Morphology of polyethylene blends: I. From spheres to fibrils and extended co-continuous phases in blends of polyethylene with styrene–isoprene–styrene triblock copolymers

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Blends containing 85% polyethylene (LDPE/LLDPE) and 15% styrene–isoprene–styrene triblock copolymers have been obtained using a single screw extruder fitted with different exit dies (annular, flat and capillary). The morphology of the blends has been investigated by scanning electron microscopy and related to the extrusion conditions (type of die, presence or absence of melt drawing). Spheres, elongated droplets, fibrils and extended co-continuous phases have been observed.

INTRODUCTION

Different parameters have been proposed to account for the morphology of incompatible polymer blends[1–9]. They are: the blending procedure, the interfacial tension between the components, the viscosity of the continuous phase, the relative viscosities of the dispersed and continuous phases, and the presence or absence of interfacial agents.

The present paper is part of a more general work concerning the degradation of polymer blends in relation to their morphology[10–14]. Blends of polyethylene with a styrene–isoprene–styrene (SIS) triblock copolymer have been processed using different blending methods. Their morphology has been investigated using scanning electron microscopy (SEM).

Although the results obtained in the present work could only be qualitatively interpreted on the basis of currently available theories and experimental data, a short summary of some representative papers on morphology and phase development in polymer blends is presented. These papers provide a key to the understanding of our observations.

EXPERIMENTAL

Polymers

LDPE and LLDPE are commercial polymers obtained, respectively, from DSM and Cdf (Chimie).

LDPE characteristics are: $M_w = 88\,200$, $M_n = 16\,800$, $d = 0.922$, melt index $(MI) = 0.85\,\text{g}/10\,\text{min}$. LLDPE characteristics are: $M_w = 109\,000$, $M_n = 26\,800$, $d = 0.919$, $MI = 1\,\text{g}/10\,\text{min}$ (ASTM D1238 65T).

The molecular weight distributions have been measured using a Waters model 150 C g.p.c. apparatus with three 10^3, 10^4 and 10^5 ultra Styragel columns and 1,2,4-trichlorobenzene at 135°C. Narrow distribution polystyrene, polyethylene and n-paraffins were used as calibration standards. Their respective Mark–Houwink constants were used to obtain a calibration in linear polyethylene.

The SIS copolymer is Shell Cariflex TR-1107. It contains 15% styrene and 85% isoprene.

Extrusion

Blends containing 15% SIS, 21.25% LLDPE and 63.75% LDPE were extruded using a Gottfert Laboratory extruder fitted with different exit dies. The annular die is 5 cm in diameter and 600 μm thick. The flat die is 22 cm wide and 600 μm thick. The capillary die is 8.83 cm long and 3 mm in diameter. The annular die was used with and without blowing. In the last case, the extrudate was allowed to fall and cool freely downwards. The temperatures in the five sections of the extruder are successively 150, 160, 170, 190 and 200°C. The temperature at the die is 220°C. The extrusion conditions are different for the capillary die: 130, 140, 150 and 160°C in the mixing chamber, 190°C at the die.

The shear viscosity *versus* shear rate data have been

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Table 1 Physical characteristics of blends of polyethylene (LDPE–LLDPE, 75/25) containing 15% SIS triblock copolymer

Processing conditions	G (s^{-1})	η_d/η_c	Q_v (ml s^{-1})	H_L (μm)	l_L or d_L (cm)	V_L/V_0	B	Longi-tudinal shrink-age (%)	Die swelling (%)	Dimen-sion phases (mean) (μm)	% Extracted
Annular die without blowing	51	0.48	0.479	1030	15	1	0.95	–	70	0.5	0
Annular die with blowing	107	0.50	1.01	70	23	5	1.46	4	–	0.1	13
	51	0.48	0.479	15	24	25	1.5	20	–	0.2	12
Flat die	34	0.5	0.453	125	16.5	6.4	0.7	0	–	0.2	4.2
Capillary die	235	1.05	0.624	5000	0.5	1	1.6	–	50	0.3	0

G = shear rate; Q_v = flow rate; H_L = film thickness; l_L = film breadth; d_L = film diameter; V_L/V_0 = draw-down ratio; B = blow-up ratio; η_d = viscosity of the dispersed phase; η_c = viscosity of the continuous phase

obtained under the same temperature conditions. The extruder was fitted with the capillary die in all cases.

The flow rate of the polymer and the breadth and thickness of the extrudates are given in *Table 1*.

Scanning electron microscopy

The samples used for SEM were prepared by freeze fracture in liquid nitrogen and covered with a thin layer of gold. Most were extracted with benzene or tetrahydrofuran for 5 days at room temperature. The weight percentage of extracted SIS was determined by weight loss measurement and by infrared spectroscopy (Bruker IFS 45). A Jeol JSM-840 scanning electron microscope was used.

MORPHOLOGY AND DYNAMICAL ASPECTS OF PHASE DEVELOPMENT IN POLYMER BLENDS

The morphology of polymer blends has been investigated both theoretically and experimentally by many research groups[1-9]. Different equations have been proposed to account for the size and shape of the dispersed phase in the matrix. Most are derived from Taylor's equation[15] concerning the dispersion of Newtonian droplets in Newtonian fluids in steady shear field. Min *et al.*[4] proposed that spheres or thin threads are formed in the matrix when the relative viscosities of the dispersed and continuous phases η_d and η_c obey the following conditions, respectively: $\eta_d/\eta_c > 2.2$, $\eta_d/\eta_c < 0.7$. When η_d/η_c ranges from 2.2 to 0.7, ondulating threads or ellipsoids have been observed. Shear flow is dominant in the experiments.

Another equation relating droplet dimension to the same parameters in steady shear and elongational flow has been proposed by Cox[16].

More parameters have been considered by Wu[17]. A master curve relating $G\eta_c R/\gamma$ to η_d/η_c where G, R and γ are, respectively, shear rate, particle diameter and interfacial tension, has been proposed for viscoelastic drops suspended in a viscoelastic matrix using a co-rotating twin screw extruder. This system is different from Taylor's (Newtonian drop in Newtonian fluids) in many respects: the drop and the matrix are both viscoelastic and the strain field is a complex combination of non-uniform, transient shear and elongational fields. A V shaped curve with a minimum corresponding to $\eta_d/\eta_c = 1$ is obtained. It obeys the relation

$$\frac{G\eta_c R}{\gamma} = 4\left(\frac{\eta_d}{\eta_c}\right)^{\pm 0.84}$$

The plus sign of the exponent corresponds to $\eta_d/\eta_c > 1$. In this case, large R values characterize systems with high interfacial tension and low matrix viscosity, the other parameters being unchanged. Few experiments corresponding to $\eta_d/\eta_c < 1$ have been reported.

The dynamical aspect of phase development in polymer blends has been considered theoretically by different authors and recently studied experimentally by Elmendorp and co-workers[5-7]. Three different interrelated steps can be considered in the development of morphology: formation and break-up of droplets; formation and break-up of threads; and coalescence of droplets.

Formation and break-up of droplets

In most blending experiments the initial mixture of the two components is subjected to a combination of shear and elongational flow, the former usually being the most important.

The break-up of Newtonian droplets in steady shear flow occurs when the viscous forces given by

$$2G\eta_c \frac{19p + 16}{16p + 16}$$

(where $p = \eta_d/\eta_c$) are equal to or exceed the surface tension γ/R (References 3 and 15). The critical shear rate for break-up G_b is given by Taylor's expression:

$$G_b = \frac{\gamma}{2\eta_c R} \frac{16p + 16}{19p + 16} \tag{1}$$

This relation was experimentally verified for polymer solutions in simple shear field[5]. It shows that large interfacial tension and low viscosity of the matrix decrease the deformability of the droplets and thus favour the stabilization of large droplets.

Non-Newtonian behaviour causes complications. No agreement can be found in the literature about the importance of the elasticity of the melt. Correction of the interfacial term by including the first normal stress difference has been proposed by Van Oene[3]. White could not obtain any evidence of the importance of this parameter[4]. A qualitative correlation between elasticity effects and droplet deformation was experimentally established by Elmendorp[6]. Elasticity of the matrix increases the deformability and hence leads to finer dispersions; elasticity of the dispersed phase leads to an increase in stability and in dimensions of the dispersion.

The theory of drop deformation in non-steady elongational flow has been discussed and experimentally studied[18]. The deformation has been shown to increase

with Weber number $\eta_c R_0 \dot{\varepsilon}/\gamma$, where R_0 is the diameter of the undeformed droplet and $\dot{\varepsilon}$ is the rate of strain tensor. At constant Weber number, the deformation increases strongly with η_d/η_c. The deformation in elongational flow thus depends qualitatively on the same parameters as the deformation in shear flow.

Formation and break-up of threads

The preceding considerations imply that an equilibrium state of dispersion is obtained for the droplets. This is, however, generally not realized in normal conditions of polymer blending. When the dispersed phase has a high viscosity under conditions of rapidly changing shear rates, droplets are stretched into elongated cylinders, which can later break into a line of droplets[6]. It has been shown experimentally[6] that these threads break according to Rayleigh's and Tomotika's treatments of capillary instabilities[19].

The breaking time of the thread varies from a few seconds to hours as a function of the interfacial tension, the viscosity of the continuous phase, the initial radius of the thread and the value of η_d/η_c. In this case the interfacial tension is the driving force to decrease the surface and thus to break up the threads, while the viscosity tends to retard the process. According to this theory, threads will be stable in blends if the time necessary to develop instabilities exceeds the time for blending and solidification.

Coalescence of droplets

Droplets can also collide and recombine. The efficiency of this shear induced process depends strongly on the flow field, the concentration of the dispersed phase, the radius of the dispersed spheres, the mobility of their surfaces and the viscosity of the continuous phase[7]. This coalescence process was shown to be very important during the single screw extrusion of blends of polypropylene with polystyrene when the concentration of the dispersed phase exceeds 0.5%; the dimensions of the dispersed phase grow from 0.2 to 2 μm when the concentration increases from 0.5 to 8%.

RESULTS AND DISCUSSION

Blending has been performed with a single screw extruder fitted with different exit dies: an annular die equipped with a drawing and blowing device, the same die used without drawing and blowing, a flat die and a capillary die. The extrusion conditions and the physical parameters characterizing each extrudate are summarized above and in *Table 1*.

Shear viscosity *versus* shear rate data are given in *Figure 1* for the blend LDPE–LLDPE 75/25 and for the triblock copolymer. They were obtained with the capillary die using temperature gradients identical to those used to obtain the different extrudates. No correction has been applied to the experimental results.

Annular die without blowing

In this first and simpler case, the experimental conditions are those described in the next section for extrusion blowing but the drawing of the melt and the blowing process are not performed. Shear flow is dominant at the die but flow is also partly elongational in the transition from extruder cross section and in
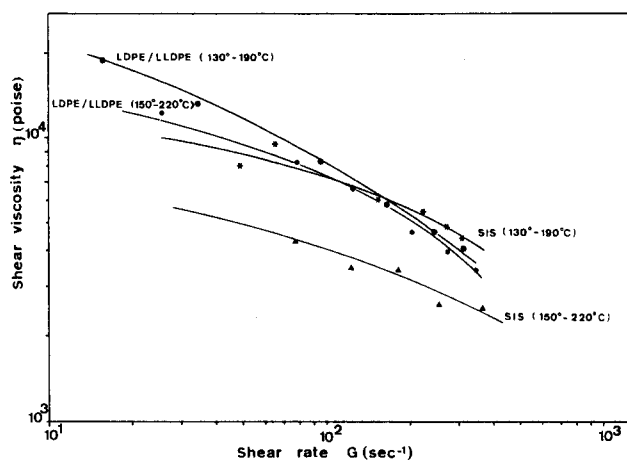

Figure 1 Shear viscosity *versus* shear rate data for the blend LDPE/LLDPE (75/25) and for the SIS triblock copolymer extruded between 150 and 220°C
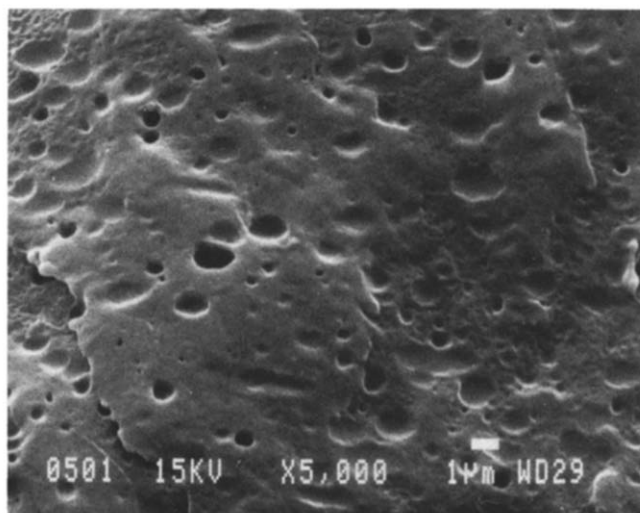

Figure 2 SEM photomicrograph of a longitudinal cross section of (LDPE/LLDPE)/SIS 85/15 (15 μm) extruded from an annular die with blowing

converging to the die lips. Both flow conditions tend to elongate the droplets but their relative contribution cannot be established. The extrudate is tubular but much thicker than that described in the next section. A die swelling of 70% due to the elasticity of the melt has been measured. No elastic recovery is observed on heating the extrudate for 0.5 h at 105°C. Indeed, relaxation of the melt occurs in the slow cooling conditions prevailing in the absence of blowing. The dispersed phase forms spheres ≈ 0.5 μm in diameter as shown in *Figure 2*. The value of η_d/η_c corresponding to the shear rate of 51 s^{-1} used in the present processing conditions is 0.48. According to Min *et al.*[4], fibrils would form instead of the currently observed spheres. The absence of fibrils can be assigned to three main processes. Thread breaking processes could occur in the elongational field at the exit of the die, as explained in the previous section. Such a process could be very efficient in the rather thick sample and inefficient cooling conditions used in the present work. These conditions together with the high concentration of the dispersed phase could also favour droplet coalescence as described in the last paragraph of the previous section. A third hypothesis is, however, the most reasonable explanation of the conversion of fibrils into

spheres: molecular relaxation of the polymer chains, which is highly probable in the absence of drawing when the rate of cooling is low, would induce this change of morphology.

Annular die with blowing

Two films of different thicknesses (15 and 70 μm) have been extruded. Highly elongated fibrillar phases are observed in both cases (*Figures 3* and *4*). This morphology is very different from the preceding one, although the shear rate at the exit of the die is the same as in the preceding case for the 15 μm film ($G = 51$ s^{-1}, $\eta_d/\eta_c = 0.48$) and only twice as large for the 70 μm film ($G = 107$ s^{-1}, $\eta_d/\eta_c = 0.50$). This is due to the important extension of the melt which occurs below the freeze line in the circumferential direction and in the machine direction during the blowing and drawing processes. Biaxial extension results from the balance of the draw-down force F_L and the bubble pressure Δp, which are given by[20]

$$F_L = 2\pi RH\sigma_{11} \cos \theta + \pi\Delta p(R_L^2 - R^2)$$

$$\Delta p = H\sigma_{11}/R_1 + H\sigma_{22}/R_2$$

wh re σ_{11} and σ_{22} are stresses in the machine direction and in the circumferential (transverse) direction, respectively, R_1 and R_2 are the principal radii of curvature of the film and the other parameters are defined in *Figure 5*.

This biaxial extension is characterized by two parameters: the blow-up ratio B given by R_L/R_0 and the draw-down ratio V_L/V_0, where R_L and R_0 are the radius of the tubular film and the radius of the die, respectively, and V_L and V_0 are the rate of drawing and the rate of displacement of the melt at the die, respectively.

The parameters B and V_L/V_0 are summarized in *Table 1*. Extension in the machine direction given by the draw-down ratio is much more important than in the transverse direction determined by the blow-up. Only a small fraction is elastically recoverable, as indicated by the decrease in length (% shrinkage) observed on annealing the film for 0.5 h at 110°C. Decreases of 20 and 4% are observed for the 15 and 70 μm films, respectively.
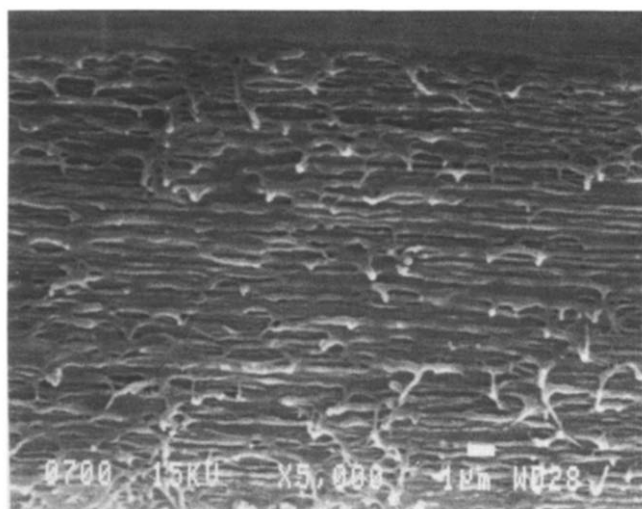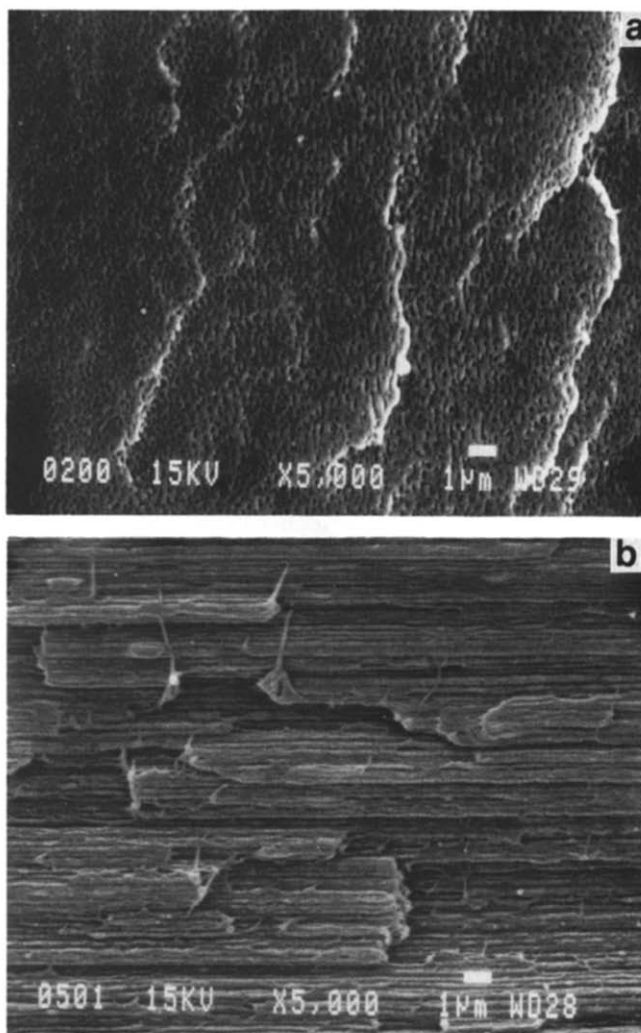

Figure 4 SEM photomicrographs of (LDPE/LLDPE)/SIS 85/15 (70 μm) extruded from an annular die with blowing: (a) transverse cross section; (b) longitudinal cross section
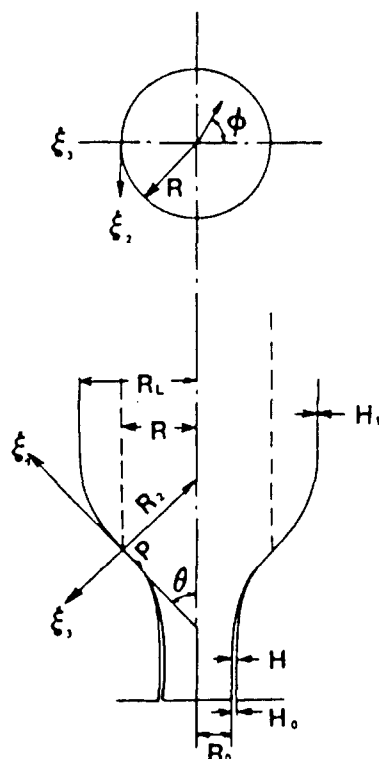

Figure 3 SEM photomicrograph of a longitudinal cross section of (LDPE/LLDPE)/SIS 85/15 (15 μm) extruded from an annular die with blowing

Figure 5 Tubular film extrusion

The morphology of the dispersed phase can now be discussed. At a draw-down ratio of 1, which corresponds to the absence of blowing, spheres $\approx 0.5\ \mu m$ in diameter are obtained (see previous section). For the 15 and 70 μm thick (blown) films, the draw-down ratios are, respectively, 25 and 5, while the corresponding fibril diameters are ≈ 0.2 and $\approx 0.1\ \mu m$, respectively. These fibrils can be supposed to be formed by extension of droplets similar to those obtained in the absence of blowing. The following relation would then be verified between the diameter of the droplet and the diameter of the fibre[21,22]:

$$\pi d_0^2 V_0/4 = \pi d_L^2 V_L/4$$

which rearranges into

$$d_L/d_0 = 1/(V_L/V_0)^{1/2} \qquad (2)$$

This relation is not verified in the present case since the fibre corresponding to the higher draw-down ratio has the largest diameter, contradicting the inverse square root dependence predicted by the previous equation. The formation of the fibre is thus a more complex process than a simple extension of the droplet.

The elongated fibrillar phases which form the 15 and 70 μm thick films exhibit another interesting property. They are co-continuous. Almost quantitative extraction (13%) of the SIS phase can be performed at room temperature using either benzene or tetrahydrofuran as selective solvent for the triblock copolymer. These extended co-continuous phases result from the biaxial extensional flow characterized by B and V_L/V_0. Indeed, co-continuity is absent when transverse extension is absent (see previous and following sections). This biaxial extension leads to sheet-like structures when the weight fraction of SIS is higher[23]. Extended co-continuous phases have, to our knowledge, never been reported in extrusion blown films. Normal co-continuous phases have been shown to form in usual internal mixer or extruder blending conditions when the following relation is obeyed[9]:

$$\eta_d/\eta_c = \Phi_d/\Phi_c \qquad (3)$$

where η_d, η_c, Φ_d and Φ_c are the viscosity and weight fraction of the dispersed phase and the continuous phase. The value of Φ_d/Φ_c is 0.18 in the present films. If the values of η_d and η_c corresponding to the effective shear rate ($51\ s^{-1}$ or $107\ s^{-1}$) used in the present extrusion conditions are taken from *Figure 1* and introduced into equation (3), co-continuity can be calculated to correspond to $\Phi_d/\Phi_c = 0.50$ instead of 0.18.

Extended co-continuous phases and fibrillar phases obeying equation (2) have been reported to develop in melt spun fibre of polypropylene–nylon and high density polyethylene–polystyrene blends[21,22].

Flat die

Extended fibrillar phases similar to those obtained by extrusion blowing are obtained with the flat die (*Figure 6*). They are not, however, co-continuous since only about one third of the dispersed phase can be extracted.

In this case, the contraction in the transverse direction is given by l_L/l_0 where l_L and l_0 are the film and die breadth: $l_L/l_0 = 0.75$. The extension in the machine direction given by the draw-down ratio V_L/V_0 has a value of 6.4, similar to that calculated for the extruded blown 70 μm film ($V_L/V_0 = 5$). The ratio η_d/η_c is also similar in both cases.
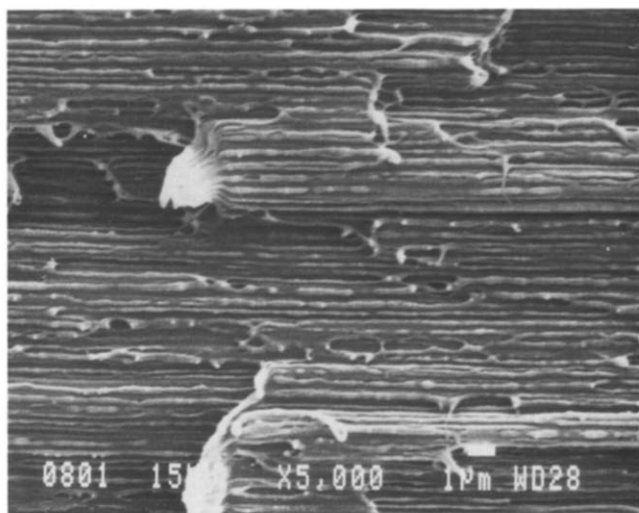

Figure 6 SEM photomicrograph of a longitudinal cross section of (LDPE/LLDPE)/SIS 85/15 extruded from a flat die
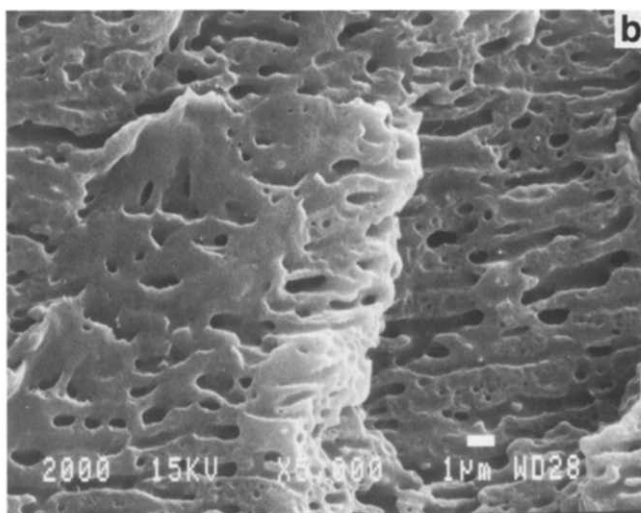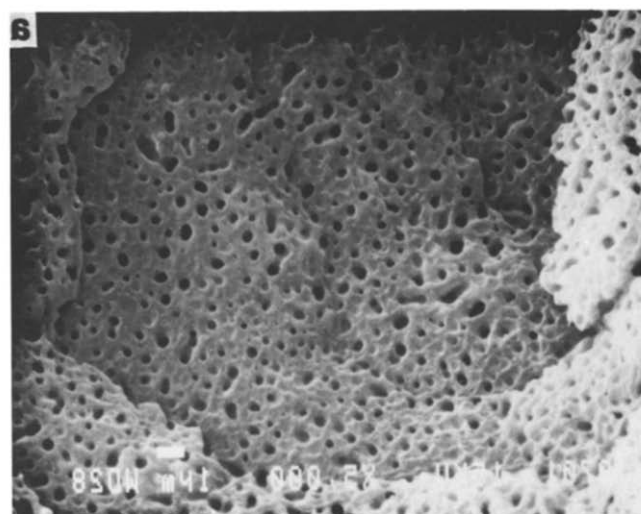

Figure 7 SEM photomicrographs of (LDPE/LLDPE)/SIS 85/15 extruded from a capillary die: (a) transverse cross section; (b) longitudinal cross section

Capillary die

Transverse cross sections (*Figure 7a*) reveal the formation of particles with a rather uniform diameter ($\pm 0.3\ \mu m$). Longitudinal cross sections (*Figure 7b*)

indicate that particles with a rather broad distribution of length are oriented in the machine direction: spheres and elongated fibrils showing a tendency to continuity are formed. Although thin elongated fibrils were expected on the basis of the value of η_d/η_c (1.05) corresponding to the shear rate of $235\,s^{-1}$, the morphology observed here agrees with the observations reported in the previous sections.

The two extrudates which are obtained without melt drawing (capillary extrusion and annular die without blowing) can first be compared: the more elongated phase corresponds to the higher value of η_d/η_c (capillary extrusion). In the other cases, melt drawing strongly modifies the morphology; similar elongated phases are observed in the rather broad range of draw-down ratio (5–25) reported here.

ACKNOWLEDGEMENTS

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