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Toughness Behaviour of Vinylester/Epoxy Thermosets with Interpenetrating Network Structure

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Summary: Vinylester/epoxy-based (VE/EP) thermosets of interpenetrating network (IPN) structure were produced by using a VE resin (bismethacryloxy derivative of a bisphenol-A type EP resin) and EP resins of aliphatic (Al-EP) and cycloaliphatic (Cal-EP) nature. Curing of the EP resins occurred either by an aliphatic (Al-Am) or a cycloaliphatic (Cal-Am) diamine compound. Dynamic mechanical thermal analysis (DMTA) and atomic force microscopy (AFM) suggested the presence of an interpenetrating network (IPN) in the resulting thermosets. AFM scans taken on the ion-etched surface of EP showed a featureless homogeneous structure. On the other hand, VE exhibited a two-phase microgel, whereas VE/EP a two-phase interpenetrating network (IPN) structure. Toughness was characterised by parameters of the linear elastic fracture mechanics, viz. fracture toughness (K_c) and fracture energy (G_c). Unexpected high K_c and G_c data were found for the systems containing cyclohexylene units in the EP network. This was attributed to beneficial effects of the conformational changes along the cyclohexylene linkages (chair/boat). The failure mode of the VE/EP thermoset combinations was studied by scanning electron microscopy (SEM) and discussed.

Keywords: atomic force microscopy (AFM); epoxy resin; fracture mechanics; interpenetrating network (IPN); vinylester resin

Introduction

A family of vinylester (VE) resins is produced by reacting bisphenol-A type epoxy resins (EP) with methacrylic acid. Although such VE resins can form a crosslinking structure without the addition of a comonomer, they are generally diluted in styrene. Styrene is an active diluent (comonomer) that crosslinks via free radical-induced copolymerisation with VE. The further role of styrene is to tailor the viscosity of the VE upon processing request. VE possesses outstanding mechanical and thermal properties but suffers of low toughness similar to most thermosetting resins. It was demonstrated that the toughness of VE can be improved without adding modifiers

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by controlling the crosslink density. This can achieved for example by using VE resins of different molecular mass [1] or by variation of the VE/ styrene ratio [2]. The toughness improvement reached by this method is, however, limited. Contrary to epoxy resins, the toughening of VE by low molecular mass polymeric modifiers was addressed only by few works. In analogy to epoxy and unsaturated polyester resins liquid functional (vinyl-, epoxy-, amino- and carboxyl-) nitrile rubbers were mostly incorporated in VE resin [3-5 and references therein]. The toughness upgrade remained often below the expectation, which was traced to the low solubility of the related rubber in the styrene diluted VE resin.

In previous works [6-8] we demonstrated that the toughness of VE-urethane hybrid (VEUH) resins may be markedly enhanced when using liquid functional (vinyl-, epoxy- and carboxyl-) nitrile rubbers and functional (vinyl- and epoxy-) hyperbranched polymers. The presence of liquid nitrile rubbers leads to reduced stiffness and glass transition temperature (T_g), which is unwanted in most applications. In this work we have considered a novel method to increase the toughness of thermosets: creation of an interpenetrating network structure (IPN). Note that IPN favours the shear deformation, which is the basic failure mode of thermosetting resins. On the other hand, it has to be stressed that IPN formation is usually accompanied also with a T_g reduction.

Experimental

Resins and their Curing

In this study the following thermosetting resins were involved: commercial VE, various EP and proprietary VE/EP (ratio:1/1) formulations [9]. The commercial VE (bisphenol-A based bismethacryloxy type) was a product of DSM Composite Resins (Daron® XP-45-A-2; styrene content: 30 wt.%, ratio of the double bonds VE/styrene=1:1.2). For its curing 0.75 phr (parts per hundred resin) dibenzoylperoxide, and 0.15 phr N,N-diethylaniline as accelerator were used.

The EP resins selected for this study were of aliphatic (Al) and cycloaliphatic (Cal) types. 1,4-butanedioldiglycidylether served as aliphatic (Al-EP) and 1,4-cyclohexane-dimethanoldiglycidylether as cycloaliphatic EP (Cal-EP) - Polypox R3 and R11, respectively, from U. Prümmer Polymer-Chemie GmbH. Al-EP was cured by a cycloaliphatic diamine (Cal-Am) procured from Vantico Ltd. (HY2954 grade: 2,2′-dimethyl-4,4′-methylenbis(cyclohexylamine)), whereas Cal-EP was cured with an aliphatic diamine (Al-Am) purchased from Aldrich (1,2-bis(2-aminoethoxy)ethane). The hardener/EP ratio was stoichiometric in all EP formulations.

The cure regime of the plaques produced in an open PTFE-mould was as follows: room temperature for 12 hours (h), 80 °C for 3 h and 150 °C for 3 h. In same cases a further post-curing step was also inserted (200 °C for 3 h) in order to check a potential improvement in T_g. Further information to the preparation of the resins and their curing is given in our papers [10].

Material Characterisation

The resins were characterised by dynamic-mechanical thermal analysis (DMTA). DMTA spectra were taken on rectangular specimens ($50x10x4\ mm^3$) in flexural mode at 10 Hz using the Eplexor 25N device of Gabo Qualimeter. DMTA spectra, viz. complex modulus (E^*), mechanical loss factor ($\tan\delta$) as a function of temperature (T), were measured in the interval T = -100...+200 °C with a heating rate of 1 °C/min. More fundamental information on the morphology of the VE, EP and VE/EP systems was expected from atomic force microscopic (AFM) studies. Polished surface of the specimens was eroded by Ar^+ ion bombardment in a secondary neutral mass spectrometer [11]. The eroded surface was scanned by AFM (Digital Instruments) in tapping mode and the related amplitude- and height-contrast images captured.

Fracture toughness (K_c) and fracture energy (G_c) were determined in accordance with the ESIS testing protocol on compact tension (CT) specimens [12]. The CT-specimens (dimension: $35x35x4\ mm^3$) were notched by sawing. The notch root of the CT-specimens was sharpened by a razor blade prior to their tensile loading (mode I) at room temperature (RT) with a crosshead speed of v=1 mm/min. Tests were performed on a Zwick universal testing machine type 1445.

In order to get a deeper understanding on the effect of morphology on the fracture mechanical response the surface of broken CT-specimens was inspected in a scanning electron microscope (SEM; JSM-5400 of Jeol). The fracture surface was coated with an alloy of Au/Pd prior to SEM investigations.

Results and Discussion

Simultaneous IPN Formation

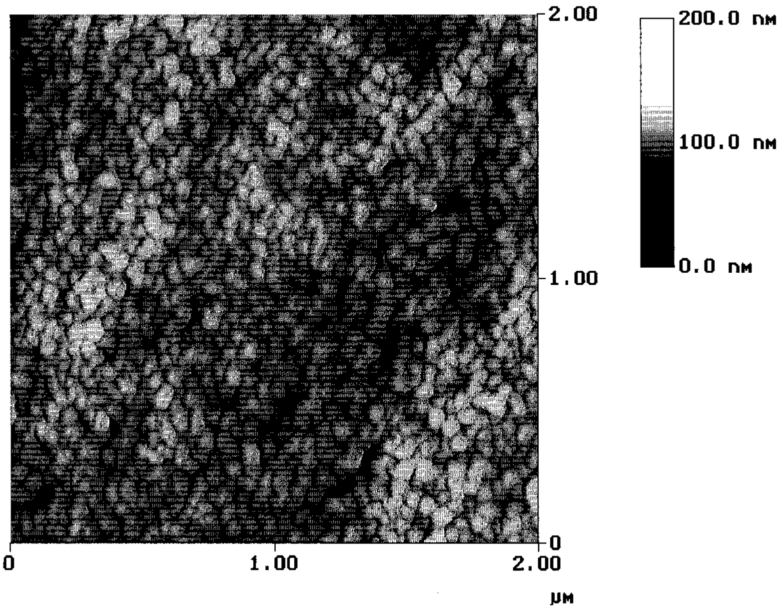

Figure 1.AFM picture (height image) taken on the Ar^+ ion-etched surface of VE

The AFM scan of the VE resin is displayed in Figure 1. Figure 1 clearly shows the nodular structure (also called microgel) of the VE. Accordingly, VE exhibits a two-phase structure. More or less spherical VE nodules are dispersed in a (poly)styrene-cocrosslinked-vinylester matrix. The size of the VE nodules is in the range of 50-70 nm. The presence of such a two-phase dispersion was shown also by Mortaigne et al. [13] who used laser ablation for the "physical etching" of VE.

Figure 2 displays the tanδ-T traces for the VE/Al-EP+Cal-Am combination cured at T = 150 and T = 200 °C. For comparison purpose the related traces of VE is also indicated. Note that the α-relaxation (T_g) peak shifts towards higher temperatures owing to post-curing. In case of an IPN structure one would expect a rather complex shape of the T_g peak. In contrast, a single α-peak was often reported for thermosets with an IPN structure [14]. So, the tanδ-T trace alone can hardly evidence the presence of IPN.

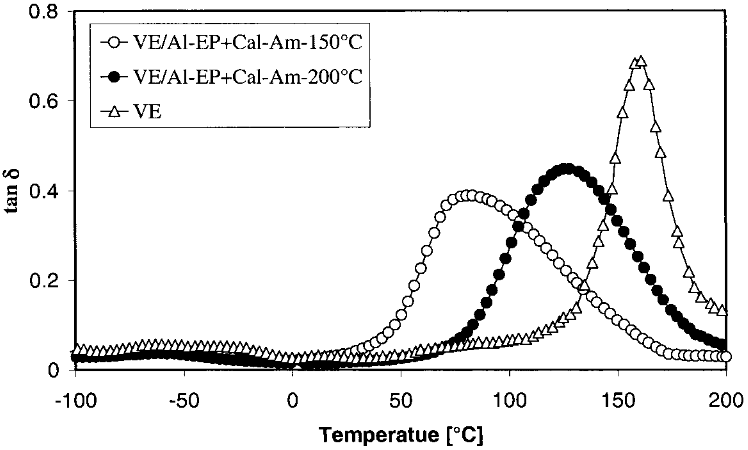

Figure 2.tan δ vs. T traces for VE/Al-EP+Cal-Am (ratio:1/1) after curing at max. T = 150 and T = 200 °C, respectively
Note: this Figure contains the related trace of VE for comparison purpose

This IPN structuring becomes, however, obvious in the height-contrasted AFM pictures in Figure 3. One can see that the IPN structure became more compact due to post-curing. This compaction upon post-curing rises the T_g (see Figure 2). However, the mean width of the IPN constituting ribbons is still in the same range (i.e. 60-80 nm) as found for VE. Note that the EP phase was less resistant to ion-etching than the VE [11].

Figure 4 shows the tanδ-T traces for the VE/Cal-EP+Al-Am systems cured at T = 150 and = 200 °C. Again, the shift in the T_g peak toward higher temperatures is prominent. Comparing the peak positions of the T_g relaxations in Figures 2 and 4 one can conclude that the rigidity of the idealized EP crosslink unit of Al-EP+Cal-Am is higher than that of Cal-EP+Al-Am. This is in line with the expectation as Cal-Am contains two cyclohexylene units, whereas Cal-EP only one. As a consequence, the idealized crosslink unit of the latter is more flexible and thus yields a lower T_g [10].

Attempts were made to modify the properties of the IPN-structured VE/EP resins from the VE side using novolak-based VE resins. However, this approach did not yield the expected result: neither considerable toughness improvement nor T_g upgrade were achieved.

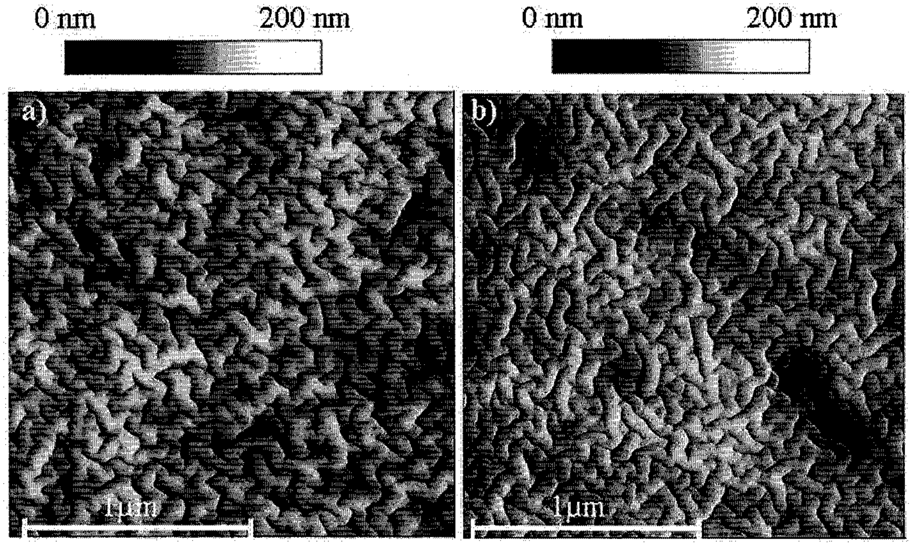

Figure 3.AFM pictures (height images) taken on the ion-etched surface of VE/Al-EP+Cal-Am after curing at max. T = 150 (a) and T = 200 °C (b)

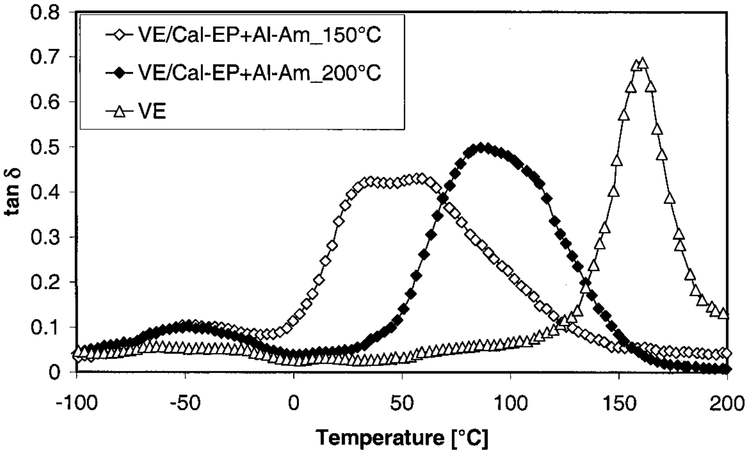

Figure 4.tan δ vs. T traces for VE/Cal-EP+Al-Am (1/1) after curing at max. T = 150 and T= 200 °C, respectively

The AFM scans in Figure 5 demonstrate the IPN formation of VE/Cal-EP+Al-Am which is again strongly compacted during additional heat treatment. It is the right place to discuss the possible driving force of this morphology compaction. One should keep in mind that albeit the VE copolymerisation with styrene is likely independent from the polyaddition reaction between the EP and hardener several by-side reactions may occur. It is probable for example that the secondary –OH groups of the VE enter in a polyaddition reaction with the epoxy groups of the EP. This means a cross-reaction between the VE and EP, which thus chemically links these two phases to each other. The related IPN structure is termed in the literature "grafted IPN".

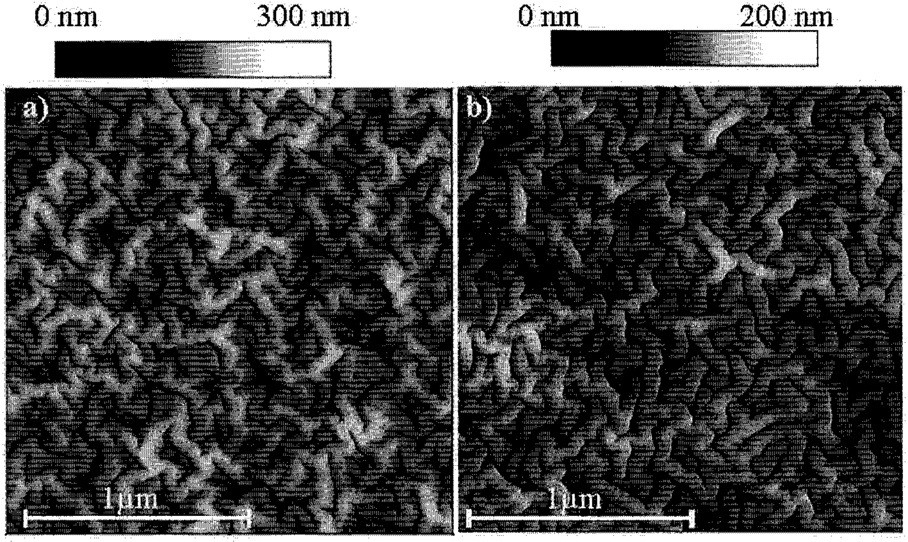

Figure 5.AFM pictures (height images) taken on the ion-etched surface of VE/Cal-EP+Al-Am after curing at max. T = 150 (a) and = 200 °C (b)

Effects of EP Formulation on the (Fracture) Mechanical Properties

Table 1 lists the basic (fracture) mechanical properties of the VE/EP compositions. The related data show the strong effect of the rigidity of the idealized crosslink unit of the EP formulation [10]. As expected, all systems are sensitive to postcuring, the effect of which is, however, different for the various EP formulations. Most sensitive indicator for this thermal treatment is the T_g. The ranking of the VE/EP systems differs when instead of the tensile mechanical, the fracture mechanical properties are taken into account. Table 1 demonstrates the benefits of EP networking on the fracture mechanical parameters when Al-EP+Cal-Am and Cal-EP+Al-Am combinations are used. Supposing that the VE crosslinking is not affected by the EP system, changes in the mechanical and fracture mechanical properties should be related to the EP network characteristics.

Table 1. Tensile mechanical properties of the VE/EP (ratio:1/1) systems studied Notes: data represent mean values derived from 5 parallel tests. T_g read from the DMTA curve as the maximum of the α-relaxation peak

Composition	Maximum Curing Temperature (°C)	Tensile Strengh (MPa)	Ultimate Tensile Strain (%)	Young's Modulus (MPa)	G_c (kJ/m^2)	K_c (MPa m$^{0.5}$)	T_g (°C)
VE/Al-EP +Cal-Am	150	50	5.5	2600	3.7	2.6	81
VE/Al-EP +Cal-Am	200	60	4.5	2700	1.1	1.6	128
VE/Cal-EP +Al-Am	150	14	38.5	700	7.3	1.3	57
VE/Cal-EP +Al-Am	200	46	5.1	2900	5.2	2.7	87

During this study which covered aliphatic and aromatic EP combinations, as well [15], it turned out that the key aspect with respect to the toughness is the presence of cyclohexylene units in the EP. This finding was traced to the chair/boat conformational changes of the cyclohexylene moieties which produce a relaxation transition at about T= -50°C (β-relaxation, cf. Figure 6). The chair/boat conformational changes along the Cal-Am hardener segments are, however, hampered as they require some co-operative motion in the Al-EP+Cal-Am formulation. This is the reason why this system exhibits outstanding strength, high K_c, high T_g and at the same time low ductility and very low G_c. The combination Cal-EP+Al-Am results in an idealized EP network unit of high flexibility. This is owing to the ether linkages and the less restricted conformational changes of the cyclohexylene groups along the EP segment. By contrast, when the EP network unit consists of Al-EP+Cal-Am then its overall flexibility (i.e. all distortion possibilities) is reduced due to the presence of two cyclohexylene groups in the hardener compared to the Cal-EP+Al-Am formulation. This arguing based on the concept of an idealized network unit of the EP phase is in line with the DMTA results – cf. Figure 6.

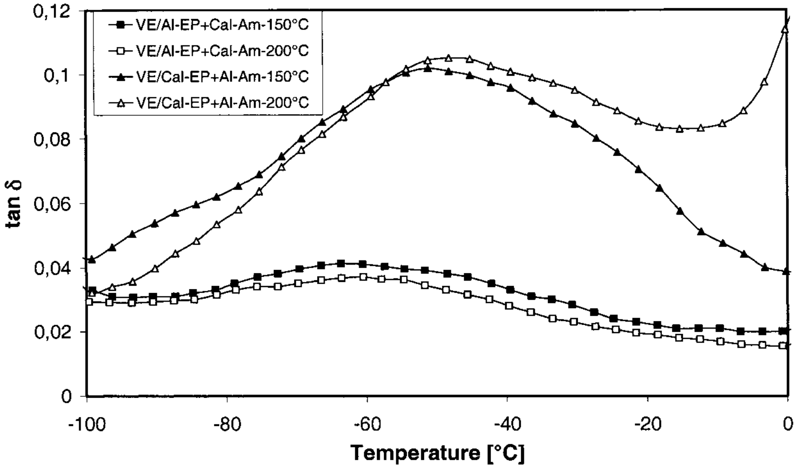

Figure 6.β-relaxation transition VE/Cal-EP+Al-Am and VE/Al-EP+Cal-Am combinations after curing at max. T = 150 and = 200 °C, respectively

Figure 6 displays that the β-relaxation of VE/Al-EP+Cal-Am is considerably less intensive than that of VE/Cal-EP+Al-Am. The intensity of the β-peak correlates with the flexibility of the idealized EP network, as discussed above. It is worth of noting that the flexibility of the EP network unit help us also to explain the changes observed after postcuring. The more flexible is the network unit, the higher the effect of the thermal treatment is. In addition, the network unit flexibility should influence the grafting reaction that occurs between the -OH(VE) and epoxy(EP) groups.

The effects of grafting and alterations in the crosslinking behavior of the VE and EP components during interpenetrating network formation are now topics of high priority in the academic research [16-18].

Failure Mode

As the basic failure mode of thermosets is shear type, the height of the river line steps on the fracture surface gives the first hint on the ductility and thus G_c of the material.

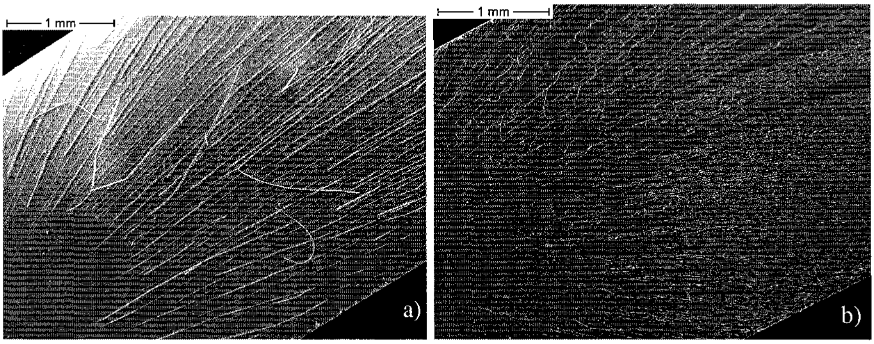

Figure 7.Scanning electron microscopic (SEM) pictures taken from the fracture surface of VE/Al-EP+Cal-Am after curing at T = 150 (a) and T= 200 °C (b)

Figure 7a shows prominent river lines on the brittle fracture surface of VE/Al-EP-Cal-Am. Both the height and width of the river lines are markedly reduced after postcuring at T = 200 °C (Figure 7b). As a consequence, G_c was also reduced which is in line with the experimental findings (cf. Table 1). Figure 8 displays the failure mode of VE/Cal-EP+Al-Am after curing at T = 150 (a) and T = 200 °C (b). The most peculiar feature of VE/Cal-EP+Al-Am is that its initial failure mode does not change with postcuring. Arrow in Figure 8b shows that the high fracture toughness is due to ductile deformation, which occurs in a much shorter range when the specimen was cured at T = 200 °C instead at T=150 °C (cf. pictures a and b in Figure 8). The fracture surface after the ductile/brittle transition still indicates for an enhanced shear deformability of this composition (see the well developed river lines in Figure 8b when compared with those in the SEM pictures of Figure 7). Considering the fact that the intensity of the β-relaxation did not change owing to postcuring (cf. Figure 6) it can be suggested that the toughness of the system correlates with the intensity of this β-relaxation transition. Accordingly, one can claim that the formation of a grafted IPN structure and the network flexibilisation of the EP constituent are excellent tools to enhance the toughness of thermosets. Note that from side of VE the possibility to tailor the morphology and thus the properties is markedly less.

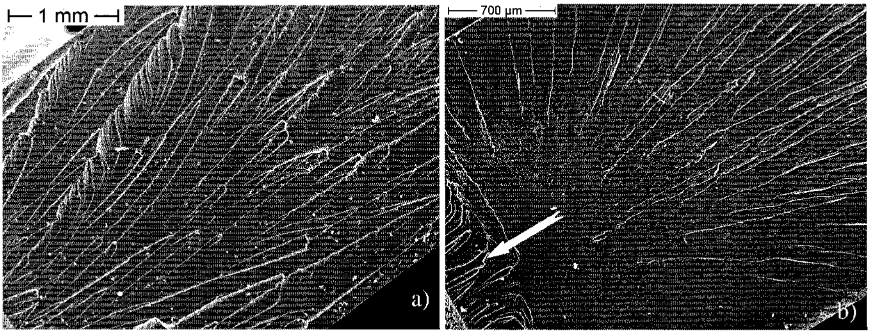

Figure 8.SEM pictures taken from the fracture surface of VE/Cal-EP+Al-Am after curing at T = 150 (a) and T = 200 °C (b), respectively
Note: arrow in picture b shows the initial ductile deformation

Conclusions

Based on this work, devoted to the study the morphology dependent toughness behavior of vinylester (VE), and VE/epoxy (EP) hybrid resins, the following conclusions can be drawn:

- cured VE has a two-phase (microgel) structure: VE nodules are dispersed in a (poly)styrene-cocrosslinked-vinylester matrix.
- the VE/EP systems at a composition ratio of 1/1 exhibited an IPN structure which became more compact with increasing curing temperature. This compaction in the morphology was traced to the formation of a grafted IPN structure.
- flexibilisation of the EP network by using EP resins or diamine hardeners containing cyclohexylene units strongly improved the toughness compared to fully aliphatic or aromatic EP versions in the VE/EP hybrids.
- the intensity of the β-relaxation, assigned to conformational changes of the cyclohexylene linkages (chair/boat transition), correlated with the toughness of the IPN structured VE/EP hybrids

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