Incompatible Ternary Blends Containing Unsaturated Polyester Resins. II. Interfacial Properties

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Synopsis

The interfacial tension (γ) in ternary blends of unsaturated polyester (UP) and rubber oligomers in styrene have been measured using three different techniques: tensiometric plate, capillary height, and drop profile methods. These experimental methods give similar results, but it has been shown that γ values "with or without skimming" are very different. The presence of small molecules, inhibitors, impurities, etc., in the interphase region can explain this discrepancy. We have observed a good correlation between γ and the Flory–Huggins interaction parameter. The elastomer chain ends have an influence on the interfacial tension: γ is reduced when the oligomers possess hydroxyl groups. An epoxy terminated butadiene–acrylonitrile copolymer, ETBN, was prepared from a large excess of diglycidyl ether of bisphenol A, DGEBA, and carboxyl terminated butadiene–acrylonitrile copolymer, CTBN, at 150°C, and without a catalyst. The excess of DGEBA was eliminated by successive precipitation in the selective solvent ethanol. Since the DGEBA blocks are miscible with the UP resin, the introduction of the ETBN copolymer drastically reduces the interfacial tension of the ternary blend of UP and rubber in styrene.

INTRODUCTION

The application of unsaturated polyester (UP) resins is often limited by their brittleness and susceptibility to catastrophic failure. Moreover, the shrinkage of the polyester polymer during crosslinking with the reactive styrene solvent leads to warpage and cracking.

Usually these problems can be solved by blending UP resins with certain additives. For example, several thermoplastic additives such as poly(methyl methacrylate) or polyvinylacetate are used to achieve a "low profile" or "low shrinkage" behavior.[1] The mechanical and fracture properties of the UP resins can be improved by the aid of elastomers.[2-4]

It is generally believed that the impact properties of thermosets may be improved by means of adding of randomly dispersed rubbery phase. In particular, the use of a carboxyl terminated butadiene–acrylonitrile random copolymer (CTBN) is quite common for toughening epoxy networks.

Direct evidence of relationships between the phase diagram, rubber particle size, and mechanical properties has been provided.[5-6] Thus, in the first part of this series,[7] the experimental ternary phase diagrams of systems consisting of

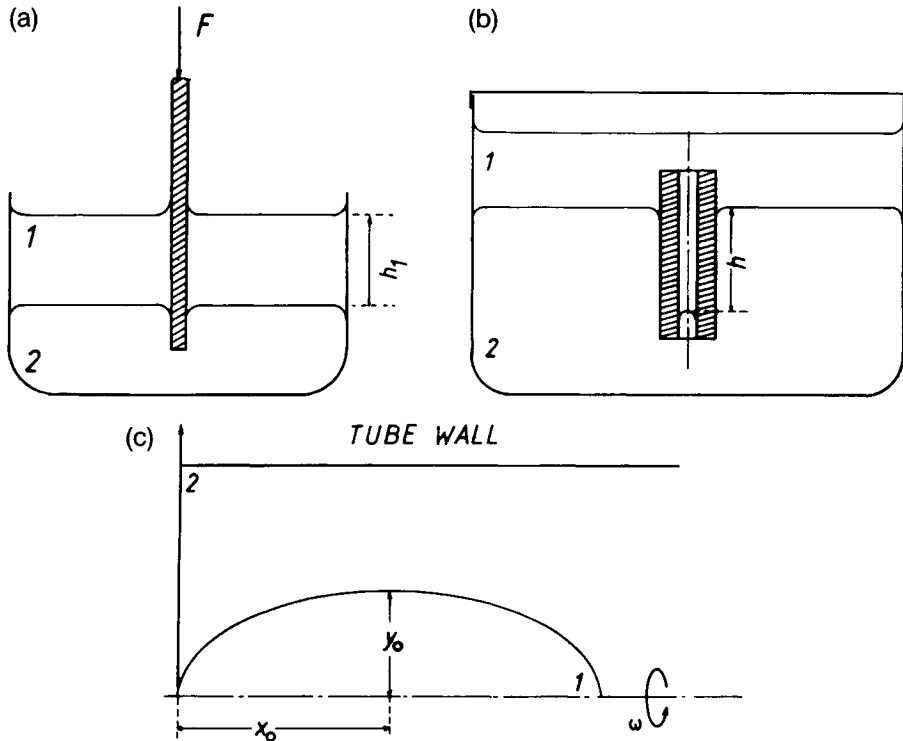(a)

(b)

(c)   TUBE WALL

Fig. 1. Schematic of the three experimental techniques used to measure interfacial tension: (a) tensiometric method; (b) capillary height method; (c) spinning drop method.

a polyester resin, based on an unsaturated polyester (UP) prepolymer in solution in styrene, and an immiscible CTBN oligomer have been determined.

Depending on the chain-ends of the UP prepolymer, there is a compatibility window, where the system is opalescent with two phases but does not exhibit sedimentation, similar to emulsion behavior. It is well known that, for high impact polystyrene materials, for example, the interfacial tension is an important factor governing morphological characteristics.[8] The late stages of phase separation depend on the interfacial tension between both phases. Thus, the aim of this second part of our study is to evaluate the interfacial properties of those demixed solutions. These interfacial properties will then be correlated with the chemical structure, specifically the type of chain-ends of the UP prepolymer and of the rubber additive. Interfacial tension measurements are quite difficult and need a lot of experimental care;[8] therefore we have used three different techniques for these measurements.

EXPERIMENTAL

Apparatus

The interfacial tension was measured using three differents methods. The equipment used for each of these methods is as follows:

i. Tensiometric plate method using a DOGNON-ABRIBAT tensiometer equipped with a platinium plate [Fig. 1(a)].

ii. Capillary height method: a calibrated capillary tube was stuck to a glass rod with a cyanoacrylate adhesive that is insoluble in styrene. A diagram of this system is shown in Figure 1(b). The capillary height was measured using a cathetometer.

iii. Drop profile method: a spinning drop apparatus manufactured by the University of Texas (Model 300), without thermoregulation. The range of the speeds used was from 12,000 to 24,000 rpm. A Gaertner traveling microscope with a filar eyepiece was used to measure the length and width of the drop [Fig. 1(c)].

Materials

The two unsaturated polyester (UP) resins used in this study were commercial formulations supplied by Norsolor. They were prepared by the condensation of isophthalic acid (IA) maleic anhydride (MA), propylene glycol (PG), and diethylene glycol (DEG), and they were available as a solution in styrene (38% of styrene by weight). The characteristics of the UP oligomers are given in Table I.

In addition, a series of telechelic reactive liquid-rubber poly(butadiene–acrylonitrile) copolymers was used. These copolymers are commercial products available from the B.F. Goodrich Co. The characteristics given by the producer are listed in Table II.

An ETBN adduct prepared from an epoxy monomer of the diglycidyl ether of bisphenol A (DGEBA, see Table III) and a reactive liquid rubber of the CTBN type with 18% by weight of acrylonitrile was also used. This adduct was prepared by reacting the carboxylic chain ends of CTBN with an excess of DGEBA. The reaction was carried out at 150°C under a N_2 atmosphere without a catalyst. The method used to follow the conversion is described in detail by Bartlet et al.[6]

Typical times for attaining an almost complete conversion were close to 5 h. This ETBN adduct was obtained by using 300 g of epoxy monomer ($\bar{n}$ = 0.15) and 200 g of CTBN 8, thus the initial equivalent ratio was eq COOH/eq epoxy = 0.07. The excess of DGEBA was eliminated by successive precipitation in the selective solvent ethanol. The number average molecular weight and the

TABLE I
Characteristics of the Unsaturated Polyester Resins with 38% by Weight
of Styrene and 170 ppm of Hydroquinone[a]

	Composition				Chain ends		Molecular weight		
Reference	IA	MA	PG	DEG	I_{OH}	$\bar{f}_{OH}$	$\overline{M_n}$	$\overline{M_w}$	I_p
UP 2437	0.4	0.6	0.74	0.45	71	1.65	2100	25,500	12
M7110i	0.4	0.6	0.7	0.3	17	1.15	3800	23,000	6

[a] I_{OH} = hydroxyl index, $\bar{f}_{OH}$ = hydroxyl functionality, and $\overline{M_n}$, $\overline{M_w}$ = number and weight average molecular weight determined by SEC (PS standards).

adduct density were calculated using a calculation method described by Verchère et al.[5] The results are $\overline{M_n}$ = 3840 g/mol and ρ = 0.979.

Sample Preparation

The ternary mixtures of UP and liquid rubber in styrene were prepared by weighing the components in a beaker and stirring vigorously with a spatula. The mixtures were then poured into 20 mL test tubes and sealed with rubber stoppers, or they were poured into 60 mm diameter dishes and carefully closed. All of the samples were placed in a temperature-controlled oven at 27 ± 0.2°C. The samples were allowed to equilibrate thoroughly; consequently, the mixtures either became homogeneous solution, or two phases separated by an interface. The time required to attain equilibrium varied from days to weeks, depending on the total polymer concentration, the nature of the elastomer, and the proximity of the critical point.[9]

When a mixture attained equilibrium, we used two different procedures to measure the interfacial tension. The first method used is called "without skimming" and involves direct measurements on the demixed solutions after sedimentation. This procedure was applied with the capillary height method and the Wilhelmy balance method. For the second procedure, called "after skimming," the top phase (dilute phase) was carefully sampled using a teat pipette. Using the same pipette, the interfacial region was carefully removed and discarded. Then, with another pipette, the bottom phase (concentrated phase) was sampled. This procedure was applied with the capillary height method and the spinning drop method.

INTERFACIAL TENSION MEASUREMENTS

Before giving any interfacial tension results, it is necessary to specify all of the experimental precautions indispensable in the evaluation of surface or interface properties.[10,11] In the case of the tensiometric method, between each measurement, the platinum plate was thoroughly cleaned with sulfochromic acid, rinsed with distilled water, and then dried at 100°C. The measurements and calculations were made using the expression of a force acting on a plate[12] [Fig. 1(a)]:

TABLE II
Characteristics of the Reactive Liquid Rubbers

Type of rubber	% acrylonitrile	Viscosity (Pa s) at 25°C	Chain ends	$\overline{M_n}$	Density (25°C)	T_g (°C)
CTB-162	0	60,000	Carboxyl	4200	0.907	−83
CTBN-8	18	150,000	Carboxyl	3600	0.948	−60
CTBN-13	26	540,000	Carboxyl	3600	0.960	−42
HTBN-7	17	140,000	Primary hydroxyl	3600	0.960	−60
VTBNX-23	16	250,000	Secondary hydroxyl Vinyl	3600	0.985	−60

TABLE III
Diglycidyl Ether of Bisphenol A Used for the Synthesis of the ETBN Block Copolymer

Reference	Formula
Bak 164	

$\bar{n} = 0.15 \overline{M_n} = 382$ g/mol.

$$F = p\gamma \cos\theta - \rho gAd \tag{1}$$

where p is the plate perimeter, γ is the surface tension, θ is the contact angle, ρ is the liquid density, g is the gravitational acceleration, A is the cross-sectional area of the plate, and d is the immersion depth.

For a clean platinum plate, θ is equal to zero. The term $p\gamma$ is the weight of liquid supported by the plate. The term ρgAd is the buoyancy correction. From eq. (1) and the force profile versus immersion depth (Fig. 2), the interfacial tension of the demixed solutions was determined.

The capillary tubes were cleaned with persulfuric acid, rinsed, and dried as before. In order to avoid styrene evaporation from the top phase, the test tubes were closed after immersion of the system [Fig. 1(b)]. The meniscus heights attained equilibrium for times shorter than 24 h, thus all of the measurements were taken 24 h after immersion. Equation (2) gives the relation between the capillary height and the interfacial tension
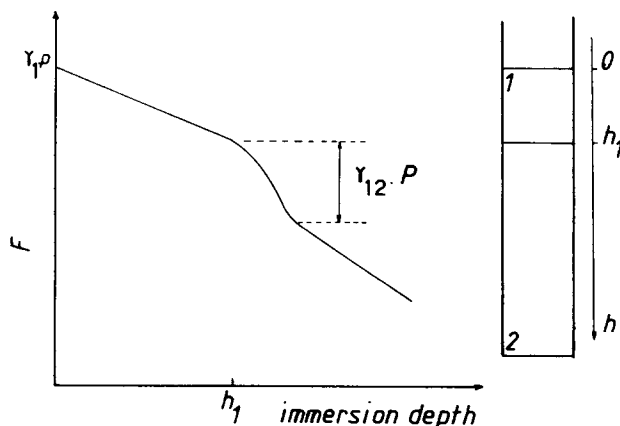

Fig. 2.   Tensiometric method: force profile vs. immersion depth.

Procedure	Tensiometric method	Capillary height	Spinning drop
Without skimming	0.8 ± 0.2	0.7 ± 0.1	—
After skimming	—	3 ± 0.1	2.7 ± 0.3

$$\gamma = \frac{\Delta\rho \cdot grh}{2} \qquad (2)$$

where γ is the interfacial tension, g is gravitational acceleration, r is capillary radius, h is capillary height measured, and $\Delta\rho$ is the density difference between the two phases. This method has been used by Langhammer and Nestler[13] for very dilute solutions.

In the spinning-drop apparatus [Fig. 1(c)], the cell is a pyrex glass tube (2.5 mm diameter). The procedure for loading the cell was to completely fill the glass tube with the more dense phase, i.e., the bottom phase, using a syringe to avoid air-bubble formation. One microliter of the less dense phase, i.e., the top phase, was then injected with a Hamilton syringe. The tube was placed in the rotor and spun at about 5000 rpm to equilibrate the drop. The interfacial tension was evaluated with Vonnegut's approximation[14] [eq. (3)] when the drop length was at least four times the drop radius.

$$\gamma = \tfrac{1}{4} \cdot r^3 \cdot \Delta\rho \cdot \omega^2 \qquad (3)$$

where r is the drop radius, $\Delta\rho$ is the density difference, and ω is angular velocity. This method has been used by Gaillard et al.[15] for the ternary system of polystyrene (PS), polybutadiene (PBD), and styrene.

RESULTS AND DISCUSSION

Comparison of the Results Obtained with Different Experimental Techniques

As mentioned by Broseta et al.[16] concerning the spinning drop technique, the major cause of errors arises from the measurement of the density difference. This is especially true for very dilute solutions, i.e., near the binodal curve, because $\Delta\rho$ is very small. Moreover, the rotating drop measurements (which essentially gives $\gamma/\Delta\rho$) can differ by 10% for the same sample. In the same way, the major cause of errors in the capillary height technique is also the density difference rather than the radius corrections.[8]

The forces measured by the tensiometric method are very low, leading to a very low precision of about 20%. Therefore, at least three independent measurements were made for each sample. The three experimental techniques for

measuring the interfacial tension were compared for a mixture containing UP2437 resin and 10 phr CTBN 8. The results are presented in Table IV.

We have observed that the experimental methods give rather similar experimental interfacial tension values if we compare the procedures "with or without skimming" separately. However, if we compare these two procedures together, the capillary height method gives very different values for γ. For all of the mixtures, we observe the presence of a thin opalescent interphase (< 0.1 mm) at the end of the experiment. During the "skimming" process, we discarded this interfacial region, which seemed to have a very important effect on the interfacial tension. We observed the same behavior for a mixture containing 10 phr CTB-162. So, we can consider that there was no fractionation due to copolymer composition and the acrylonitrile present in the CTBN.

The interfacial region ("the skim") has been analyzed by size exclusion chromatography. The chromatogram shows UP molecules, but without any fractionation phenomena, and many peaks are also present corresponding to small molecules such as hydroquinone and also unknown impurities. Moreover, when the demixed mixtures were kept in daylight for a few days, the polymerization of the UP-rich bottom phase appeared. This observation confirmed that the free radical polymerization inhibitor, hydroquinone, was no longer present in the UP-rich phase.

The mixtures tended to lower their total free energy to reach a stable equilibrium. This total free energy $\mathscr{F}$ of a two-phase system is given by a bulk and interfacial contribution:

$$\mathscr{F} = \sum N_i \cdot \mu_i + \gamma_A \tag{4}$$

where μ_i is the chemical potential of the component i and A is the interfacial area. Small molecules, i.e., hydroquinone, residues of the CTBN synthesis, impurities, etc., then go to the interphase region and decrease the interfacial tension of the system. Interfacial tension measurements with a drop profile method like the spinning drop technique automatically include the skimming process. This is not the case with other methods. Skimming seems to be the way to obtain the intrinsic interfacial tension and avoid all the perturbations in the measurements induced by the interfacial pollution. This effect is well known with respect to the surface tension measurements.[11]

Influence of Different Structural Parameters on Interfacial Tension

The interfacial tensions of a series of mixtures ("after skimming") measured by the spinning drop technique are presented in Table V. In part I of this study, we showed that the miscibility limit for these systems was around 1 phr elastomer. The first point to consider is that the interfacial tension increased with the CTBN-8 elastomer content, i.e., when the initial mixture composition moves off the binodal curve.[15,16] The values of γ reported in the literature for very dilute demixed solutions[13,15,16] are smaller than those measured in our systems with the lower styrene content. Moreover, increasing acrylonitrile content in the rubber decreased the interfacial tension from 4.9 mN/m for CTB-162 to 2.2 mN/m for CTBN-13 (26% AN).

TABLE V
Interfacial Tension, Top-phase Volume Fraction, and Phase Densities of a Series of Mixtures

Type of additive	Wt % of rubber	Top-phase volume fraction	$\rho_T \pm 0.002$	$\rho_B \pm 0.002$	γ (mN/m)
CTB-162	16.67	35	0.934	1.173	4.9 ± 0.4
CTBN-8	9.00	22	0.963	1.165	2.7 ± 0.3
CTBN-8	16.67	35	0.958	1.173	3.4 ± 0.3
CTBN-13	16.67	35	0.982	1.173	2.2 ± 0.2
HTBN-34	16.67	35	0.986	1.173	2.2 ± 0.2
VTBN-23	16.67	35	0.976	1.173	2.8 ± 0.2

The lattice theories,[17,18] the mean-field theories,[19-22] and the Cahn-Hilliard approach[16] lead to relationships between the thickness of the interface, the interfacial tension, and the Flory-Huggins interaction parameter. First, Helfand and Tagami[19] have shown that, in the limit of infinitely long chains, the interfacial thickness, AB, and the interfacial tension, γ_{AB}, of a demixed polymer blend are given by

$$\gamma_{AB} = \frac{kT}{a^2} \sqrt{\frac{\chi_{AB}}{6}} \tag{5}$$

$$\Delta_{AB} = \frac{a}{\sqrt{6\chi_{AB}}} \tag{6}$$

where a is the monomer length and χ_{AB} is the Flory–Huggins interaction parameter between polymer A and polymer B. The same calculations have been done for ternary systems containing two infinitely long polymer chains in a good solvent S, giving the same results.[22,18]

The interaction parameters χ_{AS} and χ_{BS} can be expressed in terms of the Hildebrand solubility parameter or in terms of the Hansen solubility parameter through eqs. (7) and (8)

$$\chi_{AB} = \frac{V_R}{RT} (\delta_A - \delta_B)^2 \tag{7}$$

$$\chi_{AB} = \frac{V_R}{RT} [(\delta_{d_A} - \delta_{d_B})^2 + (\delta_{p_A} - \delta_{p_B})^2 + (\delta_{h_A} - \delta_{h_B})^2] \tag{8}$$

where V_R is a reference volume, δ_k is the Hildebrand solubility parameter of the component k, and δ_{d_k}, δ_{p_k}, δ_{h_k} are the dispersive, polar, and hydrogen bonded contributions, respectively, of the Hansen solubility parameter of the component k. Thus, we calculated the Hildebrand and Hansen solubility parameters for attraction constant tables[24,25] and one molar volume table.[26] The results are shown in Table VI. In Figure 3, we plotted ln γ versus ln$(\delta_A - \delta_B).^2$

From the Hildebrand parameter from both Van Krevelen or Hoy tables, and from Hansen's parameter, we obtained straight lines, seemingly validating eq.

TABLE VI

Calculated Hildebrand Solubility Parameter δ and Hansen Solubility Parameter δ_t with the Dispersive, Polar, and Hydrogen Bonded Contributions (δ_d, δ_p, δ_h) (δ in MPa$^{1/2}$)

| | Van Krevelen | Hoy | Hansen | | | |
| | | | | | | |
Oligomers	δ	δ	δ_d	δ_p	δ_h	δ_t
UP 2437 (without styrene)	20.1	21.1	16.8	6	9.7	20.3
CTB-162	16.7	17.4	15.6	0.2	1.6	15.7
CTBN-8	18.7	18.6	15.1	3.2	3.5	15.8
CTBN-13	19.6	19.1	14.9	4.7	4	16.1

(5). The slopes are not 1/2 and depend on the calculation. For each type of calculation the results are consistent, but a systematic error is introduced by the calculation of solubility parameters. This error increases when the probability of formation of specific interactions increases. Another source of experimental error is the calculation of the molar volume.

Besides these problems, there were several assumptions made for the calculations. First, the polymer-solvent interaction parameters, which were calculated and presented in Table VII, are far from the ideal case, $\chi_{AS} = \chi_{BS} = 0$, investigated by other authors.[16,22] Secondly, when two polymers are largely incompatible, Broseta et al.[16] noticed that there is another factor of error resulting from the surfactant effect of the solvent, S, which accumulates slightly at the interface and lowers the interfacial tension. So, for all of these reasons, we are not surprised to have a slope different from 1/2.

The elastomer chain-ends have an influence of the interfacial tension. This effect is generally attributed to the formation of specific interactions at the interface.[27] The oligomeric rubbers used in this study can be classified according to their ability to lower γ:
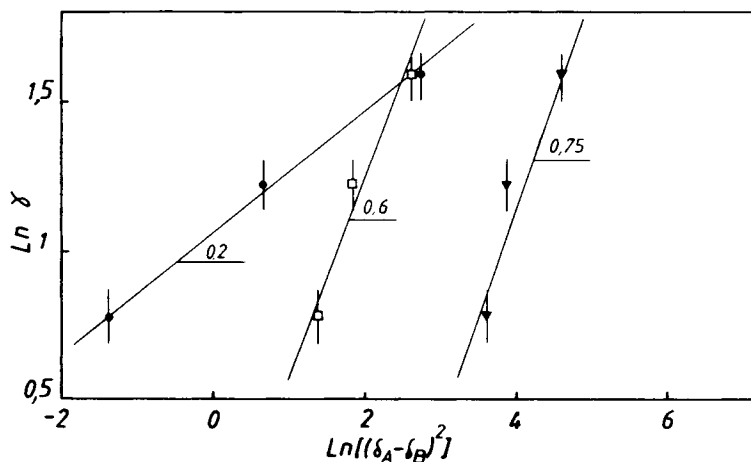

Fig. 3. $\ln \gamma$ vs. $\ln (\delta_A - \delta_B)^2$ calculated with different attraction constant tables. γ determined experimentally in mN/m and δ in MPa$^{1/2}$: (●) Van Krevelen; (□) Hoy; (□) Hoy; (▼) Hansen.

TABLE VII
Calculated Polymer/Solvent Interaction Parameters χ_{AS} and χ_{BS}

Oligomers in styrene	Hoy	Van Krevelen
UP 2437	0.9	0.5
CTB-162	0.02	0
CTBN-8	0.16	0.18
CTBN-13	0.26	0.38

CTBN < VTBN < HTBN

Similarly, the introduction of acidic chain ends in the UP prepolymer, M7110i compared to UP2437, produces an increase of γ. These observations appear in Table VIII.

It seems that acidic chain-ends tend to increase γ. On the other hand, the vinyl chain-ends of VTBN are not able to form hydrogen bonds with the UP prepolymer, but this decrease could be explained by the presence of secondary hydroxyl groups coming from the CTBN oligomer functionalization.[3]

$$H_2C=C-C-O-CH2-CH-O-C-$$

R = H or CH_3
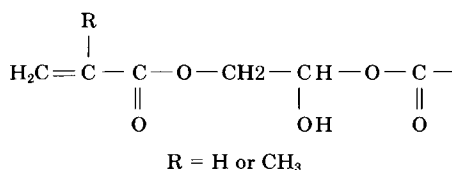
Influence of a Block Copolymer on Interfacial Tension

The influence of adding a small amount of triblock DGEBA—CTBN—DGEBA, ETBN, copolymer (83% rubber by weight) has been studied. The DGEBA blocks have the property of being miscible with the UP resins used,[28] even though the CTBN is immiscible. The system studied was a mixture containing the UP 2437 resin and 10 phr of rubber. This rubber consists of CTBN 8 and varying amounts of block copolymer ETBN. Interfacial tensions were measured using the capillary height method "without skimming" and the spinning drop method, of course, "with skimming." The results are presented in Figure 4.

TABLE VIII
Comparison of UP Chain-end Effects on the Interfacial Tension (γ in mN/m) with Different Rubber Additives and the Same Acrylonitrile Content but with Different Chain-ends

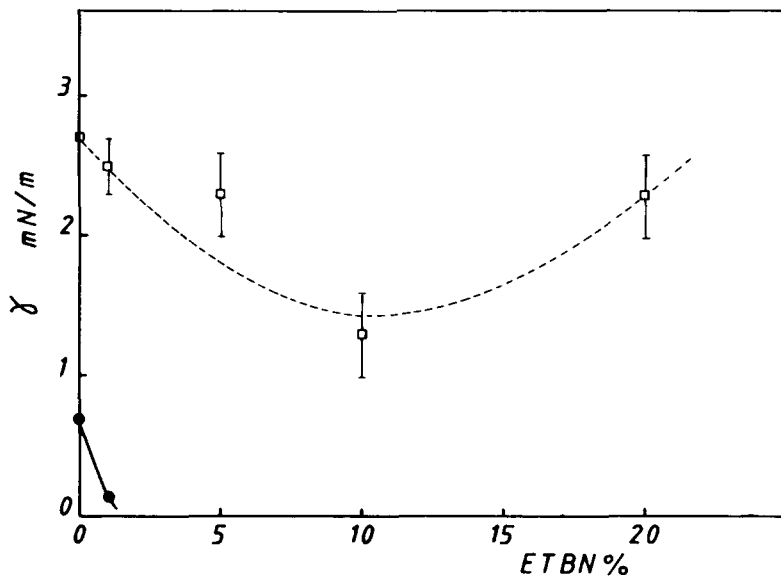| Rubber additive (17–18% AN)	CTBN-8	HTBN-7	VTBN-23
UP 2437	3.4 ± 0.3	2.2 ± 0.3	2.8 ± 0.2
M7110i	5 ± 0.3	3.8 ± 0.3	4.6 ± 0.3

Fig. 4.   Interfacial tension versus block copolymer content in the system containing UP 2437 resin and 20 phr rubber, prepared with CTBN and various amounts of the block copolymer ETBN: (■) capillary height method "without skimming"; (□) spinning drop method "after skimming" (in mN/m).

Both methods lead to a decrease of the interfacial tension due to the presence of the block copolymer. "Without skimming," the introduction of 1% by weight of block copolymer into the rubber reduced γ by an order of magnitude. It was impossible to measure γ for a higher block copolymer content using the capillary height method, because the capillary height was too small ($< \frac{1}{10}$ mm).

"After skimming," the decrease in γ was slower. We can imagine that the block copolymer ETBN present at the interface is discarded during the skimming process. The decrease of γ observed is certainly due to the excess of block copolymer initially introduced. The decrease of the demixed phase density difference $\Delta\rho$ versus block copolymer content, plotted in Figure 5, is explained by the higher density of the block copolymer than the CTBN. This is due to the presence of DGEBA blocks in the ETBN copolymer. For 10% by weight of the block copolymer ETBN, this behavior is no longer followed. We assumed that the pseudo-ternary diagram was not modified by the introduction of a small amount of block copolymer. Figure 5 indicates that this hypothesis is not valid for 20% by weight of the block copolymer ETBN in the rubber. Moreover, block-copolymer micelle formation was possible over a certain block-copolymer content (critical micelle concentration).[29] Then micelle formation wastes block copolymer, because in this case the block copolymer is not going to the interphase region. In our systems, if there was micelle formation, with regard to $\Delta\rho$ behavior, it was in the denser phase, i.e., UP-rich bottom phase. Nevertheless, no investigations have been made concerning this micelle formation.

The interfacial area depends on phase size and morphology. Therefore, it is irrelevant to compare, from a quantitative point of view, the interfacial tension obtained from our measurements and the intrinsic interfacial tension of a mix-
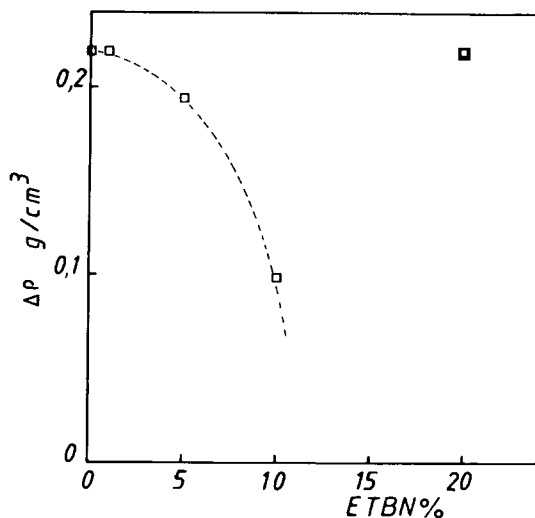
Fig. 5. Demixed phase density difference versus block copolymer content for the system presented in Figure 4.

ture composed of, for example, 10 μm rubber particles dispersed in a continuous phase. The results are self-consistent, because the same experimental procedures were always used. But these experiments are not able to give the optimum amount of block copolymer. This amount can be determined only by the morphological studies after polymerization.

CONCLUSIONS

From a technical point of view, interfacial tension measurements are quite difficult and need special considerations on whether or not to "skim" the interface. It has been shown that γ values "with or without skimming" are very different. Some experimental techniques give results directly "after skimming," but some other can give both "without skimming" or "after skimming" results, depending on the experimental process.

The chain-ends of the oligomeric components of these ternary blends have an influence on the interfacial tension. Specifically, the presence of hydrogen bonded hydroxyl functions in the blends reduces γ. Moreover, the results seems to follow the thermodynamic approaches although a complete study was impossible due to the complexity of our system.

The introduction of the triblock copolymer ETBN, prepared with two DGEBA blocks and one CTBN block, in the ternary blends drastically reduces the interfacial tension. Because of the "skimming" problem, the γ values measured in the presence of surfactants like block copolymer can only give tendencies but never intrinsic quantitative measurements.

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