

## Rheology of epoxy networks near the gel point

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### Summary

Curing and gelation of diglycidyl ether of Bisphenol A with poly(oxypropylene)-diamine (Jeffamine D 400) was followed using dynamic mechanical measurements. The gel point was determined rheologically and the characteristic value of the loss factor  $\tan \delta$  at the gel point,  $(\tan \delta)_{\text{gel}}$ , was found to depend on the structure of the polymer. A negative normal force is generated in the shear dynamic mechanical measurement at the gel point.

### Introduction

Gelation is characterized by a divergency of weight-average molecular weight or radius of gyration and by the formation of an insoluble elastic gel. Usually, rheological and mechanical techniques are used to determine experimentally the gel point (GP). The steady state shear viscosity rises to infinity at GP and elastic properties characterized by nonzero value of the equilibrium modulus of the gel fraction appear beyond GP. These quantities describe only either the liquid (pregel) or the solid (postgel) state of a sample. Determination of GP requires extrapolation of viscosity to infinity or of the equilibrium modulus to zero. Extrapolation of steady viscosity brings difficulties (1), and the determined gelation time,  $t_{\text{gel}}$ , may depend on the shear rate (2,3) also due to shear thinning at a higher rate. In practice, e.g., a viscosity of 1000 Pa·s was arbitrarily identified with GP (4). However, divergency of viscosity may also be a result of vitrification. Extrapolation of the equilibrium modulus of the gel to its zero value at GP is experimentally even more difficult because of viscoelastic effects in the very loose network.

Dynamic mechanical measurements describe both the liquid and solid state and are the best method for following rheology during the polymerization from the beginning through GP till full cure. Gillham (5) studied gelation using the torsional braid analysis. Two maxima of mechanical damping corresponding to the dynamic loss modulus  $G''$  observed during polymerization were assigned respectively to the gelation and the vitrification of the system.

Tung and Dynes (6) recorded the dynamic storage ( $G'$ ) and loss ( $G''$ ) moduli during cure of several systems and proposed their crossover to be identified with GP. The viscous properties are dominant in the liquid state, i.e.,  $G'' > G'$ ,  $\tan \delta (= G''/G') > 1$ , while the

elastic ones predominate in the solid state, where  $G' > G''$  and  $\tan \delta < 1$ . Consequently,  $\tan \delta = 1$  (the crossover point of moduli) could be expected near GP. However,  $t_{\text{gel}}$  determined by Tung depended on frequency  $\omega$  of the dynamic measurement. Moreover, the cross point cannot be generally accepted for the detection of GP because linear polymers also show such a crossover at different  $\omega$ , depending on molecular weight (7).

Winter and Chambon (8,9) revealed that the  $G'(\omega)$  and  $G''(\omega)$  curves coincided or were parallel over a wide range of frequencies near GP of poly(dimethylsiloxanes) (PDMS) and polyurethanes. The validity of a power law  $G'(\omega) \sim G''(\omega) \sim \omega^\Delta$  over the entire frequency range was assumed to be an inherent property of the state at GP. They showed that  $\tan \delta = 1$  and the critical exponent  $\Delta$  was  $1/2$  at GP in curing stoichiometric systems and in the case of excess hardener. In nonstoichiometric systems cured with an insufficient amount of a crosslinker  $\tan \delta > 1$  and  $\Delta > 1/2$  at GP. Most authors (10–13) found the critical exponent  $\Delta$  of various systems to be in close agreement with the prediction of percolation theory,  $\Delta = 0.72$ .

Harran and Laudouard (14) determined gelation from the slowing down of the rate of increase of the loss modulus  $G''$  during cure. Change of slope between two linear zones of  $\log G''(t)$  was used to detect GP.  $t_{\text{gel}}$  evaluated by this approach was independent of experimental frequency.

The rheology in the vicinity of the critical state could be affected by vitrification. In order to eliminate the possible interference of vitrification, we studied gelation of epoxy networks with a relatively low  $T_g$  value. Diglycidylether of Bisphenol A (DGEBA) was cured with a flexible poly(oxypropylene)diamine, Jeffamine D 400. We followed the influence of temperature and network structure given by the initial ratio of the functional groups of reagents on the rheology during cure.

## Experimental

Diglycidylether of Bisphenol A (DGEBA) was recrystallized from a 4 : 1 methanol : acetone mixture. The epoxy equivalent was determined by titration;  $E_{\text{epoxy}} = 171$  g/mol epoxy groups. The poly(oxypropylene)diamine (Jeffamine<sup>R</sup>) D 400 of molecular weight  $M_n = 370$  with the respective amino equivalent  $E_{\text{NH}} = 108$  g/mol amino hydrogens was used as obtained.

DGEBA was cured with the diamine at various initial ratios of functional groups  $r (= C_{\text{NH}}/C_{\text{epoxy}})$ , where  $C_{\text{NH}}$  and  $C_{\text{epoxy}}$  are concentrations of the amino hydrogens and the epoxy groups, respectively. The reactions were carried out under isothermal conditions between the plates of a rheometer. The sample was first homogenized in an oven at  $65^\circ\text{C}$  and then quickly transferred onto the preheated plates of the rheometer. The temperature equilibrium for the isothermal reaction was established within 2 minutes. The cure temperature ( $T = 70 - 110^\circ\text{C}$ ) was well above the glass transition temperature  $T_g$  of fully cured networks (15);  $T > T_g + 35^\circ\text{C}$ .

Rheometrics System Four was used to study the rheology during cure. The evolution of the dynamic shear modulus  $G^*$  during the reaction was followed by dynamic mechanical measurements using oscillatory shear deformation at constant frequency  $\omega$  ranging from 0.1 to 80 Hz (time sweep). In addition the frequency sweep ( $\omega = 0.5 - 50$  Hz) at certain time intervals during a slow reaction was measured. The shear strain was reduced gradually during the reaction in the range  $\gamma = 1 - 0.003$ , to avoid non-Newtonian

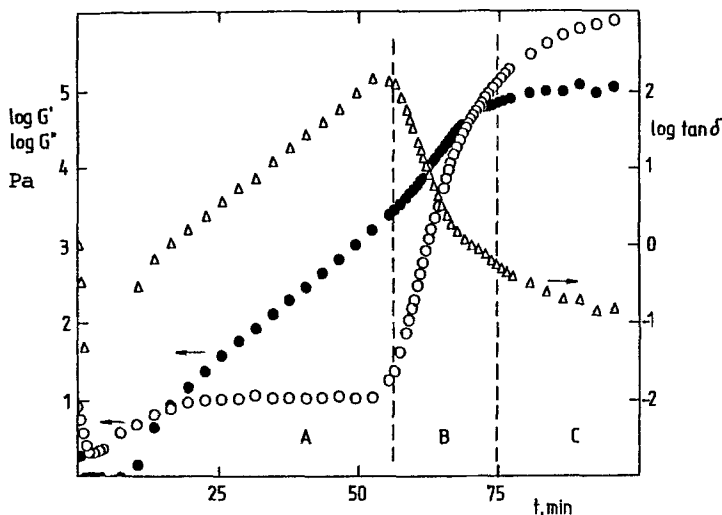


Figure 1: Evolution of the storage ( $G'$ )  $\circ$  and loss ( $G''$ )  $\bullet$  moduli and the loss factor  $\tan \delta$  ( $\Delta$ ) during the crosslinking of DGEBA with Jeffamine D 400. A – pregel stage, B – stage of gelation, C – postgel stage,  $T = 90^\circ\text{C}$ ,  $r (= C_{\text{NH}}/C_{\text{epoxy}}) = 2$ ,  $\omega = 10$  Hz.

effects and network breakdown. The strain  $\gamma = 0.1 - 0.01$  was employed near the gel point. The geometry of parallel plates (50 mm in diameter) was used.

### Results and Discussion

The chemorheological curves of curing DGEBA with D 400 at  $90^\circ\text{C}$  are shown in Fig. 1. One can differentiate three typical regions A, B and C during cure :

A) An increase in the loss modulus  $G''$  corresponding to the increase in the real part of dynamic viscosity  $\eta' (= G''/\omega)$  due to increasing molecular weight of the forming polymer. The storage modulus  $G'$  is very low and tends to zero at low frequency. The experimental values are not reproducible. Higher, reproducible values of  $G'$  were obtained only using high frequency when the unrelaxed polymer had been measured. The loss modulus  $G''$  is higher than the elastic one  $G'$  and the loss factor  $\tan \delta > 1$ .

B) A sudden increase in the storage modulus  $G'$  by several orders of magnitude, corresponding to the gel formation and increasing crosslinking density. The  $G'(t)$  curve crosses the  $G''(t)$  one when passing through this region, and  $G'$  becomes higher. Accordingly,  $\tan \delta$  decreases to values less than 1.

C) A slow increase in the storage modulus that levels off in the final stage of the reaction.  $\tan \delta < 1$  for the fully cured rubbery network.

We studied gelation of the stoichiometric system ( $r = 1$ ) and systems with excess of amine ( $r = 2$ ) and epoxide ( $r = 0.67$ ) (cf. Tab. I). The stoichiometric mixture shows the earliest structure build-up and the gel formation, along with the highest final modulus  $G'$  and the lowest final loss factor  $\tan \delta$ , as a result of the most perfect network with the highest crosslinking density.

Curing was followed at different frequencies of the dynamic measurement. Alike

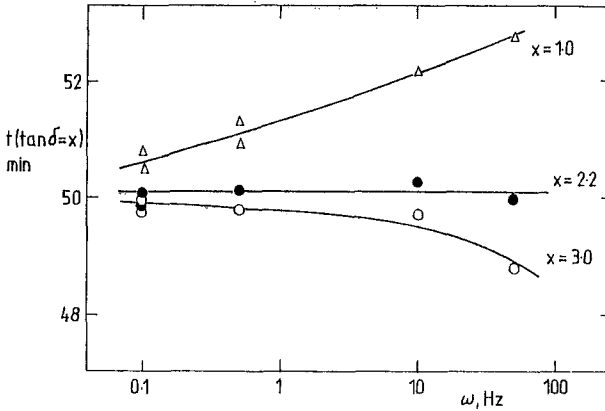


Figure 2: Time to reach the value  $\tan \delta = x$  during cure of the stoichiometric system DGEBA – Jeffamine D 400 at 90°C as a function of frequency.

Tung (6), we have found that the reaction time to reach  $\tan \delta = 1$  increases with frequency of the dynamic measurement (see Fig. 2). However, GP is a material constant and should not depend on experimental conditions. Therefore, the crossover of the moduli  $G'(t)$  and  $G''(t)$  where  $\tan \delta = 1$  does not coincide with GP. Figure 2 reveals that in the case of the stoichiometric system cured at 90°C, time to reach  $\tan \delta = 2.2$  is independent of frequency in the range  $\omega = 0.1 - 50$  Hz and we suppose this time to correspond to GP. Other dependences  $t(\tan \delta = x)$  on  $\omega$  in Fig. 2 approach asymptotically  $t(\tan \delta = 2.2)_{\text{gel}}$  at a low frequency.

$\tan \delta$  decreases during later stages of the reaction (see Fig. 1), and the rate of this decrease depends on the experimental frequency  $\omega$ . As a rough approximation,  $\tan \delta \sim 1/\omega$  in the liquid state as  $G' \sim \omega^2$  and  $G'' \sim \omega$ ;  $\tan \delta \sim \omega$  in the solid state where  $G' \sim \text{const}$  and  $G'' \sim \omega$  (7) (cf. Fig. 5). Therefore, the drop of  $\tan \delta$  during the reaction is steeper at a low frequency, as shown in Fig. 3. As a result, time to reach the given value of  $\tan \delta$  during the reaction  $t(\tan \delta = x)$  decreases with increasing  $\omega$  in the liquid state but increases with frequency in the solid state (see Fig. 3). The results in Fig. 2 may therefore be interpreted as follows: Time to reach the value of  $\tan \delta < 2.2$ , e.g.  $\tan \delta = 1$ , corresponds to the postgel, solid state, and values of  $\tan \delta > 2.2$  characterize the liquid, pregel state. Also, Tung's results (6) showing the increase in time of the moduli crossover with frequency reveal that samples with  $\tan \delta = 1$  were already beyond GP. The steeper drop of  $\tan \delta$  during cure observed at a low experimental frequency explains the asymptotic approaching of the "pregel" and "postgel" curves in Fig. 2 to the "critical state" curve. The lower the frequency the smaller the difference in time to reach a certain value of  $\tan \delta$  in the liquid  $t(\tan \delta = a)_l$  and in the solid state  $t(\tan \delta = b)_s$  (see Fig. 3).

We checked the possibility of a mechanical degradation of the forming gel due to high shear rate and large deformation. Such degradation would lead to a delay of the gelation and an increase in  $t_{\text{gel}}$  at high  $\omega$ . The reaction was carried out between plates at various frequencies of shear oscillations ( $\omega_r = 0.1 - 80$  Hz) and a single dynamic measurement using constant frequency ( $\omega = 1$  Hz) was performed at certain time intervals. It was found that the evolution of  $G'$  (measured at  $\omega = 1$  Hz) during the reaction was independent of the frequency  $\omega_r$  of the shear stress imposed on the reaction system.

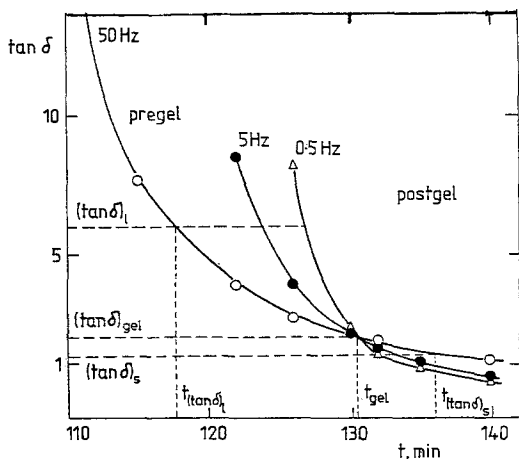


Figure 3: The decrease in the loss factor  $\tan \delta$  during cure of the system DGEBA - Jeffamine D 400 at various frequencies of the dynamic measurement.  $r = 1$ ,  $T = 70^\circ\text{C}$ ;  $\Delta\omega = 0.5 \text{ Hz}$ ,  $\bullet \omega = 5 \text{ Hz}$ ,  $\circ \omega = 50 \text{ Hz}$

Consequently, no mechanical degradation takes place during network formation under the oscillating shear stress conditions used.

Table 1 shows the results obtained for curing of mixtures with various stoichiometric ratios of the reagents and at different reaction temperatures. Unlike Winter's results on PDMS (8) and polyurethanes (16), we have found that  $(\tan \delta)_{\text{gel}} > 1$  for all epoxy systems measured, including the stoichiometric network. It is obvious that  $(\tan \delta)_{\text{gel}}$  depends on the polymer structure and decreases with increasing excess of the amine  $r (= C_{\text{NH}}/C_{\text{epoxy}})$ , which governs the structure of the polymer. The amino group of the diamine D 400 shows a significant negative substitution effect, i.e. a higher reactivity of the hydrogens in the primary  $\text{NH}_2$  than in the secondary NH group (17). As a result, at amine excess ( $r > 1$ ) the epoxy reacts mainly with the primary  $\text{NH}_2$  groups to form linear flexible chains before gelation sets in. On the contrary, at epoxide excess, a great number of secondary NH groups react in the pregel stage and a branched, more rigid structure is to be expected. The former situation may result in the entanglement formation before GP, leading to a higher storage modulus at a given frequency and a lower  $\tan \delta$  at GP. The higher storage modulus at GP,  $G'_{\text{gel}}(\omega)$ , found in the case of amine excess  $r = 2$  with respect to the stoichiometric system (see Table 1) in contrast to the fully cured samples (15) corroborates this hypothesis.

The experimentally determined  $t_{\text{gel}}$  values may, however, be affected by the viscoelastic behaviour of the polymer. The longest relaxation time of the polymer as well as the width of the distribution of relaxation times increase with increasing conversion and diverge at GP (9,18). The relative magnitude of the polymer relaxation time  $\tau$  and the experimental time of the dynamic measurement  $t_{\text{exp}} (= 1/\omega)$  are the crucial factors governing the experimental dynamic results. For a low enough frequency ( $\omega\tau \ll 1$ ), the polymer relaxes during the experiment and equilibrium values are measured (except at GP). For high frequency ( $\omega\tau > 1$ ,  $\tau > t_{\text{exp}}$ ) the polymer cannot relax and dynamic elasticity appears earlier with respect to the true gel point (2,13). One would expect the true experimental value of  $t_{\text{gel}}$  at  $\omega \rightarrow 0$  and its possible decrease with increasing frequency. Therefore, the frequency independence of  $t_{\text{gel}}$  and  $(\tan \delta)_{\text{gel}}$  over a wide frequency range need not be experimentally observed at the true GP. Moreover, an effect of vitrification is expected at high frequencies.

The frequency dependence of dynamic mechanical results is of primary importance

Table 1: Gelation of the system DGEBA – Jeffamine D 400

$T$ °C	$r$	$(\tan \delta)_{\text{gel}}$	$t_{\text{gel}}$ min	$t_n$ <sup>a)</sup> min	$G'(\omega)_{\text{gel}}$ <sup>b)</sup> Pa	$\Delta$ <sup>c)</sup>
110	1.00	$\sim 1.5$	17.8	17.7		
90	0.67	3.0	70.5	71.5	$6.60 \cdot 10^2$	$0.72 \pm 0.02$
	1.00	2.2	50.0	50.5	$1.25 \cdot 10^3$	$0.72 \pm 0.02$
	2.00	1.7	67.0	68.0	$1.80 \cdot 10^3$	
80	1.00		73.8	76–80		
70	1.00	2.1	131.0			0.71

<sup>a)</sup>time of the normal force generation

<sup>b)</sup> $\omega = 1.6$  Hz

<sup>c)</sup>critical exponent in the power law  $G'(\omega) \sim G''(\omega) \sim \omega^\Delta$

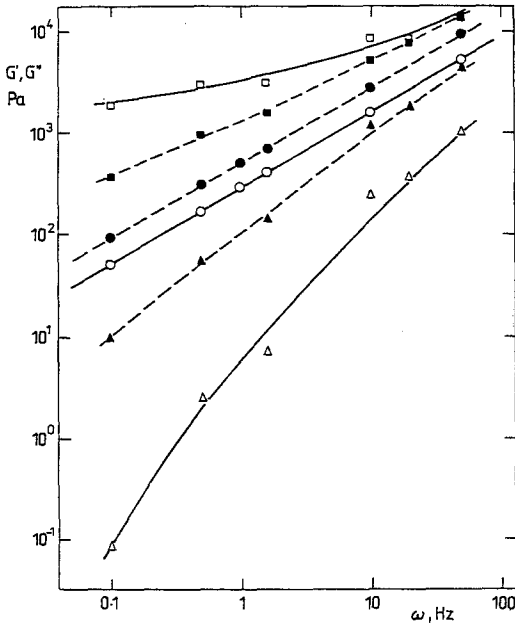


Figure 4: Storage ( $G'$ ) and loss ( $G''$ ) moduli of the sample DGEBA – Jeffamine D 400 cured for time  $t$  (time sweep) as a function of frequency.  $r = 2$ ,  $T = 90^\circ\text{C}$ .  $\square \blacksquare t = t_{\text{gel}} + 5$  min,  $\circ \bullet t = t_{\text{gel}}$ ,  $\triangle \blacktriangle t = t_{\text{gel}} - 5$  min,  $t_{\text{gel}} = 67$  min, —  $G'$ , - - -  $G''$ .

for the interpretation of data. The dependences of  $G'(\omega)$  and  $G''(\omega)$  given in Fig. 4 were evaluated by taking the values of moduli at certain reaction times from several experiments measured at different  $\omega$ .  $G'(\omega)$  and  $G''(\omega)$  are linear and parallel over the entire frequency scale measured at GP and the power law holds:  $G'(\omega) \sim G''(\omega) \sim \omega^\Delta$ . Before and after GP, the storage modulus  $G'(\omega)$  decreases rapidly to zero or shows a rubbery plateau at a low frequency, respectively. The critical parameter was evaluated to be  $0.72 \pm 0.02$ . The scatter may be attributed to difficulties with keeping exactly identical reaction conditions in all experiments. The frequency dependence of the dy-

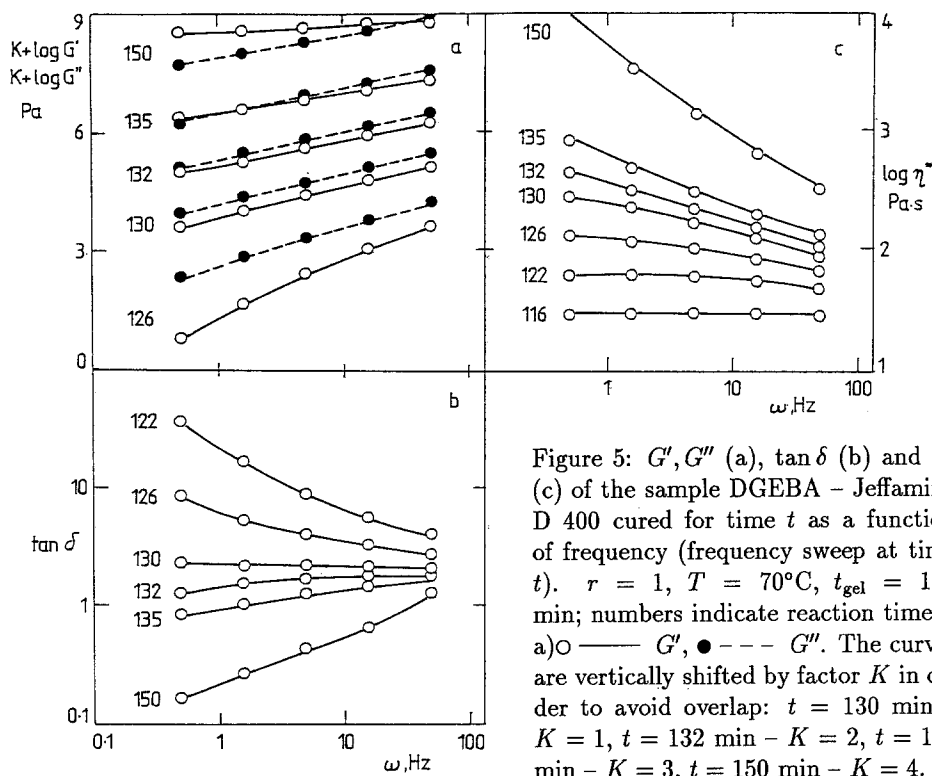


Figure 5:  $G'$ ,  $G''$  (a),  $\tan \delta$  (b) and  $\eta^*$  (c) of the sample DGEBA - Jeffamine D 400 cured for time  $t$  as a function of frequency (frequency sweep at time  $t$ ).  $r = 1$ ,  $T = 70^\circ\text{C}$ ,  $t_{\text{gel}} = 131$  min; numbers indicate reaction time  $t$ . a)  $\circ$  —  $G'$ ,  $\bullet$  - - -  $G''$ . The curves are vertically shifted by factor  $K$  in order to avoid overlap:  $t = 130$  min -  $K = 1$ ,  $t = 132$  min -  $K = 2$ ,  $t = 135$  min -  $K = 3$ ,  $t = 150$  min -  $K = 4$ .

dynamic modulus was therefore determined also using the frequency sweep in the range  $\omega = 0.5 - 50$  Hz measured at certain time intervals during a single cure at  $70^\circ\text{C}$ . The reaction is slow enough at this temperature ( $t_{\text{gel}} = 131$  min), and one can expect negligible changes of dynamic quantities due to the reaction during the short frequency sweep lasting 55 s. Figure 5 shows the evolution of the frequency dependences of  $G'$ ,  $G''$ ,  $\tan \delta$  and  $\eta^*$  of the stoichiometric system during the reaction near GP. Gelation seems to occur between  $t = 130$  and 132 min when the dynamic quantities follow the power law in frequency and  $\tan \delta$  is independent of frequency (19) over a limited experimental range (2 orders of magnitude). The critical exponent  $\Delta$  is 0.71 in agreement with some literature data (10-13), but differs from that obtained by Winter (9,16) for stoichiometrically balanced PDMS and polyurethanes. The plot of dynamic viscosity reveals that the polymer behaves as a Newtonian liquid up to 116 min of reaction time. Only then the shear thinning occurs in the frequency range used.

A negative normal force  $f_n$  is generated in the dynamic mechanical experiment just after GP (see Fig. 6). The data in Table I show a close coincidence between  $t_{\text{gel}}$  and  $t_n$ , i.e., the time of a sudden decrease in the normal force. We suppose that the volume contraction during polymerization and an appearance of equilibrium elasticity beyond GP results in drawing up the plates together leading to generation of a negative normal force.

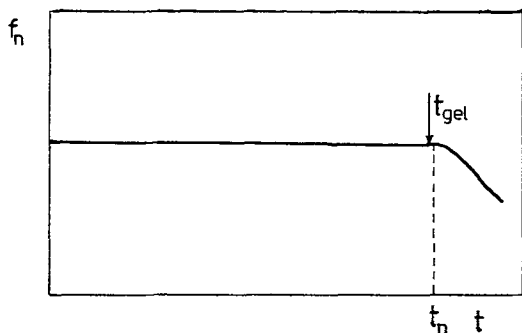


Figure 6: Evolution of the normal force  $f_n$  in the shear dynamical measurement during cure of the system DGEBA – Jeffamine D 400.  $r = 2$ ,  $T = 90^\circ\text{C}$ ,  $\omega = 50\text{ Hz}$ ,  $\gamma = 0.005$ .

### Conclusions

Gelation of the DGEBA-D 400 system can be characterized by the loss factor at GP,  $(\tan \delta)_{\text{gel}}$ , which is independent of experimental frequency. The value  $(\tan \delta)_{\text{gel}} > 1$  was determined for both the stoichiometric and nonstoichiometric systems. This value depends on the structure of the forming network given by the ratio of reagents  $r$ . The power law  $G'(\omega) \sim G''(\omega) \sim \omega^\Delta$  holds in GP and the critical parameter is  $\Delta = 0.71$ .

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