Toughness Response of Vinylester/Epoxy-Based Thermosets of Interpenetrating Network Structure as a Function of the Epoxy Resin Formulation: Effects of the Cyclohexylene Linkage

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ABSTRACT: Vinylester/epoxy (VE/EP)-based thermosets of interpenetrating network (IPN) structures were produced by using a VE resin (bismethacryloxy derivative of a bisphenol A–type EP resin) with aliphatic (Al-EP) and cycloaliphatic (Cal-EP) EP resins. Curing of the EP resins occurred either with an aliphatic (Al-Am) or cycloaliphatic diamine compound (Cal-Am). Dynamic mechanical thermal analysis (DMTA) and atomic force microscopy (AFM) suggested the presence of an interpenetrating network (IPN) in the resulting thermosets. Fracture toughness (K_c) and fracture energy (G_c) were used as the toughness characterization parameters of the linear elastic fracture mechanics. Unexpectedly high K_c and G_c data were found for the systems containing cyclohexylene units in the EP network, such as VE/Al-EP+Cal-Am and VE/Cal-EP+Al-Am. This was attributed to the beneficial effects of the conformational changes of the cyclohexylene linkages (chair/boat), which were closely analogous to those in some thermoplastic copolyesters. The failure mode of the VE/EP thermoset combinations was studied in scanning electron microscopy (SEM) and discussed. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 88: 2124–2131, 2003

Key words: vinylester resin; epoxy resin; interpenetrating network (IPN); fracture mechanics; fractography

INTRODUCTION

It was recognized early that the simultaneous formation of an interpenetrating network (IPN) in thermosets results in improved properties, especially toughness. Prerequisites for IPN formation with thermoset resins are that the curing reactions of their components do not interfere with each other and that their relative amount is well balanced (close to the phase ratio of 1:1).

IPN-structured thermosets have been synthesized by the combined use of epoxy (EP) resins and *in situ*–formed polyurethanes (PU)[1–4]; unsaturated polyester (UP) resins and PU[5–6]; EP and aliphatic acrylates[7–10]; and UP or vinylester (VE) resins with PU[11–14] or with EP resins.[10,15–19] Most of the studies were focused on improving mechanical properties, including toughness. For toughness characterization of thermosets the linear elastic fracture mechanical approach has been well established. On the other hand, there is less information in the literature on how the type and network parameters of one of the resins constituting an IPN affects the overall mechanical and thermal performance.

In a recent pioneering work it was reported that in VE(aromatic)/EP[aliphatic, cycloaliphatic, aromatic (Al, Cal, Ar)] combinations the type of EP strongly influences the toughness response.[20,21] It was also claimed that the structure of VE/EP resins at a1:1 ratio is of the IPN type. Very high toughness was reported for those VE/EP systems that contained Cal-EP or Al-EP when the EP fraction was cured by the same diamine. On the other hand, the VE(aromatic)/EP-(aromatic) system behaved in a very brittle manner. This finding was traced to the molecular mobility of the chains between the crosslinking sites. In addition, it was argued that conformational changes, a result of the presence of the cyclohexylene rings, were responsible for the strongly improved toughness.[20] This hypothesis has not yet been proved, however,. To determine whether the incorporation of cyclohexylene groups is the key, in the current study Cal-EP and Al-EP resins were selected and cured either by aliphatic (Al-Am) or cycloaliphatic (Cal-Am) diamine compounds. An additional aspect of the material selection was that the cyclohexylene linkages be in different environments and thus possess various conformational possibilities. This was the reason for the se-

lection of Cal-Am, which contains two cyclohexylene units along its chain. Accordingly, the major aim of this work was to clarify the effects of the cyclohexylene linkage within the EP network on fracture toughness (K_c) and fracture energy (G_c) in IPN-structured VE/EP-based thermosets.

EXPERIMENTAL

Materials, curing

Commercial VE resin (bisphenol A–based bismethacryloxy type; DSM Composite Resins, Zwolle, The Netherlands) was diluted in styrene (Daron® XP-45-A-2; styrene content: 30 wt %, ratio of double bonds VE/styrene = 1:1.2). For curing, 1.5 phr of peroxide (dibenzoyl peroxide; Lucidol® CH-50L of Akzo Nobel, Düren, Germany; peroxide content: 50 wt %) and 1.5 phr of accelerator (N,N-diethylaniline, NL-64-10P of Akzo Nobel; active component: 10 wt %) were used.

As aliphatic EP (Al-EP), 1,4-butane diol diglycidyl ether (Polypox R3, UPPC, Germany) was chosen; as cycloaliphatic EP (Cal-EP), 1,6-cyclohexane-dimethanol-diglycidyl ether (Polypox R11, UPPC, Mietingen-Baltringen, Germany) was selected.
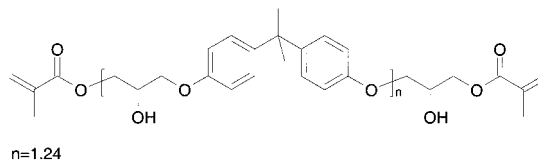
EP resins were cured by 1,2-bis(2-aminoethoxy)-ethane (Al-Am; Aldrich, Taufkirchen, Germany) and 2,2′-dimethyl-4,4′-methylenbis(cyclohexylamine) (Cal-Am; HY2954, Vantico Ltd., Wehr, Germany). The hardener/EP ratio was stoichiometric. The chemical structures of all the above compounds are summarized in Figure 1.

The resin mixtures were prepared by mixing the VE with the EP resin first. Next, the peroxide was added and the mixture homogenized. Then the EP hardener was introduced and the mixture homogenized again. Finally, the VE accelerator was added, and the resin mixture was added to a paper beaker and degassed *in vacuo* prior to being poured into open PTFE molds. The cure regime of the plaques and specimens (3 mm thick) produced in the PTFE mold was as follows: room temperature (RT) for 12 h, 80°C for 3 h, and 150°C for 3 h. In some cases an additional postcuring step was inserted (200°C for 3 h) in order to check the resistance of the thermosets to thermal aging.
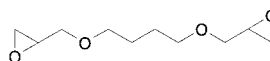
Material characterization

The phase structures of the resin combinations were characterized by dynamic mechanical thermal analysis (DMTA). DMTA spectra were taken on rectangular specimens [50 × 10 × 4 mm (length × width times; thickness)] in the flexural mode at 10 Hz using an Eplexor 150 N device (Gabo Qualimeter). The DMTA spectra, that is, the complex modulus (E^*) and its constituents (E' and E'') and mechanical loss factor (tan δ) as a function of temperature (T), were mea-
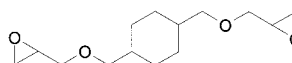

Figure 1 Chemical composition of the resins (VE, EP) and hardeners (for EP) used.

sured in the interval $T = -100°C$ to $+200°C$ at a heating rate of 1°C/min. Further information on the morphology of the VE/EP systems was expected from atomic force microscopic (AFM) studies. The polished surface of the specimens was eroded (etched) by Ar^+ ion bombardment to about 100 nm in depth. The surface profiles were scanned by AFM (Digital Instruments) in the tapping mode.

Determination of fracture toughness (K_c) and fracture energy (G_c) was done in accordance with the ESIS TC-4 testing protocol.[22] Tests were performed on a Zwick (type 1445) universal testing machine. The sawn notches of compact tension (CT) specimens (dimensions: 35 × 35 × 4 mm³), cut from the cured plates, were sharpened by a razorblade prior to their tensile loading (mode I) at RT with a crosshead speed of $v = 1$ mm/min.

Tensile mechanical characteristics (Young's modulus, strength, elongation at break) were measured on dumbbell specimens (type 1A according to EN/ISO 527/2). Their surface, which was not in contact with the PTFE mold, was polished prior to loading at RT with $v = 2$ mm/min. For the Young's modulus determination, incremental mechanical grips were positioned on the dumbbells.

To get a deeper understanding of the effect of morphology on the fracture mechanical response, the surfaces of broken CT specimens were inspected in a scanning electron microscope (SEM; JSM-5400, Jeol).
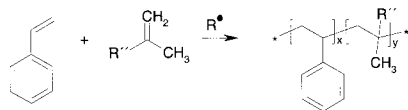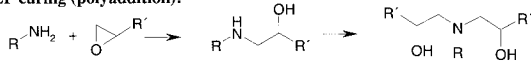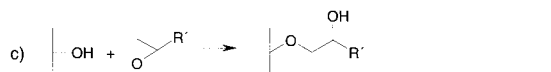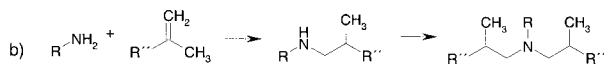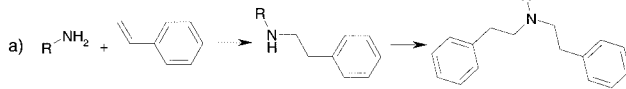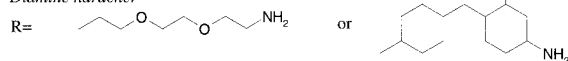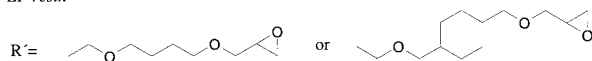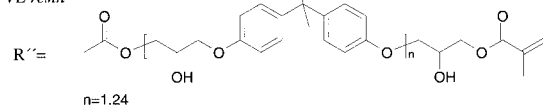
Figure 2 Possible chemical reactions during grafted IPN formation using VE and EP resins.

The fracture surfaces were coated with an alloy of Au/Pd prior to SEM investigations.

RESULTS AND DISCUSSION

Simultaneous IPN formation

Curing of VE occurs via free radical copolymerization with styrene. On the other hand, crosslinking of EP with diamine follows a polyaddition mechanism. These reactions are basically independent of one another, and as a consequence, a simultaneous IPN structure may develop. There are, however, some side reactions that make the scenario a bit more complicated. The primary amine group of the diamine hardener may react with the double bonds of styrene and VE [reactions (a) and (b) in Fig. 2]. These side reactions may reduce the crosslink density of the VE component. Their effect is possibly negligible, as styrene is present in excess, and the free radical polymerization of VE is already activated by diethylaniline and thus is very fast. The secondary —OH groups initially present in VE and formed during the polyaddition reaction of the crosslinking EP may react with the epoxy groups of the EP resin [reaction (c) in Fig. 2]. In this way a chemical link between the EP and VE

phases develops, and the related IPN is termed grafted IPN. Figure 3 highlights the difference between the IPN and grafted IPN structures. For a grafted IPN structure the related VE/EP versions should be quite sensitive to thermal treatment (postcuring). That was the reason for studying the mechanical performance of the thermoset compositions after a postcuring cycle.

Considering the DMTA spectra, more exactly the tanδ-T traces, one can recognise a shift in the α-relaxation transition (T_g) toward higher temperatures due to the annealing (postcuring) at $T = 200°C$ (Fig. 4). This shift is usual for all thermosets as new crosslinks form after the thermally-induced devitrification process. Therefore, the T_g shift can not be attributed solely to the formation of a more grafted IPN structure. A hint for the grafted IPN structure should be likely found in the range between the α- and β-relaxations. Unfortunately, not even Fourier transformed infrared spectroscopy (FTIR) can help us to show the supposed grafting, as the hydroxyl group "recovers" during the related reaction [cf. reaction (c) in Fig. 2]. Further, the tan δ-T traces in Figure 4 do not indicate unequivocally the IPN formation. It would be expected that a doubling or at least a strong asymmetry in the α-relaxation peak would occur after low-temperature curing. A double α-peak can only be recognized in VE/Cal-EP+Al-Am cured up to $T = 150°C$. Accordingly, the VE and the EP resins selected were very compatible with each other.

Attention should also be paid to the β-relaxation transition. For the system with Cal-EP+Al-Am, this peak is substantially higher than in the EP composed of Al-EP+Cal-Am. Note that in the neat VE this peak is marginal.[23] Therefore, the onset of the β-relaxation should be related to the EP network. Based on analogies (discussed later) with linear amorphous copolyesters with cyclohexylenedimethylene units along the macromolecular chain, the key parameter of the β-transition can be identified: conformational transitions of the cyclohexylene rings. The β-relaxation transitions of the VE/EP systems, shown in Figure 4, already suggest the possibility of some differences with the chair/boat transitions of the cyclohexylene groups. It is believed that this conformational change is somewhat restricted in Cal-Am, in which the movement of the two cyclohexylene rings are less decoupled from one another.

Direct evidence for the onset of IPN was provided by AFM. Supposing that the resistance of VE to Ar$^+$ ion bombardment differs from that of EP, the "ion etching" technique is a reliable way of detecting the initial morphology. Figure 5 shows AFM pictures on the ion-etched surface of VE/Cal-EP+Al-Am cured at $T = 150°C$. The morphology is obviously a cocontinuous two-phase structure. Attention should be paid to the disperse-type microstructure of VE (microgelled
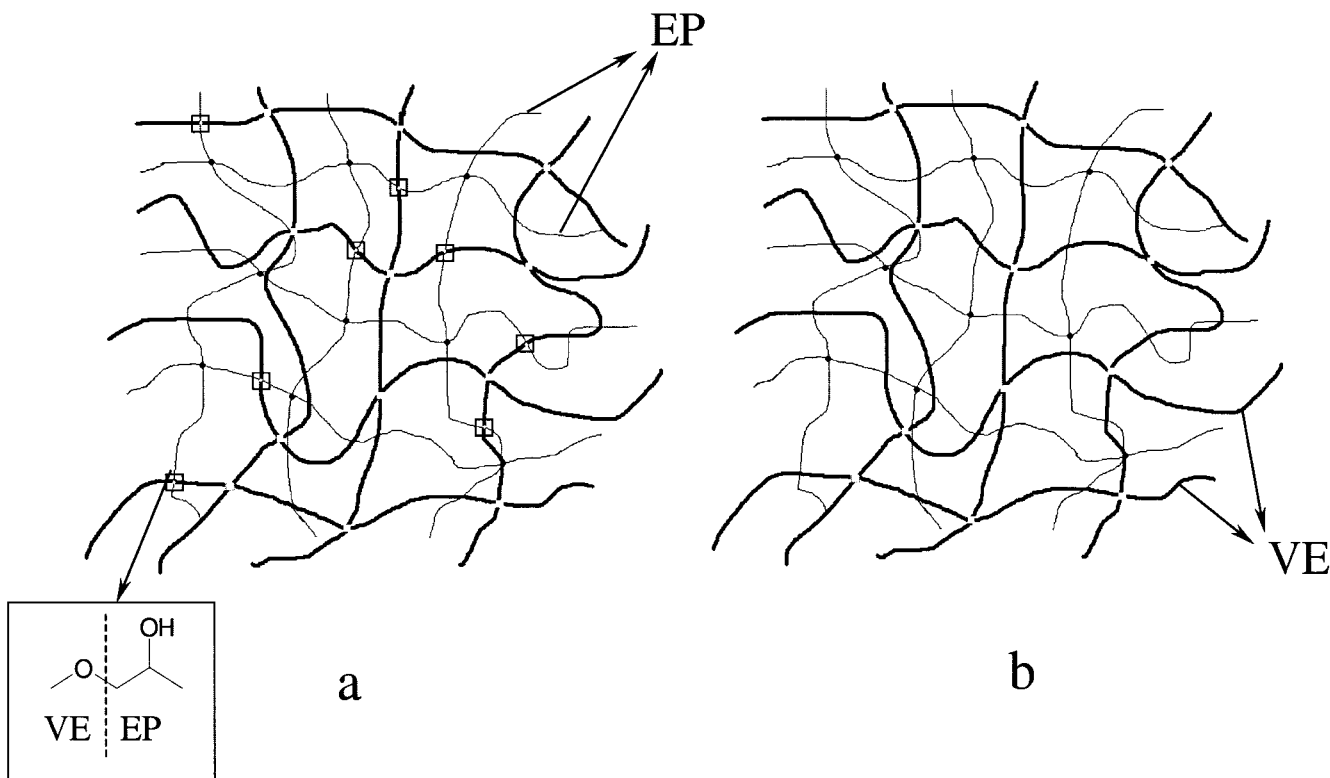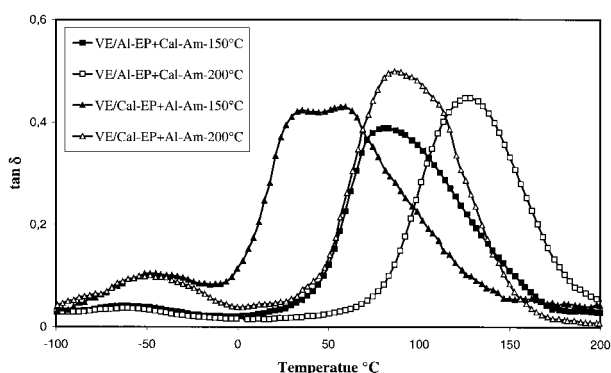
Figure 3 Difference between simultaneously formed IPN (a) with and (b) without grafting schematically.

crosslinked VE particles are embedded in a polystyrene matrix),[24] which is completely different from that which we found (cf. Fig. 5). To clarify the morphological peculiarities of the VE/EPs studied, further tests (AFM, SEM) are now in progress.

**Effects of EP formulation on (fracture) mechanical properties**

Table I lists the basic mechanical properties of the VE/EP compositions. The related data clearly suggest the strong effect of the hardener type. The use of Al-Am resulted in a thermoset with a low T_g, low stiffness, and low strength and very high ductility.

The highest stiffness, strength, and T_g associated with the lowest ductility was shown by the VE/Cal-EP+Cal-Am. As expected, all systems were sensitive to postcuring, the effect of which is different, however, for the various EP formulations. The most sensitive indicator for this thermal treatment was the T_g.

The ranking of the VE/EP systems differed when, instead of the tensile mechanical properties, the fracture mechanical properties were taken into account.

Figure 4 tan δ versus T traces for VE/EP combinations after curing at max. $T = 150°C$ and $200°C$, respectively.
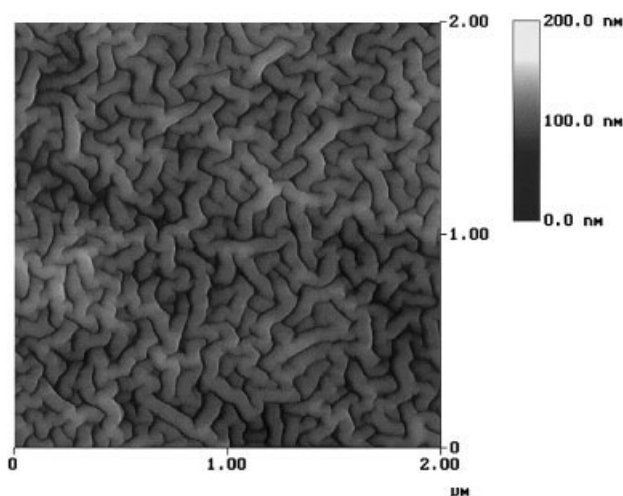
Figure 5 AFM picture (height image) showing the formation of an IPN structure with the example of VE/Cal-EP+Al-Am after curing at $T = 200°C$.

TABLE I
Tensile Mechanical Properties of VE/EP (1/1) Systems Studied

Composition	Maximum curing temperature (°C)	Tensile strength (MPa)	Ultimate tensile strain (%)	Young's modulus [MPa]	T_g (°C)
VE/Al−EP+Al−Am	150	—[a]	—[a]	—[a]	15
VE/Al−EP+Cal−Am	150	50	5.5	1311	81
VE/Al−EP+Cal−Am	200	60	4.5	1347	128
VE/Cal−EP+Cal−Am	150	54	4.5	1347	96
VE/Cal−EP+Cal−Am	200	62	4.3	1447	138
VE/Cal−EP+Al−Am	150	14	38.5	345	57
VE/Cal−EP+Al−Am	200	46	5.1	1434	87

[a] Not tested.

Notes: data represent mean values derived from five parallel tests. T_g read from the DMTA curve as the maximum of the α-relaxation peak.

Figure 6 shows the benefits of EP networking on the fracture mechanical parameters when Al-EP+Cal-Am and Cal-EP+Al-Am combinations are used. The fully cycloaliphatic version, that is, Cal-EP+Cal-Am, had a high K_c; however, it was very brittle (low G_c). On the other hand, this system was less sensitive to postcuring (cf. results in Table I and Fig. 6). It would be expected that postcuring at $T = 200°C$ would reduce G_c and increase K_c at the same time. This expectation holds for VE/Cal-EP+Al-Am but not for VE/Al-EP+Cal-Am, for which the reverse tendency was observed. On the supposition that 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. Figure 7 depicts the ideal network units of the EP systems used. The results in Table I and Figure 6 suggest that the key aspect is the presence of the cyclohexylene units. In their absence (cf. VE/Al-EP+Al-Am) a low T_g system with moderate (thermo)mechanical properties was the outcome. In addition, the EP network unit in Cal-EP+Cal-Am was rather stiff. Further, the chair/boat conformational changes along the hardener segments were hampered, as they require some cooperative mo-
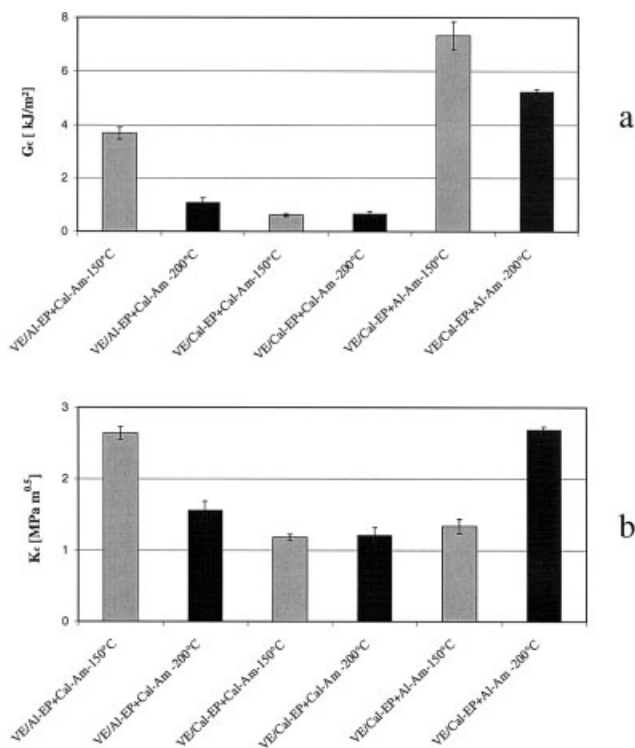

Figure 6 (a) Fracture energy, G_c, and (b) fracture toughness, K_c, of VE/EP combinations as a function of EP formulation and maximum curing temperature. Note: no valid fracture mechanical data could be determined for the VE/Al-EP+Al-Am combinations because of their high ductility at room temperature.
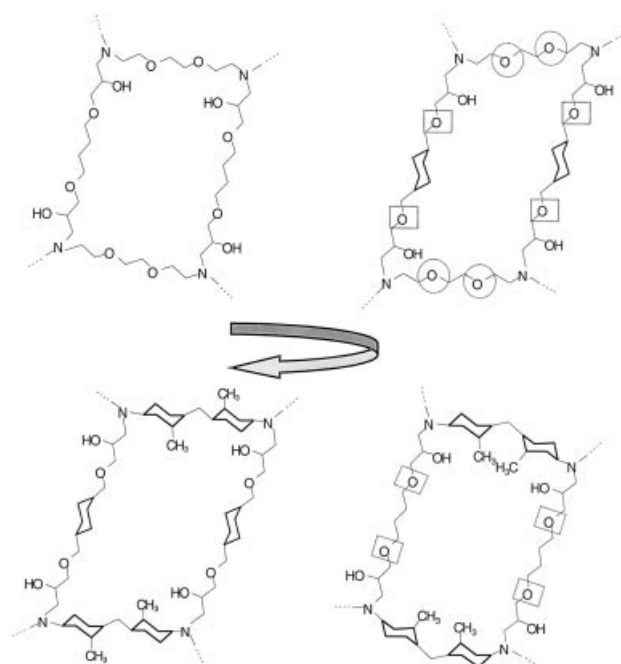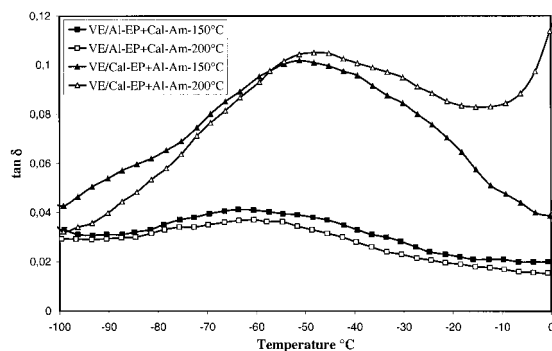

Figure 7 Idealized EP network units as a function of their constituents. Note: the unit rigidity increases in clockwise direction; flexibility increase as a result of the ether linkages is indicated.

Figure 8 β-relaxation transition VE/Cal-EP+Al-Am and VE/Al-EP+Cal-Am combinations after curing at max. *T* = 150°C and *T* = 200°C, respectively.

tion. This is why this system exhibited 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 yielded a network unit of high flexibility. This is because of the ether linkages and the less restricted conformational changes of the cyclohexylene groups along the EP segment. When the EP network unit consisted of Al-EP+Cal-Am, its overall flexibility (i.e., all distortion possibilities) was somewhat reduced as a result of the presence of the two cyclohexylene groups in the hardener, compared with the Cal-EP+Al-Am formulation. This rationale is in line with the DMTA results. Figure 8 shows that the β-relaxation of VE/Al-EP+Cal-Am was considerably less intense than that of VE/Cal-EP+Al-Am. It is worth of noting that the flexibility of the network unit also helped us to explain the changes observed after postcuring: the more flexible the network unit, the higher is the effect of the thermal treatment. In addition, the network unit flexibility should influence the grafting reaction that occurs between the —OH(VE) and epoxy(EP) groups.

Failure mode

The fracture surface of VE/Cal-EP+Cal-Am was rather smooth (cf. Fig. 9). This suggests a very low G_c, as was indeed found. The surface pattern of the river lines[25] at a high crack speed was a result of the formation of satellite cracks on slightly different planes than the dominating one. As the basic failure mode of the thermosets was shear, the height of these river line steps provided the first hint about the ductility and thus the G_c of the material. Figure 10(a) shows evidence of more ductility on the still-brittle fracture surface of VE/Al-EP+Cal-Am. Both the height and width of the river lines were strongly reduced after postcuring at *T* = 200°C [Fig. 10(b)]. As a consequence, G_c was also reduced which is in line with the experimental findings [cf. Fig. 6(a)]. Figure 11 shows the failure mode of VE/Cal-EP+Al-Am after curing at *T*
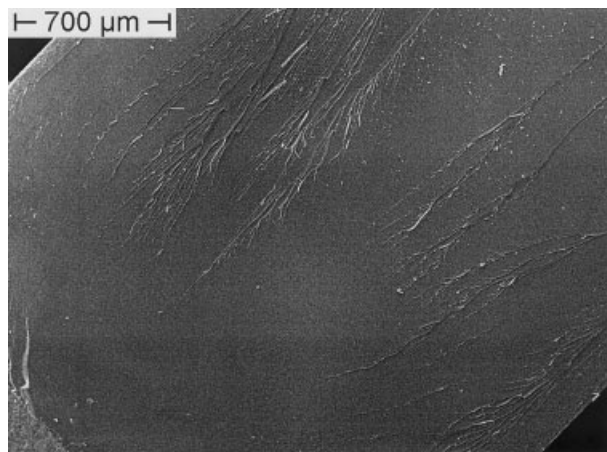
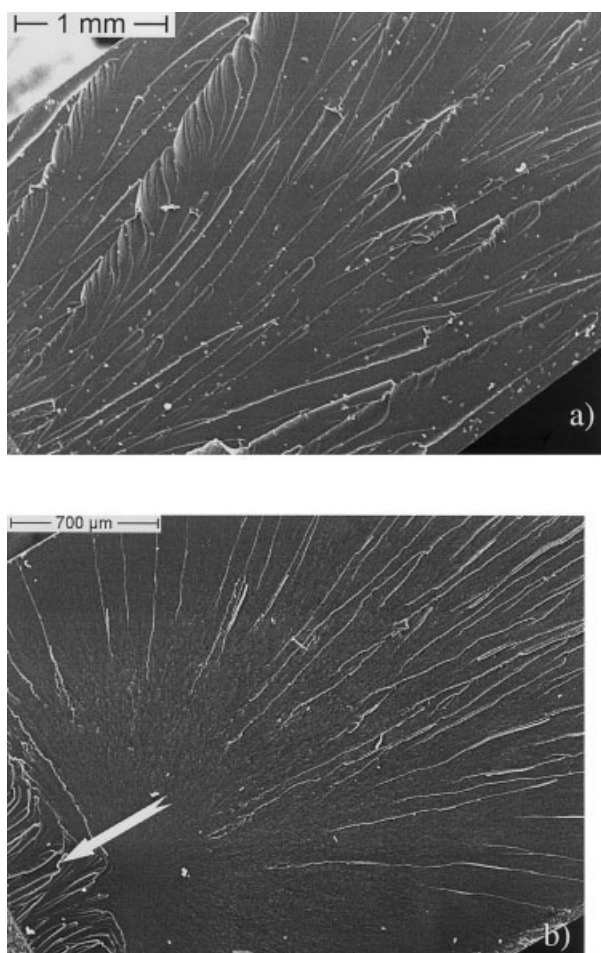**Figure 9** SEM picture taken on the fracture surface of VE/Cal-EP+Cal-Am after curing at *T* = 150°C.

= 150°C [Fig. 11(a)] and *T* = 200°C [Fig. 11(b)]. The fracture surface of the low-temperature-cured system is fully analogous with that of a linear copolyester
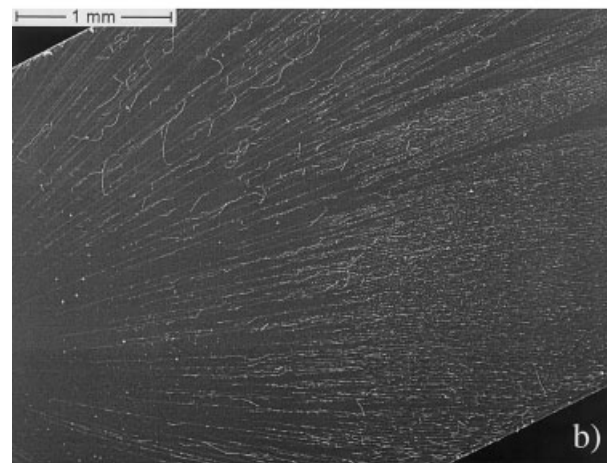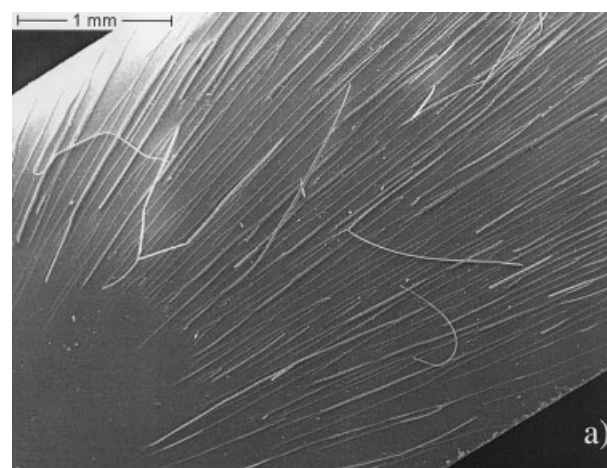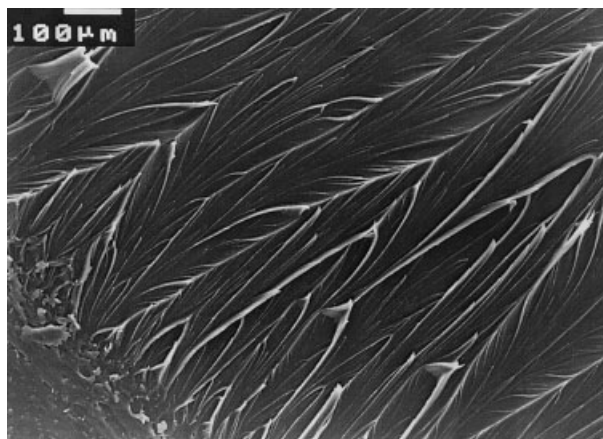

Figure 10 SEM pictures taken on the fracture surface of VE/Al-EP+Cal-Am after curing at (a) *T* = 150°C and (b) *T* = 200°C.

containing cyclohexylenedimethylene units [compare Fig. 11(a) with Fig. 12].[26] The superior toughness of this amorphous thermoplastic copolyester can be attributed to the conformational transition of the cyclohexylene group being able to couple with the motion of neighboring segments.[27–28] The strong similarity between VE/Cal-EP+Al-Am [Fig. 11(a)] and the thermoplastic copolyester (Fig. 12) can be interpreted by considering the only common component, that is, the cyclohexylene group. It should also be noted here that this amorphous copolyester always fails by shear deformation.[29] The most peculiar feature of VE/Cal-EP+Al-Am is that its initial failure mode did not change with postcuring. The arrow in Figure 11(b) shows that the high fracture toughness was a result of ductile deformation; however, this occurred in a much shorter range than in the specimen cured at $T = 150°C$ [cf. Fig. 11(a,b)]. The fracture surface after the ductile/brittle transition still indicates enhanced shear deformability of this composition [compare the river lines in Fig. 11(b) with the SEM pictures in Fig. 10].

Figure 12 SEM picture of the fracture surface of an amorphous copolyester. Note: molecular characteristics of this material are disclosed in ref. 26; fracture occurred at ambient temperature with 1 mm/min crosshead speed; notch is visible in the bottom left corner.

Figure 11 SEM pictures taken on the fracture surface of VE/Cal-EP+Al-Am after curing at (a) $T = 150°C$ and (b) $T = 200°C$. Note: arrow in picture (b) shows the initial ductile deformation.

Given that the intensity of the β-relaxation did not change because of postcuring (cf. Fig. 8), it can be claimed that the toughness of the system correlates with the intensity of this relaxation transition. Additional support for this argument is provided by previously mentioned analogy with amorphous copolyesters.[26,29] The fractographic work corroborated that the supposedly grafted IPN structure, along with the network unit flexibilization of the EP constituent, are excellent tools to enhance the toughness of thermosets.

CONCLUSIONS

Based on the results of this work, which investigated the effect of EP formulation on the toughness response of a VE/EP thermoset combination at a ratio of 1:1, the following conclusions can be drawn:

- The structure of the VE/EP is of the IPN type, as shown by the results of atomic force microscopy (see also ref. 30). However, no direct evidence was found for its grafted nature.
- Flexibilization by using an EP resin or diamine hardener containing cyclohexylene units strongly enhances the stiffness and strength compared with fully aliphatic EP versions. Though the Cal-EP+Cal-Am combination possesses high strength, but its toughness is very low when compared with "hybrid" EPs containing cycloaliphatic units in either the resin (Cal-EP+Al-Am) or the hardener (Al-EP+Cal-Am).
- The intensity of the β-relaxation correlates with the toughness. This transition was assigned to conformational changes of the cyclohexylene linkages (chair/boat transition). This finding suggests that molecular dynamics simulation may be a

valuable tool for developing thermosets that have enhanced toughness and improved mechanical and thermal properties.

References

1. Park, S.-J.; Jin, J.-S. J Appl Polym Sci 2001, 82, 775.
2. Chern, Y. C.; Tseng, S. M.; Hsieh, K. H. J Appl Polym Sci 1999, 74, 328.
3. Hsieh, K. H.; Han, J. L.; Yu, C. T.; Fu, S. C. Polymer 2001, 42, 2491.
4. Cascaval, C. N.; Ciobanu, C.; Rosu, D.; Rosu, L. J. Appl Polym Sci 2002, 83, 138.
5. Meyer, G. C.; Mehrenberger, P. Y. Eur Polym J 1977, 13, 383.
6. Hsu, T. J.; Lee, J. L. Polym Compos 1985, 25, 951.
7. Hua, F.-J.; Hu, C.-P. J Polym Sci, Part A: Poly Chem 1999, 37, 3568.
8. Vabrik, R.; Czajlik, I.; Túry, G.; Rusznák, I.; Ille, A.; Víg, A. J Appl Polym Sci 1998, 68, 111.
9. Chakrabarty, D.; Das, B.; Roy, S. J Appl Polym Sci 1998, 67, 1051.
10. Sands, J. M.; Jensen, R. E.; Fink, B. K.; McKnight, S. H. J Appl Polym Sci 2001, 81, 530.
11. Chou, Y. C.; Lee, J. L. Polym Eng Sci 1994, 34, 1239.
12. Wang, G. Y.; Zhu, M. Q.; Hu, C. P. J. Polym Sci: Part A: Chem 2000, 38, 136.
13. Chen, C.-H.; Chen, W.-J.; Chen, M.-H.; Li, Y.-M. J Appl Polym Sci 1999, 71, 1977.
14. Chen, C.-H.; Chen, W.-J.; Chen, M.-H.; Li, Y.-M. Polymer 2000, 41, 7961.
15. Dean, K.; Cook, W. D.; Rey, L.; Galy, J.; Sautereau, H. Macromolecules 2001, 34, 6623.
16. Dean, K.; Cook, W. D.; Burchill, P.; Zipper, M. Polymer 2001, 42, 3589.
17. Dean, K.; Cook, W. D.; Zipper, M. D.; Burchill, P. Polymer 2001, 42, 1345.
18. Ivankovic, M.; Dzodan, N.; Brnardic, I.; Mencer, H. J. J Appl Polym Sci 2002, 83, 2689.
19. Lin, M.-S.; Liu, C.-C.; Lee, C.-T. J Appl Polym Sci 1999, 72, 585.
20. Karger-Kocsis, J.; Gryshchuk, O.; Jost, N. SPE-ANTEC 2002, 60, 751.
21. Institut für Verbundwerkstoffe GmbH. Ger. Pat. applied for (2001).
22. Williams, J. G. In Fracture Mechanics Testing Methods for Polymers Adhesives and Composites, ESIS Publ 28; Moore, D. R., Pavan, A., Williams, J. G., Eds.; Elsevier Science: Oxford, UK, 2001; p 11.
23. Gryshchuk, O.; Jost, N.; Karger-Kocsis, J. J Appl Polym Sci 2002, 84, 672.
24. Mortaigne, B.; Feltz, B.; Laurens, P. J Appl Polym Sci 1997, 66, 1703.
25. Hull, D. Fractography, Cambridge University Press: Cambridge, UK, 199; pp 277–278.
26. Karger-Kocsis, J.; Czigány, T.; Moskala, E. J. Polymer 1997, 38, 4587.
27. Liu, J.; Yee, A. F. Macromolecules 1998, 31, 7865.
28. Chen, L. P.; Yee, A. F.; Moskala, E. J. Macromolecules 1999, 32, 5944.
29. Karger-Kocsis, J. In Handbook of Thermoplastic Polyesters; Fakirov, S., Ed.; Wiley-VCH: Weinheim, Germany, 2002; Chapter 16, pp 717–753.
30. Karger-Kocsis, J.; Gryshchuk, O.; Schmitt, S. J Mater Sci 2003, 38, 413.