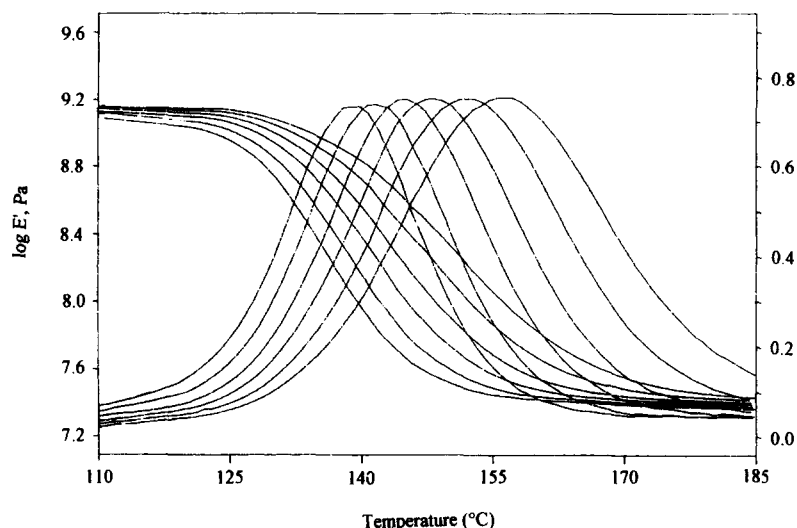
Thus, the network behaviour would depend on  $T_g$  and

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**Table 1** Characteristics of the networks under study

$A/E^a$	0.7	0.8	0.9	1.0	1.11	1.2
$x$ (mol kg <sup>-1</sup> ) <sup>b</sup>	0.22	0.87	1.49	2.09	1.593	1.23
$T_g$ (K) <sup>c</sup>	378	398	416	436	420	411
$E''_{max}$ (MPa) <sup>d</sup>	245	220	200	190	210	235

<sup>a</sup>Amine/epoxide molar ratio; <sup>b</sup>crosslink density expressed in moles of network nodes per kg, calculated according to Ref. 2; <sup>c</sup> $T_g$  taken at the maximum of  $E''$  for 1 Hz frequency; <sup>d</sup>for 1 Hz frequency.



**Figure 1** Variation of  $E'$  and  $\tan\delta$  with temperature for different frequencies from 0.1 to 20 Hz ( $A/E = 1.1$ ).

then on  $E_\infty$ , but the characteristics linked to the relaxation spectrum, essentially expressed here by the exponents  $\alpha$ ,  $\beta$ ,  $\kappa$ ,  $\kappa'$ , would be almost constant.

(c) From numerical applications, it can easily be shown that variations of these exponents lower than the observed intervals, for instance  $\Delta\alpha$  or  $\Delta\gamma = 0.01$  for the 'HN' function, lead to noticeable modifications of the shape of

Cole–Cole plots. In other words, the variations of  $\alpha$ ,  $\gamma$ ,  $\kappa$ ,  $\kappa'$  and  $Q$  are significant.

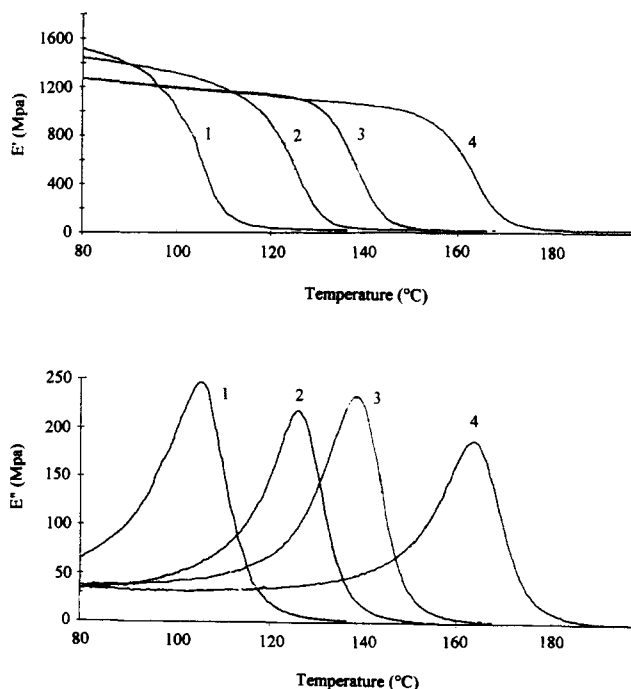
The variations of these parameters with the network structure can be tentatively analyzed keeping in mind that the values relative to the  $A/E = 0.9$  and  $A/E = 1.2$  samples are questionable.

(d) Concerning the 'HN' function, it appears that  $\alpha$  and  $\gamma$  are more or less interrelated and tend to decrease when the crosslink density increases in both sides of the stoichiometric point. According to Alvarez *et al.*<sup>9</sup> in the range where  $(1 - \alpha) > 0.40$  and  $\gamma > 0.25$ , the 'HN' function is the counterpart of the Kolrausch–Williams–Wutt (KWW) function in the time domain:

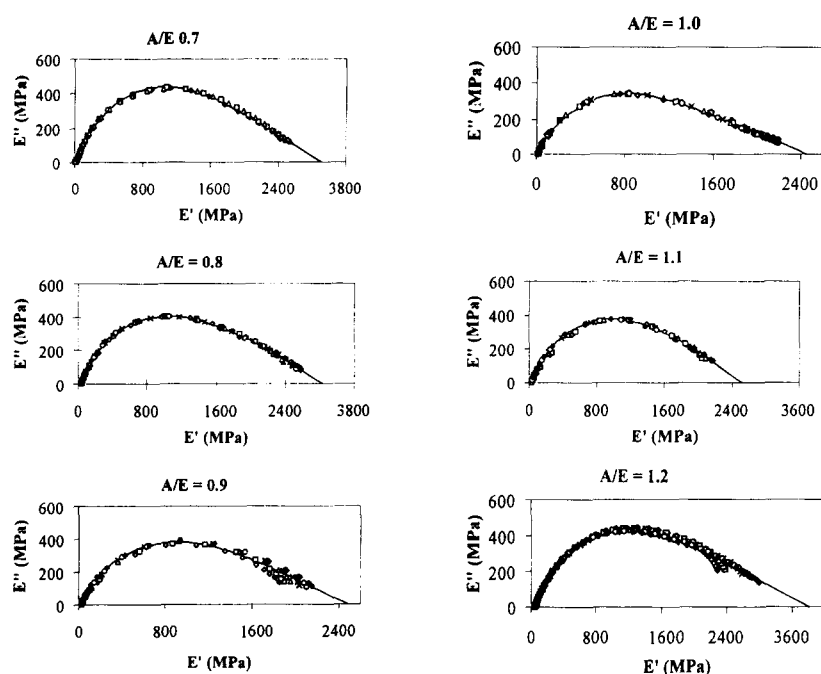
$$E_t = E_0 + (E_\infty - E_0)\exp\left(-\left(\frac{t}{\tau}\right)^\beta\right)$$

Where  $\tau$  is an average relaxation time and  $\beta$  the 'KWW parameter' linked to the width of the relaxation spectrum. Thus each pair of  $\alpha$  and  $\gamma$  'HN' parameters would correspond to one and only one  $\beta$ , KWW parameter value. Despite the fact that its generalization is questionable<sup>10</sup>, the approach of Alvarez *et al.*<sup>9</sup> opens the way to a simple expression of the 'static' or 'monotone' mechanical behaviour of the networks under study. In terms of relaxation spectra, the fact that  $\alpha$ ,  $\gamma$  and  $(1 - \alpha)\gamma$  are decreasing functions of the crosslink density seems to indicate that crosslinking induces a broadening of relaxation spectrum.

(e) With regard to the Perez function, it must first be remarked that it is not the case that the set of  $\kappa$ ,  $\kappa'$  and  $Q$  values given in Table 2 is the only one capable to fit the experimental data correctly. The values characteristic of the stoichiometric model  $\kappa = 0.20$ ,  $\kappa' = 0.625$  are, respectively, far from ( $\kappa = 0.27$ ) and close to ( $\kappa' = 0.65$ ) of the values reported by Perez<sup>8</sup> for a DGEBA–DDM network. The



**Figure 2** Variation of  $E'$  (a) and  $E''$  (b) with temperature for different  $A/E$  ( $f = 1$  Hz). (1)  $A/E = 0.7$ ; (2)  $A/E = 0.8$ ; (3)  $A/E = 1.2$ ; (4)  $A/E = 1.0$



**Figure 3** Cole–Cole plots for the samples under study. Points: experimental data, each type of symbol corresponds to the one frequency. Line: models, both models are practically undistinguishable

**Table 2** Parameters of the relations (1) and (2)

A/E	$E_0$ (MPa)	$E_\infty$ (MPa)	'Havriliak–Negami'			Perez	
			$\alpha$	$\gamma$	$\kappa$	$\kappa'$	$Q$
0.7	14	2900	0.430	0.355	0.230	0.630	0.70
0.8	30	2820	0.445	0.355	0.240	0.640	0.48
0.9	10	2520	0.405	0.330	0.220	0.620	1.00
1.0	12	2440	0.400	0.280	0.200	0.625	0.60
1.1	6	2520	0.475	0.410	0.235	0.580	0.95
1.2	30	3400	0.410	0.260	0.185	0.560	0.70

scatter of  $Q$  values in *Table 2* is impressive and it appears difficult in this case to discuss on structure–property relationships.

In conclusion, the viscoelastic properties of DGEBA–DDM networks of amine/epoxide ratio ranging from 0.7 to 1.2 and having crosslink densities from 0.2 to 2 mol kg<sup>-1</sup> ( $M_c$  between 3000 and 320 g mol<sup>-1</sup>) have been studied in the glass transition region. They are well fitted by the 'HN' and Perez functions. The parameters linked to the distribution of relaxation times do not vary much with the structure. In the case of the 'HN' function, however, a significant decrease of  $\alpha$  and  $\gamma$  with the crosslink density has been observed. In the case of the Perez function, no trend is observed in the variation of the parameter  $Q$ , which makes difficult the interpretation of the results in terms of structure effect, in the series under study.

### References

- Verdu, J., *Angew-Makromol. Chem.*, 1996, **240**, 31.
- Bellenger, V., Dhaoui, W., Verdu, J., Galy, J., Won, T. G. and Pascault, J. P., *Polymer*, 1989, **30**, 2013.
- Findley, W. N. and Reed, R. M., *Polym. Eng. Sci.*, 1977, **27**, 837.
- Morgan, R. J., *Adv. Polym. Sci.*, 1985, **72**, 3.
- Bellenger, V., Dhaoui, W., Verdu, J., Boye, J. and Lacabanne, C., *Polym. Eng. Sci.*, 1996, **30**, 321.
- Venditti, R. A. and Gillham, J. K., *J. Appl. Polym. Sci.*, 1996, **56**, 1687.
- S. Havriliak, Jr., S. Negami, *Polymer*, 8 (1967) 161.
- J. Perez, in *Physique et Mécanique des Polymères Amorphes*, TEC and DOC-Lavoisier, Paris, 1992, p. 208.
- Alvarez, F., Algeria, A. and Colmenero, J., *J. Phys. Rev. B.*, 1991, **44** (11), 7306.
- S. Havriliak, Jr., S. J. Havriliak, *Polymer*, 37 (18) (1996) 4107.