

DILUTE BLOCK COPOLYMER SYSTEMS. PROPERTIES OF OIL-EXTENDED BUTADIENE-STYRENE BLOCK COPOLYMERS

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Abstract — An investigation into the effect of butadiene-styrene block copolymer dilution with mineral oils has revealed that the variation of tensile and other properties with oil level is not monotonous. The observed changes were attributed to morphological transitions induced by diluting and assisted by the presence of oil. The determining factor for the onset of transitions seems to be the ratio between volume fractions of oil and polystyrene in the extended material.

INTRODUCTION

The study of dilute block copolymer systems and, more specifically, that of butadiene-styrene linear or star block copolymers (thermoplastic elastomers) containing a diluent of the elastic matrix such as extender oils or other plasticizers is of great practical interest in view of the fact that a considerable proportion of the present consumption of thermoplastic rubbers (TRs) is in the form of oil-extended grades. This paper will present some of the results obtained in the course of an investigation program on the properties of linear and star TRs extended with mineral oils in a wide range of concentrations.

EXPERIMENTAL

Two series of block copolymers, designated by the letters L (linear) and S (star) were investigated. The polymers were synthesized by the usual anionic polymerization techniques (1). Polymer characteristics are given in Table 1.

TABLE 1. Properties of block copolymers

| Polymer | Structure | Styrene content (wt.-%) | Molecular weight, \bar{M}_n (g.mole ⁻¹) | | |
|---------|-----------|-------------------------|---|-------------|-------------|
| | | | Total | \bar{M}_B | \bar{M}_S |
| L-1 | linear | 34.5 | 123,200 | 80,800 | 21,200 |
| L-2 | linear | 27.8 | 78,500 | 57,100 | 10,700 |
| L-3 | linear | 40.3 | 98,000 | 58,600 | 19,700 |
| S-1 | star | 42.7 | 120,000 | 68,800 | 12,800 |
| S-2 | star | 30.7 | 141,400 | 98,200 | 10,800 |
| S-3 | star | 50.8 | 180,000 | 88,400 | 22,900 |

The properties of extender oils are given in Table 2. Oil I was obtained by purification with sulfuric acid and Oil II was extracted with furfural and subsequently hydrofined.

Polymer films were spin-cast from toluene solution. Tensile properties were determined on standard dumbbell specimens at a jaw separation speed of 0.5 m/min unless specified otherwise, on a Zwick Mod. 1454 tensile tester. Hardness was measured with a dead load Zwick hardness meter in the Shore A scale. All physical and mechanical measurements were performed at 25°. Melt viscosities were measured at 170° with an Instron Mod. 3211 capillary rheometer fitted with a 0.06" x 4" capillary for which end effects were negligible.

TABLE 2. Properties of extender oils

| Property | Unit | Oil I | Oil II | Oil III |
|----------------------------|-------------------|-----------|-------------|---------|
| Color | — | colorless | pale yellow | black |
| Density at 25° | kg/m ³ | 866.5 | 897.1 | 1009.6 |
| Refractive index | — | 1.4740 | 1.4929 | 1.5785 |
| Viscosity | — | 0.134 (a) | 0.432 (a) | 118 (b) |
| Structural composition (c) | | | | |
| Aromatic C | wt.-% | 3.5 | 7 | 45 |
| Naphthenic C | wt.-% | 29.9 | 38 | 21 |
| Paraffinic C | wt.-% | 66.6 | 55 | 34 |

a). Kinematic, at 37.8° (m²/h); b). Saybolt, at 100° (deg. Saybolt); c). Calcd. from refractive index, density and mol. wt.

RESULTS AND DISCUSSION

Stress-strain properties

The stress-strain plots of butadiene-styrene TRs exhibit a series of complicating features arising from the composite nature of these elastomers. Thus, in the $G - \lambda$ and $\log(G \lambda) - \log \epsilon$ curves plotted in Figs. 1 and 2 for the first traction of a series of toluene-cast films of polymer L-1 extended with variable amounts of Oil I, the following effects can be identified:

- Yielding and drawing (plastic-to-rubber transition) at low strains, due to the disruption of the continuous phase of polystyrene (2-5);
- A hardening effect at medium strains, explained (6) by the lateral impingement of the rigid polystyrene domains.

The diluting of block copolymers alters the stress-strain behavior in a predictable way: due to a decrease in the volume fraction of polystyrene (Φ_s) the continuous glassy phase is more easily disrupted and at higher degrees of dilution the interdomain distance becomes too great to allow bridge formation. The elongation at which the hardening effect becomes visible increases with oil content. It is noteworthy that, at least for high oil contents, the critical elongation for the onset of hardening is higher than predicted by the theory of Alfonso and Pedemonte (6) (see e.g. the curves for L-1 extended with 140 phr of Oil I). This can be attributed either to a viscoelastic effect (note that throughout this paper nonequilibrium data are discussed) or to a morphological one, involving the interphase layer of the domains. Taking into account the magnitude of this layer (7) it seems more appropriate to consider the whole domain-interphase layer system (DILS) as determinant for the mechanical behavior of the material. With increasing dilution the outer shells of the DILS swell and probably become ultimately indistinguishable from the rest of the matrix, the net result of this process being a decrease in the size of the mechanically resistant DILS.

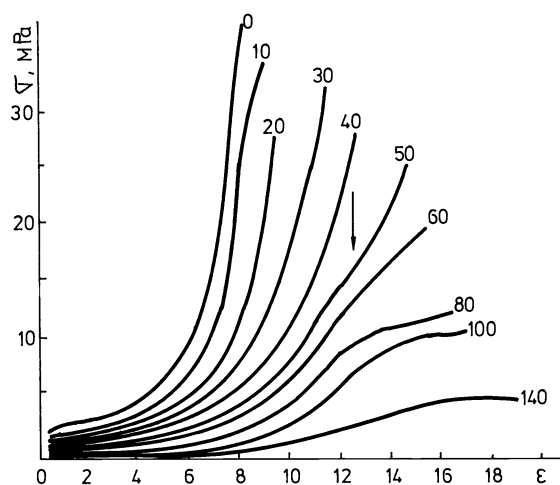


Fig. 1. Stress-strain curves for the system L-1/Oil I. Films cast from toluene, first traction. Oil concentration in phr.

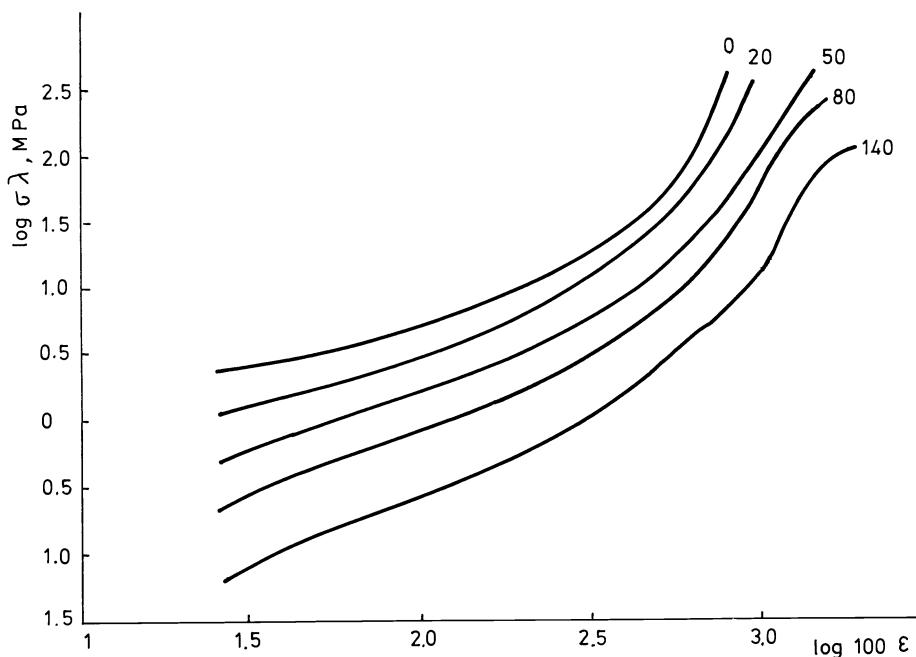


Fig. 2. Variation of true stress with extension for the system L-1/Oil I (films cast from toluene, first traction). Oil concentration in phr.

At large strains an additional effect was identified, beginning from an oil concentration of about 50 phr for the system L-1/Oil I, namely an inflexion in the stress-strain curves (marked by an arrow in Fig. 1). A tentative explanation is based on the assumption that the interphase layer of the DILS, weakened by oil absorption, yields when a critical stress is reached and undergoes an orientation in the principal direction of the strain. At even higher strains stress increases again due to the more limited deformability of the hard core of the DILS.

An attempt was made to interpret the stress-strain data in terms of the known constitutive equations for elastomers. A Mooney-Rivlin plot for the L-1/Oil I system is given in Fig. 3. It can be seen that, at low oil contents, the linear portion of the curve is rather short and the general shape of the curve, compared with the case of conventional filled and cured elastomers, is complicated by the effects already mentioned. The materials present a strong upswing at large elongations beginning at increasingly larger values of λ with increasing degrees of dilution. Also, the linear portion of the plot expands with increasing oil level. The classical two-term Mooney-Rivlin equation is of limited use save for highly diluted polymers. The applicability of the three-term constitutive equations for simple extension derived by Tschoegl (8) by expanding the strain-energy density function in terms of the invariants of the deformation tensor was tested. It was found that none of the equations gave a perfect fit for the whole curve. The best fit was obtained by using in addition to the two terms of the Mooney-Rivlin equation the cross term C_{21} . The results will be presented elsewhere; suffice it to say that the constants of the equation show an irregular variation with oil content which constitutes in our view an indication of the existence of transitions, morphological and/or of other kind.

The character of the stress-strain response is substantially altered by prestretching (2-5). A Mooney-Rivlin plot for test samples prestretched at about 80 per cent of the elongation at break is given in Fig. 4. In comparison with the curves plotted in Fig. 3 it can be seen that the linear portion of the plots has become longer. This was accompanied by a general decrease in the retractive force at the same elongation, a consequence of the breakdown of domain aggregates and also of orientation processes. In the presence of even moderate amounts of extender oil (e.g. 30 phr) the plots become practically linear up to high elongations.

Since the first elongation brings forth irreversible changes in the structure of the material, it is felt that the most adequate way for describing the stress-strain behavior of TRs would be by using a mechanical model which would include fail springs in at least one of the viscoelastic elements (9). The chemical composition of oils used for diluting thermoplastic elastomers has a marked influence on stress-strain properties. This is illustrated by the plots given in Fig. 5. At constant oil level, the higher the content of aromatic hydrocarbons in oil, the steeper is the slope of the stress-strain curve at any given elongation. This hardening effect may seem surprising in view of the known compatibility of aromatics with the polystyrene phase of TRs.

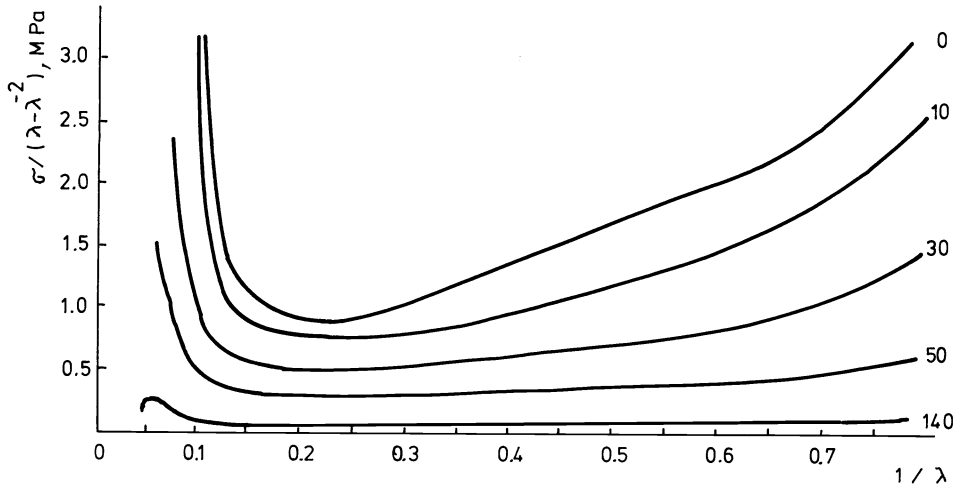


Fig. 3. Mooney-Rivlin plot for the system L-1/oil I, Films cast from toluene at first traction. Oil level in phr.

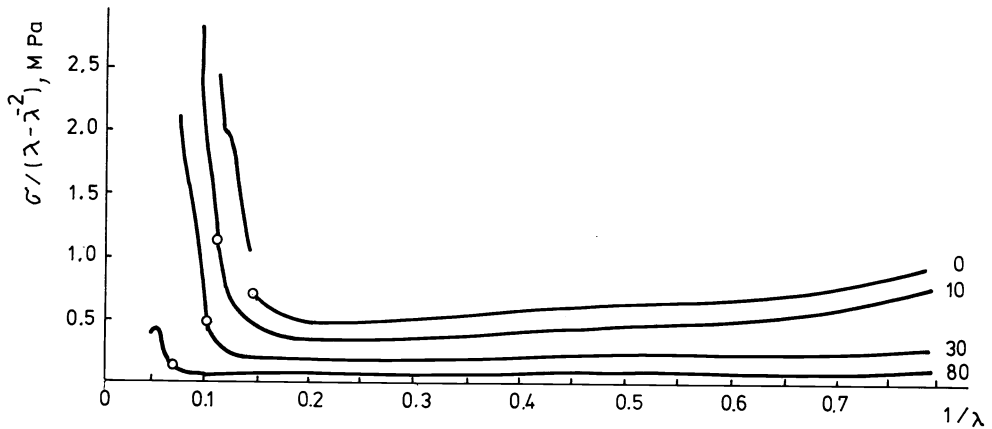


Fig. 4. Mooney-Rivlin plot for the system L-1/Oil I after prestretching at $\lambda = 0.8\lambda_B$. Maximum elongation in the first cycle is marked by open circles.

Although with increasing aromatic C content a decrease in the T_g of the glassy phase occurs (10), at room temperature the dominant factor seems to be the increased absorption of oil in the DILS which brings about an increase in the volume fraction of the hard phase, hence an increased elastic modulus of the material as a whole. Even comparatively small amount of aromatics has a rather strong effect on modulus, as seen from the data given for 50 phr oil.

Large strain "tensile modulus"

Interesting results are obtained by studying the variation of large strain "tensile modulus" with oil content (10). It should be mentioned in this context that, although not a fundamental property per se, the unit stress at fixed elongations (usually at $\lambda = 2, 4$ or 6) is widely used by rubber technologists as a measure of the elastic properties of rubber.

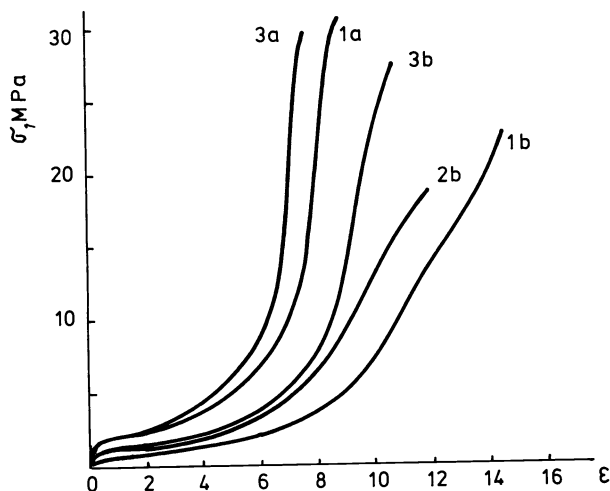


Fig. 5. Effect of oil composition on stress-strain behavior of extended films of polymer L-1 cast from toluene. 1. Oil I; 2. Oil II; 3. Oil III; a. 10 phr; b. 50 phr.

At first loading the modulus is strongly dependent on oil level. Taking the volume fraction of polybutadiene in the oil-extended matrix (Φ_R) as a measure of the degree of polymer dilution, it can be seen from the plots given in Fig. 6 that, although modulus generally decreases with increasing dilution, the dependence is not monotonous. After an initially gentler descent, at higher degrees of dilution a steeper decrease follows after a transition interval. The onset of the transition depends on the composition of base polymer, occurring at lower oil levels for polymers richer in butadiene.

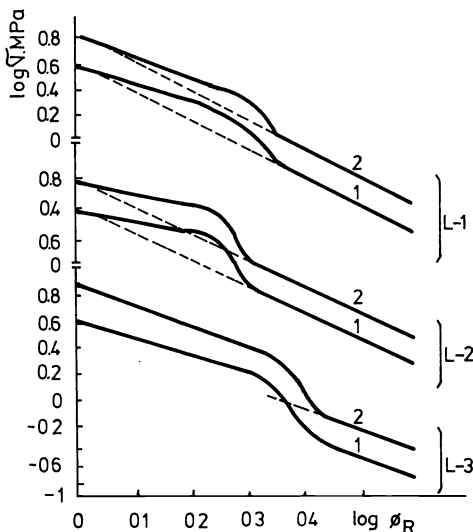


Fig. 6. Large strain "tensile modulus" for linear block copolymers as a function of volume fraction of rubber in the extended matrix. 1. $\lambda = 4$; 2. $\lambda = 6$. (From Ref. 10).

In an attempt to correlate large strain tensile modulus with oil level and initial styrene content of polymers ($\Phi_{S,0}$) it was found that, for a narrow range of λ , the unit stress can be approximated by the following equation:

$$\sigma = (C'_1 + C'_2/\lambda) (\lambda - \lambda^{-2}) \Phi_R^{1/3} (\Phi_{S,0}^{-1/2} \gamma)^n \tag{1}$$

where γ is the Guth–Smallwood function ($\gamma = 1 + 2.5 \Phi_S + 14.1 \Phi_S^2$), and C'_1 and C'_2 are constants. By

plotting $\log(\hat{\sigma} / \Phi_R^{1/3})$ against $\log \gamma$ and applying a horizontal shift factor $a_\gamma = -1/2 \log \Phi_{S,0}$, a master curve, schematically drawn in Fig. 7, was obtained with a satisfactory superposition of data for polymers with different initial compositions. The two branches of the curve, separated by the transition interval, have slopes of $n = 4$ and $n = 4/3$, respectively. The value of the exponent may be considered as an inverse measure of the retention of reinforcing ability of polystyrene domains with increasing dilution. The effect, occurring at $\Phi_S = 0.18 - 0.20$, was ascribed to a morphological transition (probably from lamellae or rods to isolated spherical domains) (10). Such a transition would be expected to take place at a constant critical value of Φ_S for all of the investigated polymers.

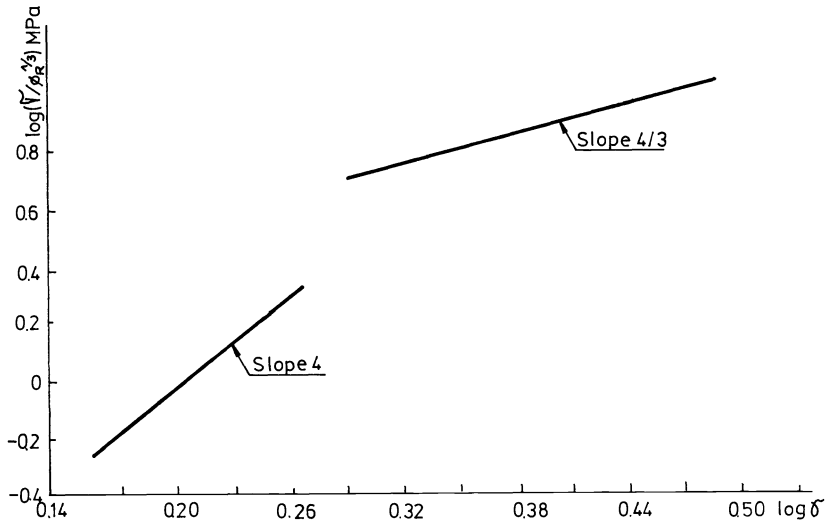


Fig. 7. Master curve of large strain "tensile modulus" dependence on the Guth-Smallwood function. All data reduced to $\Phi_{S,0} = 0.345$ and $\lambda = 6$. (From Ref. 10).

However, this is not the case as demonstrated by the lack of transition superposition for a series of polymers of varying initial composition in a $\log \hat{\sigma} - \log \Phi_S$ plot. It seems that not only the volume fraction of polystyrene domains but also the concentration of oil in the matrix exerts an influence on the onset of the transition. For the particular transition discussed here, oil migration at concentrations higher than equilibrium (e.g. at $\Phi_R \leq 0.47$ for the system L-1/Oil I) to the DILS "interface" with ensuing decrease in reinforcing capacity of the domains (11) was tentatively suspected as a possible mechanism by which oil might assist a morphological change.

In addition to the main transition discussed above, experiments performed at lower jaw separation speeds revealed the existence of smaller transitions (see Fig. 3 in Ref. 10) at 15 and 25 phr Oil I in the system L-1/Oil I, not discussed in the original paper. Although of lower amplitude, the secondary transitions are definitely larger than the experimental error, hence statistically significant.

Hardness

Hardness, usually defined as the resistance opposed by an elastic material to a deformation produced by pressing down an indenter of specified shape with a specified force, is a major specification for certain important uses of TRs such as shoe soling manufacture. In a first approximation hardness can be taken as a measure of the elastic modulus of the material.

In a quest for a quantitative relationship between hardness (H), amount of extender oil and composition of base polymer, a model similar to that used earlier for the large strain "tensile modulus" was employed (12):

$$H = H_0 \Phi_R^{1/3} (\Phi_{S,0}^a \gamma)^n \quad (2)$$

In a $\log(H/\Phi_R^{1/3}) - \log \gamma$ plot a good superposition of the curves for polymers of different initial composition was obtained by a horizontal shift corresponding to a value of $a = -0.6$, i.e. slightly higher in absolute value than the exponent found for tensile modulus. Using this value all hardness data for linear block copolymers extended with Oil I were plotted on a $\log(H/\Phi_R^{1/3})$ vs. $\log(\Phi_{S,0}^{0.6} \gamma)$ diagram yielding the master curve shown in Fig. 8. A sharp transition is identifiable at $\Phi_{S,0}^{0.6} \gamma = 4.3$, i.e. at $\Phi_S = 0.2$ for polymer L-1. The explanation given (12) for this behavior consists again in a morphological transition induced by the decreasing volume fraction of the glassy phase, from a more or less continuous phase to isolated domains dispersed in the rubbery matrix. This transition is assumed to be assisted by the presence of oil in a critical concentration.

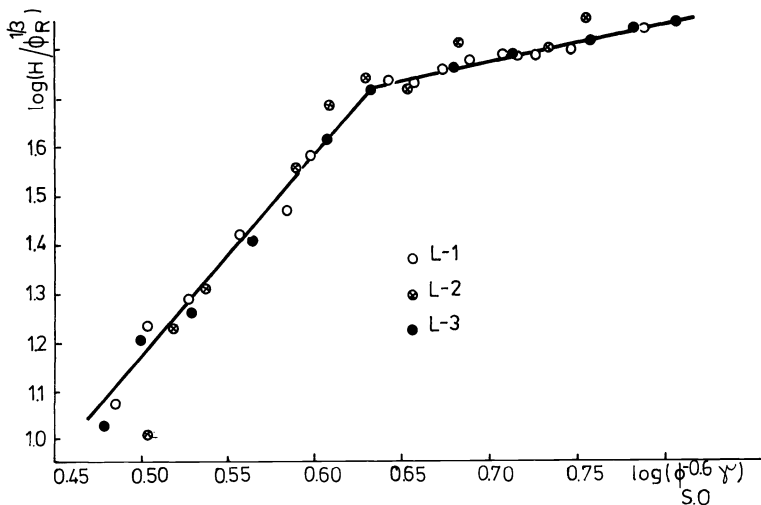


Fig. 8. Master curve of hardness dependence on oil content and composition of base polymer for linear block copolymers.

Ultimate properties

The ultimate properties of TRs, i.e. tensile strength, elongation at break and set at break vary with dilution in the expected way. This is exemplified by data plotted in Fig. 9 for the system L-1/Oil I. It can be seen that tensile strength generally decreases with increasing dilution while elongation at break increases and set at break goes through a maximum. For systems involving star block copolymers elongation at break was also found to decrease after reaching a maximum. The small increase in tensile strength recorded at low levels of oil is similar to that found for other oil-extended elastomers such as EPDM and can be assigned (13) to an

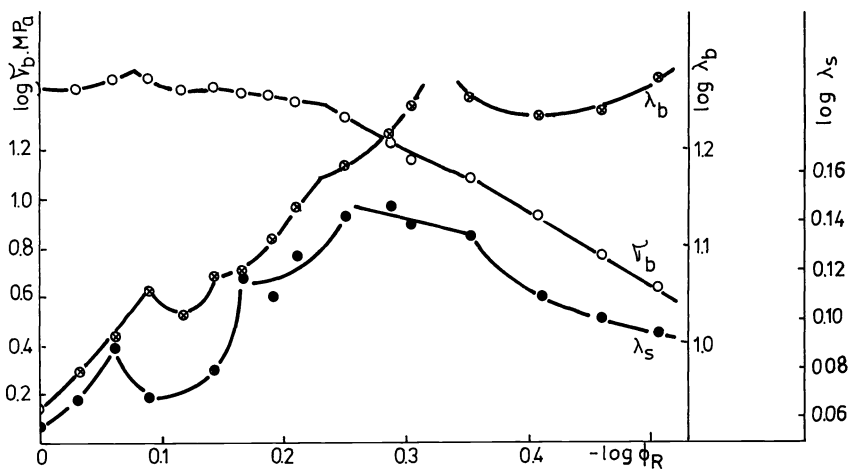


Fig. 9. Variation of tensile strength (σ_b), elongation at break (λ_b) and set at break (λ_s) with volume fraction of rubber in the oil-extended matrix for the system L-1/Oil I.

increased degree of stress-orientation of elastomeric chains, favored by the plasticizing effect of oil. A tensile strength increase in the presence of small amounts of oil is also consistent with the accepted views on the mechanism of block copolymer failure (14) according to which the glassy domains act as energy sinks, braking the propagation of cracks originating in the elastic matrix; a reduction in matrix viscosity would allow a more uniform distribution of the stress on the matrix-domain interface, preventing thus the buildup of local stress

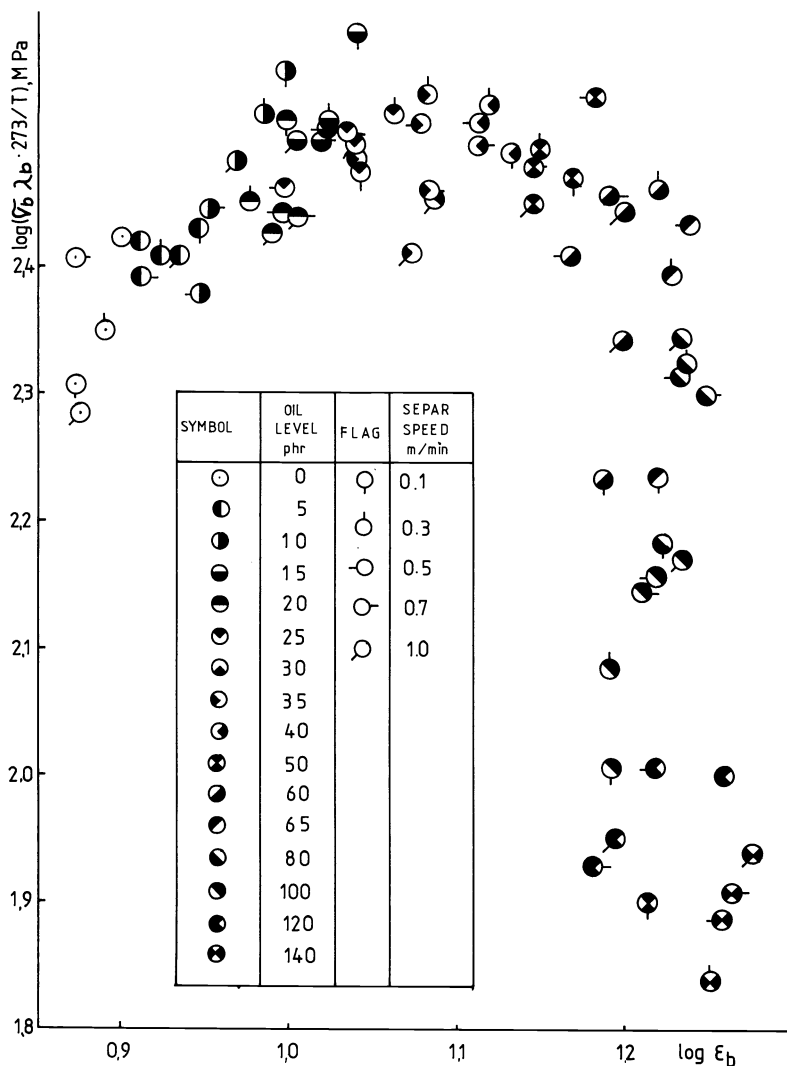


Fig. 10. Failure envelope for the system L-1/Oil I

concentrations and hence retarding the catastrophic failure of domains.

By making an analogy between the effects of temperature on the failure properties of block copolymers (14) and the effects of matrix dilution with oils, a failure envelope can be drawn by plotting true tensile strength data obtained for different oil contents and elongation rates against extension at break. An example of such a plot is given in Fig. 10. Oil content increases following the curve clockwise. Although somewhat obscured by the dispersion of experimental data, the main features of the curves for σ_b and λ_b given in Fig. 9 are still recognizable. It can be seen that the failure envelope has an approximately flat front towards ϵ_{max} , i.e. from a certain oil level upwards the extension at break remains more or less constant while accompanied by a decline in true tensile strength. Such a plot may help TR manufacturers and users to select the optimum oil level for a given base polymer in order to obtain maximum strength or maximum elongation at break. At a closer look a series of irregularities in the variation of ultimate properties with oil content (Fig. 9) can be detected. Thus, all three properties show a faster increase at beginning dilution and then pass through a minimum. Four discontinuities are found along each curve. The pattern is repeated, with minor variations, for all of the polymers investigated, as shown in Fig. 11 in a plot of the true tensile strength of polymers L-1, S-1 and S-2. This is construed as an indication of structural changes taking place in the dilute block copolymer systems which alter the physical and mechanical properties of the materials. The positions of the transition points, i.e. the concentrations of oil in the polymer at which the transitions occur, are different depending on the composition of base polymer: a given transition happens at higher oil levels for polymers initially richer in polystyrene and vice versa. This constitutes a further indication that the transitions are determined not only by the volume fraction of hard phase but also by the concentration of oil in the rubber phase as inferred earlier from modulus and hardness data. In that case the controlling factor for the onset of transitions should be the ratio between volume fractions of oil and polystyrene in the diluted material. The correctness of this assumption is demonstrated by the true tensile strength plots given in Fig. 12 as a function of $\log(1 + \Phi_0/\Phi_S)$. In this set of coordinates the transitions for the three polymers of different composition and structure are found to occur at the same values of $1 + \Phi_0/\Phi_S$.

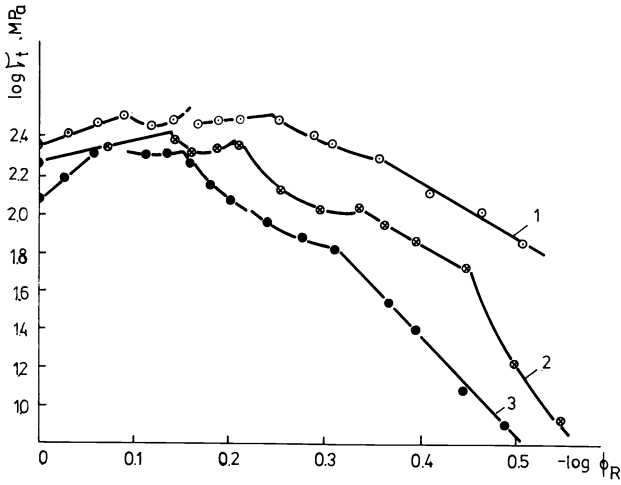


Fig. 11. True tensile strength vs. volume fraction of rubber in the diluted matrix.

- 1. L-1/Oil I;
- 2. S-1/Oil I;
- 3. S-2/Oil I.

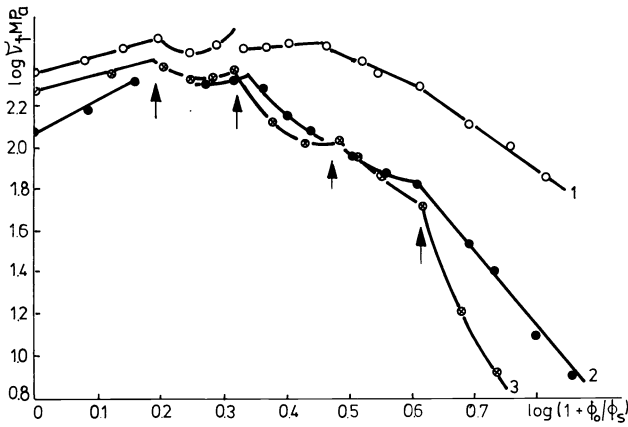


Fig. 12. Variation of true tensile strength with $1 + \phi_0/\phi_S$. Polymer/oil systems as above. Transitions are marked by arrows.

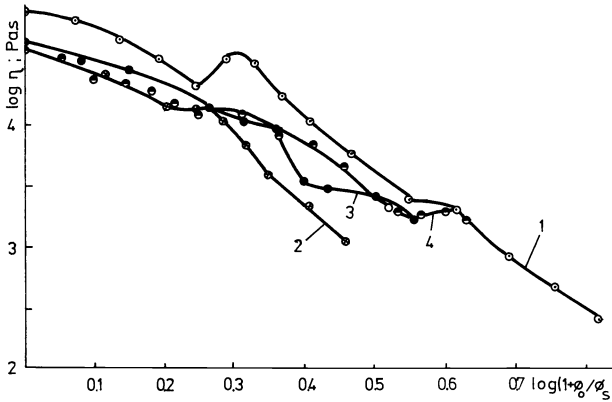


Fig. 13. Melt viscosity of oil-extended TRs as a function of $1 + \phi_0/\phi_S$. Temperature, 170° ; shear rate, 2.07 s^{-1} .

- 1. L-1/Oil I;
- 2. S-1/Oil I;
- 3. S-2/Oil I;
- 4. S-3/Oil I.

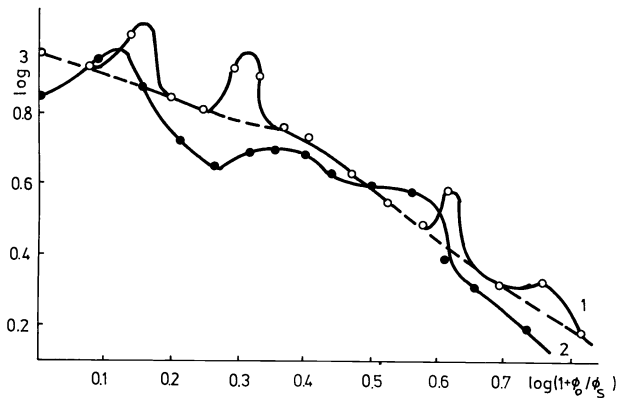


Fig. 14. Dependence of the degree of orientation on oil/polystyrene ratio. Films stretched at $\lambda = 3$.

- 1. L-1/Oil I;
- 2. S-2/Oil I.

Melt viscosity

At constant temperature, with increasing dilution melt viscosity of TRs decreases. At comparable molecular weights and styrene contents, linear triblock copolymers have higher melt viscosities than their star block copolymer counterparts (15).

The existence of an important transition occurring at $\log(1 + \Phi_0/\Phi_S) \approx 0.3$ and of a less marked one around 0.6 can be identified in the plot given in Fig. 13. A first consequence of this observation is that the materials conserved their composite nature even in melt at a comparatively high temperature (170°) (16). Secondly, it follows that the mechanisms active in triggering the transitions and the nature of the transitions are preserved in the conditions prevailing in the capillary of the rheometer (17).

Other physical properties

Other physical investigations also lend support to the existence of transitions in dilute block copolymer systems. Thus, an earlier study on the effect of dilution on the refractive index and density of butadiene-styrene block copolymers (18) has shown that the molecular refractivity of the system L-1/Oil I as a function of oil content had a discontinuity around 15 phr oil.

Interesting results were obtained by X-ray investigations on oil-extended block copolymers which have revealed a variation of the degree of orientation of macromolecular chains with maxima at oil/polystyrene ratios at which other physical and mechanical methods have also indicated the existence of transitions (19) (Fig. 14). Infrared spectra and volume resistivity measurements have led to similar results (19).

The average values of the Φ_0/Φ_S ratio for transitions observed by various methods of investigation are summarized in Table 3 (uncertain values are written in parentheses).

TABLE 3. Average values of the Φ_0/Φ_S ratio for transitions observed by various methods of investigation

| Property | Φ_0/Φ_S | | | |
|-------------------------------|-----------------|--------|--------|------|
| Tensile modulus | (0.57) | (0.96) | 1.48 | |
| Tensile strength | 0.45 | 1.12 | 1.74 | 3.40 |
| Elongation at break | 0.63 | 1.04 | 1.89 | 3.00 |
| Set at break | 0.69 | 1.11 | 2.03 | 3.50 |
| True tensile strength | 0.62 | 1.07 | 1.95 | 3.12 |
| Melt viscosity | | 1.01 | | 3.07 |
| Molecular refractivity | 0.57 | | | |
| Degree of orientation (X-ray) | 0.40 | 1.00 | 1.51 | 3.40 |
| Infrared spectra | 0.30 | | 1.51 | 3.07 |
| Volume resistivity | 0.35 | (1.15) | (1.54) | 3.00 |

In view of the diversity of methods employed for obtaining the data presented in Table 3, the coincidence of Φ_0/Φ_S values is remarkable. Further work is necessary in order to elucidate the nature of the transitions and the mechanisms involved.

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