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Rheology and Morphology of Highly Compatibilized Polymer Blends

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Summary: The rheology and morphology of highly compatibilized droplets has been studied, using both rheology and small angle light scattering. It is shown that linear viscoelastic measurements are a powerful tool to investigate the effectiveness of a compatibilizer to suppress coalescence. Moreover, such highly compatibilized droplets are insensitive to deformation and breakup. The consequences for the rheological behaviour of the blend are discussed.

Keywords: blends; compatibilization; morphology; rheology

Introduction

Polymer blends provide a economically attractive route to generate tailor-made materials that synergistically combine desired properties. One of the key aspects in the design of such materials is the proper use of compatibilizers. They can either be added to the blend (the so-called physical compatibilization route) or can be generated during the mixing step (the so-calles chemical compatibilization route). In either case, compatibilizers stabilize the morphology and provide sufficient interfacial adhesion, thus improving the mechanical properties of the blends [1–3].

During blending, several morphological processes occur simultaneously. When processing a blend with a droplet-matrix morphology, droplets can deform, breakup or coalescene. For uncompatibilized blends, consisting of Newtonian components, the morphology development is relatively well understood [4]. For their compatibilized equivalent, no complete picture is available at present although significant progress has been made recently. For instance, it is now clear that a mere reduction of interfacial tension is not the only role of a compatibilizer. The latter would simply lead to a finer dispersion because droplets could be deformed much further prior to breakup. However, Sundararaj and Macosko [5] clearly demonstrated that an important contribution of a compatibilizer is the suppression of coalescence, an hypothesis that has been confirmed by several studies. The precise mechanism for this coalescence suppression is not clear at present. Friedrich *et al.* [6] as well as Van Hemelrijck *et al.* [7,8] pointed towards the importance of interfacial rheological properties for understanding coalescence suppression. For instance, Van Hemelrijck et al. performed a set of systematic coalescence experiments, using well-defined premade block copolymers. The evolution of the morphology during coalescence was monitored by measuring the linear viscoelastic spectrum of the blend. Compared to the spectrum of uncompatibilized blends, the linear viscoelastic spectrum of compatibilized has an important peculiarity. In addition to the usual shape relaxation time of the droplets, an additional relaxation time emerges which is associated with gradients of the block copolymer concentration at the interface. These two relaxation times are nicely

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captured by the 'full' Palierne model[9] that includes a non-isotropic interfacial tension. Van Hemelrijck *et al.* [8] proposed a scaling relation that relates this additional interfacial relaxation mechanism to gradients in interfacial tension, hence pointing to the possible mechanistic role of Marangoni stresses in suppressing coalescence in compatibilized polymer blends.

Studies on the deformation and breakup of compatibilized droplets are still relatively scarce [e.g. 10,11]. Jeon and Macosko [10] visualized the compatibilizer distribution on a sheared polymer drop by using a fluorescently labeled poly(styrene-b-methylmethacrylate). They observed a higher compatibilizer concentration at the edges and tips of the droplet,. due to convection of the compatibilizer by shear flow. The mobility of compatibilizers on an interface was also confirmed by Van Puyvelde *et al.* [12] using a model PIB-PDMS blend compatibilized with a PIB-PDMS block copolymer. Observation of droplets with pointed ends was associated with the accumulation of block copolymer at the drop tips. This accumulation would indeed cause a lower local interfacial stress, giving a rise to a higher local curvature of the drops. It was also reported that PIB droplets with 10% compatibilizer did hardly show any deformation, a fact that could be attributed to a substantial Marangoni stress that immobilizes the interface at high surface coverages. In the present study, the morphology development of highly compatibilized droplets is further elaborated using a model blend consisting of PI and PDMS, compatibilized with a PI-PDMS block copolymer. Both rheology and small angle light scattering experiments will be performed to study the coalescence and breakup behaviour of highly compatibilized droplets.

Materials and Methods

The blends used in this work consist of two model components: polyisoprene (PI, Kuraray Rubber Japan) and polydimethylsiloxane (PDMS, Rhodia France). These polymers are completely immiscible over the whole temperature range relevant to this work. They are liquid at room temperature allowing their use in long-term experiments. Their molecular weight M_w, entanglement molecular weight M_e, viscosity η and first normal stress coefficient Ψ_1 at 23°C are listed in Table 1.

Table 1.
Properties of the pure components

Material	M_w (g/mole)	M_e (g/mole)	$\eta_{23\,^\circ C}$ (Pa · s)	$\Psi_{1,23\,^\circ C}$ (Pa · s^{-2})
PI	29000	5100	203	0.4
PDMS	166000	9600	208	7.9

A block copolymer of PI and PDMS is used as compatibilizer. It has been synthesized by means of sequential anionic copolymerization (see Almdal *et al.* [13] for further details). It has an overall molecular weight of 20500 g/mole (PI: 11000 – PDMS: 9500), implying that the blocks are too short to entangle with the phases of the blend.

Compatibilized blends have been prepared by adding the desired amount of compatibilizer to the minority phase after which this mixture is blended in the matrix phase. Since the blends are liquid at room temperature, mixing was performed by hand using a spatula. In the compatibilized blends, the amount of block copolymer is quoted as a fraction of the dispersed phase.

A disadvantage of physical compatibilization is the uncertainty concerning the location of the block copolymer. It is indeed not necessarily located at the interface but can also be present as micelles in one of the phases, implying that experimental results will possibly be influenced by the sample preparation. However, different sample preparation routes have been explored here (block copolymer first added to the disperse phase, block copolymer first added to the matrix phaseand simultaneously mixing the three components). It turned out that the different procedures led to the same experimental results, indicating that all the added block copolymer is located at the interface.

Rheological measurements have been performed on an ARES rheometer (Rheometric) equipped with 25 mm diameter/0.1 radian cone and plate geometry. The temperature was set at 23 °C. For the rheological experiments, blends containing 10 wt% of PDMS as the dispersed phase have been used. To support the conclusions drawn from rheological measurements, scanning electron microscopy observations were made. In these experiments, the PDSM dispersed phase has been replaced by a mixture of 80% crosslinkable vinyl-terminated PDMS (Polymer VS 165 000 from Hanse Chemie, Germany) and 20% of non-crosslinkable PDMS. To crosslink the PDMS a SiH-crosslinker (SiH 125 Hanse Chemie), a Pt-catalyst (Pt 510 Hanse Chemie) as well as an inhibitor (PT88 Wacker Chemie) have been added. It has been verified that the viscosity and moduli of the resulting dispersed phase are identical to those of the regular PDMS. After applying the appropriate shear histories, the blend is heated in the rheometer to 100 °C for 30 minutes to induce the crosslinking by hydrosilation of the vinyl ends with the SiH groups of the crosslinker. After this process the blend was recoverd and immersed in cyclohexanone to dissolve the PI matrix phase. Subsequently the material was gold coated prior to observation in a Philip XL30FEG scanning electron microscope.

Complementary to the rheological study, small angle light scattering measurements (SALS) have been used to study the deformation and break-up of droplets. Light from a He-Ne laser ($\lambda = 633$ nm) is sent through the sample that is contained in a Linkam parallel plate shearing cell (CSS 450). The scattered light is collected on a semi-transparent screen mounted underneath the cell. A high-resolution 10 bit CCD camera (Pulnix TM 1300) connected to a frame grabber (Coreco Corp.) is used to capture and to digitize the 2D light scattering patterns. In house developped software (KUL SALSSOFTWARE) is used to analyze the images.

Results and Discussion

1. Coalescence Suppression in Highly Compatibilized Droplets

To study the coalescence of droplets in compatibilized blends, the following flow protocol has been applied. First, samples are subjected to a preshear (4.8 s^{-1}) until steady state conditions are reached. Such a preshearing is necessary to wipe out the effects of mixing and loading and to generate a reproducible initial microstructure. Subsequently, the shear rate is lowered (1.2 s^{-1}) to study the flow-induced coalescence. The evolution of the morphology is monitored by interrupting the shear flow periodically and conducting linear viscoelastic measurements. A theoretical framework exists – the Palierne model [9] – that is able to extract morphological information from these measurements. This Palierne model yields information about the relaxation time of droplets. Moreover, it was shown recently that in compatibilized droplets, an additional relaxation mechanism is present that can be attributed to a non-uniform interfacial tension [6–8]. Here we will compare the behaviour of blends with low and high compatibilizer concentrations.

Figures 1^a and 1^b show the storage moduli G'_b for a 0.1% and a 10% compatibilized blend at two shear rates: the initial preshear rate and the coalescence shear rate. The curve at the coalescence shear rate of 1.2 s^{-1} is obtained after reaching steady-state conditions. As can be seen in Figure 1^a, two clear relaxation shoulders can be observed in the spectrum. As was discussed by for instance Van Hemelrijck et al. [7], the relaxation shoulder at high frequencies is associated with the form relaxation time t_f of the droplets from which the droplet dimensions can be calculated, provided the interfacial tension is known. The relaxation shoulder at low frequencies is associated with the interfacial relaxation time t_β. Based on a systematic study of the effect of molecular architecture of the compatibilizer on t_β, Van Hemelrijck *et al.* [8] proposed a scaling

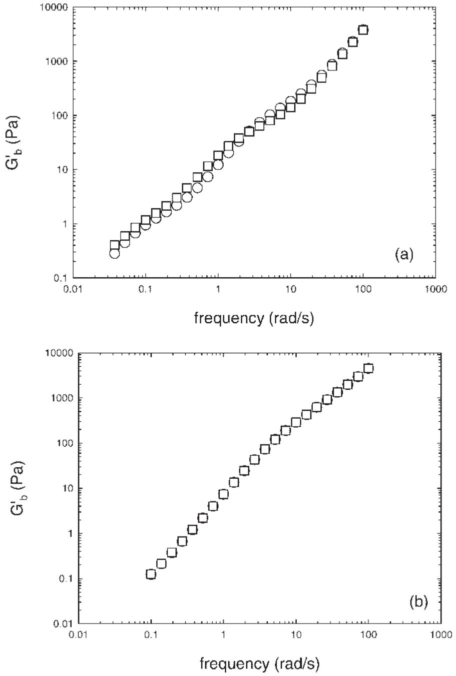

Figure 1.
Storage modulus for (a) a 0.1% compatibilized blend and (b) a 10% compatibilized blend after a preshear of 4.8 s^{-1} for 3000 strain units (○) and after shearing at 1.2 s^{-1} (□) till steady state.

relation that contains the sensitivity of the interfacial tension α to interfacial coverage c, hence pointing towards a possible link between t_β and Marangoni stresses. From Figure 1^a, it can also be seen that the form relaxation time of the droplets at a shear rate of 1.2 s^{-1} has shifted to lower frequencies, as compared to the response at 4.8 s^{-1}. This corresponds to a longer relaxation time, indicating the existence of bigger droplets. Hence, it can be concluded that in the 0.1% compatibilized blend, coalescence is still occurring. This is confirmed in Figure 2^a in which the SEM pictures are shown at the end of the preshearing period and at final steady state conditions at 1.2 s^{-1}. The interfacial relaxation time t_β did not change during the coalescence process, as was already discussed in detail by Van Hemelrijck *et al.* [8].

As can be seen in Figure 1^a, the two relaxation times are nicely separated for blends with low compatibilizer concentrations. However, Van Hemelrijck *et al.* [8] demonstrated that with increasing compatibilizer concentrations, the interfacial relaxation time becomes comparable to the form relaxation time. At intermediate compatibilizer concentrations and based on a detailed analysis of the mechanical spectrum using NLREG [14], it was still possible to discriminate between the two different relaxation mechanisms.

The situation is different for highly compatibilized blends. For instance, when comparing the moduli after preshearing at 4.8 s^{-1} and after reaching steady state conditions at 1 s^{-1}, it can be concluded that the moduli do not evolve anymore in time. Moreover, even a detailed analysis of the mechanical spectrum using NLREG did not reveal distinct relaxation times. Since the moduli did not evolve in time, it can be concluded that the radius of the droplets did not change during the coalescence experiments. This is confirmed by the SEM experiments, as can be seen in Figure 2^b. In addition, it can be noticed that the morphology of the 10% compatibilized blend is significantly smaller than the one generated in the 0.1% compatibilized blend. It can be concluded that linear viscoelastic measurements can be used to determine the efficiency of the compatibilizer, i.e. the ability of the compatibilizer to suppress coalescence.

Based on a systematic change of compatibilizer concentration, it is found that a complete coalescence suppression in this system and under these flow conditions is observed for a compatibilizer concentration beyond 1%. Assuming that all block copolymers are located at the interface and knowing the droplet radius, the interfacial coverage c_0 at a particular compatibilizer concentration can be calculated as:

$$c_0 = \frac{z \rho_d R_v N_A}{300 M_{w,bcp}} \qquad (1)$$

where z is the percentage of block copolymer added, relative to the dispersed phase. ρ_d (kg/m^3), N_A (mole^{-1}) and $M_{w,bcp}$ (kg/mole) are the density of the dispersed

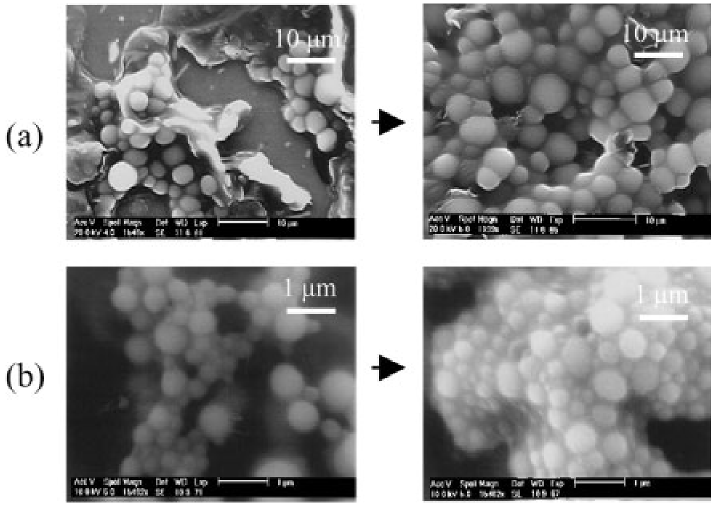

Figure 2.
SEM images of (a) a 0.1% compatibilized blend and (b) a 10% compatibilized blend after a preshear of 4.8 s^{-1} for 3000 strain units (left) and after shearing at 1.2 s^{-1} (right) till steady state.

phase, the Avogadro number and the molecular weight of the block copolymers respectively. This interfacial coverage can be compared with the maximal coverage $c_{\max}$ when the interface is fully saturated with block copolymer [15]:

$$c_{\max} = \frac{\textit{thickness}\text{ of copolymer monolayer}}{\text{volume of a single chain}} = \frac{\frac{\Lambda}{2}}{\frac{M_{\mathrm{w,bcp}}}{\rho_{\mathrm{bcp}} N_{\mathrm{A}}}} \tag{2}$$

in which Λ is the lamellar spacing in an ordered block copolymer and ρ_{bcp} the density of the block copolymer [7]. Coalescence suppression in these systems is observed beyond 1% compatibilizer concentration. Based on equations 1 and 2, this corresponds to approximately 0.2 block copolymer chains per nm^2, representing 60% of the saturated block copolymer coverage. This value is in good agreement with values reported by Lyu *et al.* [15].

2. Deformation and Break-Up in Highly Compatibilized Blends

In order to study the deformation and break-up of highly compatibilized blends, the following experimental protocol has been used. First the sample is subjected to a preshear at a low shear rate until steady state conditions are reached. Subsequently, the shear rate is suddenly increased and the transient stresses or small angle light scattering patterns are recorded as a function of time.

In Figure 3, the first normal stress difference N_1 is shown during a step-up in shear rate from 2.5 s^{-1} to 5 s^{-1} for an uncompatibilized blend (circles) and for a

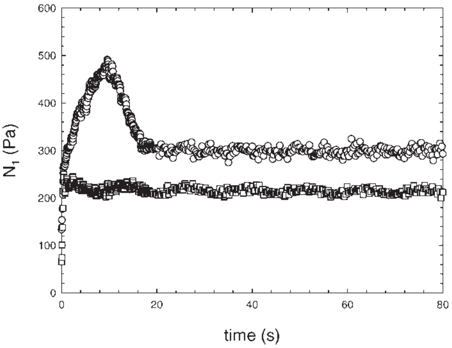

Figure 3.
Evolution of the first normal stress difference N_1 during a step-up in shear rate from 2.5 s^{-1} to 5 s^{-1} for an uncompatibilized 10/90 PDMS/PI blend (O) and for a 10% compatibilized 10/90 PDMS/PI blend (□).

10% compatibilized blend (squares). The evolution of N_1 for the uncompatibilized blend is already well understood [4]. The initial increase in N_1 is attributed to the deformation of the droplets into fibril that generate a stronger anisotropy. After some time, interfacial tension becomes dominant and the fibrils start to breakup by means of interfacial instabilities. This results in a loss of anisotropy and hence N_1 decreases. Finally, an equilibrium morphology is generated an N_1 reaches a constant value. From the stress response, detailed breakup times could be derived and scaling relations were proposed [16]. The stress response of a blend with a high compatibilizer concentration is completely different from that observed for the uncompatibilized equivalent. During the transient evolution, no overshoot is seen in N_1 indicating that no droplet deformation is measured after applying the step-up in shear rate.

Recently, the stress response of blends with intermediate compatibilizer concentrations was studied by Van Hemelrijck *et al.* [17]. The results were explained based on the occurrence of Marangoni stresses. The presence of such an extra stress alters the stress balance on a droplet. Van Hemelrijck et al. [17] proposed a modified capillary number taking into account hydrodynamic, interfacial and Marangoni stresses:

$$Ca_{comp} = \frac{\eta_{\mathrm{m}}\dot{\gamma}R}{\alpha}\left[1 - A\frac{c_0}{\alpha}\left|\frac{d\alpha}{dc}\right|\right] \qquad (3)$$

in which η_{m}, R and c_0 are respectively the matrix viscosity, the droplet radius and the uniform interfacial coverage with block copolymer. A is an unknown constant reflecting the relative importance of the Marangoni stress in the droplet deformation. The modified capillary number was able to qualitatively describe the evolution of the steady state droplet size in modestly compatibilized blends.

In order to verify the conclusions drawn from the rheological experiments, complementary small angle light scattering experiments have been performed under similar conditions. To avoid multiple scattering, the concentration of the dispersed phase was lowered to 1%. Figure 4 shows the transient SALS-patterns during a step-up in shear rate from 5 s^{-1} to 10 s^{-1} (same step-up ratio as in the rheological experiments). The first pattern is isotropic, this is logical as it was obtained after the preshearing. Shearing at the high shear rate, the pattern however remains nearly isotropic and hence no deformation is present in the system. This indicates that under these conditions the capillary number must be really small. These highly compatibilized droplets start to behave in a more suspension-like manner. A possible explanation can be found in the presence of Marangoni stresses. At a high compatibilizer concentration, these stresses can become large enough to suppress droplet deformation and will immobilize the droplets. In equation 3, this is reflected in a large $\frac{c_0}{\alpha}\left|\frac{d\alpha}{dc}\right|$ due to the high interfacial coverage c_0. This leads to a small Ca_{comp} and hence to a very small deformation.

Based on these observations, one could argue that highly compatibilized blends behave as suspensions. Hence, it is interesting to compare the steady state viscosity with the predictions of the Einstein model [18] that theoretically describes the rheology of dilute suspensions. The following equation for the viscosity of a fluid containing a small fraction of spherical solid particles should apply:

$$\eta = \eta_m\left(1 + \frac{5}{2}\phi\right) \qquad (4)$$

In principle, it would be more accurate to use Batchelor's model since we are dealing here with a particle concentration $\phi = 10\%$. It has been checked, however, that the predictions of the two models are nearly identical for this case.

Figure 5 shows the viscosity of a 5% and a 10% compatibilized blend. These two concentrations are in the regime in which no significant deformation of the droplets is observed. Hence, for these two concentrations, the material can be assumed to behave as a suspension and Einsteins

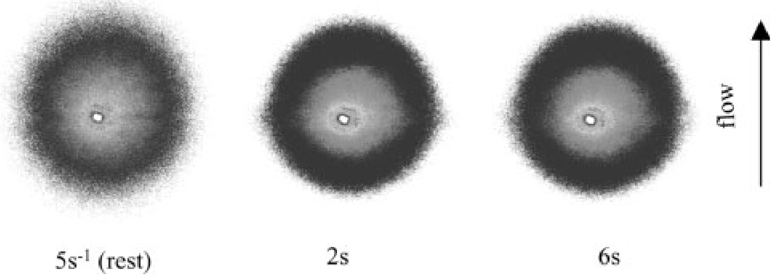

Figure 4.
SALS patterns for a 10% compatibilized 1/99 PDMS/PI blend after a step-up in shear rate from 5 s^{-1} to 10 s^{-1}. Times refer to times at the high shear rate.

viscosity model should be able to describe the viscosity. Based on Figure 5, it can be seen that the model is indeed capable of giving a reasonable estimate of the viscosity of the highly compatibilized blend.

Conclusions

In this paper, both the coalescene and deformation behaviour of highly compatibilized droplets is investigated. It is shown that linear viscoelastic measurements can provide information on the efficiency of the compatibilizer with respect to coalescence suppression. In addition, the deformation of highly compatibilized droplets is investigated both by means of rheological as well as by means of rheo-optical experiments. The time evolution of both the stress and the small angle light scattering patterns indicate that highly compatibilized droplets can be regarded as solid spheres. This suspension-like behaviour is also reflected in the steady state viscosity of the highly compatibilized material since Einstein's viscosity model gives reasonable predictions. The possible role of Marangoni stresses, not only in the coalescence suppression but also in the deformation suppression, is highlighted by means of a modified capillary number.

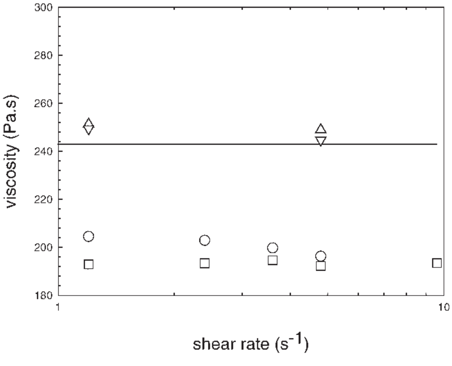

Figure 5.
Steady state viscosity of pure PDMS (o), pure PI (□), 5% compatibilized 10/90 PMDS/PI blend (∇), 10% compatibilized PDMS/PI blend (Δ). The predictions of the Einstein model are plotted as a full line.

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