Macromolecules **2006,** *39,* 2445−2448 **2445**

On Dispersions of Block Copolymer Droplets

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Received November 23, 2005
Revised Manuscript Received February 21, 2006

Dispersing immiscible fluids is a fascinating and complex physical problem which still stimulates considerable and active research. Most of these efforts aim to describe and predict the time evolution and morphology of fluid dispersions from knowledge of the flow and component fluids' characteristics. This description is essentially based on processes of breakup and coalescence of fluid droplets, which in turn implies a good knowledge of how droplets deform and how a thin liquid film drains between two colliding droplets. Since the seminal work of Taylor,[1] fluid mixing has been extensively studied, and the case of Newtonian fluids with or without surfactant molecules is now fairly well-understood.[2] The problem becomes more complex for polymer blends and is still the subject of many investigations. Both breakup and coalescence are governed by the rheology, interfacial properties, and composition of the blends. For polymer melts, droplet deformation and film drainage are very sensitive to viscoelastic effects and mobility of the droplet interface.[3,4] In this context, the peculiar properties of structured fluids such as polymer liquid crystals or ordered block copolymer melts could be of great interest. The deformation behavior and rheological and interfacial characteristics of such fluids are known to vary greatly with their composition as well as with the size, symmetries, and defects of their structure.[5] Whether and how these properties affect the dispersing mechanisms are open and challenging questions. In this short paper, we illustrate how marked differences in breakup and coalescence depend on copolymer organization. Namely, we report that a block copolymer having a three-dimensional cocontinuous structure disperses in a polymeric matrix in a manner that is qualitatively different to one having a lamellar structure, as shown by the distributions in droplet size given in Figure 1a. Interestingly, droplet coalescence is much less pronounced for the 3D cocontinuous microstructure, which prevents the formation of large droplets and allows the formation of super-tough materials where an increase in impact resistance is not accompanied by a loss in stiffness.

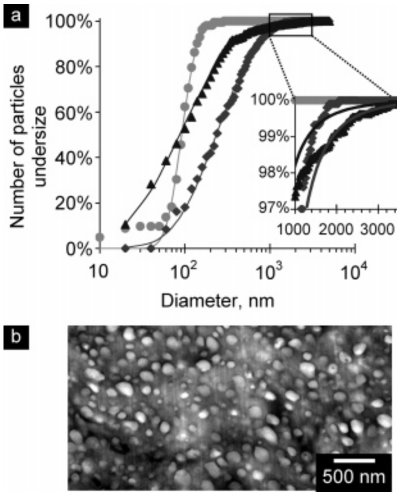

Figure 1. (a**)** Size distributions of filler droplets dispersed in a polyamide-12 matrix: reactive ethylene−propylene rubber EPRm (●), lamellar block copolymer S(B/S)S (▲), and 3D cocontinuous block copolymer SBM/SB (◆). Dispersions are obtained for a 20 wt % filler content by blending the polyamide matrix and the filler in a corotating twin-screw extruder at a melt temperature of 250 °C and a screw rotation speed of 300 rpm. Log−normal fits are represented with solid lines. (b**)** TEM micrograph of the dispersion of reactive EPRm obtained in the conditions and matrix of this study. The polyamide matrix stained with phosphotungstic acid appears in black.

Hence, the present issue is not only interesting from a fundamental point of view but also could have important practical implications. Most polymer alloys are immiscible blends obtained by dispersing one minority phase, the filler, into a majority phase, the matrix. They are usually mixed at high temperature in a molten state and quenched below the glass-transition or melting temperature of the matrix. The size and morphology of these dispersions are crucial for the macroscopic properties of the alloys such as transparency, stiffness, and impact strength. Abundant research and technological efforts have been realized to control mixing processes and find interfacial agents that yield fine dispersions that improve the matrix properties.[6] In particular, it has been shown that the presence of block copolymers at the filler/matrix interface significantly inhibits droplet coalescence and stabilizes submicron-sized dispersions.[3,4,7] Like surfactants, these copolymers, which are introduced to the initial blend or formed during blending by in situ reactions, are miscible with the filler on one part and with the matrix on the other. This is illustrated in Figure 1b, showing a fine dispersion of maleated ethylene−propylene rubber (EPRm) obtained in the polyamide-12 matrix of the study: grafted block copolymers are formed during blending at the matrix/filler interface by the reaction of maleic anhydride groups of EPRm with amine end groups of polyamide allowing to obtain an average particle size of less than 100 nm. This technology is now widely used for instance to obtain materials with improved impact resistance. Such toughening requires that droplets cavitate to induce plastic deformation of the matrix and relieve triaxial stresses that cause brittle failure.[8] As a consequence, impact fillers are usually rubbery at room temperature, and toughening is accompanied by a substantial loss in elastic modulus. Numerous strategies have been explored to alleviate this well-known toughening dilemma using rigid inorganic or structured fillers such as salami or core−shell particles in various polymer matrices.[8−10] In the present work, we disperse block copolymers that do not play a role of interfacial agent, but form structured fillers. The toughness achieved with the dispersion of the 3D cocontinuous copolymer is even better than what is attained with reactive rubbers. Moreover, high toughness is reached with little loss in rigidity since the structured filler contains little rubber.

The polymer matrix is a polyamide-12 (M_n = 25 000 and I_p = 2.3) with characteristics chosen to reduce the viscosity mismatch and achieve a good stress transfer between matrix and filler. A lamellar nanostructure was obtained with a linear polystyrene-*block*-poly(butadiene-*grad*-styrene)-*block*-polystyrene (S(B/S)S) triblock copolymer (Finaclear, Total Petrochemi-

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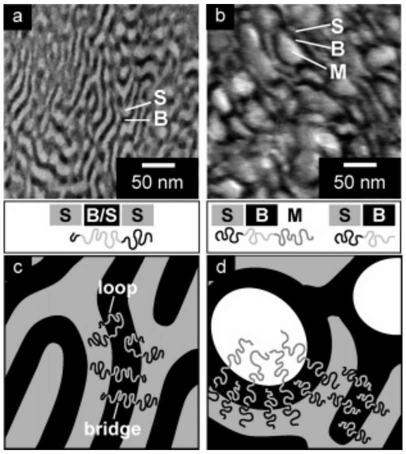

Figure 2. TEM micrographs showing the nanostructures of the S(B/S)S (a) and SBM/SB (b) triblock copolymers in the pellets before blending. Schemes c and d represent the nanostructures and chain configurations of the S(B/S)S and SBM/SB copolymers, respectively.

cals), which contains 30 wt % of polybutadiene (B) and has an average molecular weight $M_n = 93\,500$. Its highly asymmetric architecture with a random B/S middle block allows to achieve a lamellar nanostructure with a weight fraction in B as low as 30% while a symmetric ABA triblock would exhibit a cylindrical nanostructure.[11] A cocontinuous nanostructure where two continuous phases interpenetrate each other was obtained with a mixture of ABC and AB block copolymers, for which continuity can be obtained on a wider composition range than for AB and ABA block copolymers.[12] It consists of a 70/30 in wt % (i.e., 55/45 in mol %) blend of polystyrene-*block*-polybutadiene-*block*-poly(methyl methacrylate) (SBM) triblock and polystyrene-*block*-polybutadiene (SB) diblock copolymers. The S and B blocks of the diblock chain have the same block length as SB in the SBM triblock chain. The effective molecular weight of the SBM/SB mixture is $M_n = 94\,000$ with an effective composition of 32 wt % polystyrene (S), 36 wt % polybutadiene (B), and 32 wt % poly(methyl methacrylate) (M).

It is important to stress that block copolymer nanostructures not only are defined by chain composition but also strongly depend on the preparation conditions, especially for long chains which diffuse slowly and can be trapped in out of equilibrium states.[13] Accordingly, we characterized the S(B/S)S and SBM/SB nanostructures in the pellets that were used for blending. Ultrathin films were observed by transmission electron microscopy (TEM). Because of selective staining with OsO_4, B domains appear in black on the micrographs. For both copolymers, highly defective nanostructures are obtained due to the strong shearing undergone during the extrusion process used to prepare pellets. The S(B/S)S nanostructure (Figure 2a) consists of corrugated and twisted lamellae of S and B which extend in various directions for about 100 nm. Like most ABA block copolymers, the B middle block may form loops and bridges, as illustrated in Figure 2c. The SBM/SB nanostructure (Figure 2b) is more poorly defined. Spherical M domains surrounded by a cocontinuous structure of S and B appear slightly brighter due to the degradation of M under the electron beam. Despite the substantial amount of SB diblock in SBM/SB, a close inspection of TEM micrographs shows no trace of macroscopic phase separation. Thus, SB chains are well-incorporated into the SBM/SB nanostructure either at the S/B interface around the M domains or in the interstitial space between them, as schematically represented in Figure 2d. Because SBM chains are anchored to spherical M domains, this 3D cocontinuous structure differs strongly from lamellar structures which, despite a lot of defects, still allow an easier mobility of the chains. This is particularly apparent through rheological properties.

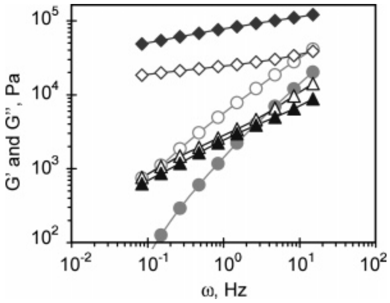

Figure 3. Storage and loss moduli, G' and G'', at 250 °C under low shear oscillatory conditions as a function of frequency, ω, for polyamide-12 (●, ○), S(B/S)S (▲, △), and SBM/SB (◆, ◇). Full and open symbols correspond to G' and G'', respectively.

Rheology was studied at the temperature of extrusion (250 °C) by low shear oscillatory measurements made in the linear regime for a 0.5% deformation in a plane−plane geometry. Particular care was taken to avoid sample degradation. Dissolution tests in chloroform were realized at various stages of the experiments to ensure that no cross-linking of B could occur during the measurements. These rheological experiments do not reproduce the complex flows and high shear rates that exist in real blending conditions. Still, they reveal the effect of the fillers nanostructure on their viscoelastic behavior. The storage and loss moduli, G' and G'', are plotted in Figure 3 as a function of the frequency, ω. The behavior of the polyamide matrix at low frequency approaches the characteristic terminal regime of homopolymer melts for which G' and G'' vary as ω^2 and ω, respectively. On the contrary, S(B/S)S and SBM/SB copolymers exhibit typical features of ordered block copolymer melts.[14] In the case of S(B/S)S, G' and G'' obey the same power law in frequency given by

$$G' \sim G'' \sim \omega^{0.53\pm0.01}$$

Such a dependence in $\omega^{0.5}$ is characteristic of unoriented lamellar structures[15] and corresponds to the relaxation times of lamellae sliding along each other.[16,19] Here, the presence of B loops and of short mobile S blocks may facilitate the reorganization of S(B/S)S lamellae. The SBM/SB structure behaves very differently, as shown in Figure 3. Compared to S(B/S)S, the higher values of G' and G'' could be partly attributed to the friction of M blocks being higher than that of S blocks. However, the most striking and important effect is related to the very nanostructure. The storage modulus is about 4 times higher than the loss modulus, and both moduli, G' and G'', vary little with the frequency as $\omega^{0.18}$ and $\omega^{0.11}$, respectively. Similar viscoelastic solidlike behaviors have been reported in cubic phases of bcc spheres.[20] Because of the symmetry and chain configurations of these structures, domains can hardly slip along each other unlike in lamellar phases, and thus relaxation mechanisms are much slower.

We prepared two polyamide blends containing 20 wt % of S(B/S)S and SBM/SB fillers in the following conditions: copolymer and polyamide pellets were extruded together in a corotating twin-screw extruder ZSK 30/41D (Werner & Pfleiderer) at a rotation speed of 300 rpm and a temperature of 250 °C. TEM observations of S(B/S)S and SBM/SB droplets (not given here) show that the initial nanostructures were preserved after blending. In particular, no phase separation occurred between SBM and SB chains, and SBM/SB particles exhibit the same

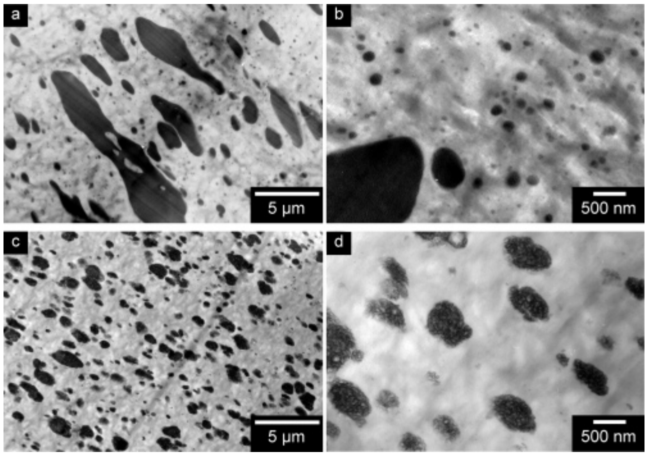

Figure 4. High- and low-magnification TEM micrographs of the dispersions of S(B/S)S (a, b) and SBM/SB (c, d) copolymers in polyamide-12. Filler droplets appear in black due to OsO_4 staining.

cocontinuous nanostructure as before blending. Because of their high molecular weight and the strong incompatibility of B with S and M, both S(B/S)S and SBM/SB copolymers remained ordered during blending so that chains could not diffuse and reorganize significantly during the short mixing times (~1 min).[13] The S(B/S)S and SBM/SB dispersions shown in Figure 4 clearly look very different. These TEM observations were quantified by image analysis over representative surfaces (>1000 μm^2) and numbers of droplets (>1000) using a method described in ref 19. The distributions in droplet size are represented in Figure 1a in a cumulative way. The shape of these distributions reveals several features about the dispersing mechanisms of these structured fillers.

Flows and shear rates are complex and nonuniform along the extruding screws. The blends alternatively underwent high shear rates for which breakup is dominant and low shear rate for which droplets collide and coalesce. Hence, the importance of breakup and coalescence can be inferred from the size of the smallest and largest droplets, respectively. For small submicron sizes, both S(B/S)S and SBM/SB distributions shown in Figure 1a are well fitted with log−normal statistical laws, which typically describe populations resulting from random breakup phenomena.[20] The smallest S(B/S)S droplets are about 10−20 nm (Figure 4b), which is comparable to what is obtained with reactive rubber (Figure 1b). For the SBM/SB copolymer, however, the smallest droplets are about 50 nm (Figure 4d), and the whole distribution is shifted by a factor of 2 toward larger sizes as compared to the S(B/S)S distribution. Such size difference between small S(B/S)S and SBM/SB droplets is intimately related to their rheological properties.[3,4] Because of the higher viscosity and elasticity of SBM/SB, the deformation and thus breakup of SBM/SB droplets were more difficult than those of S(B/S)S ones.

For large droplet sizes (>1 μm), the log−normal fit is no longer accurate. In this size range, droplets were formed by coalescence of smaller droplets as suggested by the shape of the largest droplets in Figure 4a,c. Comparing this part of the size distributions reveals that S(B/S)S and SBM/SB copolymers coalesce very differently. The coalescence of S(B/S)S droplets is significant, and large droplets extend over more than 10 μm (Figure 4a). On the other hand, the coalescence of SBM/SB droplets seems strongly inhibited as the largest SBM/SB droplet sizes hardly exceed 2 μm (Figure 4c). Of course, as for breakup, viscoelasticity of droplets affects coalescence in complex ways. In particular, the high elasticity of SBM/SB droplets may have retarded the film drainage between colliding droplets and generated elastic recoil causing colliding droplets to separate.[3,4] We argue that, besides purely rheological effects, one should consider the possible role of the copolymers nanostructure on the short-range forces leading to coalescence. Unlike homogeneous fluid droplets, the coalescence of structured droplets implies that the structures of two colliding droplets locally rearrange and merge near the contact surface. If these structural rearrangements are too slow, the adhesive forces between the colliding droplets may not be sufficient to pursue coalescence, and droplets may separate. This could have been the case of SBM/SB droplets for which chains are anchored in the M domains, and thus diffusion and slippage along the interfaces of the nanostructure are strongly hindered.

Although the influence of block copolymer nanostructure on droplet coalescence seems qualitatively clear, it will be interesting to perform experiments on model systems to explore the mechanisms of breakup and coalescence of structured fluids. From a practical point of view, the control of coalescence is essential. Here, we find that it allows to achieve remarkable impact performances. Under standard notched Charpy testing conditions at 25 °C, the neat polyamide-12 matrix is brittle with an impact strength of 16 ± 4 kJ/m^2. Like in most immiscible blends, large S(B/S)S droplets act as critical stress concentrators which trigger brittle failure of the matrix.[8] The S(B/S)S dispersion has no toughening effect, and the impact strength is reduced to 11 ± 2 kJ/m^2. On the contrary, the SBM/SB dispersion yields a ductile and supertough behavior (113 ± 4 kJ/m^2) with only a 8% reduction in elastic modulus. This is promising compared to the fine dispersion of reactive rubber shown in Figure 1b, which yields an impact strength of 61 ± 6 kJ/m^2 but at the cost of a 30% loss in elastic modulus. Hence, studying dispersions of structured polymer fluids is an open, interesting, and technologically relevant problem. We hope that future model experiments and theories will bring a new handle to tune the morphologies and properties of polymer blends.

Acknowledgment. The polyamide and copolymers were provided by Arkema and blended at the Cerdato Center. We thank V. Rebizant and F. Tournilhac for helpful comments on polyamide/SBM systems and A. Leach for revision of the manuscript. We are also grateful to R.T. Bonnecaze, M. Cloître, and N. Dufaure for stimulating discussions about rheology, breakup, and coalescence. Financial support by Arkema, CNRS, and ESPCI is gratefully acknowledged.

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MA052506D