

Toughening of vinylester–urethane hybrid resins by functional liquid nitrile rubbers and hyperbranched polymers

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Abstract

Liquid nitrile rubbers with vinyl (VTBN), carboxyl (CTBN) and epoxy (ETBN) and hyperbranched polyesters with vinyl (VHBP) and epoxy (EHBP) functionalities were added in 10 wt% to a bisphenol-A based vinylester–urethane hybrid resin (VEUH) for its toughening. The fracture energy (G_c) was determined on compact tensile specimens at ambient temperature. High toughness improvement was achieved by adding ETBN and CTBN to VEUH. It was established that a change in the initial stoichiometry of OH/NCO may affect G_c .

The combination of CTBN with other additives in 1:1 ratio yielded a synergistic effect with respect to G_c . Changes in G_c were explained by differences in the fracture mode based on fractographic inspection of the fracture surface of the specimens. It was shown the same G_c may be derived from completely different failure scenarios. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Vinylester–urethane hybrid resin; Liquid nitrile rubber; Hyperbranched polyester

1. Introduction

Vinylester (VE) resins are usually produced by reacting bisphenol-A type epoxy resins with acrylic or methacrylic acids. The VE used in this study is a dimethacrylate ester with terminal vinyl groups which is also termed epoxy acrylate-based [1] or divinyl ester resin. Although such a bismethacryloxy VE resin can form a crosslinked structure without the addition of a comonomer, it is generally diluted in styrene (St). St is an active diluent (comonomer) that participates in the crosslinking via free radical-induced copolymerization with the VE. The further role of St is to tailor the room temperature (RT) viscosity of the VE to achieve the desired processing. Cured VE outperforms the traditional unsaturated polyesters with respect to several properties (excellent resistance to hydrolysis and chemicals, low water uptake, high glass transition temperature, T_g) and challenges even epoxy resins in various application fields. The market acceptance of VE is also favoured by its easily controllable cure behaviour.

Note that the bismethacryloxy VE resins contain secondary hydroxyl groups due to the opening of the epoxy ring when reacting with methacrylic acid. They may

react with polyisocyanates. The crosslinking structure of the related resin, called vinylester–urethane hybrid (VEUH), is thus formed by a combination of free radical polymerization (via St addition on the double bonds of VE) and polyaddition (between the –OH and –NCO groups of the VE and polyisocyanate, respectively). VEUH possesses outstanding mechanical and thermal properties [2] but suffers from low toughness similar to most thermosetting resins. It was demonstrated that the toughness of VE can be improved without adding modifiers by controlling the crosslink density. This was achieved by increasing the molecular mass of the VE oligomers and by optimizing the VE/St ratio [3,4]. The related toughness improvement is, however, limited. Contrary to epoxy resins, the toughening of VE by low molecular mass polymeric modifiers was addressed by only few works. In analogy to epoxy [5,6] and unsaturated polyester resin [7,8] liquid functional (vinyl-, epoxy- and carboxyl-) nitrile rubbers were mostly incorporated in VE resin [1,7,9–11]. The toughness upgrade remained often below expectation, which was traced to the low solubility of the related rubber in the St-diluted VE resin. In order to improve solubility, other functional rubbers [12] and various end-capping strategies [1,7] were used. It should be emphasized that the solubility of the functional liquid rubbers may be better in VEUH owing to the presence of the polyisocyanate. VEUH resins may become favoured matrix materials in composites [13] if

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their toughness and ductility are thoroughly enhanced. Our previous work was devoted to screening the toughness upgrade efficiency of functional liquid nitrile rubbers and functional hyperbranched polyesters (dendrimers) [14]. It was found that those modifiers which react with the secondary OH-groups of the VE (epoxy functionality) and with the polyisocyanate (carboxyl functionality) are more suitable than those merely participating in the free radical-induced crosslinking via St copolymerization (vinyl functionality). However, no information is available on the effect of modifier combinations which affect both crosslinking reactions. Note that in the case of an eventual synergy the modifier content (which yields a reduction in stiffness and strength) could be substantially reduced. A further aspect of interest was to check whether or not the restoration of the initial NCO/OH ratio in the CTBN-containing formulations affects the toughness response. The above open questions were addressed by the present study.

2. Experimental

2.1. Materials

The VEUH resin contained a bisphenol-A based St-diluted VE of bismethacryloxy type (Daron[®] XP-45-A-2) and novolac-based polymeric isocyanate (Daron[®] XP 40-B-1) both products of DSM structural resins. The base recipe was as follows:

- 100 parts VE (Daron[®] XP 45-A-2, St content: 30 wt%, ratio of the double bonds VE/St = 1:1.2)
- 38 parts polymeric isocyanate (Daron[®] XP 40-B-1, NCO functionality: 2.7—denoted as NPI)
- 1.5 parts peroxide (dibenzoylperoxide, Lucidol[®] CH-50L of Akzo Nobel, peroxide content: 50 wt%)
- 1.5 parts accelerator (*N,N*-diethylaniline, NL-64-10P, Akzo Nobel, active component: 10 wt%)

As modifiers carboxyl- (Hycar[®] CTBN 1300X8, designated as CTBN), vinyl- (Hycar[®] VTBNX 1300X33, designated as VTBN) and epoxy-terminated liquid nitrile rubbers (Hycar[®] ETBN 1300X40 with 50 wt% St content, designated as ETBN) of Noveon Inc. (www.noveoninc.com), hyperbranched polyesters (dendrimers) with epoxy- (Boltorn[®] E1—denoted as EHBP) and vinyl-functionalities (Boltorn[®] U2—denoted as VHBP) of Perstorp Speciality Chemicals (www.perstorp.com) were used.

In the first test series all of the above listed modifiers were incorporated separately in the VEUH in 10 wt% each. In the second series the efficiency of the combinations containing CTBN and one additional modifier (5 + 5 wt%) was checked. CTBN was selected because this modifier proved to be the most efficient one in the previous work

[14]. Note that the possible reaction between CTBN and polyisocyanate has been neglected in the aforementioned test series. Therefore, in the following test additional NPI was added (by considering the possible reaction between –COOH and –NCO) in order to restore the initial stoichiometry of the base VEUH. The NPI amount calculated for the CTBN modifier has also been added to the other recipes irrespective of whether or not the related modifier may react with NPI. The reason behind this strategy was to get an experimental proof as to which reaction (*viz.* polymerization or polyaddition) the related modifier participated in. It should be noted here that the double bonds derived from the butadiene of the liquid rubbers are far less active than the terminal ones in VE and VTBN, and thus they do not enter in heteropolymerization with St.

Specimens (compact tension—CT, dumbbells) were produced by pouring the homogenized and degassed resin in steel moulds having a bolted cover plate for easy demoulding of the specimens. Curing of all resin modifications occurred under the following conditions: mixing, homogenization, degassing and filling the moulds occurred at ambient temperature, than the temperature was increased to 50 °C and kept 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.

2.2. Tests

Phase structure of the toughened VEUHs were characterized by dynamic mechanical thermal analysis (DMTA). DMTA spectra were taken on rectangular specimens (50 × 10 × 4 mm³; length × width × thickness) in flexural mode at 10 Hz using a Eplexor 150 N device of Gabo Qualimeter. The static and cyclic (sinusoidal) loading components were set for 4 and ±2 N, respectively. DMTA spectra, *viz.* complex modulus (E^*) and its constituents (E' and E''), mechanical loss factor ($\tan \delta$) as a function of temperature (T), were measured in the interval $T = -100$ to $+300$ °C at a heating rate of 1 °C/min.

Fracture toughness (K_{IC}) and fracture energy (G_c) were determined in accordance with the ESIS testing protocol [15]. 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 of the CT-specimens was sharpened by a razor blade prior to their tensile loading (mode I) at RT with a crosshead speed $v = 1$ mm/min.

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.

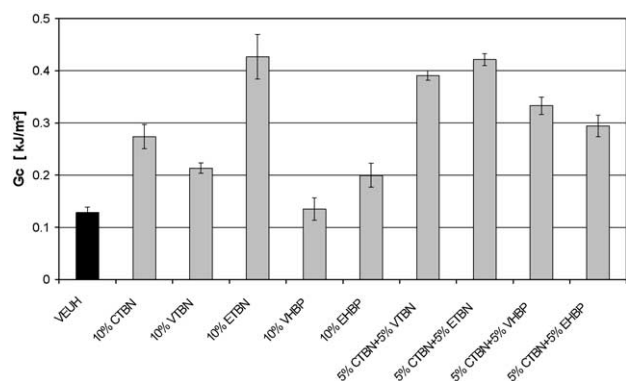


Fig. 1. Fracture energy (G_c) of VEUH resins modified by functional liquid rubbers, dendrimers and by their combinations.

3. Results and discussion

3.1. Effect of modifiers and their combinations

Fig. 1 displays the G_c values of the modified VEUH resins. Highest toughness improvement was noticed when ETBN and CTBN rubbers were added; these affect the crosslinking via the polyurethane reaction. Recall that the epoxy groups react with the secondary hydroxyl of VE and that the carboxyl groups react with the isocyanate of NPI, respectively. The efficiency of the functional (epoxy and vinyl) hyperbranched polymers is similar to that of VTBN. Note that VTBN is likely participating in the free radical polymerization of VE with St. Although the toughness improvement by EHBP is higher than by VHBP, it is still below the level reached by ETBN. This suggests some basic difference in the morphology. EHBP is probably built in the crosslinked network, whereas ETBN may form droplet inclusions owing to phase separation. However, before claiming that the toughness improvement strategy should be focused on the polyurethane route the combined action of modifiers should be clarified. For this screening CTBN was selected as base component to which vinyl- and epoxy-functionalized rubbers (VTBN, ETBN) and hyperbranched

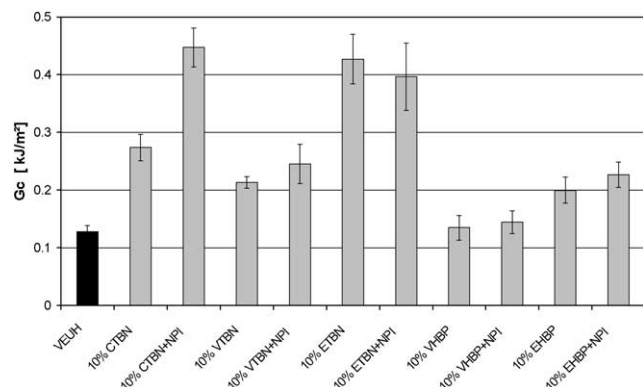


Fig. 2. Fracture energy (G_c) of VEUH resins modified by functional liquid rubbers and dendrimers in the presence of additional NPI.

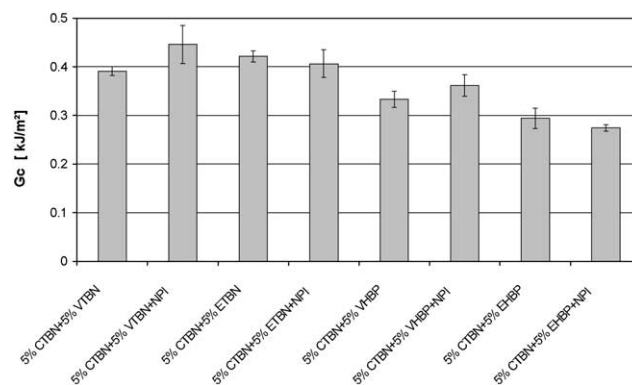


Fig. 3. Fracture energy (G_c) of VEUH resins modified by combinations of functional liquid rubbers and dendrimers in the presence of additional NPI.

polyesters (VHBP, EHBP) were added at a composition ratio of 1:1 (5 + 5 wt% other additive). By this way the toughening efficiency of liquid nitrile rubbers and hyperbranched polymers bearing the same functionalities could be compared. G_c data in Fig. 1 indicate a synergistic effect for all combinations except CTBN + ETBN. One can notice that the toughness level achieved by adding 10 wt% ETBN or CTBN can be reached by adding 10 wt% ETBN or CTBN. Attention should be paid to the good performance of CTBN + VTBN and CTBN + VHBP. This suggests that the most straightforward strategy is to use additives which affect both the heteropolymerization and polyaddition reactions.

3.2. Effect of additional polyisocyanate

It should be kept in mind that the COOH group of CTBN may react with the NCO group of NPI. By this way, however, the initial OH(VE)/NCO(NPI) ratio is destroyed. This can be restored by dosing with an appropriate amount of additional NPI. This results in a further G_c enhancement in case of VEUH modified by 10 wt% CTBN (Fig. 2). For comparison purpose the same amount of NPI was dosed in all VEUH resins modified with 10 wt% additive. Except CTBN, there is hardly any effect of additional NPI on the toughness response. This indicates that the COOH functionality of CTBN alone affected the polyurethane reaction. Interestingly, the effect of additional NPI on the toughness is marginal when using modifier combinations with CTBN (Fig. 3). This is a further argument for using a combination of modifiers affecting both the free radical polymerization and the polyaddition reactions.

3.3. Phase structure

DMTA curves of VEUH modified by functional liquid nitrile rubbers demonstrate the presence of a two-phase morphology, since the glass transitions temperatures (T_g) of both rubber (at ca. -40 °C) and VEUH matrix (at ca. 240 °C) are clearly discernible (Fig. 4). Incorporation of

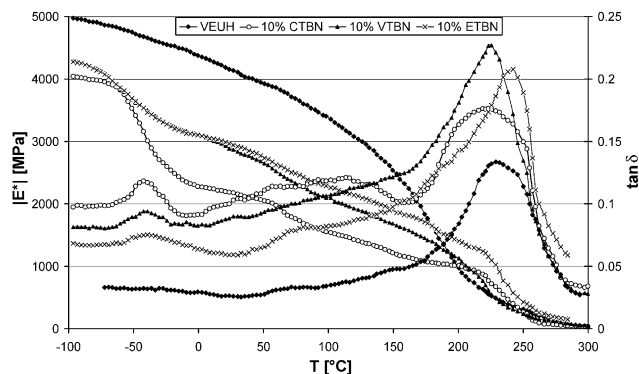


Fig. 4. E^* vs T and $\tan \delta$ vs T traces for VEUH without and with 10 wt% CTBN, VTBN and ETBN rubbers.

rubber is accompanied by a stiffness reduction. One would expect that the stiffness decrease is the largest for ETBN and CTBN which are involved in the ‘polyurethane chemistry’. This is, however, not the case with ETBN which was added in a St solution to the VEUH resin. The shoulder at about 70 °C may be assigned to a part of the crosslinked network which is less tight and highly irregular due to the incorporation of the functional rubber. The DMTA response of VEUH modified by hyperbranched polymers differs from that of the rubber modification [14]. The stiffness degradation of VEUH is less pronounced when modified by hyperbranched polymers instead of by liquid rubbers. On the other hand, the shoulder-type broad relaxation transition was also present in the VHBP and EHBP modified systems. This fact corroborates our above hypothesis, viz. the shoulder is linked to an irregular network portion in which the molecular mass between crosslinks is very high. Additional NPI enhanced the stiffness and reduced the intensity of the shoulder in the $\tan \delta$ – T curves (Fig. 5). The latter hints at the formation of a tighter, more regular crosslinked network. Furthermore, the $\tan \delta$ – T traces with and without additional NPI suggest that the shoulder is related to that part of the network structure which is controlled by the polyurethane reaction. An increase in the

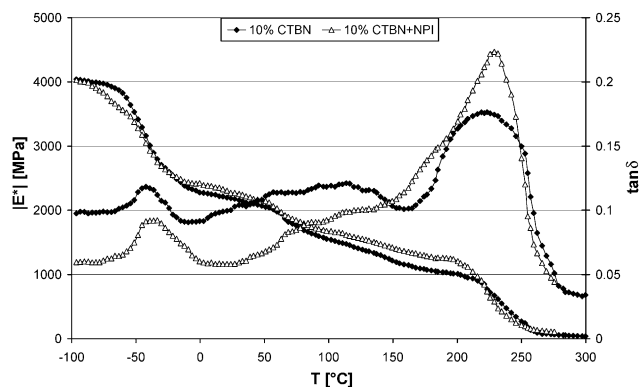


Fig. 5. E^* vs T and $\tan \delta$ vs T traces for VEUH modified by 10 wt% CTBN without and with additional NPI.

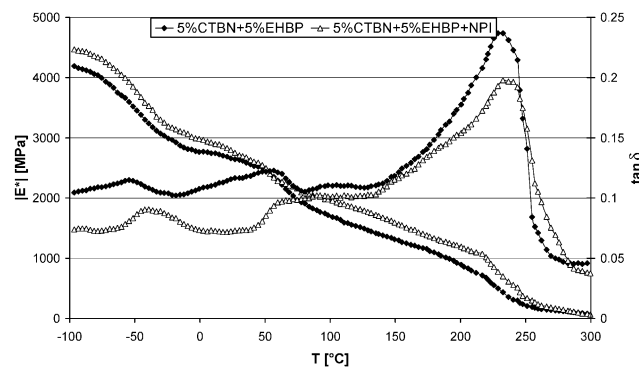


Fig. 6. E^* vs T and $\tan \delta$ vs T traces for VEUH modified by 5 wt% CTBN + 5 wt% EHBP without and with additional NPI.

crosslink density owing to additional NPI reduces the chain mobility and thus the extent of this shoulder-type relaxation transition. If the latter is related to the polyurethane reaction then the combined use of CTBN and EHBP should result in an even more pronounced change of this transition. This expectation is based on the related reactions, viz. COOH (CTBN) + NCO (NPI) and OH (VE) + epoxy (EHBP). The DMTA spectra in Fig. 6 demonstrate that this is in fact the case. The $\tan \delta$ – T traces in Fig. 6 show again that additional NPI yields a more crosslinked structure (increase in Young’s modulus and decrease in mechanical loss factor).

3.4. Fracture mechanisms

Fig. 7 compares SEM pictures taken on the fracture surface of VEUH modified by 10 wt% ETBN (a) and CTBN (b), respectively. One can see that the rubber particles in both systems are of ‘salami type’, i.e. the particles contain resin (i.e. VE) inclusions. It is also obvious that the ETBN is more finely dispersed than CTBN, and in addition ETBN is present in a quasi bimodal distribution. The fracture mechanisms in both cases are: cavitation of the particles followed by shear deformation of the matrix. Ribbs on the fracture surface of CTBN-modified VEUH evidence the onset of shear deformation (Fig. 7(b)). Crack pinning is also at work based on the characteristic appearance of tails [16]. Dosing additional NPI to the VEUH with 10 wt% CTBN results in very coarse distribution of CTBN particles of salami type (Fig. 7(c)). For the toughness improvement the same mechanisms as mentioned earlier (cavitation, matrix yielding and crack pinning) are responsible. An interesting aspect is that even the crack pinning process was accompanied by considerable shear deformation of the matrix between the particles (Fig. 7(c)). This is likely the reason for the G_c improvement reported earlier with respect to Fig. 2. On the fracture surface of VEUH modified by CTBN + ETBN the rubber particles cannot easily be resolved (Fig. 8(a)). This suggests that the rubber does not form inclusions via phase separation but acts as a ‘binding agent’ for the morphological entities of VE. Recall that the

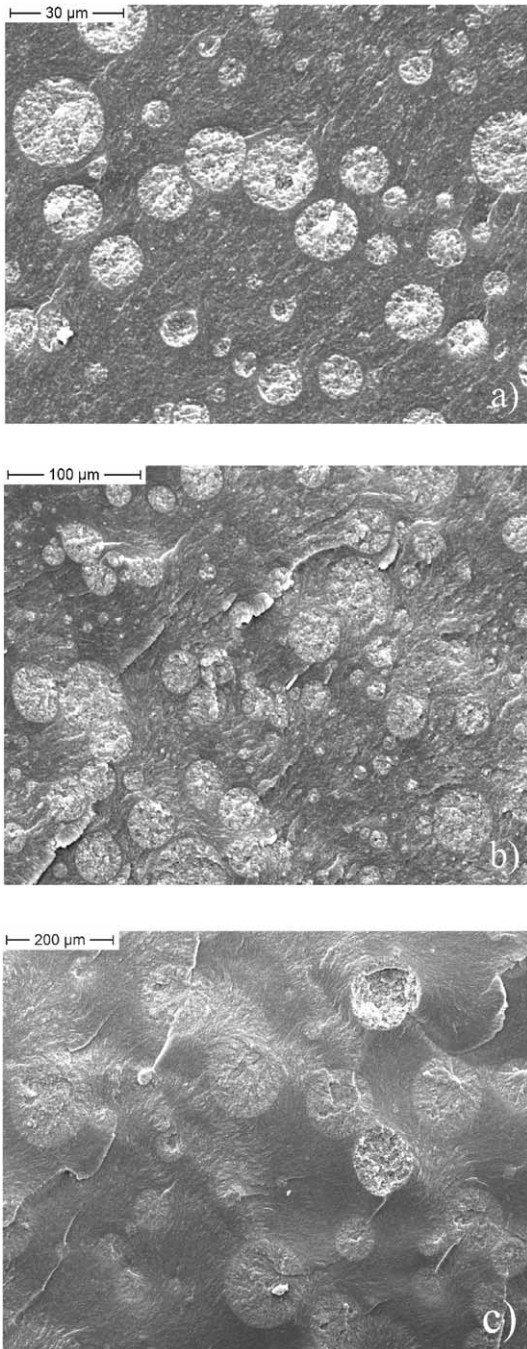


Fig. 7. SEM pictures taken on the fracture surface of VEUH modified by 10 wt% ETBN (a), 10 wt% CTBN (b), 10 wt% CTBN + NPI (c).

morphology of VE is characterized by a two-phase structure: a nodular (micrometer sized) VE network dispersed in a polystyrene phase [17]. Additional NPI, however, may restore the phase-separated structure (Fig. 8(b)). A similar scenario was found for the CTBN + EHBP combinations. The dominating fracture mechanisms in these systems is likely crack tip blunting and crack branching/bifurcation (Fig. 9). Fig. 9 makes also obvious the presence of the earlier-mentioned nodular morphology which triggers the crack bifurcation process. This is an interesting finding

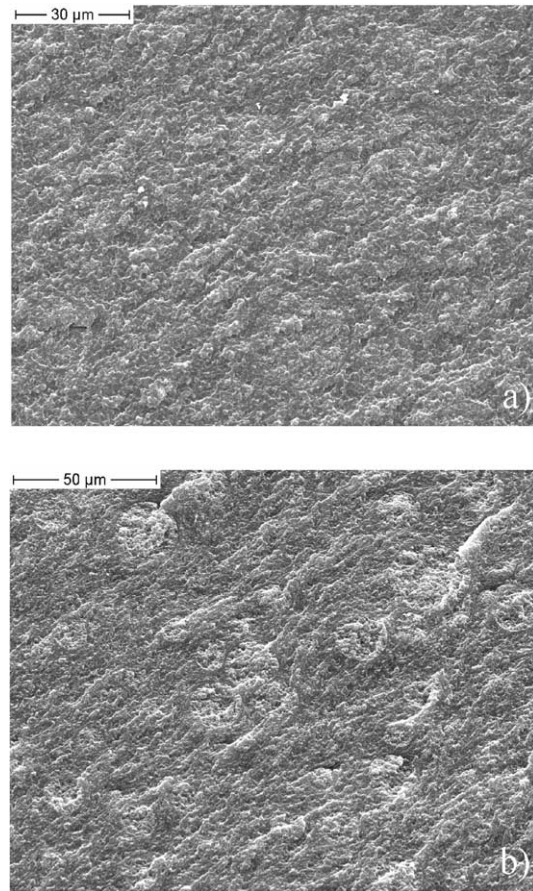


Fig. 8. SEM pictures taken on the fracture surface of VEUH modified by 5 wt% CTBN + 5 wt% ETBN without (a) and with additional NPI (b).

as usually these crack bifurcation mechanisms are believed to be markedly less efficient than the cavitation/shear deformation type. The toughness improvement by the modifier combination CTBN + VHBP is due to cavitation and crack pinning (Fig. 10(a) and (b)). It is worth noting that although the G_c values of the modifier combination (Fig. 3) were on the same level, the fracture mechanisms behind—as discussed earlier—were very different. It is, therefore, not

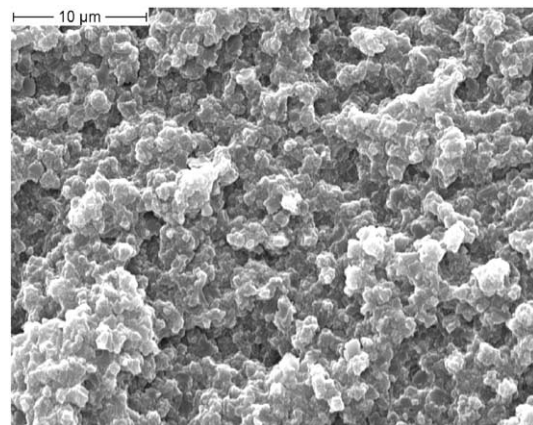


Fig. 9. SEM pictures taken on the fracture surface of VEUH modified by 5 wt% CTBN + 5 wt% EHBP.

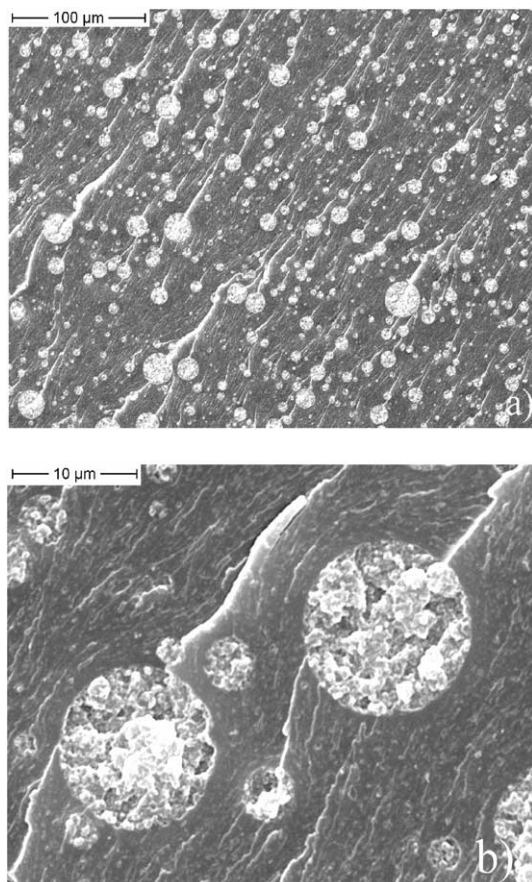


Fig. 10. SEM pictures taken on the fracture surface of VEUH modified by 5 wt% CTBN + 5 wt% VHBP.

an easy task to deduce some general rules for the toughness improving strategy of VEUH resins.

4. Conclusions

Based on this work aimed at improving the toughness of a vinyl ester–urethane hybrid resins (VEUH) by adding functional polymers which either affect the heteropolymerization of the VE with St (vinyl functionality) or the polyurethane reaction (epoxy and carboxyl functionalities), the following conclusions can be drawn:

- Most effective toughness modifiers are those combinations which participate in both reactions (i.e. free radical polymerization and polyaddition)
- The stoichiometric ratio affected by the functionality of

the modifier (in our case COOH of the CTBN) has a great influence on the fracture energy

- The phase structure governs the fracture mechanisms. Different fracture mechanisms may, however, yield the same fracture mechanical response.

Acknowledgments

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