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Coalescence in an interface-modified polymer blend as studied by light scattering measurements

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The influence of A–B diblock copolymers on coalescence in A:B blends has been studied by rheo-optical measurements and electron microscopy. Divergent criteria and experimental evidence appear in the literature on the block copolymer (BC) molecular weight (M_w) and volume fraction (φ_{bc}) when the requirement is the BC to reside at the interface. In the present study the block chain lengths were chosen shorter than the corresponding homopolymers as a starting point. For selected model systems it was found that symmetrical diblock copolymers with $\varphi_{bc} \geq 1\%$ were most effective for inhibiting coalescence. However, rheo-optical measurements revealed that the stabilization effect is not unconditional during the flow; coalescence is prevented for a time which decreases with increasing shear rate due to removal of the BC away from the interface. The origin of the observed behaviour is discussed based on various mechanisms: shear-induced mutual compatibility between components, squeeze-out/drainage of the interfacial layer, frictional pull-out of BC chains, collision-induced entrapment of BC between interfaces, encapsulation of the BC based on the concept of elastic interfacial curvature.

(Keywords: coalescence; interface; blends)

Introduction

Multiphase polymer systems constituting polymer blends and alloys have been the subject of increasing academic and industrial research for the last two decades[1]. Blending of these systems has increasingly constituted an alternative to synthesizing new polymers. The properties of the systems are to a large extent affected by the morphology, which in turn depends on the thermodynamic, rheological and interfacial properties of the constituent components, the composition and the mixing conditions. Because of the strong structure–property relationship, considerable effort has been devoted to gaining an increased knowledge on how to control the morphology during processing. In this respect the microrheology plays a key role.

From the point of view of morphology, the blends can be divided into two classes: discrete and co-continuous systems. When analysing the effects of various parameters on the morphology, a clear distinction between these classes should be observed to avoid misinterpretation of data. In this paper only discrete (distributive) systems will be discussed, i.e. systems with volume fraction of the dispersed phase below the percolation threshold for spheres (theoretically ~ 15 vol%)[2,3].

The dispersion of droplets in flow fields has been the subject of numerous investigations. In spite of these efforts the mechanism of droplet instability and break-up in viscoelastic systems is not yet fully understood. The influence of increasing particle concentration in coalescence processes has to be taken into account.

Flow-induced coalescence of the dispersed phase and its importance in the development of morphology has received less attention in the past.

Most theoretical as well as experimental work has been based on Newtonian drops in Newtonian media. Fewer contributions deal with viscoelastic drops in Newtonian or viscoelastic media. In most studies only the behaviour of non-interacting droplets has been considered while in practice the dispersed phase concentrations are too high to exclude interactions between droplets. Exact studies dealing with single-drop studies have been conducted, but only a few involved doublet interactions, while multiple interactions and coalescence have been treated semiempirically.

The problem of development of domain size distribution in selected flows has been generally formulated by Valentas *et al.*[4] in the so-called 'general population balanced equation'[5]. Silberberg and Kuhn[6], Tokita[7], Elmendorp and van der Vegt[8], Fortelny and Kovár[9], Lyngaae-Jørgensen *et al.*[10], and Huneault *et al.*[11] formulated simplified models taking both break-up and coalescence processes into account.

For polymer blends and alloys, solutions of the general population balance equations have not been published. A number of publications deal with the influence of volume fraction of the dispersed phase on polymer blend rheology, drop size and stability, namely van Oene[12], Utracki[13], Favis and Willis[14], Chen *et al.*[15] and Sundararaj and Macosko[16].

The topics considered have been summarized in a number of monographs and reviews in the last decade, notably Elmendorp and van der Vegt[17], Han[18], Utracki[1,19], Wu[20], Plochocski[21], Meijer and Janssen[22], Utracki *et al.*[23] and Søndergaard and Lyngaae-Jørgensen[24].

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In molten simple binary immiscible blends the dispersed phase has a tendency to coalesce. This leads to macrodomains, broad size distribution, and ultimately inferior mechanical properties. In order to stabilize the morphology and thus prevent gross aggregation, compatibilizers (e.g. block or graft copolymers) may be added or formed *in situ* to obtain a decreased coalescence rate and an enhanced interfacial adhesion. These overall effects have been primarily observed in the final blend structure, while only limited evidence has been provided on the behaviour during flow.

In this work, the effects of coalescence will be studied by means of light scattering measurements conducted during shear flow (also referred to as rheo-optical measurements). The rheo-optical studies constitute a valuable tool in gaining more knowledge about the microrheology and ultimately how to control the morphology of multiphase polymer systems. Results are presented concerning the effect of adding a block polymer on the coalescence behaviour in a simple binary immiscible model blend of polystyrene (PS) and poly(methyl methacrylate) (PMMA).

Background

It is experimentally established and commonly recognized that the dispersed particles in dispersive multiphase polymer systems, their size and distribution are the results of a competitive process between break-up and coalescence. Under given flow conditions an invariant morphology can be attained that represents a balance existing between particle break-up and flow-induced coalescence. The larger particles are deformed and broken up by the stresses of the flow field, while concurrently particles collide and fuse to temporarily form larger domains.

The major mechanisms of collision and coalescence of particles are considered to be flow but the effect may also take place in quiescent systems, the proposed origins being Brownian motion, dynamics of concentration fluctuation, sedimentation, temperature gradients, etc. Some of these effects may also be present during flow and they may be either enhanced or suppressed by flow[25]. However, considering the relatively high viscosity and large particles present in polymer blends, Brownian motion scarcely plays a major role in coalescence since the particle diffusion is inversely related to particle diameter and matrix viscosity. A mechanism likely to occur in polymer blends is the so-called Ostwald ripening: the large particles grow at the expense of small ones by diffusion of molecules from the smaller particles with high interfacial energy to the larger ones. This process is enhanced by flow and can be described by a scaling law[26].

The influence of other mechanisms on the blend coalescence is discussed later in the Experimental section.

Many experimental studies have shown that the observed particle size in unmodified blends is larger than predicted[7,8,14,21,27,28]. Consistent reports confirm that the droplet size increases considerably with increasing concentration of the dispersed phase. Elmendorp and van der Vegt[8] observed that only for very low concentrations (< 0.5 vol%) does the domain size approach that predicted by Taylor's theory[29]. Consequently coalescence of particles has to be taken into account.

Several theories have been proposed to describe interactions and coalescence of particles. A comprehensive treatment of the subject is given in a review by Chesters[30]. The theories of coalescence are either based on equilibrium thermodynamics or hydrodynamics: the former consider quiescent systems in which coalescence results from minimization of the total free energy by reduction of the interfacial area, whereas the latter consider flowing systems.

A set of complex population balance equations was developed for microemulsions by Valentas *et al.*[4]. Tokita used a simplified version of these equations to predict the dependence of domain size on concentration in rubber blends[7]. The approaches by both Valentas *et al.* and Tokita failed to predict the particle size quantitatively because of a key problem: the probability that collisions result in a coalescence is not directly accessible. Fortelny *et al.*[27] developed a relation for equilibrium droplet size in steady-state shearing flow following a procedure similar to that of Tokita[7]. A more pronounced coalescence was observed than that predicted. Utracki[31] carried out an extensive study on shear coagulation of latexes under steady-state shear flow, including a wide range of variables. An expression relating the coagulation time to these variables was derived. However, in order to estimate the coagulation time a parameter must be determined by doing several controlled experiments. The theory has recently been extended to polymer–polymer systems and implemented in a model of morphology evolution during polymer blending[11].

A model based on three differential equations describing the dispersion processes during steady-state and transient shear flow of viscoelastic liquid drops in a viscoelastic matrix was proposed by Lyngaae-Jørgensen *et al.*[10]. The rate equations for the dispersion process were based on a number of assumptions that were outlined in ref. 10.

Compatibilization

Compatibilization of simple binary blends is commonly recognized to have a pronounced and favourable influence on interfacial properties. The emphasized method of the interface modification is addition of a premade copolymer. The effect of other methods on the fluid properties are qualitatively equivalent.

The purpose of incorporating compatibilizers is generally to improve the physical properties that can be attributed to the following major effects: (i) to reduce the interfacial tension between phases in order to achieve an enhanced deformability of large domains and thus upon break-up gain a finer particle size dispersion during blend mixing; (ii) to stabilize the interface, thus preventing coalescence and gross aggregation of the particles during blending; and (iii) to obtain enhanced adhesion between phases in the solid state.

Compatibilizers consisting of block or graft co-polymers enhance the interfacial interaction in simple binary blends as found in earlier pioneering work[32-37]. The copolymers most often contain segments that are chemically identical or similar to the main components of the blend so as to obtain some segment miscibility in each bulk phase. The molecular weights of the copolymers are frequently chosen to be equal to or higher than those of the blend components, if it is

required that the copolymer is located at the interface between the phases[38–44]. However, divergent criteria and experimental evidence appear in the literature. At favourable conditions even a small quantity of the copolymer can yield a pronounced influence of the interfacial properties[35,37]. While block copolymers are expected to be the most effective with regard to interfacial adhesion, graft copolymers have an advantage over block copolymers in that they can be synthesized by a simpler route, e.g. by *in situ* reaction during blending or processing. Efforts within this area have been progressing considerably in recent years[45].

The effect of the compatibilization is a steric stabilization of the interface which inhibits coalescence. The force associated with the particle motions is not sufficient to squeeze and drain the interphase layer of the copolymer when the particles collide. This is associated with the yield stress usually observed in block copolymers which causes a so-called immobilization of the interphase.

The basic factors that affect the interfacial properties have been qualitatively described in terms of scaling arguments as outlined by Leibler[46]. Mean-field theories of polymer interfaces have been developed by Noolandi and co-workers[47–50] and Shull and Kramer[51]. A mean-field approximation was also proposed by Löwenhaupt and Hellman[52]. The theory of Leibler is valid for nearly miscible systems whereas the mean-field theories apply to highly immiscible ones. Noolandi and Hong also calculated the critical concentration of block copolymer for micelle formation in the bulk of a homopolymer[48]. Vilgis and Noolandi studied the case in which the blocks differ from the homopolymers[50]. The amount of the copolymer residing at the interface was expressed as $\phi_c \simeq \phi_{c,\text{total}} \exp(X_c\chi\phi_p/2)$ assuming $(X_c\chi\phi_p/2) \leq 1$, where X_c is the degree of polymerization of the copolymer, ϕ_p is the volume fraction of homopolymer $(\phi_A = \phi_B)$, and χ is the Flory–Huggins interaction parameter between A and B segments.

Decreases in the interfacial tension (and thus the interfacial energy) in the presence of copolymer have been observed experimentally in several studies[53–59]. Fleisher *et al.*[59] additionally investigated the molecular weight and end-group type on interfacial tension.

A subject of prime interest is to determine experimentally whether the copolymer actually resides at the interface and does have an effect. Some recent attempts used conventional methods such as mechanical[15,60] and rheological[61,62] testing or measurements of the interfacial tension[15,56–59,63–65]. Direct study of polymer interfaces is, however, more difficult. The techniques involved are various forms of microscopy (u.v. fluorescence, phase contrast, elemental electron loss spectroscopy, etc.) cited by Wu[53]; diverse scattering techniques that can be used to get information on the interface of bulk samples of blends and more conveniently on block copolymers[66]; i.r. spectroscopy[67] and X-ray microanalyses[68] which provide more detailed information on the composite profile; techniques based on scattering of ion beams which can be used to investigate the interface of bulk samples[69–71]; and methods involving light spectroscopic ellipsometry[72–76], X-ray[77] or neutron[74,77–80] reflection which allows short-range details of layered interfaces to be obtained.

To obtain more information on the topic of interface characterization and properties the reader may consult two recent publications edited by Feast *et al.*[81] and a monograph by Sanchez[82].

It is to be expected that the coalescence probability strongly depends upon the degree of mobility of the interface. Elmendrop and van der Vegt investigated theoretically and experimentally the influence of shear-induced coalescence on the morphology of polymer blends[8,17]. In the theoretical part of a procedure was proposed to estimate the coalescence probability. It was shown that the coalescence probability decreases considerably with increasing particle size and capillary number. It was also estimated that the probability is considerably reduced if the interface between polymers exhibits a high degree of immobility.

Recently Favis[83] determined emulsification curves for blends in accordance with the concept of Djakovic *et al.*[84]. The emulsification curves essentially follow the evolution of the dispersed phase size with interfacial modifier concentration. The critical conditions for obtaining a quasi-equilibrium particle size were determined and a critical amount of BC was estimated[85]. Equivalent experimental results have also been obtained by others[86–88].

Nakayana *et al.*[89] compared premade *versus* various reactively formed block copolymers in blends with basic components of PS and PMMA blended in a parallel plate mixer. They found the latter copolymers to be most effective in reducing the particle size. In the reactive case the blend was stabilized more quickly and a narrower size distribution was obtained. This may be ascribed to an effect of the graft copolymer at the creation of the interface between the basic components.

The influence of electron beam irradiation of the dispersed phase on the microrheology of immiscible blends was investigated by van Gisbergen and Meijer[90] and by Valenza *et al.*[91,92]. Both break-up of threads and coalescence of particles were retarded to a large extent but not as much as expected.

Using a model system of PS and PMMA with a fixed composition ratio of 10/90, the influence of adding a block copolymer with components chemically equivalent to the homopolymers was examined by the authors in simple shear flow[24]. In this system deformation and break-up of domains were also present and were accounted for using a simulation model as outlined in ref. 24. Adjustable model parameters were estimated by fitting the model to transient data of average aspect ratio of prolate spheroids obtained from rheo-optical measurements for the purpose of retrieving specific parameters. From the simulation it was concluded that addition of a block copolymer lowers the interfacial tension as well as the probability of coalescence due to collision. The block copolymer addition also seemed to stabilize the fibrils and to lower the tendency for percolation of the minor phase.

Experimental

Experiments referred to so far can be divided into investigations at quiescent conditions (e.g. annealing under the influence of gravitional force), in complex morphologies or in complex flow fields, and studies at well-defined flow conditions. The latter topic has, however, received the least attention.

Light scattering measurements at quiescent conditions and during shear flow were carried out to quantitatively

Table 1 Material characteristics

Sample	PS	PMMA	S/MMA[a] 50/50	S/MMa[b] 75/25
Source	Polysar	Rohm & Haas	KT[c]	KT[c]
Density $(kg\,m^{-3})$	1.04	1.19	1.11	1.07
Refractive index	1.49	1.59	1.54	1.51
Solubility parameter $(kJ^{1/2}\,m^{3/2})$	590	610	599	595
Weight molecular weight $(kg\,mol^{-1})$	225	87	146	91
Polydispersity, M_w/M_n	3	2	1.17	1.8

$M_{cr}(PS) \approx 30\,kg\,mol^{-1}$; $M_{cr}(PMMA) \approx 20\,kg\,mol^{-1}$.
[a] $M_w(PS) = 73\,kg\,mol^{-1}$; $M_w(PMMA) = 73\ kg\,mol^{-1}$;
[b] $M_w(PS) = 67\,kg\,mol^{-1}$; $M_w(PMMA) = 23\ kg\,mol^{-1}$.
[c] Samples produced in the authors' laboratory

examine the effect of immobilization of the interface on the particle size. In the coalescence studies presented here, attention was focused on the influence of a premade block copolymer on the interfacial properties of a model blend. The presence of the block copolymer at the interface was not measured directly, but the effect of the copolymer on the coalescence behaviour was indirectly revealed by light scattering measurements during annealing and shearing experiments. The investigations were performed with a laser rheo-optical unit in connection with a Rheometrics Mechanical Spectrometer.

Materials. The model system chosen is a binary blend of commercial grades of polystyrene (PS) and poly(methyl methacrylate) (PMMA) in the absence and in the presence of a block copolymer. Blends of these components are known to display two phase morphologies. By virtue of some similarity in the solubility parameters, one might assume that blends of these components possess some miscibility region. However, a rather sharp interface has been observed by neutron reflection measurements[74]. The material characteristics are given in *Table 1*.

In this presentation the bulk polymer composition is confined to PS/PMMA 90/10 (w/w). Besides the neat blend, a second sample was prepared by addition of a block copolymer with components chemically equivalent to the homopolymers with block chain lengths shorter than those of the homopolymers.

The block copolymers used were a symmetrical (S/MMA-50/50) and an asymmetrical (S/MMA-75/25) with similar PS block chain lengths (*Table 1*). Thus, in the blend system considered (PS/PMMA-90/10), the longest block chain of the latter penetrated the PS matrix phase.

Sample preparation. The block copolymer was produced in our laboratory by an anionic polymerization. The diblock copolymer was prepared by the procedure described by Rempp and co-workers[93] with slight modifications.

The blends were prepared by melt blending components in a Brabender Plasticorder at $10\,rev\,min^{-1}$ and $180°C$ for 20 min to obtain a dispersion of PMMA domains in a matrix. The minor component possessed the highest viscosity (zero shear viscosity ratio ≈ 8) to exclude the effect of droplet deformation and break-up in the coalescence measurements. The rheological data for the blends were published in ref. 61.

For the light scattering measurements the samples were dried in a vacuum oven at $60°C$ for at least one week before use. This procedure is important because any moisture or volatile gases present in the bulk or in microvoids strongly affect the light scattering. Pellets (0.1–0.15 mm in thickness) were formed in a hydraulic press for 4–5 min at $200°C$, followed by air cooling to ambient temperature.

Rheo-optical measurements. A rheo-optical set-up for simultaneous rheological and optical measurements was used in the experimental work. A more detailed description can be found in refs 24 and 94. The unit was built into a Rheometrics Mechanical Spectrometer (RMS), which makes it possible to detect angular distribution of scattered laser light from multiphase polymer melts during shear flow. In addition to the transmittance, the light detector measures the light in two orthogonal directions simultaneously. One direction is the flow direction. The measurements were conducted in a closed cone and plate shear cell to obtain a nearly uniform shear flow field at higher shear rates than usually accessible. The sample was placed between a glass cone and a fixed plate. The shear cell allows shear rates from 0.01 to $\sim 1 \times 10^3\,s^{-1}$ to be obtained. Dimensions of the glass geometry were: diameter 28 mm, angle of cone 0.01 rad. All measurements were carried out at $210°C$.

The data acquisition system and analysis software made it possible to construct the light scattering pattern (isointensity contours or scattering profiles) based upon two-dimensional measurements to provide a basis for visual as well as quantitative evaluation of the results.

Size exclusion chromatography (s.e.c.). The molecular weight averages of PS, PMMA and S/MMA block copolymer before and after processing in the mixer were determined using the Waters Associates model 200 s.e.c. instrument equipped with four PS gel columns of 10^6, 2×10^4, 10^4 and $10^3\,Å$ nominal porosities. The instrument was run at room temperature under the following conditions: flow rate $1\,ml\,min^{-1}$; injection volume 2 ml; sample concentration $2.5\,mg\,ml^{-1}$. Tetrahydrofuran was used as a solvent.

The s.e.c. columns were calibrated with narrow distribution PS standards from Pressure Chemical Co. and National Institute of Standards and Technology

under the above-mentioned conditions, except that the injection volume was 0.5 ml. All molecular weight data were calculated using the calibration found for PS standards and approximate 'Q factor correction'.

Electron microscopy. Samples run in the RMS were quenched after cessation of the measurement and thin slices were cut in an Reichert ultramicrotome model OMU3. Transmission electron microscopy (TEM) was performed using a JEOL, model JEM-100B-TR instrument.

Image analysis. A semiautomatic image analysis system was used to quantitatively characterize the size distribution of the particles of the discrete phase. The system consisted of a video camera coupled with a controller board installed in a computer. The analysis was performed using the program GIPS (Image Processing Software from Gade Data, Denmark).

Light scattering analysis. The approximation applied to estimate the particle size was that of Debye–Bueche[95]. An isotropic system with random two-phase structure and sharp interfaces was assumed. Here, a random structure refers to a system in which particles of random size are randomly distributed in a continuous phase. The intensity of the total scattered light from this structure can be expressed in a simplified form by the equation:

$$I(q) = C\langle\eta^2\rangle a_c^3 S(qa_c) \tag{1}$$

where C is a constant, q is the magnitude of the scattering vector, $\langle\eta^2\rangle$ is the mean square fluctuation of a scattering contrast, a_c is a correlation distance that can be related to the particle size, and S is a scaling function defined by:

$$S(x) = (1 + x^2)^{-2} \tag{2}$$

For a structure consisting of randomly distributed spherical domains of radius R and volume fraction ϕ, the following relation applies:

$$a_c = (4/3)(1 - \phi)\phi R \tag{3}$$

Under the assumptions specified above this equation correlates quantitatively the domain size with the correlation distance. The light scattering data yielded an underestimation of particle size due to multiple scattering and to a pronounced decrease in contrast between phases during flow not fully accounted for by the model. Accordingly, the data were corrected for these effects by approximative procedures. A detailed description of a stringent procedure for correction of multiple scattering is given in ref. 24 (Chapter 3).

Results and discussion

The measurements were carried out on the sample composition PS/PMMA-90/10 at 210°C in the absence and in the presence of 2 wt% block copolymer. The samples with higher copolymer concentration did not show any significant change of properties.

Prior to analysing the extent of shear-induced coalescence, investigations were carried out to elucidate any concomitant effects. The effects subject to closer examination were:

1. Ostwald ripening (large particles grow at the expense of small ones due to large differences in interfacial energy between the species concerned);
2. Stokes flow (gravitational effects);
3. Viscous flow (particle motions caused by irregular shaped interfaces), also referred to as interfacial driven coalescence;
4. Marangoni flow (temperature-gradient-induced particle motions).

Initially, recordings were performed during annealing of neat blend platelets without any pressure on the samples for up to 3 h. As can be ascertained from the lower curve in *Figure 1*, no significant domain growth could be detected. This excluded coalescence caused by processes 1 or 2 listed above. This observation was also confirmed by electron micrographs of samples taken before and after measurement. In contrast to this, a very strong domain growth was observed after having annealed the sample for 1–2 h in a simple mould cavity. Applying a small shear strain to the platelet in order to form irregular shaped collision doublets and then leaving the sample completely relaxed for 1 h did not result in any effect that could be assigned to a self-acting interfacial tension-driven coalescence (process 3). This conclusion is supported by the constant level of the integrated intensity after cessation of shear (after point b) as seen in *Figure 2*. To elucidate the effect of the remaining process (4), the measurements were carried out with temperature gradients up to $60°C\,mm^{-1}$ across a sample of 1 mm thickness in a press with one heating plate kept at a low temperature of 155°C. The size distributions of the original sample and the gradient annealed sample only indicate a slight displacement towards larger diameters for the latter, as shown in *Figure 3*.

The results of shearing measurements at low shear
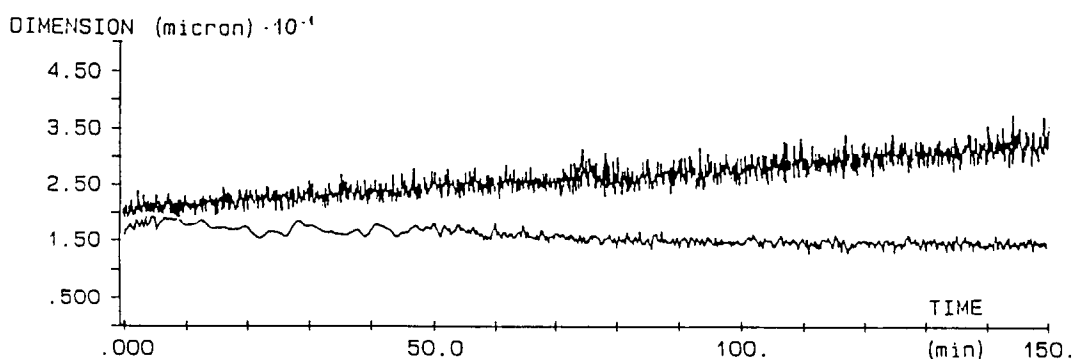
Figure 1 Particle diameter *versus* time for PS/PMMA-90/10 at 210°C. Lower curve: $\dot{\gamma} = 0\,s^{-1}$; upper curve: $\dot{\gamma} = 0.03\,s^{-1}$
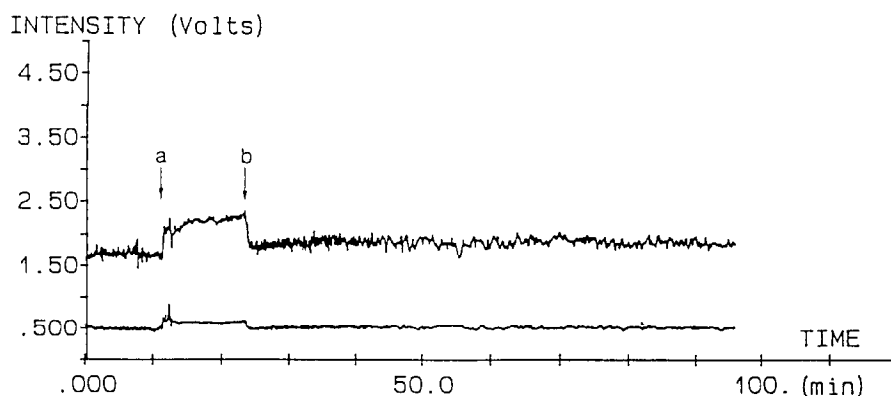
Figure 2 Test of interface-driven coalescence initially induced by shear. Upper curve is the integrated light scattering intensity. Lower curve is the transmittance. (a) Inception of shear; (b) cessation of shear and subsequent annealing (210°C)
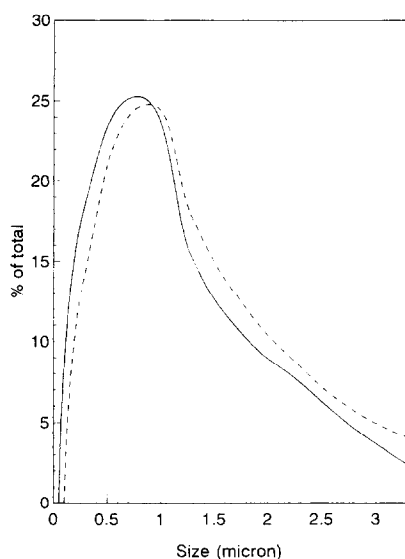

Figure 3 Size distribution curves for the neat blend obtained from image analysis: —— original sample; – – gradient annealed sample (60°C/mm, 3 h)

rates shown in *Figure 1* indicate that in neat blends the domain growth starts immediately after the onset of shearing. The increase in domain size probably levels off at some upper limit, which was assumed to decrease only slowly with shear rate. The main effect of an increased shear rate was anticipated to be an increased rate of domain growth up to a maximum where the contact time

is reduced below a critical limit, below which the interdiffusion between particles is insufficient to form a strong bond and the contact area becomes too large for the coalescence to occur.

The results on the blends with block copolymer indicate a more complex behaviour. *Figure 4* shows a time resolved trace of light scattering (parallel to the flow direction) for the blend sample with the symmetrical block copolymer originally residing at the interface. The signal stayed constant for some time followed by a marked increase which was ascribed to an onset of coalescence. In this context it should be noted that the scattering pattern (isointensity contours) stayed symmetrical during all the measurement. The observed increase of the signal may not, however, indicate an immediate increase of particle size, but merely reflects changes in optical properties due to removal of the block copolymer from the interface which in turn may result in coalescence. An increase of particle size in the present case should cause a decrease of scattering intensity. This tendency was indeed recorded by the scattering data beyond a maximum value. The result indicated that the stability of the interfacial layer is not unconditional during the flow.

In order to test various hypotheses for the observed behaviour an asymmetrical block copolymer was applied in which the long block chain (PS) penetrated the PS matrix phase so as to obtain a more sensitive measure of the effect of flow on the interfacial stability. *Figure 5* summarizes intensity-averaged recordings of time resolved traces of light scattering signals for various shear rates. Initially, it should be noted that the abrupt change in
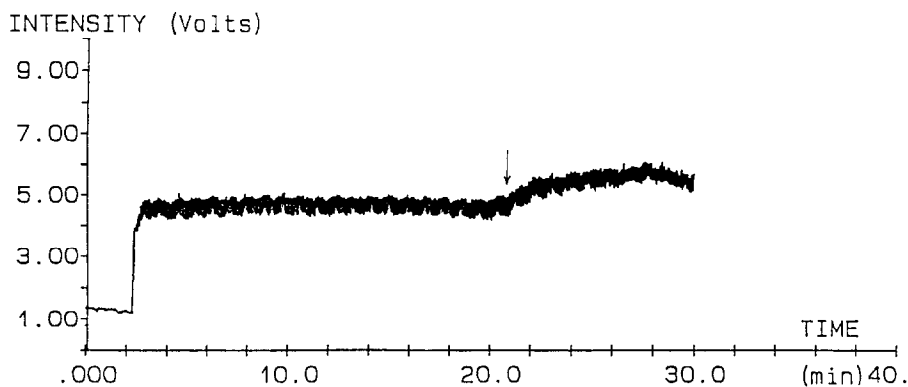

Figure 4 Trace of a light intensity signal *versus* time for S/MMA-50/50 at 210°C and $85 \, \text{s}^{-1}$. Arrow indicates onset of coalescence
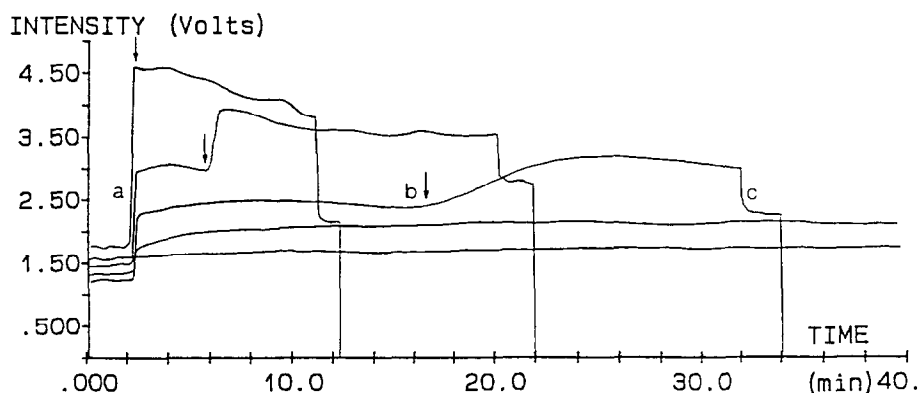
Figure 5 Traces of integrated light intensity signals *versus* time for S/MMA-75/25 at 210°C with shear rates related to curves as follows (from bottom): $8.5\,s^{-1}$; $34\,s^{-1}$; $85\,s^{-1}$; $340\,s^{-1}$; $850\,s^{-1}$. Arrows indicate onset of coalescence

intensity at inception and cessation of shear is believed to be due to a molecular orientation and relaxation, respectively, of the matrix phase, the former causing a birefringence effect. This optical effect needs to be accounted for while interpreting the signals and it has to be corrected when performing a quantitative analysis.

At low shear rates the signal was constant during all the measurement ($\sim$ 2 h) indicating that the block copolymer effectively stabilized the system against coalescence. At high shear rates, the signals were initially constant for periods of time decreasing with the increasing shear rate, followed by a marked increase. This change was, as in the previous case, ascribed to an onset of coalescence. The results indicated a somewhat shorter stability time for the asymmetrical copolymer compared to that of the symmetrical one. The shear and time dependent onset of coalescence for the copolymers are summarized in *Figure 6* showing the stability time *versus* shear rate.
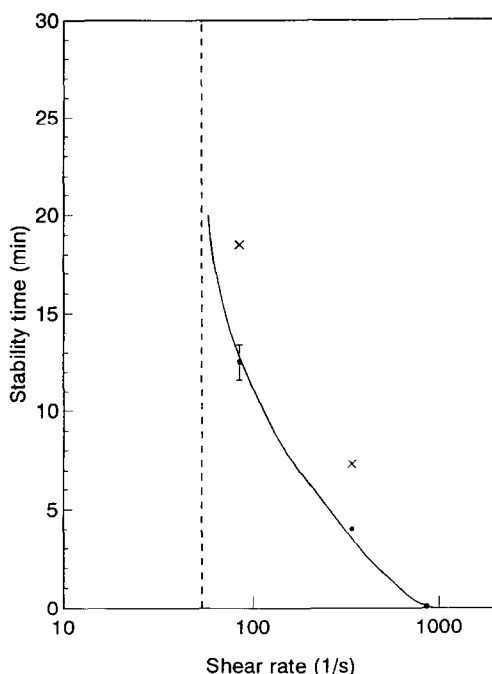
Figure 6 Stability time of diblock copolymer at the interface of a PS/PMMA-90/10 blend *versus* shear rate at 210°C: ×, SMMA-50/50; ●, SMMA-75/25. The vertical dotted line indicates the limit below which the block copolymer resides at the interface for at least 2 h
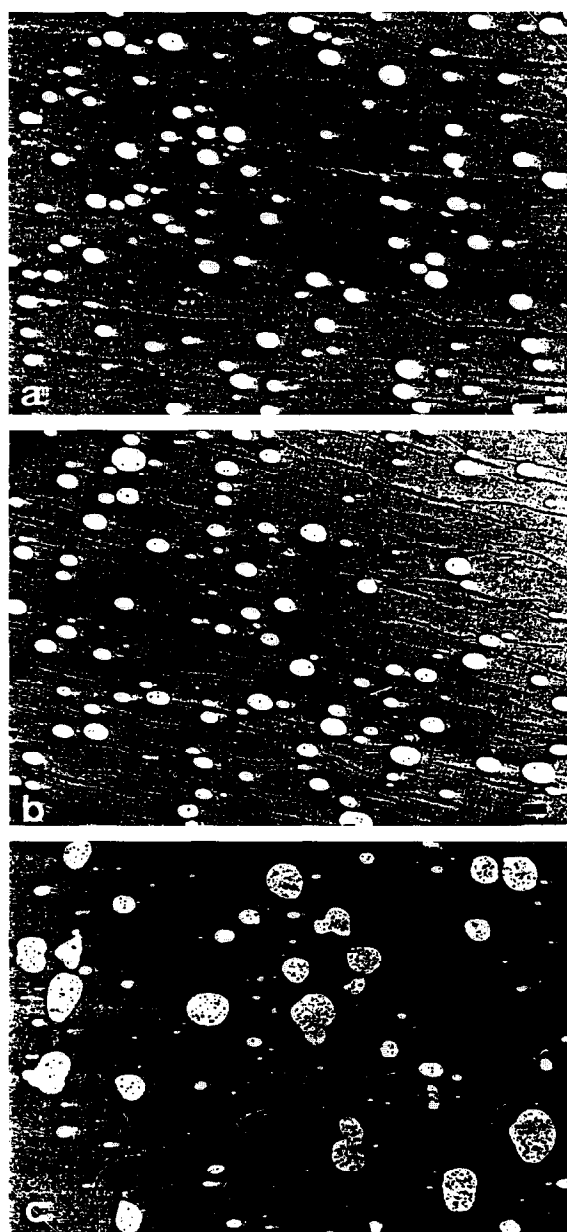
Figure 7 Micrographs of sample in *Figure 5* corresponding to various stages on the curve recorded at $85\,s^{-1}$. (a) Before inception of shear; (b) before onset of coalescence; (c) after cessation of shear. Magnification 4000×; length of bar 1 μm
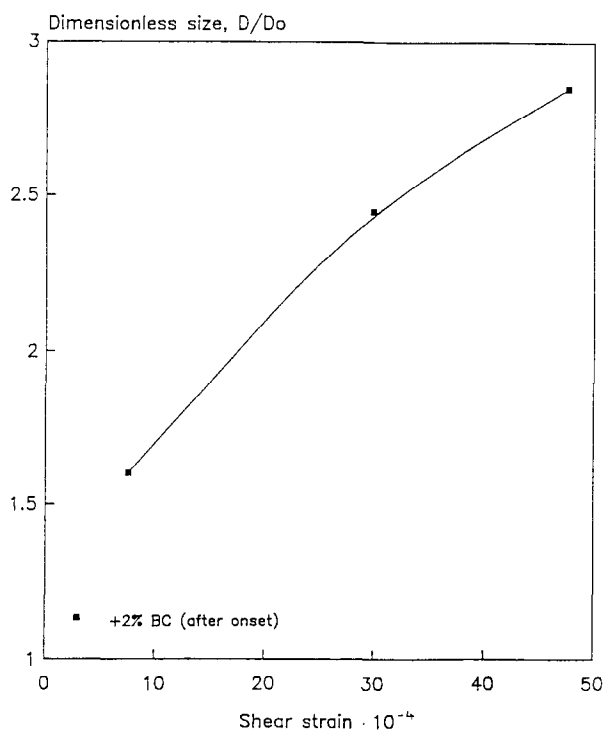
Figure 8 Dimensionless particle diameter *versus* shear strain for PS/PMMA-90/10 + 2wt% block copolymer (S/MMA-75/25) at 210°C with starting time taken at onset of coalescence

The stability of the block copolymer itself was tested by running a shear experiment on a neat copolymer sample at conditions corresponding to the measurement on the blend system at $85 s^{-1}$. The result showed only a minor decrease in molecular weight.

The interpretation of the light scattering data was further supported by micrographs of quenched samples (*Figure 7a–c*). No changes are observed from micrographs a and b taken at the times indicated by the arrows in *Figure 5*, while micrograph c, taken after the cessation of flow, shows enlarged particles at various stages of coalescence. From *Figure 7c* it should also be noted that micelles or mesophases were formed in the dispersed phase.

Several reasons may be suggested for the observed behaviour. Possible reasons for the time and shear dependent onset of coalescence may be attributed to changes in the block copolymer molecular weight due to cleavage at the interface or enhanced miscibility during flow which thermodynamically favours diffusion of copolymer molecules away from the interface. The reason for the observed behaviour may be a pull-out mechanism as suggested by Henderson and Williams[96]. The copolymer chains are gradually pulled out by frictional forces acting on the chains during the 'incubation' time until a critical concentration is reached below which the interface becomes unstable. In the case that the inclusions observed in the PMMA domains are mainly block copolymer micelles, this contradicts the above mechanism. On the other hand, the observed inclusions may also constitute a part of the matrix phase which has been entrapped between coalescing particles. Inclusions have, however, only been observed to a limited extent in neat blends with inclusions larger than typical diameters of micelles. After onset of coalescence the system essentially behaves as a neat two-component blend. One likely reason for the formation of micelles might be that some of the block

copolymer has been entrapped between coalescing particles. The influence of flow may also change the interfacial tension and, thus, the interfacial energy in a way such that the system minimizes its free energy by letting the PMMA phase encapsulate the interfacial layer of the block copolymer. This event is, however, most likely to occur in a blend system with a viscosity ratio below one.

The final results of the shearing measurements are shown in *Figure 8* in which normalized particle size as a function of shear strain is depicted with starting time at the onset of coalescence.

Concluding remarks

The rheo-optical measurements clearly recorded the effects of the block copolymer. The measurements showed that the primary and dominant mechanism of coalescence is shear coalescence in highly immiscible high-molecular-weight systems at the strong segregation limit.

The results from the shearing measurements showed that domain growth is initiated in the blend without copolymer while initially hardly any growth occurred in the blends with block copolymer. In the latter case the onset of coalescence depended on time and shear rate.

No single mechanism could be assigned to the instability behaviour, the proposed origin being an interplay of at least two mechanisms, with one dominating at low shear rates: flow-induced enhancement miscibility between copolymer and one homopolymer phase; and the other, with a higher threshold, dominating at high shear rates: a squeeze-out/drainage mechanism. Future work will incorporate the use of block copolymers with block chain lengths longer than the respective homopolymers in order to further clarify the origin of the instability.

In any case, the present work indicates that the interfacial stability is not unconditional during the flow. Thus, criteria for optimal concentration and block chain lengths for the block copolymer to reside in a thermodynamic equilibrium on the interface at static conditions should also include the effects of flow.

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