

Particle-stabilized polymer blends

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Abstract The effect of low-volume fractions of nanoparticles on the morphological processes and the rheological properties of immiscible blends are discussed. For blends of poly-isobutylene and polydimethylsiloxane stabilized by silica particles, particles help to suppress coalescence. Yet, particle bridging of different droplets has also been reported and leads to a slow build up of a gel-like structure, which could interfere with the morphology evolution under flow. We first investigated the importance of this effect under relevant conditions. To further assess the relative importance of the different processes in technically relevant polymer–polymer blends, the effect of carbon black particles on morphological processes—coalescence and break-up—in polyamide and ethylene–ethylene–methylacrylate copolymers will be studied using rheological methods. It will be shown that particles affect coalescence and break-up, suggesting that the effect of particles is linked to their effect on interfacial dynamics.

Keywords Coalescence · Break-up · Polymer blends · Particles · Emulsions

Introduction

In a recent paper, Thareja and Velankar (2007) confirmed earlier observations by some of the present authors (Vermant et al. 2004) that particles at interfaces

can be used to influence the structure and properties of polymer–polymer blends. The effects are similar to those in particle-stabilized water–oil emulsions, commonly described as ‘Pickering’ emulsions (for a recent review, see, e.g., Binks and Horozov 2006). Several mechanisms for stabilization of water–oil and oil–water emulsions by particles have been suggested, including steric (bilayer) stabilization of fully covered droplets (Binks 2002), stabilization by particle monolayers which can bridge droplets (Stancik et al. 2004; Ashby et al. 2004; Horozov and Binks 2006), effects of surface rheological properties (Reynaert et al. 2006, 2007), and even flocculation in the bulk (Binks et al. 2007). In our earlier work, it was shown that fumed silica particles can be used to suppress coalescence in blends of poly-isobutylene and poly-dimethylsiloxane. Measurements of the linear viscoelastic moduli were used to demonstrate that the silica particles alter the sensitivity of the dispersed phase–matrix microstructure to shear flow. More specifically, coalescence was shown to be suppressed or at least slowed down on a practical time scale by the presence of particles. CryoSEM observations were used to visualize particles accumulated at the interfaces and evidence was also presented that particle bridging occurred as drops were seen to be connected by a particle-laden interface (Vermant et al. 2004). Thareja and Velankar (2007) demonstrated more clearly that this ‘particle bridging’ is indeed present in similar PIB/PDMS/fumed silica systems, using optical light microscopy to reveal the presence of clusters of droplets in diluted systems. However, Thareja and Velankar (2007) also reported some apparent discrepancies between their and the published results pertaining to the low-frequency rheology and to the effects of mixing history. In the present

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communication, we will address these issues. We will also demonstrate the effects of carbon black (CB) particles on morphological processes—break-up and coalescence—in blends of technically relevant (high-temperature) polymers. Such CB-filled polymer blends form an interesting class of materials, as the use of a dispersed phase and a selective localization of CB particles at the interface (Gubbels et al. 1994) can dramatically lower the percolation threshold by a mechanism called ‘double percolation’: CB-covered droplets of the disperse phase are now readily interconnected by conductive networks in the continuous phase (Gubbels et al. 1998; Mironi-Harpaz and Narkis 2001). In the present work, we will limit ourselves to concentrations well below the percolation threshold, as the focus of this work is to demonstrate that, even at low nanofiller concentrations where the viscosities of the disperse and continuous phase are not significantly affected, the presence of the particles has an important effect on the morphological processes which in turn may be used to generate specific morphologies. By comparing the two systems, we intend to show that the most important effects of particles in polymer blends at these low filler concentrations are the effects on the morphological processes.

Experimental: PDMS–PIB blends

The first difference reported by Thareja and Velankar was the observation of ‘gel-like behavior’ in the rheology at low frequencies for silica-filled polymer blends, which was not seen in our experiments. The gel-like behavior was attributed, at least partially, to the formation of a network of particle-bridged droplets. In this study, we demonstrate that the reasons for this apparent discrepancy are twofold: First, the PDMS and PIB used by Thareja and Velankar were of lower viscosities and elasticity compared to our work, the zero shear viscosities of PIB and PDMS being, 69 and 95 Pa s (viscosity ratio $p = 0.72$) compared to 91 and 206 Pa s ($p = 0.44$). The contribution of the bridged droplets to the storage moduli in the work of Thareja and Velankar for the hand-mixed samples was on the order of 1 Pa, smaller than the lower range probed in our experiments. Secondly, as the main focus of our previous paper was on the effects of particles on coalescence, the frequency sweeps focused on the relaxation processes associated with the droplet shape relaxation (Palierne 1990), which for our systems occurred in the frequency range between 0.1 and 10 rad/s. Again, the network structure in the work of Thareja and Velankar for the hand-mixed samples were only visible at the lowest

frequencies (<0.05 rad/s), outside of the range probed in our experiments. We hence propose that a combination of factors, the lower moduli of the blend components and the relative contributions of the network structure on one hand, but more importantly the frequency ranges probed in our experiments cause the apparent discrepancy. To test this, we performed experiments extending the frequency range below 0.1 rad/s and annealing our samples of PIB/PDMS/silica. A MCR501 (Paar Physica) was used, equipped with cone and plate geometry (radius 25 mm, cone angle 4°). The results are shown in Fig. 1. Extending the frequency range indeed shows that at the lower frequencies a plateau can be observed, the magnitude of the low-frequency moduli slowly increasing as time proceeds. However, for the samples studied immediately after a preshear, as was done in our previous experiments, the magnitude of the low-frequency modulus is small, below 1 Pa, and any effect was outside the frequency range used in our previous work (the vertical line showing the low-frequency threshold used in our earlier work).

The second apparent discrepancy reported by Thareja and Velankar concerned the effects of mixing history. The latter authors showed that the low-frequency rheological properties were sensitive to blending procedures, comparing hand-blending procedures with high-shear mixing in an extruder. In our earlier work, we focused on the effect of various hand-blending procedures on the droplet morphology and showed that, by careful preparation of the systems, reproducible conditions could be obtained. Comparing the data of the hand-mixed samples in our work (our Fig. 7) with the data obtained for hand-mixed samples by Thareja and Velankar (their Fig. 5 a) shows

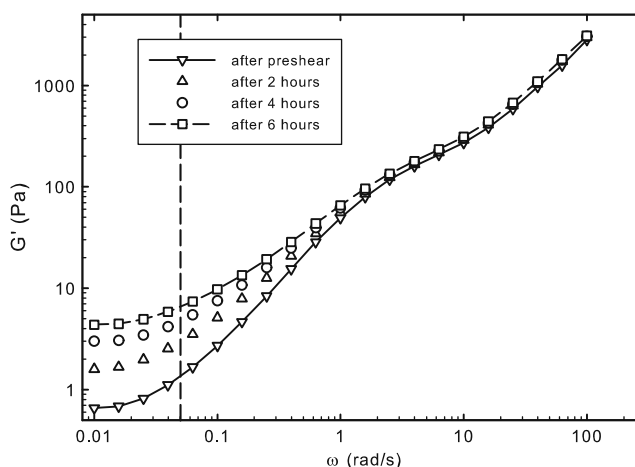


Fig. 1 Effect of annealing time on the frequency sweep at a strain of 0.25 after a preshear at 400 Pa, sheared for 2,000 s for a 30/70 PIB/PDMS blend containing 1% by weight of fumed silica

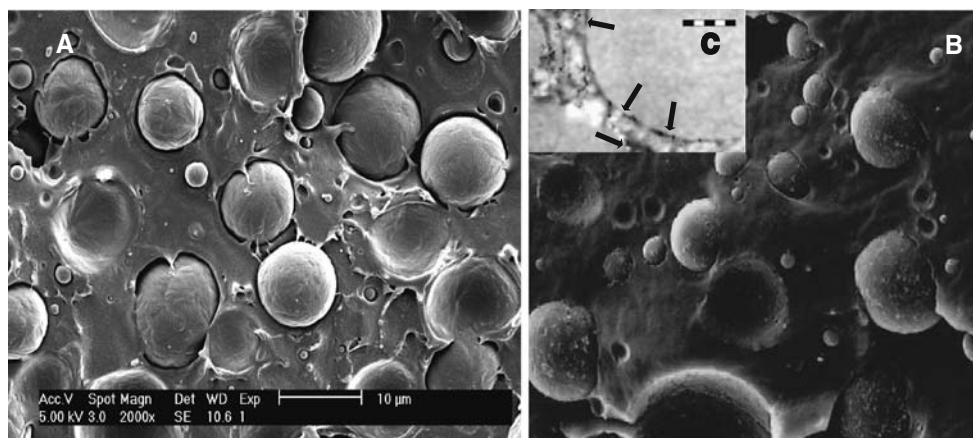
fair agreement as far as the position of the shoulders in the moduli versus frequency plots (approximately $1/\text{radii}$) are concerned. When stronger mixing flows are employed during the dispersion of the particles and generation of the matrix–droplet structure, it is not surprising that large differences are observed. We already indicated that particles can be expected to affect the morphological processes—break-up and coalescence—that establish the droplet–matrix structure, and further work is clearly required to understand how to control and tailor these processes during nonequilibrium mixing. We will demonstrate the effect of particles on break-up in more detail later. Clearly, the gel-like structure formed by bridged particles will be even more sensitive to shear history, but as indicated above, any effect on the low-frequency rheological properties was outside of the measurement range in our work, as we considered relatively mild mixing conditions and evaluated properties of the blend immediately upon cessation of flow. A final comment on the PIB/PDMS blends: we of course agree with Thareja and Velankar that studies using model systems, e.g., with particles of controlled surface chemistry and size, are useful and further research is required. The fumed silica clearly was never intended to be a model system.

Experimental: PA/PE-EMA blends

The rheological properties of particle-stabilized blends consisting of high-melt temperature components were studied for two reasons: First, to further investigate the relevance of a small, low-frequency plateau modulus that could be generated by particle-bridged droplets and secondly, to investigate if the flow-induced morphological processes in technically relevant blends are affected by the presence of nanoparticles at the interface. These systems have a higher medium

viscosity and elasticity compared to the PIB/PDMS system studied previously. Two immiscible technical polymers, a polyamide 12 (PA–Rilsan AMVO, Arkema) and a statistical copolymer of ethylene and ethylene–methyl acrylate copolymer (PE-EMA Lotryl 24MA07-Arkema) were melt blended in a ratio of 30/70 using a corotating twin screw extruder (DSM miniextruder). Rheological properties were investigated using a dynamic stress rheometer (Rheometric Scientific, USA). At a temperature of 225 °C, the zero shear viscosities amounted to 407 and 1,414 Pa s for the PA and the PE-EMA, respectively ($p = 0.3$). CB particles (Ensaco 250G) were used as filler material, and a virgin blend was compared to a system containing 1 vol.% CB. The pure polymers containing 1% CB had zero shear viscosities at 225 °C of 465 and 1,548 Pa s for the 1% CB/PA and the 1% CB/PE-EMA, respectively. The changes in viscosity and viscosity ratio are hence limited and should not dramatically affect the morphological processes. To visualize the morphologies, the samples were fractured, gold-coated, and visualized using SEM. As is shown in Fig. 2, the droplet surface was smooth for the virgin blend, whereas for the filled system, the presence of CB at the droplet surface was observed, as exemplified by the white dots on the particle surface representative of the conductive CB material. Investigation by transmission electron microscopy also revealed the predominant presence of the CB in the PA phase with a partial localization of CB at the PA/PE-EMA interface, the latter shown by the inset in Fig. 2C. An affinity for the phase with the highest surface tension, i.e., the polyamide, is observed, in agreement with literature reports (Sumita et al. 1991; Tchoudakov et al. 1996). It should be remarked that in the SEM micrographs, as in Fig. 2B, almost no bridged droplets were observed, indicating that it is at least a rare phenomenon in this PA/PE-EMA/CB system at these volume fractions of filler.

Fig. 2 SEM micrographs of a 30/70 blend of PA/PE-EMA obtained after extrusion: unfilled system (A) and system containing 1 vol.% CB (B). C TEM micrograph of a 70/30 PA/PE-EMA blend showing the localization of the CB (the scale bar in the TEM corresponds to 200 nm)



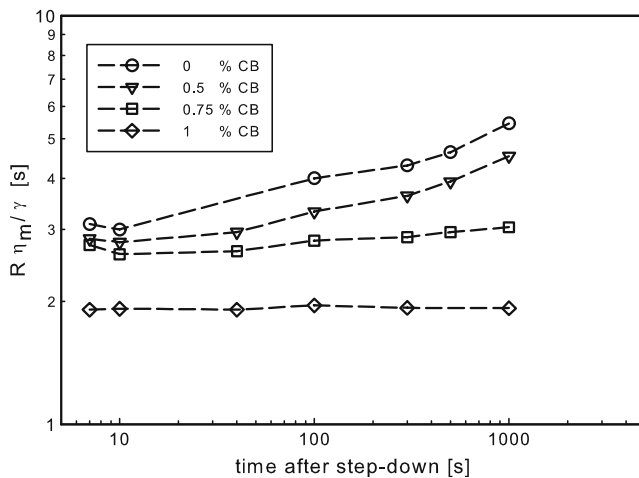


Fig. 3 Evolution of the morphology, as characterized by $R\eta_m/\gamma$, for a 30/70 PA/PE-EMA blends as a function of cumulative time at a shear rate of 0.1 s^{-1} (after a preshear at 2 s^{-1} for 800 s) for different volume fractions of CB

Similar to our earlier work, the effect of shear history on the droplet–matrix morphology was investigated; more specifically, the effect of particle volume fraction on the coalescence process was investigated. The sample was first presheared at a shear rate of 2 s^{-1} for 1,600 strain units and followed by shear flow at a lower rate of 0.1 s^{-1} . The flow was arrested from time to time and the morphology was probed using a frequency sweep. The frequency associated with the position of the ‘shoulder’ in the G' - ω curves was determined by subtracting the component contributions and determining the dominant relaxation time of the interfacial contribution which stems from the deformation of the droplet. The evolution this ‘Palierne’ time scale, which is the product of the droplet radius times medium viscosity over the interfacial tension ($R\eta_m/\gamma$) as a function of shearing time after step-down, as shown in Fig. 3. For concentrations above 0.5% CB, coalescence is slowed down on a practical time scale, even essentially suppressing coalescence at concentrations as low as 1 vol.%. Low amounts of particles, possibly leading to only sparsely covered droplets as suggested by the TEM images, may be sufficient to reduce coalescence rates, in agreement with observations for water–oil emulsions (Midmore 1998; Vignati et al. 2003) and hydrophobic silica-stabilized PP/PS blends (Elias et al. 2007).

To investigate the effect of particles on the other morphological process, i.e., break-up, the spectra were determined in a sequence where the shear rate was increased in each subsequent experiment. Break-up of the dispersed phase is expected when the capillary number at a certain shear rate is higher than the critical capillary number. This critical capillary number can be

obtained from the data of Grace (1982) and was found to be decreasing from 0.48 to 0.46 in the investigated shear rate range as a result of the shear thinning of the dispersed phase (PA), which corresponds to a critical shear rate of about 0.5 s^{-1} . Figure 4 shows the storage modulus (G' , Pa) and the elastic part of the complex viscosity (η'' , Pa s) as a function of angular frequency (ω , rad/s) of the pure 30/70 blend and the 30/70/1% CB-filled systems for a series of preshear rates. At each shear rate, the total deformation was kept fixed at a strain of 1,400. As expected, a characteristic and pronounced ‘shoulder’ appears in all the curves of Fig. 4 in a particular frequency range; it represents the shape relaxation of the deformed droplets (Palierne 1990). As in the case of the PDMS–PIB blends, the position of the shoulder in the unfilled polymer blend (Fig. 4a) is a function of the previous shear rate, shifting to higher frequencies indicative of break-up. However,

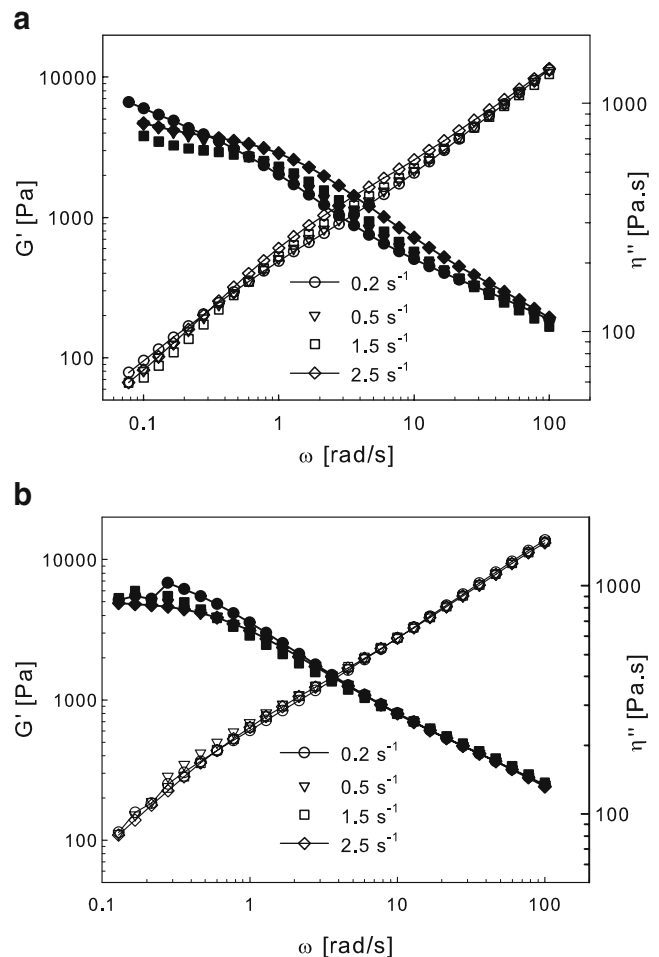


Fig. 4 Frequency dependence of the storage modulus (G' , open symbols) and the elastic part of the complex viscosity (η'' , filled symbols) at a strain amplitude of 0.05 after different preshear rates for 30/70 PA/PE-EMA blends for a virgin blend (a) and in the presence of 1 vol.% CB (b)

the effect of the same shear history on the droplet morphology is again virtually suppressed in the 1% by volume CB-filled blend systems (Fig. 4b). In the accessible frequency range, no indication for leveling of low frequencies was detected, although neither was the terminal region reached.

Although the presence of a low-frequency plateau modulus and associated yield stress because of particle bridging cannot be excluded, its effect on the rheological properties for the present system (with higher viscosities and matrix moduli compared to the PIB/PDMS) is clearly small. Recently, similar results have been obtained by Elias et al. (2007) for polypropylene/polystyrene blends containing hydrophobic silica particles. No upturn in the modulus of the complex viscosity was observed for low-silica volume fractions. Hence, under conditions which are relevant for morphology evolution and processing, no effects of bridging could be observed in this system, although at higher volume fractions, this could be the case. At higher volume fractions of filler, the effects of particles on the rheological properties of the two components will also become more important.

Conclusions

The use of nanoparticles to affect the morphology in polymer–polymer blends is a topic of great scientific and technological interest. We have tried to elucidate the source of some apparent discrepancies which were suggested by Thareja and Velankar (2007). Bridging of selected droplets was already shown in our work by CryoSEM observations; in the present work, we have confirmed that when the blends are subjected to long rest periods, particle bridging may indeed induce a gel-like behavior in the rheology of polymer–polymer–particle blends. However, the stresses involved are small and could not be detected in blends of technically relevant (high-temperature) polymers. Like for water–oil emulsions (Horozov and Binks 2006), particle bridging seems not to be a necessary condition for stabilization of the blend morphology by particles. We have now shown that both coalescence and break-up are affected by the presence of particles. Hence, optimizing the structural features of particle-stabilized blends will be possible using control of break-up during mixing and coalescence suppression.

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