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Liquid rubber modified vinyl ester resins: fracture and mechanical behavior

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Abstract

The fracture and mechanical behavior of vinyl ester resins (DVER) cured with styrene (S) and modified with two different liquid rubbers has been determined and related to the microstructure of the resulting modified thermosets. Carboxyl terminated poly(butadiene-*co*-acrylonitrile) (CTBN), a common toughening agent for epoxy resins, is an almost unreactive rubber with the DVER and S comonomers. During crosslinking the system undergoes a phase separation mechanism similar to that occurring in unsaturated polyester resins (UPE) modified with a low profile additive (LPA), such as polyvinyl acetate (PVAc). This process leads to materials, which exhibit a sharp drop in density at high CTBN concentrations (≥10% by weight) and to the development of a co-continuous microstructure in these materials. This feature is consistent with a maximum in fracture toughness as a function of the additive (CTBN) content, followed by a rapid deterioration in toughness at higher concentrations. On the other hand, the use of a reactive rubber, vinyl terminated poly(butadiene-*co*-acrylonitrile, VTBN, as the additive leads to a different morphology consisting on rubber inclusions in the thermoset matrix. This structure gradually reduces the fracture and mechanical performance of the resins modified with increasing concentration of reactive elastomer.

Keywords: Fracture properties; Mechanical properties; Modified vinyl ester resins

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1. Introduction

Thermosets resins are brittle in nature and therefore, in order to improve their fracture resistance they are usually blended or reacted with different additives and modifiers, which generally form a second dispersed phase. The most frequently used modifiers are liquid rubbers. The morphology of the final modified thermoset can significantly affect the toughening mechanism and consequently its fracture toughness.

The majority of the published results on toughened thermosets deal with epoxy resins modified by liquid rubbers and for these systems the mechanisms governing the toughening have been extensively studied and are well established [1–4]. In these thermosets, phase separation generates a morphology of spherical rubber particles in the epoxy continuous phase, which leads to toughening mechanisms: such as cavitation of rubber particles followed by void growth and consequent shear yielding of the epoxy matrix. Other thermosets like unsaturated polyesters (UPE) and divinyl esters resins (DVER) have been less studied, although some results are available in the literature [5]. The toughening of UPE and DVER crosslinked with styrene (S) has been frequently achieved using relatively inmiscible rubbers, and in some cases two phases were present from the beginning of the reaction or they were generated at low conversions of the system [6]. This condition leads to particulate morphologies of the type epoxy-rubber mentioned above. On the other hand, low profile additives (LPA) have been used to control the shrinkage of UPE resins [7,8]. In this case, the final morphologies of the modified materials are completely different and depend on the phase separation process which have been described by different authors [9–11]. The UPE-modifier-S system is homogeneous at the beginning of the reaction, as the reaction proceeds the reacted UPE-S copolymer becomes incompatible with the remaining unreacted liquid mixture and begins to separate forming nodules, where the crosslinking density increases remaining faster than in the bulk. In this process, the monomeric phase becomes enriched in the liquid rubber and different domains of copolymer and rubber-rich regions are formed. Depending on the amount of LPA utilized, the final morphology of the modified UPE corresponds to a

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Table 1
Characterization of the liquid rubber additives (data as reported by the supplier)

	CTBN 1300 × 8	VTBN × 33
% Acrylonitrile	18	18
Density (g/cm^3)	1.06	1.06
M_n (g/mole)	3600	3600
M_w (g/mole)[a]	6501	6498

[a] Calculated from the polydispersity measured by GPC.

matrix with non-spherical rubber inclusions or presents a co-continuous structure. Finally, due to the different volume contraction of the two phases during curing, microvoids develop between the rubber and the copolymer, and compensation for the resin shrinkage takes place at the cost of some microvoiding [9–11].

In this work, we have analyzed the effect of the different morphologies, generated on a DVER-S network modified with two different liquid rubbers, on the toughening of the resulting materials. The addition of an almost unreactive liquid rubber like CTBN (a toughening agent for epoxy resins), or a miscible and more reactive rubber, such as VTBN, to the vinyl ester resin was investigated. The effect of the addition on to the final mechanical properties was related to the corresponding morphologies of the two types of materials.

2. Experimental

2.1. Materials and sample preparation

A divinyl ester resin was synthesized by reacting an epoxy resin, diglycidyl ether of bisphenol A (DGEBA MY 790, Ciba Geigy, equivalent weight 176.2 g/eq) with methacrylic acid (Norent Plast S.A., laboratory grade reagent) using triphenylphosfine (Fluka A.G., analytical reagent) as the catalyst, in the presence of hydroquinone as stabilizer. The final conversion reached was higher than 93% for all batches and the formulations were stabilized with hydroquinone. The DVER molecular weight measured by gel permeation chromatography (GPC) was 583 g/mol, using polystyrene calibration [12]. The resins presented a "narrow" distribution of molecular weights ($M_w/M_n = 1.04$).

All the crosslinked samples were prepared maintaining a proportion of 55–45% by weight of DVER to S, as it is commonly used commercially [6]. The reaction was initiated using benzoyl peroxide (BPO, Lucidol 75%, Akzo Chemicals S.A.).

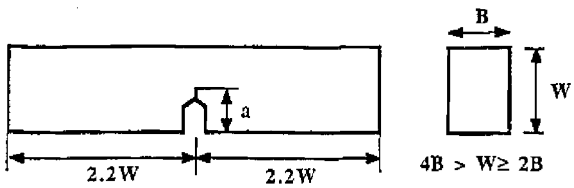

Fig. 1. Configuration of the fracture test specimens.

The liquid rubber additives were obtained from BF Goodrich Co, carboxyl terminated poly(butadiene-*co*-acrylonitrile) (CTBN, 1300 × 8) and vinyl terminated poly(butadiene-*co*-acrylonitrile) (VTBN, 1300 × 33). The characterization of the rubbers is summarized in Table 1.

In order to make samples for compression testing, the reactive mixture of monomers was injected into glass cylinders of 6 mm diameter previously sprayed with a silicone release agent. After removal from the molds, the compression specimens were carefully machined to reach the final dimensions (length/diameter > 1.5–2) and to obtain perfect parallelism for the upper and lower basis of the cylinders.

Thick plates for fracture measurements were obtained by casting the mixture into a mould consisting of two glass plates coated with a silicone release agent, spaced by a 6 mm rubber cord and held together with clamps. In order to avoid the rapid shrinkage of the sample and consequent fracture, a slow curing cycle (2 h at 50°C, 2 h at 80°C) was applied and the final material was postcured at 170°C during 1 h The test specimens were prepared by cutting rectangular bars from the slabs using a diamond saw. The thickness of the specimens was 6 mm. Central V-shaped notches were machined in the bars, then a razor blade was positioned in the notch and gently tapped to induce the growth of a natural crack ahead the blade. The samples tested were those showing a total crack length, a, in the range of $0.45 < a/W < 0.55$, where W is the width of the specimen (Fig. 1). The span to width (S/W) and the thickness to width (B/W) ratios were kept equal to 4 and 0.5, respectively [13].

2.2. Electronic microscopy

Fractured specimens were gold coated and then observed by scanning electron microscopy (SEM). Samples to be studied by transmission electron microscopy (TEM) were previously stained with OsO_4 [14] (immersed in OsO_4 solution during 7 days). Then a thin slice was obtained by microtoming the specimen and observed by TEM. Only the unreacted C=C bonds are stained by this technique. Since the DVER and S are already reacted through their unsaturations, only the less reactive internal unsaturations of the liquid rubbers are stained. Electronic microscopy was carried out using a Jeol JSM 35 CF microscope.

2.3. Physical and mechanical characterization

The densities of the cured copolymers with different compositions of elastomeric additive were determined at 20°C using picnometry in degassed distilled water.

Compression test specimens were deformed between metallic plates lubricated with molybdenum disulphide in a hydraulic INSTRON Universal Testing Machine Model 8501 according to ASTM D 695-85.

Flexural modulus and strength were measured according

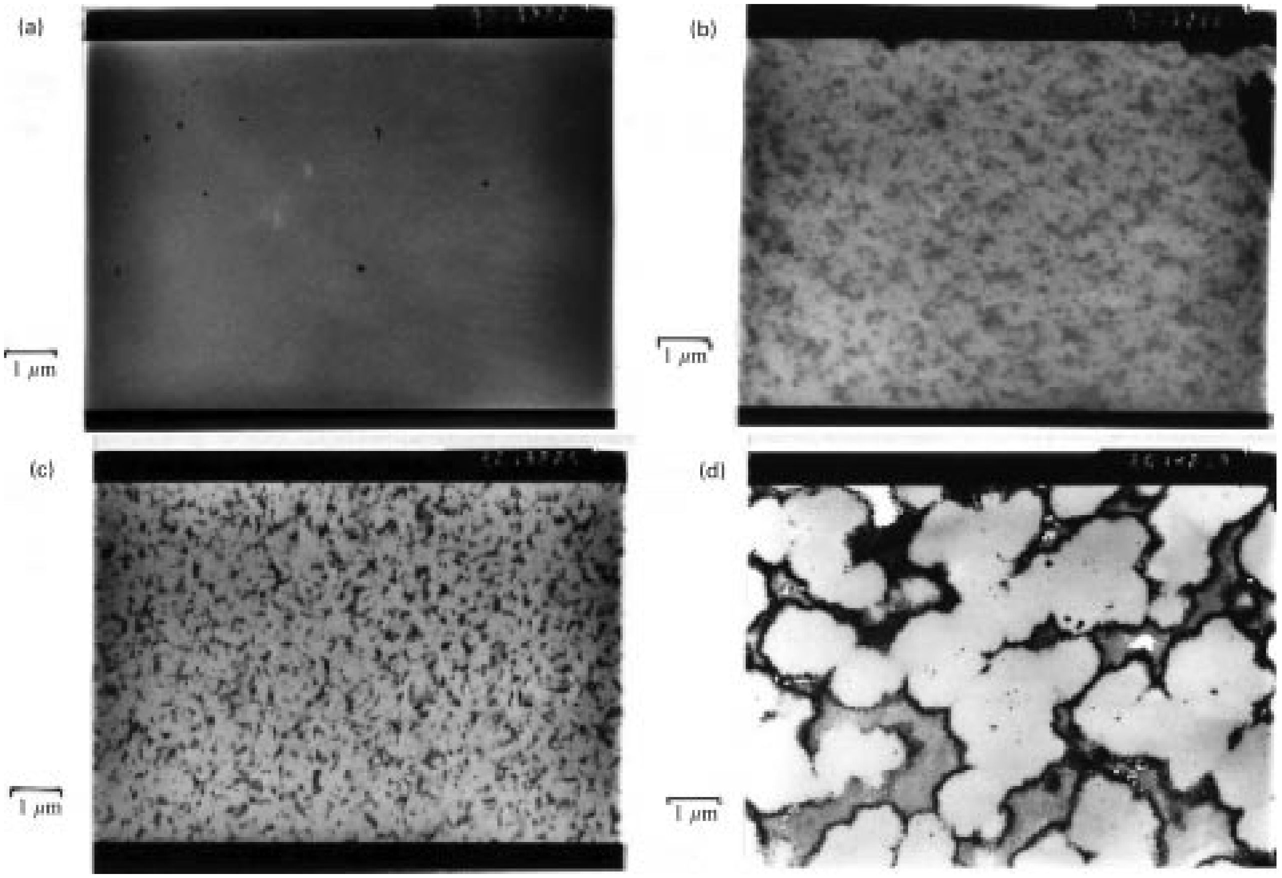

Fig. 2. TEM micrograph of a cured DVER-S sample: (a) unmodified, and containing (b) 10% by wt. of VTBN, (c) 5% and (d) 10% by wt. of CTBN.

to ASTM D 790-86 specifications, using an electromechanical INSTRON Universal Testing Machine model 4467.

Fracture mechanics measurements were made at room temperature, in three-point bending mode at a crosshead displacement rate of 10 mm/min using the universal testing machine mentioned above. The stress intensity factor at the onset of crack growth, K_{IC}, was calculated following the ESIS Protocol recommendations using single edge notched specimens (SEN) [13]. The total crack length a was measured from the fracture surface, using a profile projector with a magnification of 10 × .

3. Results and discussion

3.1. Morphology

Due to the marked differences in the morphologies induced by the two modifiers, a description of the main features of the final morphologies of the modified networks is needed to understand the properties of these materials.

The original thermoset was a transparent yellow solid. VTBN modified specimens were translucent, with cloudiness increasing gradually with the rubber content. CTBN modified samples showed similar behavior at concentration below 5% of additive. Higher CTBN concentrations produced completely opaque white samples. These features of the samples obviously have correlation with the morphology generated by phase separation induced by curing. The thermodynamic analysis of the solubility of the reactants and the evolution of the system during curing is the subject of following papers [15] In the present work, the microscopic evidence of this phase separation mechanism and its effect on the fracture properties of the materials is presented and discussed.

Fig. 2a is the TEM of the unmodified system. This micrograph is included for further comparison with the modified system and it shows no special feature. As expected, TEM indicates a single phase material.

VTBN addition generates a structure of irregular rubber domains dispersed into a DVER-S matrix, as seen by TEM (Fig. 2b), where the rubber rich regions appear dark after OsO_4 staining. Besides, the staining technique associated to TEM evidences a diffuse phase separation, not as sharp as for the CTBN-modified systems as it will be discussed below.

Addition of CTBN to the DVER-S system generates a completely different morphology. TEM of CTBN-modified resins was realized after staining of the samples, so that the rubber-rich phase should appear dark in the picture. As can

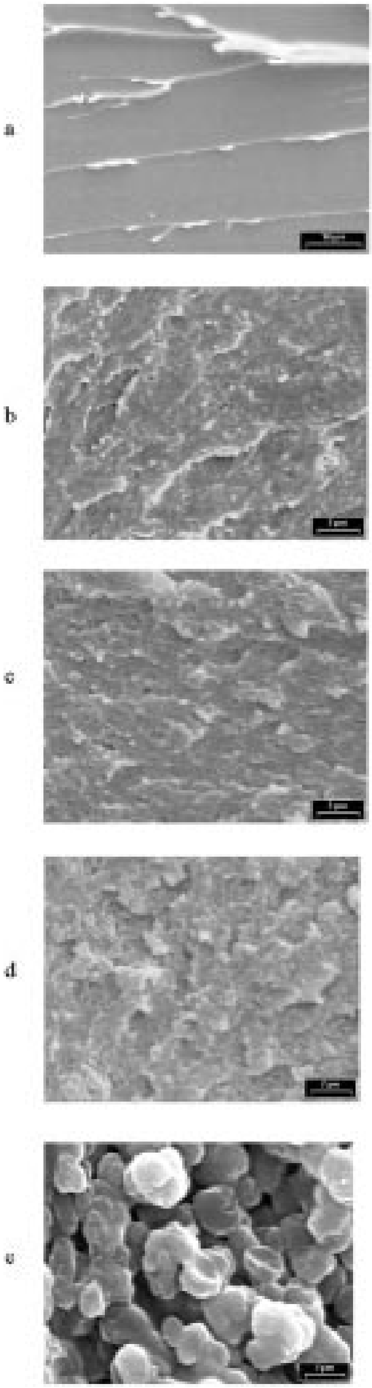

Fig. 3. SEM micrograph of the fracture surface of a cured DVER-S sample: (a) unmodified, and containing (b) 5% and (c) 10% by wt. of VTBN, (d) 5% and (e) 10% by wt. of CTBN.

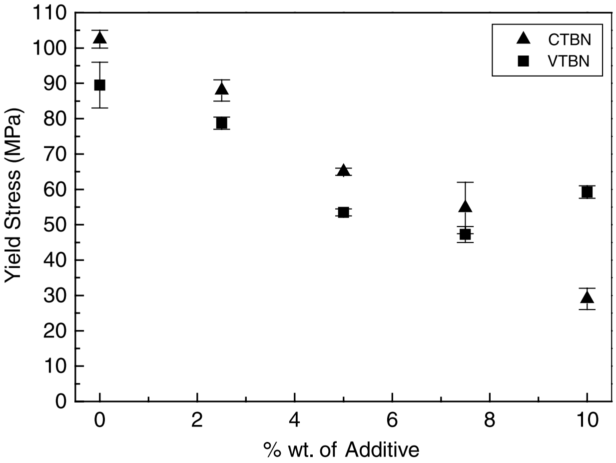

Fig. 4. Compression yield stress as a function of the rubber content: ▲ CTBN and ■ VTBN.

be seen in the two micrographs (Fig. 2c and d), at low CTBN concentrations (≤5% by weight) there are small irregular domains rich in CTBN, which appear included in a DVER-S matrix. The microstructure looks similar to the TEM of VTBN (Fig. 2b), but the definition between the phases is sharper. However, as the concentration increases (>10%) the dark areas appear larger, more localized and have the aspect of an interstitial phase between a light-gray globular DVER-S phase. This appearance is well known in LPA modified UPE-S resins, and consistent with the phase separation process described previously by other authors [9,11,16] and briefly summarized in the introduction. As the crosslinking density of the DVER rich nodules increases, more rubber is rejected and ends up surrounding the nodules. This description explains the features observed in TEM and SEM and is consistent with previous results in modified UPE-S system [7,8]. Morphological differences between these two systems can be described as follows: the UPE-S modified with LPA shows this type of nodular structure in limited isolated regions (“islands”), while this DVER-S system modified with CTBN shows this structure throughout the entire sample.

The SEM observation of the fracture surface of these materials was also indicative of the different morphologies of these materials. The unmodified thermoset resin shows a brittle fracture surface, as shown in Fig. 3a, consistent with the single phase observation by TEM.

SEM of a fracture surface of the VTBN modified material shows a rough surface consistent with the TEM indication of a fine dispersion of rubber-rich microparticles in a rigid continuous phase (Fig. 3b and c) and with the macroscopically observed opalescence of these samples.

On the other hand, SEM of samples with high CTBN concentration (higher than 5% by weight) (Fig. 3d and e) show globular nodules interconnected by what seems to be a coating film. As stated in the literature [10,11,14,16] these morphologies are essentially co-continuous and with microvoids formed during the last stages of curing (resulting from the different volumetric contraction of the two phases). When this microstructure is present in islands, it reduces the volume contraction of the overall sample (void formation reduces the high volume contraction of the thermoset). However, since in the present case the microvoids span the whole sample, the material becomes more fragile as it will be discussed further on. Moreover, the fracture surfaces of these high concentration CTBN specimens were very rough as seen by SEM. Naked eye

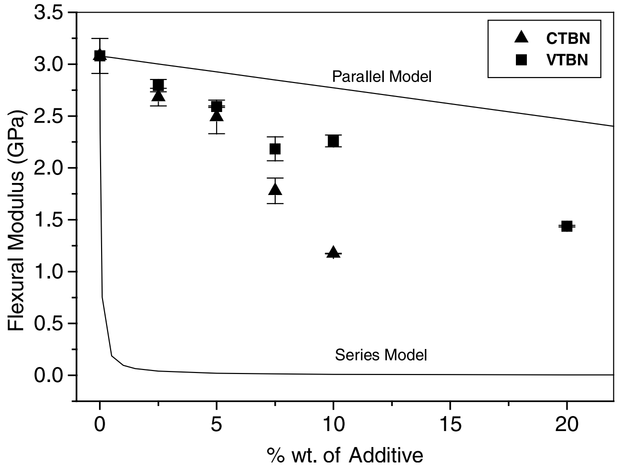

Fig. 5. Flexural modulus as a function of the rubber content: ▲ CTBN and ■ VTBN. Lines represent the predicted theoretical limits of the two phase-system, using 3.08 GPa (measured) and 1 MPa (estimated) for the DVER-S and the rubber phases, respectively.

inspection of these surfaces also indicate macroscopically rough surface with little material coherence. This morphological feature has also been described for S-UPE systems with polyvinyl acetate, PVAc, at concentrations of around 10% by weight [17,18].

Summarizing, the use of an elastomer capable of reaction with S and DVER (VTBN) enhances the compatibility of the reactants generating a morphology of very fine rubber particles dispersed in a rigid matrix. On the contrary, the addition of the esentially unreactive CTBN produces a generalized "LPA phase separation", that is, DVER-rich nodules surrounded by elastomer, which leads to the reduction of the material coherence at high concentrations of rubber.

3.2. Mechanical properties

Fig. 4 shows the compressive yield stress (σ_y) vs. the concentration of liquid elastomer added. In both cases, σ_y decreased almost linearly with the rubber concentration, and no major differences are found for both modifiers in the range of concentrations shown.

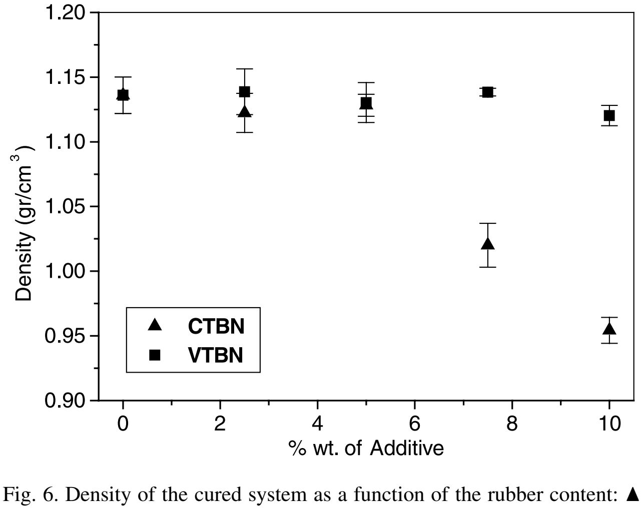

Fig. 6. Density of the cured system as a function of the rubber content: ▲ CTBN and ■ VTBN.

The small strain behavior, as represented by the flexural modulus, is shown in Fig. 5 as a function of the initial volume fraction of rubber. Values fall between the theoretical upper and lower limits (parallel and series models, respectively, for two phase-systems) [19].

VTBN modified samples show a moderate decrease trend for the whole range of concentrations studied, with about a twofold decrease in the value of the modulus at 20% of additive, with respect to that of the DVER-S copolymer.

CTBN modified systems show a similar decreasing trend up to 5% by weight of rubber. Addition of higher percentage of CTBN produces a more rapid decrease in the value of E_b. This particular behavior of the samples containing large CTBN concentrations is also consistent with density measurements. Fig. 6 shows the experimental results of density vs percentage of additive. At concentrations higher than 5% of CTBN, the samples show a steep drop in density, which can only be explained by an increased porosity of the samples and of macroscopic defects. The porosity is a direct consequence of the morphology generated, as it has been previously reported for UPE-S with LPA systems, and it leads to the catastrophic drop of properties observed at high CTBN concentrations. The VTBN modified samples have a density of about 1.13 g/cm^3 for all the formulations and these samples show essentially no dependence of density with the concentration of additive. However, the 10% CTBN sample has a density of only 0.95 g/cm^3, which indicates an important percentage of microvoids and defects. This sharp change in behavior of these samples is in agreement with the change observed in the morphology. As explained in the previous section at higher percentage than 5%, the sample becomes macroscopically opaque and white. Microstructure consists on globular nodules connected through the rubber rich phase that surrounds them and coexisting with microvoids. This microporous and probably co-continuous structure leads to the final poor performance of these materials.

Flexural strength exhibited a light dependence with rubber content at low additive concentrations, as shown in Fig. 7. An increment of about 7 and 15% in the flexural strength with respect to the neat system is registered for the 5% CTBN and VTBN modified materials, respectively. VTBN systems show a slight decrease in strength at higher additive concentrations. On the other hand, CTBN systems showed an important drop in the strength for samples containing more than 5% of additive, as it occurred also in the case of the flexural modulus, consistent with the large porosity exhibited by the material.

Summarizing, VTBN modified samples showed essentially no dependence of density with the concentration of additive. In agreement with this observation, VTBN modified systems showed gradual monotonic changes in mechanical properties that correlated well with the observed

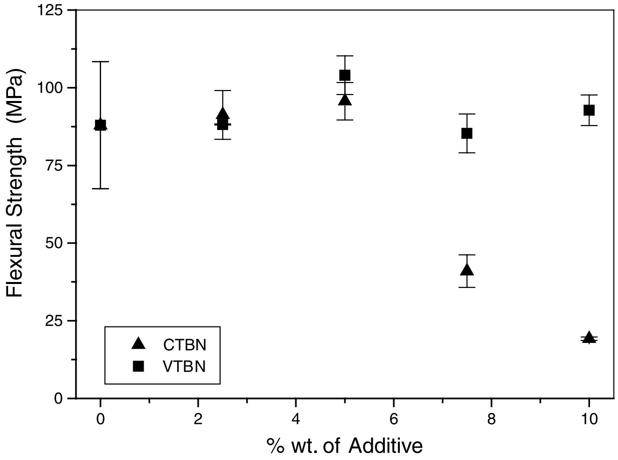

Fig. 7. Flexural strength as a function of the rubber content: ▲ CTBN and ■ VTBN.

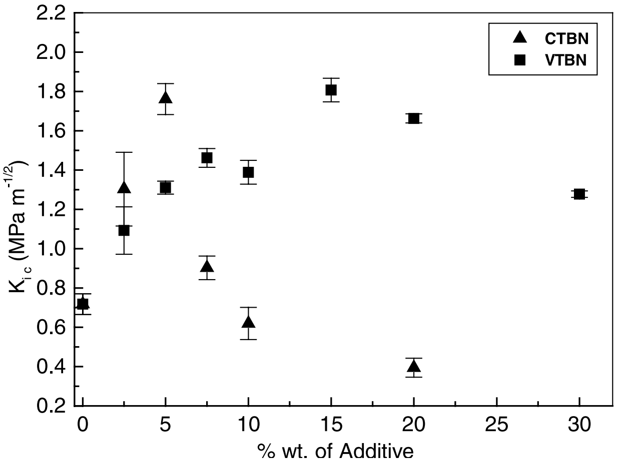

Fig. 9. Critical stress intensity factor (K_{IC}) as a function of the rubber content: ▲ CTBN and ■ VTBN.

morphologies of elastomeric inclusions for any VTBN concentrations.

On the other hand, microvoids formation (described as the final stage of phase separation in LPA-UPE-S systems) should originate samples of relatively low density.

Coincidentally with this observation, modification of DVER-S samples with CTBN, (which produced almost no changes in densities up to about 5% wt. additive), leads to a sharp decrease in the density of the material at concentrations of 10% wt. of CTBN. This drop in density keeps a close relation with the qualitative morphology change at this concentration and the rapid deterioration of the mechanical properties.

3.3. Fracture behavior

3.3.1. Fractography analysis

The examination of the fracture surfaces (Fig. 8a and b) of the broken samples reveals differences in the crack propagation modes associated with the two different phase structures developed during the synthesis stage: a dispersed rubbery phase in a continuous matrix and a co-continuous porous structure (Section 3.1).

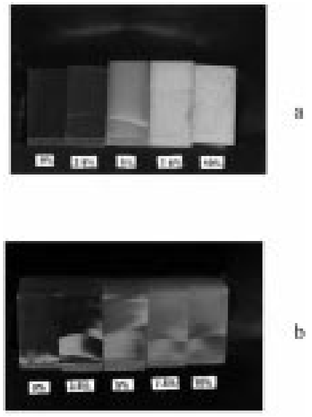

Fig. 8. Optical micrographs of the fracture surface of samples with different amounts of rubber modifiers: (a) CTBN; (b) VTBN.

Neat matrix shows a smooth “mirror-like” and featureless fracture surface without any signs of plastic matrix deformation typical of brittle fracture as usually found in unmodified crosslinked resins (Figs. 3a and 8).

Samples with the first mentioned morphology, i.e. all samples having VTBN and 2.5–5% CTBN concentrations, showed little amount of very small rubber particles, and thus, the interfacial bonding between the two phases was considered to have a negligible effect on thoughening [14]. Visual observation of fracture surface reveals a very smooth and mirror-like fracture surface with ‘stick/slip’ propagation marks on it (Fig. 8a and b). Stick/slip propagation in thermosets resins is caused by crack tip blunting due to localized plastic stretching [4]. In addition, SEM analysis (Fig. 3) confirmed the presence of several extended steps with shallow cavities and bumps typical of fast fracture growth. Only 5% CTBN-modified resin displayed a noticeable stress whitening zone around the crack tip (as shown in the macrophotography, Fig. 8a) which constitutes a clear evidence of initiation and growth of voids from the rubbery phase [4]. In fact, SEM micrographs showed larger cavities probably formed by the coalescence of neighboring voids (Fig. 3d).

In materials showing the co-continuous morphology (7, 5 and 10%, CTBN) fracture surface patterns appears completely different. Samples were opaque, rough and porous. The same feature appears through whole fracture surface and even pre-crack marks were undistinguishable (Fig. 8a). SEM micrographs (Fig. 3d and e) of the fractured samples allow to appreciate the typical pattern observed in other materials having similar co-continuous structures [20].

3.3.2. Fracture toughness

All VTBN compositions and CTBN-modified materials up to 5% show enhanced fracture properties with respect to

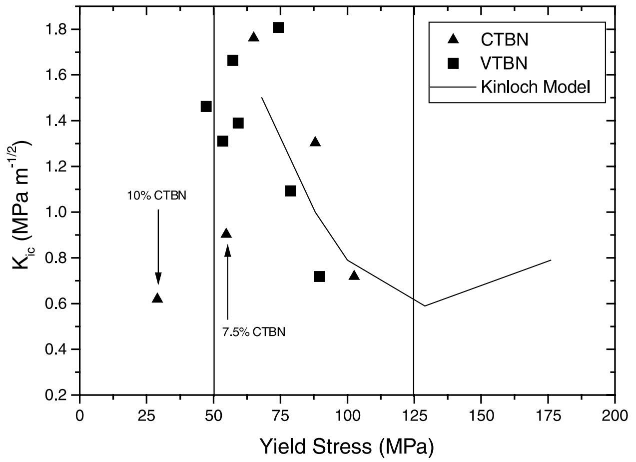

Fig. 10. Correlation between K_{IC} and σ_y for the experimental values of the DVER-S modified with different amounts of: ▲ CTBN and ■ VTBN. Continuous line corresponds to the Kinloch model.

those of the pure matrix (Fig. 9). Both modified materials show an increasing toughening trend with increasing rubber contents, at low additive concentrations. The improvement in toughness occurred together with a reduction in stiffness arising from the addition of the rubber. The maximum in fracture toughness was displayed at 5% CTBN concentration. The latter was the only sample showing a clear stress whitening, as explained in the above section. The measured value of K_{IC} was about 2.5 times higher than the one measured for the neat cured resin.

The maximum in K_{IC} for the VTBN modified system (~ 1.8 MPa m$^{-1/2}$, very similar to the maximum value found in the CTBN system) occurred at high concentrations (about 15%). The overall behavior displayed is also consistent with that proposed by Kinloch (although, this was originally proposed for epoxy-amine thermosets, only). The author presented a correlation between K_{IC} and σ_y, stating that the source of toughness is the blunting at the crack tip, which is a consequence of the low yield stress values (Fig. 10) [21].

A drastic decrease in the K_{IC} value, in coincidence with the deterioration in mechanical properties, appears at compositions of 7.5 and 10% CTBN. The drop in toughness exhibited by the co-continuous materials and the features of the fracture surfaces described in the previous section suggest that crack propagated very easily. A volume fraction of preexisting microvoids can be effective in inducing toughness [21] in intrinsically ductile low crosslinked matrices; however, an excessively high volume fraction of microvoids (as displayed at these compositions) could cause an adverse effect. The crack would eventually propagate through the voided plane, leading to the cohesive failure of the matrix without undergoing significant plastic deformation. As expected, the toughness values corresponding to these samples do not follow Kinloch model (Fig. 10), since the samples do not conform to the morphology studied and analyzed by Kinloch model.

4. Conclusions

Vinyl esters resins crosslinked with styrene were modified by the addition of two liquid rubbers with different reactivities and affinities towards the DVER and S monomers. These differences lead to two different morphologies: (a) Small rubber particles included in a DVER-S matrix. This type of morphology was observed in all VTBN samples and in samples modified with CTBN at low concentrations of additive. (b) LPA morphology, with DVER-S nodules more or less spherical connected to each other and surrounded by the additive, which results in a co-continuous microstructure at high CTBN concentrations. This last morphology was associated to a rapidly decreasing density of the sample (as a function of the CTBN content) and a correspondingly rapid deterioration in the mechanical properties.

When the rubber phase appears as a dispersed phase, some toughening was achieved even if distinct stress whitening was only observed for 5% CTBN modified samples. These results were consistent with the Kinloch model, which interpreted the improvement in epoxy resin by a crack tip blunting behavior. Porous co-continuos structure, on the contrary, was ineffective in toughening.

Finally, the use of a reactive rubber, such as VTBN, originated a more miscible system with formation of smaller rubber domains, effectively inhibiting a LPA segregation mechanism, such as it was observed in the modification with the less reactive CTBN.

Acknowledgements

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