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Effect of chemical modification on the flow behaviour of LDPE and its blends with linear LDPE

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The flow behaviour of LDPE and its blends with linear LDPE (LLDPE) chemically modified with DCP was studied as a function of blend composition and shear rate at a constant temperature using a capillary rheometer. The effect of chemical modification on the viscous and elastic properties of LDPE and two blend systems LDPE/LLDPE (80:20, 60:40) is reported. Chemical modification which is in essence a free radical process induces changes that increase melt viscosity and melt elasticity of LDPE and the two blend systems. Modification also enhances compatibility of the molten polymers. Incorporation of a small quantity of linear LDPE having a relatively narrow molecular weight distribution to the conventional LDPE having a long chain branched structure and broader molecular weight distribution lessens the shear thinning behaviour of the modified blends of the two component polymers. Melt elasticity at a constant shear stress and temperature was also investigated using die swell measurements and relating them to recoverable shear strain, normal stress and shear modulus. ©1997 Elsevier Science Ltd. © 1997 Elsevier Science Ltd.

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INTRODUCTION

In recent years there has been a great deal of commercial interest in blends based on polyolefins. One main objective in the study of such blends is to find new materials combining the beneficial mechanical and processing properties of the component polymers. The practical benefits of polymer blending has been comprehensively reviewed by Deanin[1]. The introduction of linear LDPE (LLDPE) in the early 1980s offers the possibility of obtaining a new class of blends easily processable and with good overall mechanical behaviour[2,3]. A comparison of the physical and mechanical properties of linear LDPE and LDPE is shown in *Table 1*[4].

The salient features of linear LDPE that emerge from *Table 1* are summed up as follows:

(1) even though LDPE and linear LDPE have comparable molecular weights and densities, the heat resistance of linear LDPE is considerably higher;
(2) linear LDPE is more crystalline. This is attributed to its long regular molecular chains, which facilitate the formation of large crystals;
(3) linear LDPE has a greater degree of stiffness resulting from its higher crystallinity; and
(4) the high melt viscosity of linear LDPE makes processability difficult.

Thus, from the rheological perspective linear LDPE constitutes a class of polymer which has similar physical and product properties to the other branched polyolefins (e.g. LDPE), yet differs in critical ways in its flow characteristics. We take advantage of this situation in using the rheological characteristics to assist in understanding both the structure of linear LDPE and its influence on the flow behaviour of the conventional LDPE.

Previous work on the flow behaviour of linear LDPE and its blends has been well documented in literature. Recent references[5–13] have been listed. In our previous paper[14], we compared the flow behaviour of LDPE and its blends with linear LDPE I and II differing widely in their melt flow indices. In this paper we report the effect of chemical modification on the flow behaviour of the LDPE and two blend systems LDPE/LLDPE 80:20 and 60:40, respectively.

EXPERIMENTAL

Materials

The sources of polymers investigated in this work are commercial grades of LDPE (Indothene FS 300) with MFI 6 g/10 min, density 0.922 g/cm^3 and LLDPE (Ladene 218W) with MFI 2 g/10 min, density 0.918 g/cm^3. The modifier dicumyl peroxide (DCP) was 99% pure with a density of 1.02 g/cm^3. The recommended processing temperature range is 160 to 200°C.

Blend preparation

The blends were prepared by melt-mixing in a Brabender plasticorder model PL 3S (effective chamber volume 50 cm^3) at a set temperature of 160°C and a rotation speed of 30 rev/min. for 15 min. Within this period of time a constant torque was obtained indicating a homogeneous dispersion of the polymers. Blend composition and sample codes are given in *Table 2*. Processing conditions for the

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Table 1 Typical characteristics of LDPE and LLDPE used in blown films

Characteristics	LDPE	LLDPE
Melt flow index (g/10 min)	2	1
Density	0.92	0.92
Melting temperature (°C)	110	130
Crystallinity(%)	65	70
Processability	easy	very poor

Table 2 Sample codes and composition of LDPE:LLDPE blend systems

Sample code	Composition
LDPE	100% low density polyethylene
LDPE:LLDPE(80/20)	80% low density polyethylene 20% linear low density polyethylene
LDPE:LLDPE(60/40)	60% low density polyethylene 40% linear low density polyethylene

Table 3 Processing conditions for modified samples

Sample	Processing temp (°C)	Rotor speed (rev/min)	Time (min)
LDPE	160	30	15
LDPE/LLDPE 80:20	160	30	12
LDPE/LLDPE 60:40	160	30	10

corresponding samples modified with 1 phr DCP is given in *Table 3*.

Rheological measurements

The capillary rheometer used for rheological measurements was Goettfert visco-tester 1500 with a capillary diameter of 1 mm, a capillary length of 30 mm and an entrance angle of 90°. The barrel temperature was 180°C and the measured shear rates ranged from 2.3 to 2300 s^{-1} (uncorrected). The apparent viscosity was calculated directly from the recorded force and plunger speed using capillary and barrel dimensions and without correcting for entrance and exits effects since the results in this study are of a comparative nature.

Die swell measurements were made by cutting the extrudate just below the die and measuring the diameter after solidification by means of a micrometer. The swelling ratio B was then evaluated[15].

$$B = (D_e/D)(\rho v_m)^{1/3} \qquad (1)$$

where, D_e is the diameter of the extruded sample, D the die diameter, ρ the density of the sample, and v_m the specific volume at the extrusion temperature.

RESULTS AND DISCUSSION

Flow curves

The apparent shear stress at the wall of the capillary was calculated using the expression

$$\tau_w = \Delta P/2(L/R) \qquad (2)$$

where ΔP is the pressure drop across the capillary die, L the length of the die and R its radius.

Apparent shear rate at the wall was calculated using the expression

$$\dot{\gamma}w = 4Q/\pi R^3 \qquad (3)$$

where, Q is the volumetric flow rate.

A useful form of expressing the flow behaviour is to utilize what is called the power law equation given by

$$\tau_w = K\dot{\gamma}_w^n \qquad (4)$$

where K value is a measure of consistency of the polymer, and n is the flow index. From this equation it follows that if n is unity, then K has the form identical to n and equation (4) appears as Newton's law.

equation (4) can be written in the logarithm form as follows

$$\log\tau_w = \log K + n\log\dot{\gamma}_w. \qquad (5)$$

The plot of $\log\tau_w$ versus $\log\dot{\gamma}_w$ should provide a straight line and its slope gives the value of n. The value of n indicates the extent to which the polymer deviates from Newtonian behaviour (n = 1 for Newtonian fluids).

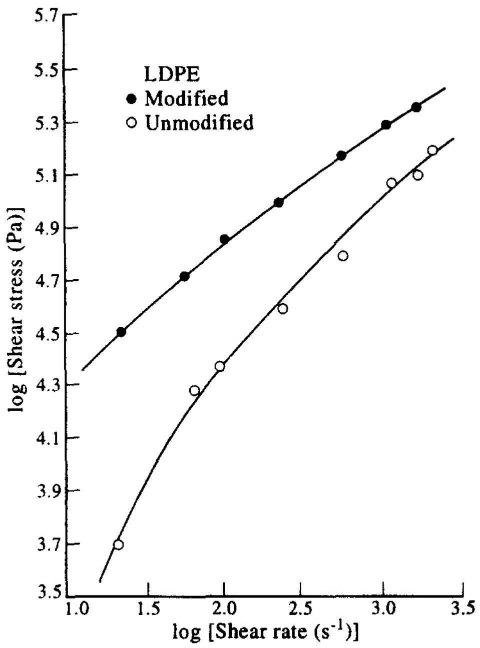

Figure 1 Shear stress versus shear rate of LDPE

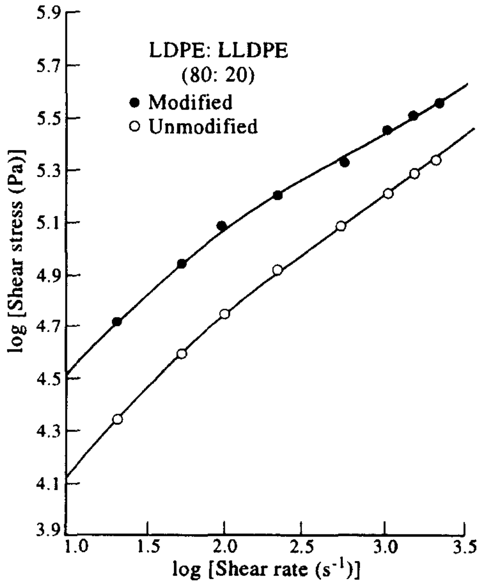

Figure 2 Shear stress versus shear rate of LDPE:LLDPE (80/20)

Plots of shear stress versus shear rate (the so-called flow curves) are shown in *Figures 1–3* for LDPE and the two blend systems LDPE/LLDPE 80:20 and 60:40. The study was thus restricted to blend compositions rich in LDPE. Higher compositions were not investigated owing to the very high melt viscosity of linear LDPE. From the figures one could observe that in the case of the two blend systems the flow curves are nearly parallel indicating that the non-Newtonian flow behaviour remains practically the same on modification.

Viscous flow

In expressing the resistance of a material to flow, the term viscosity (denoted by the symbol η) is used as a common indicator. This parameter relates the observed shear stress to the imposed shear rate (or vice versa). One of the basic laws of flow extends from Newton's law of viscosity which is given by

$$\eta = \tau_w/\dot{\gamma}_w. \qquad (6)$$

Plots of viscosity versus shear rate of LDPE and two blend systems LDPE/LLDPE 80:20 and 60:40, are shown in *Figures 5–7*. The viscosity unit used is Pa.s. Inspection of the curves indicate that the molten polymers both modified and unmodified are in the non-Newtonian flow regime. Modification increased the melt viscosity to a greater degree in the case of the pure polymer (LDPE) compared to that of the blend systems.

Plots of viscosity versus blend composition at three shear rates of increasing order (60 s^{-1}, 600 s^{-1}, 2300 s^{-1}) and a constant temperature (180°C) are shown in *Figure 4* in order to observe the effect of shear rate and blend composition on

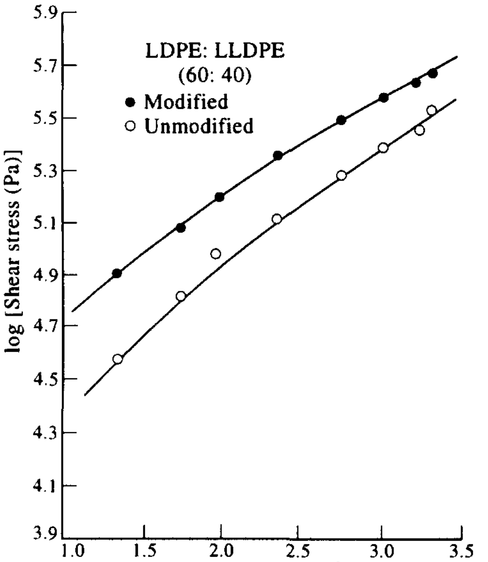

Figure 3 Shear stress versus shear rate of LDPE:LLDPE (60/40)

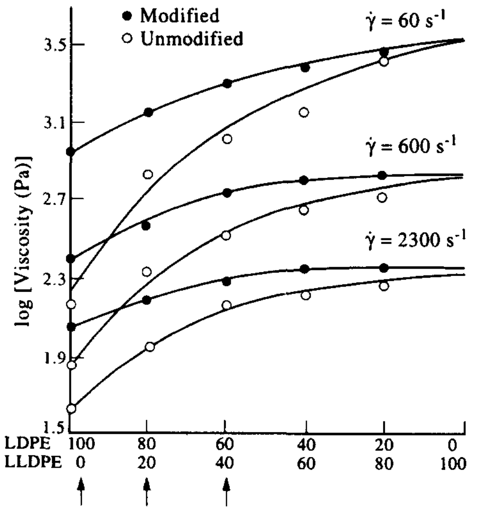

Figure 4 Viscosity versus blend composition of LDPE and LLDPE

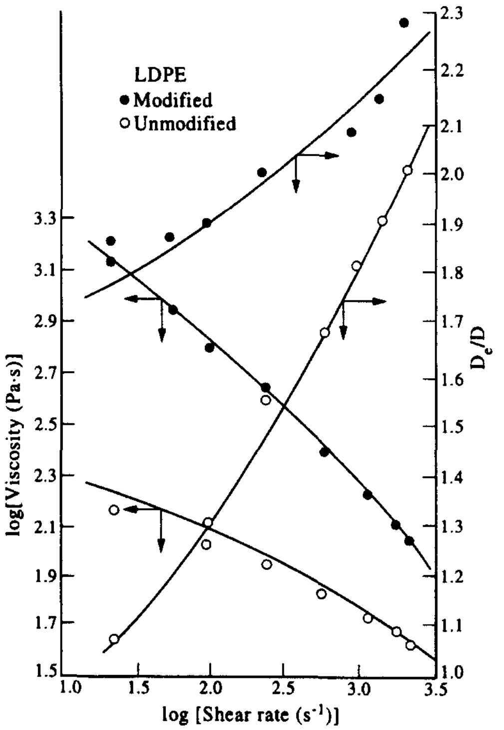

Figure 5 Viscosity and die swell versus shear rate of LDPE

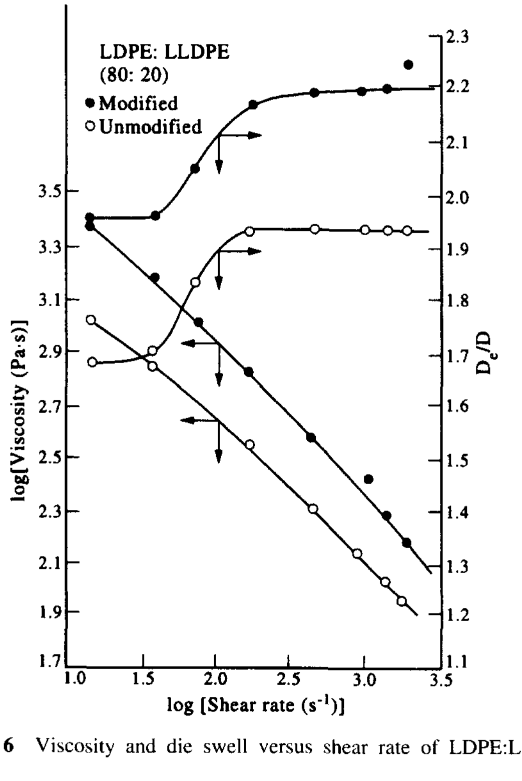

Figure 6 Viscosity and die swell versus shear rate of LDPE:LLDPE (80/20)

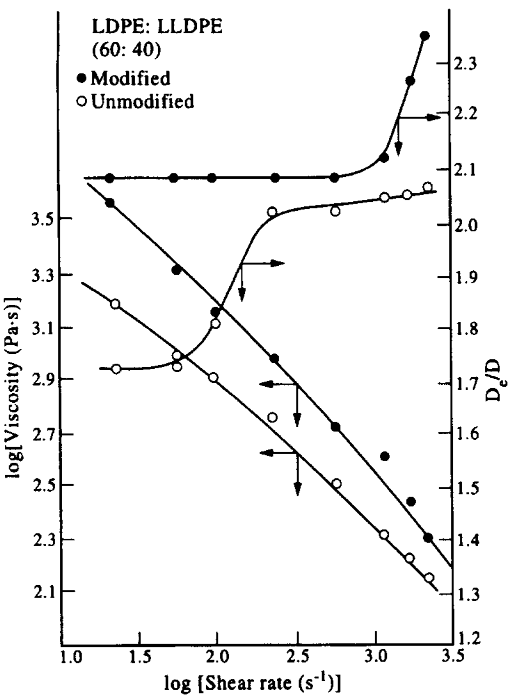

Figure 7 Viscosity and die swell versus shear rate of LDPE:LLDPE (60/40)

melt viscosity. Open circles represent data points of unmodified samples and closed circles, of the corresponding modified samples, the compositions under study indicated by arrows. First, as a function of blend composition, the modified blend systems exhibit higher values of viscosity and its variation as a function of LLDPE content is more smooth and uniform compared to that of the corresponding unmodified blend systems. This possibly indicates enhanced compatibility of the melt in the modified blend systems resulting from bonding between the long chain molecules. The term compatibility in this context refers to stronger interphase interaction between the components of the modified blends. Second, the observed differences in viscosity between the modified and unmodified homopolymers is highest for LDPE and decreases with increase in composition of linear LDPE. These results reflect a great susceptibility of LDPE to chemical modification. As a function of shear rate, the shear thinning behaviour is practically the same in the case of the modified blend systems.

Melt elasticity

The swelling behaviour of molten polymers extruded from an orifice or die is of considerable importance both in the fundamental elucidation of polymer flow and in the direct practical control of the processing characteristics of molten polymers. Mendelson *et al.* employed the theory of rubber elasticity to relate die swell to recoverable shear strain, shear modulus and normal stress. The theoretical treatment of extrudate swelling as unretarded recovery of elastic strain imparted during the extrusion process[16] utilizing rubber elasticity theory resulted in the following expressions relating recoverable shear strain γ_R and first normal stress $(\tau_{11} - \tau_{22})$ to the swelling ratio B and the wall shear stress at each shear rate:

$$\gamma_R = [(B^4 + 2)/(B^2 - 3)]^{1/2} \quad (7)$$

$$\tau_{11} - \tau_{22} = 2/3\tau_w[(B^4 + 2)/(B^2 - 3)]^{1/2} \quad (8)$$

where the factor 2/3 arises from consideration of the average shear stress (taken for a Newtonian velocity profile across the capillary cross-section) as being the appropriate value to relate to the average normal stress difference.

Shear modulus is given by

$$G = 2/3(\tau_w/\gamma_R). \quad (9)$$

The values of $(\tau_{11} - \tau_{22})$, γ_R and G defining melt elasticity calculated using equations (7)–(9) from experimental die swell measurements are shown in *Table 4*. Higher values of $(\tau_{11} - \tau_{22})$, γ_R or B and lower values of G imply greater elastic recoverability or higher melt elasticity. From the table it is clear that the modified blend systems exhibit higher values of die swell (B) and lower values of G. Thus, melt elasticity increases on modification.

Die swell behaviour as a function of shear rate is shown in *Figures 5–7*. Open symbols represent data points of unmodified samples and closed symbols, of the corresponding modified samples. Modified LDPE exhibits a systematic variation in swell, increasing continuously in the range of shears investigated (20–2300 s^{-1}). Incorporation of 20% linear LDPE changes the shape of the swell curve with a shift in the onset of swell from 20 to 60 s^{-1}, increases thereafter with shear rate and finally levels off at 600 s^{-1}. Further dilution with 40% linear LDPE shifts the onset of swell still further from 60 to 600 s^{-1}, indicating the role of linear LDPE in suppressing the swell behaviour of LDPE on modification. This progression in the shift is related to an increase in the degree of crosslinking which restricts chain mobility and hence expansion in the case of the two modified blend systems.

CONCLUSIONS

The main conclusions that result from capillary rheometer data on the viscous and elastic properties are summed up as follows:

(1) chemical modification increases both viscosity and elasticity of modified LDPE and the two blend systems with linear LDPE;
(2) modification enhances compatibility of the molten polymers;
(3) linear LDPE with a relatively narrow molecular weight distribution lessens the shear thinning behaviour of LDPE; and

Table 4 Viscous and elastic parameters of LDPE and LDPE:LLDPE blend systems at a fixed shear stress and temperature (180°C)

		η*10^2 (Pa.s)		B		$(\tau_{11} - \tau_{22})$*10^6 (Pa)		γ_R		G*10^3 (Pa)	
Sample	τ_w*10^5 (Pa)	Neat	Mod	Neat	Mod	Neat	Mod	Neat	Mod	Neat	Mod
LDPE	1.0	0.54	0.44	1.91	1.99	2.7	3.1	13.5	15.7	7.38	6.39
LDPE:LLDPE (80/20)	1.2	2.10	10.0	1.93	2.04	3.4	4.1	14.1	17.1	8.54	7.02
LDPE:LLDPE (60/40)	1.2	5.70	21.0	2.02	2.08	3.96	4.4	16.5	18.3	7.27	6.56

(4) swelling behaviour of modified LDPE is suppressed by incorporating linear LDPE shifting the onset of swell to high shear rates.

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