Die Extrusion Behavior of Carbon Black-filled Block Copolymer Thermoplastic Elastomers

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SYNOPSIS

The properties of carbon black-filled thermoplastic elastomers were studied. We compared the extrudate swell behavior and the rheological properties of carbon black-filled polymers with those of raw polymers. The shear viscosity increases with increasing amount of carbon black. The extrudate swell becomes smaller with increasing carbon black amount, indicated by the decreased elasticity of the material when adding carbon black. © 1993 John Wiley & Sons, Inc.

1. INTRODUCTION

If a viscoelastic material is forced to flow from a large reservoir through a circular tube, then the diameter of the extrudate is found to be larger than the tube diameter. Many researchers[1-5] have argued that that causes the die swell. They developed the following three points of view for the cause of the die swell: polymer chain orientation within the capillary caused by the high shear field; recovery of the elastic deformation; and viscous heat effects. The most important concept is the recovery of the elastic deformation imposed in the capillary.

Die swell must be considered for the prediction of accurate dimensions of continuous profile end products. Therefore, many studies in this field are related to plastics and rubbers.[6-11] Thermoplastic elastomers have become important commercial materials because of their good processability and high mechanical properties. However, there have been relatively few studies for thermoplastic elastomers because they exhibit complex behavior that com-

bines the elastomeric final product properties with the processing characteristics of thermoplastics.

The rheological behavior of block copolymer thermoplastic elastomers has been reported by Kraus and Rollman[12] with poly(butadiene/styrene/butadiene). Kim and Hyun[13] reported the viscoelastic behavior of SEBS. Recently, the rheological behavior of the styrene block copolymers (SBS, SIS, and SEBS) was studied by Kim and Han.[14]

In this study, we investigated the effect of carbon black on the thermoplastic elastomers SBS (styrene–butadiene–styrene), SIS (styrene–isoprene–styrene), and SEBS (styrene–ethylene/butylene–styrene). We studied both the rheological behavior of the carbon black-filled polymers and die swell phenomena.

2. EXPERIMENTAL

2.1. Materials

The characteristics of the elastomers and carbon black used in this work are summarized in Table I. Three styrene-containing thermoplastic elastomers (SBS, SIS, SEBS, manufactured by Shell Chemicals) were used. Carbon black, N330 (HAF, manufactured by Ashland), was used to prepare compounds with the thermoplastic elastomers.

Table I Materials Used in This Study

Materials	Name (Grade)	Manufacturer	Characteristics
Thermoplastic elastomer	SBS (Kraton 1102)	Shell Chemicals	Styrene/rubber ratio 31/69
	SIS (Kraton 1107)	Shell Chemicals	Styrene/rubber ratio 14/86
	SEBS (Kraton G1657)	Shell Chemicals	Styrene/rubber ratio 13/87
Carbon black	N-330 (HAF)	Ashland	Iodine adsorption 81.9 (mg/g)
			DBP absorption 101.3 (mL/100 g)

2.2. Procedure

(a) Compound Preparation

The thermoplastic elastomers were compounded with 0.1 and 0.2 volume loading of N330 carbon black, respectively, in a Haake Buchler Rheocord 750 laboratory mixer. The mixing temperature was maintained at 120°C and materials were prepared at a fill factor of 0.8. After mixing, the compound was carefully remilled into flat sheets on a two-roll mill.

(b) Measurement of Rheological Properties

Rheological behaviors of pure thermoplastic elastomers and black-filled compounds were measured in a Monsanto Processability Tester (MPT), which covers the shear rate range of 10^0 to 10^3 s^{-1}. Capillary dies (1 mm diameter) with different L/D ratios of 5, 10, and 20 were used.

(c) Extrudate Character Measurement

The investigation of extrudate swell and shape was also carried out using an MPT. At 100°C, compounds were extruded through capillary dies at a series of fixed shear rates. When the steady state was reached for a selected shear rate, the extrudate was cut and allowed to relax. The diameter of the extrudate was measured using a microscope (Gaertner Scientific Co., Model BC21).

3. RESULTS AND DISCUSSION

3.1. Rheology

The investigation of the rheological behavior of the materials is important to understand the processability. In this study, we used three styrene copolymers: SBS, SIS, and SEBS. These materials are considered to be thermoplastic elastomers as they combine the hard and soft segments of molecules in the microstructure shown in Figure 1.

The polystyrene domains (hard segment), which are chemically bound to rubbery segments, function as physical cross-links. This study concentrated on the effect of carbon black on the characteristics of the thermoplastic elastomers. Figure 2 shows the shear viscosity behavior of three copolymers. The figure also shows the shear thinning behavior of polymers. In the case of carbon black-filled polymers, the slopes are more sharply increased than
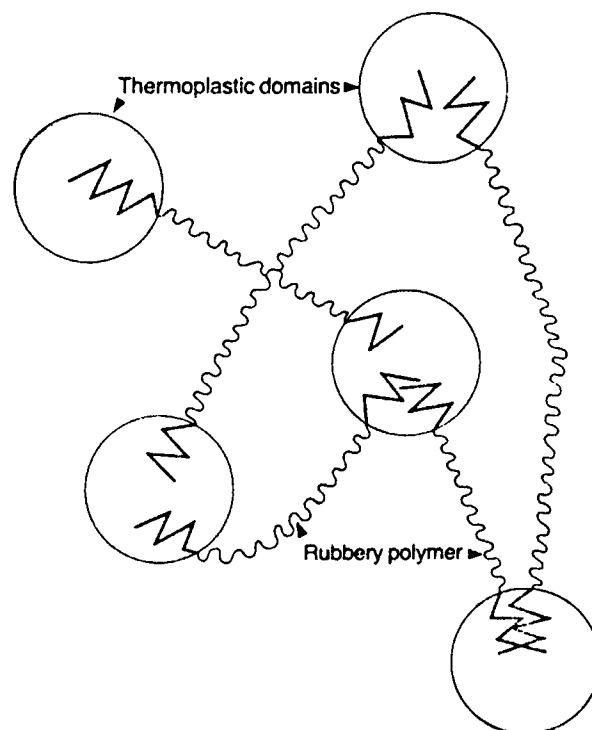

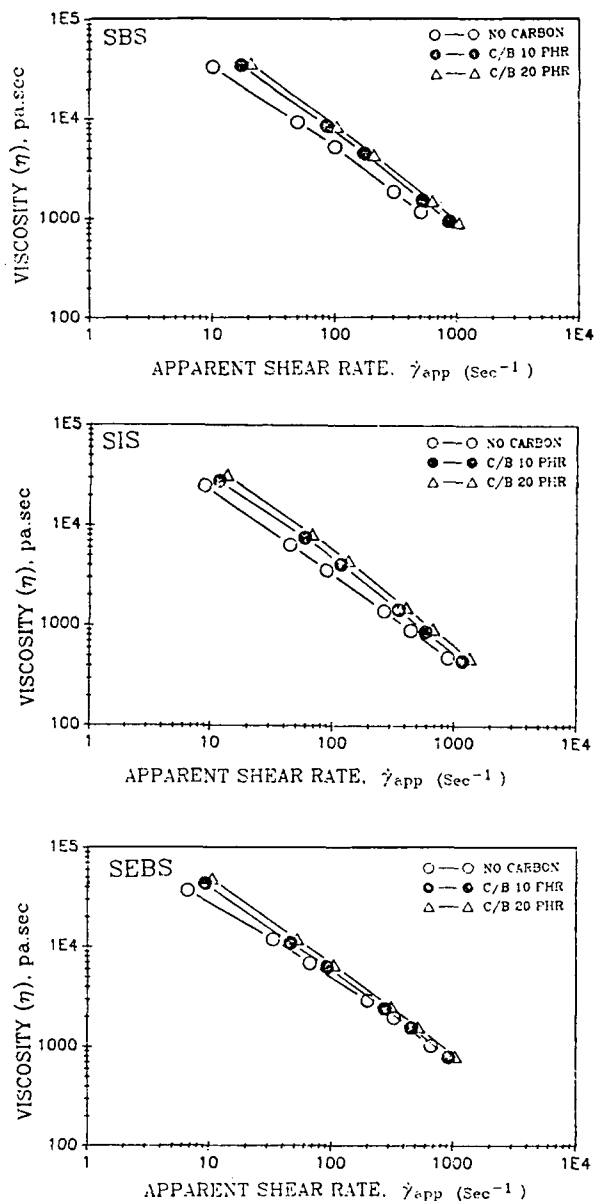**Figure 1** Phase structure of thermoplastic elastomers.

Figure 2 Rheological behavior of styrene copolymers.

ΔP_{cap}, added to the pressure loss at the entrance to the capillary, ΔP_{ent}, with the assumption of neglecting the exit pressure loss. Mathematically,

$$\Delta P = \Delta P_{cap} + \Delta P_{ent} \qquad (1)$$

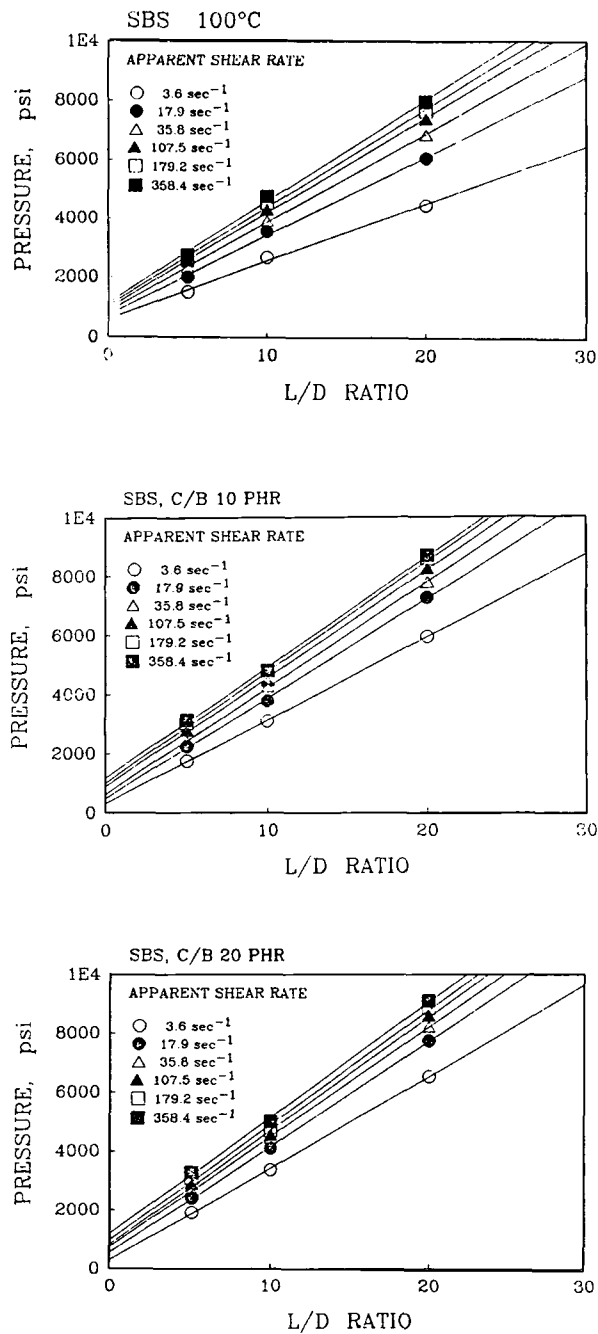The rheological property responsible for the en-

are those of the raw polymers. The viscosity of SEBS is slightly higher than that of the other polymers.

The additions of carbon black to the raw polymers are induced to increase the viscosity. The reason is that the carbon black particles within the polymer increase the fluid friction.

We now consider the entrance effects of converging flow when the fluid is moving from a large diameter reservoir into a small diameter tube. The researchers[15-18] observed the occurrence of extra pressure drops in the entrance region. The total pressure loss, ΔP, is the pressure loss in the capillary,

Figure 3 Total pressure drop vs. L/D ratio at various shear rates for SBS.
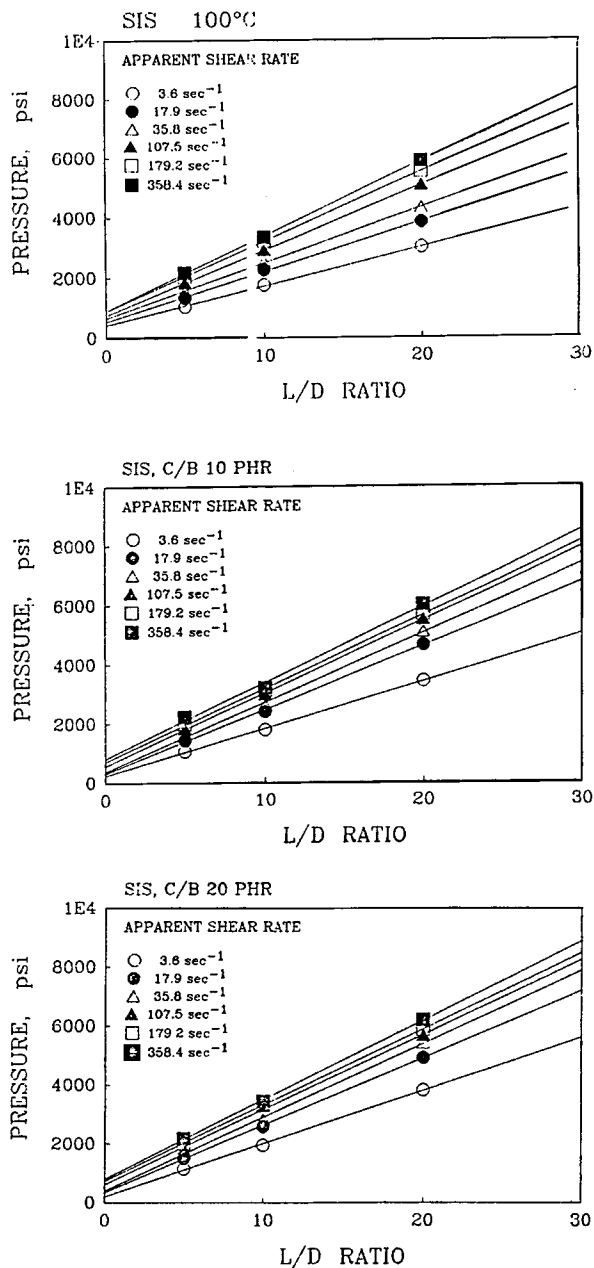
Figure 4   Total pressure drop vs. L/D ratio at various shear rates for SIS.

trance pressure drop has been argued to be melt elasticity[19]:

$$\Delta P_{ent} \cong \Delta P_{elastic} \qquad (2)$$

Bagley[20] considered that the large pressure drop at the entrance of a die may be thought of as occurring in an imaginary extension to the actual tube length. The Bagley plots are shown in Figure 3, 4,

and 5. We can determine the value of the entrance pressure drop from these figures.

The pressure losses are frequently represented in terms of a multiple of the dieland shear stress, σ_w:

$$\Delta P_{ent} = m\sigma w \qquad (3)$$

where m is called the Couette correction.
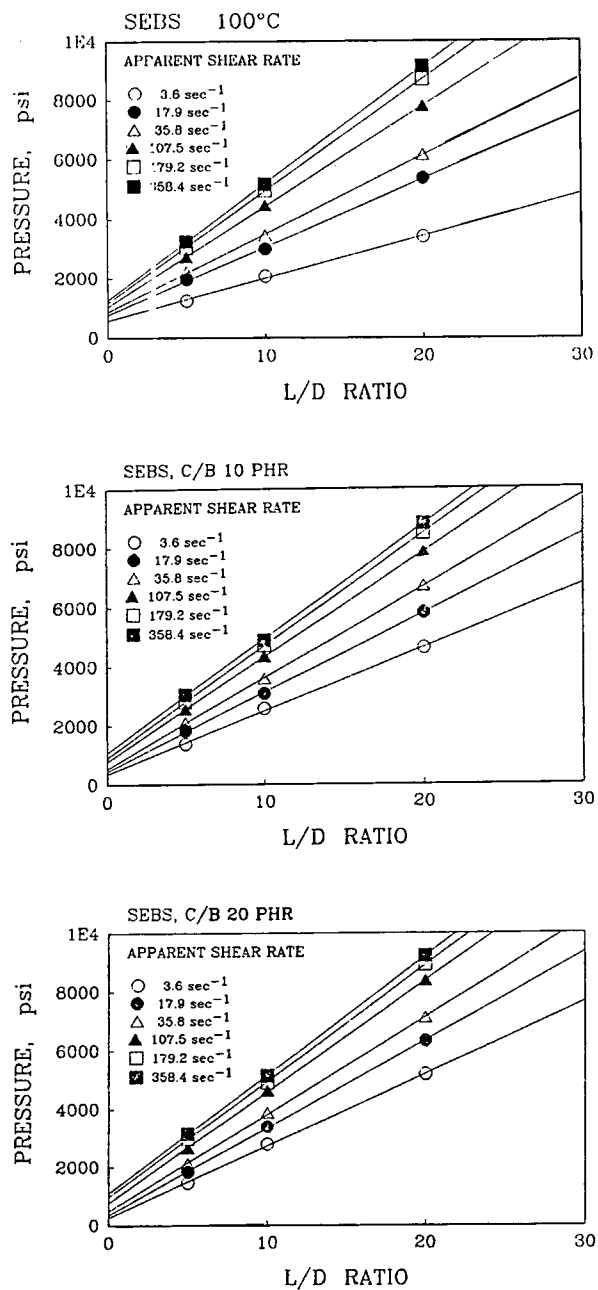
Figure 5   Total pressure drop vs. L/D ratio at various shear rates for SEBS.

The values of Couette correction for the three thermoplastic elastomers are shown in Figure 6. The results indicated that the Couette correction is decreased with adding carbon black. Therefore, it appears that the carbon black-filled polymers have less elasticity than that of the raw polymers.

3.2. Die Swell

Die swell behavior has been argued among many researchers. Today, it is generally agreed that die swell behavior is typical of viscoelastic materials. Especially, this behavior relates to their elastic properties. We photographed three thermoplastic elastomers at various die lengths and shear rates. Figure 7-9 show the extrudate distortion with various black loading at a fixed die length ($L/D = 10$).

From the photographs, we observed that more severe distortion occurs at higher shear rates. However, rough surface of extrudates at 4 s^{-1} shear rate were observed. Extrudate distortion was also more severe at lower black loading. When the die length is varied, different die swell behavior is generally observed. Figures 10-12 show the effect of die lengths. The distortion of extrudates decreased with increasing L/D ratios.

We measured the swell ratio at various shear rates and die lengths. Here, die swell ratio is defined by the ratio of the extrudate diameter, d, to the capillary diameter, D. Figure 13 shows the die swell ratio vs. shear rate, extruded in a capillary with an L/D ratio of 10. This result indicates that the carbon black-filled polymers swell less than do the raw polymers. We also know that the swell ratio increases with increasing shear rate. The effect of the die length on the die swell is shown in Figure 14. From this figure, we see the lower value of the swell ratio at longer die lengths.

4. CONCLUSION

Shear viscosity–shear rate behavior, extrudate swell, and Couette correction, which is related to the elastic property of polymeric materials of carbon black-filled styrene copolymer, were compared to those of nonfilled pure polymers to study the rheological characteristics of thermoplastic elastomers.

Styrene copolymers exhibited shear thinning behavior, and the shear viscosity was increased by the addition of carbon black because of the higher fluid friction. SEBS showed a little higher viscosity due to its unique microstructure. When carbon black was
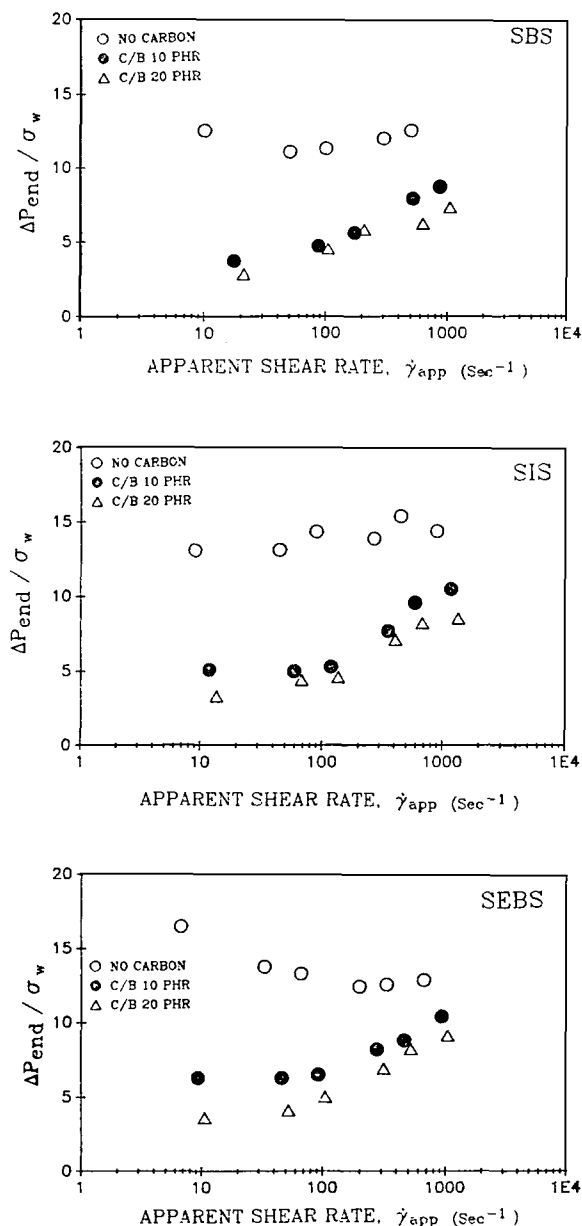

Figure 6 Couette coefficient vs. shear rate for styrene copolymers.

added, the Couette correction was decreased. This indicates that the elasticity of styrene copolymers is decreased by the loading of black.

The die cross section and extrusion rate were found to have an effect on the extrudate characteristics of styrene-containing thermoplastic elastomers. Swell and extrudate distortion decreased with increasing die length and decreasing extrusion rate. Carbon black suppressed the die swell and extrudate distortion of the styrene copolymers.
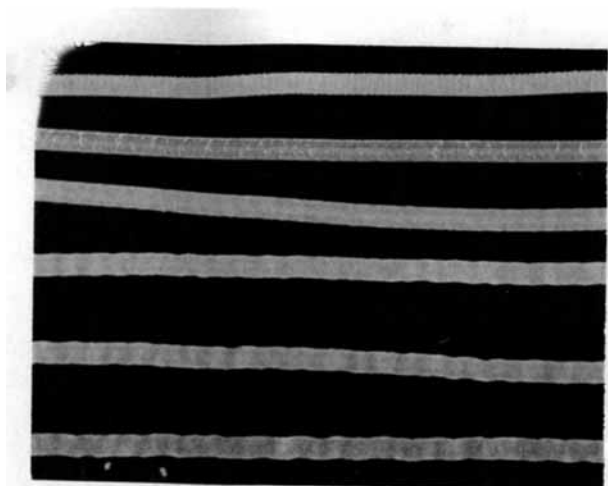
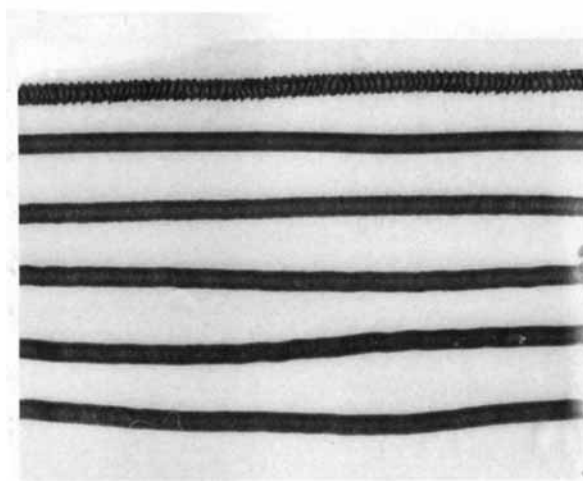**Figure 7**   Extrudate distortion of SBS ($L/D = 10$).

Shear rate
(sec^{-1})

4

18   NO CARBON

36

108

180

360

4

18   C/B 10PHR
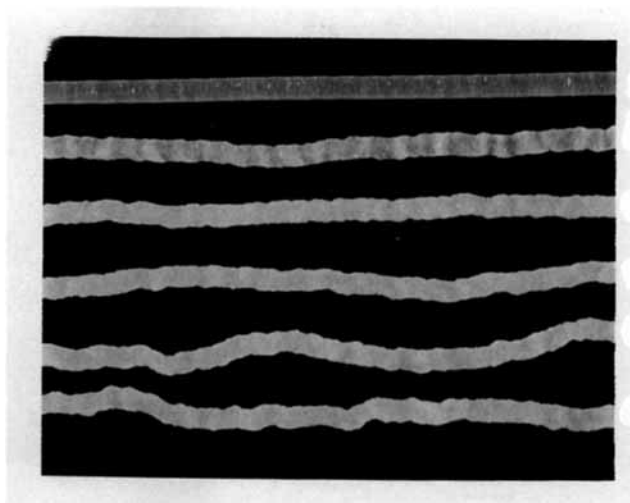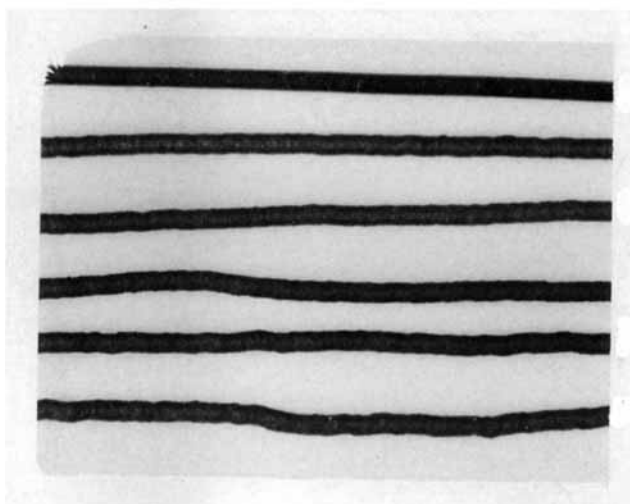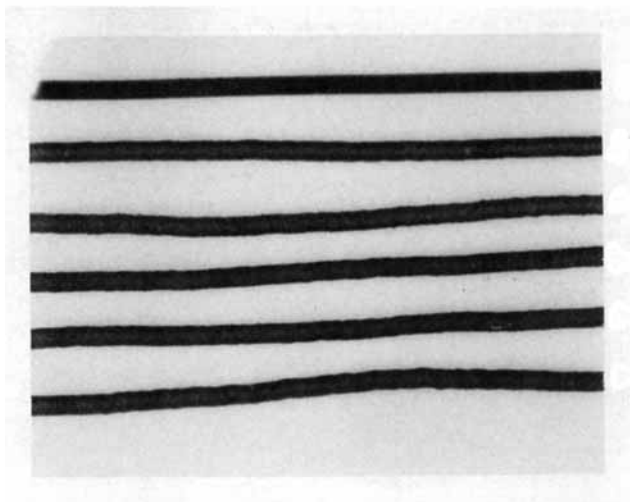
36

108

180

360

4

18   C/B 20PHR

36

108

180

360

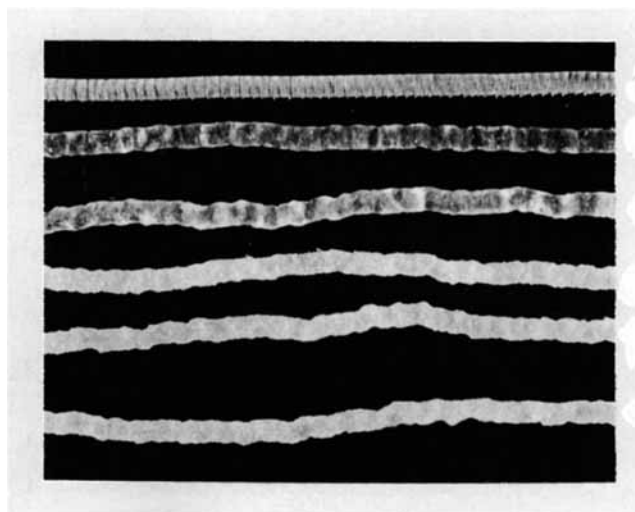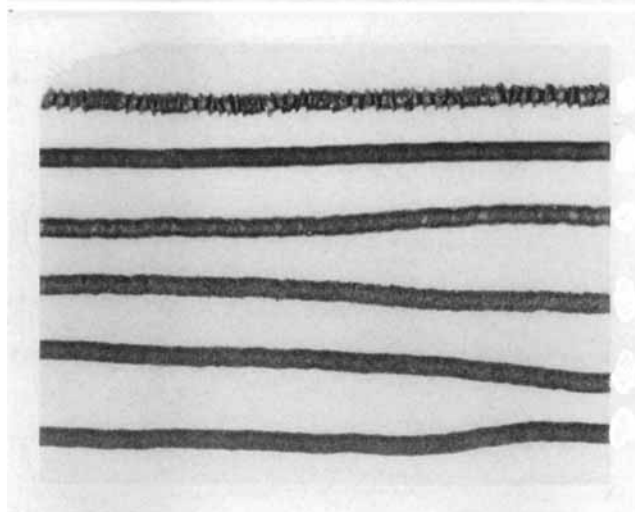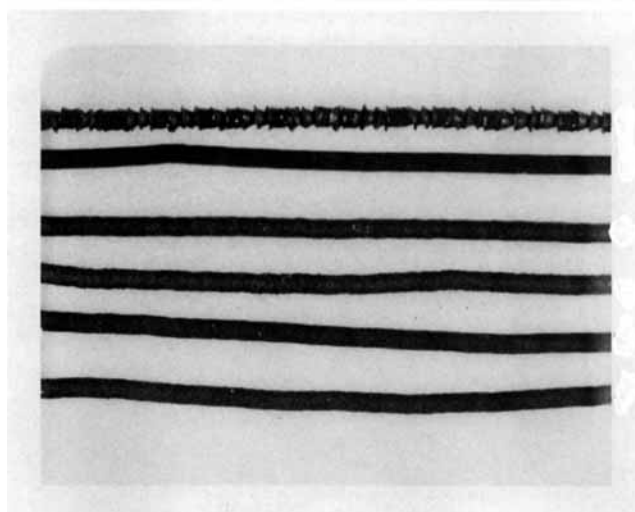**Figure 8**   Extrudate distortion of SIS ($L/D = 10$).

Shear rate
(sec^{-1})

4

18

36

108

180

360

NO CARBON

4

18

36

108

180

360

C/B 10PHR

4

18

36

108
180

360

C/B 20PHR

Figure 9   Extrudate distortion of SEBS (L/D = 10).

Shear rate
(sec^{-1})

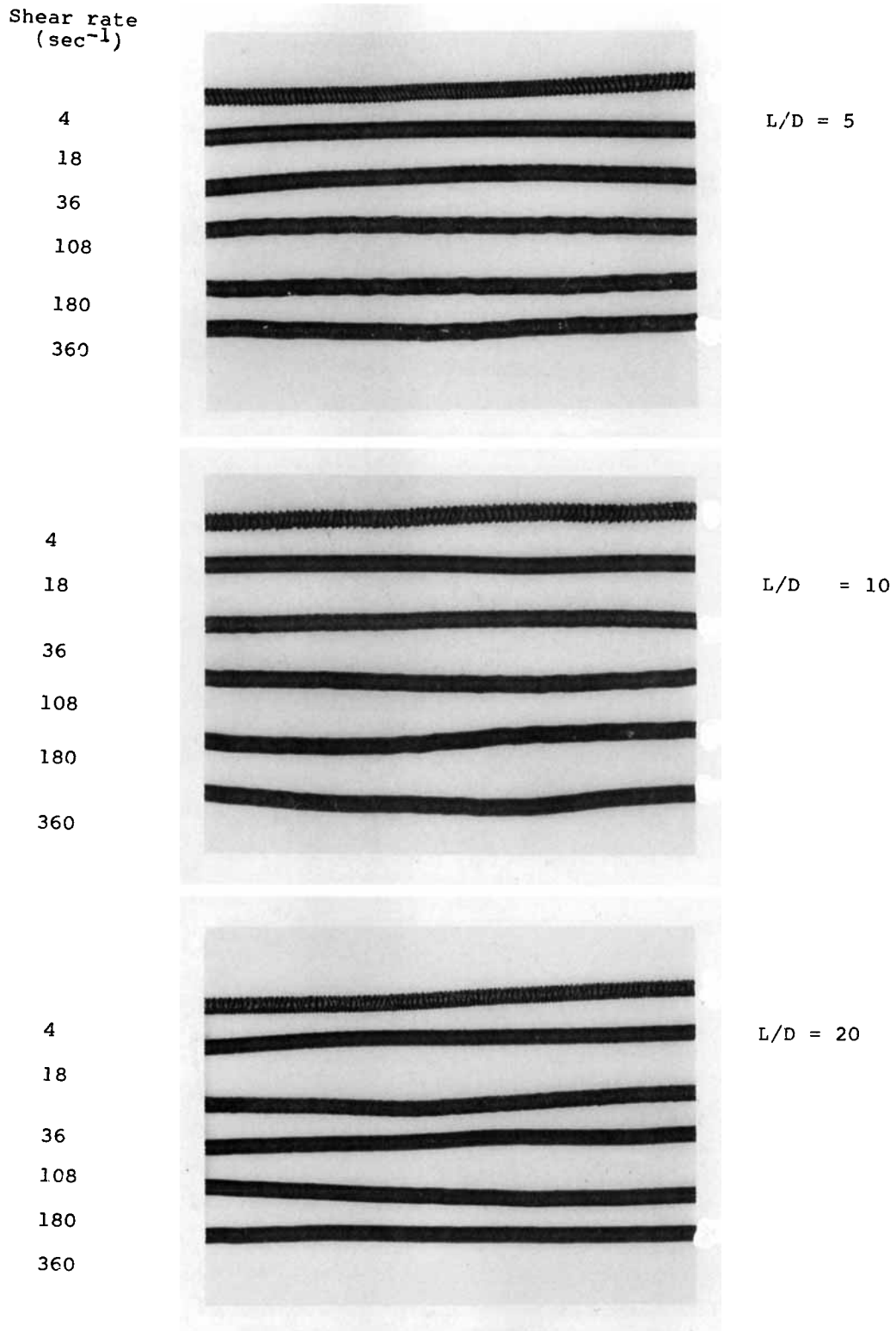Figure 10   Extrudate distortion of carbon black-filled SBS (C/B = 10 phr).

Figure 11   Extrudate distortion of carbon black-filled SIS (C/B = 10 phr).
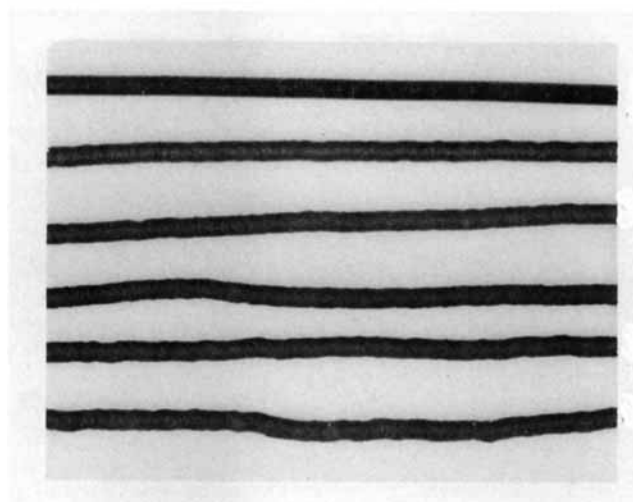
Shear rate
(sec^{-1})

4
18
36

108
180

360
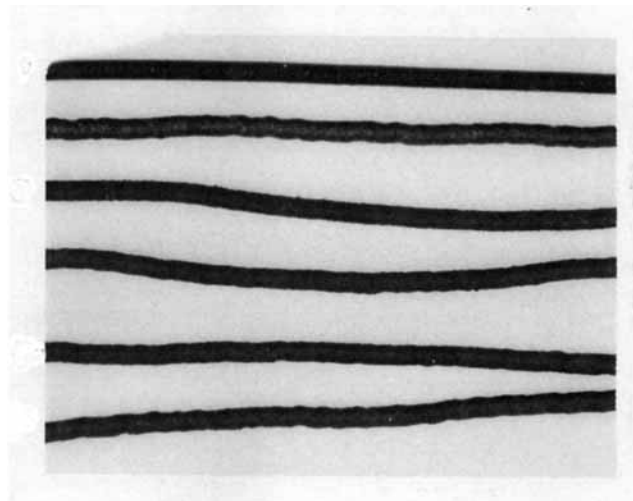
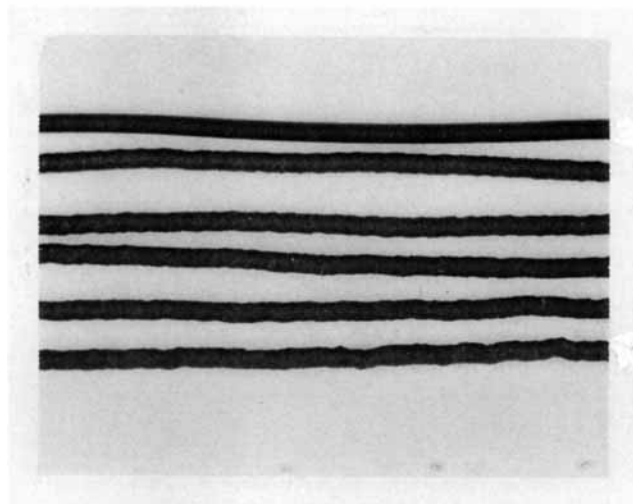L/D = 5

4
18

36

108

180

360

L/D = 10

4
18
36
108

180

360

L/D = 20

Figure 12   Extrudate distortion of carbon black-filled SEBS (C/B = 10 phr).
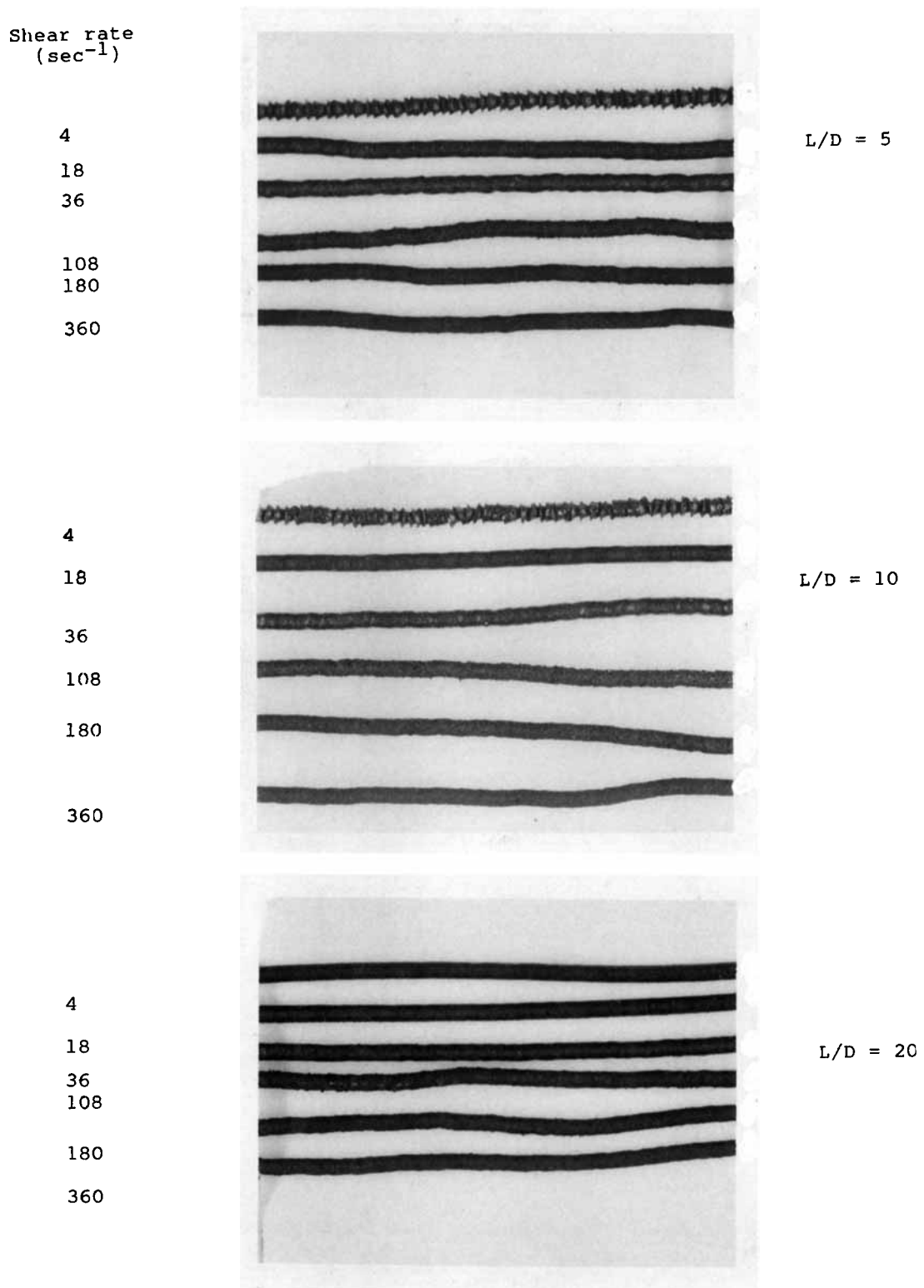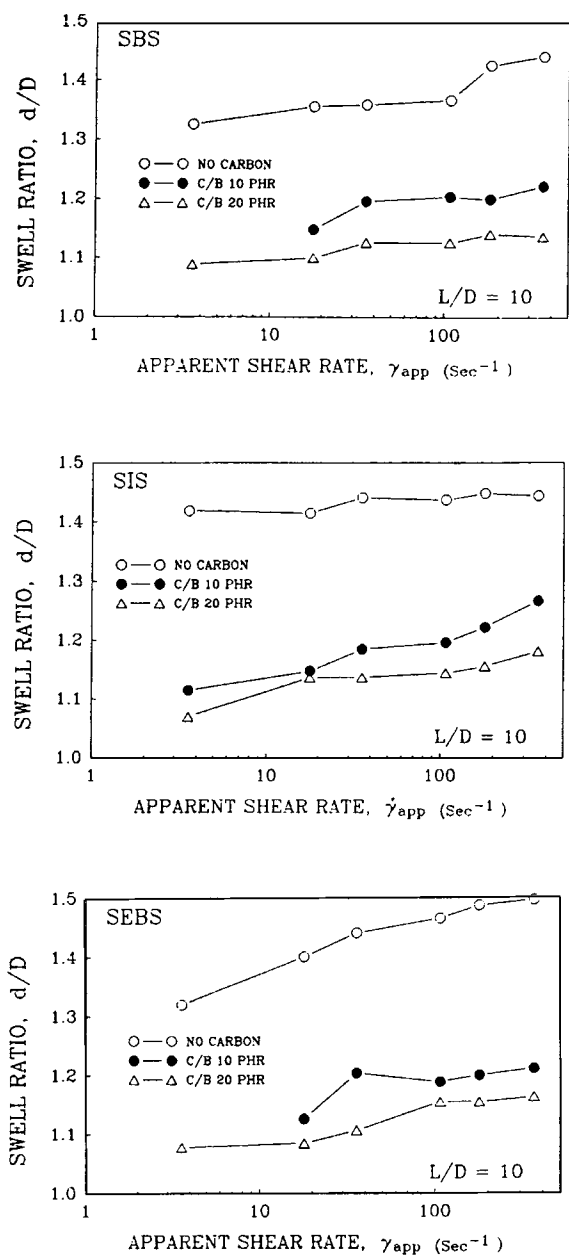
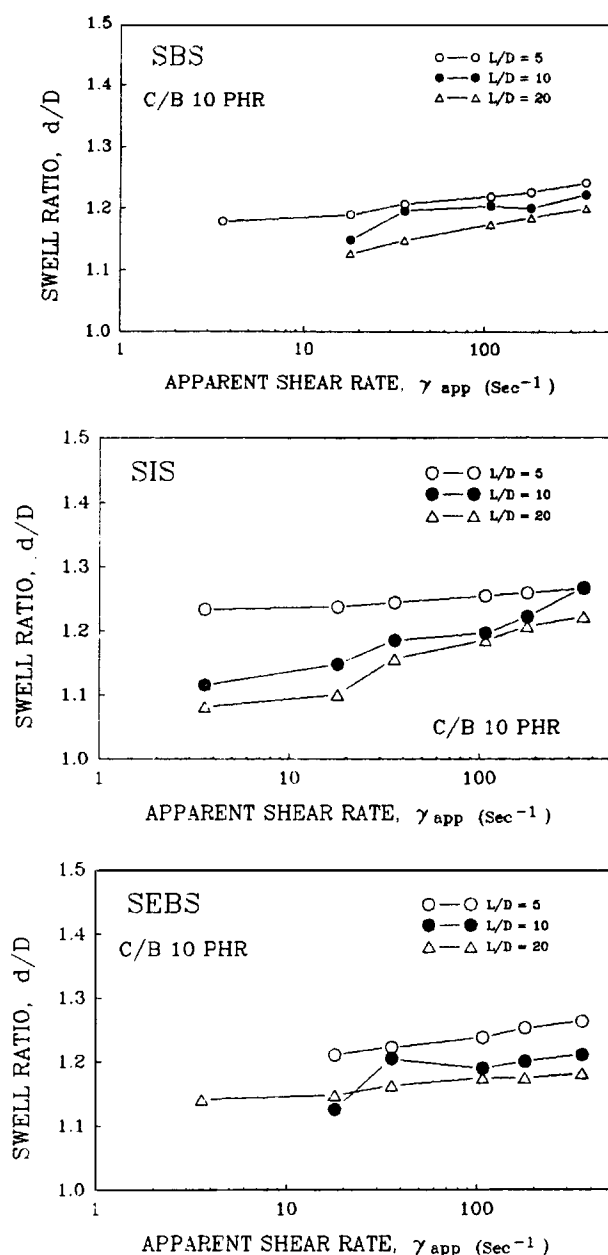**Figure 13** Die swell ratio vs. shear rate for styrene copolymers.

Figure 14 Die swell ratio vs. shear rate at various L/D ratios for styrene copolymers.

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