

Structured polymer blends

Citation for published version (APA):

Meijer, H. E. H., Lemstra, P. J., & Elemans, P. H. M. (1988). Structured polymer blends. *Makromolekulare Chemie, Macromolecular Symposia*, 16, 113-135. <https://doi.org/10.1002/masy.19880160109>

DOI:

[10.1002/masy.19880160109](https://doi.org/10.1002/masy.19880160109)

Document status and date:

Published: 01/01/1988

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
- The final author version and the galley proof are versions of the publication after peer review.
- The final published version features the final layout of the paper including the volume, issue and page numbers.

[Link to publication](#)

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license above, please follow below link for the End User Agreement:

www.tue.nl/taverne

Take down policy

If you believe that this document breaches copyright please contact us at:

openaccess@tue.nl

providing details and we will investigate your claim.

STRUCTURED POLYMER BLENDS

H.E.H. Meijer, P.J. Lemstra and P.H.M. Elemans^{*}

Dept. of Polymer Technology, Eindhoven University of Technology,
P.O. Box 513, 5600 MB Eindhoven, The Netherlands

Abstract: Various morphologies can be realized via processing of incompatible polymer blends such as droplets or fibers in a matrix and stratified or cocontinuous structures as is shown for the model system polyethylene/polystyrene. The structures induced are usually intrinsically unstable. Modelling of extrusion processes and continuous mixers yields expressions for the shear rate and shear stress but also for the limited residence time and the number of reorientations. These results could be combined with detailed knowledge of respectively distributive and dispersive mixing processes to predict the development of various morphologies as a function of time. Control of morphology is of utmost importance. In the case of droplets in a matrix, usually encountered in toughening of glassy polymers, the use of compatibilizers and/or reactions at the interphases is utilized. However, in designing specific morphologies i.e. structured polymer blends, fixation of intermediate morphologies before final processing is a prerequisite. Some preliminary results will be presented.

INTRODUCTION

Similar to rubbers and thermosets, thermoplastic polymers are hardly used in their pure form. Additives are needed to improve for example processability and lifetime (lubricants, stabilizers), modulus and strength (mineral fillers like glass beads, chalk, clay, mica or glass-fiber reinforcement), appearance and colour (pigments), conductivity (conductive fillers like steelwire, aluminium flakes or carbon) or flammability (flame retardants). Despite of the continuous development of new polymers, a large number of properties can only be obtained when different polymers are combined. Well known examples are the impact modified, (rubber) toughened polymers, where polymers with different glass transition temperatures are blended, and the group of barrier polymers for packaging, where specific polar and apolar polymers are combined in order to increase the resistance against water and gas (oxygen, carbon dioxide) transport simultaneously.

Of course there are various routes to combine polymers in order to achieve optimum properties. Polymer blends can be made directly on a microscopic scale in the reactor. The other extreme, on a macroscopic scale, is co-extrusion to produce multi-layered structures via casting, blowing, blow moulding and injection-moulding.

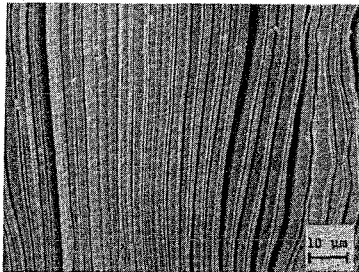
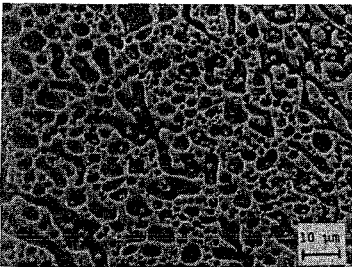
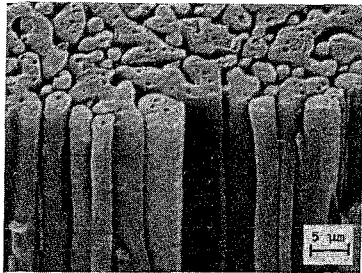
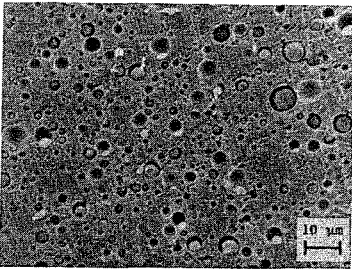
Extrusion (melt) blending is a route in between and in principle a rather flexible one. The limited miscibility of polymers complicates this processing route however. Miscibility of different types of polymers is rather an exception than rule (Ref. 1,2) due to, amongst other factors, their small configurational entropy of mixing. Unless specific interactions exist phase separation usually occurs (Refs. 3,4). Of course processing of miscible polymer systems is of interest since tailor made properties can be obtained by just changing the volume fractions. Although over 300 pairs of miscible polymers are known (Ref. 2) only a few systems have been commercialized. Well known is the successful blend PPE/PS. Other systems of commercial interest are PC/PET, PC/PBT and SMA/ABS (Ref. 5).

Polymer blends containing two crystallizable constituents which are miscible in the melt are of special interest since the morphology in the solid state can be influenced via optimized crystallization conditions. An example is a blend of nylon-6 and ethylene-vinyl alcohol copolymer (EVAL). The copolymer EVAL possesses excellent barrier properties towards oxygen but is rather brittle. The copolymer, however, is miscible with nylon-6 in the melt and after processing, extruded films can be obtained combining good mechanical properties, related to the nylon-6 matrix, with excellent barrier properties since nylon-6 crystallizes first and the EVAL copolymer concentration is enhanced in the amorphous zones (Ref. 6).

In general, however, we have to deal with incompatible polymers and depending on the processing conditions various morphologies can be obtained. Figure 1 displays some characteristic morphologies as obtained by extruding the incompatible blend of HDPE/polystyrene.

Figure 1. Scanning-Electron-Micrographs of polystyrene/polyethylene blends.
(Figs. 1a, 1b, and 1c display extrudates obtained from corotating twin screw extruder)

Figure 1d shows PS/PE composition made via Multiflux Static Mixer
see Ref. 23,24



All these morphologies were realized by extruding the model system HDPE/PS, by changing the volume fractions, viscosity ratio or processing route (Ref. 7). These structures have been classified before (Ref. 8) and found in practice, for example, with SBS block copolymers with different percentages of polybutadiene (Ref. 9,10), although there are, as one can imagine, one or two orders of magnitude difference in the scale between the incompatible system PE/PS and the blockcopolymers of SBS.

A lot of attention has been paid to obtain the morphology shown in Figure 1a. Of course the particle size is an important parameter. Experimental results have been reported by Borggreve (Ref. 11) for the system PA/EPDM, where it is clearly demonstrated that the tough-brittle transition temperature is not only depending on the amount of rubber (Figure 2) but also, at the same volume fraction, on the particle size of the dispersed phase (Figure 3). To obtain this small particle size of the dispersed rubbery phase maleic anhydride modified EPDM had to be used (Ref. 12).

On the basis of continuum and fracture mechanics, the experimental results of Figure 3 are explained in terms of local stress concentrations, caused by the low modulus of the dispersed phase, which promote a large number of small, local, overlapping crazing or shearbound deformations preventing the sample to break in a brittle manner (Ref. 13,14,15,16), stressing that the interparticle distance might be of more importance than the particle size (Ref. 14). Of course many other examples of improved impact strength for different matrices, can be given.

Structures as displayed in Figure 1b, i.e. fibrils in a matrix are aimed for reinforcement and in the fabrication of synthetic paper or artificial leather (Ref. 17,18,19).

Cocontinuous structures, Figure 1c, are usually obtained if a 50/50 blend is extruded or if the viscosity ratios of matrix and dispersion differ from one, at other mixing ratios as well (Ref. 20,21). The morphology of the cocontinuous structured is to some extent similar to, although the scale is two orders of magnitude higher than, IPN's based on direct chemistry (Ref. 22). To the authors' knowledge cocontinuous structures are not utilized as yet.

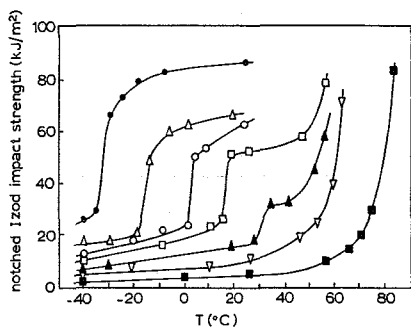


Figure 2. Brittle-tough transition in Nylon/rubber blends. Effect of rubber concentration. Data from Ref. 11.

(■ 0; ▽ 2.6; ▲ 6.4; □ 10.5; ○ 13.0; △ 19.6; ● 26.1 vol.%)

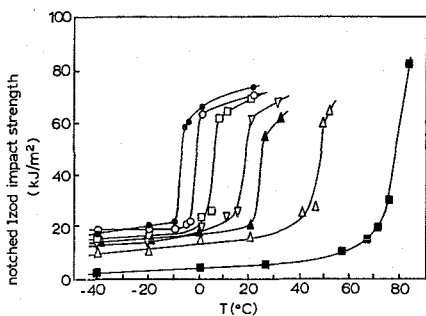


Figure 3. Brittle-tough transition in Nylon/rubber blends. Volume fraction of rubber is 26%. Effect of particle size. Data from Ref. 11.

■ Nylon-6; △ 1.59 μm ; ▲ 1.20 μm ; ▽ 1.14 μm ; □ 0.94 μm ; ○ 0.57 μm ; ● 0.48 μm

Stratified structures, see Figure 1d, can be made rather easily with specially designed static mixers like the Rossmixer or even better with the Multiflux mixer (Ref. 23,24). An example of practical use can be found in rainbow colouring luxury packaging films, where two polymers with different (light) breaking indices are combined (PMMA, PS) yielding a large number of layers of very small thickness each. The same system can, however, also be used for special barrier products, see below.

In order to understand how different morphologies in a blend of two incompatible polymers can be obtained, detailed knowledge of the processing equipment is necessary as well as an understanding of the mixing process itself. Moreover, most morphologies result from a local balance of different forces and consequently change continuously. Tools to control the morphology will be discussed after presenting details concerning the mixing processes.

MODELLING OF MIXING EQUIPMENT

From simplified flow analysis inside extruders, important overall parameters for mixing, such as residence time t , shear stress τ , shear rate $\dot{\gamma}$, total shear γ and the number of reorientations n_r can be deduced, at least locally. Especially if only melt-fed equipment is considered, all geometries such as extruder channels and clearances, but also converging flows with one or two moving boundaries, e.g. the two roll mill, have been analysed (Ref. 25,26,27,28). As a consequence the local conditions present for mixing are known even in typical compounding equipment like batchmixers, counterrotating twin screw extruders, especially Farrel Continuous Mixer, corotating twin screw extruders and reciprocating pin extruders like the Buss Cokneader.

Of course more elaborate calculations can be performed, yielding the complete three dimensional flow field in the complex geometries of the mixing sections in a corotating twin screw extruder (Ref. 29) and in the Buss Cokneader (Ref. 30,31). However, it has to be postulated a priori that these mixing sections are completely filled with melt and all calculations are still isothermal. In a recent paper we presented a more overall investigation of these continuous mixers (Ref. 32,33).

By simplifying the geometry again, the lengths which are completely filled with melt are determined dependent on the screw geometry used and on processing conditions like screw speed and (independently) metered throughput, (Figures 4 and 5). Moreover, via an averaged local heat balance the temperature rise during the compounding process can be calculated (Figure 5) and the specific energy (Figure 7), depending on processing conditions.

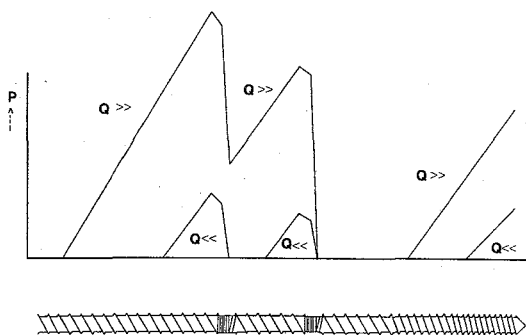


Figure 4. Pressure profiles (P) and completely filled lengths in a co-rotating twin screw extruder. Parameter: throughput (Q)

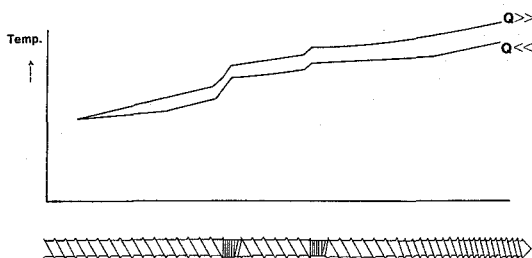


Figure 6. Calculated temperature rise in a co-rotating twin screw extruder. Parameter: throughput

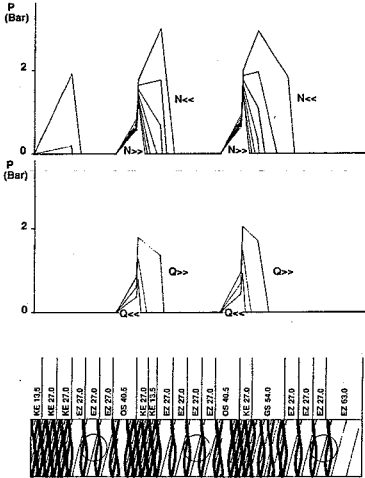


Figure 5. Pressure profiles and completely filled lengths in a Buss Cokneader with standard screw geometry. Parameter: screw speed (top) and throughput (bottom)

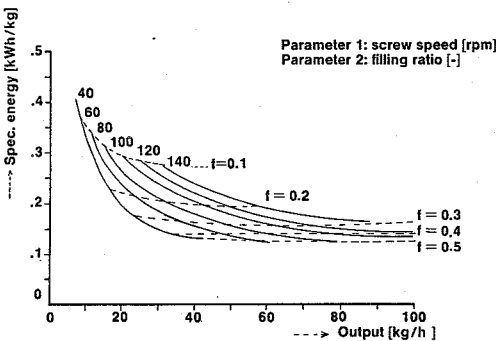


Figure 7. Specific energy in a corotating twin screw extruder as a function of throughput. Parameter: screw speed, degree of fill

If combined with criteria originating from a more complete model of the dispersion process itself, this would be sufficient to predict the morphology of an, as-processed, blend. However, despite of complicating factors like agglomeration of droplets or phase separation by crystallization, even the time effects of the dispersion process are not well understood. For the more simple dispersive mixing of carbon black in rubber (no time effects involved in breaking, no influence of particle size) in an extremely simplified geometry of a completely filled batchmixer (high shear section in series with an infinitely well mixed section), the fluid is continuously pumped from one section into the other, an interesting analysis exists (Ref. 34,35), which is later extended to two roll mills (Ref. 36). Provided that dispersive mixing of blends is better investigated, these samples may be extended to the modelling of the blending process in continuous mixers, since the mathematical tools, necessary for this kind of calculations, already exist from continuum mechanics, see for example (Ref. 37) and (Ref. 64).

DISTRIBUTIVE MIXING

For distributive mixing total shear γ and number of reorientations during the shear history are the only determining factors. This has been clearly illustrated by Ng and Erwin (Ref. 38) who performed a classical experiment which could have been done only in one's imagination as well: They place coloured slices of a polymer between two concentric cylinders and rotate one of them. The number of layers formed (measured radially) or the total interface, both measures for distributive mixing, is directly proportional to the total shear.

$$A = A_0 \gamma \quad (A = \text{surface}) \quad (1)$$

Since $\gamma = \dot{\gamma}t$, shear rate and -time are interchangeable consequently. If reorientation of the already formed layers, relative to the direction of flow, is present, mixing becomes much more effective. This is illustrated by stopping the rotation, freezing, cutting slices which are turned over 90° , an ideal reorientation consequently, heating up again and further shearing. If this procedure is repeated $n-1$ times, expression (1) reads (see Figure (8)),

$$A = A_0 (1/n \gamma)^n \quad (2)$$

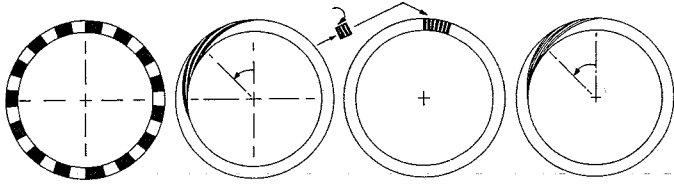


Figure 8. Shearing and reorientation during shear of black and white segments. From Rapra (Ref. 38)

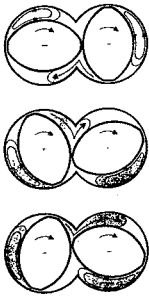


Figure 9. Mixing and reorientation in corotating twin screw extruders. (From W-P brochure)

A much more effective way of distributive mixing consequently, because reorientation does not cost energy (shear rate or -time). Static mixers are the prime exponents of mixing by reorientation n) rather than by total shear γ , but also in corotating twin screw extruders material is continuously reoriented relative to the shearing motion of the surfaces, when one screw scrapes the fluid from the other one (Figure 9). Although the pins of a Buss cokneader reorient the flow as well, see (Ref. 31), the distributive mixing is better understood by considering the local weaving action of the pins (thinking, as usual, the screw stationary and the barrel and pins rotating and reciprocating, yielding sinusoidal motions through the screw channel). Combined with an overall model of the continuous mixer (Ref. 33) this analysis directly provides insight in the distributive mixing of additives, pigments, fillers and already dispersed masterbatches in a matrix.

The number of reorientations can be estimated and form, together with the expressions for shear rate, time and total shear, the basis for scaling rules for distributive mixing in corotating twin screw extruders (Ref. 33).

DISPERSIVE MIXING

If, however, two incompatible polymers have to be blended, the interfacial tension, which is directly proportional to the mutual miscibility, becomes, during the mixing process, of the same order of the shear stress applied and dominates the resulting morphology. An order of magnitude for the interfacial tension σ is typically 10^{-2} [N/m], while the shear stress τ for polymer melts is of the order of 10^4 [N/m²]. Consequently, if local radii are in the order 10^{-6} [m], yielding $\sigma/R = 10^4$ [N/m²], both stresses are equal. The long slender bodies, induced during the first stages of the (mainly distributive) mixing, become instable due to the interfacial tension driven Rayleigh disturbances (Ref. 39), see Figure 10.

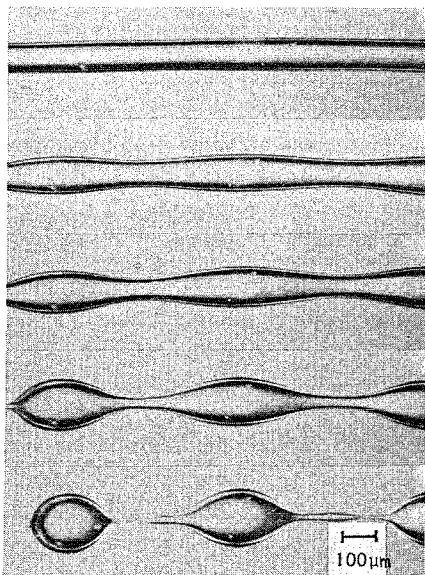


Figure 10. Sinusoidal distortions on a HDPE thread (diameter 100 μm) embedded in a PS matrix at 200°C

The droplets formed are again subjected to shear stresses counterbalanced by the interfacial tension resisting the deformation process. This process has extensively been studied in the literature (Ref. 39-45). Especially the work of Grace (Ref. 43) is worthwhile reading because of the large number of experiments performed in shear and elongational flow with liquids with a large range of viscosity ratios. The stability of droplets turned out to be strongly dependent on this viscosity ratio:

$$p = \eta_d / \eta_m \quad (3)$$

and of the rate of applied shear stress τ and interfacial tension σ/R , sometimes denoted as:

$$\Omega = \tau R / \sigma \quad (4)$$

Moreover there exists quite a large difference between the (efficiency of) shear- and elongational flows, especially if $p \neq 1$. This difference can only partly be explained by the difference in shear- and elongational viscosity (Ref. 43) but is mainly due to the difference in type of flow: weak vs. strong, respectively (Ref. 46). See Figure 11.

Although all these studies are performed with individual droplets of model liquids at room temperature, they emphasize the non-equilibrium state of the morphologies found in Figure 1a-1d. The fibrous structures found in PE/PS mixed on a corotating twin screw extruder are in between the dispersive mixing process. Moreover they are typically formed in the strong elongational flow field between screw tips and die and in the filament between the die and water quench. This is clearly illustrated in Figures 12 and 13 showing two different spots in the same filament. In one case (Figure 12) some fibrils (the smaller ones, of course) start to break up by Rayleigh disturbances while in the second case (Figure 13) one fiber has been broken up completely.

These effects, including agglomeration which is also found in Figure 12, always occur during the mixing process. The morphology will continuously change and adapt itself to local situations.

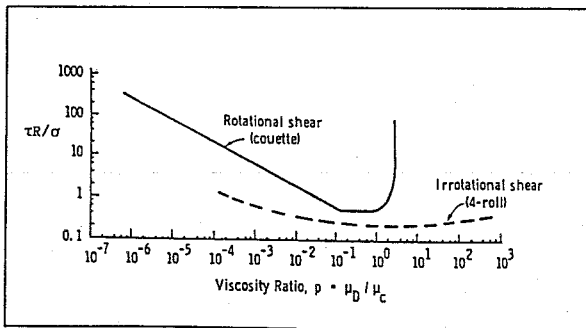


Figure 11. Comparison of effect of viscosity ratio on critical shear in rotational and irrotational shear fields. From (Ref. 43)

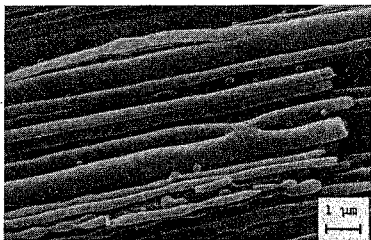


Figure 12.
Scanning electron micrograph of a fracture surface parallel to the extrudate of a 55/45 HDPE/PS blend (viscosity ratio 1). Fibrous PS is shown in different stages of break-up and coalescence

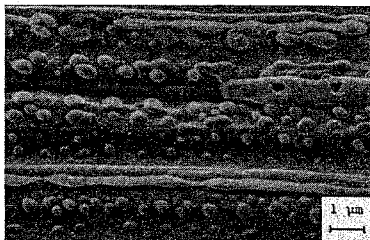


Figure 13.
As Figure 12 but with more fibers broken up

CONTROL OF MORPHOLOGY

In principle, mixing devices can be used to induce an optimum morphology in the case of incompatible blends. One could envisage that a blend in pelletized form can be produced possessing an optimum morphology. However, subsequent processing by custom moulders, could easily destroy this optimum morphology since, as discussed before, the system is inherently unstable.

In the particular case of spherical particles dispersed in a matrix, the use of compatibilizers (Refs. 47-50) or stabilizing the dispersed phase by functionalizing (Refs. 11,15) is rather successful. However, especially to fixate fibrous or stratified morphologies other tools have to be developed. Preliminary results will be presented concerning the use of radiation to fixate the dispersed phase, see below section Irradiation. At first we would like to discuss some results related to the efficiency of compatibilizers.

Compatibilizers

In order to decrease the interfacial tension in a system A/B, blockcopolymers of the type A-B are often used. To determine the efficiency of these blockcopolymers various methods have been developed. In our laboratory the so-called breaking-thread method (Refs. 51,52) was used to obtain information concerning compatibilization.

This method (see Figure 10) can be used for measuring the interfacial tension. The growth rate q of a sinusoidal distortion is directly related to the interfacial tension σ (Ref. 39,52,53,44):

$$q = \frac{\sigma \Omega(\lambda, p)}{\eta_m^D \rho} \quad (5)$$

where $\Omega(\lambda, \rho)$ is a tabulated function, λ the wavelength of the distortion, ρ the viscosity ratio of the dispersed phase (η_d) and the matrix (η_m) and D_0 the initial diameter of the fibre (Ref. 52,53,44).

Polyethylene threads were spun from a Melt-index apparatus and annealed during 24 hours at 90°C. After embedding them in the matrix (two films of PS between glass slides), the system is positioned under an optical microscope (Zeiss) in a Mettler FP2 hot stage. Results of the growth rate of a HDPE fibre in a PS matrix are given in Figure 14. The experimental reciprocal wavelength is compared with the theoretical one, to give an extra control on the experiments, in Table 1, where also the interfacial tension, calculated according to (eq. 5), is given.

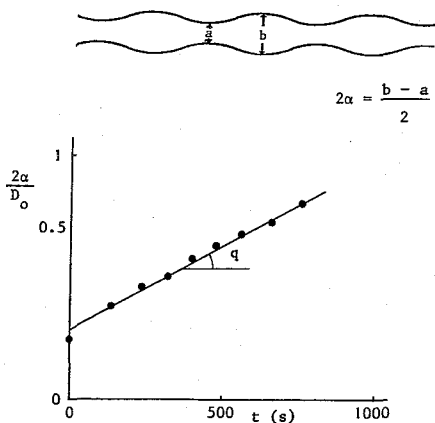


Figure 14. The relative amplitude of the distortion on a HDPE filament ($D_0 = 129 \mu\text{m}$) in a PS matrix. The filament was clamped between two PS films and measurements were performed at $T = 200^\circ\text{C}$

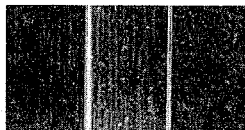
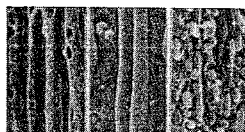
The block-copolymer PS/PE ((Mn)PS/(Mn)PE = 11.500/8.500) was introduced in polyethylene via solution-blending (0,2% and 1% respectively). The interfacial tension decreases as expected, see Table 1. For a first test on the efficiency of newly synthesized compatibilizers the breaking thread method is satisfactorily. Not so much because of its accuracy ($\pm 30\%$; also comparable with pendent drop or spinning drop methods (Ref. 52,54,55,56)), but merely because hardly any special equipment is necessary and only

small amounts of compatibilizers are needed. They can either be mixed into the polymer from which the fiber is spun or they can be dissolved wereafter the as spun fibres are dipped into the solution to give a certain amount of compatibilizer directly to the surface. As demonstrated in practice compatibilizers have a large influence on the morphology, not only because of a decrease of interfacial tension which will result in much finer dispersion because Rayleigh disturbances start at smaller fiber diameters and the same critical Ω number (sometimes referred to as Weber number) will result in smaller droplets, but also because agglomeration might be suppressed because of the presence of immobile interfaces.

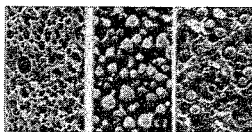
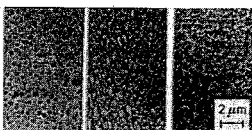
Table 1. The effect of the concentration of diblock-copolymer (wt% in the HDPE fiber) on the interfacial tension in a PS matrix ($\chi = \pi D_0/\lambda$)

Wt% block-copolymer copolymer in PE	η_m [Pas]	η_d [Pas]	X_{exp} [-]	X_{theor} [-]	$\sigma \cdot 10^3$ [Nm ⁻¹]
0	1400	1800	0,51	0,56	4,2
0.2	1400	2016	0,55	0,55	3,8
1	1400	2800	0,55	0,54	1,0
1	1400	2800	0,58	0,54	1,6
1	1400	2800	0,59	0,54	1,5

Diblock-copolymers are effective as compatibilizers (Refs. 47-50). However, the time scale during mixing the polymers A and B + compatibilizer A-B is less understood. Diffusion of compatibilizer to the interfaces is an important parameter. For example, Teyssié et al. (Ref. 50) used PS-PE diblock-copolymer in mixing PS+PE on a two roll mill. A fine dispersion was obtained. However, compounding the same system via a co-rotating twin screw extruder yields a non-equilibrium fibrillar morphology, see figures 15 and 16. The short residence time in continuous mixers compared to that on a two roll mill is prohibitive to reach the final morphology.



25/75 50/50 75/25

parallel to direction
of extrusionHDPE/PS
(reference)+ 5% PE/PS tapered
diblockcopolymer

25/75 50/50 75/25

perpendicular to
direction of
extrusion

Figure 15. Scanning electron micrographs of microtomed extrudate surfaces of the system HDPE/PS without and with compatibilizer, parallel to the direction of extrusion

Figure 16. As Figure 15, perpendicular to the direction of extrusion

It is also known from practice, that even compatibilized blends can give problems with subsequent processing, especially injection moulding. Not only are the properties, like impact strength, often influenced by the injection moulding temperature, but also delamination at the surfaces of the moulded products can occur because of orientation and deformation/agglomeration of the dispersed phase. Better control of the morphology is needed to process incompatible blends.

Irradiation

Gamma or electron-beam (EB) irradiation can be used in principle to fixate the morphology provided that the matrix is relatively insensitive for radiation treatment and the dispersed phase crosslinks preferentially.

For example, irradiation of pellets containing EPDM-rubber as the dispersed phase in a matrix of SAN or PS proved to result in a rather stable system with respect to reduced delamination of products obtained via injection-moulding (Ref. 57).

A possible processing route could be envisaged to induce first an optimum morphology in the blend in pelletized form via well-tuned mixing equipment. The pellets can be irradiated to crosslink the dispersed rubbery phase to prevent agglomeration during subsequent processing, for example injection moulding. In the case of toughening of glassy polymers this method could be of interest since low-T_g polymers (rubbers) crosslink rather easily whereas high-T_g polymers are rather insensitive to radiation. A special situation is encountered when the matrix is polypropylene, for example in the case of rubber/PP blends. The matrix PP can be degraded in a controlled manner by using radiation, improving the flow properties related to random chain-scission and consequently a narrowing of the molecular-weight-distribution.

Of course, the Dose required for fixation is an important parameter. In this respect polystyrene (co)polymers are less efficient since the aromatic side-groups trap electrons. Table 2 shows the radiation efficiency of PS/LDPE vs. Polyamide (PA)/LDPE blends. The shielding effect of polystyrene is evident.

Table 2. Crosslink efficiency of LDPE fibres dispersed in respectively a PA and PS matrix as determined via gelfraction measurements (% insoluble LDPE)

	% LDPE	dose [KGy]	% X-linked PE
LDPE/PA	25/75	50	42
LDPE/PS	18/85	50	0
	30/70	100	39
	50/50	100	43

In the case of crosslinking spherical particles, see Ref. 57, the use of EB radiation to induce crosslinks is possible, even with styrenic matrices. To fixate the morphology, crosslinking to some extent is sufficient. However, the challenge is to fixate less stable morphologies to obtain tailor-made structured blends. For example stratified layers can be

made via the Multiflux static mixer. Consequently blends can be produced in pelletized form in which a layered structure is present. Subsequent shaping processes like injection moulding, film-casting/blowing, compression moulding etc., will destroy this induced morphology immediately. Fixation via EB-crosslinking could in principle be used to survive these subsequent shaping processes. The authors hasten to add that only limited results have been obtained so far. Fig. 17 shows a scanning electron micrograph of PA-6/LDPE extrudates obtained via the Multiflux. Fig. 17b after heating to 240°C and fig. 17c shows the effect of irradiation.

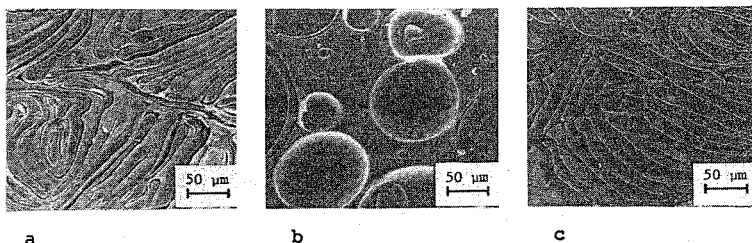


Figure 17. a. Scanning electron micrograph of a 50/50 PA-6/LDPE blend, extrudate from Multiflux, microtomed perpendicular to the direction of extrusion
 b. As 17a but compression moulded during 5 minutes (240°C)
 c. As 17b but irradiated before, dose 50 KGy

Fig. 18 shows a similar experimental result but now for the system PA-6/ethylene-vinyl alcohol copolymer (EVAL). This particular system is miscible in the melt as discerned before in the Introduction. EVAL crosslinks preferentially and after heating in the melt the layered structure remains, hence miscibility is prevented.

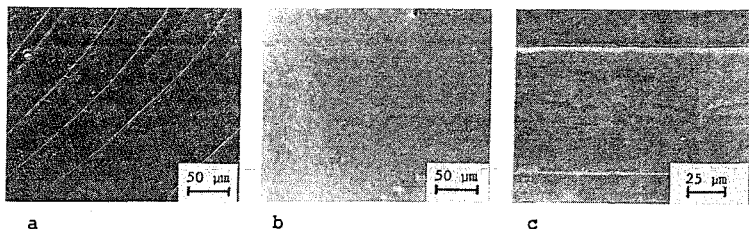


Figure 18. a. Scanning electron micrograph of a PA-6/EVAL (70/30) blend obtained via Multiflux, microtomed perpendicular to the direction of extrusion
 b. As 18a, compression moulded for 30 minutes at 240°C
 c. As 18b, but irradiated before, dose 50 KGy

The use of layered structures is important for instance in the area of packaging.

DISCUSSION

It has been shown that different morphologies can be obtained of incompatible polymers, which in general are not stable because of their dependence on volume fractions, viscosity ratios, and compatibility resulting in a local balance of stresses, but moreover especially on the processing time involved. It is worthwhile studying whether specific morphologies can be fixated. Irradiation of a blend is an interesting opportunity and in future papers we will report on the progress made in the investigation whether sufficient crosslinking for complete fixation can be established in different structured blends.

ACKNOWLEDGEMENT

Part of this publication consist of the contributions of W. de Vet (synthesis of diblock-copolymers), J. van Gisbergen (fixation of morphology by irradiation) and H. Ketels (synthesis of EVAL; EVAL blends). The authors wish to thank Prof. Ph. Teyssié and Dr. R. Fayt (Université Sart Tilman, Liège) for their help and assistance in the preparation of the block-copolymers.

REFERENCES

- (1) O. Olabisi, L.M. Robeson, M.T. Shaw, Polymer/Polymer Miscibility, Academic Press, New York (1979)
- (2) L.M. Robeson, Polymer Compatibility and Incompatibility, NMI Press (1982)
- (3) J.M. Barlow, D.R. Paul "Polyblends '87", Boucherville Canada, Polym. Eng. Sci. 27, 1482, (1987)
- (4) W.H. Stockmayer, R. Koningsveld, E. Nies in 'Equilibrium Thermodynamics of Polymer Systems' Vol. 1: Polymer Phase Diagrams, Oxford Univ. (1988)
- (5) NN, Plastics Eng. 7, 24, (1986)
- (6) H.H.T.M. Ketels, L.A.K. Kleintjens (to be published)
- (7) P.H.M. Elemans, J.G.M. van Gisbergen, H.E.H. Meijer in 'Integration of Polymer Science and Technology', Elsevier (1988)
- (8) M. Matsuo, S Sagaye in 'Colloidal and Morphological Behaviour of Block and Graft Polymers', G.E. Molau, Plenum (1971)
- (9) M. Matsuo, Japan Plastics 2, 6, (1968)
- (10) J.A. Manson, L.H. Sperling, Polymer Blends and Composites, Plenum (1976)
- (11) R.J.M. Borggreve, R.J. Gaymans, J. Schuijjer, J.F. Ingen Housz, Paper presented at the European Symposium on Polymer Blends, Strasbourg (1987)
- (12) Du Pont, US Patent 580513
- (13) S. Wu, Polym. Eng. Sci. 27, 335, (1987)
- (14) S. Wu, Polymer 26, 1855, (1985)
- (15) R.J.M. Borggreve, R.J. Gaymans, Submitted to Polymer
- (16) D. Sjoerdsma, private communication
- (17) G.V. Vinogradov, N.P. Krasnikova, V.E. Dreval, E.V. Kotova, E.P. Plotnikova, Int. J. Polym. Mat. 9, 187 (1982)
- (18) M.P.Zabugina, E.P. Plotnikova, G.V. Vinogradov, V.E. Dreval, Int. J. Polym. Mat. 10, 1 (1983)
- (19) M.V. Tsebrenko, Int. J. Polym. Mat. 10, 83 (1983)
- (20) G.N. Avgeropoulos, F.C. Weissert, G.G.A. Böhm, P.H. Biddison, ACS Rubber Division Meeting, Paper 3, New Orleans (1975)
- (21) J.G.M. van Gisbergen, P.H.M. Elemans, Poster presented at the European Symposium on Polymer Blends, Strasbourg (1987)

- (22) K.C. Frisch, D. Klempler, H.L. Frisch, Polym. Eng. Sci. 22, 17 (1982); Polym. Eng. Sci. 25, 12 (1985)
- (23) R. Sluijters, De Ingenieur 77, 15, 33 (1965)
- (24) D. Schilo, K. Ostertag, Verfahrenstechnik 6, 2, 45 (1972)
- (25) J.M. McKelvey, Polymer Processing, J. Wiley (1962)
- (26) J.M. Funt, Mixing of Rubbers, RAPRA (1977)
- (27) Z. Tadmor, I. Klein, Engineering Principles of Plasticating Extrusion, Reinhold (1971)
- (28) Z. Tadmor, C.G. Gogos, Principles of Polymer Processing, J. Wiley (1979)
- (29) W. Szydlowski, K. Brzoskowski, J.L. White, Int. Polym. Proc. 1, 207 (1987)
- (30) M.L. Booy, Polym. Eng. Sci. 15, 606 (1975); 18, 973 (1978); 20, 1220 (1980)
- (31) M.L. Booy, Y.K. Kafka, Submitted to Polym. Eng. Sci.
- (32) H.E.H. Meijer, P.H.M. Elemans, H.H.M. Lardinoye, G. Kremer in: 'Wärmeübertragung bei der Kunststoffverarbeitung', VDI Düsseldorf (1986)
- (33) H.E.H. Meijer, P.H.M. Elemans, PPS Stuttgart (1987) Polym. Eng. Sci. 28, 000 (1988)
- (34) I. Manas-Zloczower, A. Nir, Z. Tadmor, Rubber Chem. Techn. 55, 1250 (1982)
- (35) I. Manas-Zloczower, A. Nir, Z. Tadmor, Rubber Chem. Techn. 57, 583 (1984)
- (36) I. Manas-Zloczower, A. Nir, Z. Tadmor, Dispersive mixing in two roll mills (submitted)
- (37) J.M. Ottino, Polym. Eng. Sci. 23, 7 (1983)
- (38) K.Y. Ng, L. Erwin, Polym. Eng. Sci. 21, 4, (1981)
- (39) Lord Rayleigh, Proc. Roy. Soc. (London) 29, 71 (1879)
- (40) G.I. Taylor, Proc. Roy. Soc. (London) A146, 501 (1934)
- (41) R.G. Cox, J. Fluid Mech. 37, 601 (1969)
- (42) E.J. Hinch, A. Acrivos, J. Fluid Mech. 98, 305 (1980)
- (43) H.P. Grace, Chem. Eng. Comm. 14, 225 (1983)
- (44) J.J. Elmendorp, Dissertation Delft University of Technology (1986)
- (45) C.D. Han, Multiphase Flow in Polymer Processing, Academic Press (1981)
- (46) W.L. Olbricht, J.M. Rallison, L.G. Leal, J. N.N.F.M. 10, 291 (1982)

- (47) R. Fayt, R. Jerome, Ph. Teyssié, J. Polym.Sci., Polym. Lett. Ed. 19, 79 (1981)
- (48) Ibid., 19, 1269 (1981)
- (49) Ibid., 20, 2219 (1982)
- (50) Ibid., NRCC/IMRI Symposium "Polyblends '86", Montreal (1986)
- (51) D.C. Chappellear, Polym. Preprints 5, 363 (1964)
- (52) S. Wu, Polymer Interface and Adhesion, Marcel Dekker (1979)
- (53) S. Tomotika, Proc. Roy. Soc. A150, 322 (1935)
- (54) H.T. Patterson, K.H. Hu, T.H. Grindstaff, J. Polym. Sci. C34, 31 (1971)
- (55) S.H. Anastasiadis, Polym. Preprints 28, 24 (1987)
- (56) P. Gaillard, M. Ossenbach-Sauter, G. Riess, Makromol. Chem., Rapid Comm. 1, 771 (1980)
- (57) J. Schrijver, N.G.M. Hoen, P.J. Lemstra, C.A. van Gunst, NL Patent 8304162
- (58) J. Sax, J.M. Ottino, Polym. Eng. Sci. 23, 165 (1983)
- (59) P.J. Lemstra, R. Kirschbaum, Polymer 26, 1372 (1985)
- (60) P.J. Lemstra, H.E.H. Meijer, R.J.H. Burlet, NL 83 03379
- (61) D.V. Khakhar, J.M. Ottino, Int. J. Multiphase Flow 13, 7 (1987)