

**EPOXY/LAYERED-SILICATE NANOCOMPOSITES:
EFFECT OF THE MATRIX COMPOSITION
ON LARGE DEFORMATION AND FRACTURE BEHAVIOUR**

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ABSTRACT

In this paper the effect of the resin/hardener ratio on the post-yield and fracture behaviour of neat epoxy resins and epoxy/layered-silicate nanocomposites is investigated. Tensile tests, performed at room temperature and at 120°C, and DMTA tests permitted to obtain information on the filler reinforcement effect and on the materials cross-link density. The yield and post-yield behaviour was investigated in compression tests performed at room temperature up to large deformation levels. It was shown that the matrix composition and the filler presence have a substantial effect on the yield stress and on the strain softening and hardening behaviour, and these latter two appeared to be significantly ruled by the matrix cross-link density. The fracture behaviour was studied at room temperature in experiments performed at low rates. An enhanced fracture toughness and the presence of plasticity for epoxy resins with the highest cross-link density was found, whereas the other epoxies behaved in a brittle manner. With the introduction of the nanofiller different mechanisms are supposed to govern the fracture process and lead to a brittle behaviour for all the systems independently from the matrix composition.

1. INTRODUCTION

It is known that the final properties of epoxy resins depend on their chemical structure, and that the parameters related to the matrix chemical composition and the curing cycle are often varied in order to obtain optimum performances. In particular, the use of specific resin/hardener ratios is needed to achieve the best balance of properties.

Due to the possibility of understanding their molecular architecture, epoxy resins are often adopted as model systems to obtain structure-property relationships, both from an experimental and theoretical standpoint. The attention of researchers has often focused on the dependence of yield [1], post-yield [2], and fracture properties [3-4] on the material molecular structure, which is seen to have significant effects on large deformations mechanisms. Further, considerable research on the mechanical behaviour of nanocomposite materials has been done by choosing epoxy resins as matrix, in order to achieve a better understanding of the reinforcing mechanisms promoted by the addition of nanometric fillers.

Although a great enhancement of mechanical properties is expected by the addition of high interface fillers such as layered silicates, at least in the case of epoxy-based nanocomposites only moderate improvements are often observed experimentally. Such results highlight the need to investigate how the production parameters affect the performance of these materials. Whereas so far work has concentrated on topics such as the cure kinetics and the effect of changing matrix-filler interactions, only limited work has been done on the optimization of the resin/hardener ratio in nano-filled epoxy systems.

Therefore, in this work the effects of the resin/hardener ratio on the yield, post-yield and fracture properties of epoxy/layered-silicate nanocomposites were investigated.

2. EXPERIMENTAL

2.1 Materials

The materials examined were obtained by curing DER 330, a poly (bisphenol A-co-epichloridin)glycidyl end-capped ($M_{n,expt} = 363$ g/mol), with Jeffamine D230, a poly(oxypropylene) diamine ($M_{n,expt} = 248$ g/mol), using resin/hardener equivalent ratios (q , defined as equivalents of resins over equivalents of hardener) ranging between 0.75 (excess of hardener) and 1.07 (excess of resin). The resin/hardener ratio investigated were 0.75, 0.86, 0.93, 1 and 1.07. For each value of q , neat resin and a nanocomposite with 6 phr of a commercial organo-modified montmorillonite (Nanomer I30TC) were produced. Cylindrical and rectangular specimens were obtained by casting the neat and filled systems in a silicon mould and curing them firstly at 80°C for 21h, and subsequently at 120°C for 4h.

The structural characterization of the nanocomposites was carried out by wide angle X-ray diffraction (WAXD) in order to investigate the dispersion of organo-clay platelets within the matrix, and an exfoliated or a highly intercalated structure was revealed for all the filled materials.

2.2 Experiments

The mechanical behaviour of the various materials was preliminarily investigated via tensile tests and dynamical-mechanical thermal analysis (DMTA). Tensile properties were measured on rectangular bars (gauge length: 90 mm; section: 7 x 2 mm) by means of an universal testing machine (Instron, Mod. 3366). The tests were performed at room temperature (~22°C) and at 120 °C with a crosshead speed of 0.5 mm/min. The elastic modulus was evaluated by means of a contact extensometer only in the tests performed at room temperature, while at 120°C, due to a restrictions in the thermal range of utilization of the extensometer, the modulus was evaluated from data obtained by the crosshead displacement. The measurement of the ultimate properties at room temperature required additional tests, performed without the employ of the extensometer. DMTA tests were carried out on a MkII Polymer Laboratories under a single-cantilever bending mode at a frequency of 5 Hz. A temperature range between 40°C and 140°C was explored, with a heating rate of 0.5 °C/min. systems.

Yield and post-yield behaviour was investigated by means of compression tests performed on cylindrical specimens, presenting an average diameter of 7 mm and a height of 10 mm. Compressions were all carried out at room temperature adopting a crosshead speed of 0.5 mm/min up to a maximum nominal strain level of about 50%. Before each test a thin layer of paraffin oil was laid on the compression plates to minimize the friction with the specimen surfaces during the tests. In order to obtain true-stress vs. true-strain curves the changes in specimens diameter during the tests were monitored by means of a photo-camera at a sampling rate of an acquisition every 5 seconds. True-stress, σ_t , was evaluated as:

$$\sigma_t = F / A \quad (1)$$

where F and A represent the load and the specimen cross-section, respectively, as measured at a same deformation level; true-strain, ϵ_t , was evaluated as:

$$\epsilon_t = \ln \lambda \quad (2)$$

where $\lambda = l / l_0$, and l and l_0 are the actual height of a deformed cylinder and its initial height, respectively. The obtained data were also plotted as true stress vs. $\lambda^2 \cdot \lambda^{-1}$, since such a representation permits the evaluation of the strain hardening modulus [7], defined as the slope of the curve for deformations levels within the strain hardening region.

For the measurements of the fracture properties of the various materials, two different fracture mechanics methodologies were used: a linear elastic fracture mechanics approach (G_{Ic}) [5], and an elastic-plastic fracture mechanics methodology (J-integral) [6] for brittle and ductile behaviours, respectively. The fracture tests were performed by the Instron dynamometer cited above on single-edge notched in bending (SE(B)) with nominal dimensions 45 x 7 x 2 mm, at a crosshead speed of 2 mm/min and at room temperature. The sharp notches, characterized by a nominal crack depth to width ratio of 0.45, were produced on the specimens by means of a notching machine by Ceast SpA (Pianezza, Torino, Italy). The nanocomposite specimens with $q = 1.07$ were not tested since, due to their extreme fragility, it was not possible to realize a notch avoiding breakage.

3. EXPERIMENTAL RESULTS

3.1 Thermo-mechanical characterization

A mechanical characterization of neat and filled resins obtained with various resin/hardener ratios was performed in tensile tests at room temperature, and the results concerning stiffness and ultimate properties of the materials are summarized in Table 1. The resin/hardener ratio, q , has only a slight effect on the Young's modulus, which for both filled and neat resins assumes the lowest values for intermediate q ratios. For all q values neat resins display at this temperature low deformation levels at break, below 5%, and a stress at break of about 60MPa. Incorporation of the nanofiller leads only to a moderate increase in stiffness (of about 10% for each q), and to an evident reduction of the ultimate strain and, in a less significant manner, of the ultimate stress.

Table 1: Stiffness and ultimate properties measured in tensile tests on neat (0 phr) and filled (6 phr) resins with various resin/hardener ratios, q , at room temperature.

q	E_{tens} (GPa)		σ_b (MPa)		ϵ_b	
	0 phr	6 phr	0 phr	6 phr	0 phr	6 phr
0.75	3.04 ± 0.03	3.34 ± 0.08	57.7 ± 2.3	53.6 ± 5.9	0.041 ± 0.003	0.026 ± 0.005
0.86	2.94 ± 0.06	3.23 ± 0.04	60.3 ± 2.5	55.5 ± 9.9	0.050 ± 0.003	0.028 ± 0.008
0.93	2.88 ± 0.06	3.18 ± 0.08	57.5 ± 0.5	58.9 ± 3.9	0.044 ± 0.001	0.031 ± 0.004
1	2.97 ± 0.09	3.26 ± 0.10	65.9 ± 0.9	53.6 ± 1.2	0.045 ± 0.002	0.024 ± 0.002
1.07	3.08 ± 0.01	3.40 ± 0.06	58.1 ± 6.0	47.0 ± 8.2	0.029 ± 0.005	0.019 ± 0.005

A dynamical-mechanical analysis was performed on all the systems in order to gather information on the effects promoted by the resin/hardener ratio and by the nanofiller presence on the glass transition temperature. The glass transition temperature, evaluated as the peak temperature of the $\tan \delta$ traces, is reported for both neat and filled resins in Figure 1a as a function of the resin/hardener ratio, and seems to have for both epoxies

and nanocomposites a non monotonic dependence on q , with maximum values for $q = 0.93$ and 1 . The addition of the nanofiller, with exception of $q = 0.75$, does not promote significant T_g shifts.

Further tensile tests were performed at 120°C , a temperature that the E' traces from DMTA tests proved to be within the rubbery plateau region for all the materials. The elastic modulus evaluated at this temperature can be regarded as a measure of the cross-link density. It is interesting to observe that the elastic modulus of both neat resins and nanocomposites exhibits maximum values for intermediate resin/hardener ratios. This allowed us to conclude that the T_g dependence on q can be interpreted as mainly due to the changes in the cross-link density of the material.

Further, results also show that nanocomposites present for each value of q a higher tensile modulus compared with the neat matrix. With concern of such result, the future considerations on the effects of the cross-link density on the nanocomposites behaviour have to be cautiously regarded. In fact it has to be remarked that $E_{120^\circ\text{C}}$ can be reasonably considered as a measure of the network cross-link density for neat resins, but not for the nanocomposites. The modulus values presented by these latter systems are not only dependent on the matrix cross-link density, but also on a superposed reinforcement effect of the nanofiller.

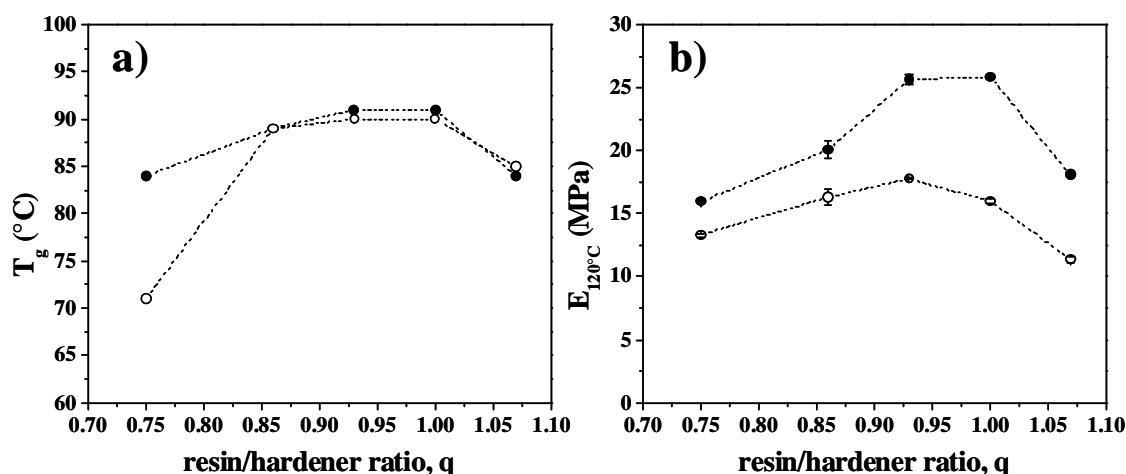


Figure 1: a) Glass transition temperature, T_g , and b) rubber-like plateau modulus, $E_{120^\circ\text{C}}$, for neat (\circ) and filled (\bullet) resins with various resin/hardener ratios.

3.2 Yielding and post-yielding behaviour

The effect of the resin/hardener ratio on yield and post-yield behaviour was investigated for all the materials in uniaxial compression tests performed. True stress vs. true strain curves were obtained, and from their representation at room temperature in Figures 2a and b it can be seen that compression tests allowed us to investigate for all materials their mechanical response for deformations up to post-yield levels.

All the systems investigated exhibit the occurrence of yielding, followed by a gradual decrease of the load in the strain softening region, and by a subsequent strain hardening, where the load increases again with the deformation. Whereas elastic modulus evaluated in these tests seem to be unaffected by q and by the presence of the nanofiller, for both neat and filled resins the resin/hardener ratio is clearly influencing the yielding and post-yield behaviour. In fact, the curves of the materials with different q differ for the yield stress value, σ_y , for the so called “yield drop”, $\Delta\sigma_y$, which represents the difference between the yield stress and the minimum stress in the strain

softening region, and finally for the slope of the stress-strain curve in the strain hardening region.

Figures 3a and b report for all the materials the yield stress and the yield drop, respectively, as a function of q . Yield stress displays an increasing trend with the resin/hardener ratio for both materials. Although for each matrix composition the values of σ_y displayed by neat and filled resins are quite similar, it is interesting to remark that the addition of the nanofiller leads to a less pronounced dependence of yield stress on q . The overall reduction of stress within the strain softening region displays a non monotonical dependence on the resin/hardener ratio, and $\Delta\sigma_y$ assumes for both families the lowest value for $q = 1$. Further, this stress decrease is observed to be reduced by the addition of the nanofiller.

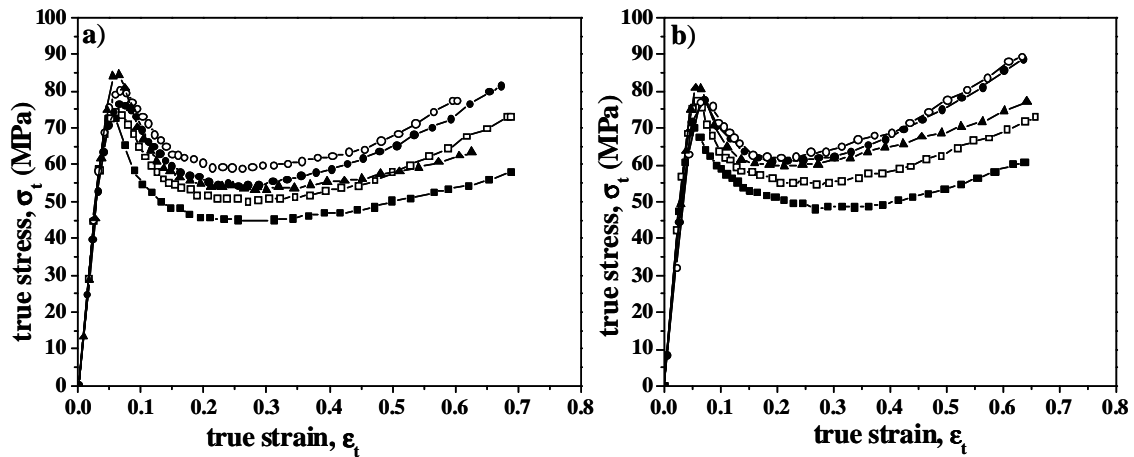


Figure 2: True stress vs. true strain curves for a) neat and b) filled resins with different resin/hardener ratios, q (■: 0.75; □: 0.86; ●: 0.93; ○: 1; ▲: 1.07).

The different dependences of σ_y and $\Delta\sigma_y$ on the resin/hardener ratio suggest that these two large deformations parameters are differently affected by the material chemical composition. Consistently with results obtained by van Melick et al. on cross-linked amorphous polymers [7], it can be concluded that yield stress, which is mainly dependent on secondary interactions between polymer chains, depends mainly by the amounts of resin added to the chemical composition but not on the epoxy cross-link density. The strain softening behaviour is ruled as well by secondary chemical interactions, but in this case the yield drop seems to be governed by the network density, so that a lower decrease in stress occurs for a higher cross-link density. Following the interpretation proposed in the cited work [7], the network structure is thought to have a stabilising effect on the softening behaviour, reducing the true stress drop as the network density increases. Further, the addition of the nanofiller seems to partially hinder the chains mobility, thus reducing, with respect to the case of the neat resin, the dependence of σ_y on q and the decrease of stress $\Delta\sigma_y$ for a same matrix chemical composition.

In the strain hardening region the slope of the stress strain curve is seen to depend for both neat resins and nanocomposites on the resin/hardener ratio. The evaluation of a strain hardening modulus was possible after having detected, for these strain levels, a linear proportionality between true stress and $\lambda^2\lambda^{-1}$, as first proposed by Mooney for rubbery elastic materials [8] and by Haward on amorphous glassy polymers [9].

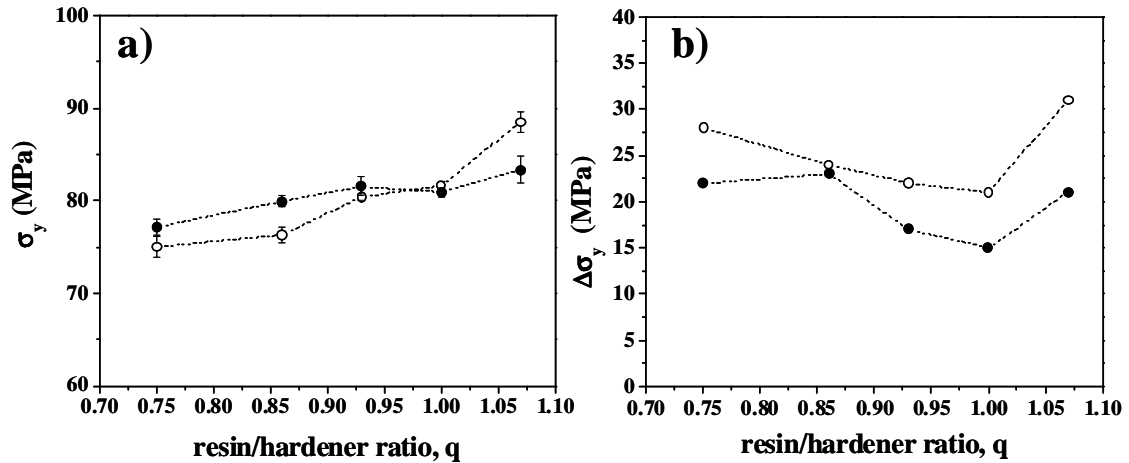


Figure 3: a) Yield stress, σ_y , and b) yield drop, $\Delta\sigma_y$, for neat (\circ) and filled resins (\bullet) as a function of the resin/hardener ratio.

Such linear trend not only helped us in achieving a proper evaluation of the strain hardening modulus, but also indicated the possibility of describing by means of a neo-Hookean (Gaussian) relationship the deformational behaviour of epoxy and epoxy based nanocomposites at large strains.

Strain hardening modulus, E_{SH} , is reported for all the materials in Figure 4a and b as a function of the resin/hardener ratio and of the corresponding rubbery plateau modulus, respectively. A non monotonic dependence of E_{SH} on q is shown for both neat and filled resins, and it is observed that the presence of the nanofiller leads to a higher strain hardening modulus for each value of q . The strain hardening modulus increases thus with the network density, as it can be understood from Figure 4 and consistently to a neo-Hookean approach to large deformations mechanics [7]. A different dependence of E_{SH} vs. q is observed for neat resin and nanocomposites follow different dependence on q , but it has to be reminded that in the case of nanocomposites the rubbery modulus can not be regarded as a measure of the crosslink density as it can be done for the pure resin, and thus further investigations have to be performed to better highlight the effect of the nanofiller presence in these systems.

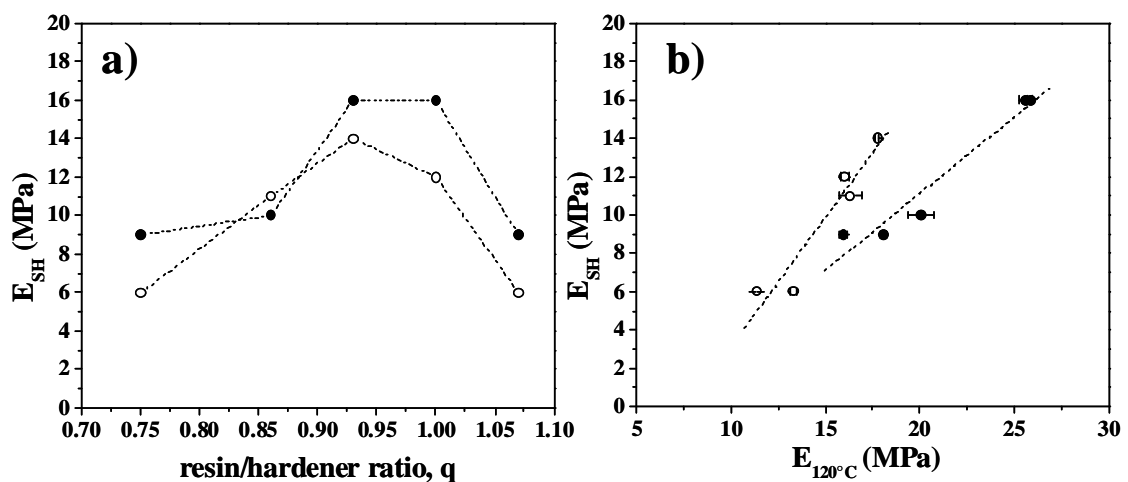


Figure 4: Strain hardening modulus, E_{SH} , as a function of a) resin/hardener ratio, q and b) $E_{120^\circ C}$ for neat (\circ) and filled resins (\bullet)

3.3 Fracture behaviour

The effect of the resin/hardener ratio on the material fracture resistance was evaluated on neat resins and nanocomposites via fracture mechanics tests performed at room temperature and at low rate. Since tensile tests performed at room temperature revealed for all the materials a brittle behaviour, fracture resistance was evaluated by tentatively adopting a Linear Elastic Fracture Mechanics (LEFM) approach [5] on SEN(B) specimens.

The load vs. displacement curves for the neat resins are represented in Figure 5, and it can be seen that the resin/hardener ratio significantly affects the materials fracture behaviour. For the values of $q = 0.75, 1$ and 1.07 the load is seen to increase linearly before an abrupt fall, confirming a brittle behaviour and the validity of the LEFM approach; by contrast, for the values of $q = 0.86$ and 0.93 a deviation from a linear behaviour is found. For these latter compositions the curves present a maximum for load values higher than those found for the other values of q , and, subsequently, a progressive decrease of the load as the displacement increases. This behaviour is also accompanied by the development of an extended plastic region at the crack tip, as can be seen by comparing the fracture surfaces of a specimen characterized by brittle behaviour (Figure 5, picture a: $q=0.75$) and a specimen with a ductile one (Figure 5, picture b: $q=0.86$). The presence of plastic deformation mechanisms occurring at the advancing crack tip is clearly evident for the ductile specimen, whereas the brittle one presents a glassy-like surface other specimen. For the resins presenting a more ductile fracture, fracture toughness was evaluated as J_{Ic} by the application of the J-integral methodology [6].

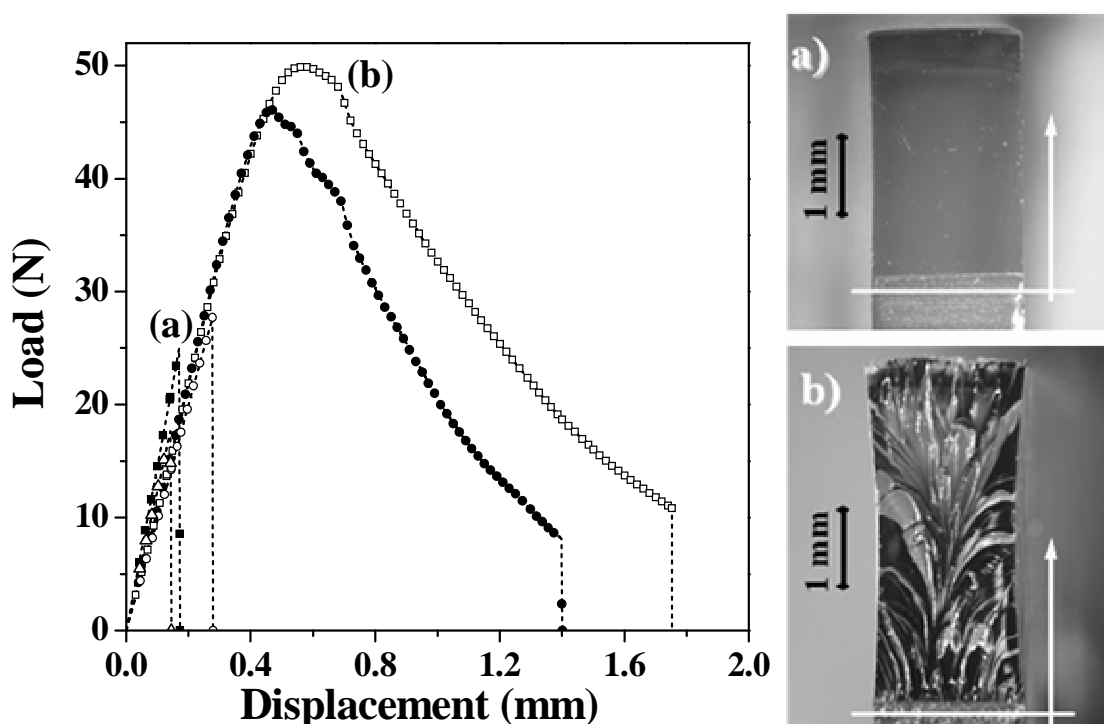


Figure 5: Load vs. displacement curves for fracture tests on SEN(B) neat resin specimens with various resin/hardener ratios, q (\blacksquare :0.75; \square :0.86; \bullet :0.96; \circ :1; Δ :1.07), and fracture surface for specimens with $q = 0.75$ (a, corresponding to curve (a)) and 0.93 (b, corresponding to curve (b)).

The nanocomposites revealed for all values of resin/hardener ratio a brittle behaviour (see Fig. 6). Only two materials ($q = 0.75-0.86$) presented a less abrupt fall of the load to zero, with anyway only a minor effect on the resistance to the fracture propagation. The behaviour can thus be considered brittle for all the materials, and the LEFM approach could be successfully applied to evaluate their resistance. The fracture surface can be described for all the materials as a plane surface characterized by the presence of a certain roughness; the picture in Fig. 6 reports, as an example, the fracture surface of a specimen with $q = 0.75$.

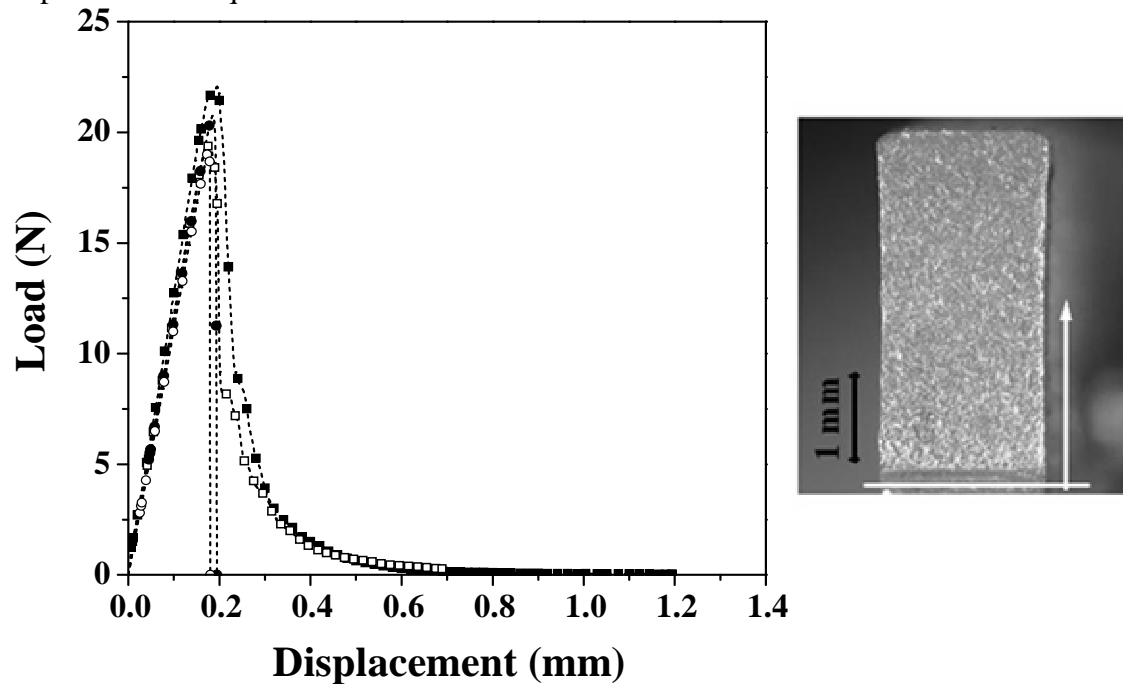


Figure 6: Load vs. displacement curves for fracture tests on SEN(B) nanocomposite specimens with various/resin hardener ratios, q (\blacksquare :0.75; \square :0.86; \bullet :0.93; \circ :1), and fracture surface for a specimen with $q = 0.75$.

The values of fracture resistance measured on all the materials are presented as a function of the resin/hardener ratio for both neat resins and nanocomposites in Figure 7a.

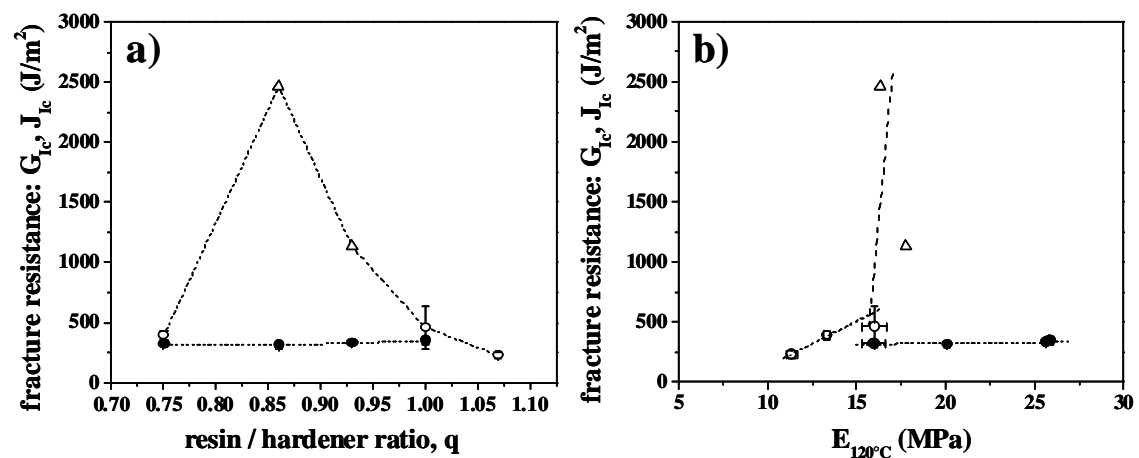


Figure 7: Fracture resistance (\circ , \bullet : G_{Ic} ; Δ : J_{Ic}) for the neat (open symbols) and filled (full symbols) resins as a function of a) resin hardener ratio, q , and b) rubber-like modulus, $E_{120^\circ C}$.

The resin/hardener ratio has an evident influence on the fracture resistance of neat resins, which present a maximum resistance for intermediate q values. On the other hand, the fracture resistance of the nanocomposites is not affected by q , and it can be seen that the presence of the nanofiller reduces the fracture resistance for each q value with respect to that measured on the corresponding neat resin. Ductile matrices undergo a significant embrittlement when the nanofiller is added, and such an effect might be interpreted as due to local confinement of the polymer chains, whose possibility of deforming plastically is severely hindered. Further, it is interesting to note that also when the matrix has brittle behaviour, the presence of the filler reduces, even if only slightly, the material fracture resistance. In spite of similar fracture resistances, neat and filled resins present also different fracture surfaces, suggesting that with the introduction of the filler different fracture mechanisms are governing the behaviour of the nanocomposites.

Figure 7b represents the fracture resistance of the various materials as a function of their corresponding rubbery plateau moduli to evidence possible effects the material cross-link density. The fracture resistance of the nanocomposites, due to the brittle behaviour promoted by the filler, seems to be unaffected by the apparent matrix cross-link density. On the other hand, for the neat resins, interestingly, the peak in fracture resistance is found for the materials with the highest cross-linking degree, although the reason of such an effect is not fully understood and further experiments are required to explain this behaviour.

4. CONCLUSIONS

The investigation of post-yield and fracture behaviour of neat and filled resins evidences the dependence of the materials mechanical response on the matrix composition. Further, for a same value of the resin/hardener ratio, the addition of a layered-silicate nanofiller is seen to influence the material behaviour. As concerns yielding, whose nature is ruled by secondary interactions, it is seen that as the amount of epoxy resin is increased with respect to the hardener fraction, the yield stress increases, and that such an increase is more pronounced in neat epoxies than in the nanocomposites. The strain softening and strain hardening behaviours of both neat and filled resins are also dependent on the cross-link density of the obtained resins. For a neat resin a lower yield drop and a higher strain hardening modulus are exhibited for a higher cross-linked density. Further, for each value of the resin/hardener ratio, the addition of the filler leads to a reduction of the yield drop, and to a higher strain hardening modulus, and these effects are interpreted as a local hindrance of the molecular mobility exerted by the filler. As concerns fracture, the neat resin behaviour is seen to be significantly dependent on the resin composition. An enhanced fracture resistance, accompanied by an evident plastic deformation at the advancing crack tip, is found for the resins obtained with resin/hardener ratios of 0.93 and 1, whereas a brittle behaviour is observed for the other neat resins. Interestingly, the resins characterized by a ductile fracture behaviour are those with the highest cross-link density. The introduction of the nanofiller into the matrix, on the other hand, leads to a brittle behaviour for all the matrix compositions investigated and to a reduction in fracture resistance with respect to the corresponding neat epoxy. For the nanocomposites, the values of fracture resistance are practically independent from the value of q . In any case, the visual inspection of the fracture surfaces produced on the specimens of the nanocomposites with that of the neat resins which exhibited no sign of ductility suggests that the mechanisms which govern the fracture of nanocomposites differ from those of a brittle neat epoxy.

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