Morphology of polyethylene blends: 3. Blend films of polyethylene with styrene–butadiene or styrene–isoprene copolymers obtained by extrusion–blowing

M. Getlichermann and C. David*
Faculté des Sciences, Campus Plaine, CP 206/1, Université Libre de Bruxelles, B-1050 Bruxelles, Belgium
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The morphologies of blends of polyethylene (PE) with a range of copolymers with different basic structure (diblock, triblock, starblock or statistical) have been compared in order to assess the relative importance and interrelation of rheological and molecular parameters. The development of well defined dispersed phases in extruded–blown PE films results from two successive steps. The first is the dispersion step, dominated by shear force fields and shear viscosity in the extruder barrel and die. The second step involves drawing of the melt and freezing of the structures. If the dispersed phase is characterized by a high value of the shear viscosity ratio η_d/η_m and hence by a low deformability, elongation can be performed in neither step. This was observed for diblock styrene–butadiene (SB) in a low viscosity PE matrix, for SBS_{r2} and for StatSB which all give spheres or ellipsoids. The dimension of the spheres is governed by the viscosity of the matrix and by the value of η_d/η_m according to the Wu equation. If the dispersed phase is highly deformable ($\eta_d/\eta_m < 1$), it is elongated in one or two dimensions at the exit of the die. For a Newtonian melt, these structures break during the elongation time preceding freezing of the structures if the breaking time given by Tomotika's theory is shorter than the elongation time. Broken filaments have indeed been observed for SBS at 240°C and also for styrene–isoprene–styrene (SIS) at 270°C. For a non-Newtonian dispersed phase, stabilization of the structures occurs by different mechanisms involving the elastic contribution of the elongational viscosity. It is related to entanglements and increases with molecular weight. Yielding or tension thickening behaviour can be involved. This is illustrated by the formation of co-continuous elongated structures when the high-molecular-weight diblock SB and triblock SIS are blended with PE, respectively at 240 and 220°C. Two starblock copolymers, SBS_{r1} and SBS_{r3}, although non-Newtonian and characterized by a rather low value of η_d/η_m, do not give continuous structures. This is attributed to the low molecular weight of the branches which does not allow the formation of a sufficient number of entanglements.

(Keywords: polyethylene blends; styrene–butadiene; styrene–isoprene)

INTRODUCTION

The primary purpose of this work was to develop photodegradable polyethylene (PE) blend films for agriculture using an unsaturated polymer as the dispersed phase to initiate their photodegradation and fragmentation. Different PEs and one styrene–isoprene–styrene (SIS) triblock copolymer were used as dispersed phase and the results reported previously[1–3].

It soon appeared that the mechanism of photo-oxidation and the type of fragmentation of the film depend on the morphology of the blend. A new elongated co-continuous morphology was identified. In the degraded film it induces fragmentation in long, narrow ribbons in the direction of extrusion. When the dispersed phase is present in the form of small spheres, isotropic fragmentation occurs in the heavily degraded film. Initiation of the photodegradation of PE was found to occur by a new mechanism involving diffusion of small fragments of the oxidized central block of SIS from the dispersed phase to the PE phase.

The purpose of the present work is to explore the morphologies induced in PE by a broad range of styrene–butadiene (SB) copolymers. This research presents a dual interest. Polybutadiene is an unsaturated polymer which could, as polyisoprene, initiate the degradation of PE. Also, since it is commercially available as triblock, diblock, starblock or random copolymers, it allows a deeper insight into the relation between structure of the copolymer and morphology of the blend. The initial idea was that continuous morphologies would be favoured by increasing the number of terminal styrene blocks per macromolecule. Co-continuous structures would then be favoured in the order starblock > triblock > diblock > random. The study of blend morphologies is considered in the present paper. Photo-oxidation results will be published elsewhere[4].

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* To whom correspondence should be addressed

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EXPERIMENTAL

Polymers

Two different low-density PEs (coded LDPE-1 and LDPE-3) and one linear low-density PE (coded LLDPE) were used as the matrix phase. These PEs were utilized separately, or in a 75/25 blend only for LDPE-1 and LLDPE. LDPE-1, LDPE-3 and LLDPE are commercial polymers obtained respectively from DSM, DSM and Atochem. LDPE-1 characteristics are: $M_w = 88\,000$, $M_n = 19\,000$, density = 0.922, melt index (MI) = 0.85 g/10 min. LDPE-3 characteristics are: $M_w = 121\,000$, $M_n = 18\,000$, density = 0.923, MI = 4.4 g/10 min. LLDPE characteristics are: $M_w = 113\,000$, $M_n = 31\,000$, density = 0.919, MI = 1 g/10 min (ASTM D1238 65T. Cond. E).

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

Copolymers of various structures and molecular weight were used as the dispersed phase. *Table 1* gives their characteristics. The molecular weight values have been obtained from industry.

Extrusion

Blends containing different weight percentages of copolymers (5, 10, 15 and 25 wt%) were extruded using a Gottfert Laboratory extruder fitted with an annular blown film die (inner diameter = 5 cm, thickness = 600 μm).

Unless otherwise stated, the temperatures in the different sections of the extruder and at the die (last two sections) are successively for PE–SIS: 150-160-170-190-200-220-220°C and for the other blends: 150-170-190-215-220-240-240°C.

The draw-down and blow-up ratio are respectively 5 and 1.5 in all cases.

Viscosity

The shear viscosity–shear rate data have been obtained in the conditions of temperature used for the extrusion. The extruder was fitted with a capillary die (diameter = 0.3 cm, length = 8.83 cm) in this case.

The measurements of dynamic viscoelastic properties were carried out with a rheogoniometer in the parallel plate mode. It was used to measure G' (dynamic storage modulus) and G'' (loss modulus) at the temperature imposed at the die and for a deformation of 3%.

Scanning electron microscopy (s.e.m.) and extractions

The samples used for s.e.m. were prepared by freeze-fracture in liquid nitrogen and covered with a thin layer of gold. They were extracted with tetrahydrofuran (THF) (24 h) at room temperature after fracture. A Jeol JSM-840 scanning electron microscope was used. The weight percentage of extracted SIS was determined by weight loss measurement and by infra-red spectroscopy (Bruker IFS 45) for samples extracted with THF over 3 days at room temperature.

Dimension of the dispersed phase

When possible, the diameter (d, dimension of the transverse direction) and length (l, dimension in the extrusion direction) of the phases have been quantified through the definitions of number-average (subscript n) and weight-average (subscript w) disperse-phase dimensions[5]:

$$d_n = \sum_i N_i d_i / \sum_i N_i$$

$$d_w = \sum_i N_i d_i^2 / \sum_i N_i d_i$$

The values of d_n, d_w, l_n and l_w have been determined using 50 dispersed structures for each system.

RESULTS

In the first section, the morphologies will be compared at constant composition (15 wt% dispersed phase) as a function of their rheological parameters (η_d/η_m, where η_d and η_m are the shear viscosities of the dispersed and matrix phases respectively, η_m, Newtonian or non-Newtonian behaviour of the melt, interfacial tension). In the second and third sections, they will be tentatively related to the chemical structure of the unsaturated constituent unit and to the basic structure of the copolymers (diblock, triblock, starblock, statistical). Blend composition will be considered in the last section. The purpose of this discussion is to assess the relative importance and the interrelation of the global rheological parameters and of the molecular parameters to the morphology of the blend.

Effect of the viscoelastic properties of the melt on the morphology of the blend

The rheological curves for the polymers used in the present work are given in *Figures 1* to *3*. *Table 2* shows the viscosities obtained from these curves and the values of G' and G'' obtained by plate-and-plate rheometry. All

Table 1 Characteristics of the unsaturated copolymers

Copolymer	M_w	M_n	Structure	Styrene content (%)	Melt index (g/10 min)	Microstructures (%)			
						1,2	3,4	1,4-*cis*	1,4-*trans*
SIS (Cariflex TR 1107—Shell)		140 000	Triblock	15	9.0 (ASTM D1238/G)	6–7	1	92–93	
SBS (Cariflex TR 1102—Shell)		70 000	Triblock	28	6.0 (ASTM D1238/G)	10	–	35	55
SBS_{r1} (Finaprene 417—Fina)	119 000	58 000	Starblock	30	1.5 (ASTM D1238/P)	13	–	33	54
SBS_{r3} (Finaprene 414—Fina)	105 000	58 000	Starblock	40	0.5 (ASTM D1238/P)	13	–	33	54
SB (Finaprene 315—Fina)	140 000	132 000	Diblock	70	3.5 (ASTM D1238/P)	13	–	36	51
Stat SB (Finaprene 1204—Fina)	243 000	163 000	Statistical	25	56 (ASTM D1646ML) (1 + 4) (100°C)[a]	30	–	27	43

[a] Mooney viscosity given for this copolymer

the polymers considered here are non-Newtonian in shear with the exception of the triblock SBS at 240°C and of the triblock SIS at 270°C, which are then above the order–disorder transition temperature (T_r) and hence Newtonian.

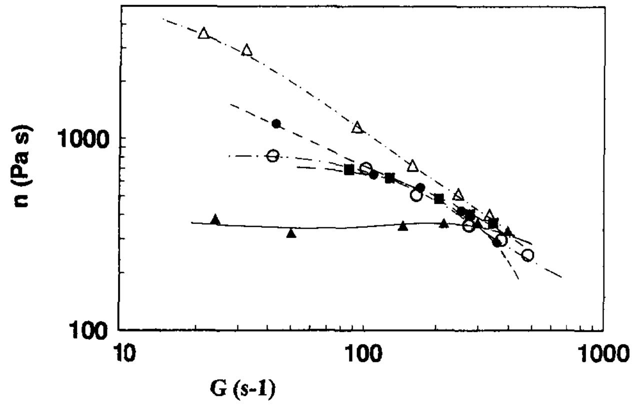

Figure 1 Shear viscosity–shear rate data at the indicated die temperature: (●) LDPE-1/LLDPE (75/25) 240°C; (▲) SBS 240°C; (■) SBS_{r1} 240°C; (△) SBS_{r2} 240°C; (○) SBS_{r3} 240°C

Examination of *Table 2* which summarizes the obtained morphologies shows that dispersed spheres or ellipsoids are only obtained when $\eta_d/\eta_m > 1$ (blends 7 to 9) whereas fibrils of various lengths are usually obtained if $\eta_d/\eta_m < 1$ (blends 1 to 6). Transition from one type of structure to the other can be promoted by changing only the viscosity of the continuous phase as exemplified by blends 6 and 9 which both involve the diblock SB. When this copolymer is blended with a high-viscosity PE (LDPE-1/LLDPE: $\eta_m = 6 \times 10^2$ Pa s; $\eta_d/\eta_m = 0.8$), long fibrils are obtained (blend 6); when it is blended with a lower viscosity PE (LDPE-3: $\eta_m = 2.4 \times 10^2$ Pa s; $\eta_d/\eta_m = 2.3$) rather large spheres or ellipsoids are formed (blend 9). The spheres result from the low deformability of the dispersed phase, first in the complex shear field of the extruder and die and then in the elongational field at the exit of the die. Shear viscosity ratio η_d/η_m is thus a prominent parameter since it characterizes the deformability of the dispersed phase.

The dimensions of the dispersed structures are similar for blends 7 and 8 and much larger for blend 9. They are governed by the viscosity of the matrix and by the

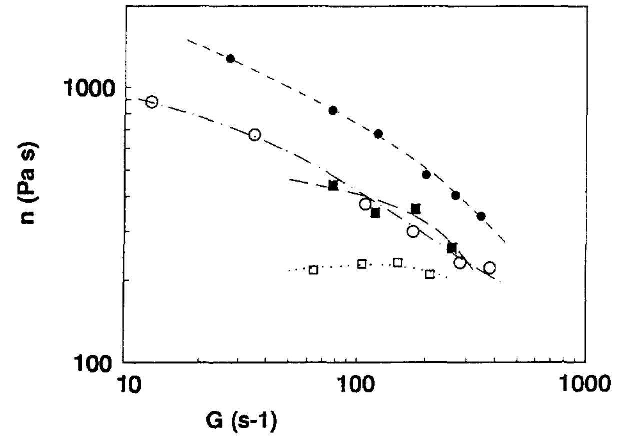

Figure 2 Shear viscosity–shear rate data at the indicated die temperature: (●) LDPE-1/LLDPE (75/25) 220°C; (○) LDPE-1/LLDPE 270°C; (■) SIS 220°C; (□) SIS 270°C

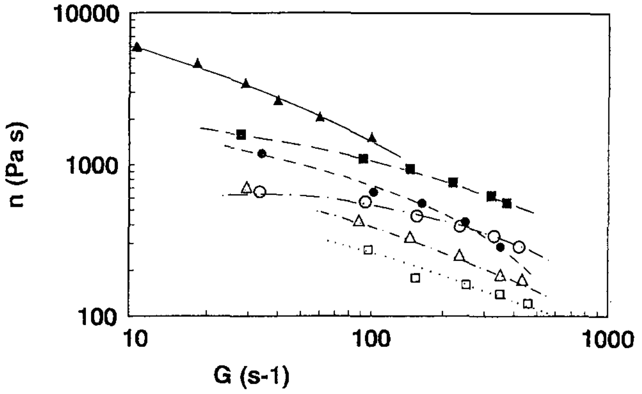

Figure 3 Shear viscosity–shear rate data at the indicated die temperature: (●) LDPE-1/LLDPE (75/25) 240°C; (△) LDPE-1 240°C; (■) LLDPE 240°C; (□) LDPE-3 240°C; (○) SB 240°C; (▲) StatSB 240°C

Table 2 Morphology of the blends containing 15% copolymer

Blend	Film	Styrene content (%)	M_n ($\times 10^3$)	M_w ($\times 10^3$)	T_{die} (°C)	G' (10^4 Pa)	G'' (10^4 Pa)	η_m (10^2 Pa s)	η_d/η_m	Morphology					Copolymer extracted (%)
											l_n (μm)	l_w (μm)	d_n (μm)	d_w (μm)	
$\eta_d/\eta_m < 1$															
	LDPE-1/LLDPE				220	6	3.5	6.5 (nN)							
					240			6.5 (nN)							
					270			4.2 (nN)							
1	+SIS	15	140	–	220	4	3.0	3.3 (nN)	0.5	CFS	>10	>10	0.1	0.2	87
2	+SIS				270	–	–	1.9 (N)	0.5	SF	1.3	1.7	0.1	0.17	9
3	+SBS	28	70	–	240	2.8	2.9	3.9 (N)	0.6	mF	6.0	8.0	0.1	0.2	17
4	+SBS_{r1}	30	58	119	240	10.0	5.6	5.9 (nN)	0.9	mF	5.0	7.0	0.1	0.2	7
5	+SBS_{r3}	40	58	105	240	3.5	1.5	5.9 (nN)	0.9	E	1.4	1.8	0.3	0.5	10
6	+SB	70	132	140	240	–	–	5.5 (nN)	0.8	1F	>10	>10	0.2	0.3	40
$\eta_d/\eta_m > 1$															
	LDPE-1/LLDPE				240			6.5 (nN)							
7	+SBS_{r2}	40	77	147	240	–	–	8.5 (nN)	1.3	S to E	0.6	0.8	0.4	0.5	9
8	+statSB	25	163	243	240	14.0	6.8	15.5 (nN)	2.3	S to E	0.7	0.8	0.4	0.6	12
	LDPE-3				240			2.4 (nN)							
9	+SB	70	132	140	240	–	–	5.5 (nN)	2.3	S to E	3.0	4.0	1.2	1.7	15

N, Newtonian; nN, non-Newtonian; CFS, continuous fibrillar structure; SF, short fibrils; 1F, long fibrils; mF, medium fibrils; E, ellipsoïds; S, spheres value of η_d/η_m, as will be calculated in the discussion using the Wu equation[6]. The lengths and diameters (in μm) of the structures for these blends are respectively: 0.6, 0.4; 0.7, 0.4; 3.0, 1.2. Interfacial effects are not very important in the present blends of non-polar polymers but may become determining when blends of polar and non-polar polymers are involved.

We shall now consider blends 1 to 6 which are characterized by $\eta_d/\eta_m < 1$ and discuss the influence of the Newtonian or non-Newtonian behaviour of the molten copolymer on the morphology of the blend and mainly on the formation of very long fibrils ($l > 10\,\mu$m) and co-continuous elongated structures. Examination of *Table 2* shows that such structures are not obtained with SIS at 270°C (blend 2) and SBS at 240°C (blend 3) which are Newtonian at these temperatures. Broken fibrils are indeed observed. In contrast, co-continuous phases and long fibrils are respectively obtained for the non-Newtonian systems PE–SIS (blend 1) and PE–SB (blend 6) at 240°C. Co-continuous phases are characterized by an oriented fibrillar morphology from which the copolymer can be extracted almost quantitatively by a selective solvent without destruction of the film. S.e.m. photomicrographs of extended co-continuous morphologies are given in refs 2 and 3. Another example (*Figure 4*) is given in this work. Nevertheless, other blends incorporating the starblocks SBS_{r1} and SBS_{r3} do not give these structures even though they are non-Newtonian. Non-Newtonian behaviour is thus a necessary but not a sufficient condition to obtain co-continuous extended structures and long fibrils. Non-Newtonian behaviour in shear indicates the presence in the melt of any kind of network and particularly of entanglements.

Effect of a change of the chemical structure of the central unsaturated triblock copolymer: comparison of SIS and SBS

SIS (blend 1), extensively investigated in a previous paper[2,3] and SBS (blend 3) are compared here. The matrix is the same in both cases. The processing conditions are also the same with the exception of a difference of 20°C in the die temperature (220 and 240°C). However, the copolymers differ in their molecular weights (140×10^3 and 70×10^3), styrene content (15 and 28%) and order–disorder transition temperature (230 and 220°C). The non-Newtonian behaviour of SIS indicates the presence of a network or entanglements. At 220°C and a shear rate of $100\,s^{-1}$, the network structure is probably destroyed and only entanglements remain. On the contrary, SBS is above T_r at the blending temperature; the Newtonian character of the blend indicates that thermal and flow-induced disentanglement has occurred. *Table 2* shows that co-continuity is observed for SIS while moderately elongated fibrils (6 μm) are formed in the case of SBS. The percentage of copolymer extracted by a selective solvent of the copolymer (respectively 87 and 17%) indicates that co-continuity is far from realized in the case of SBS although the values of η_d/η_m are similar for SIS and SBS blends.

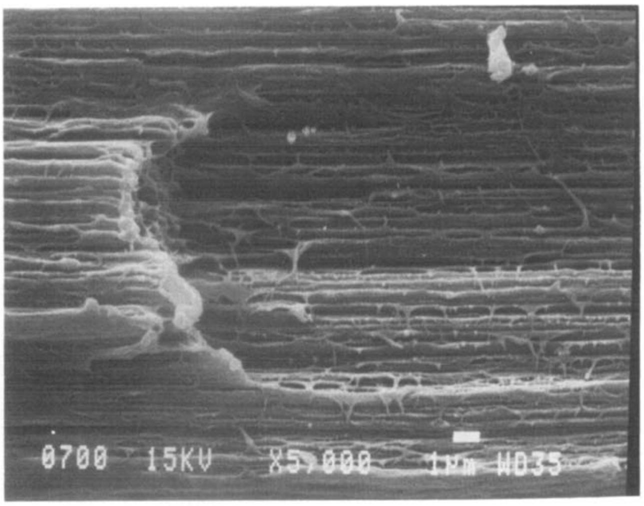

Figure 4 S.e.m. photomicrograph of LDPE-1/LLDPE (75/25) containing 25% diblock SB (longitudinal cross-section)

What is the reason for this difference? The unsaturated block is the continuous phase in the phase-separated structure of the block copolymer in both cases. Interfacial tensions between LDPE and SIS or SBS have not been measured in the conditions used in the present work but can be assumed to be not very different from each other. This suggests that co-continuous structures are not directly related to the chemical structure of the copolymer. They are favoured by the non-Newtonian behaviour of the dispersed phase in cases where a low value of η_d/η_m ensures the deformability of this phase as discussed in the previous section.

This hypothesis is supported by the fact that SIS extruded with LDPE-1/LLDPE at higher temperature (270°C; blend 2) is Newtonian at this temperature. The short fibrils observed under these conditions could result from the breaking of larger filaments.

The chemical structure of the central block has thus no importance by itself but only through the rheological, and in some cases the interfacial, properties that it imparts to the melt.

Effect of the basic structure of the copolymer: comparison of triblock, diblock and starblock copolymers

Blends 3, 4, 5 and 6 of *Table 2* are considered here. They were all obtained at the same temperature (240°C) and in the same conditions. The continuous phase is the same (LDPE-1/LLDPE) and η_d/η_m is < 1 in all cases.

The diblock SB differs largely from the others in composition (richer in styrene) and molecular weight (exceeding by a large margin the critical molecular weight for entanglement formation). In the conditions used to obtain blend 6, it is non-Newtonian; this blend approaches co-continuity as indicated by the high percentage of copolymer that can be extracted (40%) (it will be shown below that co-continuity is indeed obtained in blends containing 25% SB).

Starblocks SBS_{r1} and SBS_{r3} are non-Newtonian at this temperature but the molecular weight of the branches is low. The non-Newtonian properties of the melt are probably due to the presence of small star-shape domains which are present below the order–disorder transition[7] and which are destroyed in the elongational field at the exit of the die. Entanglements, if present, are not formed in a sufficiently large number to resist this field. Indeed, SBS is tension-thinning below T_r. As a consequence, filaments break during elongation and the structures obtained with SBS_{r1} and SBS_{r3} are shorter than those observed with diblock SB. SBS_{r3} is richer in styrene than SBS_{r1} and gives shorter but thicker structures. These could be tentatively assigned to a higher interfacial tension between the PE matrix and the SBS_{r3} dispersed

Table 3 Classification of results

η_d/η_m	Deformability	Copolymer content (%)	N/nN	Mol. wt	Morphology	Film
>1	Low	15			Spheres Ellipsoids	SBS_{r2} StatSB SB
<1	High	15	nN	High	Co-continuous	SIS SB (25%)
<1	High	15	nN	Low	Broken filaments	SBS_{r1} SBS_{r3}
<1	High	15	N	All	Broken filaments	SIS (270°C) SBS
<1	High	5	nN[a]		Spheres	SIS
<1	High	7.5–15	nN[a,b]		Broken filaments of increasing length	SIS
<1	High	>25	nN[a]		PE dispersed phase	SIS

N, Newtonian; nN, non-Newtonian

[a] Newtonian systems not studied

[b] See ref. 3

Table 4 Effect of composition on the morphology of blends of PE with unsaturated copolymers

			Morphology					
Blend	Film	η_d/η_m	Shape[a]	l_n (μm(	l_w (μm)	d_n (μm)	d_w (μm)	Copolymer extracted (%)
	LDPE–LLDPE							
10	5% SIS	0.5	E	0.1	0.19	0.07	0.08	8
1	15% SIS	0.5	CFS	>10	>10	0.1	0.2	87
11	25% SIS	0.5	nhFS	–	–	–	–	89
12	+5% SB	0.8	E	1.1	1.7	0.3	0.5	15
6	+15% SB	0.8	lF	>10	>10	0.2	0.4	40
13	+25% SB	0.8	CFS	>10	>10	0.2	0.4	92

E, ellipsoids; CFS, continuous fibrillar structure; nhFS, non-homogeneous fibrillar structure; lF, long fibrils

phase which is known to be lamellar for this composition of the starblock. The difference is, however, very large to be assigned to interfacial factors only.

Triblock SBS and SBS_{r1} have similar styrene content and similar morphologies although the first is Newtonian and has a high molecular weight and the second is non-Newtonian with low-molecular-weight branches. The only possible interpretation is that these different properties finally result in the same number of entanglements.

The results are summarized in *Table 3* according to the following arguments. Non-Newtonian behaviour is a qualitative indicator of the presence of entanglements. When the molecular weight exceeds the critical molecular weight for entanglement formation, the number of entanglements and hence the elastic properties of the melt rise with molecular weight. They stabilize the filaments and increase the probability of obtaining long filaments and extended co-continuous phases. Examination of *Table 3* shows that a rough semi-quantitative interpretation of the results could be obtained in this way.

According to these results, it is proposed that a high molecular weight which favours the formation of entanglements is an important parameter for the formation of elongated, co-continuous structures.

Effect of the composition of the blend

Three compositions have been studied for blends containing SIS or diblock SB. The morphology and the quantity of copolymer which can be extracted by a selective solvent are given in *Table 4* and analysed in *Table 3*. Examination of the results shows that SIS and PE are co-continuous when the blend contains about 15% SIS. For PE containing the diblock SB, 25% SB has to be present to allow co-continuity.

DISCUSSION

Two steps are important for the development of morphologies in extruded–blown blend films:

- dispersion of the minor phase in the complex shear and elongational field of the extruder barrel and die;
- elongation of the molten blend at the exit of the die and freezing of the morphology by rapid cooling.

The theoretical approaches proposed in the literature for these steps will be briefly summarized here and applied to our systems.

Dispersion

During extrusion, the materials undergo complex shear and elongational force fields and temperature profiles along the barrel and the die. Deformability and dispersion of the droplets have been discussed by many authors (references 8–11 and references cited therein). Since these parameters depend on experimental conditions, the reported behaviour can only be considered as roughly indicative. It is often admitted that long filaments and discrete droplets are formed if η_d/η_m values are respectively low (>0.7) and high (>2.2). In the intermediate range, short threads are observed.

Master equations correlating the size of non-Newtonian particles in a non-Newtonian matrix in the case of a co-rotating twin-screw extruder have been proposed by Wu[6] and will be given here since they are the best approximations to our conditions that we could find in the literature:

$$G\eta_m a/\gamma = 4(\eta_d/\eta_m)^{0.84} \quad \text{if } \eta_d/\eta_m > 1 \tag{1}$$

where G is the shear rate, a is the diameter of the particle and γ is the interfacial tension. Few experimental results support the part of the curve corresponding to $\eta_d/\eta_m < 1$. It was approximated by the same equation fitted by the exponent, 0.84. This equation shows that the abscissa $Gn_m a/\gamma$ increases with η_d/η_m for $\eta_d/\eta_m > 1$. It also means that for a given system characterized by a given value G, η_m and γ, the diameter of the particles increases with η_d/η_m, indicating that the particles are less easily deformed and broken when η_d/η_m increases. In the same way, it can be deduced that the smaller particles are obtained when $\eta_d/\eta_m = 1$.

For $\eta_d/\eta_m < 1$ (blends 1 to 6), the droplets are highly deformable. Deformation of the droplets in the shear field of the extruder but also during drawing and blowing at the exit of the die (see below) is followed by breaking if the time-scale of the experiment allows Tomotika's mechanism[12,13] to be operative in the case of Newtonian melts or if shear thickening or yielding behaviour are absent in the case of non-Newtonian melts. The transient morphologies obtained at the exit of the die before elongation have not been isolated in the present work.

Elongation

For long filaments or co-continuous elongated structures to be formed, the initial droplet of dispersed phase has to undergo elongation without breaking, respectively in one or two directions. The problem of formation and break-up of filaments has been revisited recently by Elmendorp[12]. It can occur by various mechanisms.

In the case of Newtonian matrix and dispersed phase, a sinusoidally distorted filament is formed. When the distortion wavelength exceeds the circumference of the thread, the interfacial area decreases when the distortion amplitude increases. For this reason the thread is unstable. It breaks when the distortion amplitude is larger than the average radius of the thread. The time necessary to break, t_b, is given by:

$$t_b = \frac{1}{q} \ln \frac{0.8R_0}{\alpha_0} \tag{2}$$

where R_0 and α_0 are the initial radius and amplitude. The parameter q is a complex function which decreases by increasing the viscosity of the matrix, the radius of the undisturbed filament or η_d/η_m. It increases by increasing the interfacial tension. For the PE–SBS blend processed in conditions where SBS is Newtonian (240°C), t_b can be evaluated to be very short (<0.15 s) by comparison with an example reported by Elmendorp[12]. Since the elongation time can be evaluated to be of the order of 4 s in our extrusion conditions, breaking of the filament will occur.

In the case of non-Newtonian dispersed and continuous phases, filament stabilization is explained either by tension thickening of the dispersed phase or by the existence of a yield stress in the stress–rate of elongation curve. The first point is straightforward: tension thickening leads to filament stabilization whereas tension thinning leads to filament breaking. The importance of yield stress has been emphasized by Elmendorp[12]. An elongated sinusoidally distorted thread will not break if it exhibits a yield stress greater than or equal to the pressure difference P_s between positions in the thread with maximal and minimal radius. This pressure difference results from interfacial effects.

Non-Newtonian elongational viscosity η_E which governs elongation and breaking of the filaments can now be related to the molecular properties of the filament. It has conveniently been separated into two contributions by Schlund and Utracki[14]. The first (η_{EL}) is due to linear viscoelastic response, the other (η_{ES}) originates in the structural changes of the specimen during deformation. This last component is due to intermolecular interactions and entanglements. It thus gains importance with increasing molecular weight and branching as is well known for LDPE, is higher for polar polymers than for non-polar ones and could be favoured below the order–disorder transition of triblock and starblock copolymers.

Concerning the polymers used in the present work, LDPE is well known to be tension thickening. For block copolymers, elongational properties have only been reported for SBS at 150°C, i.e. below the order–disorder transition. At the blending temperature used in the present work (240°C), it is Newtonian and the observed breaking of the filaments is explained by Tomotika's theory developed in the preceding paragraph. Broken filaments are also observed with the two starblock copolymers SBS_{r1} and SBS_{r3} although branching could favour tension thickening in these cases. The molecular weight of the internal PB blocks is higher than the critical molecular weights for entanglement formation (6000) and thus also favourable to tension thickening. However, the star structure probably limits the mobility of the branches and sterically hinders the formation of entanglements. This probably justifies filament breaking in these last two non-Newtonian systems. Two non-Newtonian copolymers (SIS and diblock SB) yield co-continuous structures. Their molecular weight is higher than that of the other copolymers and also higher than the critical molecular weight for entanglement formation. This could favour tension thickening and also the existence of yield points. A comprehensive study of the elongational behaviour of molten block copolymers is urgently needed to have a definitive interpretation of these results.

Effect of increasing copolymer concentration: co-continuity and phase inversion

A detailed investigation of the morphology of the PE–SIS blend has shown that the volume and shape of the dispersed particle increases with the weight fraction of the dispersed phase[3].

Phase inversion has often been found to occur[8,15] in shear fields when the relation:

$$\eta_d/\eta_m = \phi_d/\phi_m \quad (3)$$

(where ϕ_d and ϕ_m are the volume fractions of the dispersed phase and of the matrix, respectively) is verified. A theory of shear flow-induced phase inversion was proposed[8] and showed that the empirical relation (equation (3)) is a good approximation. In fact, continuity settles progressively through a broad range of sample composition where increasing fraction of the dispersed phase can be extracted by a selective solvent. Co-continuity between the two phases corresponds to phase inversion. It is realized when each phase can be quantitatively extracted by a selective solvent.

In the present work co-continuity is observed for SIS and SB blends when the values of η_d/η_m are respectively about 0.18 and 0.33, instead of 0.5 and 0.8 predicted by equation (3). In the present case, however, there is an important contribution of the elongational flow to the generation of co-continuous phases. It can readily be realized that the composition corresponding to phase inversion and thus to the formation of co-continuous phases will be different for an increasing number of randomly distributed spheres, of randomly distributed anisotropic particles like filaments or for the oriented anisotropic filaments that are formed in the elongational fields which determine the morphology of this blend. The degree of phase continuity can be assimilated to the accessibility of a dispersed phase as discussed by Goheen and Wool[16]. Co-continuity corresponds to 100% accessibility; accessibility can be calculated as a function of composition by computer simulation, as has been done recently by this author for spherical starch particles in a PE matrix. This could also be done but has, to our knowledge, never been published, for an oriented fibrillar dispersed phase in a continuous matrix.

The PE–SBS blends are far from co-continuous, even when 25% SBS is present. The behaviour of this blend is explained by the Newtonian behaviour of SBS in the melt and attributed to the short breaking time of the transient filaments as discussed in the preceding sections.

CONCLUSIONS

Long filaments or elongated co-continuous structures can be obtained by extrusion–blowing of styrene–butadiene or styrene–isoprene copolymers in PE if the η_d/η_m values are low enough to promote efficient deformation and dispersion of the minor component in the matrix before the exit of the die. This constitutes the first step of blend processing. Extension followed by breaking of the filaments was observed for the Newtonian SBS; breaking time according to Tomotika's theory can indeed be evaluated as being shorter than the elongation time in the processing conditions used in the present work. Extension without breaking in one or two directions at the exit of the die is possible only if the dispersed phase is non-Newtonian in the elongation conditions. Ideally the elastic component of the melt viscosity counteracts filament breaking by Tomotika's mechanism either through the existence of a yield stress or by tension thickening. In the present work, co-continuous structures have been obtained for non-Newtonian SIS and diblock SB copolymers. This is attributed to the high molecular weight of the polybutadiene and polystyrene blocks in SB and of the polyisoprene block in SIS.

Dispersed ellipsoids which could initiate random fragmentation of photodegraded films[1,4] are obtained for highly dispersible SIS copolymers ($\eta_d/\eta_m < 1$) present at low concentration to prevent coalescence. For a given value of η_d/η_m, and whatever this value, the dimensions of the ellipsoids increase with interfacial tension and decrease with shear rate and viscosity of the matrix.

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REFERENCES

1 Getlichermann, M., Trojan, M., Daro, A. and David, C. *Polym. Degrad. Stab.* 1993, **39**, 55

2 Trojan, M., Jacobs, R., Piens, M. and David, C. *Polymer* 1991, **32**, 510

3 David, C., Getlichermann, M. and Trojan, M. *Polym. Eng. Sci.* 1992, **32**, 6

4 Getlichermann, M. and David, C. *Polym. Degrad. Stab.* 1994, **43**, 343

5 Min, K., White, J. L. and Fellers, J. F. *Polym. Eng. Sci.* 1984, **24**, 1327

6 Wu, S. *Polym. Eng. Sci.* 1987, **27**, 335

7 Ghijsels, A. and Raadsen, J. *Pure Appl. Chem.* 1980, **52**, 1359

8 Utracki, L. A. 'Polymer Alloys and Blends', Hanser, Munich, Germany, 1990

9 White, J. L. and Min, K. *Makromol. Chem. Macromol. Symp.* 1988, **16**, 19

10 Taylor, G. I. *Proc. R. Soc. (London) A* 1934, **46**, 501

11 Elmendorp, J. J. and Maalcke, R. J. *Polym. Eng. Sci.* 1985, **25**, 1041

12 Elmendorp, J. J. *Polym. Eng. Sci.* 1986, **26**, 418

13 Tomotika, S. *Proc. R. Soc. (London) A* 1935, **150**, 322

14 Schlund, B. and Utracki, L. A. *Polym. Eng. Sci.* 1987, **27**, 359, 380

15 Miles, I. S. and Zurek, A. *Polym. Eng. Sci.* 1988, **28**, 896

16 Goheen, S. M. and Wool, R. P. *J. Appl. Polym. Sci.* 1991, **42**, 2691