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Molecular analysis of yielding in pure and antiplasticized epoxy-amine thermosets

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The yielding behavior of epoxy-amine thermosetting resins was investigated by a study of the stress-strain curves in compression mode, recorded at various temperatures and strain rates. The materials under study included pure resins of variable chain flexibility and cross-link density, as well as dense resins modified by the addition of antiplasticizers in the initial monomer mixture. Two types of antiplasticizer were examined, depending on whether they remain miscible to the network or give rise to nano-scale phase separation along network construction and lead to materials of improved toughness. Data analysis was performed on the molecular scale, by putting emphasis on the correlation existing, as in thermoplastic amorphous polymers, between the yielding and segmental mobility associated to the β-relaxation processes. © *2002 Kluwer Academic Publishers*

1. Introduction

Yielding can be regarded as a key mechanism in the deformation of polymeric materials. Indeed, the yielding may control toughness, a mechanical property of practical interest, through its influence on the crazing and micro-crack propagation mechanism. For this reason, there is an interest to understand, on the molecular scale, how the stress-strain behavior of polymers depends on such parameters as chemical structure, temperature, and strain rate.

In the case of thermoplastic polymers, recent studies performed in our laboratory [1–6] have emphasized the connections existing between the yielding behavior and nature of the polymer chain motions involved in the main mechanical relaxation (α) and in the sub-T_g secondary relaxations (β, γ). A unique line of reasoning proved to be suitable for polymers as different from each other as polystyrene, poly(methyl methacrylate), polycarbonate, semi-aromatic polyamides, poly(vinyl chloride), etc.

In the same way, the well-known tendency towards brittleness of thermosetting resins has been interpreted by Cook *et al.* [7, 8] as resulting from the lack of molecular mobility inherent to their highly cross-linked network structure. For such materials, it is necessary to separate the cross-link density effect from the chain flexibility effects, which both affect, for instance, the value of the glass transition temperature T_g. As proposed by Cook [7, 8] and by many others (see for instance reference [9]), this can be achieved by useing mixtures of primary diamine and homologous primary monoamine or secondary diamine as the hardener instead of pure primary diamine. Doing so, it has also been possible to get a deeper insight into the β relaxation of model epoxy networks [10–12]. It is known for a long time that this broad β relaxation involves mechanically active hydroxypropylether motions [13]. Combination of dynamical mechanical analysis [10, 11], solid-state nuclear magnetic resonance (NMR) [11], and creep experiments [12] allowed us to demonstrate that the relevant torsion motions are isolated (i.e. decoupled from each other) in the low temperature part of the relaxation. By contrast, they present a more and more cooperative character in the high temperature part of the relaxation. Origin of the cooperativity was ascribed to the possible mobility of nitrogen atom cross-links, sometimes called network effect.

Recently, some earlier observations of Daly *et al.* [14] on the antiplasticization of epoxy networks by certain low molecular weight unreactive additives were revisited in our laboratory. As anticipated from Daly's results, cure of diglycidylether of bisphenol-A (DGEBA) with diaminodiphenylmethane (DDM), diaminodiphenylsulfone (DDS) or hexamethylenediamine (HMDA) in the presence of the product of reaction of glycidylphenylether with acetamidophenol (so called additive A in Table I) led to networks presenting a higher glassy-state modulus than the regular formulations without additive [15, 16]. The molecular origin of this phenomenon, called antiplasticization for a long time [17], has been elucidated, thanks to solid-state NMR experiments [15, 18]. It turns out

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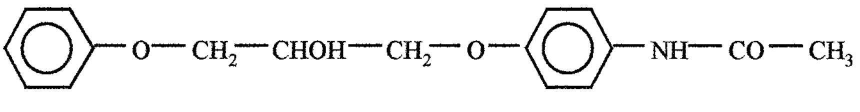
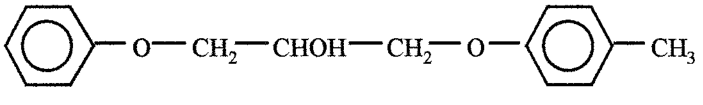
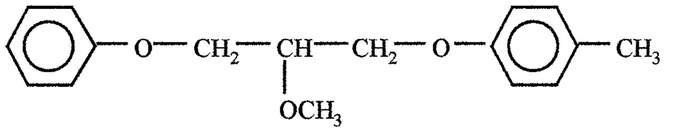
TABLE I Chemical formulae of the epoxy-amine antiplasticizers used in this study

Additive	Chemical formula
A (reference [14])	
C	
O	

that the additive molecules of A, distributed at random within the sample, are likely to immobilize the network nitrogen cross-links lying in their neighborhood and therefore to hinder the cooperative hydroxypropylether motions. With this respect, the net effect of the antiplasticizing additive on the β relaxation is identical to that observed in the case of loosely cross-linked networks prepared with amine mixtures. Interestingly, replacement of the additive A by two other additives of lower polarity, so-called C and O in Table I, was reported to yield networks of markedly increased toughness [19,20], as the result of nano-scale phase separation.

Summarizing, it is obvious that the influence of molecular mobility on the yield behavior is not as well understood yet for thermosetting resins than for linear thermoplastics. Therefore, we decided to study in more details the stress-strain behavior of epoxy-amine networks, focusing firstly on samples of same chain flexibility and variable cross-link density, and then on densely cross-linked networks antiplasticized by the additives A, C, and O.

2. Experimental

2.1. Materials

2.1.1. Chemicals

The epoxide DGEBA used in this study was Rutapox 0162, purchased from Bakelite Co. Five amines were used as curing agents, namely: diaminodiphenylmethane (DDM) and its homologous chain extender 4-benzyl aniline (BAN), hexamethylenediamine (HMDA) and the chain extender n-hexylamine (HA), and finally diaminodiphenylsulfone (DDS). Four of them are commercially available: DDM (Acros Organics), HMDA (Aldrich), HA (Aldrich), and DDS (Ciba-Geigy, grade HT 976-1). The last one, BAN, was synthesized in our laboratory according to a well-documented procedure [21]. The additives A, C, and O were also synthesized in our laboratory. The additive A was prepared by following the procedure well documented by Daly *et al.* [14], and based upon the reaction of glycidylphenylether with p-acetamidophenol in the presence of diethylamine hydrochloride as the catalyst. The same procedure was used to prepare the additive C, by replacing the reactant p-acetamidophenol by p-cresol, and then purifying the reaction material by distillation under reduced pressure. Purity of both A and C additives was checked by the absence of the band characteristic of the epoxide ring at 915 cm^{-1} on the Fourier-transformed infrared spectrum. Finally, the additive O was prepared from the additive C by methylation of its residual alcohol function by methyl iodide in the presence of silver oxide [19]. After distillation of the reaction material under reduced pressure, yield of the etherification reaction was investigated by ^{1}H and ^{13}C NMR, and estimated to about 90%.

2.1.2. Network preparation

The composition of the different formulation used for network preparation is given in Table II. Typically, DGEBA was heated at 50°C and briefly degassed under vacuum before the rest of the chemicals (amines and eventually additive) were added at 80°C (or 35°C in the case of HMDA). Usually, the resins were cured up to 80°C for 10 hours and then post-cured for 24 hours at a temperature exceeding by about 30°C the expected ultimate glass transition temperature of the network. A peculiar cure cycle was retained for the samples based on DDS, because of the low diamine reactivity and the high network sensitivity to thermal degradation [22]. As a compromise, DDS resins were cured at 150°C for 6 hours and then post-cured for 3 hours, at 200°C in the case of S100 and at 160°C in the case of S100/A-62 and S100/C-62.

2.1.3. Network characteristics

For all the networks under study, it has been verified that the overall extent of epoxide-amine reaction after post-cure is equal to or larger than about 0.90, as determined by NMR or Fourier-transformed infrared spectroscopy [23, 24]. Thus, one may consider that the samples represent a well-controlled architecture and are not significantly influenced by the presence of unreacted pending groups. It is worth pointing out that this finding holds in the presence of additive molecules also [22]. In addition, as checked by NMR, the additives do not react with the DGEBA epoxide functions along the step of network construction [15, 25]. The values of the main mechanical relaxation temperature, T_α, of the

TABLE II Designation and formulation of the networks under study

Code name	Composition: Diepoxide	Composition: Primary diamine	Composition: Co-hardener or additive	Relaxation temp. (°C)
H100	DGEBA (2 mol)	HMDA (1 mol)	None	$T\alpha = 119$
H40	DGEBA (5 mol)	HMDA (1 mol)	HA (3 mol)	$T\alpha = 70$
H5	DGEBA (5 mol)	HMDA (0.125 mol)	HA (4.75 mol)	$T\alpha = 56$
M100	DGEBA (2 mol)	DDM (1 mol)	None	$T\alpha = 186$
M40	DGEBA (5 mol)	DDM (1 mol)	BAN (3 mol)	$T\alpha = 115$
M5	DGEBA (5 mol)	DDM (0.125 mol)	BAN (4.75 mol)	$T\alpha = 86$
S100	DGEBA (2 mol)	DDS (1 mol)	None	$T\alpha = 220$
M100/A-29	DGEBA (2 mol)	DDM (1 mol)	Additive A (0.29 mol)	$T\alpha = 138$
M100/A-62	DGEBA (2 mol)	DDM (1 mol)	Additive A (0.62 mol)	$T\alpha = 106$
M100/A-66	DGEBA (2 mol)	DDM (1 mol)	Additive A (0.66 mol)	$T\alpha = 1.04$
M100/A-96	DGEBA (2 mol)	DDM (1 mol)	Additive A (0.96 mol)	$T\alpha = 90$
M100/M-62	DGEBA (2 mol)	DDM (1 mol)	Additive M (0.62 mol)	$T\alpha = 114$; $T_\mu = 65$
M100/O-62	DGEBA (2 mol)	DDM (1 mol)	Additive O (0.62 mol)	$T\alpha = 110$; $T_\mu = 50$
S100/A-62	DGEBA (2 mol)	DDS (1 mol)	Additive A (0.62 mol)	$T\alpha = 125$
S100/M-62	DGEBA (2 mol)	DDS (1 mol)	Additive M (0.62 mol)	$T\alpha = 130$; $T_\mu = 63$

networks [21], and of the second relaxation temperature, T_μ, of the phase separated systems [20] as well, are recalled in the last entry of Table II. Conventionally, they have been taken at the maximum of the loss modulus E'' in dynamic mechanical measurements performed by subjecting the samples to small amplitude sinusoidal deformations of frequency 1 Hz.

2.2. Stress-strain measurements

2.2.1. Mechanical testing conditions

Mechanical testing was carried out in compression mode on a MTS 810 hydraulic testing system equipped with a temperature chamber. The regular deformation rate for the experiments was 2×10^{-3} s^{-1}. However, some additional measurements were performed over the range 4×10^{-5} s^{-1}–2×10^{-1} s^{-1}.

Experiments were performed on parallelepipedic samples, with a 4×4 mm^2 section area and 8 mm high (compression direction). Samples were cut with a diamond saw very carefully, as a lack of parallelism of the faces would greatly disturb the shape of the stress-strain curves. Stress-strain curves were collected at temperatures ranging from −90°C to T_α. Before tests, samples were left at the chosen temperature for 30 min.

Because the levels of strain involved in the experiments are quite small, typically less than $\varepsilon = 0.150$, the values of nominal stress calculated by the computer were supposed, as a first approximation, to be identical to the true stress and used instead of them without further manipulation.

2.2.2. Analysis of the stress-strain curves

Fig. 1 shows the general shape of the stress-strain curves of the materials under study. Whatever the variable be under consideration, temperature (Fig. 1a) or strain rate (Fig. 1b), all curves present the same profile. Namely, an initial linear evolution, typical of the elastic response, then a curvature corresponding to the inelastic response before the yield point, is attained at the maximum stress σ_y, and finally some strain softening until reaching the plateau, characterized by the plastic flow stress, σ_{pf}.

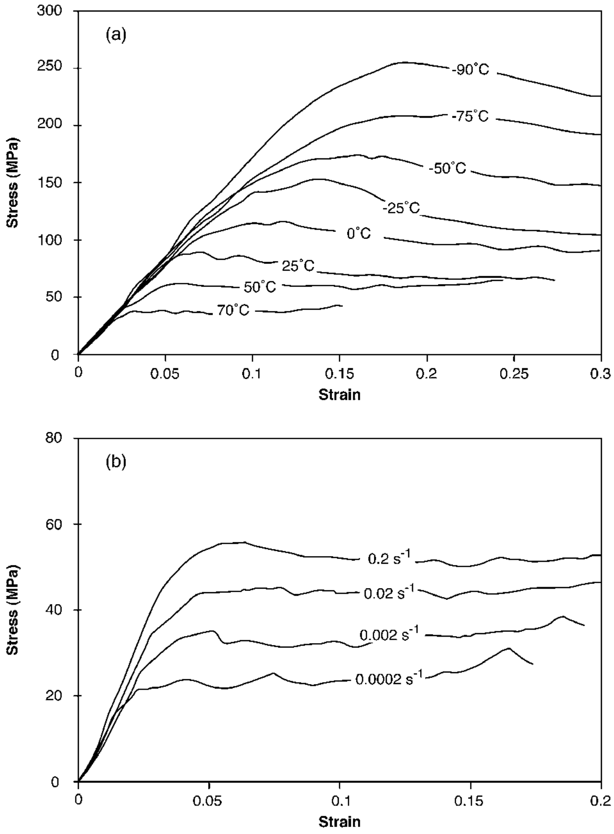


Figure 1 Typical stress-strain curve relative to the sample M100/A-96. (a) Effect of temperature at a strain rate of 2×10^{-2} s^{-1} and (b) effect of strain rate at a temperature of 70°C.

The present work deals mainly with the analysis of the three quantities σ_y, σ_{pf} and SSA ($= \sigma_y - \sigma_{pf}$). However, experimental determination of these characteristics is sometimes difficult:

- on the one hand, the lowering of the plasticity threshold as T_g is approached reduces the elastic deformation range. Therefore, the error bars on the value of modulus E strongly increased, even by performing the experiments in triplicate.
- on the other hand, as discussed below, the stress-softening phenomenon tends to be hidden for certain formulations and (or) temperature conditions.

An account for the effect of strain rate is given by assuming the validity of an Eyring type equation [26]:

$$\dot{\varepsilon} = \dot{\varepsilon}_0 \exp(-\Delta G_a / RT) \tag{1}$$

in which ΔG_a is the stress- and temperature-dependent activation free energy of deformation.

ΔG_a, in turn, obeys the equation:

$$\Delta G_a = \frac{\Delta H_0 + (T/\mu)(\mathrm{d}\mu/\mathrm{d}T)V_0\sigma}{1 - (T/\mu)(\mathrm{d}\mu/\mathrm{d}T)} \tag{2}$$

where ΔH_0 is the activation enthalpy, μ is the shear modulus, and V_0 is the activation volume. Basically, V_0 is an index of the sensitivity of the plastic deformation to strain rate according to the equation:

$$V_0 = RT\left(\frac{\mathrm{d}\ln\dot{\varepsilon}}{\mathrm{d}\sigma}\right)_T \tag{3}$$

Accordingly, V_0 was calculated from the slope of the plots of stress versus logarithm of strain rate (Fig. 2). The calculations were performed at the yield point ($\sigma = \sigma_y$). It was impossible to do the same at the plastic flow stress ($\sigma = \sigma_{pf}$), because σ_{pf} could not be evaluated systematically.

Finally, ΔH_0 was calculated according to the equation:

$$\Delta H_0 = -TV_0\left(\frac{\mathrm{d}\sigma_y}{\mathrm{d}T}\right) \tag{4}$$

The bases for Equations 2–4 have been detailed some years ago by Haussy *et al.* [27]. All measurements were performed on samples subjected to the same thermal history in order to satisfy the required isostructural conditions.

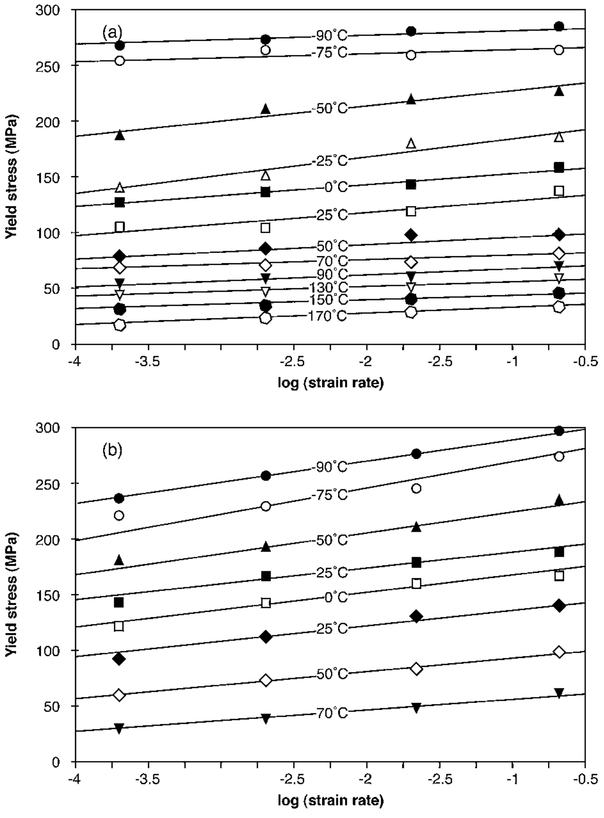


Figure 2 Yield stress versus logarithm of strain rate at different temperatures. (a) Samples M100 and (b) samples M100/A-96.

3. Results and discussion

3.1. Networks without additive

The nominal stress-strain curves of these networks exhibit exactly the features already reported by Mayr *et al.* [7]. For the systems with low cross-link density (H5, H40, M5, M40), a well-defined yield stress maximum was systematically observed. On the other hand, this maximum was less and less apparent as long as the cross-link density was increased up to the case of densely cross-linked networks (H100, M100, S100).

Focusing on the σ_y values of systems differing by network architecture and (or) chemical formula, it is worth restating the arguments presented firstly by Lesser and Kody [28] and then by Mayr *et al.* [7]. These authors claimed that molecular mobility is the factor governing the yield stress and that the main role of cross-link density on yielding should be in its effects on molecular mobility and hence on glass transition temperature. In accordance to these ideas, they suggested to use the plots of σ_y (T) versus $T_g - T$ for system comparison purpose. Application of this data analysis procedure was performed for both series of flexible semi-aromatic resins H and of rigid aromatic resins M. In each series, the results cross-check the earlier findings [7, 28]: at constant chain flexibility, the lower the cross-link density, the higher the σ_y value. Comparison, in the same way, of samples of roughly identical cross-link density but quite different chain flexibility is based on the plots of σ_y (T) versus $T_\alpha - T$ given in Figs 4a–c. No influence of chain flexibility is observed while comparing the weakly cross-linked resins M5 and H5. By contrast, for the dense networks, flexibility dependence of σ_y is evidenced almost all over the $(T_\alpha - T)$ range, the rigid resin M100 presenting a weaker resistance to yielding than the more flexible resin H100. The case of the loosely cross-linked resins M40 and H40 is intermediate: no influence of chain flexibility is observed at moderate departure from T_α, and then σ_y becomes higher in the case of the most flexible resin.

Comprehensive interpretation of this set of results can be achieved by using the molecular line of reasoning, which has proven to be suitable for the thermoplastic polymers [1–6].

Obviously, the β-type relaxation motions play a prominent role in this analysis: at given $(T_\alpha - T)$ and network chemical structure, the observed increase in σ_y with decreasing cross-link density (Fig. 3) results directly from the relevant loss of the cooperative β motions [10, 11]. Indeed, if most of the large-scale mobility sites disappear, then the initiation of yielding becomes more difficult and, in turn, σ_y increases.

Let us now assume, as a first approximation, that, at given $(T_\alpha - T)$, the σ_{pf} values, which are governed by the α-relaxation motions, do not depend too much on the network cross-link density at fixed chemical structure. Then, the increase in σ_y would be responsible for most of the strain softening SSA, which increases as well with decreasing cross-link density. As far as some

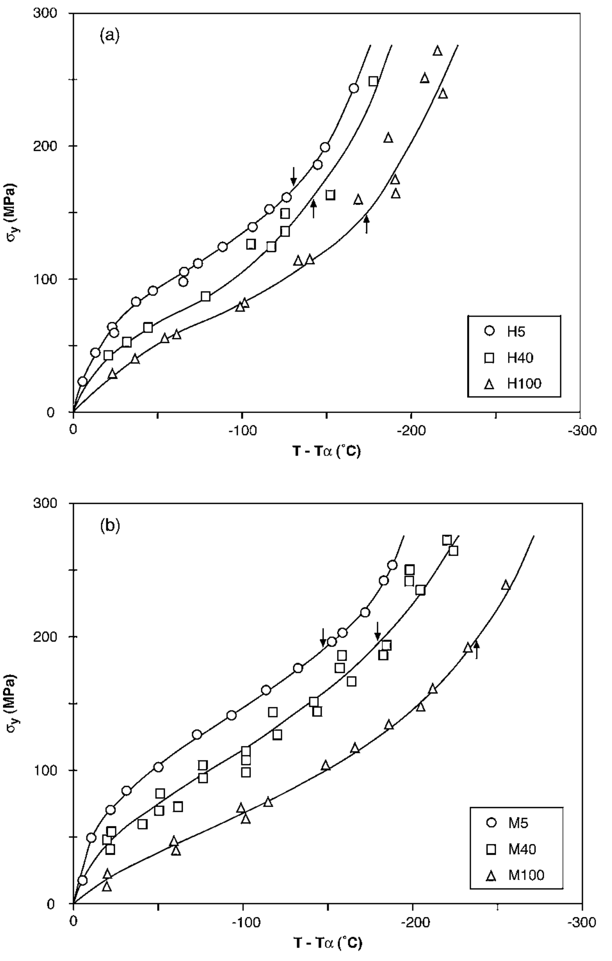


Figure 3 Yield stress versus departure from main mechanical relaxation temperature, $T - T_\alpha$ (the arrows indicate the location of the maximum of the β-relaxation at 1 Hz.) (a) Samples H5, H40, and H100 and (b) samples M5, M40, and M100.

differences are observed between the resins compared in Figs 3 and 4, it can be accounted for them by considering the position of the β relaxation maximum [29], marked by an arrow on the plots. It turns out in any case that σ_y values relative to $T_{\beta\,\max}$ are roughly identical. Finally, further evidence for the implication of β relaxation motions in yielding processes can be given by inspecting the profiles of activation volume, V_0, and activation enthalpy, ΔH_0. As illustrated in Fig. 5 on the example of the resin M100, both quantities present marked jumps, much larger than the error bars on the calculations: first at the onset of the β relaxation, then on the temperature range where highly cooperative motions appear, and finally at the approach of T_g. The features are consistent with earlier reports on the subject [30, 31].

3.2. Networks M antiplasticized by the additive A

The case of samples containing the additive A is the simplest to analyze, as we are dealing with homogeneous materials, in which the antiplasticizing character of the additive has been clearly evidenced [16, 19, 24]. The yield stress, σ_y versus $T - T_\alpha$ and compressive modulus, E versus $T - T_\alpha$ for the samples containing two different proportion of the additive A, namely M100/A-66 and M100/A-96 are shown in Fig. 6. Data relative to the neat network M100 are also given, for sake of comparison. These figures clearly indicate that additive A behaves as a true antiplasticizer for a given departure of T_α: as the content of A in the network increases, then both yield stress and compressive modulus values increase. In other words, yield stress curves arrange themselves by following the modulus order: the more cohesive the material, the larger its resistance to plastic deformation. From a quantitative viewpoint, it is interesting to examine the quantity σ_y/E, reported

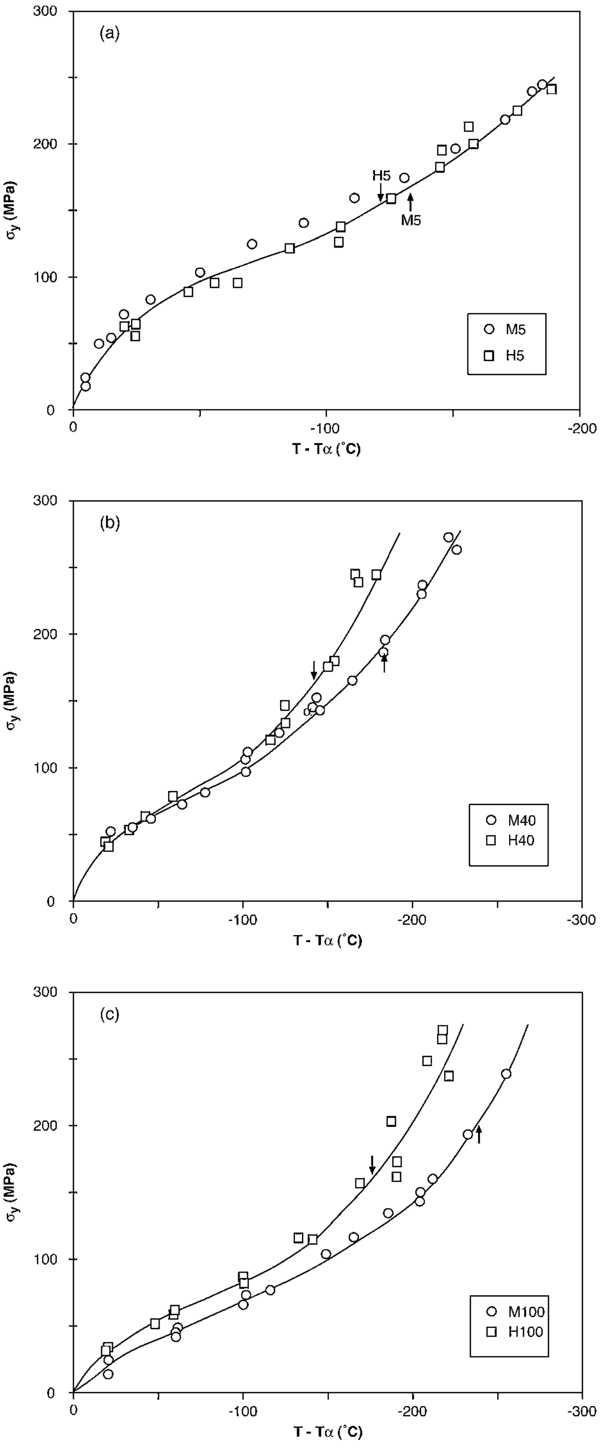


Figure 4 Yield stress versus departure from main mechanical relaxation temperature, $T - T_\alpha$ (the arrows indicate the location of the maximum of the β-relaxation at 1 Hz.) (a) Samples H5 and M5, (b) samples H40 and M40 and (c) samples H100 and M100.

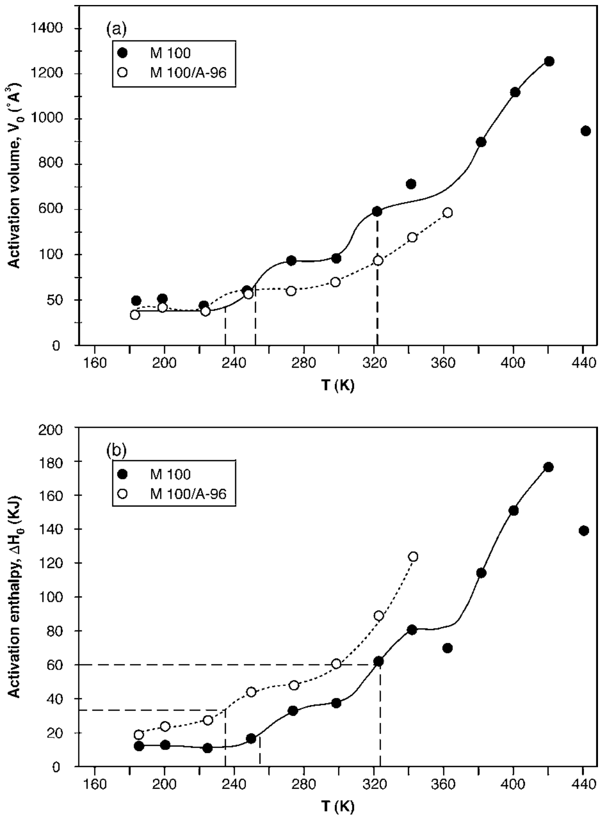


Figure 5 Activation volume and activation enthalpy versus temperature for the pure resin M100 (solid line) and for the antiplasticized network M100/A-96 (dotted line). (a) Activation volume, V_0 and (b) activation enthalpy, ΔH_0.

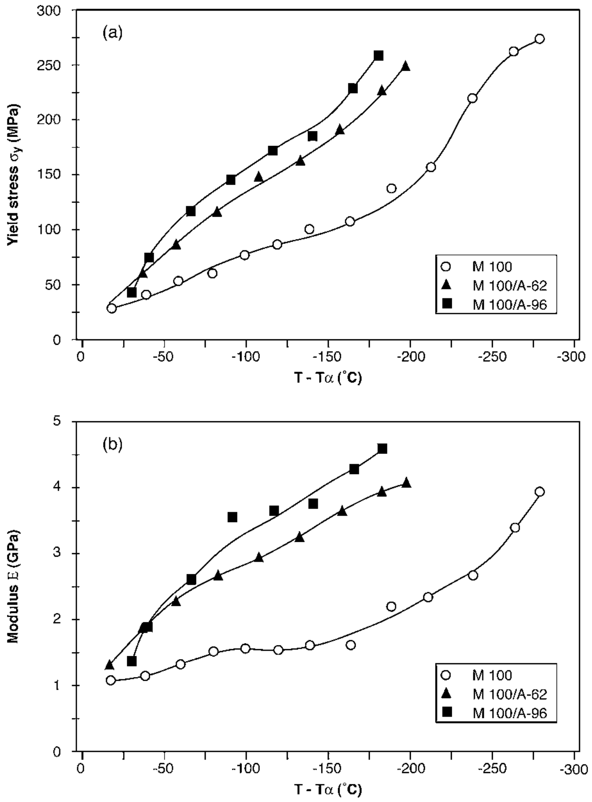


Figure 6 Yield stress and elastic modulus versus $T - T_\alpha$ for the samples M100 (circle), M100/A-62 (triangle) and M100/A-96 (square). (a) Yield stress, σ_y and (b) elastic modulus, E.

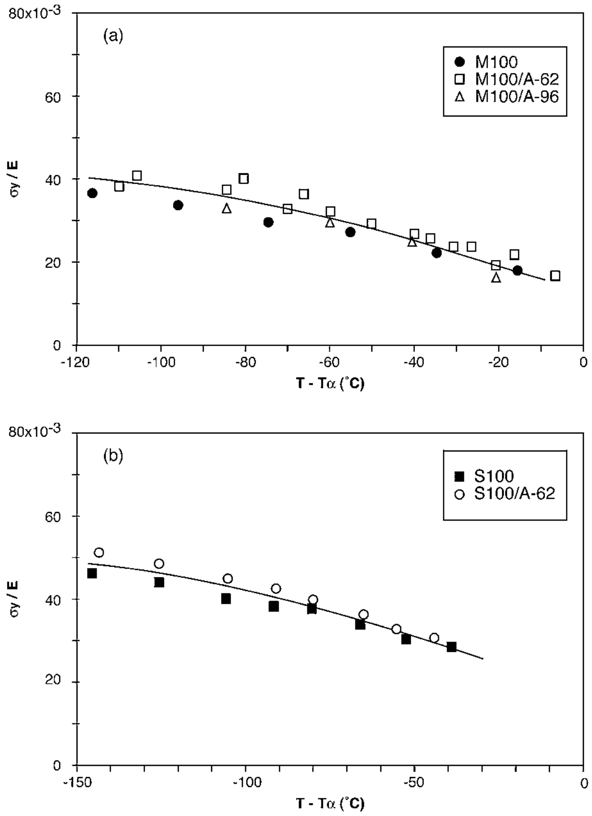


Figure 7 Effect of additive A on the plots of yield stress normalized by the elastic modulus, σ_y/E versus $T - T_\alpha$. (a) Pure and modified resins of the series M and (b) pure and modified resins of the series S.

directly as a function of $T - T_\alpha$ (Fig. 7). Within the experimental error on the measurements, data relative to the pure and antiplasticized resins fall on a unique master curve. Similar conclusion have been obtained for many systems including polystyrene [1], polycarbonate and semi-aromatic polyamides [4], plasticized poly(vinyl chloride) [6]. In these cases, no coupling exists between the α and β relaxation processes, exactly as in the antiplasticized epoxy resins.

In addition, one may observe that strain softening, which is almost lacking in M100, appears in the materials M100/A-29 to M100/A-96 (Fig. 1). This feature can be interpreted by the disappearance of the cooperative β motions. The fact that antiplasticization and introduction of primary monoamines in the formulations have the same effect on the strain-softening phenomenon (see previous section) support well this conclusion. The same trends have already been reported for methyl methacrylate-based random copolymers [1, 2]: in that case, strain softening was shown to increase dramatically as long as the α motions are decoupled from the β motions.

Furthermore, let us compare the activation volume, V_0, and the activation enthalpy, ΔH_0, of the modified networks to those of the pure resin (Fig. 5a and b). The ΔH_0 value is about two times larger for the antiplasticized network M100/A-96 than for the neat one, in good agreement with the increased resistance of the material to plastic deformation. At the same time, V_0 value becomes lower for the antiplasticized networks than that of the neat ones because the spatial extent of the mobility sites associated to the β relaxation is reduced. It is worth noting, in addition, that jumps in V_0 and ΔH_0 ascribed to the cooperative β motions in M100, disappear in M100/A-96 profiles, as expected.

3.3. Networks S antiplasticized by the additive A

As reported elsewhere [19, 24], the additive A is a quite good antiplasticizer of the matrix S, to which it remains miscible all along the network construction. Stress-strain measurements were carried over a narrower range of temperatures ($-20°\text{C} < T < 80°\text{C}$) than for the resin M. However, this range was wide enough to validate the findings deduced from the study of series M resins. Indeed, the temperature dependence of σ_y is comparable to the M and S resins whether they are pure or modified; the antiplasticizing power of additive A induces a marked increase in σ_y. Moreover, normalization of σ_y values by modulus brings back the different curves to a unique profile as a function of $T - T_\alpha$ (Fig. 7b). Comparison of Fig. 7a and b also shows that, at given $T - T_\alpha$, the values of σ_y/E do not depend markedly on the chemical nature (S or M) of the matrix. This observation reinforces the idea that mobility and cohesion effects mainly govern yield behavior of these materials.

3.4. Networks antiplasticized by the additives C and O

Irrespective of the series of resins (M or S) under consideration, analysis of their yield behavior in the presence of additives C and O is complicated by the biphasic character of the materials [19, 20, 24]. According to these reports, one should bear in mind that the so-called μ phase is spread within the matrix in the form of very small domains, markedly enriched in additive; flexibility in these domains is quite high, as indicated by the low value of the T_g, around 50°C. By contrast, the continuous phase, so-called α, is more rigid (T_g around 110–120°C, depending on the formulation) and lightly impoverished in additive. Let us give an order of magnitude of phase composition on a selected example: for the samples M100/C (or O)-62, it has been reported [20] that the weight fraction of additive, which equals about 0.15 in the initial mixture of monomers, would be around 0.13 and 0.30 in the α and μ phase, respectively.

Actually, when compared at same nominal amount of additive, the profiles of σ_y versus $T - T_\alpha$ rank the networks modified by the additives C and O just in between those relative to the pure network and the network modified by the additive A. This observation holds for the resins M (Fig. 8a) and for the resins S as well (Fig. 8b). A priori, two explanations may account for these features. Firstly, one could argue that σ_y is lower for the additives C and O than for the additive A, because of the presence of the new μ phase sites of mobility, which favor yield initiation. And secondly, one could suggest that the effect is imputable to the α phase, which is less antiplasticized by the additive because of its lower amount in this phase. These two arguments are not exclusive form each other and, maybe, both effects contribute to the observed behavior. However, the former seems to be weaker, inasmuch as no evident drop in σ_y is observed while passing T_μ, marked by arrows in Fig. 8a and b.

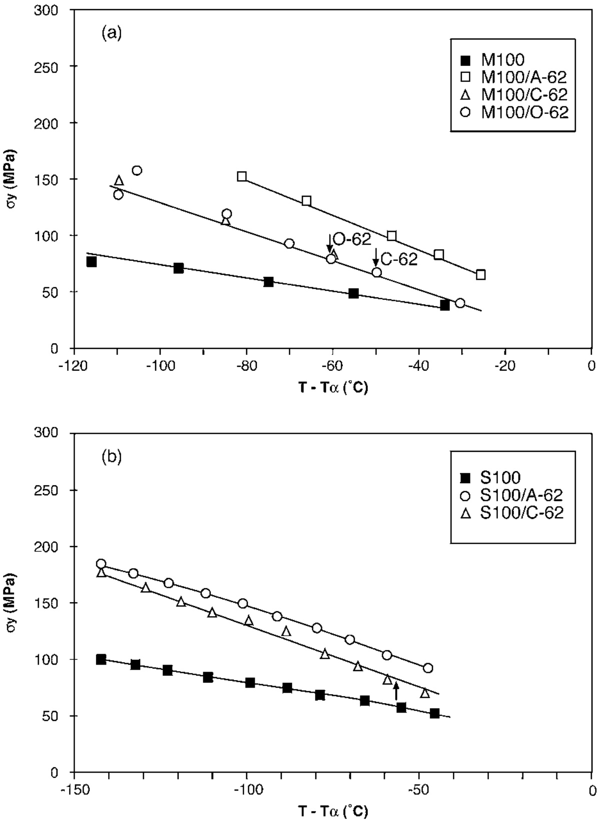


Figure 8 Effect of additives C and O on the plots of yield stress, σ_y versus $T - T_\alpha$ (the arrows indicate the location of the maximum of the β-relaxation at 1 Hz). (a) Pure and modified resins of the series M and (b) pure and modified resins of the series S.

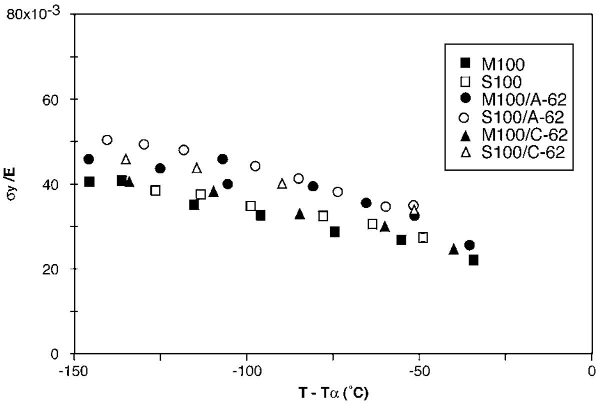


Figure 9 Comparison of plots of σ_y/E versus $T - T_\alpha$, irrespective of network formulation.

Anyway, it is clear from Fig. 9 that all the plots of σ_y/E versus $T - T_\alpha$ lie, at least as a first approximation, on a unique master curve, irrespective of the homogeneous or biphasic character of the materials. This observation is consistent with the idea that the yield initiation events probably occur in the α-phase.

By the way, it is interesting to confront the yield behavior of the networks modified by the additives C and O with their reported improved toughness [19, 20]. While comparing toughness of the pure resin with that of the C and O modified ones, it does not matter to do that on the direct temperature scale or on the $(T - T_\alpha)$ scale, because the stress intensity factor, K_{Ic}, exhibits a very weak temperature dependence [20]. Thus, the observed increase in K_{Ic} cannot be connected with a lower resistance by yielding: the plots of Fig. 8, indeed, reveal higher σ_y values for the modified than for the pure resins at given ($T - T_\alpha$). As tentatively proposed in reference [19], toughening would just result here from the special morphology of the phase μ, which is unlikely to affect the yield behavior.

4. Conclusions

Similar to various amorphous thermoplastic polymers, yielding properties of epoxy-amine thermosets are strongly influenced by the β-relaxation motions, which develop below room temperature in these materials.

In particular, occurrence of sub-T_g cooperative motions, characterized by a larger spatial extent than the well-known isolated ones, favors the initiation of plastic deformation processes and, therefore, decreases the yield stress values, σ_y, at given departure ($T - T_\alpha$) from the main mechanical relaxation T_α. Addition in the formulations of primary monoamines or of antiplasticizing additives, which are two equivalent routes towards the disappearance of the cooperative β-motions, leads to increase of the resistance to plastic deformation, in the form of an increase in σ_y values. In the same time, strain softening shows up on the stress-strain curves.

All the networks under study present almost the same profile of evolution of σ_y/E as a function of ($T - T_\alpha$), and that, irrespective of the network cross-link density, of the possible presence of an antiplasticizer, and of its state of dispersion within the matrix. This finding emphasizes the influence of molecular cohesion on the yield behavior of these materials.

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