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The effects of shear rate and capillary length-to-diameter ratio on isothermal extrudate swell of polymer melts

تأثير معدل القص ونسبة طول الأنبوب لقطرة على جهاز البثق المتساوي الحراره للبوليمر المنصهر

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Abstract

The objective in this article is to establish useful composition-processing structure-property relationships for predicting the rheological properties of automotive type multi-component polymer liquids, and to determine the effects of shear rate and capillary length-to-diameter ratio on isothermal extrudate swell of polymer melts.

ملخص

ان الهدف من هذه الدراسة هو تقصي علاقات مفيدة بين تركيب وتصنيع وبناء وخواص المبلمرات السائلة المتعددة المكونات وذلك ليساعد علىالتنبؤ بخواصها الريولوجيه ولتحديد آثار معدل القصر ونسبة القطر لطول الأنبوبة على المبلمرات المصهورة في حالة ثبوت الحرارsة.

Introduction

The extrusion process is widely used in manufacturing automotive components such as tubing, hoses, cables, side moldings and seals. In this process a pressurized polymer melt flows through a die with a given configuration. Owing to the viscoelastic properties of polymer melts, the dimensions of an extruded melt are often larger than those of the die. This is the well-known "die-swell" phenomenon [1, 3, 20]. In the last three decades, effort was devoted to the determination of the mechanisms that led to extradite swell and to the development of useful relationships for predicting the die swell ratio of extradites [3, 23, 27].

In general, the die swell ratio can be defined as the ratios between the dimensions of a completely relaxed extradite perpendicular to its flow direction and those of the die. It is generally agreed [2, 4-6, 9] that the die swell of a polymer extradite can be attributed to the relaxation of the normal stress components of extradite. For the case of capillary extrusion, the values of die swell (defined by the ratio of completely relaxed extradite diameter, d_j, to the capillary diameter, D) of such polymer melts as filled and unfilled thermoplastics, elastomer gums and reinforced elastomer, increase with increasing shear rate or decreasing capillary length-to-diameter ratio, (LID). As an example, we show in figure 1, the data of the die swell ratio (d_j/D) versus the shear rate (γ) of a high-density polyethylene (HDPE) extruded in a capillary die [with (L/D) = 20] at 180°C [20]. Experimental data of the HDPE melt also showed [15] that the value of die swell ratio decreased rapidly at low values of (L/D) and leveled off as (L/D) increased further. A plot of the die swell ratio of the HDPE at 180°C as a function of (L/D) ratio is shown in Figure 2. From the Rheological point of view, the above die swell results imply that the amount of recoverable elastic energy in the melt while flowing in the capillary increases with increasing shear rate or with decreasing (L/D) ratio [20]. From the viewpoint of composition, further investigation on the effect of composition and microstructure (such as polymer-filler interaction and polymer chain cross links) on extradite swell would help in the development of polymer compositions and in the optimization of extrusion processes.

The purpose of this work is therefore to measure experimentally some rheological properties, such as shear stress, viscosity and die swell ratio of reinforced polymer melts and to correlate these rheological properties with such processing parameters as the flow rate (or correspondingly, the shear rate) and the capillary length-to-diameter ratio. These results may be used to devise new technologies for developing polymer compositions with enhanced processing characteristics.

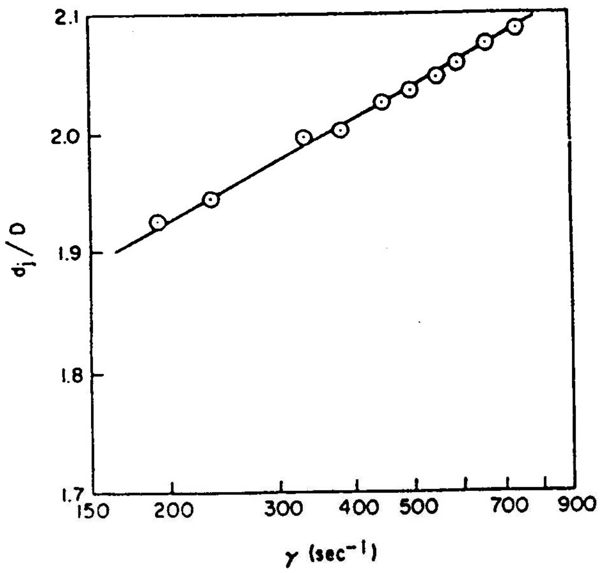

Figure 1: Die Swell ratio (d_j/D), versus shear ratio (γ), for high-density polyethylene in capillary extrusion (L/D = 20) at 180 °C [20].

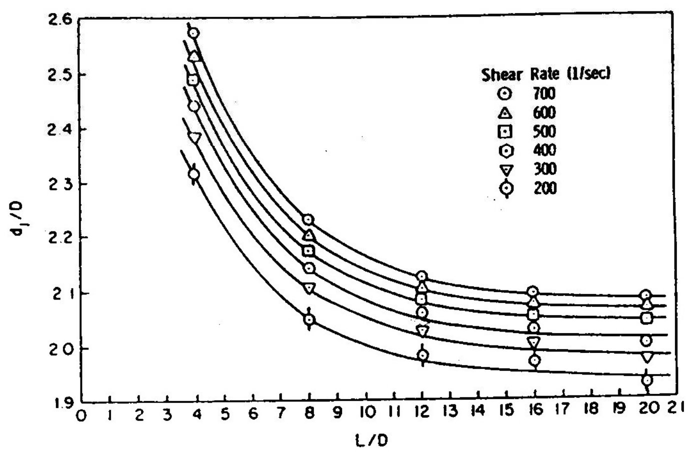

Figure 2: Die Swell ratio (d_j/D), versus capillary length ratio (L/D), for high-density polyethylene at 180 °C and various shear rates [20].

Experimental

Material and Sample Preparation

A carbon black filled ethylene-propylene-dine elastomer (EPDM) composition was investigated in this work. A peroxide cure system was used in the EPDM composition, and the volume concentration of carbon black was 10%. In order to enhance the degree of mixing of the filler in the polymer matrix, the EPDM master batch was prepared using a cyclic heating cooling mixing method [21] in a 1.2 kg Ban bury internal mixer. The master batch was then sheeted out on a two-roll (152.4 x 304.8 mm) mill.

Test Procedure

Steady-shear viscosity and extrudate die swell of the EPDM elastomer master batch were measured using the Monsanto Process ability Tester (MPT), a microprocessor-controlled capillary rheometer. The set-up of the piston, barrel, and extrudate chamber are illustrated in Figure 3. The test temperatures for the barrel, the piston and the chamber were set at 80°C.

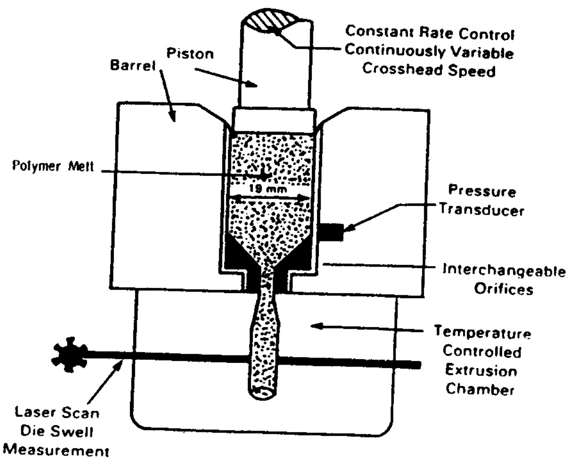

Figure 3: The piston barrel, and extrudate chamber assembly of the Monsanto process ability tester.

Three capillary dies with different length-to-diameter ratios (L/D) were used, and the dimensions of each capillary are listed in Table 1. Each test required thirteen to fifteen grams of elastomer, which was cut into cubical pieces of approximately 8 x 8 x 8 mm^3 to facilitate loading of the MPT barrel. Values for the viscosity and the die swell ratio were measured at various shear rates from 10 to 1200 (l/sec). A laser die swell detector (He/Ne laser, 1 mill watt class II, Laser Product) located in the extrusion chamber (see Figure 3) was used to measure the die swell ratio of the extrudate.

Table 1: Dimensions of Capillary Dies

Capillary	**Capillary**	**Capillary**
Diameter (mm)	Length (mm)	Length-to-Diameter Ratio (L/D)
1.00	30.0	30.0
1.51	30.2	20.0
2.00	32.0	16.0

Results and Discussion

Die Swell Ratio of Capillary Extrudate

Using the MPT at 80°C, we determined values for the die swell ratio (d_j/D) of the EPDM composition as a function of shear rate (γ) and capillary length-to-diameter ratio of the die (L/D). The die swell data are summarized in Table 2, and plotted in Figures 4 and 5.

Table 2: Values for the Die Swell Ratio of Ethylene-Propylene-Dine Elastomers Measured at Various Shear Rates (γ) and with Different Capillary Length-to-Diameter Ratios (L/D)

Logarithmic Shear Rate	**Die Swell Ratio (d_j/D) (L/D)**		
Log (γ)(1/sec)	**30**	**20**	**16**
1.70	1.284	1.255	1.179
2.30	1.256	1.227	1.159
2.60	1.241	1.213	1.149
2.78	1.231	1.205	1.143
2.90	1.227	1.199	1.138
3.00	1.223	1.195	1.135

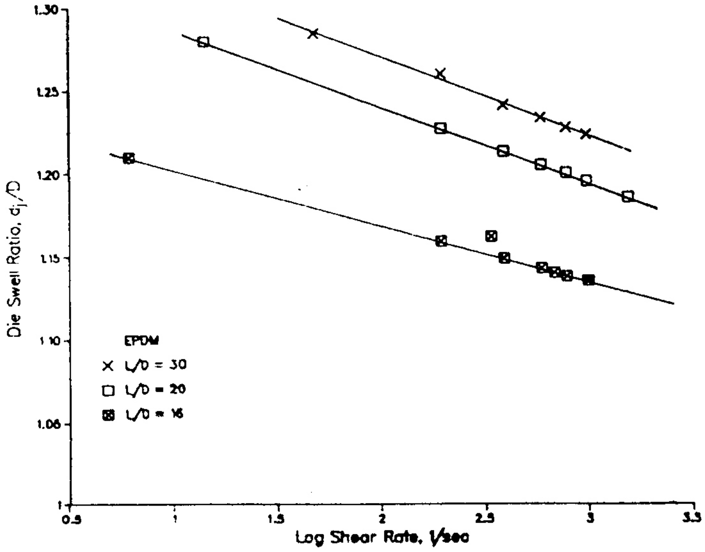

Figure 4: Die Swell ratio versus shear rate for ethylene – Propylene – Dine Elasttomer extruded in various capillary dies at 80°C.

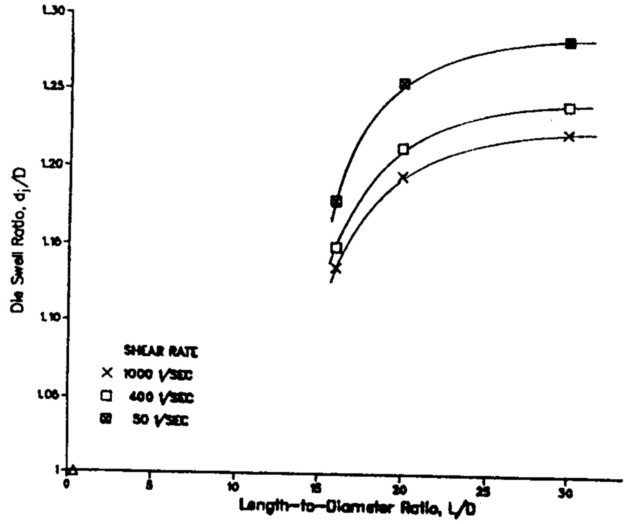

Figure 5: Die Swell ratio (d_j/D), versus capillary length to diameter ratio, for Ethylene-propylene-Dine Elastomer at 80°C and various shear rates.

Based on these results, we conclude that the value of die swell ratio decreases with increasing logarithmic shear rate, log (γ), or with decreasing (L/D) ratio. Physically, this means that the amount of recoverable elastic energy put into the melt decreases as the shear rate increases or the (L/D) ratio decreases. The inverse effect (die swell ratio) is a decreasing function of shear rate). This was reported by Middleman and Gavis [6] for Newtonian liquids at Reynolds numbers greater than 16 and by Metzner et al. [7] for several polymer solutions in the shear rate range above 8 x 10^3(1/sec). These results imply that the decrease in die swell ratio at high shear rates may result from the inertial effect of the fluid at high flow velocities [6, 7].

Effect Shear Rate (γ) on Shear Stress (τ_w) and End Pressure Drop (ΔP_{end}) of HDPE and EPDM Melts

The determination of Rheological properties of polymer liquids using a capillary rheometer often requires the measurement of the pressure drop through the capillary tube (see Figure 3). Experimentally, the total pressure drop between a point upstream in the reservoir and the exit of the tube consists mainly of three parts as shown below [23, 24].

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

Where

ΔP = total pressure drop,

ΔP_{ent} = pressure drop at the entrance to the capillary,

ΔP_{cap} = pressure drop in the capillary, and

ΔP_{exit} = pressure drop at the exit.

The pressure drop in the capillary ΔP_{cap} is believed due entirely to viscous dissipation. The pressure drop at the entrance to the capillary ΔP_{ent} and the pressure drop at the exit ΔP_{exit} are often referred to as the end pressure drop ΔP_{end} , i.e.,

$$\Delta P_{end} = \Delta P_{ent} + \Delta P_{exit} \quad (1a)$$

It is generally agreed that the end pressure drop ΔP_{end} is attributed to the viscoelastic nature of polymer melts. It is also found [l5, 16, 18, 20] that the value of the entrance pressure drop ΔP_{ent} is much greater than that of the exit pressure drop ΔP_{exit}. Therefore, it is reasonable to assume in this work [20] that the value of ΔP_{ent} equals that of ΔP_{end}. Bagley [1] proposed a useful equation for calculating the true wall shear stress (τ_w) of polymer liquids in capillary extrusion. The equation can be rewritten as

$$\tau_w = \Delta P/2\ [(2L/D) + e] \qquad (2)$$

In which ΔP is the total pressure drop as shown in Equation (1), (L/D) is the capillary length-to-diameter ratio, and e is the Bagley end correction factor which can be obtained by plotting the total pressure drop versus the (L/D) ratio [1,20]. Furthermore, it has been shown that the end pressure drop ΔP_{end} can be calculated using the equation shown below [15, 20].

$$\Delta P_{end} = 2e\tau_w \qquad (3)$$

Using Equations (1), (2) and (3), in conjunction with experimental data on the total pressure drop, ΔP, Han et al. [15, 20] determined the true wall shear stress, τ_w, and the end pressure drop, ΔP_{end} of the HDPE melt at 180°C as a function of shear rate and capillary (L/D) ratio are agree with our results plotted in Figures 6 and 7.

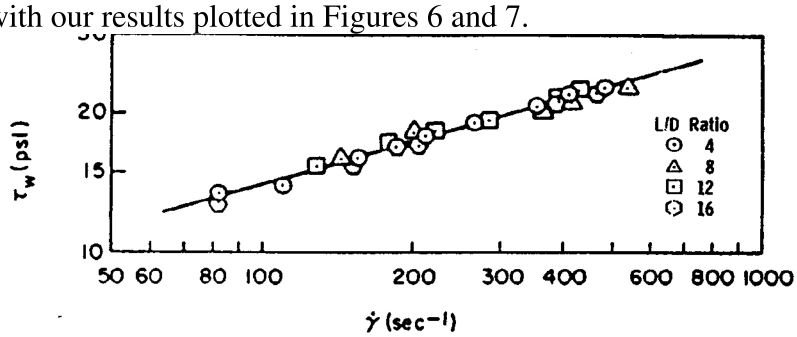

Figure 6: True wall shear stress (τ_w), versus shear rate (γ), for high-density polyethylene at 180 °C, corrected with correction factor [20].

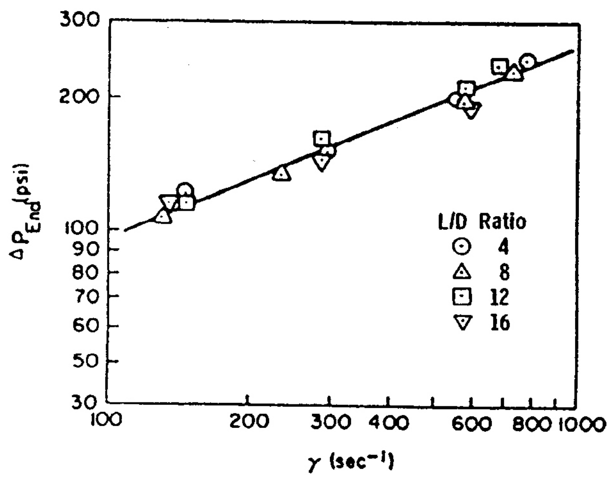

Figure 7: End pressure drop (ΔP_{end}), versus shear rate (γ), for high-density polyethylene at 180 °C.

In this work, we also employed the same method [as shown in Equation (1) through Equation (3)] and determined the true wall shear stress, τ_w, and the end pressure drop, ΔP_{end}, of the EPDM melt at 80 ^oC as a function of the shear rate, γ, and the capillary (L/D) ratio. These data, along with values for the Bagley end correction factor, are summarized in table 3.

Table 3: Values for the True Wall Stress (τ_w), the Bagley End Correction Factor (e) and the End Pressure Drop (ΔP_{end}) of Ethylene-Propylene-Dine Elastomers Measured at Various Shear Rates (γ) and with Different Capillary Length-to-Diameter Ratios (L/D)

(L/D)	e	Log (γ)(1/sec)	Log (ΔP_{end})(Pa)	Log (τ_w)(Pa)
30	32.0	1.70	6.93	5.12
30	28.0	2.30	7.05	5.30
30	26.0	2.60	7.10	5.39
30	24.8	2.78	7.13	5.44
30	24.2	2.90	7.16	5.47
30	23.6	3.00	7.18	5.50
20	32.0	1.70	6.93	5.12

...Continue table (3)

(L/D)	e	Log (γ)(1/sec)	Log (ΔPend)(Pa)	Log (τw)(Pa)
20	28.0	2.30	7.03	5.29
20	26.0	2.60	7.08	5.37
20	24.8	2.78	7.11	5.42
20	24.2	2.90	7.13	5.45
20	23.6	3.00	7.15	5.47
16	32.0	1.70	6.93	5.12
16	28.0	2.30	7.05	5.30
16	26.0	2.60	7.11	5.39
16	24.8	2.78	7.14	5.45
16	24.2	2.90	7.17	5.48
16	23.6	3.00	7.10	5.51

The data were plotted and are shown in Figure 8. Based on the results shown in figures 6,7 and 8, we conclude that there exist linear relationships in the plots of logarithmic shear stress, log (τ_w), versus logarithmic shear rate, log (γ), at different capillary (L/D) ratios. It is noteworthy that values for the slope of these logarithmic plots are positive.

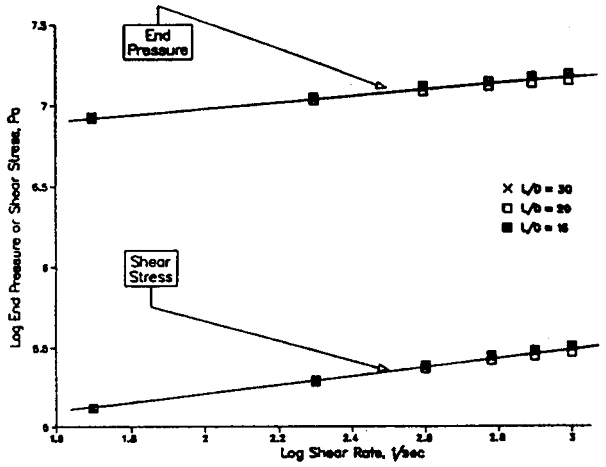

Figure 8: End pressure drop and True wall shear stress versus shear rate for Ethylene-propylene-Dine Elastomer in various capillary Dies at 80 °C.

The new Rheological theory for capillary extrusion showed that the extrudate swell is attributed to the viscoelastic properties of polymer liquids [1-20, 22-24]. The effect of shear rate (γ) on the value of die swell ratio (d_j/D) is generally believed due to the shear-dependent viscosity and the shear-dependent melt elasticity of polymer liquids**.** A power-law model often describes the shear-dependent viscosity of pseudoplastic liquids, such as polymer melts. In steady flow, the power-law model [25-27] can be written as:

$$\eta \propto \gamma^{(1/n-1)} \tag{4}$$

Where

η = Steady shear viscosity of polymer liquids,

γ = Shear rate, and

n = material coefficient defined as the stress-sensitivity coefficient [27].

The shear-dependent melt elasticity at steady flow can be described as function of the shear-dependent relaxation time [25-27]. It has been suggested that the shear-dependent relaxation time λ_1 can be expressed by the following [25-27]:

$$\lambda_1 \propto \gamma^{(1/m-1)} \tag{5}$$

The parameter, m, in the exponent of Equation (5) is a material coefficient and its value can be positive, zero or negative, depending on the rate change in morphological chain structures [28] such as primary and secondary entanglements and chemical cross links of polymers. The rheological relationships for predicting shear stress at wall (τ_w), end pressure drop (ΔP_{end}) and die swell ratio (d_j/D) at various shear rates (γ) and different values of the material coefficients, n and m. These relationships [22] can be summarized as follows:

$$\tau_w \propto \gamma^{(1/n)} \tag{6}$$

$$\Delta P_{end} \propto \gamma^{\left(\frac{1}{m}+\frac{1}{n}\right)} \tag{7}$$

$(d_j/D) \propto [1 + \beta\gamma^{2/m}]^{1/6}$ (8)

The parameter, β, in Equation (8) is a material coefficient whose value is always positive [22,25,26]. The Values for the Rheological Coefficients, m and n, of the High-Density Polyethylene (HDPE) Melt at180 ^{0}C and the Ethylene-Propylene-Dine Elastomer (EPDM) Melt at 80 ^{0}C are shown in table 4.

Table 4: Values for the Rheological Coefficients, m and n, of the High-Density Polyethylene (HDPE) Melt at180 ^{0}C and the Ethylene-Propylene-Dine Elastomer (EPDM) Melt at 80 ^{0}C

Melts	**1/n***	**(1/m) + (1/n)†**	**1/m**	**n**	**M**
HDPE	0.32	0.44	0.12	3.13	8.33
EPDM	0.29	0.19	-0.10	3.45	-10

* The value of (1/n) equals the slope of the line in the plot between the logarithmic true wall shear stress and the logarithmic true wall shear stress and the logarithmic shear rate (see Figures 6 and 8).

† The value of (1/n) + (1/m) equals the slope of the line in the plot between the logarithmic end pressure drop and the logarithmic shear rate (see Figures 7 and 8).

The predictions from the above equations can be summarized as follows:

1. The slope of the plot--logarithmic shear stress, log (τ_w), versus logarithmic shear rate, log (γ)--equals (l/n), where n is the stress sensitivity coefficient.
2. The slope of the plot--logarithmic end pressure drop, log (ΔP_{end}), versus log (γ)--equals [(l/m) + (l/n)] [see Equation (7)].
3. The die swell ratio (d_j/D) is an increasing (or decreasing) function of shear rate, when the material coefficient, m, is greater (or less) than zero.

Some Remarks on the Inverse Rheological Effect

Using a capillary rheometer (Monsanto Process ability Tester), we have determined the Rheological properties of a carbon black reinforced ethylene-propylene-dine elastomer (EPDM) melt having peroxide cure agents. Experimental data clearly show the inverse effect of shear rate and capillary length-to-diameter ratio on the value of die swell ratio of the EPDM melt (see Figures 4 and 5), when compared with the die swell phenomena of the high-density polyethylene (HDPE) melt (see Figures 1 and 2) .The Rheological explanation for the above inverse effect is that the relaxation time of the EPDM melt is more shear-dependent [the value of m in Equation (5) being negative] than that of the HDPE melt [the value of m in Equation (5) being positive].

As a reminder, the coefficient m describes the shear-dependence of the relaxation time of a polymer liquid. Previous investigations [28] have shown an increase in die swell with increasing shear rate for carbon black filled rubbers containing sulfur curatives, and mixed by conventional mixing methods. The inverse effect found in this work may be attributed to: (1) the EPDM melt investigated being filled with peroxide curatives and (2) the EPDM batch being mixed using a cyclic heating-cooling mixing procedure [21] for enhancing the degree of mixing of the filler particles in the matrix.

Summary and Conclusions

Results show that values for the die swell ratio of the EPDM composition decrease with decreasing (L/D) ratio, which is the reverse from that reported for polymer melts such as a high-density polyethylene (HDPE). This inverse rheological effect can be described by a new rheological theory. The results also show that the relaxation time of the EPDM composition is more shear-dependent than that of the (HDPE) melt. This extra shear-dependence of relaxation time for the EPDM composition prepared using the cyclic mixing method indicates that new polymer compositions or optimum processing conditions can be developed for achieving the desired extradite die swell.

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