

Rheological Behavior of Short Carbon Fiber-Filled Thermoplastic Elastomer Based on Styrene–Isoprene–Styrene Block Copolymer

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SYNOPSIS

The rheological behavior of styrene–isoprene–styrene block copolymer filled with short carbon fibers has been studied with the Monsanto Processability Tester (MPT). Carbon fibers of 6 mm length were used in the range of 0–20 phr. The rheological studies were carried out in the temperature range of 150–180°C and the shear rate range of 50.6–401.2 s^{-1} using three different capillaries with varying L/D ratio. The die swell was automatically recorded using a laser scanning system attached to the MPT. The results show that the composites behave as pseudoplastic materials and follow the power-law model. The shear viscosity of the composites decreases up to 10 phr fiber loading and then either increases or remains constant with further increase of fiber concentration. The die swell decreases with increase of fiber loading and L/D ratio of the capillary. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Short carbon fiber-reinforced thermoplastic elastomers are important engineering materials because of their improved mechanical properties and easy processability in conventional polymer processing machinery. The choice of suitable processing conditions in various processing equipment is guided mainly by the rheological behavior of the composites. A number of investigations on the rheological behavior of short fiber-reinforced thermoplastics and elastomers have been reported in the last few decades.^{1–6} However, thermoplastic elastomers reinforced with short fibers have been studied only scantily.^{7,8} Crowson et al.^{1,2} reported extensively on the flow behavior of short glass fiber-reinforced thermoplastics during injection molding. They showed that converging flow produces a high alignment of fibers, whereas diverging flow causes a 90° rotation of previously aligned fibers. They also reported that the composite viscosity is considerably influenced by fiber loading and fiber length at lower

shear rates than at higher shear rates. Melt rheology of polymers containing carbon fibers and glass fibers has been studied by Kitano and co-workers⁹ and Chen and co-workers,¹⁰ respectively. Gupta and co-workers¹¹ reported that both melt viscosity and elasticity increase with fiber loading in the short glass fiber-reinforced polypropylene–EPDM blends.

In our earlier communication,⁷ we presented the results of rheological properties of short carbon fiber-filled thermoplastic elastomer based on NR–HDPE blends. In the present investigation, the rheological behavior of short carbon fiber-reinforced styrene–isoprene–styrene (S–I–S) block copolymer is reported. The effects of temperature, fiber concentration, and length-to-diameter ratios of the die on the melt flow behavior of the composites is investigated.

EXPERIMENTAL

Styrene–Isoprene–Styrene Block Copolymer (S–I–S)

Kraton D-1107 with specific gravity of 0.92 and styrene–rubber ratio of 14/86 was obtained from Shell Development Co., U.S.A.

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Table I The Values of Power-law Constants Derived from Apparent Shear Stress and Apparent Shear Rate Data

Temperature	Sample No.	<i>L/D</i> Ratio					
		20 : 1		10 : 1		1 : 1	
		<i>n</i>	<i>k</i>	<i>n</i>	<i>k</i>	<i>n</i>	<i>k</i>
150°C	<i>S</i> ₀	0.27	1.72	0.28	1.69	0.36	1.81
	<i>S</i> ₅	0.29	1.64	0.30	1.63	0.39	1.80
	<i>S</i> ₁₀	0.30	1.60	0.32	1.58	0.42	1.79
	<i>S</i> ₂₀	0.32	1.55	0.34	1.52	0.39	1.93
165°C	<i>S</i> ₀	0.29	1.58	0.30	1.56	0.38	1.66
	<i>S</i> ₅	0.34	1.42	0.33	1.49	0.38	1.74
	<i>S</i> ₁₀	0.30	1.45	0.36	1.38	0.45	1.58
	<i>S</i> ₂₀	0.32	1.46	0.33	1.47	0.44	1.69
180°C	<i>S</i> ₀	0.35	1.36	0.35	1.36	0.50	1.30
	<i>S</i> ₅	0.38	1.26	0.39	1.27	0.55	1.25
	<i>S</i> ₁₀	0.40	1.17	0.41	1.18	0.49	1.41
	<i>S</i> ₂₀	0.40	1.17	0.39	1.24	0.52	1.31

Carbon Fiber

Grade RK-30 carbon fibers were obtained from RK Carbon Fibres Ltd., U.K. The fiber has the following

characteristics: epoxy-treated; density, 1.78 gm/cc; tensile strength, 3.0 GPa; tensile modulus, 220–240 GPa; and carbon content, 95% mass.

Table II The Values of Power-law Constants Derived from True Shear Stress and True Shear Rate Data

Temperature	Sample No.	<i>L/D</i> Ratio					
		20 : 1		10 : 1		1 : 1	
		<i>n</i>	<i>k</i>	<i>n</i>	<i>k</i>	<i>n</i>	<i>k</i>
Average Value of <i>n</i> = 0.27; Average Value of <i>k</i> = 1.59; % Deviation in <i>n</i> = ±10; % Deviation in <i>k</i> = ±9.0							
150°C	<i>S</i> ₀	0.27	1.63	0.27	1.64	0.25	1.73
	<i>S</i> ₅	0.27	1.59	0.25	1.62	0.27	1.65
	<i>S</i> ₁₀	0.27	1.56	0.28	1.54	0.27	1.61
	<i>S</i> ₂₀	0.30	1.48	0.31	1.44	0.28	1.57
Average Value of <i>n</i> = 0.30; Average Value of <i>k</i> = 1.41; % Deviation in <i>n</i> = ±15; % Deviation in <i>k</i> = ±11.0							
165°C	<i>S</i> ₀	0.28	1.52	0.28	1.54	0.26	1.58
	<i>S</i> ₅	0.33	1.33	0.32	1.37	0.35	1.27
	<i>S</i> ₁₀	0.28	1.41	0.30	1.37	0.34	1.41
	<i>S</i> ₂₀	0.31	1.39	0.29	1.40	0.31	1.44
Average Value of <i>n</i> = 0.37; Average Value of <i>k</i> = 1.19; % Deviation in <i>n</i> = ±11; % Deviation in <i>k</i> = ±11.0							
180°C	<i>S</i> ₀	0.34	1.32	0.35	1.29	0.36	1.30
	<i>S</i> ₅	0.36	1.22	0.35	1.24	0.37	1.22
	<i>S</i> ₁₀	0.36	1.11	0.39	1.10	0.38	1.16
	<i>S</i> ₂₀	0.39	1.12	0.37	1.16	0.42	1.06

Preparation of the Composite

The composites were prepared in a Brabender Plasticorder (Model PLE-330), using a cam-type rotor, with a speed of 50 rpm and the mixer chamber temperature of 150°C. Initially, the S-I-S was melted in the mixer for 2 min and then chopped carbon fibers (6 mm in length) were added to it and mixed for another 3 min. The mix was then taken out and sheeted through a laboratory mill with a nip setting of 2 mm. The sheeted material was remixed in the plasticorder under similar conditions for 2 min to ensure uniform dispersion of the fibers and homogeneity of the blend and, finally, sheeted out through the two-roll mill. The sheeted-out stock was compression-molded between aluminum foils in an automatic Toyoseiki Labo-press at 170°C for 3 min. At the end of the molding time, the sample still under compression was cooled by circulating water at room temperature through the platens. Aluminum foils

were used between the mold surface to reduce shrink marks on the sheet. The measurements were carried out with 0, 5, 10, and 20 phr of fibers and the corresponding samples were designated as S_0 , S_5 , S_{10} , and S_{20} , respectively.

Measurement of Rheological Properties

Rheological measurements of gum and filled systems were carried out by using the Monsanto Processability Tester (MPT).¹² Testing was conducted with circular dies having a 1.50 mm diameter and length-to-diameter (L/D) ratios of 20, 10, and 1 (for calculating Bagley's correction), at four different apparent wall shear rates (50.6, 101.2, 202.4, and 401.2 s^{-1}) and three temperatures (150, 165, and 180°C). The extrusion chamber was kept at 120°C to avoid sudden cooling of the extrudate. Shear rates were calculated from the piston speed and dimensions of

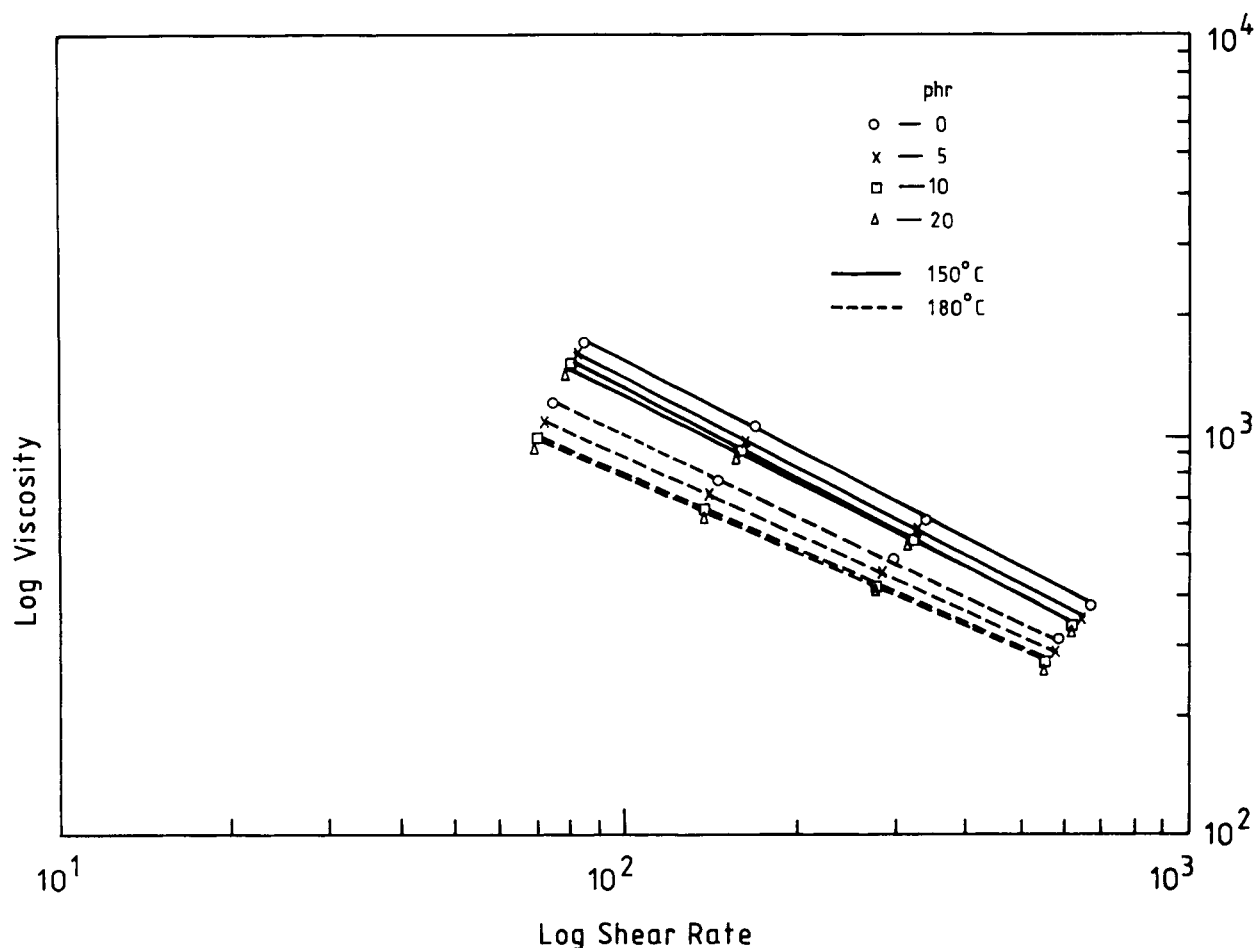


Figure 1 Variation of viscosity with shear rate for the S-I-S carbon fiber composites at 150 and 180°C using the capillary of the L/D ratio equal to 20 : 1.

the barrel and capillary. The running die swell (the die swell at the exit of die as soon as the extrudate comes out) data were directly recorded with the laser scanning system. The detailed procedure of measurements by using the MPT has been described elsewhere.^{13,14}

RESULTS AND DISCUSSION

The apparent wall shear stress τ_{wa} and shear rate $\dot{\gamma}_{wa}$ values were calculated from the direct measurements using standard relations.¹⁵ True wall shear stress τ_w and true wall shear rate $\dot{\gamma}_w$ were obtained

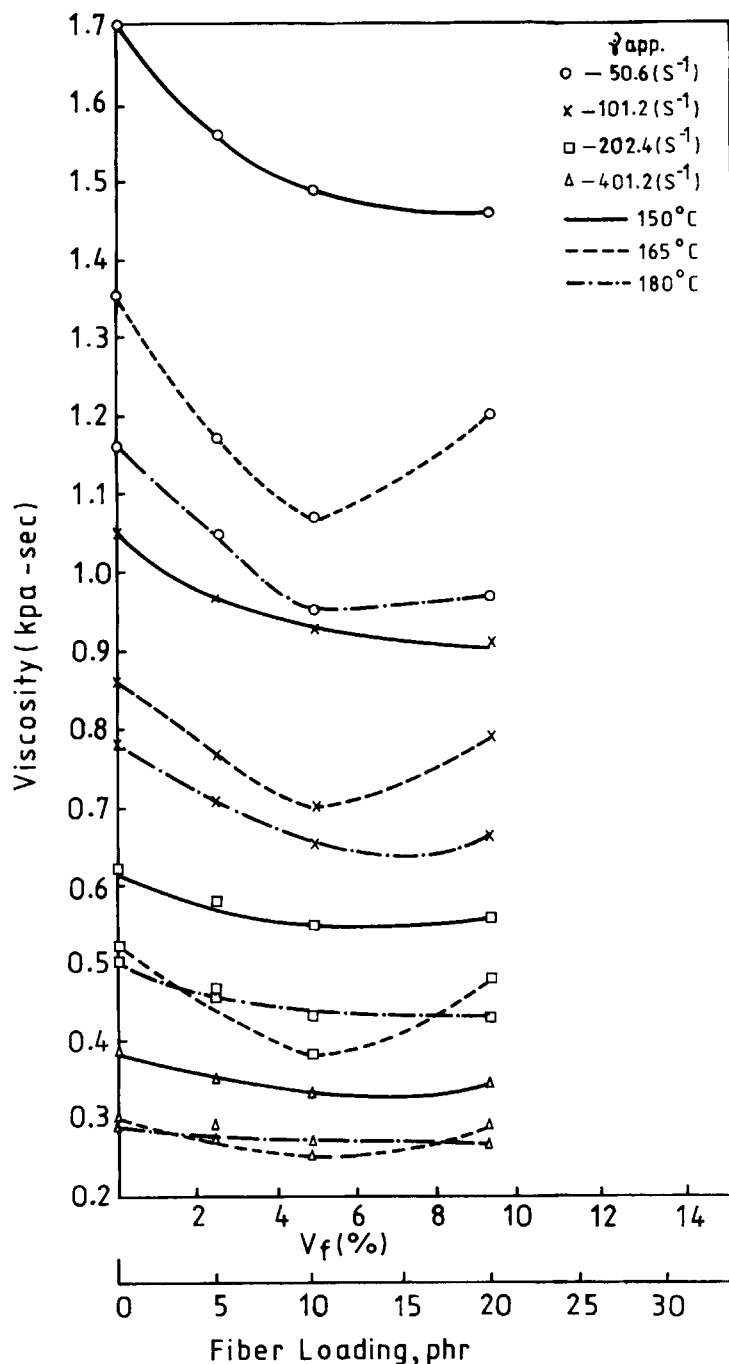


Figure 2 Variation of viscosity with fiber loading at different temperatures and rates of shear. L/D of capillary equal to 20 : 1.

by applying Bagley's correction¹⁶ to τ_{wa} and Rabinowitsch¹⁷ correction to $\dot{\gamma}_{wa}$, respectively. All the systems investigated have been found to obey the power-law relationship in the measured shear rate range:

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

with $n < 1$ indicating the pseudoplastic behavior of the melts. The values of the power-law constants n and k based on τ_{wa} and $\dot{\gamma}_{wa}$ are given in Table I and those based on τ_w and $\dot{\gamma}_w$ are tabulated in Table II. It can be seen from the tables that the n and k values based on apparent shear stress and shear rates vary with fiber loading and the L/D ratio of the capillary used. However, the true shear stress and shear rates for different systems and L/D ratios more or less superimpose, giving almost constant values of these parameters, as shown in Table II. At a particular temperature, the values of n and k give about a $\pm 10\%$ deviation. However, with the increase of temperature, n increases and k decreases.

The melt viscosity of the composites was calculated from the following equation:

$$\eta = \tau_w / \dot{\gamma}_w \quad (2)$$

Figure 1 represents the plot of log viscosity against log shear rate of the composites and unfilled system at two different temperatures (150 and 180°C) and an L/D ratio of 20 : 1. It is evident from the figure that viscosity decreases with shear rate, temperature, and also fiber loading at both the temperatures studied. The reasons for the variations of viscosity with shear rate and temperature are well established; however, its reduction with fiber loading is somewhat unusual.

Figure 2 shows the plot of viscosity against fiber loading at different temperatures and shear rates. It is interesting to note that the viscosity initially decreases with fiber concentration and then either remains constant or increases, giving a minimum value at around 10 phr ($\vartheta_f = 0.05$) fiber loading. The minima in viscosity is especially prominent at 165°C. The incorporation of the fibers in the rubber matrix introduces two opposing effects, i.e., (i) increased fiber-rubber interaction that increases the viscosity and (ii) increased wall slip¹⁸⁻²⁰ due to the presence of longitudinally oriented fibers along the

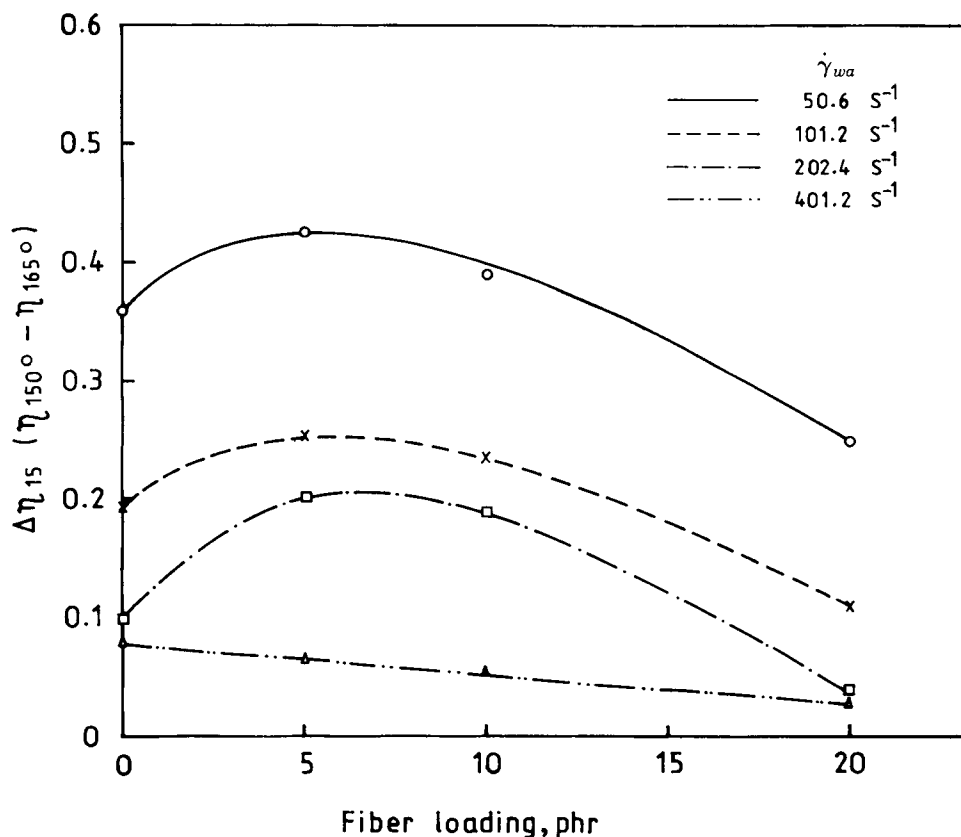


Figure 3 Plot of difference of viscosity ($\Delta\eta_{15}$) with fiber loading at different shear rates.

Table III Values of Coefficients K_1 and K_2 of Eq. (3) at Different Temperatures and Shear Rates

Apparent Shear Rate	150°C		165°C		180°C	
	K_1	K_2	K_1	K_2	K_1	K_2
50.6	-3.94	25.4	-7.57	69.15	-5.5	38.8
101.2	-3.58	22.5	-6.85	63.5	-5.1	36.0
202.4	-3.38	24.4	-10.7	105.7	-4.2	28.9
401.2	-4.20	32.25	-5.6	53.4	-2.1	14.5

wall-melt interphase, which decreases the viscosity. At low fiber concentration (< 10 phr), the effect of fiber orientation is predominant over the fiber-melt interaction, giving a reduction in viscosity. As the fiber loading is increased beyond the 10 phr level, these two effects either balance each other (at lower temperature of 150°C), giving constant viscosity, or conversely (at higher temperatures), causing the viscosity to increase.

For the same increase in temperature ΔT (165–150°C) of the system, the corresponding decrease $\Delta\eta_{15}$ ($\eta_{150} - \eta_{165}$) in the viscosity is a function of ap-

parent rate of shear and fiber loading (Fig. 3). At lower $\dot{\gamma}_{wa}$ values, $\Delta\eta_{15}$ initially increases with fiber loading, possibly due to the increased wall slip because of favorable fiber orientation, and then decreases because of increased fiber-rubber interaction. At a higher rate of shear, however, $\Delta\eta_{15}$ marginally decreases with fiber loading. A further increase in temperature (from 165 to 180°C) gave much smaller values of $\Delta\eta_{15}$ (Fig. 2), at all values of $\dot{\gamma}_{wa}$ and fiber loading.

The variation of relative viscosity with fiber loading at different temperatures and rates of shear

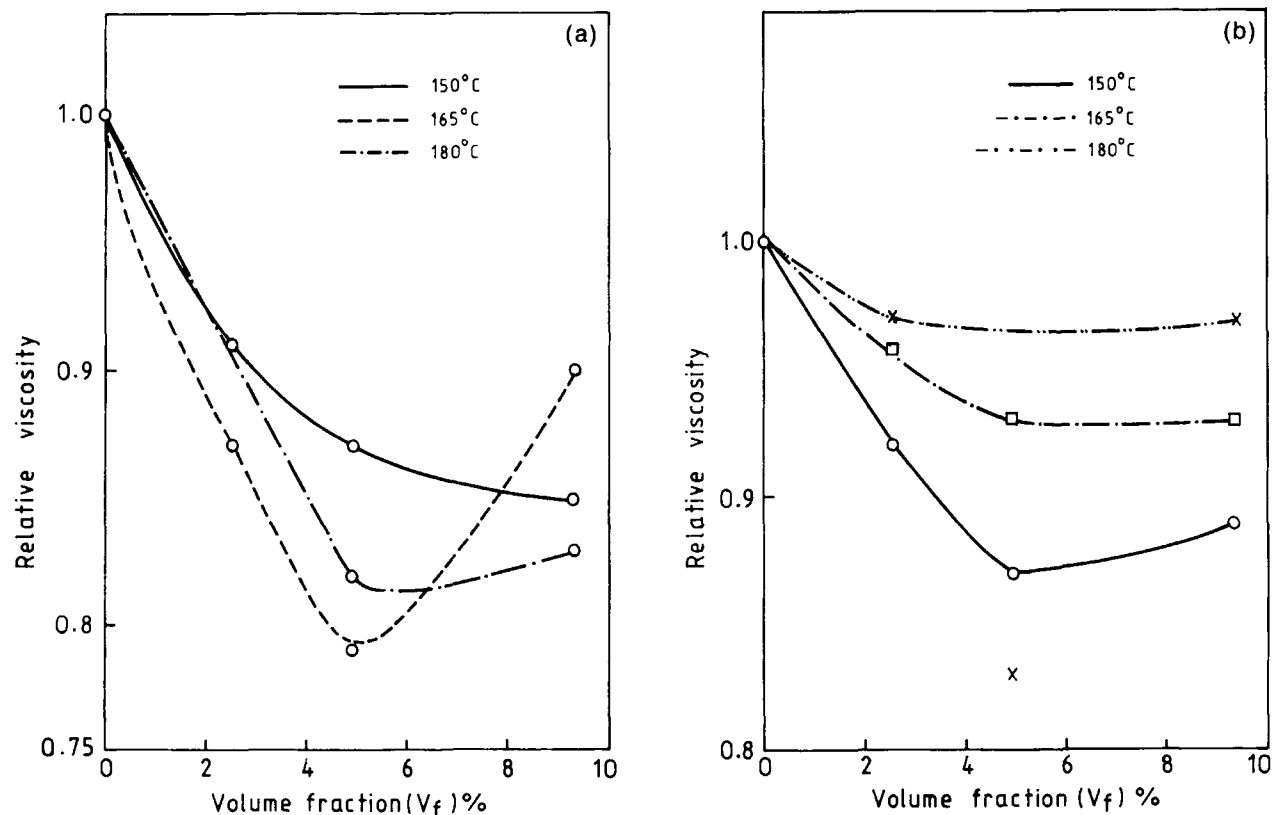


Figure 4 Plot of relative viscosity with volume fraction of fiber at (a) 50.6 s^{-1} and (b) 401.2 s^{-1} .

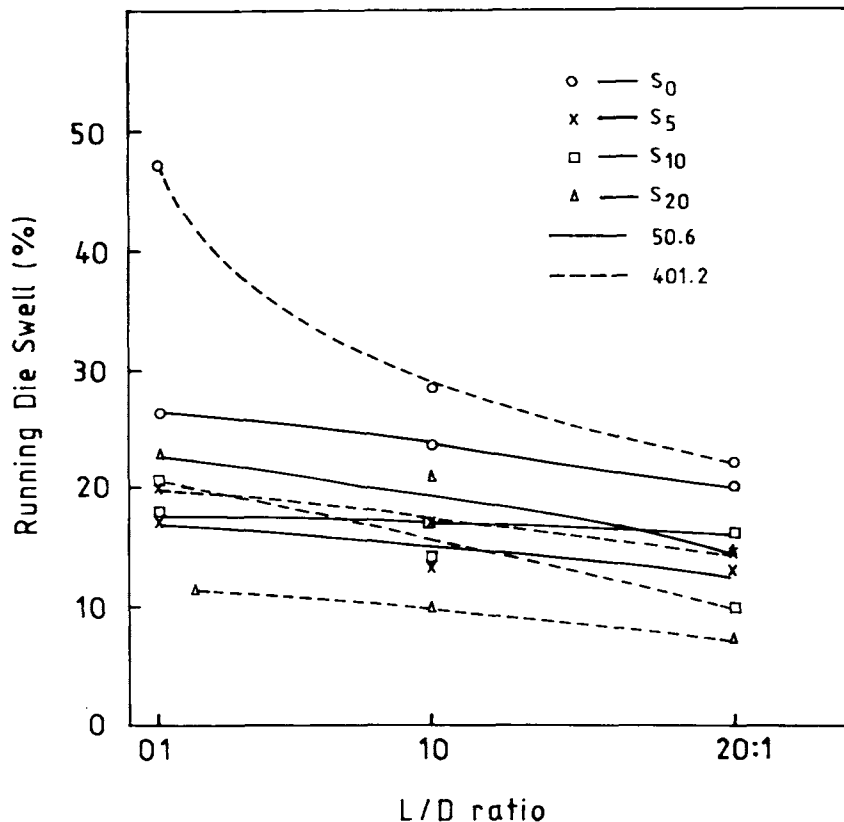


Figure 5 Plot of running die swell against L/D ratio of the composites at 150°C and shear rate of 50.6 and 401.2 s^{-1} .

has been fitted in a second-degree polynomial type of equation:

$$\frac{\eta_f}{\eta_g} = 1 + K_1 \vartheta_f + K_2 \vartheta_f^2 \quad (3)$$

where K_1 and K_2 are functions of rate of shear and temperature; η_f and η_g , the viscosities of the filled and gum systems, respectively, and ϑ_f , the volume fraction of fiber in the composite. The values of K_1 and K_2 are tabulated in Table III. The negative values of K_1 are due to the wall slip because of the orientation of fiber along the direction of flow. The variation of relative viscosity with fiber loading at different temperatures and apparent rates of shear are shown in Figure 4.

Elastic Effects

The elastic effects of the polymer melts are manifested in the form of die swell. The instantaneous increase in diameter of the extrudate as soon as it comes out of the capillary is known as the running

die swell. The plot of the running die swell against the L/D ratio of the capillary at 150°C and the apparent shear rate of 50.6 and 401.2 s^{-1} for both the unfilled and filled compound is shown in Figure 5. It is evident from the figure that die swell values decrease with the increase of the L/D ratio and fiber loading. Similar behavior was also reported in our earlier study⁷ for the NR-HDPE-carbon fiber system. Such die swell behavior may be explained by assuming that the elastic strain is larger at the entry of the die than that within the die. The elastic strain begins to relax in the duct, and when the die length is relatively large compared to die diameter, equilibrium exists.¹⁴ Therefore, a die with a low L/D ratio gives higher die swell values than those of a higher L/D die.

CONCLUSIONS

1. The S-I-S composites show pseudoplastic behavior and obey the power-law equation.
2. The viscosity of the composites decreases

with the fiber concentration up to 10 phr fiber loading, and at higher concentration, it either increases or remains constant, depending on the temperature.

3. The reduction of viscosity with fiber loading is more prominent at low shear rate; however, at higher shear rate, the change in viscosity is marginal.
4. The die swell value decreases with fiber concentration into the matrix as well as with the L/D ratio of the die.

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