Macromol. Symp. ***147***, *221–234 (1999)*

YIELDING AND FRACTURE IN CROSSLINKED EPOXIES

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SUMMARY: From a comparison of tensile properties of two epoxy networks crosslinked, respectively, with an aromatic diamine or an anhydride and from the available literature data on the fracture properties of thermosets, it has been tried to establish structure-property relationships in this field. Attention was focused on possible specific aspects of the crosslinked polymers. Surprisingly, the crosslink density does not seem to play a crucial direct role in fracture. In contrast, there is a relation between toughness and T_g: aliphatic networks of low T_g are generally tougher than aromatic ones. The local mobility plays a very important role because it partly controls the value of Poisson's ratio (which determines the relative importance of dilatant stresses and shear stresses responsible, respectively, for brittle rupture and yielding) and, presumably, the activation volume of yielding (which partly determines the broadness of the temperature interval of ductility).

INTRODUCTION

Industrial thermosets are often brittle. For instance at ambient temperature, polyesters, vinyl esters or phenolics have tensile ultimate strains generally lower than 5 % and critical rates of the elastic energy release G_{Ic} lower than 200 J m^{-2} in crack propagation experiments. Epoxies generally display higher toughnesses[1-6], but they remain, in most cases, less ductile than thermoplastics of comparable T_g values, such as polycarbonates or polysulfones. Is it licit to generalize this observation and to claim that brittleness is a general property of thermosets ? To answer this question, it is first important to remark that certain thermoplastics, for instance polystyrene, are very brittle. From a detailed investigation of relationships between structure and fracture behaviour of linear polymers, Wu showed that polymers displaying the highest ductilities and toughnesses are most densely crosslinked (crosslinking being due to entanglements in theses cases)[7]. In fact, Wu demonstrated that the crosslink density is associated with the chain tortuosity[8], the latter being related to the height of the conformational energy barriers[9]. There is thus a key difference between linear and three-dimensional polymers: in the former, the crosslink density is a consequence of the conformational structure, whereas in the latter, both characteristics are independent since the

CCC 1022-1360/99/$ 17.50+.50/0

crosslink density is first determined by the chemistry of the systems. There is, however, no reason to exclude the hypothesis of existence of networks (with covalent crosslinks), in which the conformational behaviour would be favorable to ductility, according to Wu's theory. In this case, it would be abusive to claim that a given material is brittle because it is densely crosslinked. Our aim is first to bring some new experimental data relating to the temperature effect on yielding and fracture properties of two epoxy networks based on diglycidyl ether of Bisphenol A (DGEBA) and crosslinked with *cis*-5-norbornene-*endo*-2,3-dicarboxylic anhydride (NA) or 4,4'-diaminodiphenylsulfone (DDS).

The essential reason for this choice is that both materials strongly differ in their local mobility, as revealed by the intensity of their β-transition: very low in DGEBA-NA (shear modulus G ~ 1.3 GPa at 20 °C) and high in DGEBA-DDS (G ~ 1.0 GPa at 20 °C). Since many authors have suggested that the local mobility could play a crucial role in yielding and fracture[10,11], it seems important to compare materials with very distinct characteristics in this domain. It can be recalled that unsaturated polyesters and vinyl esters, which are very brittle, are characterized by low-intensity secondary transitions (typically G ~ 1.25-1.50 GPa for styrene-crosslinked polyesters and vinyl esters at 20 °C), and thus are closer to DGEBA-NA (which is a polyester) than to DGEBA-DDS. The presentation of experimental results is followed by a discussion on structure-fracture properties relationships.

EXPERIMENTAL

Materials

Both networks under study were obtained from a diepoxide, diglycidyl ether of Bisphenol A (DGEBA) having a degree of polymerization $\overline{DP}_n = 0.15$. Network A was hardened with *cis*-5-norbornene-*endo*-2,3-dicarboxylic anhydride (NA) under the following conditions: 5-min mixing at 120 °C in oil bath, 10-min degassing in vacuum at 120 °C, casting in a mold cavity having the shape and dimensions of an ISO/1 tensile specimen, 10-h cure at 160 °C, and 30-min post-cure at 180 °C. Network B was hardened with 4,4'-diaminodiphenylsulfone (DDS) under the following conditions: 20-min mixing at 140 °C in oil bath, 30-min degassing in vacuum at 140 °C, casting in the same mold cavity, 2-h cure at 160 °C, and 2-h post-cure at 200 °C.

In both cases, samples were cast-molded in metallic molds in order to obtain ISO/1 tensile dogbone bars. The sample edges were polished in order to limit the sample roughness and thus the presence of large defects capable of initiating cracking. Some physical characteristics of the samples under study are summarized in Table 1.

Table 1 Physical characteristics of the networks under study

Network	Code	T_g (K)	ρ (g cm^{-3})	E (MPa)
DGEBA-NA	A	418	1.23	3600
DGEBA-DDS	B	493	1.21	2880

Tensile testing

Tensile tests were performed on an Instron 4502 tensile machine equipped with a thermostatic chamber regulated within ± 1 °C. Two series of experiments were realized for each material: First, in the region of low strains, using a two-dimensional mechanical extensometer to determine elastic properties. Second, in the region of large strains to determine the yield and fracture properties. Here, the crosshead displacement was considered sufficiently accurate to determine strains. In all the cases, only the engineering properties (not corrected for section changes), were reported. The tests were performed at the tensile rate ($\dot{\varepsilon}$) of $2.77.10^{-3}$ s^{-1}. Common effects of $\dot{\varepsilon}$ variation on moduli and yield stresses were observed but they will not be reported here.

Physical characterization

Glass transition temperatures T_g were determined by DSC using a Netzsch apparatus at the 10 K min^{-1} scanning rate. T_g was taken at the inflection point. Thermomechanical spectra were recorded in the flexural mode at 1 Hz frequency and the scanning rate 2 K min^{-1}, using a Netzsch thermomechanical analyser.

RESULTS

Some examples of tensile curves are shown in Fig. 1a (sample A) and 1b (sample B).

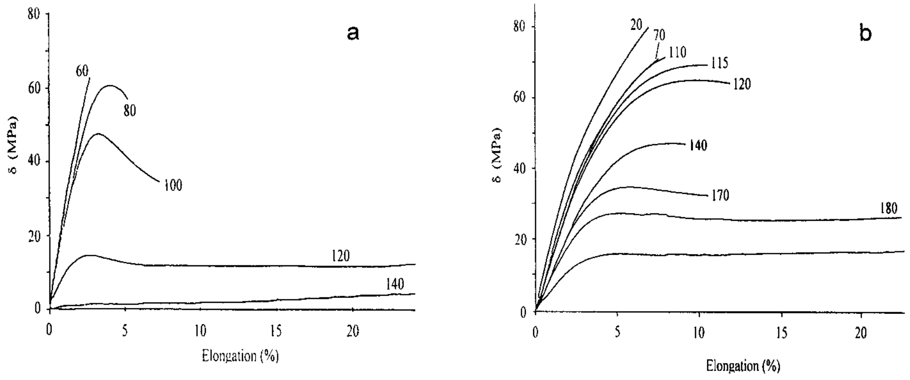

Fig. 1 Examples of tensile curves for samples A (a) and B (b) at the strain rate $2.77.10^{-3}$ s^{-1} at temperatures indicated (°C)

They display yielding and plastic deformation above approximately 80 °C (sample A) and 120 °C (sample B).

The maximum (engineering) stress σ_M, e.g. the ultimate stress σ_R in the case of brittle rupture and the yield stress σ_Y in the case of plastic deformation, was plotted against temperature for both systems (Fig. 2). In both cases, one can easily distinguish two fracture regimes in the temperature dependence of σ_M: The 'brittle' regime for which $\Delta\sigma_M/\Delta T < 0.1$ MPa K^{-1} and the 'plastic' regime for which $\Delta\sigma_M/\Delta T < 1$ MPa K^{-1} (sample A) or 0.7 MPa K^{-1} (sample B). In the latter regime, the yield stress varies almost linearly with temperature according to the relationship established by Kambour[12] for linear amorphous polymers, $\sigma_y = C\,(T_g - T)$.

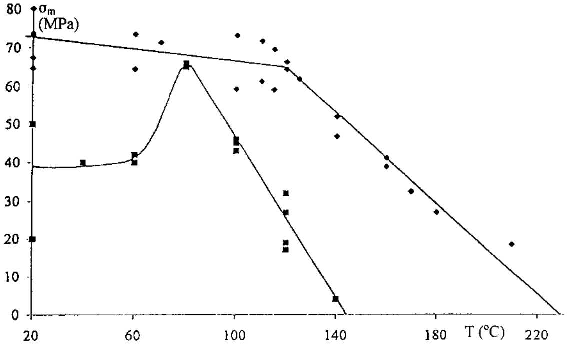

Fig. 2
Maximum stress vs temperature for samples A (■) and B (◆) (strain rate $2.77.10^{-3}$ s^{-1})

There is a great difference between the ultimate stress values in the brittle regime: about 70 MPa for the amine-cured (B) and 40 MPa for the anhydride-cured network (A). Both samples also differ by the shape of the curve $\sigma_M = f(T)$ in the transition region between both regimes. The curve displays a very marked maximum for sample A whereas it can be described as a simple intersection of two straight lines for sample B. No doubt, this difference can be attributed to the yield behaviour of both materials: the tensile curves display a noticeable overboost in sample A (Fig. 1a), and virtually no maximum in sample B (Fig. 1b). It is well known that this maximum is essentially associated with physical ageing[13], which is here confirmed by the fact that in sample A, σ_y strongly depends on the thermal history. Physical ageing is especially fast in sample A for reasons which remain to establish. Anyhow, one can interpret the difference between A and B by the fact that B is closer to thermodynamical equilibrium than A.

In Fig. 3, the ultimate elongation ε_R was plotted against temperature for samples A and B. For both systems, a small but significant increase in ε_R was observed at temperatures higher than the transition temperature T_{BP}, between the 'brittle' and the 'plastic' regime of rupture. It can be reasonably assumed that both regimes correspond to those which were called respectively 'brittle stable' and 'brittle unstable' by Kinloch[2] in a study of the crack propagation characteristics of DGEBA - aliphatic amine systems. Ductility appears when temperature approaches (T_g-20) K (sample A) or (T_g-40) K (sample B). Then, ε_R abruptly increases reaching values close to 0.25 - 0.30 (versus 0.02 - 0.05 in the 'brittle' regime) for both systems.

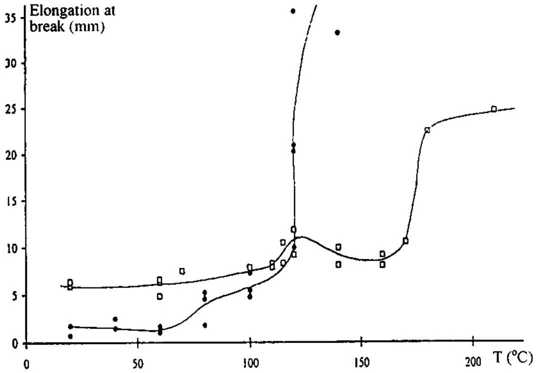

Fig. 3
Ultimate elongation versus temperature for samples A (●) and B (□) (strain rate $2.77.10^{-3}\ s^{-1}$)

A detailed study of the elastic and viscoelastic properties of these materials led to the following results:

The bulk modulus is virtually temperature-independent between 200 K and (T_g-30) K for both systems (B = 6 GPa for sample A and 7 GPa for sample B). The difference can be attributed to the difference in cohesive energy densities, higher in sample B (due to the presence of hydroxy groups[14] than in sample A.

Poisson's ratio ν is almost temperature-independent between 220 K and (T_g-40) K for sample A. For sample B, ν is 0.40 - 0.41, increasing from about 0.41 to about 0.45 between 220 and 340 K and then remaining almost constant up to (T_g- 40) K (Fig. 4).

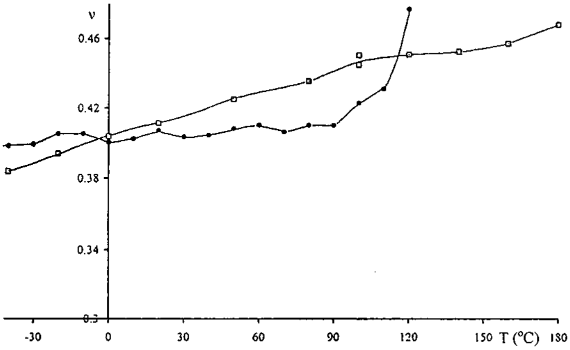

Fig. 4
Temperature variation of Poisson's ratio for both samples A (●) and B (□) (strain rate $2.77.10^{-3}\ s^{-1}$)

The amine-cured sample (B) displays a considerably stronger β-transition than the anhydride-cured one (A) (Fig. 5), which explains the temperature effect on ν in sample B, whereas ν appears almost temperature-independent in sample A.

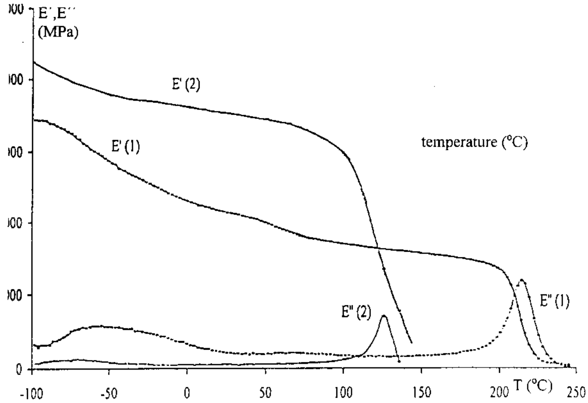

Fig. 5
Shape of the β–dissipation peak in DMTA spectra (frequency 1 Hz): A (2), B (1)

DISCUSSION

Let us consider possible influent parameters in the case under study.

Limited chain extensibility due to the high crosslink density

This argument, inspired by rubber studies, is the most frequently used to explain the brittleness of thermosets. In the frame of this theory, rupture would occur when the network chains are fully extended, which corresponds theoretically to a maximum draw ratio proportional to $M_c^{1/2}$ (neglecting possible effects of the polydispersity of network chain lengths). One expects, in this case, that the physical quantities characterizing the fracture behaviour, for instance determined from crack propagation experiments[3,4,6], are scaled by M_c. Plastic deformation would occur at the crack tip and stretching of network chains would predominantly contribute to the crack propagation energy. In other words, yielding being assimilated to a devitrification, it is expected that thermosets behave, in this respect, as rubbers. This is effectively observed in two of the above cited structural series[3,6], but not in the third one[4].

In the case of tensile testing on unnotched samples, one can clearly see that the ultimate elongation in the brittle regime ($\varepsilon_R = 0.05$) is considerably lower than its maximum possible value ($\varepsilon_R \geq 0.2$ at $T \geq (T_g - 30)$ K (Fig. 5). Thus the brittleness of thermosets at ambient temperature does not result directly from the limited extensibility of network segments. If there are peculiarities of the fracture behaviour of thermosets, they are to be searched in their brittle-ductile transition rather than in characteristics at a given temperature.

Glass transition temperature

Let us consider the three above cited structure series[3,4,6]. In those where toughness characteristics increase[3,6] regularly with M_c, the main structural variable is effectively M_c (e.g., the crosslink density), the chain stiffness being approximately constant. However, in the third series studied by Pascault et al.[4], the main structural variable is the chain flexibility: the networks are based on aromatic (DGEBA)/aliphatic (DGEBD) epoxide mixtures with variable DGEBA/DGEBD molar ratios. Here, M_c decreases, and the toughness increases with the DGEBD fraction. It appears thus that the only common feature of these three structure series is that the fracture toughness is a decreasing function of T_g. As a matter of fact, if the chain flexibility is almost constant, T_g is expected to be a monotonic, decreasing function of M_c. On the contrary, if both variables, chain flexibility and crosslink density change at the same time, it is not surprising to find cases where chain flexibility effects on T_g predominate[15] as found in the series under consideration[4].

One can also observe a general tendency of the fracture toughness to be a decreasing function of T_g in stoichiometric systems differing essentially by the aromatic/aliphatic content[2]. It is noteworthy that aliphatic or semialiphatic epoxy networks are tougher than aromatic ones of close (or possibly lower) crosslink density. For instance, the critical rate of energy release G_{Ic} is of the order of 1000 J m^{-2} for the DGEBD-DDS system[1], versus less than 300 J m^{-2} for the majority of DGEBA - aromatic diamine systems. The key role of T_g can be associated with the well-known effect of temperature on yielding as expressed by Kambour's relationship, $\sigma_y = C (T_g \sim T)$, and well confirmed in our results (Fig. 2), where C is a constant independent of T_g at least in a first approximation. According to this relationship, σ_y is an increasing function of T_g in a given structural series, except for unexpected very large variations of C.

If, then, the fracture behaviour is considered as resulting from the competition between a 'brittle' process, in which the ultimate stress is almost independent of temperature, and a 'plastic' process in which the yield stress is a decreasing function of temperature (as shown in Fig. 2), it can be seen that the 'plastic' process is more and more favored as σ_y is lower and lower and thus as T_g is lower and lower.

Elastic and viscoelastic properties

From the analysis of the behaviour of epoxy samples in multiaxial states of stress[16,17], one can interpret the ductile-brittle transition as a result of competition between the hydrostatic (dilatant) component of the stress tensor, responsible for cavitation, which initiates brittle fracture, and the shear component responsible for plastic yielding. Poisson's ratio ν, contributing to the relative importance of both stress components, is thus a key quantity[18]. One can observe, in the case of linear polymers, that brittle polymers such as polystyrene (ν = 0.35 - 0.37) have generally Poisson's ratios lower than ductile polymers such as polycarbonate (ν = 0.42). Unrelaxed Poisson's ratio values, as determined from the 5 MHz ultrasonic propagation velocity, have the value of 0.370 ± 0.004 for a large family of amine-epoxide networks[14] and do not seem to vary with the crosslink density. However, a recent study of the tensile properties of thermosets[19] showed a very important effect of the local mobility on Poisson's ratio as schematized in Fig. 6.

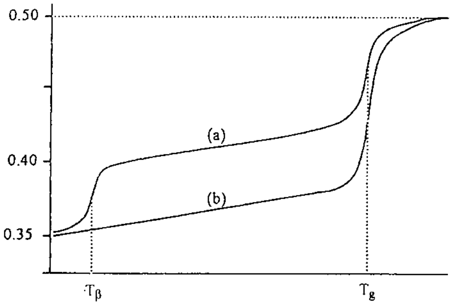

Fig. 6

Theoretical shape of the Poisson's ratio variation with temperature for polymers displaying a strong (a) or low (b) secondary transition

For most of the polymers, ν is of the order of 0.35 just below the β–transition. Two extreme cases can be schematized: for the polymers displaying a β–transition of low mechanical activity (low-intensity β–dissipation peak), such as typically polystyrene or unsaturated polyesters (UP) and vinyl esters (VE), ν increases slowly with T and takes values generally lower than 0.40 at ambient temperature. For the polymers displaying a β–transition of high mechanical activity such as typically polycarbonate (PC), polysulfone (PSO) or certain stoichiometric amine-crosslinked epoxies, ν increases at the β–transition and takes values ranging typically between 0.41 and 0.44 at ambient temperature.

This behaviour can be easily understood recalling that the bulk modulus B is not influenced by β–motions[19]. Then, one can write from the basic relationships of continuum mechanics:

$$\nu = \frac{3B - 2G}{2G + 6B}$$

(G is the shear modulus, which is the elastic quantity directly affected by the molecular mobility).

The mechanical activity of the β–transition can be represented by the corresponding modulus gap ΔG_β.

By deriving the above relationship, one obtains $$\frac{d\nu}{dG} = -\frac{1}{2B}\left(\frac{1}{1+(G/3B)}\right)^2$$

Here, $G/3B \leq 0.1$ so that, in a first approximation, $\Delta\nu_\beta = -\Delta G_\beta/2B$.

One can see that Poisson's ratio gap at the β–transition is grosso modo proportional to the shear modulus gap. The already reported favorable effect of the local (β) mobility on the failure behaviour[10,11] could be thus explained by the following schematic causal chain

high mobility → high Poisson's ratio value at ambient temperature → low shear modulus value → low yield stress → easier plastic deformation → higher ductility.

In practice, there are relatively simple tests to estimate the mechanical activity of the β–transition, for instance:

(i) Determination of the area of the β dissipation peak in DMTA spectra at a chosen frequency (for instance, 1Hz): $A_\beta = \int_{T_1 < T_\beta}^{T_2 > T_\beta} \tan\delta \, dT$

Typical A_β values are: 0.75 k for PC, 1.0 - 2.4 k for amine-crosslinked epoxies, 0.08 k for DGEBA-NA and 0.1 k for UP.

(ii) Determination of the ratio unrelaxed/relaxed (E_U/E_R) tensile modulus ratio; E_U can be, for instance, determined from ultrasonic velocity measurements[14], E_R can be determined from classic tensile measurements at moderate strain rates ($\dot{\varepsilon} < 10^{-3}s^{-1}$).

(iii) One can remark that $b=\frac{E_U}{E_R}=\frac{2G_U\left(1+\nu_U\right)}{2G_R\left(1+\nu_R\right)} = \frac{G_U}{G_R}\frac{1}{1+\frac{\Delta\nu_\beta}{1+\nu_U}}$ where $\Delta\nu_\beta = \nu_R - \nu_U$.

Since $\Delta\nu_\beta/(1+\nu_U) < 0.05$, one can use the approximation $b = E_U/E_R \sim G_U/G_R$. Hence it comes $b - 1 = \Delta G_\beta/G_R$.

Typical values of $(b - 1)$ are generally less than 0.2 in polymers of the 'brittle' family (PS, UP, VE, etc.) and of the order of unity in polymers of the 'ductile' or 'semiductile' family (PC, PSO, epoxide-amine networks, etc.).

Temperature interval of yielding

In the case of linear polymers, Wu[7] has proposed a relationship between both limits, T_g and T_B, of the domain of ductility, involving a single structural variable, C_∞ (characteristic ratio of the chains, associated with their tortuosity):

$T_B/T_g = a + bC_\infty$ where a and b are constants ($a = 0.135$, $b = 0.082$) and T_B is the brittle-ductile transition temperature.

This relationship can be rewritten:

$\Delta T/T_g = (1 - a) - bC_\infty$ where $\Delta T = T_g - T_B$ is the temperature interval of ductility.

Could such or an equivalent relationship be established for glassy networks? To our knowledge, data on C_∞ values for the chains constituting the industrial thermosets are not available but it can be yet remarked that the networks containing polystyrene chains (with an especially high C_∞ value, $C_\infty \sim 10$), UP and VE, are especially brittle: no yielding can be observed[20] until 20 - 30 K below T_g.

For thermosets, the problem can be reconsidered on the basis of the above presented concept of competition between brittle fracture and plastic yielding in its simplest version where the brittle stress σ_R is temperature-independent whereas σ_y obeys Kambour's relationship. The 'brittle-plastic' transition temperature T_{BP} is thus given by $\sigma_R = C\,(T_g - T_{BP}) = C\Delta T$. Thus, the knowledge of σ_R and C would allow to predict many important features of the fracture behaviour. Let us try to analyze the relationships between both characteristics and the network structure.

Brittle stress σ_R. In the brittle domain, the concepts of linear elastic fracture mechanics are valid so that one can write $\sigma_R/E = f(h)$ where h is the defect size and f(h) a function tending towards a limit when h tends towards zero. According to Struik[21], this limit could be of the order of 1/30 versus the limit here, $\sigma_R/E \sim 1/80$ (DGEBA-NA) and 1/40 (DGEBA-DDS). Here, both samples were prepared in the same mold. They were free of visual defects (bubbles, etc.) and they were polished by the same method so that it appears difficult to explain the difference in σ_R values (40 MPa for DGEBA-NA, 70 MPa for DGEBA-DDS) by differences in the flaw size.

When deformation is almost completely free of viscoelastic effects, one expects theoretically that E is proportional to the cohesive energy density e. For epoxy networks, it was found[14] that $E \sim 0.78\ B \sim 8.5\ e$. So, according to Struik[21] we would have $\sigma_R \sim 0.28\ e$.

The cohesive energy density can be estimated in various ways[14]. It is higher for DGEBA-DDS (e ~ 550 MPa), owing to the presence of hydrogen-bonded hydroxy groups, than for DGEBA-NA (e ~ 450 MPa). Thus, a part of the difference between the σ_R values of both networks could be explained by their difference in cohesivity. It appears, however, difficult to assume that only this characteristic is responsible for the whole difference.

It is noteworthy that, in the tensile conditions under study, the DGEBA-NA behaviour is almost purely elastic, whereas there is a highly active β-transition in the case of DGEBA-DDS. Are viscoelastic effects responsible for such a difference of σ_R values ? This point would merit a supplementary investigation.

Temperature dependence of the yield stress. Is it possible to predict the value of $C = - d\sigma_y/dT$ from the structure ? From the group interaction modelling approach, Porter[22] obtains $d\sigma_y/dT = 1 - \tan^{1/2} \Delta_\beta$ where $\tan \Delta_\beta$ is the 'cumulative loss tangent' essentially associated, in the case under study, with the amplitude of the β–dissipation peak. We find, once again, the crucial importance of the local motions, which explains, at least partly, why C is higher for DGEBA-NA (1 MPa K^{-1}) than for DGEBA-DDS (0.7 MPa K^{-1}) and considerably higher for a styrene-crosslinked vinyl ester ($C = 2.0$ MPa K^{-1}, ref. 20) than for the epoxies under study. But does crosslinking influence C ?

A possible way to discuss this point could start from the observation that C is directly linked to a more fundamental parameter, the activation volume of yielding. As a matter of fact, Kambour's law can be considered equivalent to Eyring's law at constant strain rate $\dot{\varepsilon}$:

$\dot{\varepsilon} = \dot{\varepsilon}_0 \exp[-(H-V\sigma_y)/RT]$ where $\dot{\varepsilon}_0$, H and V are constants for a given material. Then, $\sigma_y = (R/V) \lg (\dot{\varepsilon}_0/ \dot{\varepsilon}) \{[H/(R \lg (\dot{\varepsilon}_0/ \dot{\varepsilon}))] - T\} = C(T_g - T)$.

C would be thus inversely proportional to the activation volume V: the lower is V, the higher is C and the sharper is the ductility temperature interval, all the other parameters being equal. According to Lefebvre and Escaig[23], V could be lower for thermosets (~ 0.1 $l.mol^{-1}$) than for thermoplastics (~ 1 l mol^{-1}). If this observation can be generalized, we would have here one of the (very scarce) specific effects of the crosslink density on the mechanical behaviour of polymers (together with the well-known effect on T_g). Unfortunately, recent results on aliphatic amine-crosslinked epoxies revealed V values close to those for linear polymers[17].

Topological defects in the network

The above discussion concerns essentially 'perfect' networks, such as networks in which most of the segments are elastically active. In the case of amine-epoxide networks for which the cure is almost free of secondary reactions, one can easily show that when the amine/epoxide functional ratio varies, one can distinguish schematically two situations: $2 > r \geq 1$ for a perfect network or $r < 1$ for a network with dangling chains.

It can be shown, for instance in Drzal results[24], that both situations are not symmetric. The fracture properties decrease rapidly when r becomes lower than unity, whereas they are almost unchanged or sometimes increase when r becomes higher than unity.

This aspect could be important in our comparison of DGEBA-NA and DGEBA-DDS. As a matter of fact, it is impossible to obtain a 'perfect' network with anhydride hardeners, even in the stoichiometric case, because the epoxide-anhydride reaction is equilibrated[25]. In contrast, epoxide-amine systems such as DGEBA-DDS can be almost completely reacted and the network structure is near to the 'perfection'.

Toughness and ductility as non-equilibrium properties

It is well known that physical ageing induces an increase in σ_y and thus favours the brittle rupture relatively to plastic deformation[13]. In initially ductile networks such as DGEBD-DDS[1], the decrease in G_{1c} upon physical ageing is very impressive. This indicates that the fracture characteristics are non-equilibrium properties, which complicates the analysis of the structure-property relationships in this field and leads to new questions about possible crosslinking effects on physical ageing. We have observed for instance in the case of DGEBA-NA that physical ageing leads to an especially high increase[26] in σ_y. However, we lack data in this field to be able to generalize.

CONCLUSION

On the basis of literature data and experimental data on tensile properties of two epoxy networks hardened, respectively, with an aromatic diamine (DDS) and with a cycloaliphatic anhydride (NA), we have tried to investigate the structure - fracture properties relationships in thermosets. The role of the following physical factors has been examined:

Crosslink density - It is clear that the fracture behaviour of the thermosets under study around the ambient temperature cannot be interpreted in terms of limited extensibility of network segments linked to the high crosslink density. As a matter of fact, these materials display relatively high draw ratios when they are stretched at temperatures close to T_g.

Glass transition temperature - Compilation from several literature sources indicate that the network toughness is generally a decreasing function of T_g. Aliphatic systems are generally tougher than aromatic. This behaviour can be easily understood since the yield stress is generally an increasing function of T_g.

Elastic and viscoelastic properties - There are two important interrelated parameters: the β–mobility (as assessed for instance by the intensity of the β–dissipation peak), and Poisson's ratio ν. The temperature variation of the latter can explain the existence of a critical temperature T_{BP}, above which shear yielding plays a predominant role and below which cavitation associated with the dilatant component of the stress tensor is responsible for the brittle rupture.

Competition between brittle rupture and yielding - Here also, the local mobility plays a very important role since viscoelasticity has apparently a positive effect on the brittle rupture. Furthermore, the temperature effect on yield stress also depends on the intensity of the β–dissipation peak in such a way that the 'ductility interval' (T_g - T_B) increases when the mobility increases. A specific effect of crosslinking on the activation volume of yielding could be suspected from results obtained by Lefebvre and Escaig but it is too early to generalize this observation.

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