

Toughening of Vinylester–Urethane Hybrid Resins Through Functionalized Polymers

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ABSTRACT: Liquid nitrile rubber, hyperbranched polyester, and core/shell rubber particles of various functionality, namely, vinyl, carboxyl, and epoxy, were added up to 20 wt % to a bisphenol-A-based vinylester–urethane hybrid (VEUH) resin to improve its toughness. The toughness was characterized by the fracture toughness (K_{Ic}) and energy (G_c) determined on compact tensile (CT) specimens at ambient temperature. Toughness improvement in VEUH was mostly achieved when the modifiers reacted with the secondary hydroxyl groups of the bismethacryloxy vinyl ester resin and with the isocyanate of the polyisocyanate compound, instead of participating in the free-radical crosslinking via styrene copolymerization. Thus, incorporation of carboxyl-terminated liquid nitrile rubber (CTBN) yielded the highest toughness upgrade with at least a 20 wt % modifier content. It was, however, accompanied by a reduction in both the stiffness and glass transition temperature (T_g) of the VEUH resin. Albeit functionalized (epoxy and vinyl, respectively) hyperbranched polymers were less efficient toughness modifiers than was CTBN, they showed no adverse effect on the stiffness and T_g . Use of core/shell modifiers did not result in toughness improvement. The above changes in the toughness response were traced to the morphology assessed by dynamic mechanical thermal analysis (DMTA) and fractographic inspection of the fracture surface of broken CT specimens. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 84: 672–680, 2002; DOI 10.1002/app.10392

Key words: vinylester–urethane hybrid resin; toughening mechanisms; fracture mechanics; CTBN; hyperbranched polyester; core/shell rubber; crosslinking; modification; thermosets

INTRODUCTION

Nowadays, bisphenol-A-based vinylester (VE) resins are widely used as matrix materials of composites for demanding applications for which unsaturated polyester resins are less suitable (low strength, moderate environmental resistance, low glass transition temperature, T_g), and

epoxy resins are too expensive. Among others, VE resins are produced by reacting bisphenol-A type epoxy (EP) resins with acrylic or methacrylic acids.^{1–2} This reaction leads to double bonds (unsaturation) at terminal positions of the molecules which participate in the free-radical (co)polymerization with styrene. Styrene is thus present as an active diluent in VE resins. These bisacryloxy or bismethacryloxy VE derivatives contain secondary hydroxyl groups for which a polyurethane chemistry, namely, reaction with polyisocyanates, can be adopted. The resulting resins are termed vinylester–urethane hybrids (VEUH). Note that the crosslinked structure in VEUH resins is formed by a combination of free-radical

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polymerization (via styrene addition on the double bonds of VE) and polyaddition (between the —OH and —NCO groups of the VE and polyisocyanates, respectively).³ VEUH resins are marketed by DSM-BASF Structural Resins (Zwolle, The Netherlands) under the trade name of Daron®. They have outstanding physicomachanical and thermal properties but possess low toughness, similar to all commodity thermosets.

The state of knowledge on the toughening of thermosets is based on results achieved mostly on EP resins. It is generally accepted that the modifier particles, produced by phase segregation during crosslinking or added in the preformed state, act as stress concentrators, release the local triaxial stress state (via cavitation, debonding processes), reduce the crack speed (crack bifurcation, crack pinning), and promote shear deformation in the crosslinked resin itself (e.g., refs. 4–9). Incorporation of rigid inorganic or organic fillers (e.g., thermoplastic powders, core/shell type rubbers with and without functionalization) is widely practiced for impact modification of EP resins. Microvoids produced via solvent vapor-induced phase separation¹⁰ can also fulfill the role of a toughness modifier. A very efficient method is to add functionalized liquid rubbers, like carboxyl- or amine-functionalized nitrile or silicon rubbers (e.g., refs. 4, 6, 7, 11, and 12) to the crosslinking EP resin. These rubbers are mostly soluble in EP but precipitate in the form of droplets during crosslinking of the EP. The mean size of the droplet inclusions is crucial in respect to the desired toughness upgrade. The size and size distribution of the particles produced by phase separation depend on several factors (type, functionality and amount of the rubber, type of the hardener, crosslinking conditions, etc.). The related problems have triggered considerable R&D activity to use preformed particles, the particle size and distribution of which are well controlled.

Contrary to EP resins, much less information is available on the toughening of VE^{13–16} and no open literature is known by the authors for toughened VEUH resins. It was reported that modifiers, well established for EPs, are less efficient in unsaturated polyester^{17,18} and VE resins,¹³ for which some special modifiers and preparation routes have been recommended.^{13,19,20} Other reports, however, claimed that some traditional EP modifiers worked well both in traditional unsaturated polyester and VE resins.^{21–24} The possible reason behind this controversy is likely related to the solubility and phase segregation of the modi-

fier in the styrene-containing polyester and VE resins. This scenario may be, however, completely different for VEUH resins in which polyurethane chemistry is also involved (polyisocyanate compound is added). It is important to note that the VEUH resin exhibits a crosslinked structure composed of styrenic and —NH—CO—O— crosslinks and has nothing in common with interpenetrating networks produced of unsaturated polyester and polyurethane (e.g., refs. 25 and 26).

The research philosophy of this work was to check the feasibility of two toughening ways in VEUH: (a) phase separation upon crosslinking and (b) production of the second phase by preformed particles. In both cases, attention was paid to the use of functional polymers which impart either the radical polymerization of styrene (via vinyl functionality) or the polyaddition-type crosslinking between the —OH and —NCO groups (via carboxyl and EP functionalities). Accordingly, this work was aimed at screening the toughening of a VEUH resin by adding liquid nitrile rubbers and hyperbranched polymers with vinyl and EP functionalities as well as by incorporating core/shell rubber particles of vinyl, carboxyl, and EP functional surfaces. Note that amine-functionalized polymers, although available, were not involved in this study. Their fast reaction with polyisocyanates and the acceleration effect on the free-radical polymerization obstruct this option.

EXPERIMENTAL

Materials

The VEUH resin contained a bisphenol-A-based styrene-diluted VE of bismethacryloxy type (Daron® XP-45-A-2) and a novolac-based polymeric isocyanate (Daron® XP 40-B-1), both products of DSM-BASF Structural Resins. The base recipe was as follows: 100 parts VE (Daron® XP 45-A-2, styrene content: 30 wt %, ratio of the double bonds VE/styrene = 1:1.2); 38 parts polymeric isocyanate (Daron® XP 40-B-1, NCO functionality: 2.7); 1.5 parts peroxide [dibenzoyl peroxide, Lucidol® CH-50L of Akzo Nobel (Dueren, Germany), peroxide content: 50 wt %]; and 1.5 parts accelerator (*N,N*-diethylaniline, NL-64-10P, Akzo Nobel, active component: 10 wt %).

It should be mentioned that this recipe was used for screening the efficiency of the modifiers, that is, the functionality of the latter was not

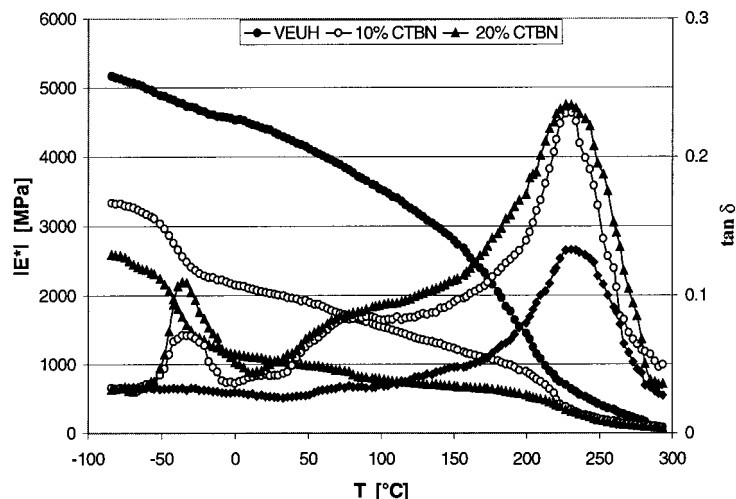


Figure 1 E^* versus T and $\tan \delta$ versus T traces for VEUH without and with 10 and 20 wt % CTBN rubber.

considered. As modifiers, carboxyl- (Hycar[®] CTBN 1300X8, designated as CTBN) and vinyl-terminated liquid nitrile rubbers (Hycar[®] VTBNX 1300X33, designated further on as VTBN) of BF Goodrich (Oevel, Belgium; www.bfgoodrich.com), dendritic (hyperbranched) polyesters with EP (Boltorn[®] E1—denoted as EHBP), and vinyl functionalities (Boltorn[®] U2—denoted as VHBP) of Perstorp Speciality Chemicals (Perstorp, Sweden; www.perstorp.com) and nonreactive (Paraloid[®] EXL-2300—denoted as CS) and reactive core/shell rubbers of butyl acrylate/methyl methacrylate (Paraloid[®] EXL-2314—denoted as CS-E as having EP functionality) of Rohm and Haas Co. (Frankfort, Germany; www.rohmandhaas.com) were selected.

Specimens [compact tension (CT), dumbbells] were produced by pouring the homogenized and degassed resin in steel molds having a bolted cover plate for easy demolding of the specimens. Curing of all resin modifications occurred under the following conditions: Mixing, homogenization, degassing, and filling of the molds occurred at ambient temperature; then, the temperature was set to 50°C for 15 min, 80°C for 30 min, 140°C for 30 min, and, finally, 200°C for 60 min. This curing cycle considered the recommendations of the VEUH supplier.

Tests

The phase structure of the toughened VEUHs was characterized by dynamic mechanical thermal analysis (DMTA). DMTA spectra were taken

on rectangular specimens (50 × 10 × 4; length × width × thickness) in a flexural mode at 10 Hz using an Eplexor 150 N device of Gabo Qualimeter. The static and cyclic (sinusoidal) loading components were set for 2 and ±1 N, respectively. DMTA spectra, namely, the complex modulus (E^*) and its constituents (E' and E'') and the mechanical loss factor ($\tan \delta$) as a function of temperature (T), were measured in the interval $T = -100$ to $+300^\circ\text{C}$ at a heating rate of $1^\circ\text{C}/\text{min}$.

Fracture toughness (K_{Ic}) and fracture energy (G_c) were determined in accordance with the ESIS testing protocol.²⁷ The tests were done with a Zwick universal testing machine type 1445. The CT specimens (dimension: 35 × 35 × 4 mm³) were notched by sawing. The notch root was sharpened by a razor blade prior to tensile loading (mode I) of the CT specimens at room temperature (RT) with a crosshead speed of $v = 1$ mm/min.

To obtain a deeper understanding of the effect of the 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 the SEM investigations.

RESULTS AND DISCUSSION

DMTA Behavior

Figure 1 shows the E^* versus T and $\tan \delta$ versus T traces for the VEUH resin modified by various

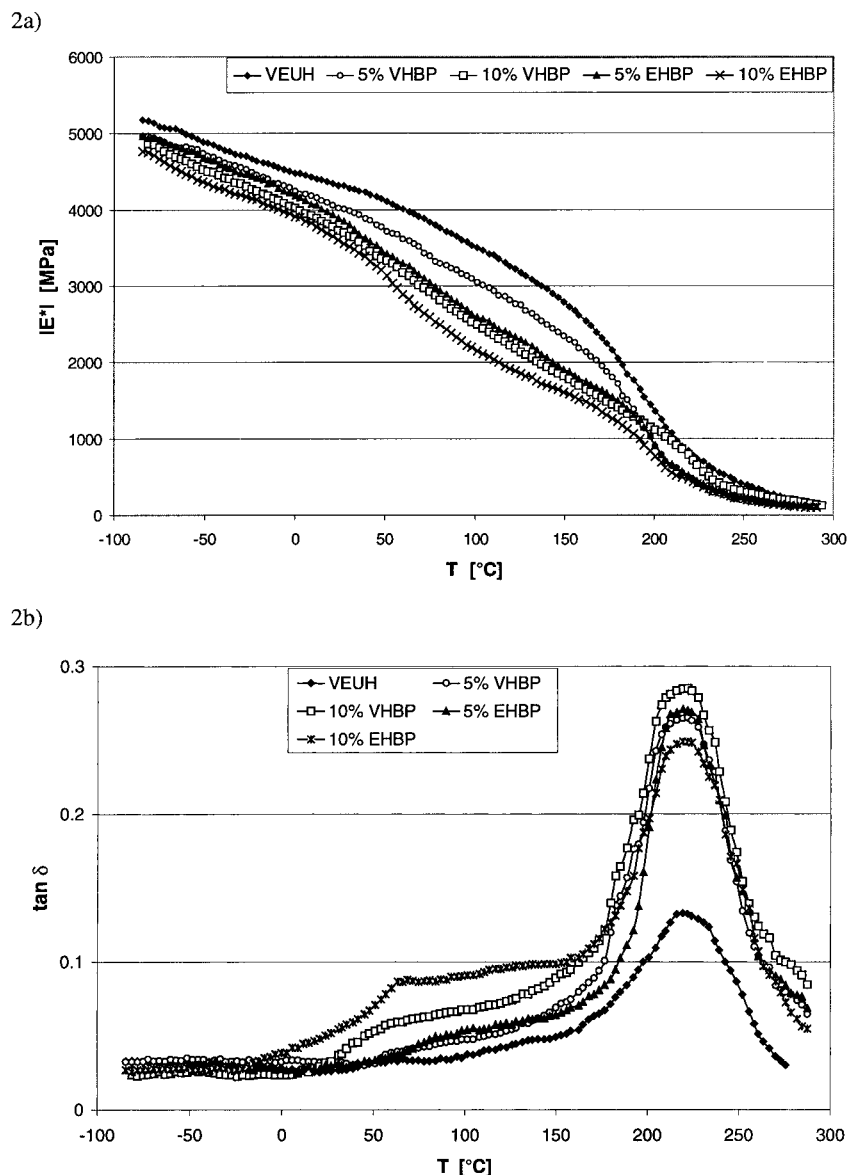


Figure 2 (a) E^* versus T and (b) $\tan \delta$ versus T traces of VEUH modified by various amounts of VHBP and EHBP, respectively.

amounts of CTBN rubber. One can see that incorporation of CTBN results in a stiffness decrease at $T \approx -35^\circ\text{C}$, which is the glass transition temperature (T_g) of this rubber under the experimental conditions (Fig. 1). In Figure 1, the T_g of both the CTBN and VEUH matrices ($T_g \approx 230^\circ\text{C}$) are clearly visible. Incorporation of CTBN increases not only the T_g relaxation of the rubber, but it also results in a well-developed shoulder on the T_g relaxation of the base resin. This transition is likely linked to the interphase between the rubber and the VEUH matrix. The onset of this broad relaxation transition suggests that the morphol-

ogy of the CTBN-modified VEUH should be rather complex.

The DMA response of the systems modified by hyperbranched modifiers is completely different. Either VHBP or EHBP cause a significant decrease in the stiffness of the VEUH [Fig. 2(a)]. Attention is drawn to the difference between VHBP and EHBP. EHBP impacts the crosslinked network structure more markedly than does VHBP [Fig. 2(b)]. Recall that the secondary hydroxyl groups of the VE resin may react directly both with the isocyanate groups of the polyisocyanate and the EP functionality of the EHBP. The

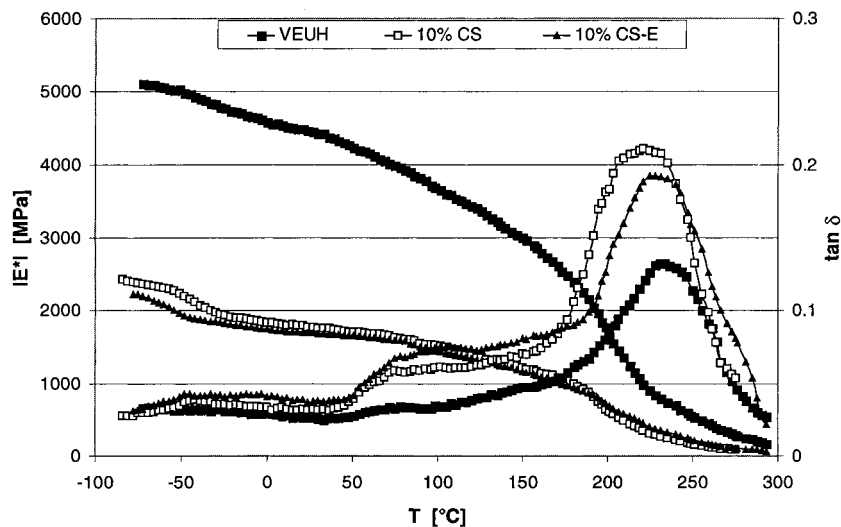


Figure 3 E^* versus T and related $\tan \delta$ versus T traces for VEUH without and with 10 wt % CS and CS-E rubber, respectively.

latter yields a further secondary hydroxyl group which may enter in the same reactions as mentioned above. This should result in a network structure of varying crosslink density. As the segmental motion within is also different, one thus expects the appearance of a peak or shoulder below the T_g relaxation of the base VEUH similarly to the CTBN modifier. Figure 2(b) shows that this is the case. VHBP, on the other hand, is not involved in the urethane reaction but is involved only with the free-radical styrene copolymerization.

Figure 3 shows the DMTA spectra of CS- and CS-E-modified VEUH. The T_g of these CS rubbers is at $T \approx -50^\circ\text{C}$. Again, the T_g of the VEUH resin is only slightly influenced by the incorporation of the core/shell rubbers. This is similar to the cases with CTBN and functionalized hyperbranched polyesters and suggests that this transition is controlled by the free-radical polymerization reaction. The shoulder peak of the CS-E is far more pronounced than is the nonreactive CS version. This observation helps us to trace the reason for the appearance of the shoulder in the $\tan \delta$ versus T curves. The interphase region between the preformed functional CS rubber is less crosslinked than is the VEUH bulk. It is intuitive that the situation is very similar to that of the CTBN modification (cf. Fig. 1). However, in the case of CTBN, the interphase region should be markedly larger than with a preformed rubber of given particle size. In comparing Figures 1 and 3, one can guess that the particle distribution of the CTBN

in the VEUH resin is highly inhomogeneous (being controlled by the crosslinking conditions), which, per se, should result in a broad relaxation transition (which is the case—see Fig. 1).

Fracture Mechanical Response

Table I lists the K_c and G_c data as a function of the modifier type and content. K_c monotonously increases with an increasing CTBN and EHBP content and CTBN seems to be the most efficient toughness improver. Recall that both these modifiers affect the crosslinking via the “polyurethane route” and compete with the reaction between $-\text{OH}$ (VE) and $-\text{NCO}$ (polyisocyanate). The variation of K_c as a function of VTBN content is less pronounced. This suggests that, among the liquid nitrile rubbers, the carboxyl-terminated type should be selected. On the other hand, both EP- and vinyl-functionalized hyperbranched polyesters performed quite well in respect to toughness improvement. Interestingly, the core/shell rubbers did not improve the fracture toughness at all.

The above ranking, namely,

$$\text{CTBN} > \text{EHBP} \approx \text{VHBP} > \text{VTBN} \\ > \text{CS, CS-E} \approx \text{VEUH}$$

holds also when the fracture energy, G_c , is considered (cf. Table I). Figure 4, showing the course of G_c normalized to the unmodified VEUH, emphasizes the above tendency. The fact that the

Table I Fracture Mechanical Data, That Is, K_{Ic} and G_c Values, of the Compositions Studied

Composition	K_{Ic} (MPa m ^{1/2})	G_c (J/m ²)	G_c^* (J/m ²)
VEUH	0.53	128	80
5% CTBN	0.55	199	94
10% CTBN	0.68	274	219
20% CTBN	0.90	946	780
5% VTBN	0.56	162	129
10% VTBN	0.55	195	150
20% VTBN	0.63	261	239
5% VHBP	0.60	136	114
10% VHBP	0.58	135	114
20% VHBP	0.83	424	360
5% EHBP	0.47	119	81
10% EHBP	0.67	200	203
20% EHBP	0.74	446	390
5% CS	0.57	159	128
10% CS	0.53	175	139
5% CS-E	0.57	175	152
10% CS-E	0.54	183	136

G_c^* was calculated by $G_c^* = K_{Ic}^2/E$, where E is the Young's modulus. E was determined in static tensile tests on dumbbells using an incremental extensometer with mechanical grips. Scatter range of the data is less than $\pm 20\%$ (cf. also Fig. 4).

experimentally determined G_c values agree fairly well with those calculated by $G_c = K_{Ic}^2/E$ (valid for the plane stress state) is a clear hint that the prerequisites of the linear elastic fracture mechanics (i.e., brittle fracture at a given maximum

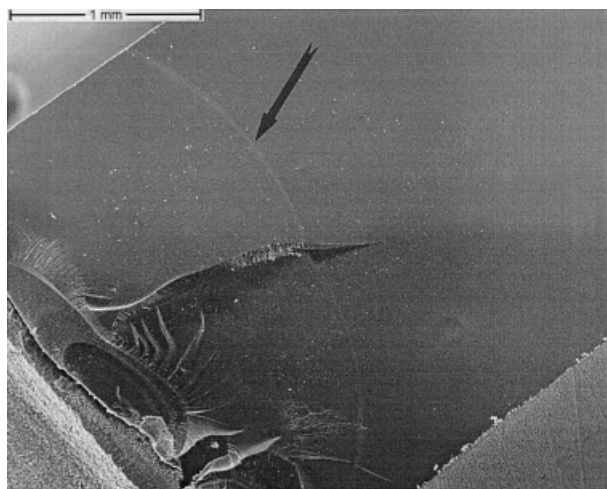


Figure 5 SEM picture taken on the fracture surface of the neat VEUH resin. Notes: The razor notch is visible on the bottom left of this picture. The crack arrest line is indicated by the arrow.

load) are met in our case. It is obvious that the above ranking of the modifier can be deduced from changes in the failure mode of the related systems. Therefore, extensive fractographic work was devoted to clarify this issue.

Fractography

Figure 5 demonstrates that the neat VEUH underwent brittle failure. Near to the notch, one can recognize a shell/chevron-type pattern which can

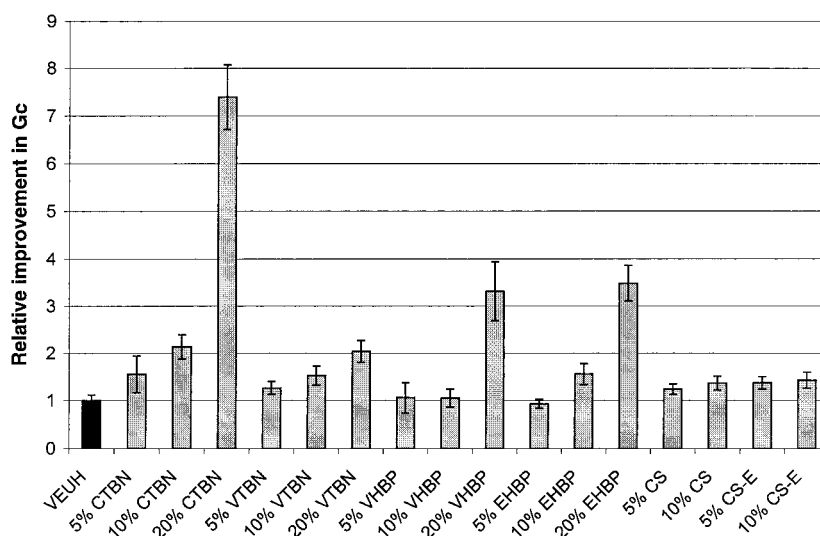


Figure 4 Relative change in the fracture energy (G_c) as a function of modifier type and content. Note: The normalization value was 120 J/m².

be traced to crack initiation and advance on slightly different planes. This affects the crack speed across the thickness in its early stage. The arrow in Figure 5 indicates an arrest line. Note that such arrest lines develop if the speed of the advancing crack is below a critical value, which results in some relaxation of the local stress.²⁸

Figure 6(a,b), taken from the fracture surface of a CT specimen of VEUH with 10 wt % CTBN, shows that the CTBN modifier is present in a dispersion of a broad particle size. CTBN particles as large as 50 μm in diameter are frequent [cf. Fig. 6(b)]. The fracture surface at the notch region shows that some crack tip blunting occurred prior to fast fracture [indicated by the arrow in Fig. 6(a)]. Figure 6(b) shows that the CTBN particles consist not only of rubber but also contain a considerable amount of VEUH. One can assume that the crosslinking degree in the particle is substantially lower than in the bulk. As a consequence, the broad shoulder in the $\tan \delta$ versus T curves (cf. Fig. 1) should be attributed to the complex feature of the CTBN dispersion instead of the interphase solely as presumed initially. At a higher CTBN content, one can expect even some phase inversion. Figure 6(c), taken from the fracture surface of a specimen of VEUH with 20 wt % CTBN, demonstrates that this is indeed the case. Accordingly, the failure mechanism in CTBN-modified VEUH is crack tip blunting due to stretching of the rubber particles of large size and complex ("salami") structure—see Figure 6(a). Crack bifurcation/deflection dominates the fast fracture range, especially at a high CTBN content [Fig. 6(c)].

Figure 7 compares the fast fracture range of VEUH modified by 10 wt % EHBP [Fig. 7(a)] and 10 wt % VHBP [Fig. 7(b)]. One can recognize that EHBP works as a finely dispersed modifier with good bonding to the matrix. EHBP forces the crack to deflect and bow during its propagation [cf. Fig. 7(a)]. On the other hand, VHBP is incorporated into the VEUH matrix and thus contributes to its shear deformation [cf. Fig. 7(b)].

Figure 8 shows why the CS modifier did not improve the toughness of the VEUH resin. The fracture surface is smooth without evidence of crack bifurcation. Further, the effect of crack pinning (crack bowing) is also negligible. Note that the tail ribs behind the particles evidence the onset of the crack tip pinning mechanism. Possible reasons for this behavior are too large particles with poor bonding to the VEUH matrix.

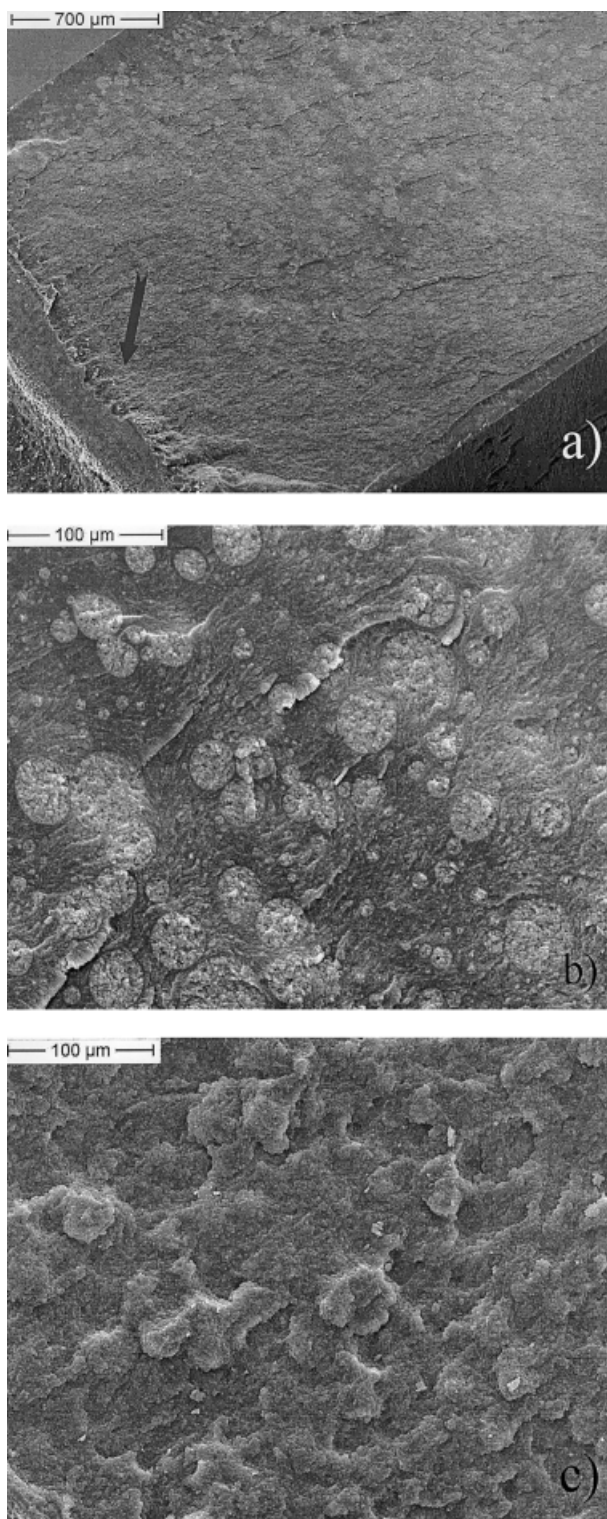


Figure 6 SEM pictures taken on the fracture surface of VEUH modified by (a,b) 10 and (c) 20 wt % CTBN rubber.

The fractographic inspection corroborates our previous note in respect to the new relaxation transition observed in the DMTA spectra [cf. Figs. 1, 2(b), and 3]. This is, in fact, an effect of the interphase and morphology of the dispersed phase, which obviously affects the failure mechanisms. Recall that among the latter mechanisms crack blunting followed by crack deflection/bifurcation proved to be the most efficient ones. Considering the fracture mechanical data in Table I and the $\tan \delta$ versus T traces of the related compounds [Figs. 1 and 2(b)], one can claim that high toughness correlates with the extent of the new relaxation peak.

CONCLUSIONS

Based on this work devoted to the toughness improvement of a VEUH resin by adding various

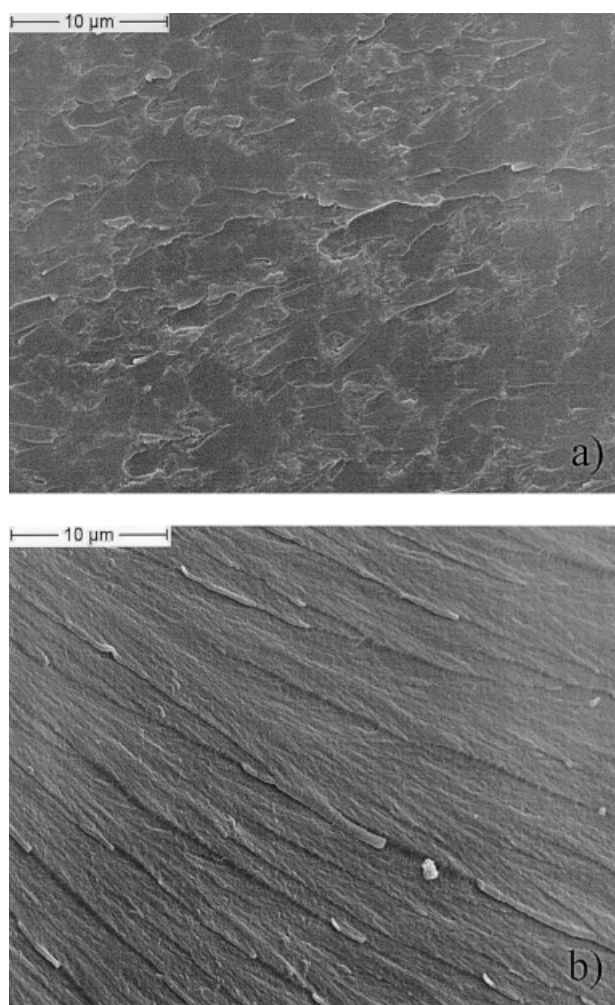


Figure 7 SEM pictures from the fast fracture range of VEUH containing 10 wt % (a) EHBP and (b) VHBP.

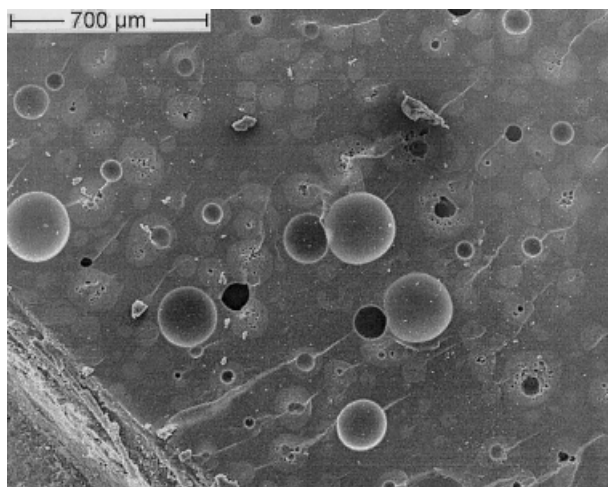


Figure 8 SEM pictures taken on the fracture surface of VEUH modified by 10 wt % CS rubber. Note: Razor notch is visible on the bottom left of this picture.

modifiers which either impart the free-radical polymerization (vinyl functionality) or urethane formation (EP, carboxyl functionalities), the following conclusions can be drawn:

- The most efficient modifiers, participating in the urethane chemistry, have carboxyl (CTBN) or EP functionalities (EHBP). Contrary to CTBN, the incorporation of EHBP does not result in a reduced stiffness and glass transition temperature (T_g).
- The related failure mode is crack tip blunting favored by rubber stretching and enhanced shear deformation of the VEUH matrix. The fast crack growth in systems with CTBN and EHBP modifiers is governed by crack deflection and pinning. Crack pinning alone did not yield toughness improvement as showed by the examples of VEUH containing preformed core/shell rubbers.

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