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Violation of the power-law dynamic mechanical behaviour at the gel point threshold in non-stoichiometric epoxide systems

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Summary

The dynamic mechanical behaviour of fully cured off-stoichiometric epoxy systems prepared from poly(oxypropylene)diamine (Jeff D-400) or -triamine (Jeff T-403) and diglycidyl ether of Bisphenol A (DGEBA) with initial ratios of reactive amine (NH_2) and epoxide (E) groups, r_H = (2[NH_2])/[E] ranging from 2.4 to 4.3 was investigated in the gelation threshold region. The evolution of the dynamic behaviour of two stoichiometric samples with r_H = 1 with reaction time, t_r, was also studied. The critical ratios for gelation, r_H^c , of fully cured samples were determined from extraction experiments (r_H^c = 2.54 for Jeff D-400/DGEBA and r_H^c = 4.15 for Jeff T-403/DGEBA systems, respectively). For both stoichiometric critical gel (CG) structures obtained by changing the curing time t_r, a power-law rheological behaviour ($G' \sim G'' \sim \omega^n$, G' and G'' are the storage and loss moduli, respectively, ω is angular frequency and n is a critical exponent) with the loss tangent, tan $\delta = G''/G'$ independent of frequency, was found. On the other hand, both CG off-stoichiometric systems with r_H^c ratios show a small dependence of tan δ on ω, so that the critical power-law behaviour is not exactly obeyed. More complex CG structure in these samples, formed due to differences in the structure growth process, was suggested to account for violation of the power-law behaviour.

Introduction

During a crosslinking reaction, the number-average and the weight-average molecular weights, M_n and M_w, in the system increase and at the critical conversion (at the gel point, GP), M_w increases to infinity (1-3). In the pre-gel state the system is soluble while after passing the GP, the insoluble gel fraction, w_g, with finite equilibrium modulus, G_e, is formed. The material at the GP, termed the critical gel (CG), is an intermediate state between liquid and solid.

In the systems prepared by an alternating stepwise addition reaction of reactive end groups, such as in epoxy systems from polyamines and polyepoxides, two ways of reaching the CG exist (4-6). Both ways follow from the GP equation valid for independent reactivities of amine hydrogens and epoxy groups in reactants (1-3)

$$\alpha_H^c \, \alpha_E^c (f_{w,H} - 1)(f_{w,E} - 1) = 1 \qquad (1)$$

where α_H^C and α_E^C are critical conversions of amine hydrogens and epoxy groups, and $f_{w,H}$ and $f_{w,E}$ are the reduced second moments of functionality distribution (weight-average functionalities) of polyamine and polyepoxide reactant, respectively.

The first, classical way of reaching the GP is an increase in conversion (increase in reaction time, t_r) at a constant composition of the reacting system. The GP takes place at critical conversion of amine hydrogens, α_H^C, or epoxy groups, α_E^C ($\alpha_H^C \cdot r_H = \alpha_E^C$, r_H is the initial molar ratio of amine hydrogens to epoxy groups in the system, r_H = (2[NH_2])/[E]).

The second way of reaching the GP is the critical molar ratio (CMR) method, consisting of finding such initial composition of the system at which the GP occurs just at full conversion of minority reactive groups (3,4-7). If epoxy systems are prepared with an

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excess of amine hydrogens ($r_{\mathrm{H}} > 1$), then the CG is reached at critical ratio r_{H}^{C}, for which from Eq.(1) it follows

$$r_{\mathrm{H}}^{c} = \left(\alpha_{\mathrm{E}}^{c}\right)^{2} \left(f_{w,H} - 1\right)\left(f_{w,E} - 1\right) \qquad (2)$$

Systems with $r_{\mathrm{H}} > r_{\mathrm{H}}^{c}$ are soluble and those with $r_{\mathrm{H}} < r_{\mathrm{H}}^{c}$ contain both the sol and the gel. While the change in conversion at constant composition leads to reacting structures with time, the CMR method gives structurally stable systems (8).

The dynamic mechanical behaviour of CG structures obtained by a change in conversion have been extensively studied in the literature (9-12). It was found that CG is characterized by a power-law dependence of the storage G' and loss G'' moduli on frequency (10-12)

$$G'(\omega) = G''(\omega)/\tan\delta = \Gamma(1-n)\cos\delta\, S\, \omega^{n} \qquad (3)$$

where S (Pa s^{n}) is the gel strength (specific material parameter), $\Gamma(x)$ is the gamma function, n is the critical exponent and the phase angle $\delta = n\pi/2$ is independent of frequency. Equation (3) is in accord with theoretical expectations from the percolation theory (13) applied to dynamic of polymer clusters at the GP. The exponents n are widely scattered and depend on chemical systems; the values n from 0.2 to 0.9 can be found, in the literature (8,12-14). As no universal value n was experimentally found it was suggested that the scaling failure is due to local properties which can depend on the distance from the threshold. Moreover, our dynamic mechanical measurements (8) obtained on two off-stoichiometric polyurethane systems prepared from poly(oxypropylene)triols and a diisocyanate, in which CG were obtained by CMR method, have shown a small frequency dependence of the loss tangent, so that the power-law behaviour (Eq.(3)) was not exactly obeyed. On the other hand, measurements of Randrianantoandro et al. (15) on similar polyurethane CG systems prepared by a CMR method have shown a power-law behaviour.

In this paper we have studied the extraction and dynamic mechanical behaviour of two epoxy systems based on poly(oxypropylene)diamine or -triamine and diglycidyl ether of Bisphenol A in the vicinity and at the GP threshold reached by the CMR method. For comparison, an evolution of viscoelastic behaviour with reaction time, t_r, for two stoichiometric mixtures with $r_{\mathrm{H}} = 1$ of both epoxy systems was also investigated.

Experimental

Sample Preparation. Two epoxy series were prepared from the diglycidyl ether of Bisphenol A (DGEBA, epoxy equivalent $\gamma_{\mathrm{E}} = 1754$ g/mol epoxy, $M_n = 350$ g/mol and number-average functionality $f_{n,E} = 2$ and $f_{w,E} = 2$) and poly(oxypropylene)diamine (Jeffamine® D-400, $\gamma_{\mathrm{A}} = 106.4$ g/mol H, $M_n = 370$ g/mol, $f_{n,H} = 3.75$ and $f_{w,H} = 3.87$) with initial molar ratios of amine hydrogens to epoxy (E) groups, $r_{\mathrm{H}} = (2[\mathrm{NH_2}])/[\mathrm{E}] = 2.42 - 2.60$, or poly(oxypropylene)triamine (Jeffamine® D-403, $\gamma_{\mathrm{A}} = 78$ g/mol H, $M_n = 427$ g/mol, $f_{n,H} = 5.36$ and $f_{w,H} = 5.69$) with the ratios $r_{\mathrm{H}} = 3.95 - 4.30$. The procedures used in the purification and characterization of the starting compounds were described earlier (6). The reaction proceeded at 90 °C for 16 h in closed Teflon moulds. Spectroscopic measurements revealed that no epoxy groups were present after the reaction. Before rheological measurements, moulds were cooled down to -50 °C and the sheets (10 x 10 x 0.2 cm) were removed; samples 50, 30 and 10 mm in diameter were used in the parallel-plate geometry measurements.

Dynamic Mechanical Measurements and Extraction. The measurements of the storage, G', and loss, G'', components of the complex shear modulus, $G^{*} = G' + iG''$, of structurally stable off-stoichiometric systems were carried out with Rheometrics SYS-4 apparatus in the parallel-plate geometry. Strains between $\gamma = 0.2$ and 0.001 were used (linear viscoelastic behaviour). The angular rates ω varied from 10^{-2} to 10^{2} rad s^{-1}, and temperatures changed from -50 °C to 120 °C. While in the main transition and glassy region, 10-mm diameter plates were used, in the rubbery and flow regions, 30- and 50-mm diameters were employed.

By applying the frequency-temperature superposition, the superimposed curves of $G_p' = G'b_T$ and $G_p'' = G''b_T$ vs. reduced frequency ωa_T, shifted to the reference temperature T_o = 30 °C, were obtained. The horizontal shift factor, a_T, was obtained mainly from the superposition of loss tangent (since $\tan \delta_p = \tan \delta$), while the vertical shift b_T was obtained from the superposition of G_p' and G_p''.

The curing reaction of two stoichiometric samples was followed in a rheometer at $\omega = 1$ to 10^2 rad s^{-1} with 50 mm diameter at reaction temperature T_r = 60 °C. The shear strains changed with ω from γ= 1 to 0.005 to avoid network breakdown. A series of frequency sweeps (one run took 60 s) during curing reaction was measured.

The extraction was carried out with a large excess of toluene, xylene and tetrahydrofuran at room temperature for several days. The polymers were placed inside a Teflon mesh sieve and immersed in a large excess of the solvent. After extraction, the mesh with the extracted sample was dried under reduced pressure at 60 °C and the weight fraction of the gel, w_g, was determined.

Results and discussion

Extraction and Critical Mole Ratios of Reactive Groups. The weight fraction of gel, w_g, as a function of the reactive group ratio r_H in both structurally stable series is shown in Fig. 1. As expected, with increasing r_H, the gel fractions w_g decrease and the values of the critical ratio of reactive groups, r_H^c, can be determined. While samples with $r_H < r_H^c$ are networks, those with $r_H > r_H^c$ are soluble. Due to lower functionality of diamine, the decrease in the weight fraction of gel, w_g, of D-400/DGEBA samples is located at lower r_H values than that of T-403/DGEBA networks. Therefore, the critical r_H^c value found for samples from D-400 is lower than that found for samples with T-403 (r_H^c = 2.54 vs. r_H^c = 4.15). As follows from Eq.(2) experimental r_H^c values are considerable lower than would correspond to theoretical expectations (if $\alpha_E^c = 1$, then r_H^c should be 2.87 for D-400 and 4.69 for T-403 system, respectively). There are two possible explanations of lower experimental r_H^c values: (a) Eq.(1) was derived for a ring-free case and it may be assumed that some bonds at the GP are lost in intramolecular cycles. From experimental r_H^c values and Eq.(2) the value r_H^c = 0.94 can be calculated for both systems. This means that approximately 6% of bonds wasted in cycles can explain the differences; (b) In the primary amino group there exists a difference in reactivity of the first and the second

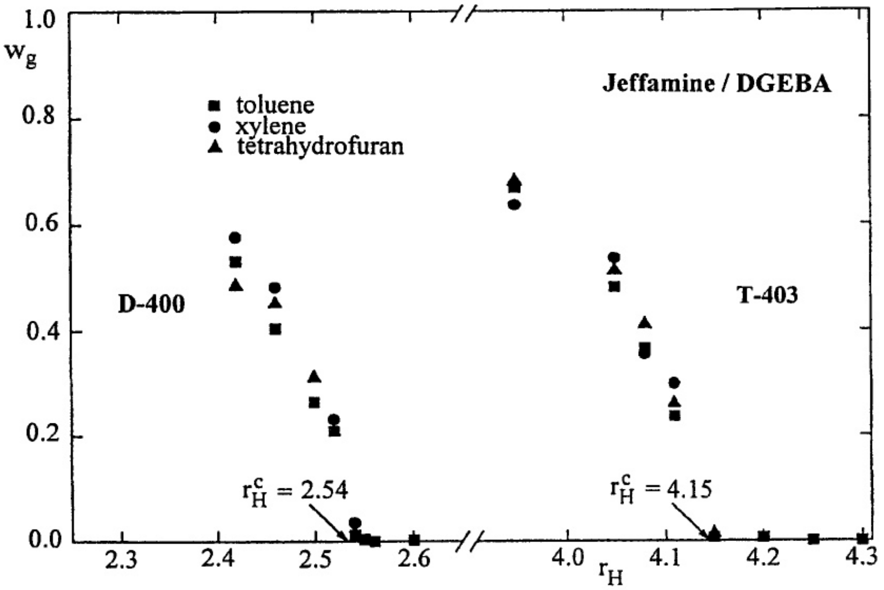

Fig. 1. Dependence of the weight fraction of the gel, w_g, on the ratio of the reactive groups r_H (r_H^c are the critical ratios for the gel point)

hydrogen. Lower reactivity of the second hydrogen (negative substitution effect) was found earlier for amines used in our systems (6); this fact means that linear structures are preferred at the beginning of the reaction before the GP. In such way both points (a) and (b) lead to experimental r_H^c values lower than theoretically predicted ones.

Dynamic Mechanical Behaviour of Structurally Stable Systems Prepared by the CMR Method. For all samples of both series, the frequency-temperature superposition could be easily performed and the horizontal shift factor a_T (T_o) satisfied the Williams-Landel-Ferry (WLF) equation in the form (16)

$$\log a_T(T_o) = (-1/2.3 f_{30})(T - T_o)/(f_o/\beta_f + T - T_o) \qquad (4)$$

where f_{30} is the fractional free volume at T_o = 30 °C and β_f is the thermal expansion coefficient of the free volume (Fig. 2).

As follows from Fig. 2, both free-volume parameters f_{30} and β_f are practically independent of the molecular weight of Jeffamines and of the r_H ratio, and attain the values found for other amorphous systems (16). As no abrupt changes in dependences of these parameters on r_H can be found at critical ratios r_H^c, the GP has no specific effect on the temperature dependence of the relaxation times. Similar results were reported earlier (17) for poly(dimethylsiloxane) systems at the gelation threshold where an activation energy of the zero shear viscosity independent of the distance from the GP was found.

An example of superimposed curves of G_p' and G_p'' moduli vs. the reduced frequency ωa_T is shown in Fig. 3 for D-400/DGEBA samples. The shape and position of the main transition region (located at high frequencies) on ωa_T are only slightly dependent on the ratio r_H. On the other hand, a large change in the shape of the G_p' and G_p'' vs. ωa_T dependence can be seen in the rubbery and flow regions (at lowest ωa_T). Similar results were obtained for T-403/DGEBA system.

In Fig. 4, the superimposed loss tangent, tan δ_p, vs. ωa_T dependences are shown for both stable series. The frequency position of tan δ_p maxima and their frequency shape are practically independent of r_H. Large changes in tan δ_p can be seen in the low ωa_T region. While for all crosslinked samples, ($r_H < r_H^c$), tan δ_p decreases with decreasing ωa_T (solid-like behaviour), for soluble samples ($r_H > r_H^c$) tan δ_p increases with decreasing ωa_T (liquid-like behaviour). At the same time in network samples, non-zero equilibrium storage modulus G_e' can be found by extrapolation (Fig. 3). Surprisingly, for both off- stoichio-

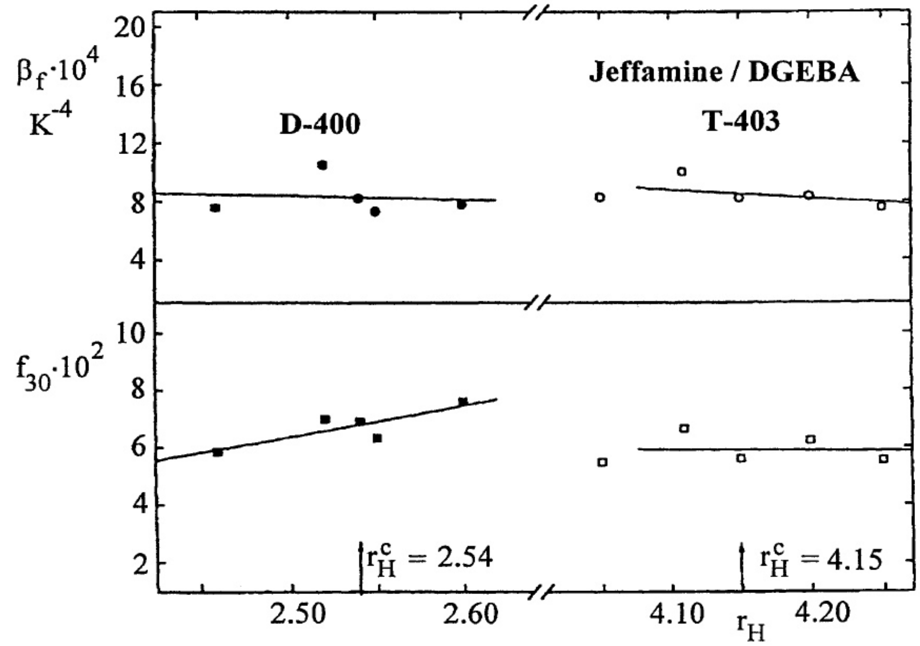

Fig. 2. Dependence of the fractional free volume, f_{30}, and of the free volume temperature expansion coefficient, β_f, on the ratio r_H (r_H^c are the critical ratios for the gel point).

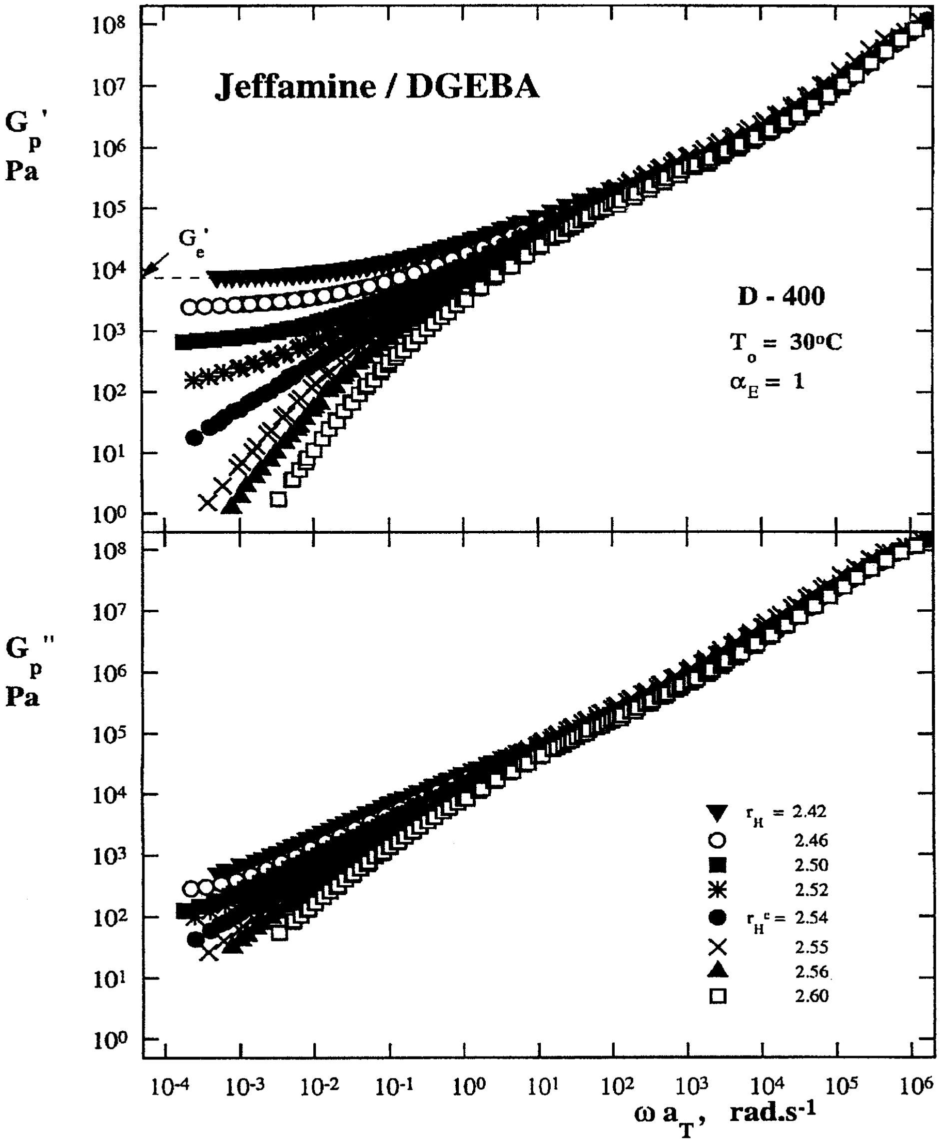

Fig. 3. Dependence of the reduced storage, G_p', and loss, G_p'', moduli on the reduced frequency ωa_T for D-400 series with indicated r_H values.

metric CG structures with r_H^c values, a small increase in tan δ_p with decreasing ωa_T can be found in the lowest frequency region (Fig. 4). In the first approximation, we can write

$$\tan \delta_p = (\omega a_T)^m \qquad (5)$$

where exponent m = -0.04 for D-400 and m = -0.05 for T-403 system. Similar results were found earlier for off-stoichiometric polyurethane CG systems (8). We can thus conclude that the power-law behaviour (Eq. 3) with frequency-independent tan δ_p is not exactly obeyed for CG epoxide structures prepared by the CMR method.

Dynamic Mechanical Behaviour of Reacting Systems with Stoichiometric Ratio. Generally, stoichiometric mixtures show the earliest structure build-up and gel formation along with the highest equilibrium G_e' moduli and $w_g \rightarrow 1$ (most perfect networks). An example of the results obtained in curing of a stoichiometric T-403/DGEBA mixture is shown in Fig. 5; similar results were obtained for D-400/DGEBA mixture. The critical gelation times (the crossover of phase angle 2 δ/π curves, Fig. 5c) t_c = 509.4 min for D-400 and t_c = 497.4 min for T-403 were found. Relatively long gelation times correspond to a slow crosslinking reaction. Figures 5a and 5b show the frequency dependences of moduli and of the loss tangent at reaction times near the GP. As can be expected, tan δ increases with ω in the solid state ($t_r > t_c$) and decreases with ω in the liquid state ($t_r < t_c$);

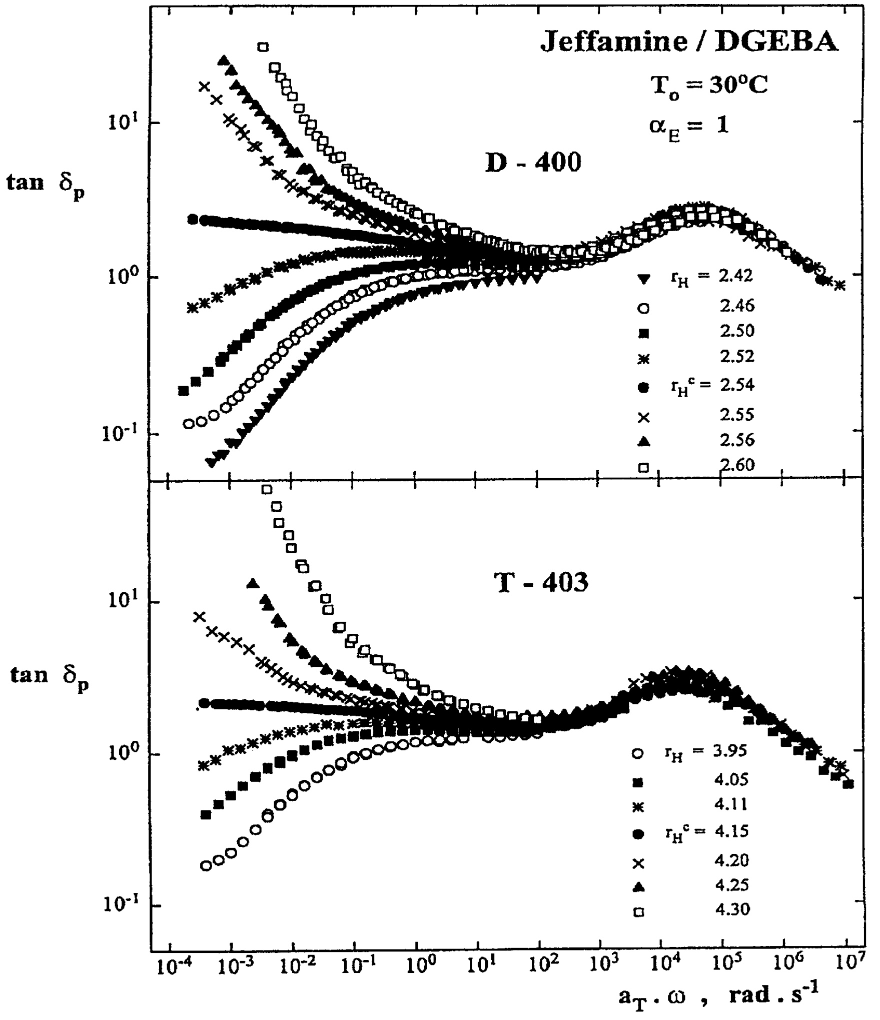

Fig. 4. Dependence of the reduced loss tangent, tan δ_p, on the reduced frequency ωa_T for samples of both series prepared at indicated r_H values.

at the critical time, tc, tan δ is frequency-independent. The dependence of moduli *G'* and *G''* on ω shows a power-law behaviour for the CG at t_c. While before the GP, the *G'* value decreases with decreasing ω, after GP it shows a rubbery plateau. The relaxation exponents calculated from the phase angle (Fig. 5c) using Eq.(3) are $n = 0.67$ for D-400 and $n = 0.678$ for T-403 CG structures. The moduli *G'* and *G''* of CG structures were further used for the calculation of the gel strengths *S*. Corresponding *S* values calculated from Fig. 5a and similar results obtained for the D-400 CG system are $S = 1500$ Pa s^n for D-400 and $S = 2950$ Pa s^n for T-403. In accord with previous results (8,12), the CG rheological parameters *n* and *S* are not universal and depend on structure of initial reactants.

As was discussed previously (8), due to differences in the structure growth process the weight-average molecular weight, M_w, and the polydispersity (M_w/M_n value), in systems formed by change in the r_H ratio in vicinity of the GP are higher than those formed by an increase in conversion at constant distance from the GP. Therefore, we can expect more complex GP structures (more and longer dangling chains present on the longest molecule) in off-stoichiometric systems than in stoichiometric ones. As it is known (16,18), viscoelastic properties in the rubbery plateau and terminal zones are dominated by the presence of topological constraints (entanglements), the molecular weight M_w and its distribution strongly influence the dynamic mechanical behaviour. In such way more complex GP structures in off-stoichiometric systems probably account for violation of the power-law behaviour in the measured frequency region.

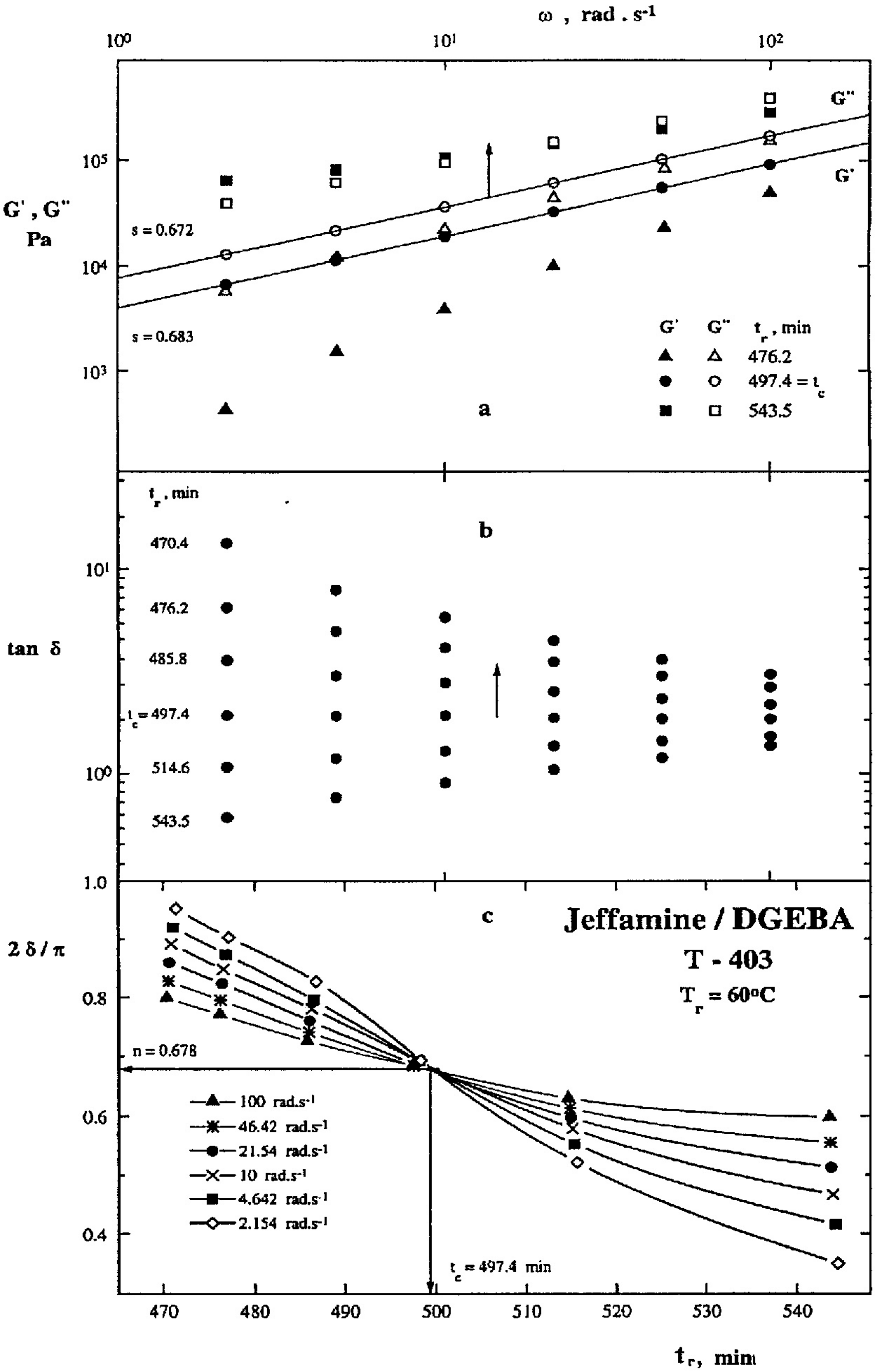

Fig. 5. Dependence of the moduli $G'$and G'' (a) and of the loss tangent, tan δ (b), on frequency ω; (c) shows dependence of the ratio $2\delta/\pi$ on the reaction time t_r (stoichiometric T-403/DGEBA sample).

Analysis of Storage Compliance Functions. In our previous paper (8), an interesting frequency behaviour of the superimposed storage J_p' compliance in the rubbery and flow regions was shown. The dependences of J_p' and J_p'' compliances are shown in Fig. 6 for both epoxy off-stoichiometric systems. For crosslinked samples with $r_H < r_H^c$, the limiting equilibrium compliances J_e' can be extrapolated from the data for $\omega a_T \to 0$. For soluble samples with $r_H > r_H^c$, the limiting steady-state compliance J_{e0}' can be determined (8,16). As in the case of polyurethane systems, both epoxy CG samples with r_H^c show the highest J_p' values with $J_e' = J_{e0}' \to .\infty$ The same conclusions can be also deduced from the frequency dependences of the storage compliances J' for both stoichiometric systems,

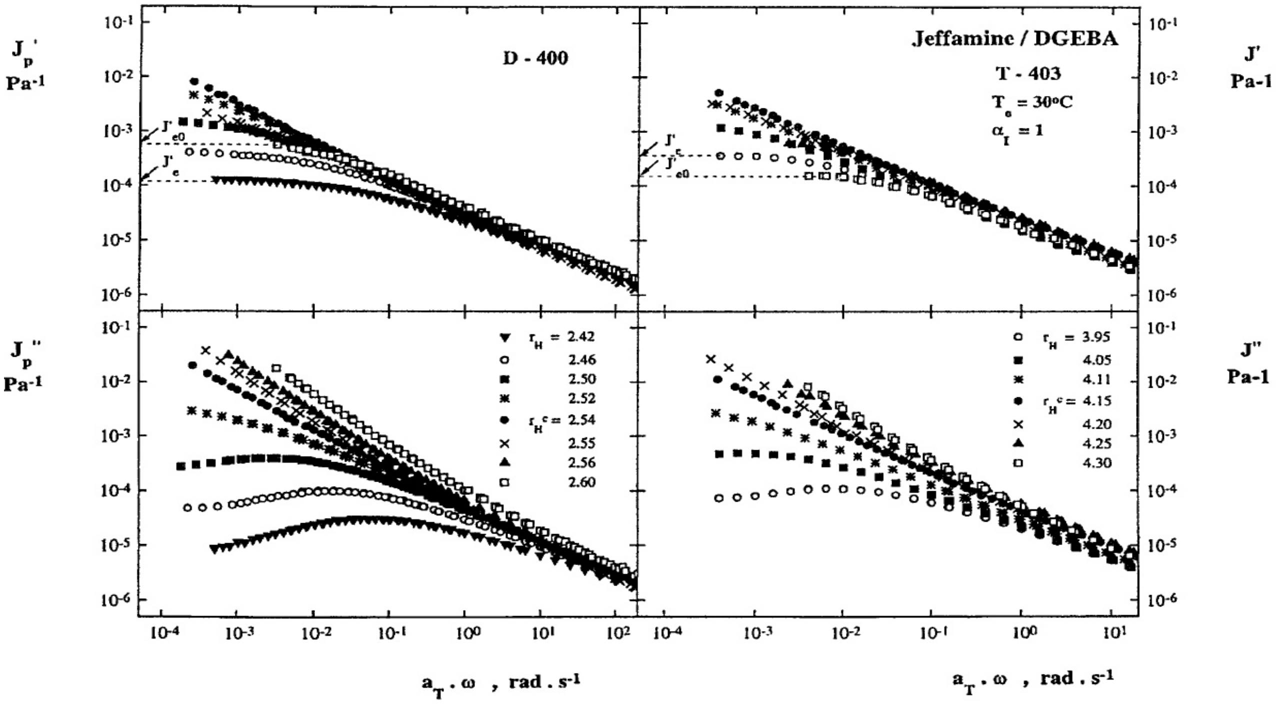

Fig. 6. Dependence of the reduced storage, J_p', and loss, J_p'', compliances on the reduced frequency, ωa_T, for samples of both series prepared at indicated r_H values

where the highest J' values at given ω and infinite extrapolated values of J_e' and J_{eo}' can be observed for CG structures at t_c. We believe that in particular the highest J_p' values at given ωa_T represent the critical dynamic mechanical behaviour of GP structures obtained by the CMR method.

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