

Incompatible Ternary Blends Based on Unsaturated Polyester Resins.

I. Phase Diagrams

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Synopsis

We have determined pseudo ternary phase diagrams for blends based on unsaturated polyester resins and an elastomeric additive. Size exclusion chromatography analysis is a well-known method for quantifying the demixed phase composition in the case of isomolecular polymers. But when some fractionation occurs, our results show that this analysis becomes inapplicable. In our systems, due to the presence of nitrogen atoms in the elastomer, elemental analysis has been used, and, with the help of the percent of styrene, this leads to the determination of the pseudo ternary phase diagrams. The major cause of this fractionation is the high polydispersity of the UP prepolymer. Lowering the molecular weight of the UP prepolymer leads to a partial miscibility with styrene. This unexpected phenomenon may be attributed to a chain-end effect rather than a real molecular weight effect. Finally, we have defined a compatibility window between 1–3 or 1–7 phr of elastomer, where the solutions are two-phase systems but without any sedimentation processes, even after several weeks. This compatibility window is certainly limited by binodal and spinodal curves. The higher limit, 3–7 phr of elastomer, depends strongly on the type of chain ends (hydroxyl or carboxyl) of the UP prepolymer.

INTRODUCTION

The use of unsaturated polyester (UP) resins in many applications is often limited by their brittleness and susceptibility to catastrophic failure. Moreover, the shrinkage of the polymer during crosslinking with the reactive styrene monomer leads to warpage and cracking. The concept of blending UP resins with additives is often used to achieve a “low profile” or “low shrinkage” behavior by adding selected thermoplastics of controlled structure,¹ or to improve mechanical and fracture properties by adding elastomers.^{2–4}

It is generally believed that the impact properties of thermosets may be improved by means of incorporating a randomly dispersed rubbery phase. The use of a carboxyl terminated butadiene-acrylonitrile random copolymer (CTBN) is especially common for toughening epoxy networks. Direct evidence of some relationships between the phase diagrams, rubber particle size, and mechanical properties have been exhibited.^{5–7}

To explain the “low profile” effect of polyvinyl acetate in their systems, Bucknall et al.⁸ give a schematic representation of the phase diagrams including the polymerization phenomenon. But, to our knowledge, no experimental ter-

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nary phase diagram for an unsaturated polyester prepolymer with an additive in a styrene solution has been previously published.

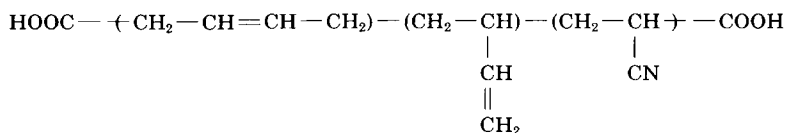
The aim of this work, rather than to evaluate the morphological and mechanical properties of a toughened UP network, is to evaluate the phase diagram equilibria of a ternary system with the aid of size exclusion chromatography and elemental analysis. The system chosen for this study consists of an unsaturated polyester (UP) and CTBN in styrene as the solvent.

EXPERIMENTAL

Materials

The two unsaturated polyester (UP) resins used in this study were commercial formulations obtained from Norsolor and prepared by the condensation of isophthalic acid (IA), maleic anhydride (MA), propylene glycol (PG), and diethylene glycol (DEG). Both were available as solutions in styrene (62% prepolymer, 38% styrene by weight). An experimental unsaturated liquid polyester prepolymer of low molecular weight was also used, and was prepared by Norsolor through the condensation of isophthalic acid (IA), fumaric acid (FA), and diethylene glycol (DEG). The characteristics of the UP resins are summarized in Table I.

We used a reactive liquid-rubber poly (butadiene-acrylonitrile) that is carboxyl-terminated (Goodrich CTBN 1300x8) containing 18% wt acrylonitrile, possessing a molecular weight of 3600 g/mol, a functionality of 1.8 and the chemical formula:



The styrene was used as received from Prolabo; it contains 0.001% wt of *ter*-butyl-4-pyrocatechol as an inhibitor.

TABLE I
Characteristics of the Unsaturated Polyester Resins

	Monomers				% Styrene by weight	% Hydroquinone (ppm)	Hydroxy chain ends		Molecular characteristics		
	IA	MA	PG	DEG			I_{OH}	f_{OH}	\overline{M}_n	\overline{M}_w	$I_p = \overline{M}_w/\overline{M}_p$
UP2437	0.4	0.6	0.74	0.45	38	170	71	1.65	2100	25,500	12.1
M7110i	0.4	0.6	0.7	0.3	38	170	17	1.15	2800	23,000	8.2
Oligomer	0.2	0.2 ^a	None	1 ^b	None	None	265	1.65	835	1142	1.4

IA = isophthalic acid; MA = maleic anhydride; DEG = diethylene glycol; PG = propylene glycol; I_{OH} = hydroxyl index; f_{OH} = hydroxyl functionality; \overline{M}_n , \overline{M}_w : number and weight average molecular weight (PS standards).

^a In this case maleic anhydride is replaced by fumaric acid (FA).

^b The excess of DEG necessary to obtain a low molecular weight is eliminated by evaporation.

The size exclusion chromatography (SEC) mobile phase, tetrahydrofuran (THF), was filtered through a 0.5 μm Millipore filter.

Apparatus

Quantitative polymer SEC analyses of the ternary mixtures were performed using a Waters SEC equipped with an Ultraviolet (UV) detector, using a monochromatic light of wavelength 254 nm and a differential refractive index (RI) detector. The detectors were positioned in series, and their outputs were graphically recorded. The SEC was operated with four columns packed with ultrastyrage: 10^5 , 10^4 , 10^3 , and 500 Å. For styrene concentration determinations, an evaporation method was used, which employed a Mettler furnace (DSC TA3000) to provide controlled heating of the samples under an argon stream. The second quantitative analysis of the ternary sample mixtures was done using elemental analysis.

A light transmission device was used to obtain a binary cloud-point (CP) curve. The apparatus and accuracy of the measurements are given in detail elsewhere.⁷

Sample Preparation

The ternary mixtures of varying composition 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 and placed in a temperature-controlled oven at $27 \pm 0.2^\circ\text{C}$. The samples were allowed to equilibrate thoroughly; consequently, the mixtures either became a homogeneous solution, or two phases separated by a distinct interface. The time required to reach equilibrium varied from days to weeks depending on the total polymer concentration and the proximity to the critical point.⁹ When the mixture was equilibrated, the top phase (the 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 (the concentrated one) was sampled.

Sample Analysis

Two different techniques were used to make quantitative analyses of the ternary mixtures: the elemental analysis was done on samples of the two demixed phases of one system, i.e., the top and the bottom phase; in order to obtain quantitative results from the SEC output, it was necessary to calibrate the apparatus in a unique fashion. Samples of the UP resin or oligomer UP/styrene blend were injected into the SEC equipment, and the UV and RI output areas for each of these chromatograms were calculated using a digitized planimeter coupled with a HP85 computer. The resulting plots were linear over the entire range of concentrations studied. An identical procedure was followed for a series of CTBN 8 samples, where the UV response at 254 nm was found to be zero, and the RI response was found to be a linear function of concentration.¹⁰ Thus, the measurements of UP concentration were done on UV outputs. We ensured that the molar absorption coefficient of the UP was constant along the chromatogram by plotting the ratio of the height of the UV response to the height

of the RI response (h_{UV}/h_{RI}) versus elution time. The results are given in Figure 1. The SEC analysis was coupled with the measurements of styrene fraction by evaporation. For the fraction determinations by evaporation, samples of about 5 mg of each phase were placed in DSC pans. They were then thermal treated for 30 min at 120°C under an argon stream. The samples were weighed before and after thermal treatment. The styrene fraction was determined from an average of five measurements. From both styrene and UP prepolymer concentrations, we determined the phase compositions.

RESULTS

(1) The first series of mixtures considered represents the practical case of introducing an elastomeric component in a UP resin. Thus we studied the ternary system UP2437 resin (38% by weight of styrene) mixed with different amounts of CTBN. No fractionation is visible on the UV chromatograms of the top phase (the dilute phase), and the phase diagram presented in Figure 2 was determined by quantitative analysis of SEC chromatograms and styrene loss. The diagram shows equilibrium tie lines for all the compositions of the mixtures studied. The initial blend separated into a concentrated UP-rich bottom phase and a dilute CTBN-rich top phase. The calculation of the Flory-Huggins interaction parameter (χ) from the Hildebrand solubility parameter (ϕ) are presented in Table II using both Hoy's¹¹ and Van Krevelen's¹² values. The coexistence curve is asymmetric and the tie lines slope downward towards the UP-styrene axis representing the binary system with the larger interaction parameter. This observation agrees qualitatively with other experimental findings.⁹

(2) In the second series of mixtures considered, the total polymer concentration varied between 20 and 50% by weight (more dilute solution), but the UP2437 prepolymer/CTBN weight ratio remained constant at 50 : 50. The mixtures separated. The UV chromatograms of the top and the bottom phases

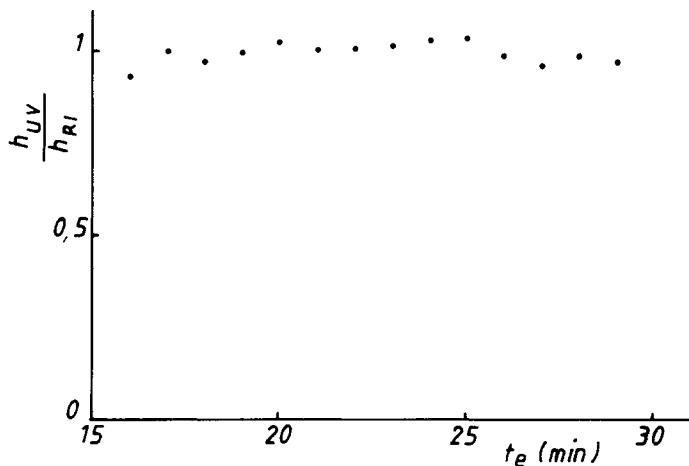


Fig. 1. UP 2437 resin. Ratio of UV to RI output heights versus elution time.

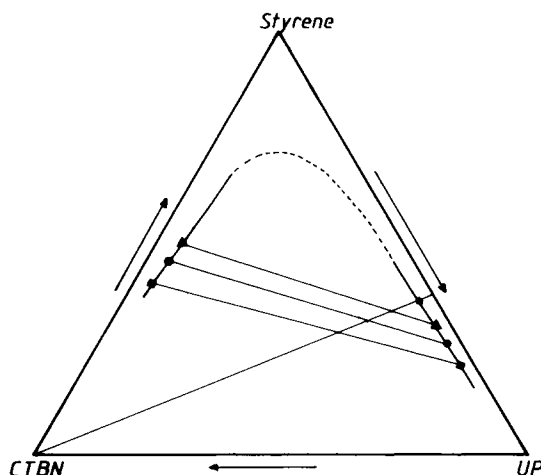


Fig. 2. Ternary phase diagram determined by SEC quantitative analysis of the system UP 2437 resin (38% wt styrene)/CTBN 8: (▲) 8 phr; (●) 16 phr; (■) 24 phr.

are presented in Figures 3 and 4. An important new fact appears: the higher molecular weight molecules of the UP prepolymer were found in the UP-rich bottom phase, and the lower molecular weight molecules of UP prepolymer were found in the CTBN-rich top phase. This fractionation phenomenon was enhanced when polymer concentration decreased. Thus, the use of quantitative analysis of SEC chromatograms to determine phase composition was impossible. The phase diagram was therefore obtained from elemental analysis. CTBN is the only component of the system having nitrogen atoms in the macromolecular chain. Therefore, by measuring the nitrogen content of one phase, we could determine the CTBN content. However, the UP prepolymer fraction was measured from oxygen content and while taking into account the CTBN fraction determined previously. All of the elemental analysis results are presented in Table III. The phase diagram is given in Figure 5. As before, the mixtures separated into a concentrated UP-rich bottom phase and a dilute CTBN-rich top phase. Moreover, we noticed the absence of tie lines. The explanation could be that the UP corner of the diagram is not qualitatively representative of the UP prepolymer present in each demixed phase of one mixture. In addition, due to the fractionation, we can consider that the phase diagram obtained is the sum of $n \times m$ binodal curves, where n is the number of different molecular

TABLE II
Polymer-solvent Interaction Parameters at 25°C Calculated from the
Attraction Constant Tables of Hoy¹¹ and Van Krevelen¹²

Binary systems	χ_{Hoy}	$\chi_{\text{Van Krevelen}}$
UP 2437/styrene	0.9	0.5
Oligomer UP/styrene	3.3	4.2
CTBN 8/styrene	0.16	0.18

The reference molar volume chosen is the styrene molar volume of 113.4 cm³/mol.¹³

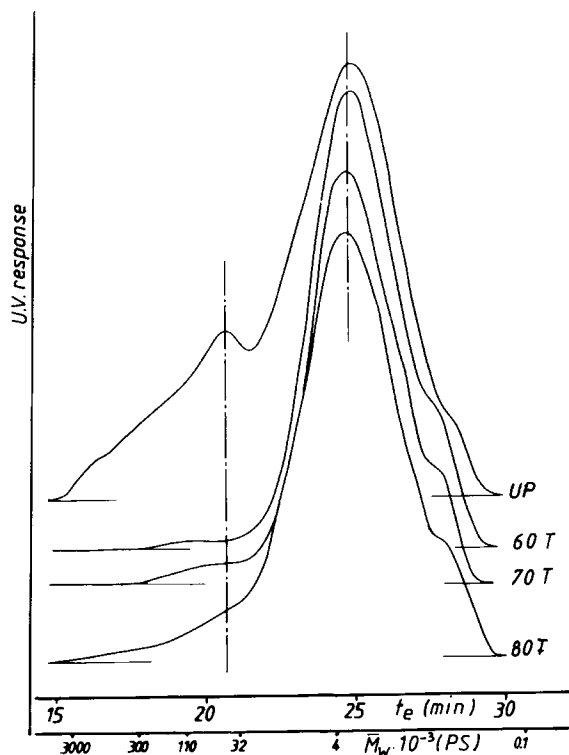


Fig. 3. UV chromatograms of the CTBN-rich top phase of samples containing a constant 50 : 50 prepolymer UP 2437/CTBN 8 weight ratio with 60, 70, and 80% by weight of styrene.

weight species in the UP prepolymer, and m the same number in CTBN.¹⁴ We have a pseudo-ternary phase diagram, so it is not possible to superpose Figure 5 on to Figure 2. Moreover, the elemental analysis gives the real weight fraction of CTBN, but we have no information about a weight fractionation of CTBN or about a hypothetical fractionation involving the acrylonitrile content. Nevertheless, we believe that the major factor with regard to fractionation is the high initial polydispersity of the UP prepolymer.

(3) In order to evaluate the influence of the UP molecular weight on the phase diagrams, we considered ternary mixtures with a constant oligomer UP/CTBN 8 weight ratio (Table I) but with different styrene fractions. The UV chromatograms of the bottom phase exhibit a slight tendency to fractionation up to 70% wt styrene. But a quantitative analysis of the SEC chromatograms remains possible, and the phase diagram is presented on Figure 6. According to Tompa,¹⁴ this binodal curve is characteristic of a ternary system exhibiting a partial miscibility between one polymer and a solvent. Logically, this partial miscibility is observed on the axis representing the binary polymer/solvent system with the larger interaction parameter (see Table II). Lowering the molecular weight of the UP leads to a partial miscibility with styrene. This unexpected phenomenon may be attributed to the effect of the chain ends rather than a real molecular weight effect. The cloud-point (CP) curve of the oligomer UP/styrene system is shown in Figure 7. We noticed that the CP

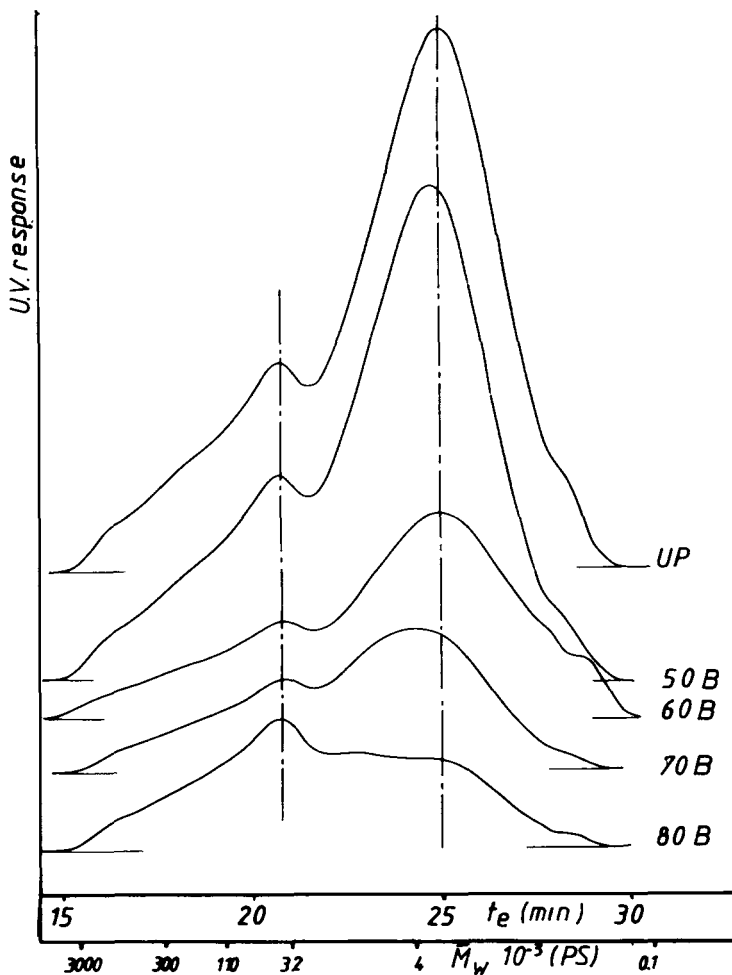


Fig. 4. UV chromatograms of the UP-rich bottom phase of samples containing a constant 50 : 50 prepolymer UP 2437/CTBN 8 weight ratio with 50, 60, 70, and 80% by weight of styrene.

curve is asymmetric, and that the maximum (called precipitation threshold) does not coincide with the calculated critical point ($\phi_{\text{crit}} \cong 42\%$ by weight). According to Koningsveld¹⁵ and others,⁵ these phenomena are due to polymer polydispersity.

(4) A macrophase separation of the UP2437 resin/CTBN 8 system around 7 phr (parts of additives per 100 parts of resin, by weight) has been observed. With at least 1 phr of CTBN the solution is opalescent, and between 1 phr and 7 phr the system is biphasic, but without any sedimentation processes, even after several weeks (like a stable emulsion). The miscibility limit is located at 1 phr; between 1 and 7 phr we have a compatibility window, and after 7 phr we have spinodal demixing. This behavior is represented in Figure 8. With another UP resin (M7110i) having the same chemical structure but with more acid chain-ends instead of alcohol, the same miscibility limit is observed, but with a narrower compatibility window (see Fig. 9). We speculate that some

TABLE III
Elemental Analysis Results of the Demixed Phases (T: top, B: bottom) of the Ternary System
Containing a Constant 50 : 50 Prepolymer UP 2437/CTBN 8 Weight
Ratio with Different Styrene Content from 80 to 50% by Weight

Solutions	C (%)	H (%)	N (%)	O (%)	Total (%)
Pure styrene	94.30	7.70	0	0	100
Pure CTBN 8	83.08	10.28	4.45	2.46	100.69
80 T	86.61	7.75	0.55	3.40	98.31
	86.89	7.67	0.55	3.49	98.60
75 T	84.46	7.89	0.83	3.17	96.33
	84.58	7.79	0.84	3.10	96.31
70 T	86.67	8.83	1.33	2.78	99.61
	86.50	8.71	1.19	2.90	99.30
65 T	87.16	8.48	1.52	2.94	100.10
	86.86	8.39			99.71
60 T	86.97	8.55	1.86	2.72	100.1
55 T	86.64	8.63	2.42	2.80	100.49
	86.57	8.63			100.42
50 T	86.03	8.84	2.37	2.74	99.98
80 B	75.88	6.88	0.41	15.58	99.75
	76.12			15.90	99.31
75 B	74.72	6.75	0.40	18.14	100.01
	74.65				99.94
70 B	72.28	6.44	0.15	19.95	98.82
	72.16	6.43		20.19	98.93
65 B	70.07	6.51	0.13	21.92	98.63
	70.09	6.45		21.84	98.51
60 B	66.80	6.18	0.10	26.08	99.16
	66.58	6.17		25.82	98.67

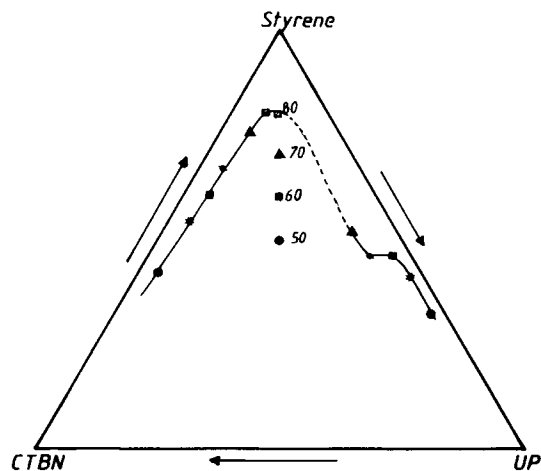


Fig. 5. Pseudoternary phase diagram obtained by elemental analysis of the system containing a constant 50 : 50 prepolymer UP 2437/CTBN 8 weight ratio but with different styrene contents: (□) 80%; (▲) 70%; (○) 65%; (■) 60%; (★) 55%; (●) 50%.

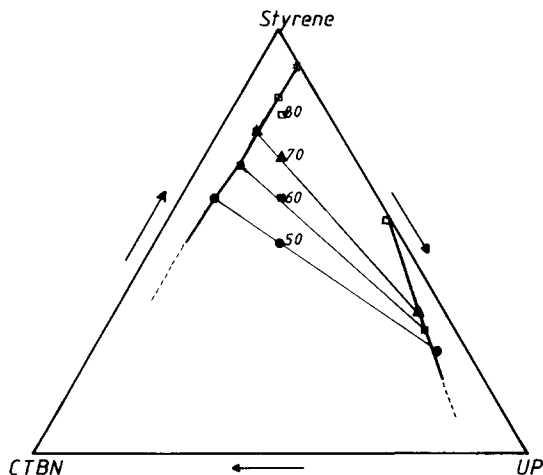


Fig. 6. Ternary phase diagram obtained by quantitative SEC analysis of a mixture containing a constant 50 : 50 oligomer UP/CTBN 8 weight ratio and with different styrene contents.

surfactant effects exist with the assumption of some specific interactions.¹⁶ This particular point will be the subject of the second paper of this series.

DISCUSSION

The introduction of an incompatible elastomeric additive like CTBN up to 1 phr into UP resins leads to phase separation. Each phase composition is fixed by the thermodynamics of the initial mixture. In our case, the lower binary

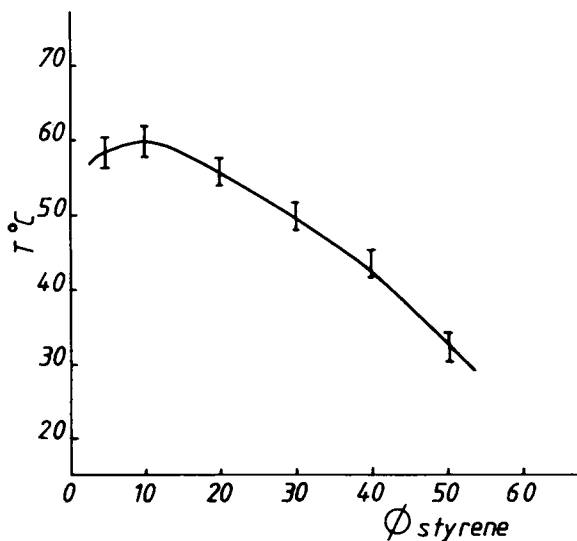


Fig. 7. Cloud point curve of the binary system oligomer UP/styrene.

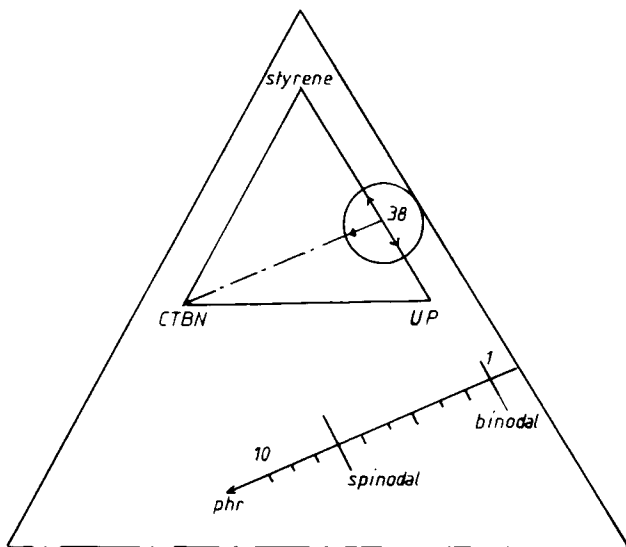


Fig. 8. Comparison of the miscibility limit and the compatibility window for the system UP 2437 resin (38% by weight of styrene)/CTBN 8.

interaction parameter is that for the UP2437 prepolymer/styrene. Therefore, the downward slope of the tie lines towards the UP2437 prepolymer/styrene axis signifies the formation of a prepolymer UP-rich phase with a lower styrene content than in the initial UP resin. According to HAN,¹⁷ the UP resin polymerization kinetics increases with the fraction of styrene monomer. Thus, the

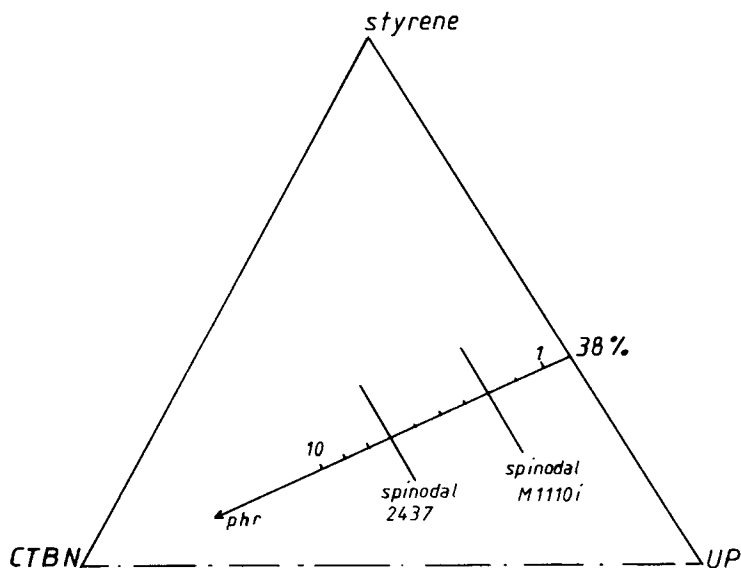


Fig. 9. Comparison of the compatibility windows for UP 2437 and UP M7110i resins (38% by weight of styrene) with CTBN 8.

polymerization kinetics of our systems containing a UP resin and an additive may be slower than that for the pure UP resin. This phenomenon has been observed in other experimental findings¹⁸⁻²¹ when an incompatible polymer was added to UP formulations.

The toughening effect of similar incompatible reactive liquid rubber additives to UP systems has been investigated.² The shape of the initial phase diagram indicates the initial compositions of the phases, but the question remains as to what are the compositions of the phases after polymerization.

Since the systems are immiscible, the second step of this study will be to investigate interfacial properties between the demixed phases.

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