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Rheological properties of a star-shaped butadiene-styrene block copolymer

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With 6 figures

1. Introduction

In melting state, butadiene-styrene block copolymers present a very singular behaviour which, despite an evident interest for the processing, has stimulated relatively few studies. Unusual melt rheological properties of these block copolymers have been shown up by several previous investigations (1–6), and are currently attributed to the multiphase structure resulting from the thermodynamical incompatibility between polystyrene and polybutadiene segments.

The high viscosity, high elasticity and strongly non-newtonian behaviour of butadiene-styrene block copolymers are usually attributed to a conservation of the multiphase structure, persisting in the melting state. In fact, the flow mechanism of these materials is not well understood at this time, in this sense that, if melt flow of these products results from a softening of thermoplastic domains with the temperature increase, an homogeneous mixture of polybutadiene and polystyrene segments rest unlikely, according to the thermodynamical incompatibility.

In this study, we investigated the melt rheology of a star-shaped butadiene-styrene block copoly-mer, as a function of the temperature, using a slit die rheometer. Furthermore, slit die rheometry possibilities have been used to obtain some elastic characteristics in melting state, namely entrance pressure drop and exit pressure.

2. Experimental

A variable depth slit die rheometer, well described in a previous publication (7) has been used to study the rheological properties of the butadiene-styrene block copolymer. Essentially the slit die rheometer gives wall pressure measurements during the extrusion flow, which permit to obtain pressure profile into the die, entrance pressure drop and exit pressure. Extrusion experiments were performed at 160, 180, 200 and 220 °C, with dies of same length (85 mm) and same width (10 mm) but different depths (.509 mm, .725 mm and 1.005 mm).

The studied sample was a star-shaped butadiene-styrene block copolymer, SOLPRENE 415, supplied by the Phillips Petroleum Company. It has an intrinsic viscosity of .97 dl/g (in toluene, at 25 °C), a styrene content of 40% by weight and a molecular weight $\bar{M}_w$ of 153000 (by GPC), with a polydispersity $\bar{M}_w/\bar{M}_n$ of 1.24 (8).

3. Results and discussion

True flow curves for SOLPRENE 415 at 160, 180, 200 and 220 °C are given in fig. 1. The same shape is generally observed for each
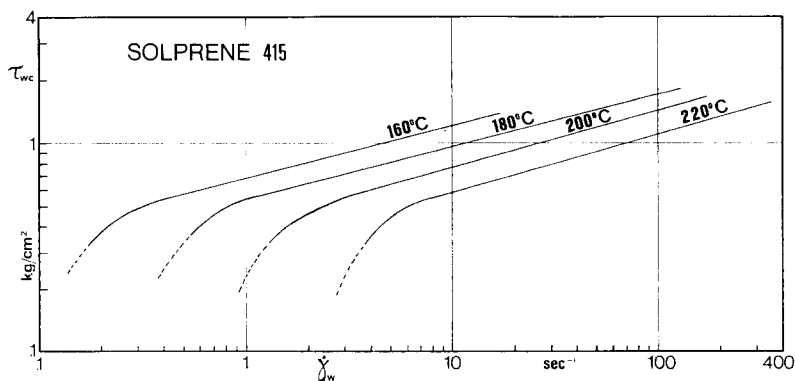

Fig. 1. Shear stress at wall versus true shear rate, at different temperatures, for SOLPRENE 415. Broken lines indicate discrepancy between data from different depths slit dies

curve, with a transition for a shear stress of .56 kg/cm^2 (5.5 × 10^5 dyn/cm^2). Above this critical shear stress, flow curves follow a power law, and below $\tau_w = 5.5 \times 10^5$ dyn/cm^2, a marked curvature is observed with a discrepancy between data from different depths slit dies. The transition in the flow curves at a critical shear stress for the star-shaped butadiene-styrene block copolymer agrees very well with a similar observation on linear triblock S-B-S copolymers by *Holden, Bishop* and *Legge* (1). Thus, the existence of two particular melt flow states, for butadiene-styrene block copolymers, do not depend on their macromolecular structure.

The shear rate-temperature superposition was attempted for the flow curves and the viscosity functions. The reference temperature was arbitrary chosen as 160 °C, and the shift factors at 180, 200 and 220 °C were graphically determined for $\tau_w = 1$ kg/cm^2. The results of the superposition are given in fig. 2, with the shift factor as a function of the temperature. The temperature dependence of the shift factor $a_T(T_0)$ is well expressed by an exponential law, as follows:

$$a_T(160) = \frac{\dot{\gamma}_w(T)}{\dot{\gamma}_w(160)} = 6.96 \times 10^{-4} e^{0.045 T},$$

$(\dot{\gamma}_w$ at $\tau_w = 1$ kg/cm$^2)$. [1]

The superposition is excellent above the transition shear stress, and a discrepancy is observed below $\tau_w = 5.5 \times 10^5$ dyn/cm^2.

The viscosity functions are given in fig. 3. Below the transition shear stress, a maximum is observed, and above $\tau_w = 5.5 \times 10^5$ dyn/cm^2, the temperature dependence of the viscosity follows an Arrhenius equation, as shown in fig. 4 [η_a for $\tau_w = 1$ kg/cm^2], which permits to

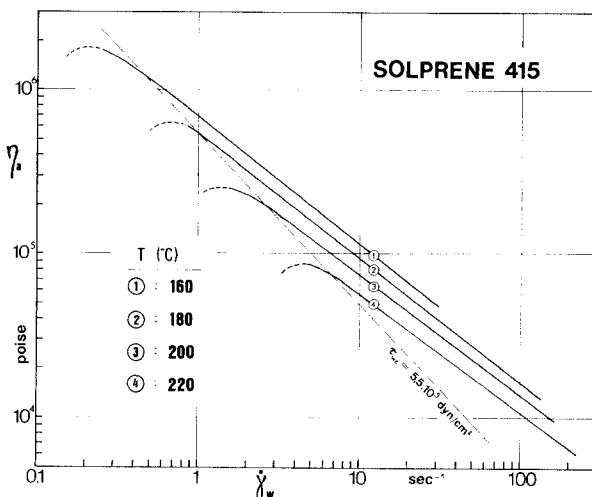calculate a flow activation energy of 19.2 kcal/ mole.

Fig. 3. Apparent viscosity versus shear rate at different temperatures, for SOLPRENE 415

By comparison, *Arnold* and *Meier* (4) showed that for linear SBS block copolymers, the activation energy depends on the polystyrene content; for samples with PS content above 35%, the activation energy is 38 kcal/mole, and when PS < 31%, E_τ is 19 kcal/mole. Our star-shaped block copolymer (with 40% PS) has an activation energy equal to the one of a linear material of PS < 31%. Thus the radial structure has the effect to reduce the flow energy, by comparison to the linear structure, at same PS content. This explains why radial block copolymers are less viscous in melting state, and suggests that the involved flow mechanism is strongly macromolecular structure dependent. One hypothesis could be that the star-shaped material presents an aggregates flow.
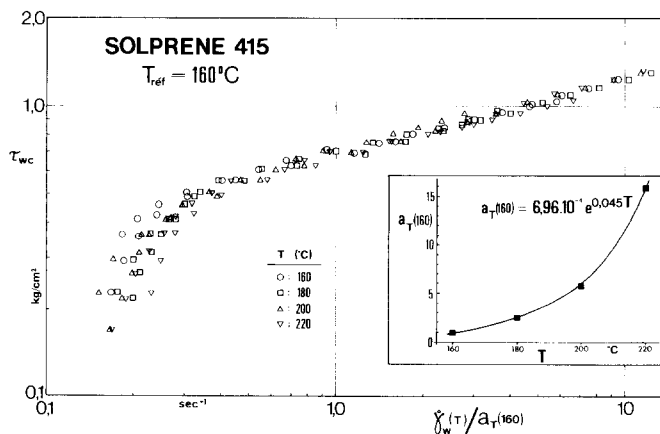
Fig. 2. Shear rate – temperature superposition for flow curves of SOLPRENE 415, and temperature dependence of the shift factor $a_T(160)$
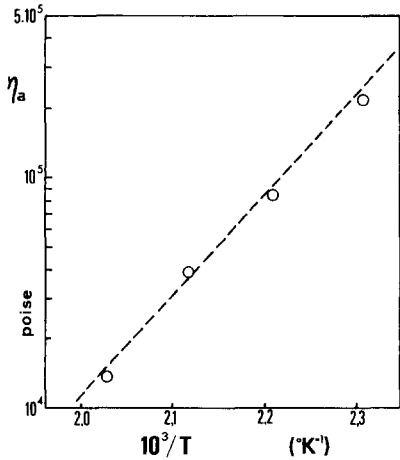
Fig. 4. Apparent viscosity at $\tau_w = 1\ \mathrm{kg/cm^2}$ versus $1/T$ for SOLPRENE 415

Wall pressure measurements into a slit die rheometer permit to deduce exit pressure by extrapolating the so called "pressure profile", i. e. the plot of measured wall pressures versus the longitudinal distance. It has been suggested by several authors to use the exit pressure as a measurement of the melt elasticity (9), and to deduce the first normal stress difference following (10):

$$\tau_{11} - \tau_{22} = P_{exit} + \tau_w\,\frac{dP_{exit}}{d\tau_w}.\qquad [2]$$

A plot of the first normal stress difference versus the shear stress does not depend on the melt temperature, and this is in complete agreement with results of *Han* (11) with other polymers. But we have noted a slit geometry dependence as shown in fig. 5a. At a given shear stress, values of the first normal stress difference as computed from exit pressure measurements, decrease as the slit depth increases. Multiplicating $(\tau_{11} - \tau_{22})$ by h, the slit depth, a single curve is obtained, as shown in fig. 5b. Earlier, *Han* and coworkers (12) have obtained a correlation between the exit pressure and the L/D ratio in capillary rheometers, but to the author's knowledge, no reference has been made to such a correlation between slit die geometry and exit pressure. In fact, some well known observations on die swell at the exit of slit dies are consistent with our observations of the slit depth dependence of the exit pressure (and thus the first normal stress difference); also die swell (and

wall pressure) at the center of the long side is greater than that at the center of the short side, in a rectangular duct (13). In other words, die swell decreases when the slit depth increases, as well as the exit pressure (and the first normal stress difference).
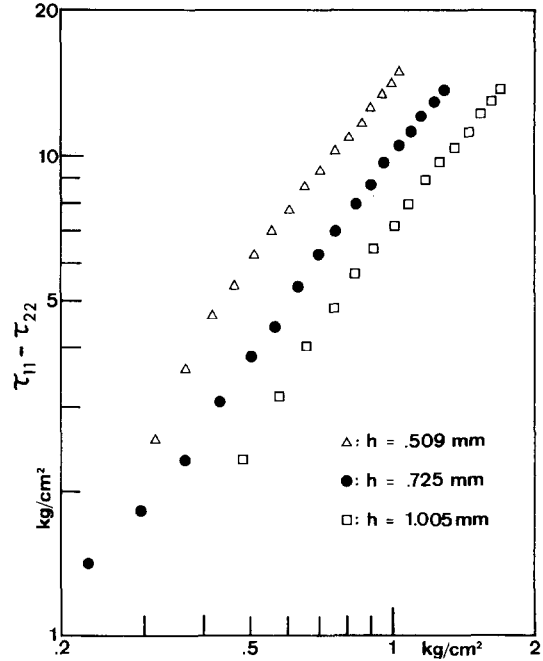

Fig. 5a. First normal stress difference versus shear stress in different depths slit dies, for SOLPRENE 415
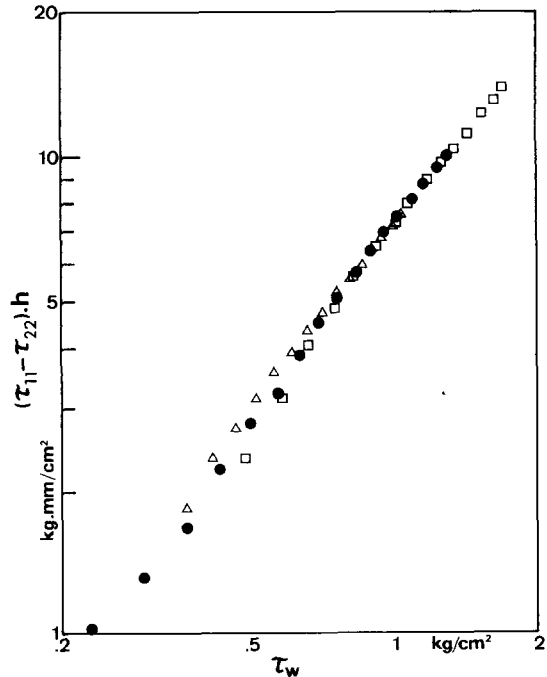

Fig. 5b. Product of the first normal stress difference by the slit depth versus the shear stress

With the slit die rheometer, we can estimate easily the pressure drop at the entry of the die, by considering the difference between the applied pressure into the barrel (P_a) and the first pressure measurement (P_I) into the die. A plot of the exit pressure P_0 versus $P_a - P_I$ shows a linear dependence between the two quantities (fig. 6). Thus the pressure drop at the entry and the exit pressure appear to have the same origin: the elasticity of the melt. This indicates that an elastic perturbation at the entrance has a direct consequential effect at the exit.
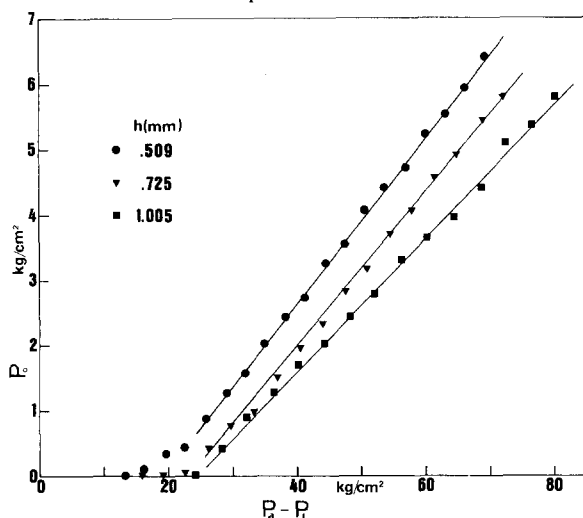

Fig. 6. Exit pressure versus entrance pressure drop in different depths slit dies, for SOLPRENE 415

4. Conclusions

Rheological properties of the star-shaped butadiene-styrene block copolymer have been studied with a slit die rheometer. Flow curves and viscosity functions at 160, 180, 200 and 220°C show, for a shear stress of 5.5×10^5 dyn/cm^2, a singularity which could indicate a modification in the structure of the melt.

By a classical shear rate-temperature superposition method, the flow activation energy at constant shear stress has been obtained, 19.2 kcal/mole. This value of the activation energy indicates that the star-shaped structure has the effect to reduce the flow energy, by comparison with a linear triblock copolymer. Moreover, this suggests an aggregate flow mechanism for the star-shaped block copolymer.

Exit pressure and pressure drop at the entry were determined for the block copolymer melt. First normal stress difference as a function of the shear stress shows a dependence on the slit depth, but a single curve can be obtained,

expressing the product $(\tau_{11} - \tau_{22}) \times h$ as a function of τ_w.

Summary

Flow curves and viscosity functions at 160, 180, 200 and 220 °C have been determined for a star-shaped butadiene-styrene block copolymer, by means of a slit die rheometer. At a critical shear stress, a transition occurs in flow curves, which suggests a modification in the melt structure. The flow activation energy is deduced by a classical shear rate – temperature superposition method, and the obtained value suggests an aggregates flow mechanism for the star-shaped product. Exit pressure and entrance pressure drop are obtained and show a dependence on the slit depth.

Zusammenfassung

Mit Hilfe eines Schlitz-Düsen-Rheometers werden die Fließkurven und Viskositätsfunktionen eines stern-förmigen Butadien-Styrol-Blockpolymerisats bei 160, 180, 200 und 220 °C bestimmt. Bei einer kritischen Schubspannung tritt in den Fließkurven ein Übergang auf, der auf eine Modifikation der Schmelzstruktur hindeutet. Die Fließ-Aktivierungsenergie wird mit einer klassischen Schergeschwindigkeits-Temperatur-Superpositionsmethode abgeleitet; der erhaltene Wert macht für das Stern-Polymerisat das Vorhandensein eines Aggregat-Fließmechanismus wahrscheinlich. Austritts-druck und Eintrittsdruckabfall werden gemessen und zeigen eine Abhängigkeit von der Schlitztiefe.

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