Measuring of Coalescence in Polymer Melt Blends Flowing Through Converging Channels

Yuri P. Miroshnikov, Alexey K. Egorov, Mariya V. Egorova

Department of Chemistry and Physics of Polymers and Polymeric Materials, M.V. Lomonosov Moscow State Academy of Fine Chemical Technology, 86 Vernadskyi Avenue, Moscow 119571, Russia

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ABSTRACT: Droplets of polymer blends flowing through convergent channels undergo collisions and coalescence because of the appropriate wineglass-shaped flow paths with essential flow constriction at the entrance zone. Therefore, an attempt has been undertaken to use capillary flow for studying coalescence phenomena in polymer blends. When the initial drop diameters in a barrel (before extrusion), d_b, and in the extrudate, d_e, are measured, coalescence efficiency can be easily calculated as $E_c = d_e^3/d_e^3$, provided that no breakup of elongated domains occurs. Compared with methods employing simple shear flow, it has several advantages. For example, the convergent flow pattern combining both shear and extensional flows is directly related to industrial processing operations like extrusion, injection molding, blowing, etc. The method imposes minor limitations on processing parameters and materials used. Applicability of the technique proposed was verified by systematic studies of coalescence in PMMA/PS binary melts blends during capillary extrusion and by comparing these results to theoretical predictions and experimental data from literature. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 120: 2724–2733, 2011

Key words: polymer blends; coalescence; convergent flow

INTRODUCTION

For the past few decades a great deal of both experimental and theoretical studies devoted to blending mechanisms and phase morphology evolution in immiscible polymer blends have been made.[1,2] The main effort in these works has been focused on better understanding the behavior of droplet populations in flowing emulsions, undergoing simultaneous acts of deformation, breakup and coalescence. It is clear that in order to obtain a complete picture of droplet behavior, each individual mechanism should be studied in detail. There are no principal obstacles when one deals with individual droplets. Alternatively, in real emulsions consisting of droplet ensembles, separate studies of blending mechanisms which are interdependent, encounter serious difficulties.

As far as studies of coalescence in droplet populations are concerned, a question that has first to be answered is how to distinguish coalesced drops from virgin domains. In case this problem is solved, the efficiency (or coefficient) of coalescence is easily measurable as the ratio of the average volume of the coalesced domains to that of the virgin ones. These days, two main procedures for studying coalescence in emulsions are known. One of these deals with labeled dispersed phase, whereas another one makes use of the shear rate step-down technique. Both approaches will be discussed in more detail below.

In this work we are going to propose an alternative method of studying coalescence induced by converging flows. To prove the applicability of this model systematic studies on coalescence of the inner phase domains in poly(methyl methacrylate)/polystyrene (PMMA/PS) melt blends have been performed. The dependences of coalescence efficiency on material, geometrical and processing variables, have been evaluated and the data obtained are compared with the results known from literature. Besides, some data on visualization of droplet interactions and on coalescence in quiescent melt blends are also discussed.

In the following section, we will briefly examine recent publications, both experimental and theoretical, concerning droplet coalescence in flowing emulsions.

Previous works

As it was mentioned above, there are two well known techniques employed in studying droplet coalescence in polymeric emulsions. A complicated

Correspondence to: Y. P. Miroshnikov (yupm@mail.ru.).
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(and, to our knowledge, still exclusive) technique had been proposed by Roland and Böhm[3] in their study on coalescence in 5/95 polybutadiene/polychloroprene (PB/PCP) blends. Two similarly sized thin sheets of properly preblended mixtures, in one of which PB is fully protonated and in the other one PB is fully deuterated, are brought together and subjected to one-step passes through a two-roll mill a varying number of times. The loss of the initial isotopic purity caused by flow-induced fusion of dissimilar PB droplets was measured by small angle neutron scattering and interpreted in terms of the extent of coalescence.

The results obtained showed very high rate of coalescence. Only 10 one-step passes through the roll mill gap induced drop coalescence in approximately 2/3 of the dispersed phase domains. Coalescence was enhanced on the increase of the shear rate and the decrease of the viscosity of the dispersed phase.

The second approach that has become popular employs steady shear flows in two modes. First, an emulsion is subjected to relatively high shear rates ensuring droplet deformation and breakups under conditions when critical value of the capillary number is exceeded, i.e.:

$$\mathrm{Ca} = \frac{\eta_m R\dot{\gamma}}{\sigma} >> \mathrm{Ca}_{\mathrm{cr}} \tag{1}$$

Here, η_m is the viscosity of the matrix phase, $\dot{\gamma}$ is the shear rate, R is the droplet radius and σ is the interfacial tension. After that the shear rate is stepped down to a lower level ($Ca < Ca_{\mathrm{cr}}$) at which only flow-induced coalescence takes place.

The results obtained in these works, employing simple[4–10] or complex[11] shear flow fields, show that the efficiency of coalescence, E_c, increases with decreasing shear rate and increasing content of the dispersed phase. Furthermore, the rate of coalescence of the smaller drops was higher compared to that of the larger drops.[6] Besides, E_c was depressed by the increase of the droplet size ratio.[7] It was shown also[7] that the dependence of the coalescence efficiency on the phase viscosity ratio, μ ($\mu = \eta_d/\eta_{\mathrm{m}}$, where η_d and η_m are viscosities of the dispersed phase and the matrix respectively), was described by a convex curve with a maximum at $\mu \sim 1$. Alternatively, Caserta et al.[8] argue that, provided the matrix viscosity is constant, a decrease of the phase viscosity ratios from 2.38 to 0.1 results in a gradual increase of the coalescence rate. The work[9] also reports that in emulsion with a bimodal droplet size distribution the rate of coalescence between small and large domains is higher than that between similar sized drops. Moreover, the deformed droplets coalesced slower than spherical ones.[10]

There are few attempts to study droplet coalescence phenomena other than in simple shear flow fields.[11–14] In particular, it was shown[11] that models developed for simple shear flow are applicable to qualitative description of coalescence in complex flows. Significant decrease of coalescence efficiency on increasing phase viscosity ratio and the shear rate in a mixer with chaotic flows was observed.[13] The authors also report[14] that in flow through capillary dies coalescence mostly occurs along the intermediate axial zone away from both die walls and axis.

Theoretical works on coalescence in polymer blends are still in slow progress. Most models developed so far deal predominantly with isolated doublets of undeformed or slightly deformed Newtonian drops forming flat contact surfaces upon collision. As a rule, a classic ballistic theory by Smoluchovski[15,16] is used as a starting point for the most part of coalescence theories. According to this theory, the number of collisions, N_c, of equally sized spherical drops in a simple shear flow per unit volume and per unit time reads:

$$N_c = \frac{3\phi^2\dot{\gamma}}{\pi^2 r^3} \tag{2}$$

where ϕ is the volume fraction of the dispersed phase, r is the radius of drops. This means that the rate of collision is proportional to the shear rate and the volume fraction squared and inversely proportional to droplet radius cubed. It is clear that collision frequency in eq. (2) can not be related to the extent of coalescence quantitatively, unless N_c is modified with a function describing the probability of coalescence. The latter is a complex parameter, which includes deformation of colliding drops and their hydrodynamic interactions in various flow fields, modes of collision, viscoelastic and surface properties of both phases, drainage and breakage of separating matrix film, etc.

Attempts towards accomplishing these tasks have mainly taken two directions. One of them deals with corrections to the Smoluchovski's theory considering hydrodynamic interactions between colliding droplets[17,18] and deformability of domains in flow[19,20] which are related to the trajectories of domains in flow. These approaches, called "trajectory" theories, predict decreasing E_c with increasing phase viscosity and droplet diameter ratios as well as with deformation of colliding domains.

The second direction, representing "drainage" theories, deals with the intimate mechanisms of approach and interaction of colliding drops which are controlled by the rate of drainage of the intervening matrix film and by mobility of the interfaces. According to the drainage theory, the coalescence efficiency for systems with partially mobile interfaces is predicted by the equation[16,21–23]:

$$E_c = \exp\left(-0.077\left(\frac{\eta_m d\dot{\gamma}}{\sigma}\right)^{1.5}\left(\frac{d}{h_c}\right)\left(\frac{\eta_d}{\eta_m}\right)\right) \quad (3)$$

where h_c is the critical thickness of liquid film separating colliding drops, below which this film raptures; d is the average diameter of drops. As one can observe, eq. (3) documents decreasing E_c with the phase viscosity ratio, the capillary number, and the ratio of the average domain diameter to minimal thickness (h_c) of the separating film.

Theoretical works by Fortelny and Zivny[24] show that known theories describing droplet behavior in simple shear flow are to be applicable to coalescence analysis in extensional flow.

Few attempts to combine different theories are known.[25,26] For example, the combination of trajectory and deformation approaches predicts[25] a decrease of coalescence efficiency with increasing shear rate and with decreasing particle size ratio.

Lyu et al.,[23] employing a population dynamic equation,[27] have developed a numerical approach with the aim to compare experimental results on PS/HDPE melt blends[7] with the Smoluchovski, trajectory and drainage theories. Besides, this work provides a sound critical review of the theories together with corresponding references. The overall conclusion made from this study is that none of the above theories enable quantitative description of droplet coalescence in simple shear flow. Moreover, they are not consistent with the experimental results by the authors[7] concerning extremal dependence of coalescence efficiency on the phase viscosity ratio. At the same time, the Smoluchovski's theory was accounted to be reflecting the major aspects of coalescence phenomena.

Keeping in mind the information obtained from the literature, the following conclusions may be offered. Some experimental results are still contradictive, probably, because of either different flow fields and materials used or other reasons. Therefore, a further intense effort is needed in this direction. The experimental works and the theories reviewed are both consentaneous in that the coalescence efficiency increases with increasing component ratio. The drainage theory predicting reduction of the coalescence efficiency with the shear rate is in line with the experimental data obtained in simple shear flows, but contradicts the data obtained in complex flows.[3] Finally, all the theories fail to predict extremal dependences of coalescence efficiency on the phase viscosity ratio.[7]

As far as techniques for studying coalescence are concerned, one of them, dealing with labeled component[3] is, at least, too complicated. Another one, employing step-down of the shear rate, is limited to very low shear rates. Besides, it does not represent, in general, the real flow fields (i.e., superimposed shear and extensional) occurring in conventional processing apparatus.

In the following sections, an alternative technique for studying of coalescence in converging flows will be proposed and the results obtained will be compared with corresponding data from literature.

EXPERIMENTAL

Technique

Because of the appropriate velocity and shear stress profiles, a fluid flowing through a converging channel undergoes both shear and extensional deformation. While approaching the entrance zone from a barrel, the distances between wineglass-like streamlines become increasingly closer.[28] Assume two liquid drops follow their own streamlines as shown in Figure 1(a). In the upper region of the barrel, drops 1 and 2 deform slightly because of the action of local shear stress but still do not interfere. In the lower, convergent regions, because of narrowing of the flow, drop 1 can collide with drop 2, provided the distance between the flow paths became smaller than the sum of radii of the deformed drops. This picture illustrates the basic idea of the model technique that was preliminarily tested in our experiments on simulation of collisions of drops in converging channels.[29]

Thus, on extrusion, two populations of drops are considered, the initial (reference) one being in the

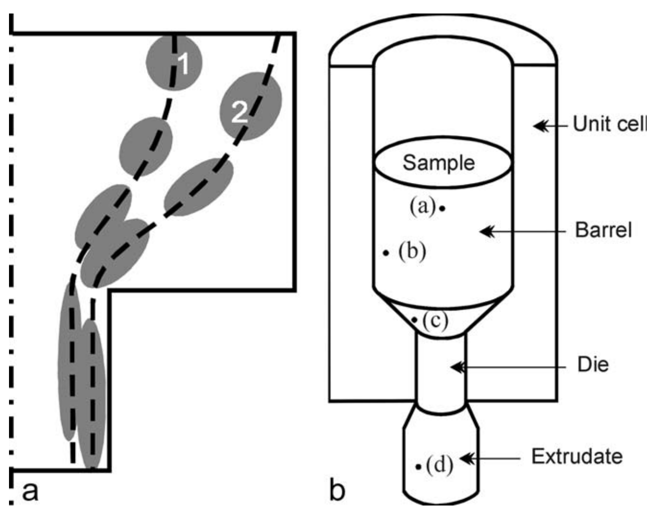

Figure 1 Sketches of: (a) a pair of liquid drops undergoing collisions and coalescence in a convergent flow on their way from a wide barrel into a narrow capillary die; (b) one half of a take apart barrel/capillary unit cell with a blend sample which can be removed after quenching. The positions of microvolumes, from which ultrathin sections in the direction of the flow for TEM analyses have been prepared, are labeled by dots and letters a–d.

TABLE I
Properties of Individual Polymers and Their Blends

Property	PMMA1	PMMA2	PS1	PS2	PS3	PS4	PS5	PS6
M_w (kg/mol)	78	36	200	166	151	87	53	42
η (kPa s) at $\dot{\gamma} = 8.0\ s^{-1}$ and 180°C	12.6	0.99	4.54	3.69	2.28	0.40	0.09	0.03
$\mu = \eta_{PS}/\eta_{PMMA2}$			4.57	3.72	2.29	0.40	0.09	0.03
log μ			0.66	0.57	0.36	−0.40	−1.04	−1.5

upper part of a rheometer barrel and the final one (having suffered partial convergent flow induced coalescence) being in an extrudate. If the drop diameters, d_b (or the drop volumes, V_b), in a barrel and these in the quenched extrudate (d_e or V_e) are measured, the coalescence efficiency can be calculated as follows:

$$E_c = \frac{V_e}{V_b} = \frac{d_e^3}{d_b^3} \qquad (4)$$

Apparently, E_c denotes the average number of domains fused into a single drop upon the flow of emulsion through a converging channel.

The technique proposed is assumed to be adequate as long as the coalesced drops will undergo no further breakups during extrusion and subsequent quenching of the extrudates. The accessible way to suppress such breakage of liquid filaments is to use relatively short capillaries and fast quenching of the extrudates.

Materials and procedures

The polymers used were samples of bulk-polymerized atactic poly(methyl methacrylate), PMMA, and atactic polystyrenes, PS, of different molecular weights listed in the Table I. Commercial grades of PMMA1, PMMA2, and PS1 were purchased from Rohm and Haas Co. (Plexiglas VO52 and VS11) and Dow Chemical Co. (Styron 634) respectively, whereas the remaining samples of bulk-polymerized PS were obtained from domestic suppliers. Mainly, blends PMMA1 with PS1 were studied, whereas PS(1-6)/PMMA2 compositions were used in the experiments on the effect of phase viscosity ratio on E_c only.

All polymer samples and their blends were dried overnight in a vacuum oven at 80°C before use. Blends of PS/PMMA and PMMA/PS were prepared on a two-roll mill at 185°C, grinded, placed into the rheometer barrel and preheated at 185°C for 20 min. Such annealed blend morphology before extrusion with the measured droplet diameter d_b will be considered as the reference one.

A capillary weight rheometer MV-2 with the diameter of a barrel D_b = 9.5 mm has been used. A variety of capillary dies with flat entrance angles (α = 180°) with diameters D_c = 0.97, 1.36, 2.20, 2.85, and 3.32 mm and constant length to diameter ratio L_c/D_c = 21.0 ± 0.6 as well as those with D_c = 2.2 mm and L_c/D_c = 6.8, 13.6, and 21.0 were used. Additionally, a capillary die with D_c = 2.2 mm, L_c/D_c = 6.8 with α = 100° has been employed. To prevent changes in final morphologies small portions of the extrudates (3–4 mm long) were cut off at the die orifice and immediately dropped into iced water.

A take apart convergent unit cell shown in Figure 1(b) has been custom-made and implemented to study phase morphology evolution in different places of the converging zone and capillary die. Assembled with two parts, this unit cell comprises a rheometer barrel with a diameter of 9.5 mm conjugated to a capillary die with D_c = 2.2 mm, L_c = 26 mm (L_c/D_c = 11.8) and α = 100°. After the flow arrest the unit cell can be quickly removed from the rheometer oven and quenched in a large bath of iced water.

Transmission electron microscope (TEM) Tesla BS242E and conventional techniques of sample preparation have been used throughout this study. Because a strong dependence of the phase structure upon radial distance in a die exists, the microtome sectioning of the extrudates to measure the final volume average domain diameters, d_e, has always been performed in the direction of the flow at a distance of half a radius from their outer surfaces with the accuracy of ±2 μm. PMMA/PS blends are known to develop self-contrast under the electron beam, so no additional staining was needed.

An interactive computer image analysis was used to quantify the scale of dispersion of the blends. To obtain statistically significant results on domain sizes, no less than 300 particles were measured for each experimental point. Also, 3–5 parallel experiments were usually performed for estimation of experimental scatter shown by the error bars on some graphs. As a rule, values of E_c were calculated on the basis of average drop diameters.

RESULTS AND DISCUSSION

Behavior of droplets in converging zones

Inhomogeneous shear fields in Poiseuille flow where the velocity of a fluid increases and the shear stress

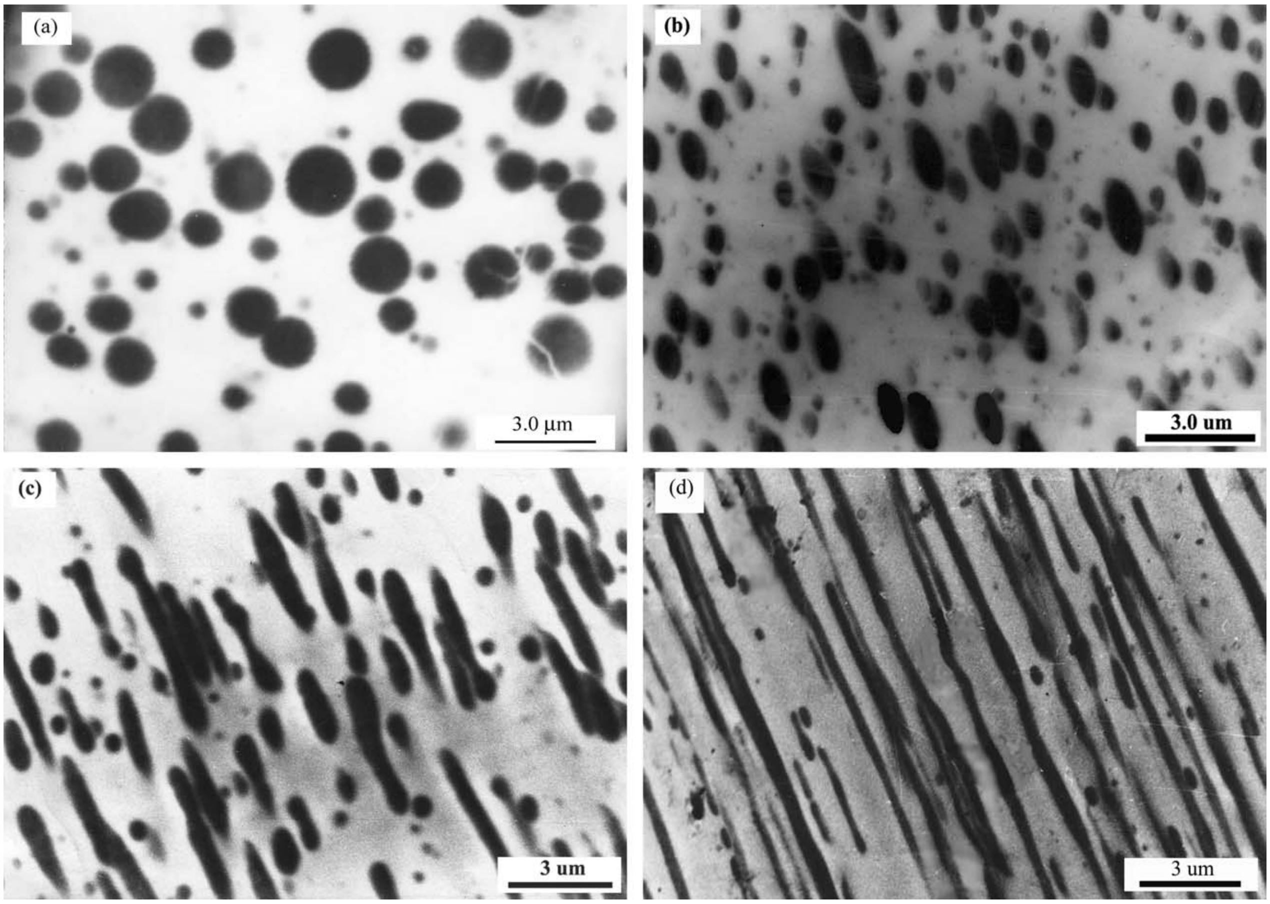

Figure 2 Representative TEM photographs of ultrathin sections of a 15/85 PS1/PMMA1 blend ($\mu = \eta_{PS}/\eta_{PMMA} = 0.4$) taken from the microvolumes a–d. Extrusion at temperature $T = 185°C$ and shear rate $\dot{\gamma} = 3.0\ s^{-1}$.

decreases in radial direction from the tube wall to the tube axis become even more complex in converging channels.[28] Although rectilinear streamlines transform into the wineglass-shaped ones, the higher, compared with barrel, fluid velocity in a narrow die creates a significant portion of extensional flows. Apparently, the drops of emulsion flowing in different zones of a converging channel are subjected to different stress fields, which determine particular features of domain deformation and interactions.

The main purpose of morphological studies made in this work was to locate flow zones where coalescence takes place upon extrusion. Besides, it was important to make sure that upon subsequent capillary flow and extrudate solidification no noticeable filament breakage occurred. These experiments have been performed at constant shear rate of 3.0 s^{-1} with the use of a take apart unit cell [Fig. 1(b)] and a 15/85 PS1/PMMA1 blend ($\mu = 0.4$). After establishing steady state extrusion, the flow was abruptly arrested, the unit cell filled with a melt blend was quickly removed from the heater and quenched in iced water. Since this operation takes only a few seconds, no significant change of blend morphology (primarily, thread breakups) is assumed to take place. After the unit cell is disassembled, the released solid sample of the blend comprising portions of material resided in a barrel, the entrance zone and capillary die was precisely cut along the diametric (center line) plane followed by fine polishing under micrometric control. Finally, small portions of the material were cut from many different places of the sample and subjected to microtome sectioning. For the sake of brevity, the morphology in only four microvolumes labeled by dots and letters (*a*)–(*d*) in Figure 1(b) will be discussed here.

Corresponding typical TEM micrographs in Figure 2(a–d) show that the portion of the blend situated in the upper axial region of a barrel [spot *a*, Fig. 2(a)] is represented by the dispersion of spherical submicron sized drops of PS (dark areas) with minor (if any) traces of coalescence. Having examined photographs and the corresponding distribution curves (not shown here) belonging to spots *a*–*d*, we may conclude that some coalescence already starts in the upper peripheral regions of a barrel [spot *b*, Fig. 2(b)] and proceeds the more effectively the closer the studied volume to the entrance capillary zone. As expected, the most intensive coalescence within the converging region [spots *c*, Fig. 2(c)] takes place.

Morphology of the blend in the extrudate (spot *d*, Fig. 2 days) is represented by long and slim thread-like domains aligned with flow direction. Similar fiber-like morphology is detected in the capillary die (not shown).

A micrograph in Figure 2(d), and dozens of other images obtained from the areas of the capillary die and extrudates, show no noticeable signs of the filament breakups in this blend. Minor differences of volumetric diameters of the threads found in a capillary die and in the extrudate are proved quantitatively by comparing corresponding domain size distribution curves.

TEM analysis evidences that coalescence in the convergent zone may be assumed completed at the horizontal level which is a bit lower than the spot *c* in Figure 2(b). Then, strong extensional flows, acting in the vicinity of the die entrance, deform larger drops formed due to coalescence into long slim filaments.

Thus, the morphological studies obtained allow for some considerations having direct concern with the validity of the proposed technique. These data show that minor coalescence takes place during slow flow in the barrel. In these regions, where $Ca < Ca_{crit}$, no drop breakups would be expected at all. Much higher shear rates in the converging zone enlarge Ca beyond Ca_{crit} which makes the breakups possible. But the key point is that the drop deformation is conjugated here with simultaneous intensive coalescence leading to the formation of thick elongated filaments [see Fig. 2(c)] whose times to break are higher than the residence times in this zone. Flowing down to the die entrance region these domains are subjected to substantial longitudinal extension followed by molecular orientation. It is well known that this fact, and the flow itself, stabilizes liquid polymer threads markedly. Most probably, there are capillary die and the extrudates before solidification where the filament breakups might be expected. As it was mentioned above, these problems have been solved using relatively short dies and fast cooling of the extrudates.

Effects of processing and material parameters

Influence of convergence geometry

The influence of flow convergency on the coalescence efficiency, E_c, is illustrated in Figure 3. This dependence was obtained by varying of the ratio of the diameter of a barrel to that of a capillary die, D_b/D_c, while keeping length to diameter ratio $L_c/D_c = 21.0$ constant. One can observe that growth of the D_b/D_c ratio (i.e., an increase of convergency) from 2 to 10 results in more than twofold increase of E_c. This effect may be due to corresponding relative reduction of the distances between streamlines within the entrance zone which enhances a collision frequency. These data could be a matter of technological interest because they show how to vary coalescence on extrusion.

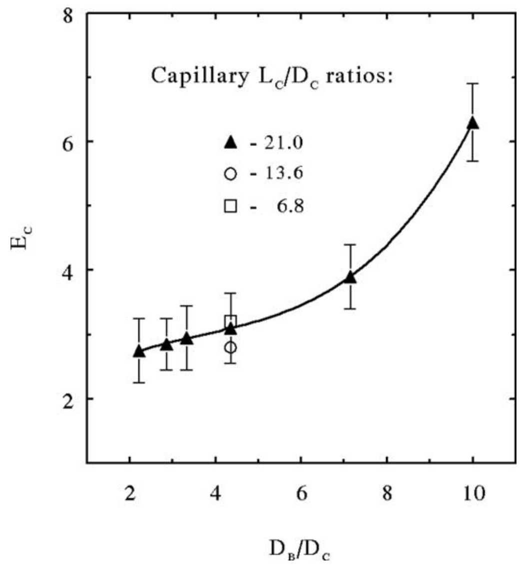

Figure 3 Influence of flow convergency represented by the barrel/capillary die diameter ratios, D_b/D_c, on the coalescence efficiency, E_c, for a 15/85 PMMA1/PS1 blend ($\mu = 2.8$) extruded at $\dot{\gamma} = 1.8\ s^{-1}$. Three experimental points placed at $D_b/D_c = 4.5$ belong to three capillary dies with the same diameter, 2.2 mm, but different lengths ($L_c = 46.2$, 29.9, and 15.0 mm).

The other two experimental points placed on this graph at $D_b/D_c = 4.5$ relate to the capillaries with the same diameter (2.2 mm) but different lengths. Independence, within the experimental error, of the E_c upon capillary length once again proves the absence of noticeable breakage of the stretched drops upon capillary flow (at least, in this particular blend).

Temperature, shear rate, and entrance angle

According to our data, there is, at least, power law increase of the coalescence efficiency with extrusion temperature. Almost 10-fold growth of E_c has been detected when the temperature was raised from 160 to 195°C. As far as phase viscosity ratio of the blend experiences minor change with temperature it is clear that the reduction of the viscosities of both phases upon flow favors coalescence.

The influence of the extrusion shear rate, $\dot{\gamma}$, on the convergent flow driven coalescence is illustrated in Figure 4. Blends of 15/85 PMMA1/PS1 ($\mu = 2.8$) were extruded through the capillary dies having similar length to diameter ratios but different entrance angles, $\alpha = 180°$ and $\alpha = 100°$. When plotted in linear coordinates shown in Figure 4, these results indicate a fast increase in E_c, at low and moderate

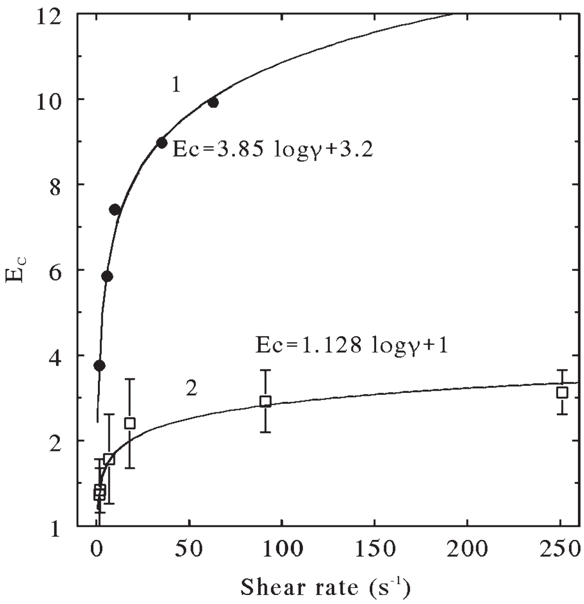

Figure 4 Dependences of the coalescence efficiency, E_c, on the extrusion shear rate for a 15/85 PMMA1/PS1 (μ = 2.8) melt blends; $L_c/D_c = 12.0$ and capillary entrance angle α = 100° (curve 1) and α = 180° (curve 2); $T = 185$°C.

shear rates, followed then by a tendency towards asymptotical leveling-off of E_c at higher shear rates. Here, the experimental points are labeled by symbols, whereas solid lines are the best fits with equations shown next to each curve. Following a well-reasoned opinion that the shear stress rather than shear rate should be used in studying the emulsion behavior, we have plotted E_c versus shear stress as well (not shown for brevity). The shapes of these curves were similar to those disposed in Figure 4.

Data presented in Figure 4 are in line with both experimental work by Roland and Böhm[3] (in which similar flow pattern on a two-roll mill has been used) and a classic Smoluchovski theory.[15] At the same time, the most part of experimental works employing simple shear flow reports a decrease in coalescence efficiency with increasing shear rate.[4–10] Since such behavior is usually explained in terms of the drainage theory, the following brief analysis of the subject might be worthwhile.

The Smoluchovski's theory [eq. (2)] predicts a linear increase of the rate of collisions (which favors coalescence) with increasing shear rate. On the other hand, according to Chesters,[16] the growth of the shear rate results in larger flattened contact area between colliding drops which, in turn, reduces the rate of squeezing flow of the matrix film and, finally, leads to coalescence suppression. Combining these approaches and ignoring quiescent coarsening, Janssen and Meijer[21,22] have arrived to the following conclusions. In the very low shear rate region ($Ca \ll Ca_{crit}$), no coalescence has to be expected because no collision of droplets occurs. Upon further growth of the shear rate, the increase of the collision rate results in corresponding increase of coalescence probability. Finally, at high shear rates coalescence is being progressively suppressed because of flattering contact areas and corresponding increase of drainage time.

Evidently, our E_c versus $\dot{\gamma}$ dependence correlates qualitatively well with the above predictions except for high shear rates where a leveling off rather than reduction of coalescence has been detected. This effect may be attributed to the constrained converging flow in which droplets of emulsion pushed through tapering channels may undergo a kind of "forced" coalescence driven by lateral compression stresses normal to flow direction.

Figure 4 demonstrates also that the coalescence efficiency experiences almost fivefold increase when the entrance angle of the die is reduced from 180 to 100 degrees. This phenomenon may be due to the increase of the length of the convergent zone. The latter, other conditions being equal, enlarges the residence times of the drops in this specific area and favors the completion of time consuming process of drainage of the separating matrix films.

Initial domain size

Different PMMA1 drop sizes in 15/85 PMMA1/PS1 blends (μ = 2.8) were prepared by varying the duration of melt mixing on a two-roll mill from 8 to 28 min at 185°C. After preheating, the melts were extruded through a capillary die with $L_c = 30.0$ mm; $D_c = 2.2$ mm and α = 180° at $T = 185$°C and $\dot{\gamma} = 6.0$ s^{-1}. A plot of E_c versus average diameters of the initial drops depicted in Figure 5 shows very sharp

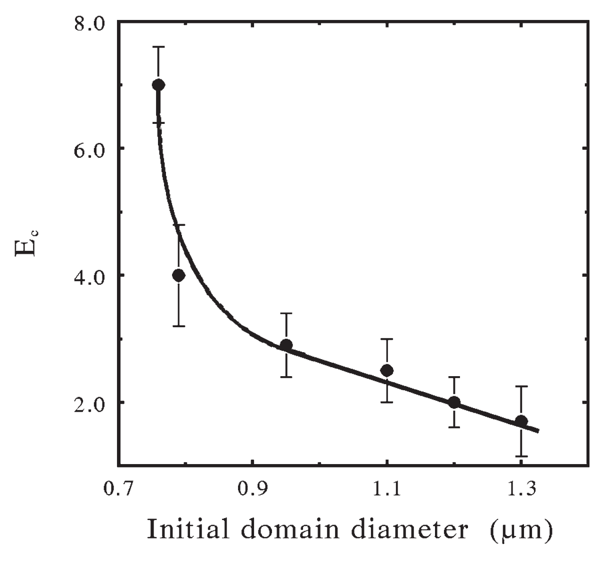

Figure 5 Dependence of E_c on the average initial domain diameter in 15/85 PMMA1/PS1 melt blends (μ = 2.8) extruded at $T = 185$°C and $\dot{\gamma} = 6.0$ s^{-1} through a capillary die with $L_c = 30.0$ mm; $D_c = 2.2$ mm and α = 180°.

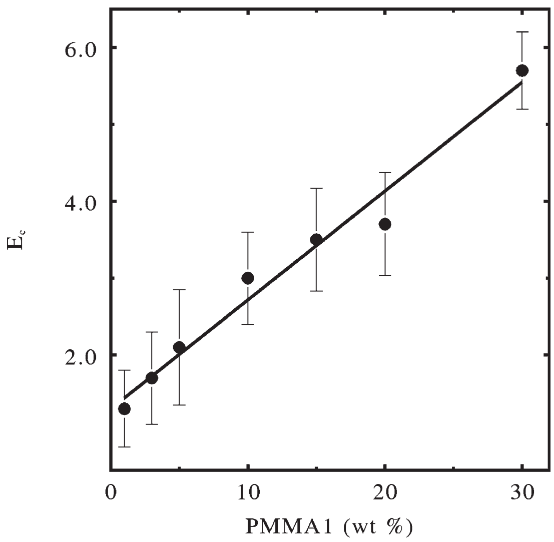

Figure 6 Influence of the component ratio on coalescence efficiency in PMMA1/PS1 blends (μ = 2.8) extruded at T = 185°C and $\dot{\gamma}$ = 1.8 s^{-1} through a capillary die with L_c = 30.0 mm; D_c = 2.2 mm and α = 180°.

growth of the coalescence efficiency with the decrease of the droplet sizes. More specifically, these data mean that coalescence in populations with smaller average drop sizes proceeds more readily than that in populations with larger droplets.

Unfortunately, no domains with initial average diameters less than 0.76 μm have been studied here, because initially fine emulsions suffered fast thermal coalescence in a barrel during the blend preheating stage. An attempt to approximate the experimental data with Smoluchovski's eq. (2) reveals (the curve is not shown here) that the dependence of E_c versus reciprocal average domain radius cubed fits satisfactorily all the experimental points shown in Figure 5 except the one with the minimal droplet size d_b = 0.76 μm. At this point the experimental E_c was higher than the predicted value. Nevertheless, taking into account large experimental scatter, one may conclude that, at least, a qualitative correlation between our data and both the Smoluchovski's theory and experimental data from literature is observed.

Blend composition ratio

According to our data shown in Figure 6, the coalescence efficiency grows approximately linearly, rather than squared as the Smoluchovski's theory [eq. (2)] predicts, with concentration of the dispersed phase. The effect is, evidently, due to inequality of the initial drop sizes in blends with different component ratios. Probably, the situation illustrated by Figure 6 is a result of competition between two opposite tendencies which can be analyzed qualitatively on the basis of eq. (2). Indeed, the rate of collision is proportional to concentration squared, on the one hand, and inversely proportional to cube of domain size, on the other hand. As long as the domain diameter is a growing function of the inner phase concentration, the interplay of these tendencies results in a particular dependence shown in Figure 6. To eliminate the uncertainty that this graph obviously bears, one has to fix the initial drop size while varying blend composition ratio. Needless to say that, at least in this case, this is scarcely feasible.

Phase viscosity ratio

Phase viscosity ratio, μ, is one of the primary variables predetermining the behavior of emulsions. Experiments have been performed on the influence of μ on the coalescence efficiency in the model blends with fixed component ratio of 15/85 PS/PMMA2. The blends were composed in such a way that the matrix was always formed by PMMA2, although six samples of PS of different molecular weights served as the dispersed phases. As it follows from data listed in the Table, the values of phase viscosity ratios of the blend samples ranging from 0.04 to 4.57 have been realized. All the blends were prepared in a manner similar to that described in previous sections and then extruded at a shear rate of $\dot{\gamma} = 2.2$ s^{-1} and T = 185°C through a capillary die with L_c = 30.0 mm; D_c = 2.2 mm and α = 180°. A relatively low shear rate in these experiments has been chosen with the only aim to avoid deformation of drops beyond TEM image frames, making the measuring of their actual volumetric sizes excessively time consuming.

As Figure 7 shows, the dependence of E_c on log μ is highly nonlinear and described by a U-shaped curve. According to these data and contrary to both theoretical and experimental works cited above, the coalescence efficiency is minimal at $\mu \approx 1$ and goes up when the viscosity of the inner phase is considerably lower or higher than that of the matrix.

Actually, the left part of the curve indicating the growth of E_c with decreasing phase viscosity ratio at $\mu < 1$ correlates qualitatively well with both the trajectory and drainage [eq. (3)] theories and with most experimental works mentioned earlier. Contrary to all predictions, the right branch of the curve at $\mu > 1$ again shows an increase of the coalescence efficiency with increasing viscosity of the inner phase.

Nevertheless, a kind of logical explanation of this effect could be proposed. Since in these experiments the viscosity of drops was changed by varying molecular weights of the PS samples, the increase of their viscosity is followed by the increase of elasticity. More elastic drops undergo less deformation both in flow and upon collisions. Therefore, the near-spherical surfaces of more viscous drops

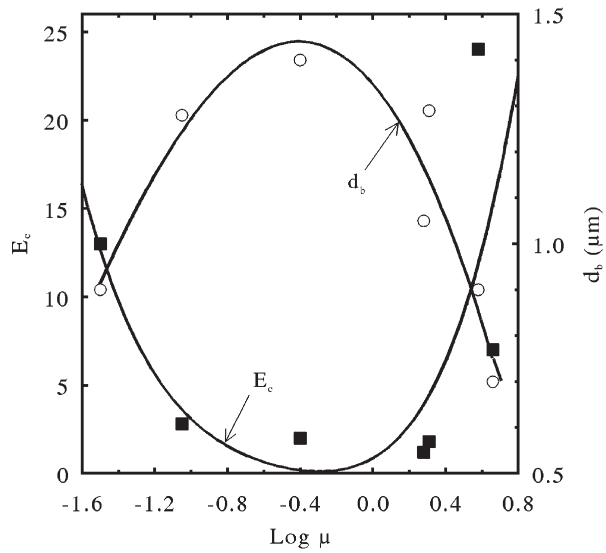

Figure 7 Influence of the phase viscosity ratio, μ, on the coalescence efficiency, E_c in blends 15/85 PS(1-6)/PMMA2 (see Table I) upon extrusion at $T = 185°C$ and $\dot{\gamma} = 2.2\ s^{-1}$ through a capillary die with $L_c = 30.0$ mm; $D_c = 2.2$ mm and $\alpha = 180°$ and on the initial average drop diameter, d_b measured after preheating in a barrel for 20 min at $T = 185°C$ before extrusion for the same blends.

experience less flattering upon collisions. This might lead to faster drainage of the separating matrix film and, consequently, to more effective coalescence.

Another probable reason that may be responsible for the observed phenomenon is that the average initial domain diameter before extrusion, d_b, in all the blends has not been maintained constant. To obtain knowledge about what is happening to droplet dimensions after preheating of the virgin blends in a rheometer barrel the values of d_b were measured and plotted as a function of phase viscosity ratio in Figure 7. It is interesting that the shape of this curve is inversed with respect to the E_c versus μ dependence. If one relies upon both the literature data reviewed earlier and our results depicted in Figure 5, showing increasing coalescence efficiency with the reduction of the droplet diameters then, a simple though formal explanation of the observed phenomenon may be proposed. As long as smaller domains coalesce more readily, a concave curve for d_b is transformed to a convex curve for E_c after extrusion.

Meanwhile, the key question about whether U-shaped E_c versus μ curve in Figure 7 actually describes this dependence or originates from the nonequal-sized initial domains remains open until similar experiments at d_b = const are carried out.

CONCLUSIONS

A novel technique for studying coalescence stimulated by converging flows has been proposed and tested experimentally. To ascertain the validity of the method dependences of the coalescence efficiency, E_c, upon converging geometry, shear rate and shear stress, average initial droplet diameter, extrusion temperature, component and viscosity ratios have been analyzed. Overall, our results obtained with the model melt blends of PS/PMMA are in line with existing experimental and theoretical findings. However, some discrepancies between our data and the results from literature have been observed. For example, the dependence of E_c on the phase viscosity ratio disagrees partially with the drainage theory and existing experimental data. Nonequal initial domain diameters and/or specific flow fields in narrowing channels may be responsible for this discrepancy. Therefore, the proposed technique may be considered as an alternative method which allows to diversifying our knowledge about coalescence upon processing of polymer blends.

Like any simulation method, this technique bears both advantages and shortcomings which can be formulated as follows:

Benefits:

1. Simple and predictable.
2. Model flow field is operative, at least partially, in real industrial mixers and in molding operations.
3. Seems to adequately represent basic dependencies of coalescence on composition ratio, shear rate, and initial drop sizes.
4. Easily adjustable for studies of various flow geometries, processing and material parameters.
5. Assumed to be useful for studies on particular coalescence mechanisms, effects of different additives, etc.

Shortcomings:

1. One-step extrusion technique implies, unlike real blending, no dynamic balance between breakup and coalescence of drops.
2. Suppressing simultaneous breakage of the extended drops in flow and during melt blend solidification is a necessity.
3. Difficulties associated with maintaining constant initial drop sizes in comparative experiments (effects of concentration, phase viscosity ratio, elasticity, etc.), which, as a matter of fact, can be referred to in any other reviewed technique.
4. Excessively time-consuming when electron microscopy is used for monitoring phase morphology.

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