

Polymer Melt Mixing: Liquid–Liquid Mixing

In polymer processing, melt blending of homopolymers is a common route towards materials with specific properties. Most polymer pairs are thermodynamically immiscible in the molten state and the blend is characterized by its morphology, the spatial distribution of the constituting polymers. As the morphology is crucial to the material properties, it is key to understand the development and stability of multiphase morphologies, or more generally the dynamics of liquid–liquid mixing.

The basic mechanisms to be considered are the stretching and breakup of liquid domains, immersed in another immiscible liquid, and the eventual coalescence of formed small drops upon collision. In the area of interest, inertia and buoyancy can be neglected with respect to viscous and interfacial effects. Key dimensionless parameter is the capillary number Ca : the ratio of shear stress τ imposed on a drop by the external flow field, and the interfacial stress σ/R (with σ the interfacial tension, an intrinsic property of the liquid–liquid pair, and R the local radius of the dispersed domain):

$$Ca = \frac{\tau}{\sigma/R} = \frac{\eta_c \dot{\gamma} R}{\sigma} \quad (1)$$

with η_c the viscosity of the continuous phase (the immersing liquid) and $\dot{\gamma}$ the local shear rate. An illustration of the competition between viscous and interfacial forces is given in Fig. 1. Note that studies are often performed using model liquids at room temperature in idealized flow fields (e.g., simple shear flow or elongational flow). An additional dimensionless parameter key to the dynamics of liquid–liquid

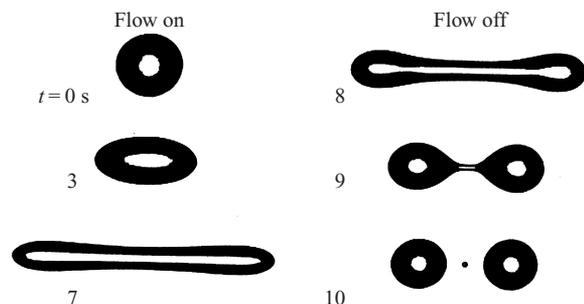


Figure 1

Deformation and breakup of a drop in elongational flow: initially interfacial tension tries to balance the deforming stress; upon cessation of the flow, interfacial tension drives towards retraction and necking (castor oil drop of 1.5 mm in silicone oil matrix, both of viscosity 0.7 Pa s).

mixing is the viscosity ratio (p) between dispersed and continuous phase:

$$p = \frac{\eta_d}{\eta_c} \quad (2)$$

For example, the critical value of the capillary number Ca_{crit} , indicating above which steady shear stress a drop will irreversibly stretch and break up, is strongly dependent on the viscosity ratio.

1. Stretching ($Ca \gg 1$)

In the initial stage of mixing, the dispersed domains are generally large (millimeter size) and so is the capillary number; the shear stress overrules the interfacial stress. If the critical capillary number for breakup is exceeded sufficiently, i.e., at Ca/Ca_{crit} above 5 or so, interfaces behave “passively” and liquid domains are stretched affinely with the external flow field; the rules for distributive mixing hold, i.e., the extent of drop deformation depends only on the total strain applied; deformation rate and time are interchangeable. In steady elongational flow, affine stretching proceeds exponentially in time with an associated fast reduction of striation thickness. However, in simple shear flow stretching progresses only linearly. The reason is the rotational nature of simple shear: the orientation of a stretching domain turns away from the principal axis of strain (45°) towards the streamline direction, so that the stretching efficiency of a specified domain decays to zero. Interestingly, at viscosity ratios deviating from one, dispersed domains stretch either slower (if $\eta_d > \eta_c$) or faster (if $\eta_d < \eta_c$) than the surrounding continuous phase.

Practical mixers are often dominated by simple shear flow rather than elongation. Nevertheless, exponential stretching can be achieved by applying folds, just like a baker who is kneading the dough, forcing the number of striations to double at each fold. Figure 2 illustrates the deformation of passive tracer drops in a two-dimensional cavity subjected to periodic movement of top and bottom walls, one after the other. Streamlines taken at different moments in time cross each other, thus changing the direction of the flow locally and generating a fold in a bundle of stretched filaments. Note that in this so-called chaotic mixing, periodic points can be identified (returning to their original position after each period of motion) that are of either hyperbolic or elliptic nature, representing areas of exponential mixing or undeformed islands respectively.

Practical applications of stretching and folding may be space-periodic rather than time-periodic. Examples can be found in static mixers, reciprocating single-screw extruders (Buss Co-Kneader) and so-called

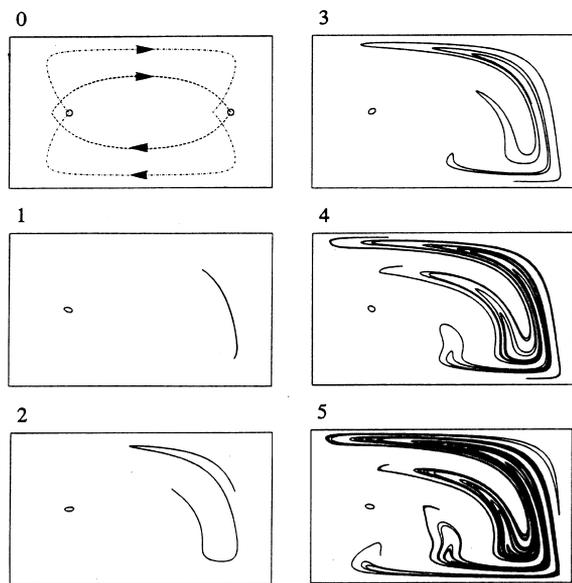


Figure 2
Deformation of two passive tracer drops in a periodic cavity flow, moving top and bottom wall alternately over a certain distance in their own direction. Initial drop positions are chosen at periodic points, and dashed curves indicate their trajectories during one period. One drop is initiated in an island and remains undeformed; the other one is stretched and folded, quickly covering a large area.

chaos screws for single-screw extrusion (having undercut, secondary flights); co-rotating intermeshing twin-screw extruders generate folds and reorientations at the take-over of material from one screw to the other. The common theme in effective distributive mixers is that they apply large strains without large stresses, thus avoiding excessive viscous dissipation with its consequent temperature rise.

2. Breakup ($Ca \sim 1$)

Once the dispersed domains have been stretched into long slender liquid threads (μm), the interfacial stress (σ/R) becomes important. Small disturbances at the interface grow, leading to breakup of the threads into lines of droplets (dispersive mixing). In the case of a viscous thread in a viscous matrix which is quiescent, the amplitude, α , of the sinusoidal waves grows exponentially with time:

$$\alpha = \alpha_0 \exp(\Omega t / t_\sigma) \quad (3)$$

with α_0 the initial amplitude and Ω the dimensionless growth rate; note that the time t is taken relative to t_σ , the characteristic timescale for σ -driven processes ($\sim \eta_c R / \sigma$). In fact, disturbances of all wavelengths (λ)

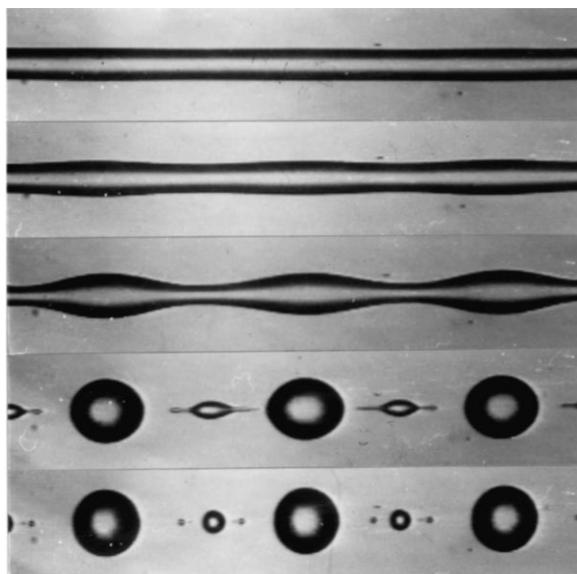
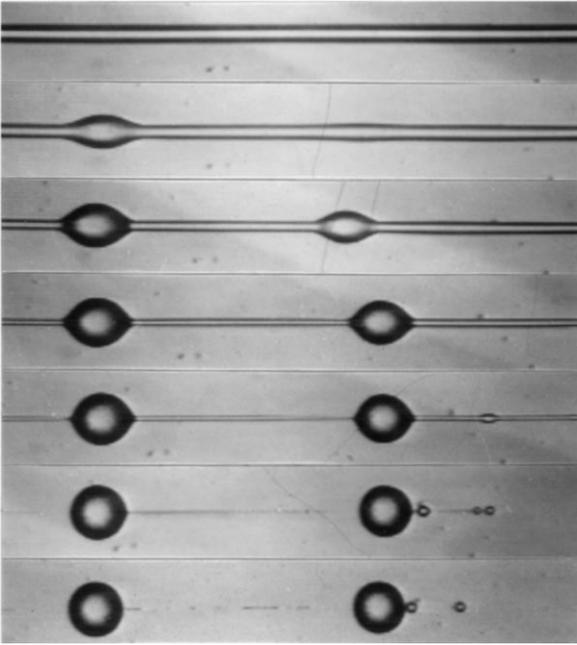


Figure 3
Disintegration of a viscous thread of 0.35 mm diameter (castor oil, $\eta_d = 0.74 \text{ Pa}\cdot\text{s}$) in a quiescent viscous matrix (silicone oil, $\eta_c = 0.94 \text{ Pa}\cdot\text{s}$, $\sigma = 4.1 \times 10^{-3} \text{ N}\cdot\text{m}^{-1}$); photographs were taken every second.

are present at an initial amplitude level α_0 , and the growth rate Ω is a function of the wavenumber ($x = 2\pi R / \lambda$) and the viscosity ratio (p). For each value of the viscosity ratio there is one specific wavenumber having the maximum growth rate Ω ; this dominant wave will lead to breakup. Note in Fig. 3 that in the final stage of thread breakup, so-called “satellite droplets” emerge in the fine filaments between adjacent drops.

Viscoelasticity of the dispersed phase may retard the thread breakup process dramatically. At a certain stage of disturbance growth, elongational stresses build up in the necks that are being drained into the emerging drops. Locally, the flow stagnates and typical dumbbell shapes appear, as can be seen in Fig. 4. A simple set of requirements for viscoelasticity to play a role demands that (i) stresses build up faster than they relax ($\dot{\epsilon}\theta > 1$, with $\dot{\epsilon}$ the stretching rate and θ the relaxation time); and (ii) the total strain is substantial ($\dot{\epsilon}t > 1$). The polymer solution in Fig. 4 clearly fulfills these requirements, whereas polymer melts may exhibit the phenomenon to a less pronounced extent.

In a more realistic case, continued stretching of a disintegrating thread largely retards the breakup process. Now, the thread radius continuously decreases and the evolving waves are stretched. At each moment in time a different disturbance becomes dominant; “old,” stretched-out waves damp and are overruled by “new” ones, again and again, until the thread is so thin that a critical disturbance finally


Figure 4

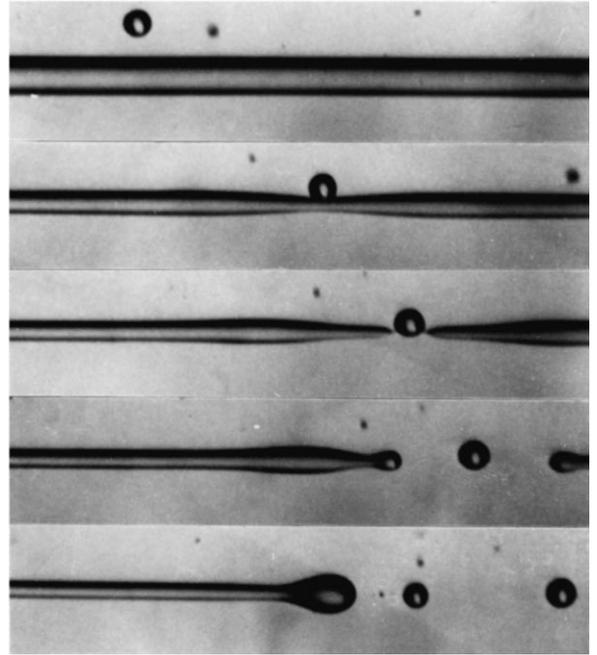
Disintegration of a 0.07 mm thick viscoelastic thread (corn syrup/water mixture with 0.01% polyacrylamide) in a quiescent viscous matrix (silicone oil, $\eta_c = 2.0 \text{ Pa}\cdot\text{s}$, $\sigma = 18 \times 10^{-3} \text{ N}\cdot\text{m}^{-1}$); photographs were taken every 3 seconds.

becomes fatal. For viscous liquids the resulting drop size decreases almost proportionally with the stretching rate and, interestingly, the more viscous the liquids are (either dispersed or continuous phase), the stronger is the effect of postponing breakup, resulting in even smaller droplets.

A final point of attention for thread breakup is the level of the initial disturbance amplitude α_0 . As a minimum the effect of temperature fluctuations can be estimated, giving values of $\sim 10^{-9} \text{ m}$. However, in a realistic situation, multiple drops and threads may easily influence one another, impose large disturbances, and trigger early scission and breakup as shown in Fig. 5.

After stretching and breakup of liquid filaments, the drops (typically $1 \mu\text{m}$ in polymer blends) are subjected to shear stresses, and may break up further if the critical capillary number is still exceeded. As mentioned, Ca_{crit} is a strong function of the viscosity ratio p and of the flow type; in elongational flows $Ca_{\text{crit}} \sim 1$ over a wide range of p , whereas simple shear flow is less effective: Ca_{crit} is larger, especially when $p \neq 1$. For sufficiently high drop viscosity ($p > 4$) it is even impossible to reach breakup as $Ca_{\text{crit}} \sim \infty$.

It is interesting to compare the two breakup mechanisms discussed here: (i) a one-step route of thread breakup during stretching, i.e., applying maximum deformation rate right away; and (ii) a stepwise


Figure 5

Collision of a drop onto a stretching thread; early scission leads to end-pinching, producing relatively large drops. Both liquids are viscous, with $p = 0.35$; photographs were taken every 2 seconds.

sequence increasing the deformation rate up to the same maximum level, breaking drops in two, just at Ca_{crit} , again and again. The one-step route generally gives a finer morphology and seems more applicable in the regime of polymer compounding. Moreover, the one-step route implies that the morphology becomes finer upon increasing the viscosity of either phase, even if the viscosity ratio goes far above one: a conclusion quite different from the usual suggestion that a viscosity match ($p = 1$) is best, as based on the stepwise quasi-equilibrium route.

3. Coalescence ($Ca < 1$)

Finally, attention is focused on the dynamic character of the morphology. Small drops formed may break up again (if the local capillary number is large enough), or coalesce (at small values of the capillary number). Modeling the coalescence process consists of two aspects: (i) collision of dispersed drops, and (ii) drainage and rupture of the separating liquid film between colliding drops, leading to confluence (see Fig. 6). Evidently, the collision frequency is favored by both a larger volume fraction ϕ of the dispersed phase and a larger deformation rate. A simple way of defining the probability (P_{coll}) that a collision happens within a certain process time is to compare the typical

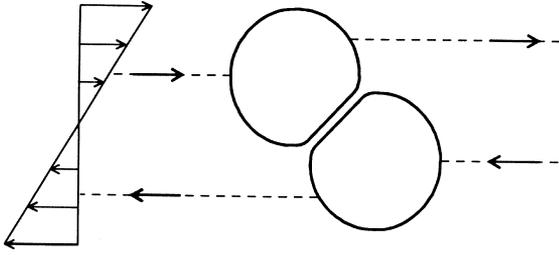


Figure 6
Collision of two deformable liquid drops in simple shear flow with drainage of the liquid film in between, before confluence can occur.

time scale between collisions (t_{coll}) with the available process time (t_{proc}):

$$P_{\text{coll}} = \exp(-t_{\text{coll}}/t_{\text{proc}}) \quad (4)$$

ranging from 0 up to 1 as t_{coll} becomes smaller than t_{proc} , i.e., upon increasing either ϕ or $\dot{\gamma}$.

As soon as the drops “notice” each other, they tend to flatten and the liquid film is squeezed out, until it is so thin ($\sim 5 \times 10^{-9}$ m) that van der Waals forces cause sudden film rupture, leading to coalescence of the drops. However, this critical film thickness needs to be reached within the available interaction time of the collision, otherwise the drops simply tumble around and move on individually. Similarly to the collision probability, one can now define the probability for successful film drainage (P_{drain}) by comparing the required drainage time (t_{drain}) with the available interaction time (t_{int}):

$$P_{\text{drain}} = \exp(-t_{\text{drain}}/t_{\text{int}}) \quad (5)$$

ranging from 0 up to 1 as t_{drain} becomes smaller than t_{int} . For the interaction time, one could simply take something like $1/\dot{\gamma}$. However, for the film drainage time two considerations have to be made. First, it should be noted that the flattened area increases as the drops are bigger or as the collision is faster (higher collision force). Furthermore, the mobility of the interfaces between drops and matrix largely influences the drainage rate; drainage is slower if interfaces are less mobile, either by high drop viscosity or by a surfactant at the interface. The consequence of the above is that at high deformation rates, the drops flatten significantly, requiring a long time for drainage, while the duration of the collision is only short; the drops will only “kiss and tumble.” Soft collisions will more readily lead to coalescence.

Combining both probabilities, the overall coalescence probability is obtained:

$$P_{\text{coalesce}} = P_{\text{coll}}P_{\text{drain}} = \exp\left(-\frac{t_{\text{coll}}}{t_{\text{proc}}} - \frac{t_{\text{drain}}}{t_{\text{int}}}\right) \quad (6)$$

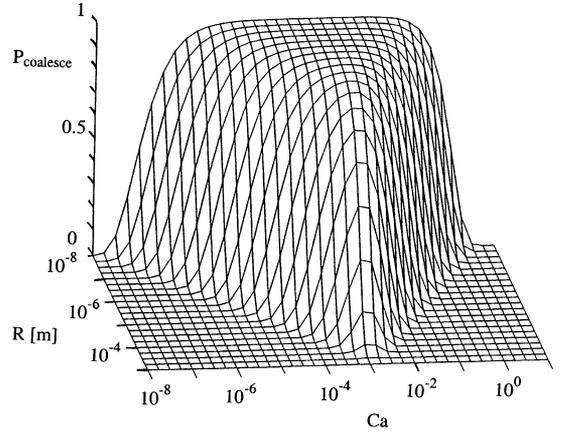


Figure 7
Coalescence probability as a function of the drop radius and the capillary number. Conditions: simple shear flow, $t_{\text{proc}} = 50$ s, $\eta_d = \eta_c = 1$ Pa s, $\sigma = 10^{-2}$ N m $^{-1}$, $\phi = 0.1$, drainage model with partially mobile interfaces.

with a typical example in Fig. 7. Left of the hump, the flow is too slow to generate enough collisions ($P_{\text{coll}} = 0$). Right of the hump, collisions occur but the flow is too fast: the available interaction time has reduced below the required drainage time ($P_{\text{drain}} = 0$). Note that for small droplets the coalescence window is wide, whereas large drops have no chance to coalesce. It now also becomes obvious that coalescence takes place in different regimes ($Ca < 1$, “weak zone”) than drop stretching and breakup ($Ca \geq 1$, “strong zone”). Figure 8 shows a number of coalescence events of relatively large drops that are pushed together extremely gently: no flattening, long interaction time.

4. Discussion

For application to a practical mixer, the dynamic microrheological models for stretching, breakup, and coalescence need to be coupled with an overall flow simulation of the compounder. Useful insights can be obtained already from a simple two-zone model: let a population of dispersed domains pass cycles through alternating “strong” and “weak” zones. In the strong zone, exponential stretching occurs with eventual thread breakup; in the weak zone, thread breakup and coalescence may occur. For example, in the general competition between breakup and coalescence, it becomes clear that increasing any of the viscosities leads to a finer morphology, even though the viscosity ratio may deviate from one. The reason is the delay of thread breakup during stretching and, equally as important, the suppression of coalescence. It is clear that a multiphase morphology cannot be predicted from the critical capillary number only.

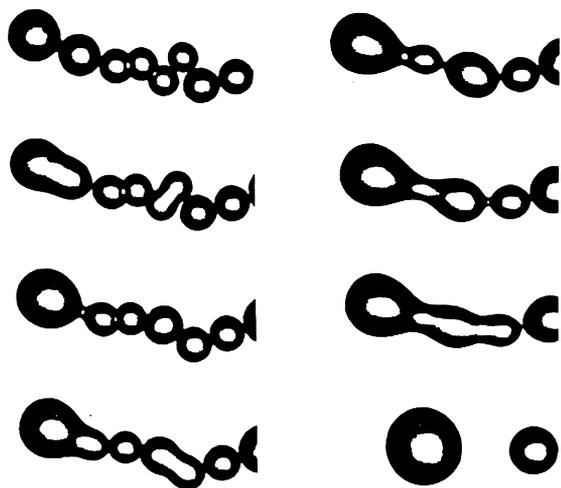


Figure 8

A cascade of coalescence events in a string of drops that is pushed together; both liquids are purely viscous. Note that each confluence of drops seems to trigger the next film rupture.

In the melt blending of polymers, the initial size reduction may be largely governed by the melting process, which is not included in the present article. The order of addition and the sequence of sticking or melting play a key role. Still, in the final stage, it is the dynamic competition between breakup and coalescence that governs the morphology.

A final consideration is the fact that a polymer blend morphology may easily change during subsequent processing steps: e.g., a fine morphology obtained in a compounder may coarsen during molding, unless it is stabilized in some way. Forming a compatibilizer *in situ* is a powerful strategy to “lock in” a fine mor-

phology once formed. Thus the material properties become more robust with respect to shaping of the final plastic part.

See also: Polymer Melt Mixing: Distributive Mixing; Polymer Melt Mixing: Agglomerate Dispersion; Polymer Melt Mixing in Static Mixers

Bibliography

- Chesters A K 1991 The modelling of coalescence processes in fluid-liquid dispersions: a review of current understanding. *Trans. Inst. Chem. Eng.* **69A**, 259-70
- Grace H. P. 1982 Dispersion phenomena in high viscosity immiscible fluid systems and application of static mixers as dispersion devices in such systems. *Chem. Eng. Commun.* **14**, 225-77
- Janssen J M H 1997 Emulsions: the dynamics of liquid-liquid mixing. In: Meijer H E H (ed.) *Processing of Polymers*, Materials Science and Technology, Vol. 18. Wiley-VCH, New York. Chap. 3.
- Janssen J M H, Meijer H E H 1995 Dynamics of liquid-liquid mixing: a 2-zone model. *Polym. Eng. Sci.* **35** (22), 1766-80
- Ottino J M 1991 Unity and diversity in mixing: stretching, diffusion, breakup, and aggregation in chaotic flows. *Phys. Fluids A* **3** (5), 1417-30
- Scott C E, Macosko C W 1995 Morphology development during the initial stages of polymer-polymer blending. *Polymer* **36** (3), 461-70
- Stone H A 1994 Dynamics of drop deformation and breakup in viscous fluids. *Annu. Rev. Fluid Mech.* **26**, 65-102
- Taylor G I 1934 The formation of emulsions in definable fields of flow. *Proc. R. Soc. London* **A146**, 501-23
- Tjahjadi M, Ottino J M 1991 Stretching and breakup of droplets in chaotic flows. *J. Fluid Mech.* **232**, 191-219
- Tomotika S 1936 Breaking up of a drop of viscous liquid immersed in another viscous fluid which is extending at a uniform rate. *Proc. R. Soc. London* **A153**, 302-18

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