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Temporary droplet-size hysteresis in immiscible polymer blends

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Abstract

The droplet size distribution during steady shearing of model polymer blends is examined in situ by optical microscopy. The volume-average steady-state droplet size during shear is essentially inversely proportional to shear rate, as expected. When the shear rate is increased suddenly, the droplets break up, through a process that involves the transient formation of threads, and rapidly establish a new steady state, comprising ellipsoidal droplets that are extended slightly in the direction of shear. When the shear is stopped, the droplets quickly relax to a spherical shape, but virtually no coalescence is observed, because neither Brownian nor buoyant forces are significant and the volume fraction of the dispersed phase is low. Slow shear, however, induces droplet collisions that lead to coalescence. The coalescence process is much slower than breakup. In contrast to some predictions, however, there is no permanent droplet size hysteresis. The steady-state size produced by breakup of initially larger droplets is eventually produced at large strain by coalescence of initially smaller droplets. The lack of permanent hysteresis has implications concerning appropriate mathematical models of coalescence behavior.

Keywords: Temporary droplet-size hysteresis; Immiscible polymer blends; Mathematical models

1. Introduction

Blending of polymers with different physical properties presents the possibility of enhancing the overall properties of a material through a synergistic combination of the desirable properties of each component in the system. The mechanical and optical properties of immiscible polymers depend critically on the disperse phase morphology [1]. During shear flow, the droplet size is a direct result of droplet breakup [2,3] and coalescence [4,5] processes. Under transient conditions either breakup or coalescence predominates. For example, breakup occurs when the shear rate is suddenly increased, and the shear forces exerted on the droplet overcome the interfacial forces that tend to maintain the droplet in a spherical shape. The balance of these forces was described by Taylor [2,3] through the capillary number, $\mathrm{Ca} = \eta_\mathrm{m}\dot{\gamma}\mathrm{R}/\nu$, where η_m is the matrix phase viscosity, $\dot{\gamma}$ is the applied shear rate, R is the droplet radius, and ν is the interfacial tension between the two phases. Once Ca exceeds a critical value approximately 0.5 [5], breakup occurs under steady shear until a stable steady-state droplet diameter, D_s, is achieved. The steady-state droplet diameter is defined as:

$$D_\mathrm{s} = \frac{2\nu\,\mathrm{Ca}_\mathrm{crit}}{\eta_\mathrm{m}\dot{\gamma}} \approx \frac{\nu}{\eta_\mathrm{m}\dot{\gamma}}. \tag{1}$$

However, when the average droplet size D, is smaller than the steady-state size D_s, coalescence dominates. For example, if a mixture is sheared rapidly first to break up the droplets, subsequent shearing at a lower rate induces coalescence. Coalescence is relatively complex, because it consists of up to three steps. Shear induces droplet “collisions”, the efficiency of which depend on hydrodynamic interactions. When the droplets are much smaller than their steady-state size, Ca is also small and the droplets are presumed to remain spherical throughout collision, and the second and final step of coalescence is rupture of the microscopic film separating two droplets. However, at larger Ca (larger droplet size) an intervening step occurs, because the shear force is sufficiently strong that it presses the droplets together and forms a flattened contact region, in which the two droplets are separated by a thin (macroscopic) film of the continuous matrix. The continuous fluid drains during this step until the droplet interfaces are close enough to each other that the film can undergo rupture. If film drainage and rupture are not completed, the droplets tumble past one another, and are convected away from one another by the shear flow.

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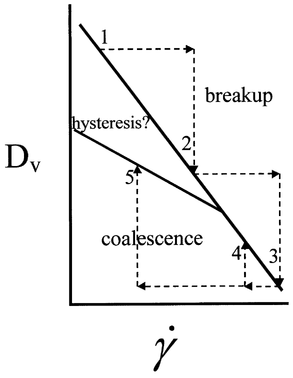

Fig. 1. Schematic log–log plot of droplet diameter versus shear rate. The upper solid line is the breakup curve, as predicted by Taylor. The lower solid line is the coalescence curve derived from a binary assumption that equates drainage and interaction times (Eq. (3)). At shear rates greater than the critical shear rate where the two lines intersect, the drainage time is not significant compared to the droplet interaction time. Below this rate, drainage is significant, and a hysteresis is predicted. The dashed lines represent steps of the experimental protocol, as described in the text.

To predict whether film drainage is completed, the film drainage time and the time of contact are calculated. While the latter is always approximately $1/\dot{\gamma}$, several different expressions for the film drainage time have been developed to describe different hydrodynamic situations [4]. For example, for viscous fluid droplets [4],

$$\frac{t_{\mathrm{drain}}}{t_{\mathrm{contact}}} \sim \frac{\eta_{\mathrm{d}}}{\eta_{\mathrm{m}}}\left(\frac{\eta_{\mathrm{m}}\dot{\gamma}}{\nu}\right)^{3/2}\frac{\sqrt{6}}{32}\mathrm{D}^{5/2}\frac{1}{h_{\mathrm{c}}}, \tag{2}$$

where $\eta_{\mathrm{d}}/\eta_{\mathrm{m}}$ is the relative viscosity of the droplet, and h_{c} is the final thickness of the film before film rupture. A simple binary assumption is logical: i.e. if $t_{\mathrm{drain}} < t_{\mathrm{contact}}$, then coalescence occurs, otherwise the droplets tumble over one another. Using this assumption, Eq. (2) can be rearranged (after setting $t_{\mathrm{drain}} = t_{\mathrm{contact}}$) to predict that the steady-state droplet size produced by coalescence

$$D_{\mathrm{coal}} \sim \dot{\gamma}^{-3/5}, \tag{3}$$

differs from that produced by breakup (Eq. (1)). Note that since t_{drain} depends significantly on D (Eq. (2)), the film drainage step becomes a significant limitation only for large droplet size, i.e. low shear rates (see Eq. (3)). Therefore, when film drainage becomes limiting at sufficiently low shear rates, a droplet size hysteresis is predicted [5], such that at the same shear rate, the steady-state size resulting from the coalescence of initially small drops is smaller than that from the breakup of initially large drops (Fig. 1). Other expressions analogous to Eqs. (2) and (3) have been developed for other limiting cases, including inviscid or solid droplets [4].

Unfortunately, t_{drain} and t_{contact} have not been calculated precisely. Indeed, even for a monodisperse droplet population, a distribution of times is expected, because they depend upon the relative separation of the far-field streamlines of the droplet pair, i.e. the so-called impact parameter [6]. The contact time decreases as the droplet streamlines are more widely separated. To account pragmatically for these uncertainties, a continuous film drainage probability can be formulated. For example, the following expression has been proposed [7,8]:

$$P_{\mathrm{drain}} = \exp\left[\frac{-t_{\mathrm{drain}}}{t_{\mathrm{contact}}}\right]. \tag{4}$$

Because this probability remains finite even for large $t_{\mathrm{drain}}/t_{\mathrm{contact}}$, no hysteresis is expected. However, though there is a distribution of t_{drain} and t_{contact}, it has not been rigorously demonstrated that a continuous probability such as Eq. (4) is valid. Perhaps there remain limits on t_{drain} and t_{contact} such that droplet size hysteresis can occur.

Recent quantitative measurements of droplet size in polyisobutylene/polydimethylsiloxane systems [9] were suggested to indicate that hysteresis does occur and increases with increasing the viscosity ratio $\eta_{\mathrm{d}}/\eta_{\mathrm{m}}$, as suggested by Eq. (2). Through measurements of dynamic moduli, these authors calculate the volume-averaged droplet diameter according to the Palierne theory [10]. Vinckier et al. [11] corroborated these results by direct measurements of the droplet diameter by optical microscopic techniques for similar systems.

In this investigation, we probe quantitatively the *steady-state* morphology of immiscible binary mixtures by direct measurements (optical microscopy) under steady shear conditions with a particular goal to characterize any droplet size hysteresis between droplet breakup and coalescence. In this report, we study some factors that influence the rate of droplet coalescence in polymer blends.

2. Experimental

2.1. Materials

Four types of homopolymers were used for this investigation: poly(dimethylsiloxane) (PDMS; United Chemical Technologies), polyisobutylene (PIB; Polysciences), poly(ethylene glycol) (PEG; Polysciences and donated by Union Carbide), and poly(propylene glycol) (PPG; Fisher Scientific and donated by Arco Chemical). These materials were advantageous for in-situ optical microscopy for several reasons: their relatively low viscosity produced a convenient combination of droplet size and shear rate, experiments could be conducted at relatively low temperature, and their indices of refraction were sufficiently different from one another. The systems investigated were Newtonian over the entire range of shear rates examined (Table 1). Several different molecular weights were

Table 1
Physical properties of the materials used in this study

Polymer	η (Pa s) at $\dot{\gamma} = 0$	ρ (kg m^{-3})
PIB(0.5k)	0.57 (25°C)	894 (20°C) [23]
PIB(0.8k)	10 (25°C)	894 (20°C) [23]
PDMS(28k)	0.90 (25°C)	971 (23°C) [24]
PDMS(49.35k)	4.1 (25°C)	973 (23°C) [24]
PDMS(62.7k)	8.2 (25°C) 0.41 (90°C)	974 (23°C) [24]
PEG(10k)	2.5 (90°C)	1069 (80°C) [25]
PEG(18.5k)	15. (90°C)	
PPG(12.2k)	5.3 (25°C) 0.50 (90°C)	1005 (25°C) [26]

obtained to investigate the effects of viscosity and viscosity ratio (Table 1).

In this report, we denote the composition of a blend system as follows: for example, PDMS(62.7k)5%/PPG(12.2k), where the first component is the disperse phase, the numbers in parentheses are the molecular weights, and the percentage is the concentration of disperse phase expressed in weight percent. Various procedures were used to produce a uniform, whitish, bubble-free mixture before loading into the shear cell: the PDMS/PEG and PPG/PEG systems were melted and subsequently stirred in a petri dish; the relatively low-viscosity PDMS(28k)/PIB(500) system was shaken vigorously; and all other systems were stirred at room temperature.

2.2. Experimental method

The blend systems were investigated under steady shear conditions using a Linkam CSS-450 Cambridge shearing cell which was mounted upon an Olympus BX-60 optical microscope, which was operated in bright-field transmission mode, using a 20X long working distance objective. A CCD video camera was used to acquire in situ observation of the breakup and coalescence processes. The shear cell consists of two glass parallel plates with an adjustable gap setting (chosen as 50 μm for most of these experiments). The upper (smaller) plate has a radius of 15 mm. The observation window is a fixed at a radius of 7.5 mm. The total sample volume was approximately 35 μl. The gap, shear rate, and temperature were all regulated by a control unit which is connected to a computer. Image acquisition was performed through the use of Vision Explorer software purchased from Graftek Imaging, Inc. The droplet sizes were analyzed through the use of Labview general instrumentation

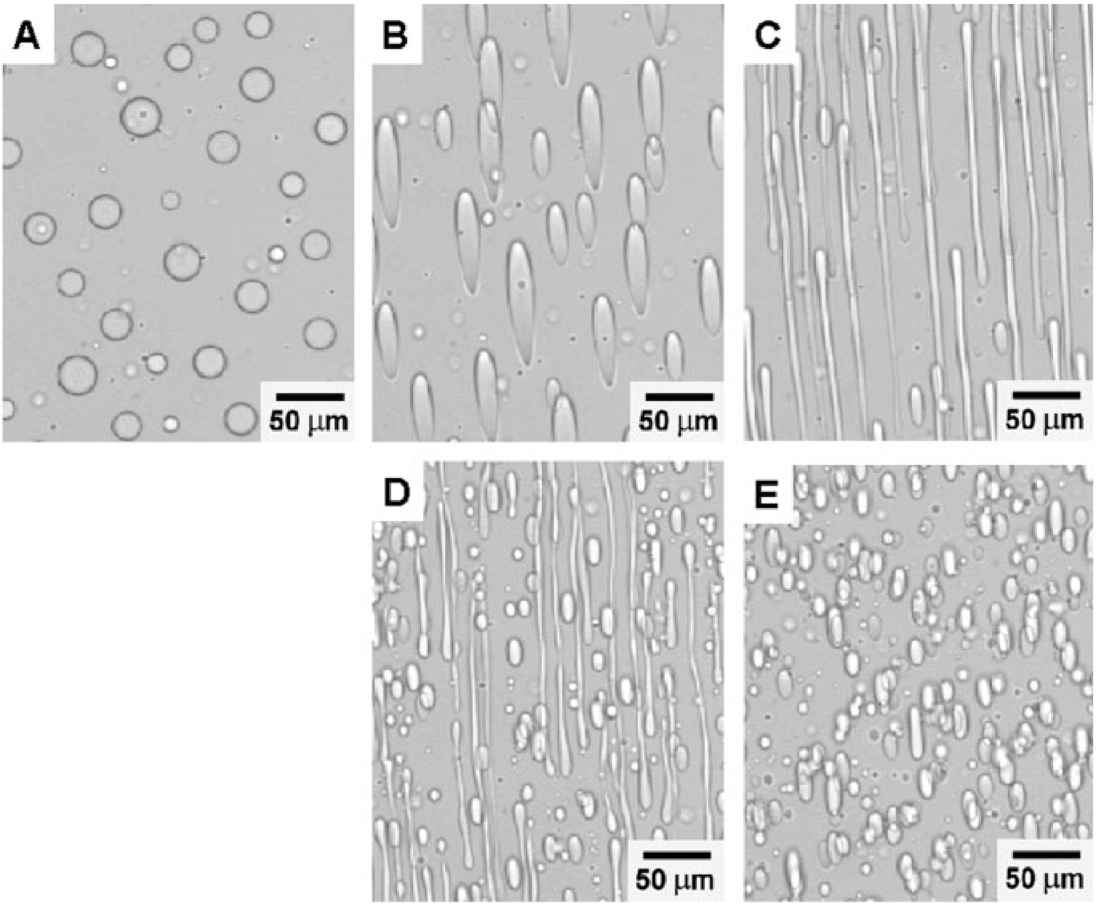

Fig. 2. Optical bright field micrographs of droplet shapes during the startup of shear flow. (A) The PDMS(28.5k)5%/PIB(0.5k) mixture at rest, prior to shearing to 40 s^{-1}. Snapshots taken during shear at shear strain equal to (B) 4, (C) 27, (D) 60, and (E) 195.

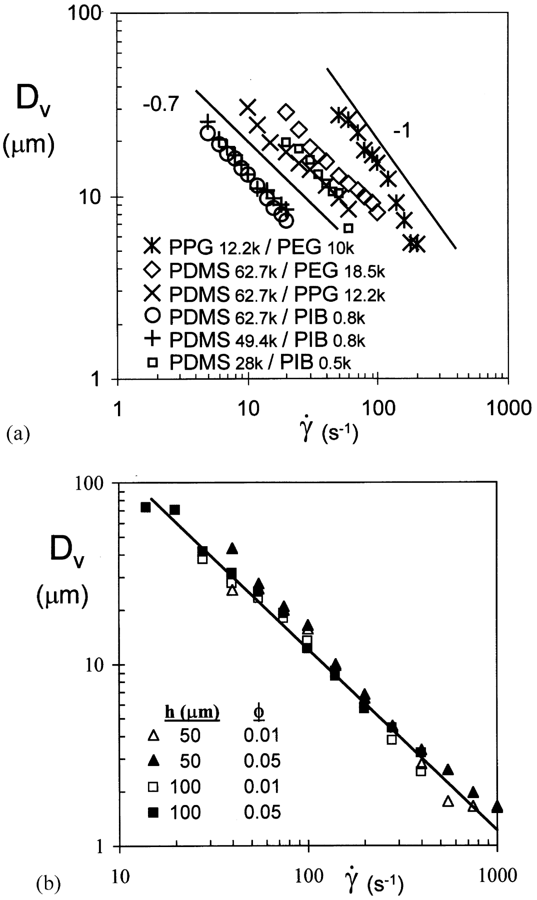

Fig. 3. (a) Breakup curves for several blend systems studied. (b) Breakup curves for 1 and 5%PPG(12.2k) in PEG(10k) at 90°C. Symbols are defined in the inset table, where h is the gap spacing and ϕ is the weight fraction of PPG. Data at 50 and 100 μm gap spacing are consistent. The line represents the Taylor equation (Eq. (1)) with $\nu = 3.1$ mN m^{-1} and $\mathrm{Ca}_{\mathrm{crit}} = 0.5$.

software (IMAQ Vision 4.0), and the number and volume-average droplet diameters were calculated:

$$D_{\mathrm{n}} = \frac{\sum_{i=1}^{n} n_i D_i}{\sum_{i=1}^{n} n_i}; \qquad D_{\mathrm{v}} = \frac{\sum_{i=1}^{n} n_i D_i^4}{\sum_{i=1}^{n} n_i D_i^3}. \tag{5}$$

The minimum measurable droplet diameter was somewhat less that 2 μm, and typically 500–2000 droplets were counted to compute the averages.

The primary advantage of Labview in these experiments was the use of a circularity function (Danielsson operator) that calculated the curvature of individual droplets within the thresholded image. The Danielsson operator resolves the situation of overlapping droplets in the thresholded image plane by considering the cluster as a group of overlapping discs. Through calculation of the curvature of each object comprising the cluster, the routine effectively separates the overlapping discs and calculates their respective radii [12]. This function allows quantitative investigation of mixtures having disperse phase volume fractions up to several percent, so that coalescence phenomena could be studied effectively.

3. Results and discussion

Each of the binary systems that we investigated displays the same general phenomena (Fig. 1), albeit with differences in characteristic time scales. To prepare to study breakup, the mixture was sheared slowly in order to establish a large initial droplet size. The shear rate was then stepped up, and the droplet size distribution was measured after a specified amount of strain (e.g. Fig. 1, point 1). The shear rate was then increased sequentially to acquire additional points (e.g. Fig. 1, points 2 and 3) of the breakup curve. The droplet size measured at a particular shear rate did not depend on how much slower was the previous shear. That is, the same point 3 was achieved with or without shear at the intermediate point 2.

The breakup process is portrayed in Fig. 2. Fig. 2A represents the morphology of 5%PDMS(28.5k) in PIB(500) at rest just prior to shear. The droplets of PDMS are spherical and randomly distributed. Immediately after shear begins, the droplets stretch along the flow direction (Fig. 2B). The degree of stretching (Fig. 2B) is nearly affine for the largest droplets, and less for the smaller sized droplets, as expected. If the flow is ceased at this point, the ellipsoidal droplets simply retract to their spherical shape [13]. (In other investigations, droplet retraction has been analyzed to yield a measure of interfacial tension [14,15].) If shearing does not cease, the droplets continue to stretch until long filaments of PDMS are formed (Fig. 2C). These have nearly constant radii, except near the ends where they are slightly more bulbous. If the flow is arrested here, then the filaments immediately begin to breakup by a capillary instability, another process which has been analyzed to yield a measure of interfacial tension [16,17]. The breakup of the filament during shear is suppressed by its continuous stretching, which damps growing oscillations [5,18,19]. Eventually, the filament becomes thin enough that oscillations can grow more rapidly. Fig. 2D represents a point in time when some filaments have broken (producing trains of small droplets) and others have visible oscillations. Finally, all threads are broken, and droplets are randomly distributed. At steady state, the largest droplets are ellipsoidal, while those that are substantially smaller than the critical size are spherical (Fig. 2E). A distribution of droplet sizes is produced during shear, because primary and secondary oscillations of the filament diameter lead to the formation of larger and smaller droplets, respectively [20]. The amount of strain required to achieve steady state depends on several factors including initial droplet size, interfacial tension, and viscosities. (Under conditions of greater compatibility, others have found the filaments to be very long-lived [18].) During our experiments, the strain to

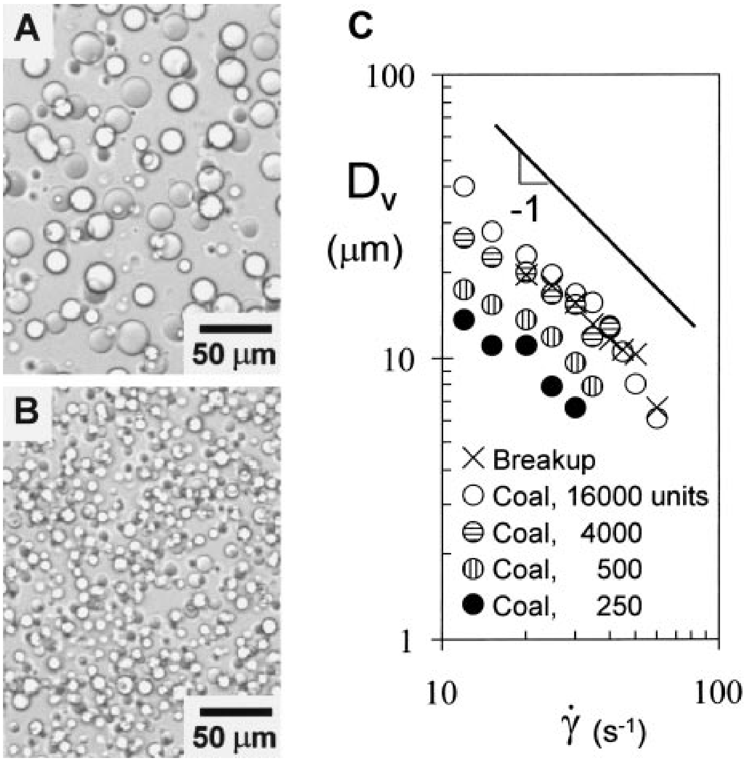

Fig. 4. Steady-state and transient droplet sizes in the PDMS(28.5k)10%/PIB(0.5k) system. Optical micrographs (A and B) were taken after different shear histories. (A) The shear rate was stepped up to 25 s^{-1} (after 250 shear units at 20 s^{-1}), and the mixture was sheared for 250 units of strain. The droplet size distribution represents steady state. (B) The shear rate was stepped down to 25 s^{-1} (after 250 units at 60 s^{-1}), and again sheared for 250 units of strain. The droplet size is smaller than in (A). (C) X symbols represent measurements of the steady-state droplet size produced by initially larger droplets as a function of shear rate. The circles represent droplet sizes after first shearing 250 units of strain at 60 s^{-1} and then immediately at a slower rate (as denoted by the abscissa) for the amount of strain as indicated in the legend. After sufficient strain, the droplet sizes produced by breakup and coalescence coincide.

achieve complete thread breakup and apparent steady state was approximately 100–200 shear units. When the shear is finally arrested, all droplets return to a spherical shape. At the concentrations that we investigated, coalescence events resulting from this relaxation occur only in the most inviscid mixtures and in that case only rarely. After this rapid initial relaxation, the droplets in the quiescent state were stable for hours, during which time quiescent coalescence occurred very infrequently. Therefore, a snapshot taken immediately after shearing provided an accurate representation of the droplet sizes, if not shapes, during shear. Spherical droplet shape facilitated quantitative analysis of the micrographs, as described in the experimental section. The steady-state droplet size produced by breakup was measured for several systems (Fig. 3a), as a function of shear rate.[1] The effect of gap spacing and the dispersed phase concentration were also investigated (Fig. 3b). The steady-state droplet size produced by breakup is independent of both these parameters, indicating that wall effects are not significant and that both 1 and 5% mixtures can be considered to be dilute. Indeed, fitting the Taylor equation (Eq. (1)) yields reasonable values of the critical capillary number (Fig. 3b).

Following establishment of the breakup curves (Fig. 3), the droplet distribution at the most rapid shear rate (schematically depicted in Fig. 1 as point 3) was used as the initial droplet size distribution. The shear rate was “stepped down” to a predefined shear rate, and the distribution was measured after the same amount of strain used for the breakup measurements (point 4, Fig. 1). The system was sheared once again to point 3, after which the shear rate was stepped down to a lower rate, and the distribution was measured once again (point 5). The distributions measured in this fashion constitute a coalescence curve that is characteristic of a certain starting droplet size distribution and amount of strain. As drawn, points 4 and 5 (Fig. 1) represent two different conceivable situations. For point 4, the droplet size reaches the breakup curve at steady state. Point 5 on the other hand represents the possibility that film drainage may limit the ultimate growth of the droplet, so that the steady-state size achieved by coalescence is less than that achieved by breakup at the same shear rate.

Fig. 4 illustrates two snapshots, taken directly after shearing a mixture of 10%PDMS(28.5k) in PIB(0.5k) at 25 s^{-1} for 250 shear units, after either a step up (from 20 s^{-1}, Fig. 4A) or step down (from 60 s^{-1}, Fig. 4B) in shear rate. The effect of the prior droplet size distribution is apparent. The droplets are noticeably smaller (Fig. 4B) after a step down in

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[1] Note: in agreement with Minale et al. [9], the volume average size is not strictly inversely proportional to the shear rate.

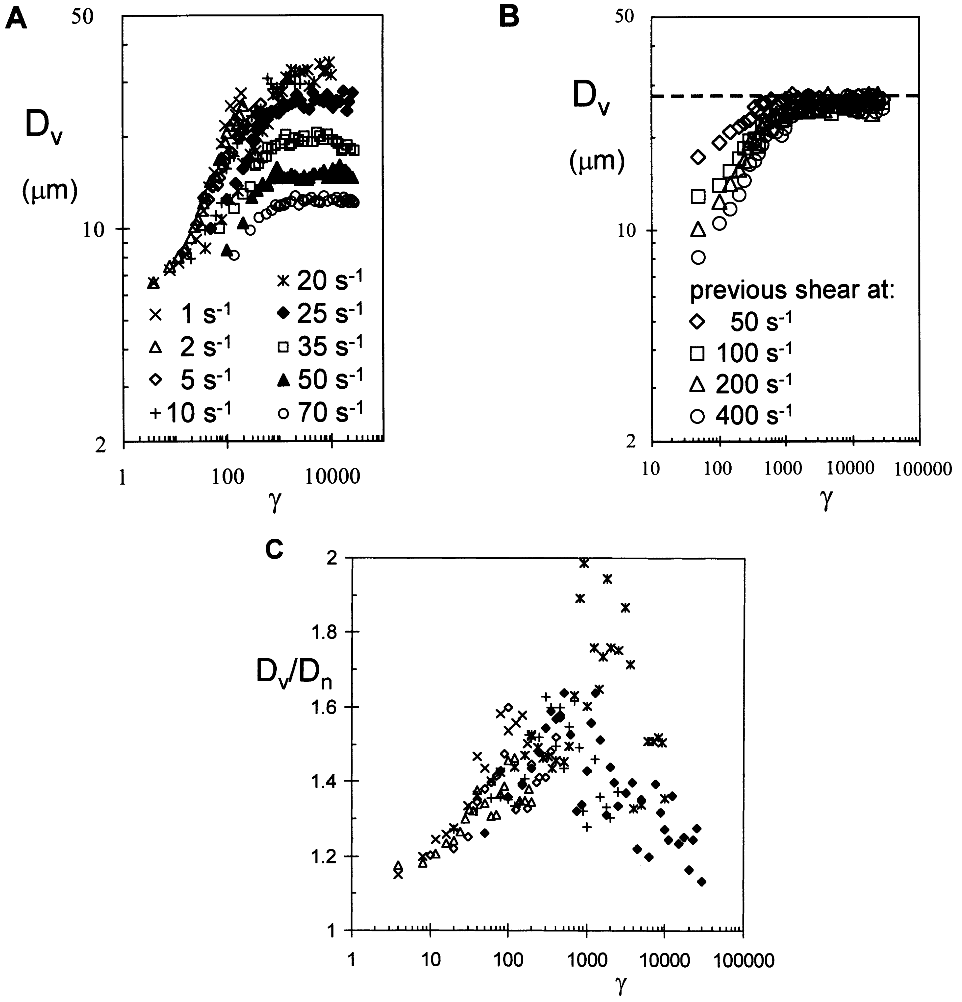

Fig. 5. Coalescence in the PDMS(62.7k)5%/PEG(18.5k) system. (A) Droplet growth as a function of increasing strain after a step down in rate. Prior to the step down, the droplets were broken up at a shearing rate of 100 s^{-1} for 2000 shear units. (B) Droplet growth as a function of increasing strain after a step down to the same rate (25 s^{-1}). The droplets were previously broken up during 2000 units of strain at 50, 100, 200, and 400 s^{-1}. (C) Droplet size polydispersity D_v/D_n versus shear strain, using symbols as defined in figure A.

shear rate (coalescence) than the droplets produced by breakup of larger droplets after a step up to the same shear rate (Fig. 4A).

Similar behavior is observed at other shear rates (Fig. 4C). The coalescence curve so obtained is approximately parallel to the breakup curve, because the droplet growth rate is faster at slower shear rates. When the step down ratio ($\dot{\gamma}_{\text{prior}}/\dot{\gamma}$) is small, e.g. 2, the droplet size does not grow significantly, and D_v has essentially the same value as produced by the previous breakup shear at 60 s^{-1}. However, these results do not represent steady-state coalescence behavior. When the shear is allowed to continue longer (viz. 500, 4000, or 1600 shear units), the droplets produced by coalescence continue to grow (Fig. 4C). The coalescence curve essentially reaches the breakup curve at approximately 4000 shear units. Thereafter, the breakup and coalescence curves superpose within the scatter of the data (Fig. 4C). When the volume fraction of the disperse phase was reduced in half (i.e. to 5%), the coalescence rate was also halved, while the breakup line was unchanged. A comparison of the kinetics of breakup and coalescence clearly supports that these two processes take place by two completely different mechanisms.

The rate of coalescence, of course, is a strong function of the blend constituents. Faster rates are observed for the PDMS(62.7k)5%/PEG(18.5k) mixture at 90°C (Fig. 5), while much slower rates are observed for the PDMS(62.7k)5%/PPG(12.2k) mixture at 25°C (Fig. 6), for which typically more than several thousand units of shear are required to achieve steady state. This difference may arise in part from the greater viscosity of the PDMS phase at room temperature (see Eq. (2) and Table 1).

When the droplet size is investigated as a function of applied shear strain at a variety of shear rates (Figs. 5A and 6), three stages (shown schematically in Fig. 7) are observed. The first stage is observed only if the step down ratio is very large (e.g. >20), so that the initial droplet size is

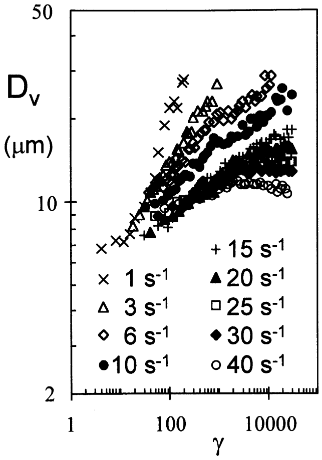

Fig. 6. Coalescence in the PDMS(62.7k)5%/PPG(12.2k) system; droplet growth as a function of increasing strain after a step down in rate. Prior to the step down, the droplets were broken up at a shearing rate of 60 s^{-1} for 2000 shear units. For shear rates of 40, 30, 25, 20, and 15 s^{-1}, steady state was achieved after proximately 2000, 2400, 4400, 8000, and 24 000 shear units, respectively. Steady state was not achieved at lower shear rates.

much smaller than the steady-state size. During this stage, the droplet grows exponentially with increasing shear strain, i.e. with constant coalescence efficiency. For example, the data at small strain for shear rates 1, 2, and 5 s^{-1} superpose and exhibit exponential growth of droplet size (Fig. 5A). First-stage behavior has been observed in all of the systems that we have studied; its further analysis is discussed elsewhere [21]. During the second stage, the droplets grow further according to a quasi-power law, and finally, in the third stage, the droplet size reaches steady state. Since coalescence eventually produces the steady-state droplet size established by droplet breakup, there is no permanent droplet size hysteresis. Lack of permanent hysteresis seems to be universal, because, as we discuss in another report [21], film drainage is a dominant effect on the coalescence rate during the second stage. As the droplet size increases, the drainage probability (and therefore the coalescence efficiency) continuously decreases Eqs. (2) and (4). Therefore, the film drainage effect, while dramatically slowing coalescence, cannot produce permanent hysteresis.

The number average droplet size grows more slowly than does the volume average, so that the polydispersity of the droplet size distribution reaches a maximum shortly before D_v reaches steady state (Figs. 5A and C). After D_v reaches steady state, D_n continues to grow slowly, and the distribution narrows again (Fig. 5C).

The quasi-power law associated with stage 2 droplet growth depends on the initial droplet size (Fig. 5B). In each case, the droplets grow essentially to the steady-state size produced by breakup at that shear rate. When the initial size is larger, the amount of strain to reach steady state is less. However, this difference is minimal, since the growth rate is faster when the droplets are further from their steady-state size, and the growth rate slows as the steady size is approached.

This observation raises a question concerning whether the coalescence behavior depends on previous conditions, or simply on the prevailing conditions, i.e. the current droplet size and shear rate. If one assumes a monodisperse (or any scale invariant [22]) droplet size distribution, how that size was produced by previous conditions is irrelevant. Instead, the current coalescence behavior is dictated by the current conditions. In such case, the coalescence behavior of initially very tiny droplets would map out a master curve

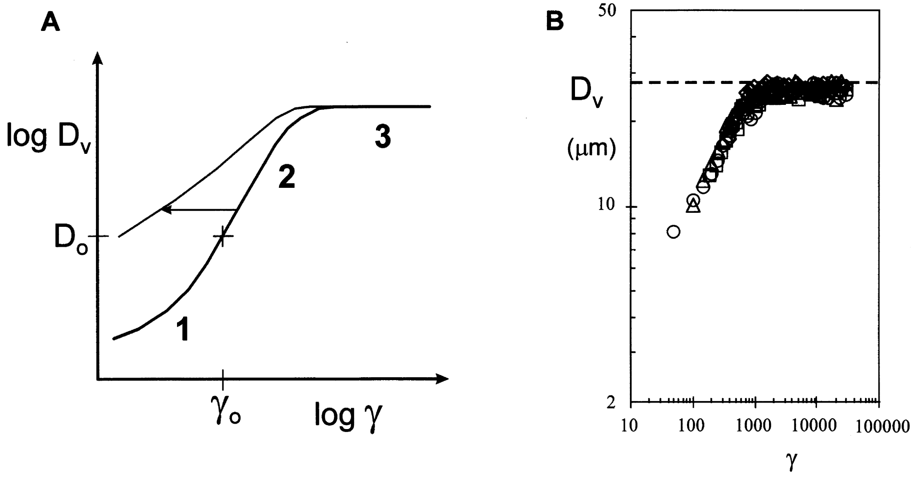

Fig. 7. (A) Schematic of the three stages of shear-induced coalescence: (1) exponential droplet growth, (2) quasi power law growth, and (3) steady state. The black sigmoidal curve represents a master curve that includes each of the stages, as indicated. This master curve is applicable when starting with small droplets. However, if the initial droplet size is D_0 (within stage 2), the droplets will grow according to a different quasi power law (gray curve) reaching the steady-state value. The gray curve may be conceived as being generated by subtracting γ_0 from the master curve. (B) Data in Fig. 5B replotted to demonstrated the superposition of droplet sizes during the quasi power law growth stage. 350, 140, and 50 shear units have been added to the data points representing initial breakup during 2000 units of shear at 50, 100, and 200 s^{-1}, respectively. See Fig. 5B for definition of symbols.

(Fig. 7). This curve should predict all other situations for which the initial droplet size is bigger, because at any given point (e.g. γ_0, D_0), the shear can be stopped and then recommenced, and the droplet growth monitored anew. Consider a droplet size D_0, which would be obtained on a master curve after a shear strain equal to γ_0. If the system starts with droplet size equal to D_0, then the subsequent growth of the droplets is already determined from the master curve. Therefore to predict the droplet size as a function of strain, one would simply subtract γ_0 from the master curve, thus transforming the black master curve in Fig. 7 to the gray curve.

Conversely, to test this hypothesis, we add a certain amount of strain from one growth curve to superpose it with another (Fig. 7B). We find that addition of 50, 140, and 350 shear units, respectively, adequately superposes the curves representing the growth of droplets initially broken up at 200, 100 and 50 s^{-1} with that for droplets initially broken at 400 s^{-1} (Fig. 7B). This same procedure applies to the other systems for which we tested and demonstrated this hypothesis, e.g. PDMS(28.5k)5%/PIB(0.5k). This superposition also demonstrates that the growth curve during stage two is not a true, but a quasi power law.

4. Conclusions

Shear-induced droplet breakup and coalescence processes were examined directly by optical microscopy. Most importantly, we demonstrate that no permanent droplet size hysteresis occurs: the steady-state droplet size produced by coalescence is essentially equal to that produced by breakup. However, the kinetics of coalescence can be slow compared to that of breakup. The growth of the droplets during coalescence occurs in stages: at first they grow exponentially with shear and then according to a quasi power law. For a given blend system, the strain required for steady state depends weakly on the strain rate, except for very small step down ratios. However, it varies significantly for each system, ranging from a few hundred to nearly 100,000 shear units in more viscous mixtures.

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