

# Measurement of the Rheological Properties of Thermoplastic Elastomers

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## Synopsis

Using the Han slit/capillary rheometer, measurements were taken of the rheological properties of commercially available thermoplastic elastomers, namely, styrene-butadiene-styrene (SBS) block copolymer (Shell, Kraton), ethylene-propylene copolymer (Exxon, Vista), olefinic-type thermoplastic rubbers (UniRoyal, TPR 1600, TPR 1900, and TPR 2800), and urethane thermoplastic elastomers (UniRoyal, Roylar A863 and Roylar E9). The rheological properties determined were shear viscosity and first normal stress difference at various melt temperatures. Depending on the material and the melt temperature tested, the range of shear rates tested was 50 to 700  $\text{sec}^{-1}$ , and the range of shear stresses tested was  $10^5$  to  $10^6$   $\text{dyn/cm}^2$ . For comparison purposes, rheological measurements were also taken for a few materials using the Weissenberg rheogoniometer although its use was limited to low shear rates (or shear stresses). It was demonstrated clearly that the Han slit/capillary rheometer is a unique instrument for determining the rheological properties of thermoplastic elastomers in the range of high shear rates (or high shear stresses) often encountered in various polymer processing operations.

## INTRODUCTION

During the past decade, thermoplastic elastomers have received much attention from both the resin-producing and the resin-processing industries. The commercially available thermoplastic elastomers fall into two categories: (1) the block copolymers and (2) the physical blends. The elastomeric block copolymers can further be categorized, according to their chemical structure, as (a) styrene-diene (A—B—A) type; (b) ester-ether  $\{A—B\}_n$  type; and (c) urethane-ester or urethane-ether  $\{A—B\}_n$  type. The elastomeric properties of these block copolymers are attributed to their two-phase morphology in the solid state.<sup>1</sup> These materials behave as vulcanized rubbers at room temperatures and yet can be processed as thermoplastics at elevated temperatures. Moreover, the transition between melt-like and vulcanizate-like behavior is entirely reversible.

Of the several thermoplastic elastomers commercially available today, the A—B—A-type block copolymers of styrene and butadiene, i.e., styrene-butadiene-styrene (SBS) and butadiene-styrene-butadiene (BSB), are perhaps the most extensively studied. The SBS copolymers have been reported to possess unique rheological properties<sup>1,2</sup> because of their two-phase domain structure, which persists to a significant degree in the molten state. Kraus et al.<sup>3</sup> determined the steady shear and dynamic viscosities of SBS- and BSB-type block copolymers of styrene and butadiene. They found that, at a constant molecular weight and total styrene content, viscosities were greater for the polymer terminating with styrene blocks than for the polymer terminating with butadiene blocks. They reported also that the viscoelastic behavior of these polymers is

determined by the length of the terminal block and not by the total molecular weight.

Dynamic viscosity measurements<sup>4-6</sup> of SBS block polymers, over a wide range of temperature, indicate that a transition occurs from highly non-Newtonian flow behavior at low temperature to Newtonian flow behavior at elevated temperature. This transition is attributed to a structural change from a multiphase structure at low temperature to a homogeneous structure at elevated temperature.

Futamura and Meinecke<sup>7</sup> have studied the effect of central block structure on the rheological properties of ABA-type copolymers containing polystyrene end blocks. They found that the molecular weight and the glass transition temperature of the central block have a negligible effect on the melt viscosity, whereas the difference in solubility parameter between the central block and the terminal block, which governs the miscibility of the two phases, has a large influence on melt flow properties.

Thermoplastic polyurethane block copolymers contain short blocks of amorphous polyesters or polyethers and hard blocks of paracrystalline polyurethane. The latter aggregate into hard domains and serve as network junctions for the soft, rubbery polyether or polyester matrix. Polyurethane elastomers have high melting points and hardness because of strong hydrogen bonds holding in the paracrystalline polyurethane domains. The major difference between the SBS-type elastomers and the polyurethane elastomers lies in that the latter contain hard crystalline polyurethane segments which are much shorter than the amorphous polystyrene blocks of the SBS-type elastomers.<sup>8</sup>

Recently, UniRoyal Chemical Company introduced a new family of polyolefin-based thermoplastic elastomers<sup>9</sup> called TPR thermoplastic rubbers. These materials are believed to be a physical blend of a crystalline polyolefin (e.g., polypropylene or high-density polyethylene) and an elastomeric copolymer. The morphology of these elastomers is expected to be similar to that of elastomeric block copolymers. However, as TPR thermoplastic rubbers constitute a physical blend containing a chemically crosslinked elastomeric network, they may exhibit rheological behavior distinctly different from that of block copolymers. Although a few studies<sup>10,11</sup> report the viscous property of TPRs, little has been discussed about their elastic behavior in the molten state.

As part of our continuing program for determining the rheological properties of polymeric materials, we very recently carried out rheological measurements on several commercially available thermoplastic elastomers, and in this paper we report the highlights of the study.

## EXPERIMENTAL

The apparatus used for the rheological measurements was the Han slit/capillary rheometer,\* which provides measurement of wall normal stresses along the die axis. The principles and applications of the rheometer are well documented in a number of publications by Han<sup>12-15</sup> and in the recent monograph by Han.<sup>16</sup>

The materials investigated were three grades of olefinic-type thermoplastic

\* A commercial version of this rheometer is available from Seiscor Division, Seismograph Service Corporation, Tulsa, Oklahoma 74102.

rubber (UniRoyal TPR 1600, TPR 1900, and TPR 2800), two grades of urethane thermoplastic elastomer (UniRoyal Roylar A863 and Roylar E9), an SBS block copolymer (Shell Kraton G2701), and an ethylene-propylene copolymer (Exxon Vista).

For comparison purposes, rheological measurements were also taken for a few materials using the Weissenberg rheogoniometer, although its use was limited to low shear rates (or shear stresses).

## RESULTS AND DISCUSSION

Figures 1 and 2 give plots of viscosity  $\eta$  versus shear stress  $\tau_w$  and first normal stress difference  $\tau_{11} - \tau_{22}$  versus shear stress  $\tau_w$  for Kraton at three melt temperatures. In preparing these plots from the data obtained from the Han slit/capillary rheometer, the theoretical expressions developed earlier by Han<sup>15</sup> were used, and they are summarized in Table I. Readers who are not familiar with the methods of preparing the plots given in Figures 1 and 2, using the data obtained with the Han slit/capillary rheometer, should consult previous publications by Han.<sup>15,16</sup>

It is seen in Figure 1 that Kraton follows non-Newtonian behavior and that its viscosity decreases as the melt temperature increases. It is of interest to note in Figure 2 that  $\tau_{11} - \tau_{22}$  increases with  $\tau_w$ , giving rise to a single correlation which is independent of melt temperature. Such a correlation has been demonstrated repeatedly by Han,<sup>13-16</sup> who used not only homopolymers but also polymer blends and filled polymers.

Very recently, Leblanc<sup>17,18</sup> used a slit die, basically the same as that constructed by Han<sup>13</sup> and used extensively by Han and co-workers<sup>15,16</sup> in determining the rheological properties of a butadiene-styrene block copolymer (Solprene 415, Phillips Petroleum Co.). Leblanc obtained nonlinear pressure profiles, indicating that flow was *not* fully developed in the slit die. However,

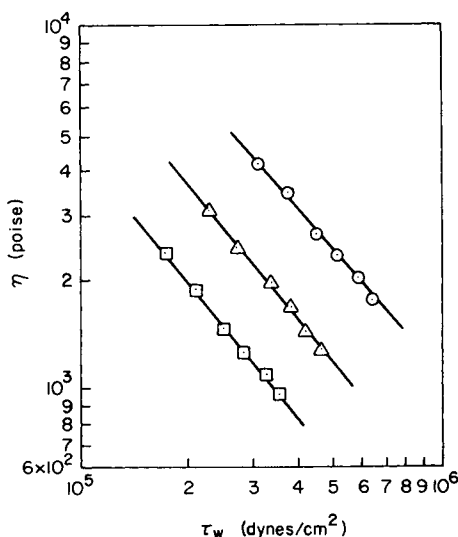


Fig. 1. Viscosity vs shear stress for Kraton at various temperatures: (○) 140°C; (△) 160°C; (◻) 180°C.

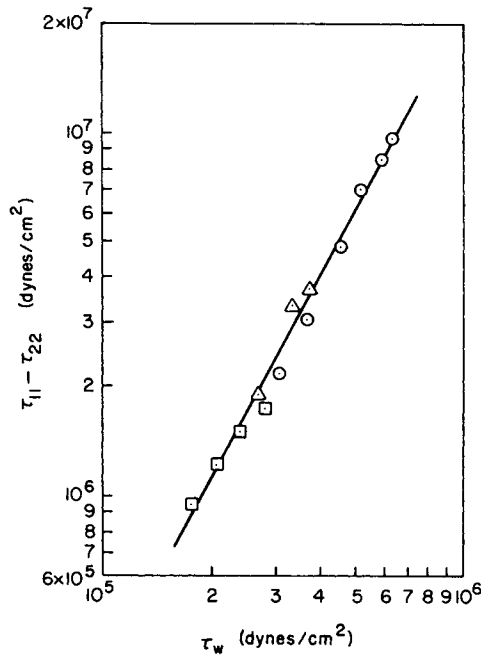


Fig. 2. First normal stress difference vs shear stress for Kraton at various temperatures: (○) 140°C; (△) 160°C; (□) 180°C.

TABLE I  
Summary of Theoretical Equations for Slit/Capillary Rheometry<sup>a</sup>

Rheological variables	Slit rheometry	Capillary rheometry
Apparent shear rate $\dot{\gamma}_{app}$	$\frac{6Q}{wh^2}$	$\frac{32Q}{\pi D^3}$
Wall shear stress $\tau_w$	$\left(\frac{-\partial p}{\partial z}\right) \frac{h}{2}$	$\left(\frac{-\partial p}{\partial z}\right) \frac{D}{4}$
True shear rate $\dot{\gamma}$	$\left(\frac{2n+1}{3n}\right) \dot{\gamma}_{app}$	$\left(\frac{3n+1}{4n}\right) \dot{\gamma}_{app}$
Viscosity $\eta$	$\frac{\tau_w}{\dot{\gamma}}$	$\frac{\tau_w}{\dot{\gamma}}$
Normal stress difference $\tau_{11} - \tau_{22}$	$P_{exit} + \tau_w \frac{dP_{exit}}{d\tau_w}$	$P_{exit} + \tau_w \frac{dP_{exit}}{d\tau_w}$

<sup>a</sup>  $Q$  is the volumetric flow rate,  $w$  is the slit width,  $h$  is the slit thickness,  $D$  is the capillary diameter,  $-\partial p/\partial z$  is the pressure gradient,  $n$  is defined as  $d \ln \tau_w / d \ln \dot{\gamma}_{app}$ , and  $P_{exit}$  is the exit pressure.

Leblanc<sup>17</sup> curve fitted his nonlinear pressure profiles to a parabolic equation. He then calculated wall shear stress and also shear viscosity, unfortunately without realizing apparently that he should have obtained varying wall shear stress (hence varying shear viscosity) along the longitudinal axis of the die. The nonlinearity of the pressure profiles obtained by Leblanc appears to have resulted from his third pressure transducer (position III), which was mounted close to

the entrance of the die. It should be pointed out that determination of steady shear viscosity from nonlinear pressure profiles in a slit die (or in a capillary) does not make sense, and therefore the validity of Leblanc's data on shear viscosity is in serious doubt. Apparently using the same data collected for determining shear viscosity, Leblanc<sup>18</sup> published another paper reporting the first normal stress difference, using exit pressure. Again, the exit pressures he used were obtained by extrapolating the nonlinear pressure profiles to the die exit, apparently without realizing that the theoretical expression he used requires fully developed flow, i.e., linear pressure profiles. Therefore, the validity of Leblanc's data on  $\tau_{11} - \tau_{22}$  is in serious doubt. No wonder that he obtained a  $\tau_{11} - \tau_{22}$  that depends on the slit depth.

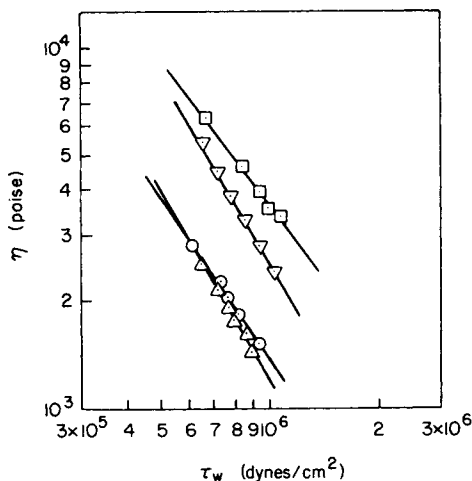


Fig. 3. Viscosity vs shear stress at 240°C: (Δ) TPR 1600; (○) TPR 1900; (▽) TPR 2800; (□) E-P copolymer.

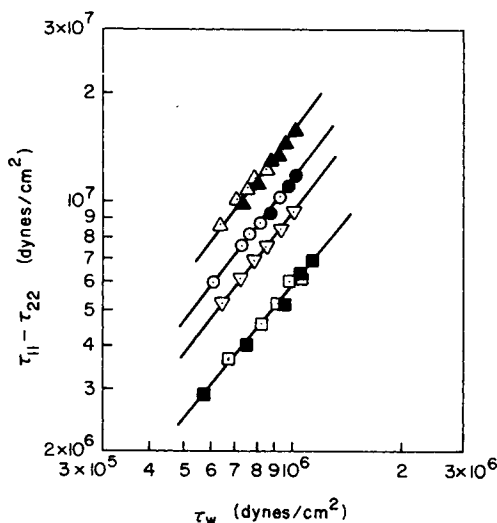


Fig. 4. First normal stress difference vs shear stress at different melt temperatures. Closed symbols for 220°C and open symbols for 240°C: (Δ, ▲) TPR 1600; (○, ●) TPR 1900; (▽) TPR 2800; (□, ■) E-P copolymer.

Figures 3 and 4 give plots of  $\eta$  versus  $\tau_w$  and  $\tau_{11} - \tau_{22}$  versus  $\tau_w$  for the three TPRs and the ethylene-propylene copolymer. It is of particular interest to note that the material which is the least viscous of the three TPRs is the most elastic, and the material which is the most viscous is the least elastic. That is,

$$\eta_{\text{TPR1600}} < \eta_{\text{TPR1900}} < \eta_{\text{TPR2800}}$$

and

$$(\tau_{11} - \tau_{22})_{\text{TPR1600}} > (\tau_{11} - \tau_{22})_{\text{TPR1900}} > (\tau_{11} - \tau_{22})_{\text{TPR2800}}$$

The structural characteristics of the TPRs used in the present study are very little discussed in the published literature. The TPRs are believed to be blends of a partially crosslinked ethylene-propylene-diene tercopolymer and a crystalline polyolefin.<sup>9</sup> The differential scanning calorimetric (DSC) thermograms obtained with the three TPRs used are given in Figure 5, together with the DSC thermograms of a high-density polyethylene (Union Carbide DMDJ 4306) and a polypropylene (Amoco Chemicals 6014). It is evident in Figure 5 that all three TPRs contain a crystalline component having a melting point peak at about 166°C, which is very close to the melting point of 167°C obtained for polypropylene. Also, the heights of the melting point peaks for TPR-1600, TPR-2800, and TPR-1900 are in an increasing order, indicating that they contain a crystalline component, most probably polypropylene, in the same increasing order of concentration.

It is of interest to mention that the TPR-2800 having an intermediate amount of crystalline component is the most viscous and yet the least elastic of the three TPRs and that the TPR-1600 having the least amount of crystalline component is the least viscous and yet the most elastic of the three TPRs investigated. Similar trends in the rheological properties of polymer blends have been reported by Han and co-workers,<sup>19,20</sup> who noted that the viscosity and elasticity of polymer blends may go through a maximum or minimum at a certain blend ratio. They

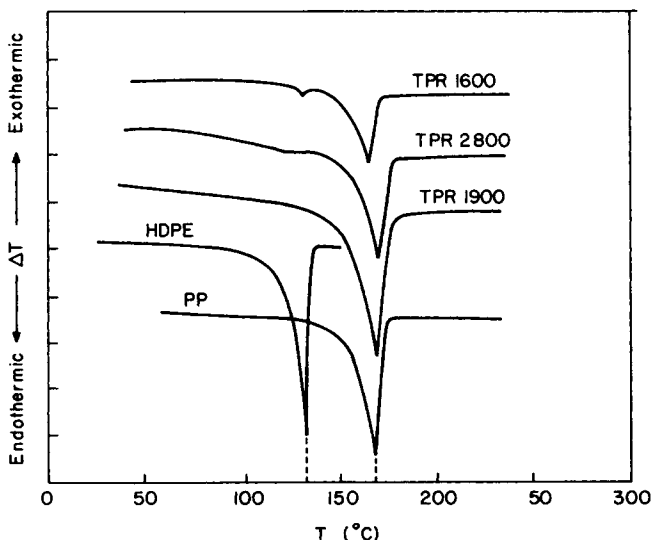


Fig. 5. Differential thermal analysis thermograms of TPRs. Heating rate 10°C/min;  $\Delta T$  scale with 0.5°C/in.; weight of sample 20 mg.

noted that such seemingly peculiar behavior depends, among many factors, on the state of dispersion. Such an observation is of practical importance to the development of elastomeric polymer blends with controlled rheological properties.

Figures 6 and 7 give plots of  $\eta$  versus  $\tau_w$  and  $\tau_{11} - \tau_{22}$  versus  $\tau_w$  for the two urethane thermoplastic Roylar elastomers investigated. It is seen that

$$\eta_{\text{Roylar A863}} < \eta_{\text{Roylar E9}}$$

and

$$(\tau_{11} - \tau_{22})_{\text{Roylar A863}} > (\tau_{11} - \tau_{22})_{\text{Roylar E9}}$$

Comparison of Figure 6 with Figures 1 and 3 reveals that the "shear thinning" behavior of the Roylars is much weaker than that of the Kraton and TPRs.

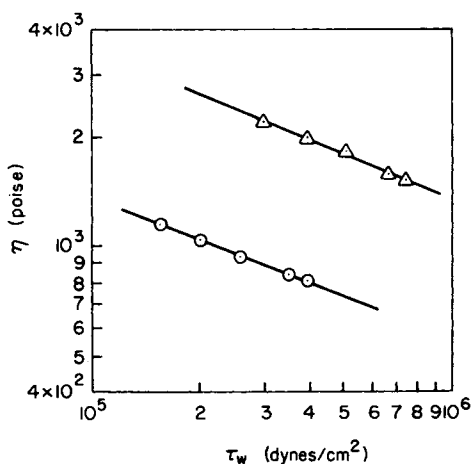


Fig. 6. Viscosity vs shear stress at 180°C: (○) Roylar A863; (Δ) Roylar E9.

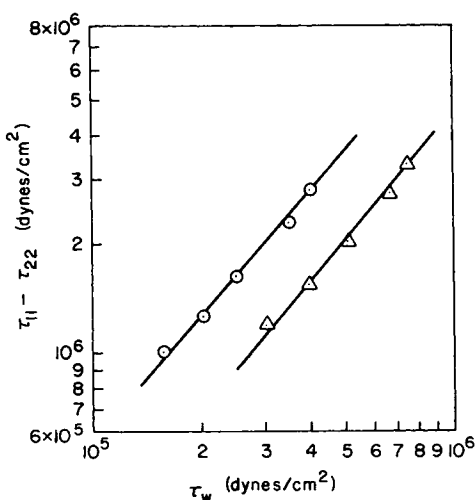


Fig. 7. First normal stress difference vs shear stress at 180°C: (○) Roylar A863; (Δ) Roylar E9.

TABLE II  
Power Law Constants of Polymers Investigated

Polymer (manufacturer)	Sample code	Melt temp., °C	$K$ , dyn sec <sup><i>n</i></sup> /cm <sup>2</sup>	$n$ , dimension- less
SBS copolymer (Shell Chemicals)	Kraton	140	$0.444 \times 10^5$	0.45
		160	$0.328 \times 10^5$	0.45
		180	$0.251 \times 10^5$	0.45
Thermoplastic rubber (UniRoyal)	TPR 1600	220	$1.668 \times 10^5$	0.37
		240	$0.820 \times 10^5$	0.37
	TPR 1900	220	$1.098 \times 10^5$	0.39
		240	$0.724 \times 10^5$	0.39
	TPR 2800	240	$1.181 \times 10^5$	0.36
Ethylene-propylene copolymer (Exxon Chemicals)	E-P copolymer	220	$0.842 \times 10^5$	0.46
		240	$0.621 \times 10^5$	0.46
Urethane thermoplastic elastomer (UniRoyal)	Roylar A863	180	$0.428 \times 10^4$	0.75
		200	$0.157 \times 10^4$	0.75
	Roylar E9	180	$0.903 \times 10^4$	0.71

Table II gives material constants evaluated for the various resins investigated, using the empirical power law model represented by

$$\tau_w = K \dot{\gamma}^n \quad (1)$$

It is believed that Roylar A863 is a polyether urethane based thermoplastic elastomer and that Roylar E9 is a polytetramethylene ether glycol-based thermoplastic elastomer. In these elastomers in the solid state, the strength is derived from the hard crystalline polyurethane segments held together by strong hydrogen bond forces. The lengths of the crystalline polyurethane segments are relatively short (molecular weight of about 900) compared to those of polystyrene blocks (molecular weight of about 10,000) in SBS copolymers. Hence, in the molten state, when the hydrogen bond forces are no longer effective, polyurethane elastomers exhibit insignificant network structure and possess low melt viscosity and much weaker shear thinning behavior. On the other hand, the TPR thermoplastic elastomers contain highly associated molecular structures due to the chemical crosslinks and hence are characterized by high melt viscosity and strong shear thinning behavior.

Information on the temperature sensitivity of melt viscosity is useful in controlling extrusion and injection molding operations. The activation energy of shear flow,  $\Delta E$ , at a constant wall shear stress of  $6 \times 10^5$  dyn/cm<sup>2</sup>, was calculated using the Arrhenius relation  $\Delta E/R = d \ln \eta / d(1/T)$ , in which  $R$  is the gas constant,  $\eta$  is the viscosity, and  $T$  is the absolute temperature. Table III gives  $\Delta E$  values for TPR-1900, Roylar A-863, and Kraton. It is seen that the TPR-1900, which contains thermally insensitive chemical crosslinks, has the lowest  $\Delta E$  value, and hence its melt viscosity is least sensitive to variation in melt temperature. Holden et al.<sup>1</sup> reported that at low temperatures (about 100°C) the activation energy of SBS block copolymers approaches that of homopolystyrene ( $\Delta E = 82$  kcal/mole), whereas at high temperatures (about 200°C) it approaches that of polybutadiene ( $\Delta E = 4.5$  kcal/mole). The activation energy of 12.8 kcal/mole obtained for Kraton is in agreement with the above observation. Roylar A863 has an activation energy of 23.6 kcal/mole, indicating that its melt viscosity is quite sensitive to variation in temperature.



TABLE III  
Activation Energies for Shear Flow of Thermoplastic Elastomers

Polymer	Temperature, °C	Activation energy, <sup>a</sup> kcal/mole
TPR 1900	220	11.34
Roylar A863	180	23.42
Kraton	180	12.49

<sup>a</sup> Determined at constant shear stress of  $6.0 \times 10^5$  dyn/cm<sup>2</sup>.

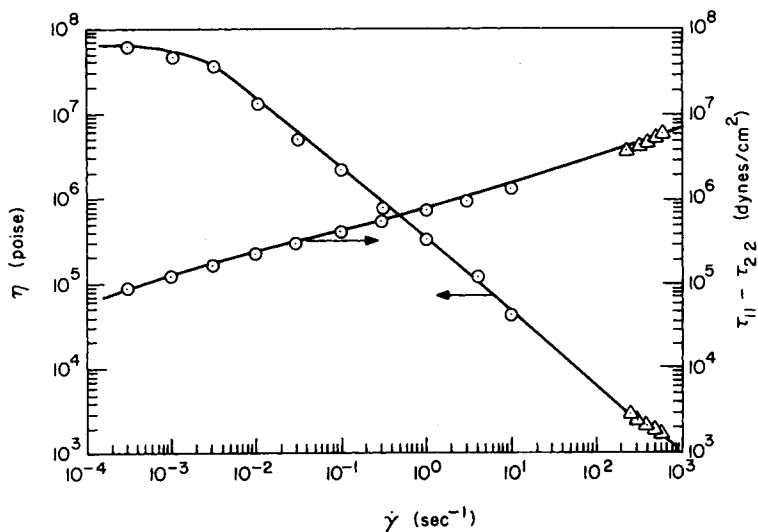


Fig. 8. Viscosity and first normal stress difference vs shear rate for TPR 1900 at 200°C: (○) Weissenberg rheogoniometer data; (Δ) Han slit/capillary rheometer data.

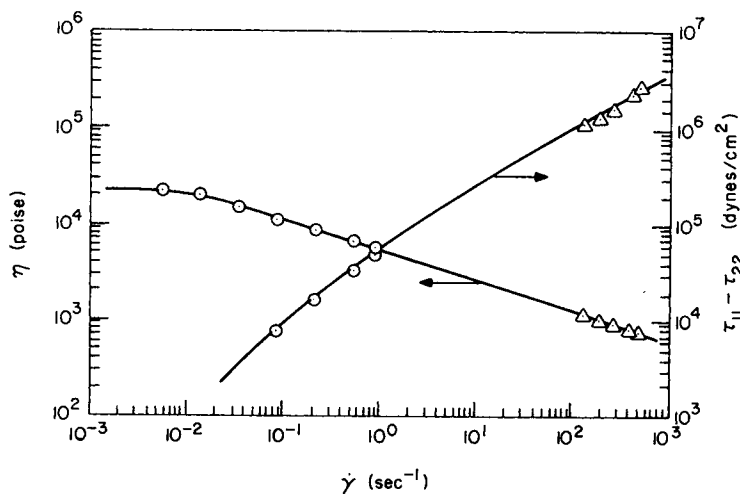


Fig. 9. Viscosity and first normal stress difference vs shear rate for Roylar A863 at 180°C: (○) Weissenberg rheogoniometer data; (Δ) Han slit/capillary rheometer data.

Figures 8 and 9 give plots of  $\eta$  versus shear rate  $\dot{\gamma}$  and  $\tau_{11} - \tau_{22}$  versus shear rate  $\dot{\gamma}$  for TPR 1900 and Roylar A863, respectively. These plots are given to check the consistency of the two different experimental devices, namely, the Han slit/capillary rheometer and the Weissenberg rheogoniometer. It should be pointed out that the use of the Weissenberg rheogoniometer (and all similar rotational-type instruments) is limited to low shear rates (or low shear stresses). Therefore, its usefulness in determining the rheological properties of thermoplastics, for example, at high shear rates (or high shear stresses), is limited. However, the use of the Han slit/capillary rheometer has no such limitation.

As may be seen in Figure 8, the melt elasticity (i.e.,  $\tau_{11} - \tau_{22}$ ) of TPR 1900 increases relatively slowly with shear rate. Comparison of Figures 8 and 9 shows that as the shear rate is increased, the rate of increases in  $\tau_{11} - \tau_{22}$  is much greater for Roylar A863 than for TPR 1900, whereas the shear sensitivity of Roylar A863 is quite low compared to that of TPR 1900. These differences must be explained in terms of the molecular configurations under deformation, and explanation awaits future research.

To summarize, what has been demonstrated above is that the Han slit/capillary rheometer is a unique instrument for determining the rheological properties of thermoplastic elastomers in the range of high shear rates (or high shear stresses) often encountered in various polymer processing operations.

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