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Kinetics of Flow-induced Coalescence and Form Relaxation in Polymer Blends as studied by Rheo Small Angle Light Scattering

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SUMMARY: The kinetics of flow-induced coalescence in PS/PMMA (polystyrene/polymethylmethacrylate) blends containing 1 wt% and 5 wt% PMMA was measured by rheo small angle light scattering under conditions of non-deformed droplets. The results are in agreement with a coalescence model which includes binary hydrodynamic interactions. Under conditions where droplet deformation occurs, coalescence is suppressed and the interfacial tension was determined from the form relaxation time on the basis of the Palierne model.

Introduction

Flow-induced coalescence is one of the basic processes which determine the final morphology during processing of polymer blends. Rheooptical techniques as small angle light scattering (SALS)1) and microscopy2) are powerful methods to study the kinetics of this process. The recent study by SALS3) was motivated by a new kinetic model of flow-induced coalescence in which hydrodynamic interactions are explicitly taken into account4). Rheooptical techniques are also powerful for studying transient phenomena in melts as flow-induced deformation and breakup of particles or shape relaxation of deformed droplets. The study of these phenomena are relevant because of their connection with interfacial tension.

Experimental

The measurements were carried out with a Bohlin stress rheometer with integrated SALS device and 2D detection by a CCD camera. The apparatus described elsewhere5) was modified for the study of typical thermoplastic blends at high temperatures6). We report here on investigations on blends of polystyrene (PS) and poly(methyl methacrylate) (PMMA) with low content of PMMA (≤ 5 wt%) (Table 1). Blends were prepared by melt-blending in a Randcastle Microextruder at 220°C.

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Table 1. PS/PMMA homopolymers and blends

	$\overline{M}_W$ [Da]	η_0 [Pas]
PS100[a)]	100 000	$2.4\cdot10^3$ (at 210°C)
PMMA28[a)]	28 000	$1.0\cdot10^4$ (at 210°C)
PS158[b)]	158 000	$1.2\cdot10^5$ (at 175°C)
PMMA25[b)]	25 000	$6.5\cdot10^4$ (at 175°C)

[a)] Blend system (1 and 5 wt% PMMA) for coalescence experiments
[b)] Blend system (2 wt% PMMA) for form relaxation experiments

Coalescence[3)]

From PS100 and PMMA28 (Table 1) blends containing 1wt% and 5wt% PMMA were prepared. By evaluation of TEM micrographs (Fig. 1) it was found that the initial size distribution was quite narrow with an average radius of 100 nm which was taken as the initial droplet radius in the simulation of the experimental data. After shearing for a long time the size distribution is broadened considerably by flow-induced coalescence. The kinetics of coalescence during shear flow was monitored by recording the light scattering patterns. For shear rates $\dot{\gamma} \leq 0.8\ \mathrm{s}^{-1}$ the intensity distribution is isotropic at all times, i. e. the coalescing droplets are not deformed. The circular averaged intensity distributions were analysed according to the Debye-Bueche theory in terms of the correlation length a_c which is connected to the second and third moments of the droplet size distribution by

$$a_c = \frac{4}{3}(1-\phi)\frac{<r^3>}{<r^2>} \qquad (1)$$

The evolution of the correlation length for various shear rates is displayed in Fig. 2. Before shearing (t <0 min) the droplet sizes are stationary and in agreement with the size measured by TEM. The data scale with total strain $\gamma = \dot{\gamma}\,t$ as shown in Fig. 3 which also displays simulated curves. Strain as well as the time dependence are in excellent agreement with the simulation of the droplet size distribution by a model of flow induced coalescence which takes into account binary hydrodynamic interactions[4)]. If hydrodynamic interactions are neglected the particle growth is much faster than experimentally observed.

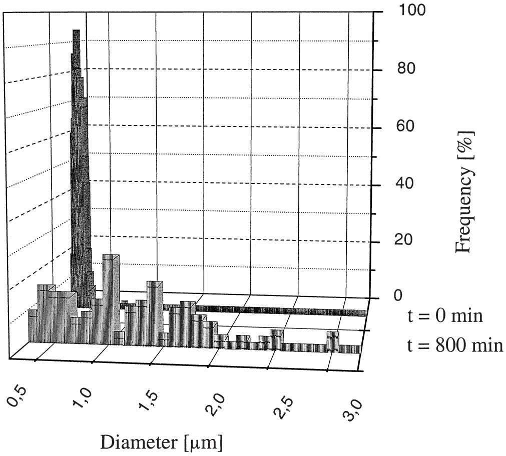

Fig. 1: Histograms of 2D diameters obtained from TEM images of a blend with 1% PMMA before shearing (t=0) and after shearing for t=800 min at a shear rate $\dot{\gamma}$ = 0.02 s^{-1}.

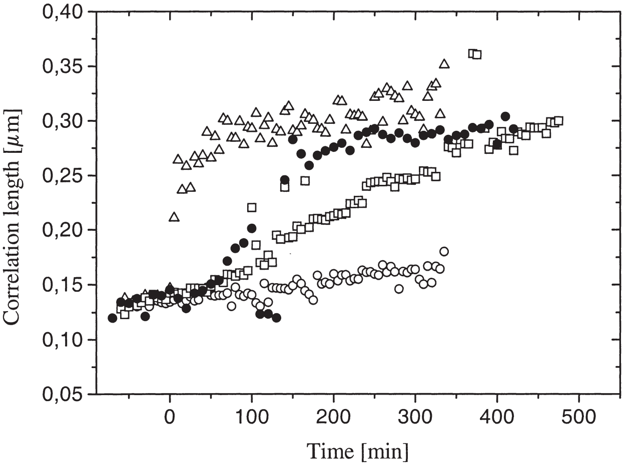

Fig. 2: Evolution of the correlation length at different shear rates as a function of time (0.0019 s^{-1} (○), 0.036 s^{-1} (□), 0.043 s^{-1} (●), 0.47 s^{-1} (Δ)), $\phi_{PMMA} = 0.05$).

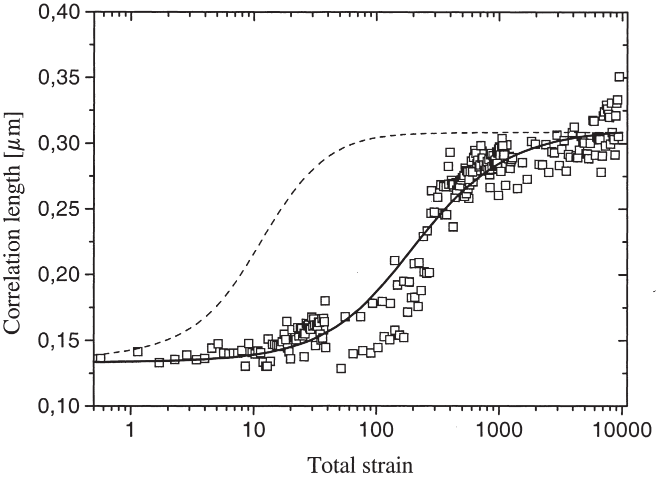

Fig. 3: Correlation length as a function of total strain. Shear rates and volume fraction as in Fig. 2 (experimental data (□), simulation with (——) and without (----) hydrodynamic interactions for $\phi_{\mathrm{PMMA}} = 0.05$ and $N = 12$).

Two factors set limits to the spatial resolution of the experiments. One factor is the wavelength of light (632 nm) setting a lower limit (~ 50 nm), the other is multiple scattering setting an upper limit. The latter is the reason why the correlation length in Fig. 3 saturates at about 0,3 μm for a blend with 5wt% PMMA. This limit is much lower than the resolution of the instrument (1.5 μm). The apparent upper limit of the droplet size in Fig. 3 is simulated by the maximal number of units N of the initial droplet volume of the discretized size distribution of the kinetic model. It was shown that slope of the curves as function of time or strain are not dependent on the artificial parameter N. The experimental growth rates as a function of strain rate are displayed in Fig. 4 for two concentrations. The ratio of the slopes of the linear fits is in agreement with the ratio of the volume fractions.

Form relaxation

For shear rates $\dot{\gamma} \leq 0.8\ \mathrm{s}^{-1}$ the droplet size remains practically stationary after shear stop for a long time. If the shear rate is increased or the viscosity ratio is decreased an ellipsoidal scattering pattern is observed. Fig. 5 shows a typical measurement for the blend of PS158 and PMMA25 at 175°C. The increase of the correlation length in the direction of flow is not accompanied by a corresponding decrease of the correlation length in the neutral direction as expected for constant volume of the droplets. We assume that the dimensions in this direction are below the lower resolution limit of the instrument.

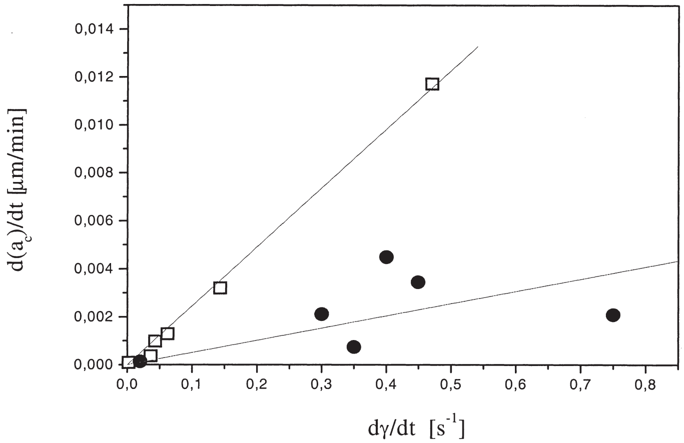

Fig. 4: Experimental growth rates as a function of shear rates for 5 wt% (□) and 1 wt% (●) PMMA28 in PS100. Lines represent linear fits of the data.

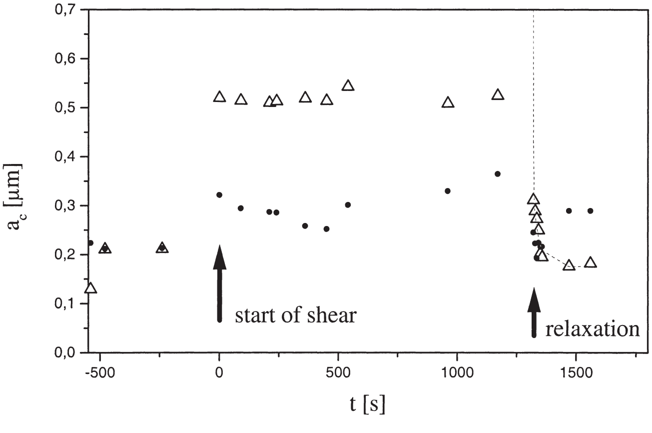

Fig. 5: Correlation lengths as a function of time in flow direction (Δ) and in neutral direction (•) for a blend of PS158 containing 2 wt% PMMA25; shear rate = 0.29 s^{-1}. The dashed line represents a fit with a 1st-order exponential decay function.

Unlike the experiments of the previous section the flow-induced structure relaxes back to the original state. We interprete the observed anisotropy during shear as a stationary deformation of the droplets which retract to the original spherical shape after shear stop.

This implies that coalescence of deformed droplets at low concentration is markedly suppressed which was also confirmed by recent computer simulations$^{7)}$.

Relaxation of a deformed droplet is essentially determined by the ratio of the interfacial tension and the particle radius. Therefore the interfacial tension of immiscible polymer blends can be measured if the droplets have a well defined initial size. Measurements on individual droplets have been performed by optical microscopy$^{2)}$. An alternative way is to observe the relaxation in reciprocal space by small angle light scattering (SALS) on an ensemble of dispersed particles, provided the initial particle size distribution is sufficiently uniform and processes other than deformation such as breakup or coalescence of droplets can be excluded. These conditions are fulfilled in the present case since the initial size is uniform, the capillary number (i. e the ratio of viscous stress and interfacial stress) is sufficiently small, and the experiments show that the initial size distribution is restored after cessation of shear.

In polymer blends the viscoelasticity of the components influences their deformation and relaxation behaviour. This has been taken into account in the model of Palierne$^{8)}$. According to the model, the form relaxation time τ after shear stop for small deformations is given by

$$\tau = \frac{\eta_m R_v}{4\sigma} \frac{(19k+16)(2k+3-2\phi(k-1))}{10(k+1)-2\phi(5k+2)} \tag{2}$$

where η_{m}, R_{v} and σ are the viscosity of the matrix, the radius of the droplets, and the interfacial tension, respectively, k is the viscosity ratio of the droplets and the matrix, and ϕ is the volume fraction of the dispersed component. On the basis of Palierne's model the interfacial tension of PS/PMMA has been determined from the dynamic moduli. A value of $2\cdot10^{-3}$ N/m was obtained in accordance with results from other methods$^{9)}$. With this value, R = 125 nm (derived from the stationary correlation length of about 170 nm before and after shearing) and the experimental parameters (Table 1) a relaxation time of 27 s is determined from eq. (2). If a 1st-order exponential decay is assumed, an average relaxation time of 25 s is obtained from Fig. 5, a second experiment gave reproducible results with a similar relaxation time of 20 s. The resulting mean value of $\tau = 22.5\,\mathrm{s}$ compares well with the theoretical relaxation time calculated by the Palierne model (27 s), indicating that form relaxation experiments can be used to determine so far unknown interfacial tensions from relaxation times of immiscible blends

As compared to the measurement of shape relaxation of individual droplets by optical microscopy the advantage of measurement by SALS is that a statistical analysis of a representative number of particles is not necessary because light scattering already averages over a large droplet population. A similar approach was followed recently where the authors studied the retraction and breakup of droplets that were highly stretched to filaments by combined dichroism and small angle light scattering$^{1)}$. They determined the interfacial tension by measuring the breakup time and analysed this parameter on the basis of Tomotika's theory of fibril breakup. As the authors point out the analysis can only be applied to Newtonian Systems for which the theory is valid. Their experiments indicate that the elasticity of the thread has the effect to increase the measured interfacial tension

Conclusion

It was shown that rheo small angle light scattering can be used to measure coalescence kinetics in a typical blend of thermoplastic polymers at typical processing temperatures for low concentrations. Although the observation window is limited by multiple scattering from above and by the wave length of light from below the measurements can be quantitatively analysed. The method also allows the measurement of relaxation times in a stopped flow experiment from which the interfacial tension can be determined. Though data are still limited the good agreement with values from other methods is encouraging to use SALS as additional method to determine this important quantity.

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