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Tensile moduli of co-continuous polymer blends

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Abstract

Co-continuous blends of polyethylene with polypropylene or polystyrene are shown to exhibit high tensile moduli. The experimental results exceed predictions of the moduli using existing models for co-continuous morphologies, and approach the level of the parallel model. These high moduli are found to be isotropic to a good degree, in contrast to fibrillar polymer blends which can have such high moduli only in one direction. © 1999 Published by Elsevier Science Ltd. All rights reserved.

Keywords: Co-continuous morphology; Mechanical properties; Tensile modulus

1. Introduction

Blending of polymers is an effective way of tailoring materials for specific applications. Most polymers are immiscible and blending usually leads to heterogeneous morphologies. The type and scale of these morphologies determine the properties of the blend [1]. This holds especially for mechanical properties such as the tensile modulus. In the case of a droplet–matrix morphology the tensile modulus of a blend will largely be determined by the modulus of the matrix phase. The modulus of a fibrous blend can, however, be largely determined by the modulus of the dispersed (fibrous) phase, especially in oriented samples [2,3]. Co-continuous blends are expected to fall in between these extremes: neither of the blend components is expected to dominate the moduli of the blends, however, relatively high and isotropic values may be expected because of their interpenetrating phase structure.

The purpose of this study is to demonstrate that co-continuous morphologies are characterised indeed by high isotropic tensile moduli, exceeding values as predicted by existing models for co-continuous structures. In previous papers [4–7] we have discussed formation, conditions for existence and stability of co-continuous polymer blends. In the present paper we report tensile properties of polyethylene–polypropylene (PE–PP) and polyethylene–polystyrene (PE–PS) blends as a function of composition and morphology, and compare these with existing theoretical models. In a forthcoming paper results for blends with thermoplastic elastomers will be shown and a new model for the moduli of co-continuous structures will be introduced [8].

2. Theory

Tensile moduli of polymer blends are strongly dependent on the composition and morphology. In literature several models can be found which describe tensile moduli of blends as a function of the composition [9–15]. Most of these models are valid for a given morphology, others leave the morphology unspecified. Changes of morphology with composition are common in polymer blends, such as the transformation of a dispersed morphology into a co-continuous morphology. For this reason most models are applicable only within limited composition ranges.

The moduli of polymer blends generally range between an upper bound, E_U, given by the parallel model [9]:

$$E_U = \phi_1 E_1 + \phi_2 E_2 \quad (1)$$

and a lower bound, E_L, given by the series model [9]:

$$\frac{1}{E_L} = \frac{\phi_1}{E_1} + \frac{\phi_2}{E_2} \quad (2)$$

in which E_i and ϕ_i are the modulus and the volume fraction of phase i. Although the parallel and series models are, strictly speaking, valid only for simple and idealised structures, they are frequently used as limiting models regardless of morphology.

For particle/matrix morphologies the relation between modulus and composition has been given by Halpin [10]. Particles of the second blend component of uniform aspect

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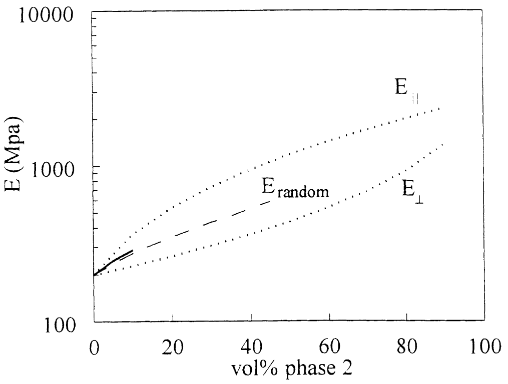

Fig. 1. Modulus versus composition with $E_1 = 200$ MPa and $E_2 = 2500$ MPa: (…) represents $E_{\parallel}$ and $E_{\perp}$ with $L/D = 10$ up to 90 vol.% phase 2 as calculated from Eqs. (3a) and (3b); (--) and (—) represent E_{random} with $L/D = 10$ and 40 upto $\phi_{\mathrm{m}} = 45$ and 10 vol.% phase 2, respectively, as calculated from Eqs. (4a) and (4b).

ratio L/D are supposed to be oriented in one direction. The modulus in this direction, $E_{\parallel}$, is given by:

$$E_{\parallel} = E_1 \frac{1 + AB\phi_2}{1 - B\phi_2} \tag{3a}$$

with:

$$A = 2\frac{L}{D}; \qquad B = \frac{(E_2/E_1) - 1}{(E_2/E_1) + A}. \tag{3b}$$

The modulus according to Eqs. (3a) and (3b) is plotted in Fig. 1 for $L/D = 10$. For aspect ratios larger than 100 the calculated moduli approach the upper bound (Eq. (1), which was confirmed experimentally by Crevecoeur [3]. The modulus perpendicular to the direction of orientation, $E_{\perp}$ is also given by Eqs. (3a) and (3b), if $A = 0.5$ is used instead of $2L/D$ [10]. $E_{\perp}$ is much lower than $E_{\parallel}$, as is shown in Fig. 1.

The tensile modulus for a randomly oriented dispersion is given by [11]:

$$E_{\mathrm{random}} = \frac{2}{\pi} \int_0^{\pi/2} E_{\theta}\, \mathrm{d}\theta \tag{4a}$$

in which E_{θ} is the angular dependence of the tensile modulus. This modulus is:

$$E_{\theta} = \frac{E_{\parallel} E_{\perp}}{E_{\parallel} + (E_{\perp} - E_{\parallel}) \cos^4 \theta} \tag{4b}$$

in which $E_{\parallel}$ and $E_{\perp}$have the same meaning as that defined earlier. Two examples of moduli of random blends are shown in Fig. 1, for different aspect ratios. Eqs. (3) and (4) are applicable at concentrations of the dispersed phase up to the maximum packing density of the dispersed particles. In the case of a hexagonal packing of parallel rods this maximum packing density can be up to about 90 vol.% whereas it is much lower for randomly oriented rods or for spheres. The maximum packing density of randomly oriented rods depends on their aspect ratio L/D and is given by [5,16]:

$$\frac{1}{\phi_{\max}} = 1.38 + 0.0376\left(\frac{L}{D}\right)^{1.4}. \tag{5}$$

An increase in the aspect ratio of the dispersed phase leads to a decrease of the maximum packing density and, consequently, to a smaller range of validity of Eqs. (4a) and (4b). This is illustrated in Fig. 1 for values of $L/D = 10$ and $L/D = 40$ limiting the maximum composition for Eqs. (4a) and (4b) to $\phi = 43$ and 12 vol.%, respectively.

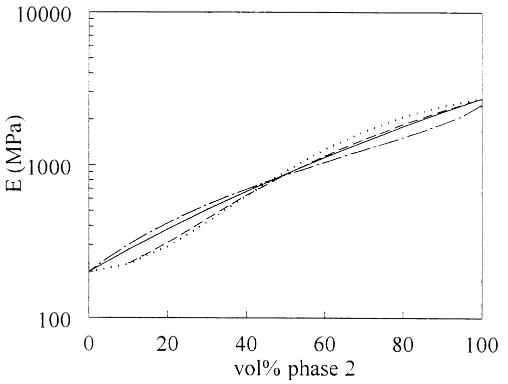

Fig. 2. Modulus versus composition with $E_1 = 200$ MPa and $E_2 = 2500$ MPa: (—), (…), (--) and (- - -) calculated with Eqs. (6) and (7) with $(n - 1)/n = 0.5$, Eq. (8) with $T = 1.9$ and $\phi_{\mathrm{cr}} = 0.01$, and Eq. (9), respectively.

For co-continuous polymer blends different equations for the tensile modulus as a function of the composition have been proposed. The relation given by Davies [12], assuming the blend to be macroscopically homogeneous and isotropic, takes the shape:

$$E^{1/5} = E_1^{1/5}\phi_1 + E_2^{1/5}\phi_2. \tag{6}$$

It is supposed to be applicable for co-continuous structures without specifying any details. Coran and Patel [13] proposed an equation which is intended to account for phase inversion at a certain composition of the blend. The modulus is expressed as a function of the upper and lower bounds using a fit parameter, n, which is supposed to depend on wetting and compatibility and to give the point of phase inversion as $\phi = (n - 1)/n$:

$$E = \phi_2^n (n\phi_1 + 1)(E_{\mathrm{U}} - E_{\mathrm{L}}) + E_{\mathrm{L}}. \tag{7}$$

Lyngaae-Jørgensen et al. [14] have given a relation for the moduli of blends above the percolation threshold of the minor component:

$$E = E_1 + (E_2 - E_1)\left[\frac{\phi_2 - \phi_{\mathrm{c}}}{1 - \phi_{\mathrm{c}}}\right]^T \tag{8}$$

in which $T = 1.7$–1.9 and $\phi_{\mathrm{c}} = 0.16$, for fibres ϕ_{c} is much lower. Kolarik [5] introduced the cross orthogonal skeleton (COS) model for the mechanical properties of a

Table 1
Trade names and shear viscosities at $\dot{\gamma} = 22\, s^{-1}$ of the polymers used [5,6]

Sample code	Trade name (manufacturer)	Viscosity (Pa s) at 200°C
PS1	Hostyrene N2000 (Shell)	780
PS2	Hostyrene N7000 (Shell)	2400
PE1	Stamylan LD 2100TN00 (DSM)	1860
PE2	Stamylan LD 2102TN26 (DSM)	960
PP	Stamylan PP 19MN10 (DSM)	520

co-continuous morphology. The modulus of the COS model is:

$$E = E_1(1-f)^2 + E_2 f^2 + \frac{2f(1-f)}{(1-f)/E_1 + f/E_2} \tag{9}$$

in which f is related to the volume fraction as $\phi_1 = (1-f)^2(1+2f)$ [15].

The moduli calculated with Eqs. (6)–(9) are shown in Fig. 2. Despite the different background, the predictions of these theories with $E_1 = 200$ MPa and $E_2 = 2500$ MPa do not differ very much.

Any relation for the tensile modulus of a polymer blend requires a proper definition of the structure to which it applies. A gradual change in structure from dispersed to fully co-continuous takes place in heterogeneous polymer blends on increasing the volume fraction of the minor component [5,13]. In dilute systems droplet–matrix structures prevail. At higher volume fractions, starting at the percolation threshold, interconnected structures of the minor component develop until at a still higher volume fractions all of the minor component is incorporated in a single continuous phase network inside the matrix component and a fully co-continuous morphology is obtained. This co-continuous morphology can exist over a range of compositions, depending on the blending conditions [5]. Beyond this range, at still higher volume fractions, the phase network of the erstwhile matrix component starts breaking down until finally this component becomes dispersed.

From this picture it will be clear that Eqs. (6)–(8)cannot be expected to give a proper description of the moduli of the blends over a broad composition range. The relation of Lyngaae-Jørgensen et al. [14] does indeed account for the onset of percolation, however it does not account for the onset of full co-continuity. The COS-model [15] does account for full co-continuous morphologies, but its predictions hardly differ from the values obtained by Eqs. (6)–(8).

In fully co-continuous blends both components form single continuous and interpenetrating structures. For low volume fractions of the minor component such a fully continuous structure can exist only if the ligaments of the phase network have an extended shape. By depicting this continuous phase network as a random assembly of rod-like particles at their maximum packing density, one obtains a crude model of a continuous phase network [5]. The limiting volume fraction for existence of such a phase network will be given by Eq. (5) relating the composition limits to the aspect ratio of the network ligaments, which in turn can be related to the blending conditions [5]. By applying Eq. (5) to both blend components a composition range is obtained within which fully co-continuous structures can exist. These fully co-continuous blends will have tensile moduli which are determined by the moduli of both components. As these blends show interpenetrating network structure we expect these tensile moduli to exceed predictions by the traditional models for dispersed and co-continuous structures. Outside the composition range for full co-continuity the phase network breaks down and a gradual decrease of the moduli of the blends may be expected.

Table 2
Blend components, the expected volume fractions for the upper limit of co-continuity, ϕ_U, (estimated) and for the lower limit of co-continuity ϕ_L (measured)

Series	Blend components	ϕ_u (vol.%) upper limit (estimated)	ϕ_l (vol.%) lower limit (experimental)
I	PS1, PE1	56	35
II	PS1, PE2	56	46
III	PS2, PE2	78	56
IV	PE2, PP	79	27

3. Experimental

Two grades of PS, two grades of low density PE and one grade of PP, shown in Table 1, were used to prepare the PE–PS and PE–PP blend series shown in Table 2. Nine different compositions (9, 17, 27, 35, 46, 56, 67, 78 and 88 vol.% PS in PE and 9, 18, 28, 37, 47, 58, 69, 79 and 89 vol.% PE2 in PP) were made by extrusion at 200°C. The mixing equipment consisted of a 20 mm Collin laboratory extruder equipped with a transport screw, and a static mixer in series with the extruder containing 10 Ross ISG 15 mm diameter mixing elements. Each element contains four channels with a radius of 0.135 cm. The average shear rate in the channels was estimated to be 22 s^{-1}. The extruder was equipped with a film extrusion die with an opening of 100 mm width and 1.5 mm thickness. Directly after leaving the extruder the film was cooled rapidly by compressed air. The film was collected with take up rolls.

Co-continuity in the blends was checked by extraction experiments. The strands were broken in liquid nitrogen

Table 3
Percentage of PS or PE extracted from the blends of series I–III and series IV, respectively, as a function of the volume fraction

% PS in blend	% PS extracted (series I)	% PS extracted (series II)	% PS extracted (series III)	% PE in blend	% PE extracted (series IV)
9	39	15	34	9	76
17	65	49	48	18	65
27	83	76	63	28	100
35	100	95	84	37	100
46	100	100	93	47	100
56	100	100	100	58	100

and extraction was performed in a Soxhlet extraction apparatus for 3 days. This was sufficient for complete removal of the soluble fraction. Five pieces of the extruded strands were used to obtain an average value. The samples were checked whether they were self supporting after extraction. The PS can be extracted from the PE–PS blends with 2-butanone and PE can be extracted from the PE–PP blends with iso-octane. In the case of co-continuity 100% of the PS phase from the PE–PS blends or 100% of the PE phase from the PE–PP blends can be extracted [17]. It was not possible to extract the PE phase from the PE–PS blends or the PP phase from the PE–PP blends without damaging the remaining phase. For that reason the upper limit for the composition range of co-continuity could not be determined experimentally and was estimated on the basis of stability of the sample after extraction.

From the extruded films several test pieces were punched out parallel and perpendicular to the original flow field. The test pieces were dumbell shaped (ISO/DIS 8256A); the cross section being 2.5 × 1.5 mm and the length being approximately 60 mm. The tensile measurements were done with an Instron Universal testing machine. Stress–strain curves were determined at a speed of 10 mm min^{-1}. From these curves the tensile modulus and strength were determined. Five test bars were tested for each composition both parallel and perpendicular to the original flow direction.

4. Results and discussion

The blend systems PE–PS (series I, II and III) and PP–PE (series IV) were chosen for their differences in composition range for full co-continuity [5,6]. Apart from checking the validity of Eqs. (6)–(9) this enabled a comparison of blends with the same composition but with different morphologies. The results of the extraction experiments are shown in Table 3 and the corresponding lower limiting volume fractions together with the estimates for the upper limits are shown in Table 2. From this table it can be seen that co-continuity in series I, II and III can be found at 35–56 vol.% PS1 in PE1, 46–56 vol.% PS1 in PE2, 56–78 vol.% PS2 inPE2 and 28–79 vol.% PP in PE2. The properties of these blends are compared and are discussed in detail later.

4.1. PE–PS blends

The moduli of the blends of series I, II and III as a function of the composition are shown in Figs. 3–5, respectively, both for samples taken parallel and perpendicular to the original flow direction. The values of these moduli are compared with the values predicted by Eqs. (6)–(9). For the sake of simplicity only the predictions of Eq. (6) are shown in Figs. 3–5.

Co-continuity in blends of series I is found at 35–56 vol.% PS1 in PE1. The moduli of the blends exhibiting

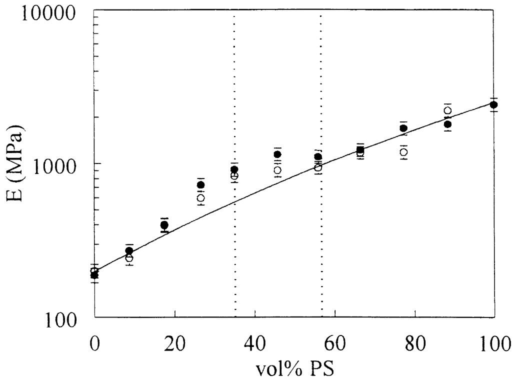

Fig. 3. Young's modulus versus composition for PE–PS blends (Series I): ● and ○ represent the modulus parallel and perpendicular to the original flow field. The experimental values are compared with Eq. (6) (full line). The composition limits for co-continuity are indicated with (…).

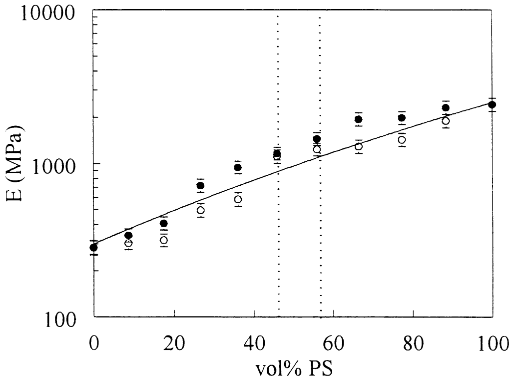

Fig. 4. Young's modulus versus composition for PE–PS blends (Series II): ● and ○ represent the modulus parallel and perpendicular to the original flow field. The experimental values are compared with Eq. (6) (full line). The composition limits for co-continuity are indicated with (…).

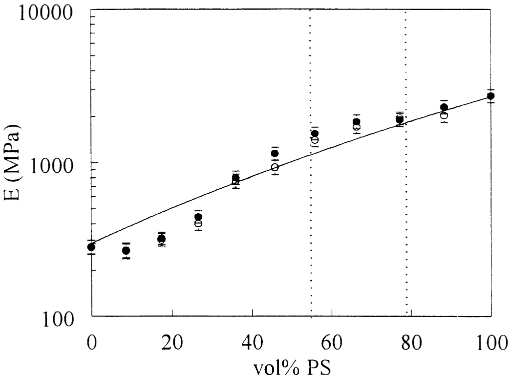

Fig. 5. Young's modulus versus composition for PE–PS blends (Series III): ● and ○ represent the modulus parallel and perpendicular to the original flow field. The experimental values are compared with Eq. (6) (full line). The composition limits for co-continuity are indicated with (…).

a co-continuous morphology are higher than the one calculated with Eqs. (6)–(9). Above 56 vol.% PS some anisotropy can be seen which is due to some skin-core effects. Although no fully continuous PS phase was obtained the modulus of the samples with 27 vol.% PS is obviously raised to a higher level. In this blend more than 80% of the PS phase was extracted.

The blends of series II exhibit a co-continuous morphology in a narrow composition range: 46–56 vol.% PS1 in PE2. In contrast to the blends of series I the blends of series II have anisotropic properties caused by the skin core structures. Only in the case of full continuity of the PS phase in the blend with 46 and 56 vol.% PS an isotropic material was obtained. The modulus of this isotropic material is higher than the values calculated with Eqs. (6)–(9).

Co-continuity in series III was found within a composition range of 56–78 vol.% PS. Above 36 vol.% PS the modulus of the blend is already raised. Although no full co-continuity was found more than 80% of the PS phase could be extracted. The moduli of the blends in case of full co-continuity were higher than the equivalent moduli of series I with the same composition where no co-continuity was found. Again, predictions of Eqs. (6)–(9) cannot be used in this case.

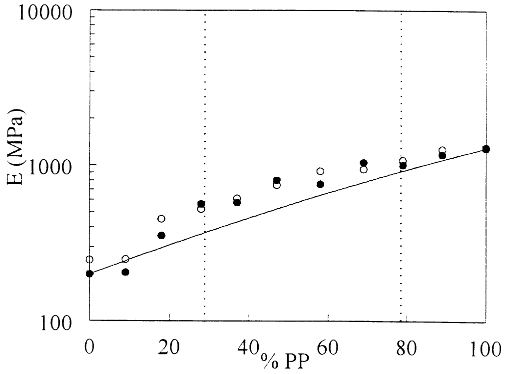

Fig. 6. Young's modulus versus composition for PE–PP blends (Series IV): ● and ○ represent the modulus parallel and perpendicular to the original flow field. The experimental values are compared with Eq. (6) (full line). The composition limits for co-continuity are indicated with (…).

4.2. PE–PP blends

The moduli of the blends of series IV as a function of the composition are shown in Fig. 6. Co-continuity in these blends is found within a broad composition range; 28–79 vol.% PP in PE2. The moduli of the blends exhibiting a co-continuous morphology are higher than the ones calculated with Eqs. (6)–(9) just as for blends of PE–PS. The PE–PP blends exhibit this behaviour over the entire broad composition range within which full co-continuity can be generated.

5. General discussion

Fully co-continuous blends are found to be characterised by values of their Young's moduli which are high and isotropic. These large values exceed the predictions of existing models and are nearer to the upper bound for mixtures. This is illustrated in Fig. 7 which summarises the results for the PE–PS blends. These high moduli of co-continuous blends are probably the result of a very effective stress transfer in the fully interpenetrating phase networks. This is not accounted for by existing models for moduli of polymer blends, perhaps with exception of the COS model. However, the COS model appears to predict values approaching the upper bound only if the moduli of the blend components differ many orders of magnitude, which is not the case in our blends.

The level of the moduli of co-continuous blends approaches the parallel model and appears to be isotropic, which means that in these blends both phases fully contribute to the blend modulus in all directions. Such a level cannot otherwise be obtained in polymer blends, except in fibrous blends and then only in one direction provided these blends are perfectly oriented. This makes co-continuous morphologies much more effective than fibrous morphologies for reinforcing purposes.

The high level of moduli and isotropic behaviour of co-continuous blends is not confined to one single composition, but can be achieved over a wide composition range, depending on processing conditions [5,6]. Beyond this range a gradual decrease in values of the moduli is observed, down to the level of droplet–matrix systems, depending on the degree of continuity. Also, a more pronounced anisotropy is observed beyond this range, associated with distinct skin/core structures.

By creating a co-continuous structure instead of a droplet–matrix structure in a given blend the modulus of the blend can be significantly raised, depending on the ratio of the moduli of the blend components and the composition.

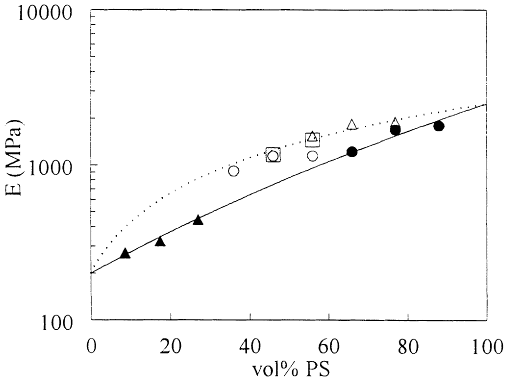

Fig. 7. Young's modulus versus composition for PE–PS blends in the case of co-continuous morphologies (○, □ and △ represent series I, II and III, respectively) and a dispersion (● and ▲ represent series I and III, respectively) These experimental values are compared with Eq. (1) (……) and Eq. (6) (full line).

For example, in a blend of 30% PS in PE changing the droplet–matrix structure into a fully co-continuous structure will raise the modulus from approximately 400 MPa to approximately 750 MPa, resulting in almost a doubling of the stiffness of the material. This makes co-continuous morphologies a versatile means of obtaining new materials.

6. Conclusion

Blends of polyethylene–polystyrene and polyethylene–polypropylene with a co-continuous morphology show high isotropic tensile moduli. These high moduli exceed predictions by the models valid for co-continuous morphologies and approach the parallel model. Changing the structure from a droplet–matrix to a co-continuous structure at a given composition can result in a quite significant increase in modulus.

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