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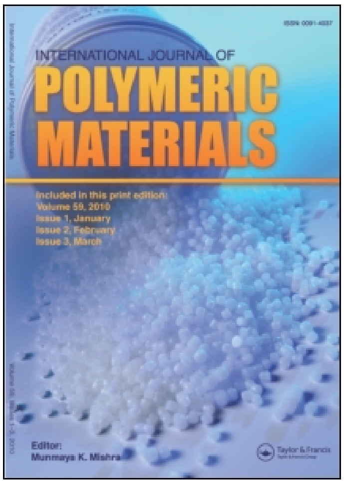

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Stress–Strain Characteristics and Ultimate Strength Properties of the SBS-Type Block Copolymer at Temperature Below and a Little Above the T_g of Polystyrene Blocks†

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The paper presents a summary of the results of study into the stress–strain relationship and ultimate strength characteristics of a SBS block copolymer (Cariflex TR-1200). The polymer has been investigated at uniaxial extension in the range of temperature from 20 up to 90°C. Two types of the stress-strain curves have been observed: S-shaped and the curves with a maximum corresponding to necking. The stress dependence on strain and time can be factored as $\sigma(\varepsilon, t) = h(\varepsilon)\, G(t)$. Viscosity has been measured. There exists a yield value of the stress above which it can be registered rather strong fall of viscosity. The yield value increases with decrease of temperature that is attributed to difficulties of break-down of the copolymer structure as temperature decreases. The long term durability of the block copolymer varies following a pattern typical of cured rubbers. The formation of specimens from solutions in various solvents may perceptibly affect this pattern, whereby the long term durability and the associated ultimate strength may change three- to ten-fold. These findings are ascribed to variations in the two-phase structure of the block copolymer due to conditions of its formation.

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† Presented at the XIth All-Union Symposium on Polymer Rheology held May 12–16, 1980 in Suzdal (U.S.S.R.).

INTRODUCTION

This work presents a study of the SBS copolymer, namely Cariflex-TR-1102, produced by Shell in the Netherlands. It is a further development of the collaborative investigation of the copolymer at temperature above T_g when it can be processed as the molten thermoplastic. It has been done under the auspices of the Macromolecular Division of the IUPAC.[1]

The polybutadiene and polystyrene in the copolymer are mutually incompatible thus resulting in a two-phase composite structure.[2–4] The nominal block length in molecular weight units is $1.1 \times 10^4 - 5 \times 10^4 - 1.1 \times 10^4$. At temperature below T_g (in the case of investigated block copolymer it is +60°C) the glassy polystyrene domains being dispersed in a polybutadiene matrix act as crosslinks thus creating a network. In such conditions thermoelastoplastic behaves like a cured rubber.

Such materials have found broad application as thermoelastoplastics behaving as filled rubbers at temperatures below the glass transition temperatures of the S blocks, while above T_g they can be processed as thermoplastics. The two-phase structure of the thermoelastoplastics may change under the effect of mechanical fields and temperature. It is, therefore, the purpose of this work to examine the thermoelastoplastics under various uniaxial strain conditions in broad ranges of strain rates and applied stresses. Different methods of formation of the block copolymer from melt and solutions were used.

2. EXPERIMENTAL

According to the available data,[4] the structure of such a block copolymer after its extrusion includes cylindrical polystyrene domains of colloidal dimensions, packed in a hexagonal pattern in a polybutadiene matrix. The specimens to be tested were extruded from a melt at 130°C and 0.3 MPa with subsequent annealing at 90°C, as well as cast from 10% solutions in various solvents at room temperature with vacuum drying at 60°C. Used as solvents were toluene which is a good solvent of polystyrene and polybutadiene, cyclohexane which is a poor solvent for polystyrene, and dioxane which is a poor solvent for polybutadiene.[5] The measurements were taken with uniaxial stretching of specimens at a constant strain rate ($\dot{\varepsilon}$ = const) and at a constant true stress (σ = const), using devices described earlier.[6,7] The total strain (ε) of the specimen was separated into its recoverable (ε_e) and irrecoverable (ε_f) components, as was described earlier,[8] and expressed according to Hencky as $\varepsilon = \ln(l/l_0)$, $\varepsilon_e = \ln(l/l_f)$ and $\varepsilon_f = \ln(l_f/l_0)$, where l_0 is the initial and l and l_f, respectively, total and irrecoverable components of the specimen length at a given point in

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time. The tests were conducted in broad ranges of $\dot{\varepsilon}$ (from 10^{-4} to 10^{-1} s^{-1}) and σ (up to 3.10^8 Pa) at temperatures ranging from 20 to 90°C.

3. RESULTS

3.1 Extension at $\dot{\varepsilon}$ = const

One of the most important mechanical characteristics of polymers is the true stress–strain relationship. In the case of SBS specimens formed from a melt there are two types of the stress–strain dependences: S-shaped curves typical of cured rubbers and $\sigma(\varepsilon)$ curves with a maximum σ_n corresponding to necking and onset of non-homogeneous deformation of the specimen. The latter is typical of glassy polymers.[9–11] The trend of the $\sigma(\varepsilon)$ curve of the SBS-type block copolymer is determined by the strain rate to temperature ratio. A drop in temperature down to 20°C brings about S-shaped $\sigma(\varepsilon)$ curves. A rise in temperature results in $\sigma(\varepsilon)$ curves with a maximum σ_n. A similar effect is produced by a decrease in $\dot{\varepsilon}$, which can be seen from the data obtained at 60°C (Figure 1).

Characteristically, the necking of the stretched SBS-type block copolymer

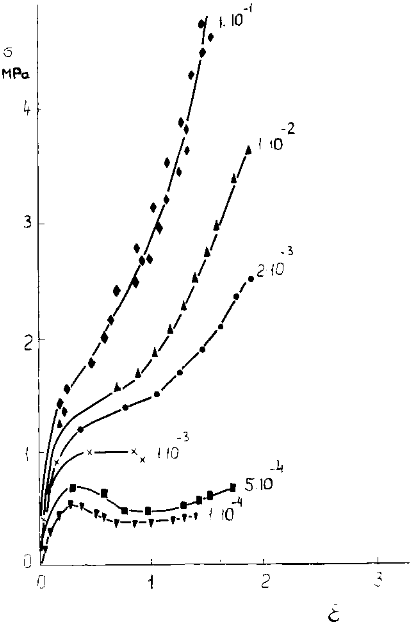

FIGURE 1 True stress versus strain at 60°C and various strain rates $\dot{\varepsilon}$ s^{-1}: ▼—1×10^{-4}; ■—0.5×10^{-3}; x–1×10^{-3}; ● 2×10^{-3}; ▲ 1×10^{-2}; ◆ 1×10^{-1}.

specimen occurs at values of the total strains equal to 0.4+0.5 ($\Delta l/l_0 = 50 + 60\%$) and are independent, in the first approximation, of temperature and $\dot{\varepsilon}$. Just as in the case of glassy polymers,[9,10] the value of σ_n decreases linearly with increasing temperature, tending to zero at the glass transition temperature of polystyrene and increasing in accordance with $\sigma_n = A + B \ln \dot{\varepsilon}$ where A and B are empirical constants ($B = 0.5$). The necking of glassy polymers is attributed to the development of forced elastic strains in the material.[11] In this case the considerable increase in $\dot{\varepsilon}$ eventually leads to a brittle fracture of the polymer at small strains before necking.

In the case of the SBS-type block copolymer, the necking seems to be due to plastic deformation of the material under the effect of overstresses localized at specimen inhomogeneities. However, the accompanying high-elastic strains check the growth of local inhomogeneities of the specimen, thereby suppressing necking at sufficiently large values of ε_e which is well known for polymer melts.[12]

Figure 2 represents the curves showing the stress versus deformation time $t = \varepsilon/\dot{\varepsilon}$ derived from the experiments at fixed values of $\dot{\varepsilon}$. Note that the data represented in Figure 2 have been obtained during the first stretching of specimens. The matter is that when the specimen is stretched again without rest, the hysteresis phenomena are observed. As can be seen from the results obtained at 20°C, relations log σ – log t are described by parallel straight lines at all strains. A similar picture is observed at other temperatures. This is illustrated by two parallel lines corresponding to strains of 0.4 and 1.8 and temperatures ranging from 20 to 70°C (reduction to 20°). The slopes of the

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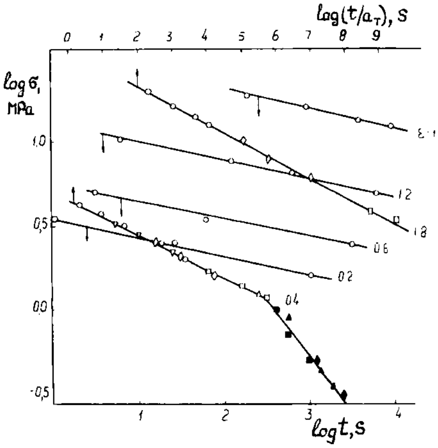

FIGURE 2 True stress versus deformation time at various temperatures and strains: ○ 20°C; ▽ 40°C; ◇ 50°C; □—60°C; △ 70°C. The figures near the lines stand for strain values. Black symbols correspond to necking. Reduction temperature – 20°C.

lines derived at different temperatures coincide, and the dependence $\sigma(t)$ can be represented in a temperature-invariant form including those approaching the process of necking (the right part of the curve for the value of deformation equal to 0.4). These data suggest that in the rubberlike state the strain behavior of the SBS-type block copolymer specimens formed from a melt is independent of the amount of stretching when it varies within a broad range. Thus the dependence of stress on the deformation and time can be represented as $\sigma(t, \varepsilon) = G(t) \cdot h(\varepsilon)$, where $G(t)$ is a time function and $h(\varepsilon)$ is a strain function. It should be emphasized that such a separation of the variables is consistent with Smith's data for the SBS-type block copolymer[13] and is well known for cured rubbers.[14]

The break on the $\log \sigma^* - \log t$ curve derived at $\varepsilon = 0.4$ corresponds to the moment of necking, while the curve portion to the right of the break corresponds to the dependence of σ_n on the deformation time.

3.2 Extension at σ = const.

Figure 3 represents compliance versus time ($\varepsilon/\sigma - t$) at 25 to 85°C for specimens formed from a melt. It can be seen that compliance versus time is described by straight lines in wide ranges of applied stresses (10^5 to 10^6 Pa at 85°C and 10^6 to 3×10^8 Pa at 25°C). Characteristically, just as in the case of creep of noncrosslinked rubbers with a narrow molecular-weight distribution,[15] the data for regular extension and fracture (blackened dots in Figure

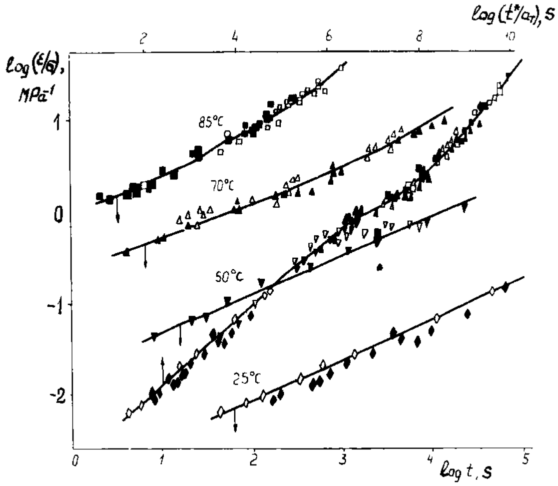

FIGURE 3 Compliance versus time at various temperatures: ◇ -25°C; ▽ - 50°C; △ - 70°C; □ - 85°C. Black symbols correspond to compliance at fracture. Reduction temperature 25°C.

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3) fall on the same lines. The creep dependence can be represented in the form of a temperature-invariant master curve A (Figure 3) by normalizing time with the aid of a temperature reduction factor α_T.

3.3 Viscosity

The experiments show that the SBS-type block copolymer may easily accumulate irrecoverable deformation below but not too far from the glass transition temperature of the styrene block. The accumulation pattern depends strongly on σ and temperature. Figure 4 shows the longitudinal viscosities (λ) versus the true stresses. Viscosity is defined as $\lambda = \sigma/\dot{\varepsilon}_f$ where $\dot{\varepsilon}_f$ is the flow strain rate. It is known that the longitudinal viscosity of polybutadiene with a narrow molecular mass distribution (MMD) is practically independent of σ[15] at temperatures far above T_g. But when temperature decreases substantially non-Newtonian behavior is displayed.[21]

In the region of lower stresses λ tends to a constant initial value. At high stresses, λ of the SBS-type block copolymer decreases with increasing σ. Attention must be drawn to the fact that by decrease of temperature there occur simultaneously increase of viscosity and the critical (yield) value of the stress at which viscosity begins to descend. This obviously depends on the difficulties of breaking the structure of the copolymer at temperatures far below T_g. It should be pointed out in this connection that at temperatures above 100°C the SBS-type block copolymer behaves like structurized dispersed systems and filled polymers whose yield point falls into the region of low stresses.[16,17] Analysis of the obtained data indicates that in the examined range of temperature (T) the variation of λ with T is of Arrhenius-type law. The initial values of λ at temperatures ranging from 20 to 30°C become as high as 10^{13} to 10^{14} Pa·s that is typical for polymeric glasses.

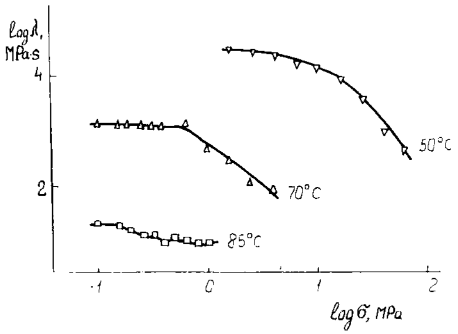

FIGURE 4 Longitudinal viscosity versus true stress at various temperatures: ▽ — 50°C; △ 70°C; □ 85°C.

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3.4 Long term durability of block-copolymer

One of the most important strength characteristics of polymers is their long term durability (t^*). It has been measured at conditions of σ = const. Figure 5 shows long term durability versus stress for specimens formed from a melt and cast from solutions in various solvents. As can be seen these curves are described for all specimens except those cast from solutions in dioxane, in a broad range of times and at various temperatures by formula $t^* = K\sigma^{-\alpha}$ where K and α are constants well known for rubbers[9,10] and noncross-linked elastomers.[14] Parameter $\alpha = 2.3$ approaches the value of α for unfilled and noncross-linked rubbers and is much lower than in the case of filled cross-linked elastomers. In the latter case $\alpha = 6$[9,10] for rubbers based on random butadiene-styrene copolymer SBR-30. The preparation of SBS-type block copolymer specimens from solutions in various solvents may be a factor producing a marked effect on the value of t^* and even on the trend of the $t^*(\sigma)$ curve. Such behavior stems from the effect of the affinity of the solvent to polystyrene and polybutadiene on the structure of the SBS-type block-copolymer films formed from the solution. This materially affects the strain behavior of the SBS-type block-copolymer.[3,18] Cyclohexane, which is a poor solvent of polystyrene and a good solvent of polybutadiene, is conducive to polystyrene forming a separate phase when a film is cast, as a result of which the long term durability of the films coincides with t^* of films formed from a melt. Toluene, which is a good solvent for both SBS blocks, improves the compatibility of the blocks and makes their segregation difficult when the solvent is evaporated. This results in a less regular structure, which reduces the long term durability of the block copolymer film as compared to t^* of the films cast from the cyclohexane solution. Dioxane, which is a poor solvent of polybutadiene and a good solvent of polystyrene, causes coiling of the macromolecular segments forming the rubber phase into separate domains.

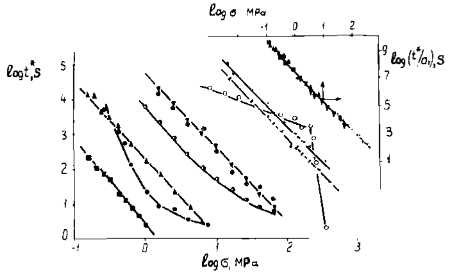

FIGURE 5 Long term durability versus true stress at various temperatures. Specimens formed from a melt: ▼—50°C; ▲—70°C; ■—85°C. Specimens formed from solutions in various solvents: + cyclohexane, 25°C; ⊕ -cyclohexane, 50°C, ∗ toluene, 25°C, ○ dioxane, 25°C, ◑—dioxane, 50°C, ●—dioxane, 70°C. Reduction temperature 25°C.

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As a whole, the SBS films become highly inhomogeneous and their structure changes under the effect of stress and temperature. Consequently, a break is observed on the log $t - \log \sigma$ curve at 25°C and a departure from linearity of this curve at higher temperatures and the stress. In general, depending on the type of solvent used in the casting of block copolymer specimens, the long term durability may vary five- to ten-fold with a three- to four-fold variation in the material strength. The long term durability data of specimens formed from a melt and cast from cyclohexane solutions can be represented in a temperature-invariant form with t^* being normalized with the aid of the temperature reduction factor α_T (Figure 5).

4. DISCUSSION

Thus, the foregoing is indicative of a dual mechanical behavior of the SBS-type block copolymer. On the one hand, the block copolymer behaves like cross-linked rubber at widely ranging $\dot{\varepsilon}, \sigma$ and temperatures, the last varying from room temperatures to those approaching the T_g of polystyrene, and in some cases its behavior is similar to that of non-cross-linked one-phase elastomers. In this case it appears that the temperature-time reduction procedure can be applied to the derived data. Analysis of all results suggests that the values of temperature reduction factors α_T of the strain and strength properties coincide and are determined by the temperature-induced changes in the initial viscosity. The temperature dependences of α_T and viscosity in the examined range (20 to 90°C) are described by the Arrhenius relation with an activation energy equal to 230 kJ/mole. This is suggestive of a unified relaxation mechanism of deformation and viscous flow of the block copolymer at uniaxial extension.

On the other hand, the SBS-type block copolymer exhibits, under certain conditions, properties typical of structurized multiphase systems with a structure changing under the effect of high values of σ and depending on the specimen preparation technique. Some investigators suppose[19] that the application of the temperature-time superposition procedure to such systems is questionable from the physical point of view because every phase is characterized by its own relaxation mechanism. At the same time, the applicability to the obtained data of a temperature-time superposition with the same value of α_T in broad ranges of $\dot{\varepsilon}, \sigma$ and ε at various strain modes suggests that, at least in the case of specimens formed from a melt, the predominant role in the relaxation behavior of the SBS-type block copolymer at the experimental temperatures is played by a single complex mechanism involving mobility of the polybutadiene phase and joint motion of the polybutadiene and polystyrene segments along the phase boundary.[20] Final

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solution of this problem though, calls for further experimental and theoretical studies.

In conclusion, we should like to sum up that, depending on the ratio of the strain rate to temperature, two types of strain curves are possible for the block polymer, one being typical of cross-linked elastomers and the other of glassy polymers. In the course of creep the block copolymer starts to flow irreversibly, the viscosity of this flow being sensitive to changes in stress and temperature. The long term durability of the SBS block copolymer varies following a pattern typical of rubbers. In this case, the factor of formation of the polymer from its solutions in various solvents strongly influences the long term durability.

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