Transient phenomena in dispersive mixing

Citation for published version (APA):

Elemans, P. H. M., Bos, H. L., Janssen, J. M. H., & Meijer, H. E. H. (1993). Transient phenomena in dispersive mixing. *Chemical Engineering Science*, 48(2), 267-276. <https://doi.org/10.1016/0009-2509%2893%2980014-H>, [https://doi.org/10.1016/0009-2509\(93\)80014-H](https://doi.org/10.1016/0009-2509(93)80014-H)

DOI:

[10.1016/0009-2509%2893%2980014-H](https://doi.org/10.1016/0009-2509%2893%2980014-H)

[10.1016/0009-2509\(93\)80014-H](https://doi.org/10.1016/0009-2509(93)80014-H)

Document status and date:

Published: 01/01/1993

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
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TRANSIENT PHENOMENA IN DISPERSIVE MIXING

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ABSTRACT

The deformation and breakup processes of single droplets in well-defined fields of flow have been extensively studied in the literature. In spite of the fact that in real mixers the conditions are far from equilibrium, most studies are confined to (Newtonian) systems undergoing almost stationary deformation. The transient character of the dispersive mixing process is much less documented. In a Plexiglas-walled Couette-apparatus, the time-dependent deformation of Newtonian droplets into extended threads has been studied. When the shear rate is very slowly increased, allowing for almost equilibrium deformation, the results of the critical capillary number Ca_{crit} as a function of viscosity ratio, as reported in the literature, are reproduced. However, in transient flows at capillary numbers $Ca \gg Ca_{crit}$, droplets are deformed into long slender bodies which continue to extend, until the shear has stopped. They then disintegrate into lines of droplets because of interfacial tension-driven disturbances. The time scale for deformation and breakup is important for a better understanding of the dispersive mixing process, e.g., during polymer blending in screw extruders.

KEYWORDS

droplet breakup; liquid-liquid mixing; interfacial tension; dispersive mixing

INTRODUCTION

When a blend of two incompatible polymers is subjected to shearing forces, e.g., in a corotating twin-screw extruder, droplets of the dispersed phase will deform into long, threadlike particles, which can break up into smaller droplets (Grace, 1982; Elmendorp, 1986; Elemans, 1989). The ultimate morphology - the relative distribution of the constituents - depends on volume or weight fraction (Bohm *et al.*, 1977; Elemans *et al.*, 1987), viscosity ratio of both polymers and the type of flow (Grace, 1982). The word 'polymer', deliberately used in the former paragraph, in contrast with 'liquids' as mentioned in the title, suggests a similarity in the behaviour of systems used in emulsion rheology as well as in polymer rheology.

Therefore, we will review some of the literature on time-dependent deformation and breakup of (Newtonian) droplets. The emphasis will be on isolated particles in shear flow (coalescence of droplets will not be considered). An attempt will be made to transfer the results from model experiments to the processing conditions of a polymer blend in a screw extruder.

AFFINE DEFORMATION OF DROPLETS IN SIMPLE SHEAR FLOW

The deformation of droplets depends on the ratio of the shear stress $\tau = \eta_c \dot{\gamma}$ and the pressure due to the interfacial tension σ/R . This ratio is usually referred to as the capillary number Ca . For large capillary numbers ($Ca = \eta_c \dot{\gamma} R / \sigma$), and for viscosity ratios $p < 1$, droplets will deform affinely with the matrix. Their deformation can be expressed in terms of the total shear γ ($\gamma = \dot{\gamma} \cdot t$), imposed by the flow field (Starita, 1972). In simple shear flow, a spherical droplet having an initial diameter 'a' will deform into an ellipsoid with length L and width B :

$$L/a = \sqrt{(1 + \gamma^2/2 + (\gamma/2) \cdot \sqrt{(4 + \gamma^2)})} \quad (1)$$

$$B/a = (L/a)^{-0.5} \quad (2)$$

hence, by defining the deformation $D = (L - B)/(L + B)$,

$$D = \frac{(L/a)^{1.5} - 1}{(L/a)^{1.5} + 1} \quad (3)$$

Figure 1 shows these properties L/a , B/a and D as a function of γ .

Fig. 1. Relative length L/a , relative width B/a and deformation D of an affinely deformed droplet as a function of γ . The dashed line shows the influence of periodical reorientation on B/a .

Periodical reorientation of the already deformed droplet increases the efficiency of the mixing process drastically (Ng and Erwin, 1981). This is illustrated by the dashed line in Fig. 1, which shows the influence of reorientation on the decrease in width of a droplet in simple shear flow.

BREAKUP OF THREADS

Until now, the shear rate $\dot{\gamma}$ and the time t have been interchangeable. Once the droplet has become highly extended, it will exhibit initially small sinusoidal (so-called Rayleigh) distortions, each possessing a wavelength λ along the thread. Depending on the viscosity ratio $p = \eta_d/\eta_c$, one wavelength, λ_m , will turn out to be dominant and will cause breakup (Rayleigh, 1879; Tomotika, 1935; Elmendorp, 1986). For a Newtonian thread of infinite length in a fluid matrix which is at rest, the time for breakup, t_b , can be calculated using the theory of Tomotika (1935).

$$t_b = 1/q \ln (/(2/3) R_0/\alpha_0) \quad (4)$$

where

R_0	the initial thread radius	
α_0	the initial distortion amplitude	
q	the growth rate of the distortion	$q = q(R_0)$

The factor $(/(2/3)$ stems from the condition that breakup occurs when the amplitude is equal to the average thread radius (Elmendorp, 1986).

Fig. 2. Sinusoidal distortions on a polyamide-6 thread (diameter 55 μm) embedded in a PS matrix at 230 $^{\circ}\text{C}$ (Elemans *et al.*, 1990). The photographs were taken at: $t = 0, 15, 30, 45, 60$ s. Reprinted with permission of the Society of Rheology.

Predicting the stability of a thread in a matrix which is deforming is more difficult, since the wavelength λ is changing with time. For instance, at low deformations in shear flows the distortions are swept away, whereas at high deformations in elongational flows a potentially dominant wavelength will be extending so fast with the matrix (Tomotika, 1936; Kalb *et al.*, 1981; Elmendorp, 1986) that its effect will be damped out before having been able to cause breakup.

BREAKUP OF DROPLETS

Starting with the work of Taylor (1932, 1934), numerous studies have been devoted to the deformation and breakup of small droplets in a matrix undergoing simple shear flow or hyperbolic extensional flow. Good reviews of the relevant experimental and theoretical work reported in the literature can be found in the work of Rallison (1984) and Elmendorp (1986). Recommended as well is the almost 'classical' work on droplet breakup by Grace (1982), who used a Couette-type apparatus and a four-roll mill to generate simple shear flow and hyperbolic extensional flow, respectively.

More recently, Bentley *et al.* (1986a, 1986b) developed a computer-controlled four-roll mill. The continuous adjustment of the speed of each individual roller enabled them to position a droplet almost anywhere in the apparatus and to keep it there for a considerable period of time. Moreover, they succeeded in (approximately) generating a wide range of flows, characterized by a single parameter α , which is correlated to the ratio of deformation rate to vorticity (Giesekus, 1962). The conclusions of their experiments on steady droplet deformation and breakup are in general agreement with those of earlier authors.

Continuing Bentley's work, Stone *et al.* (1986) study transient effects in droplet breakup. By slowly increasing the shear rate, droplets are brought to a certain elongation ratio L/a . The flow is then stopped. Under the influence of interfacial tension, the droplets may return to their original shape or alternatively break up into several fragments. For a broad range of viscosity ratios p ($0.01 < p < 10$), the breakup mechanism via Rayleigh distortions is only observed for values of $L/a > 15$. For lower L/a values, ($6 < L/a < 15$), the droplets exhibit 'end-pinching', as shown in Fig. 3 (see Stone *et al.*, (1986) for experiments, and Stone and Leal (1988) for numerical calculations on this phenomenon). The ends of the droplet become spherical while the overall length decreases. The ends pinch off, and the newly formed fluid thread relaxes further, disintegrating (in general) more slowly, because of the larger thread radius. The time scale for end-pinching is thus shorter than that for the growth of Rayleigh distortions. A beautiful demonstration of end-pinching in a mixing apparatus is given by Tjahjadi and Ottino (1989).

Fig. 3. Relaxation and breakup of a molten high density polyethylene thread (diameter $20\ \mu\text{m}$) in a polystyrene matrix at $T = 200\ ^\circ\text{C}$. The photographs were taken at regular intervals and cover a range of 216 s. Reprinted with permission of the Society of Rheology.

EXPERIMENTAL

Breakup experiments with Newtonian systems were performed in a Plexiglas-walled Couette-type apparatus. The purpose of the experiments was twofold: (i) to investigate the behaviour of droplets during deformation and breakup under non-equilibrium conditions; (ii) to check the time-dependent deformation of droplets at low capillary numbers.

Although limited in direct practical applicability, these experiments give insight into the time scales involved in the deformation of droplets in real mixers, e.g., in the strongly varying flow field between the kneading flight and the barrel of a twin-screw extruder.

EXPERIMENTAL SETUP

A simple shear flow is generated in a Couette-type apparatus. It consists of two counterrotating concentric cylinders. The speed of both the inner and outer cylinder can be adjusted to keep a droplet at the same position in the gap while being deformed at a shear rate $\dot{\gamma}$, which for a Newtonian flow is given by (Trevelyan and Mason, 1951):

$$\dot{\gamma} = \frac{2 (R_1^2 \omega_1 + R_2^2 \omega_2)}{(R_2^2 - R_1^2)} \quad (5)$$

where $R_{1,2}$ the radius of the inner, resp. outer cylinder
 $\omega_{1,2}$ the angular velocity of the inner, resp. outer cylinder

In the present apparatus, $R_1 = 50$ mm, $R_2 = 63.2$ mm. The height of the gap is 120 mm, which is enough to avoid disturbance of the flow field due to the bottom. Shear rates up to 20 s^{-1} can be obtained. The deformation of a droplet can be studied from above by a microscope plus a video system, connected to a high-resolution monitor.

MODEL FLUIDS

Table 1 lists the characteristic properties of the Newtonian fluids used in the experiments. As continuous phase, silicon oil (Rhodorsil, Rhone-Poulenc) was used. As disperse phase, solutions of Corn Syrup (Globe 01138) in water were used. Viscosities at 23°C were determined on a Bohlin Vor dispersion rheometer. Newtonian behaviour was observed up to approximately $\dot{\gamma} = 10 \text{ s}^{-1}$. The interfacial tensions between the Corn Syrup (C.S.) solutions and the silicon oil was measured using a Du Nouy-ring tensiometer.

RESULTS

Experiments with model fluids in simple shear flow will be discussed first, each representing a stage of the dispersion process that occurs on a distinct time scale. Only the most important results will be presented here. Details can be found in reports by Bos (1988) and Janssen (1989).

Table 1. Viscosities of the Newtonian model fluids at 23 °C. In brackets is the interfacial tension between the Corn Syrup (C.S.) solutions and (any of) the silicon oils.

		$\eta_{23^\circ\text{C}}$	$\sigma \cdot 10^3$
		(Pa.s)	(N.m ⁻¹)
continuous phase	Rhod V 60000	63.3	
	Rhod V 30000	29.9	
	Rhod V 12500	12.5	
	Rhod V 5000	4.95	
	Rhod V 1000	1.04	
disperse phase (wt.% C.S./wt.% H ₂ O)	96/4	28.0	(40.0)
	95/5	16.25	(40.0)
	90/10	4.06	(41.4)
	85/15	1.13	(46.7)
	83/17	0.75	(47.0)

AFFINE DEFORMATION

A spherical droplet (typical diameter about 1 mm) is suddenly subjected to a supercritical simple shear flow, i.e. $Ca > Ca_{\text{crit}}$. Ca_{crit} is the capillary number for breakup under steady conditions. For $0.1 < p < 1$, $Ca_{\text{crit}} = 0.5$ (Grace, 1982). The length L or, at deformation $D > 0.8$, the width B , is measured from the monitor. The deformation, D , can be determined and compared with the theoretical prediction as given by Eq 3. Affine deformation occurs at $Ca/Ca_{\text{crit}} \geq 2$, see Fig. 4.

Fig. 4. Affine deformation at supercritical capillary number. Viscosity ratio $p = 0.135$. The drawn lines represent the deformation calculated from Eq 3.

BREAKUP OF THREADS IN SIMPLE SHEAR FLOW

A supercritical simple shear flow, with $Ca \gg Ca_{crit}$, is stepwise applied to a spherical droplet, which will deform affinely into a thread. At a certain moment, the thread will exhibit sinusoidal distortions which will cause breakup. The time for breakup, t_b , is defined as the elapsed time between the onset of the flow and the moment at which a line of separate droplets has been formed in the central region of the thread. Figure 5 compares the results concerning the dimensionless time for breakup with data from similar experiments by Grace (1982). Upon exceeding Ca/Ca_{crit} , the time for breakup does not decrease, as in Grace's experiments. Grace might have observed end-pinching, which indeed yields a much smaller value for t_b . This may explain the large difference shown in Fig. 5.

Fig. 5. The effect of exceeding Ca_{crit} on dimensionless burst time $t^* = t \cdot \sigma / (\eta_c \cdot R_0)$. Symbols indicate the value of the viscosity ratio p . Open symbols represent data from Grace (1982), whereas closed symbols refer to data from Elemans (1989). The dashed line represents $p = 1$.

CONCLUSION

In the case of Newtonian droplets in a Newtonian matrix, affine deformation occurs in simple shear flow at $Ca/Ca_{crit} \geq 2$. The time required for deformation can be calculated from Eq 1 (with $\gamma = \dot{\gamma} \cdot t$). Upon cessation of the flow, the time for breakup of highly extended droplets ($L/a > 15$) can be calculated using Tomotikas theory (Eq 4), see also Elemans *et al.* (1990). For moderately extended droplets ($6 < L/a < 15$), the numerical calculations of Stone and Leal (1988) apply.

If viscoelasticity is introduced, deformation and breakup of droplets is more complicated. Some scouting experiments with Boger fluids have been performed by Bos (1988). Results of a more systematic study can be found in the work by De Bruin (1989), giving an increased Ca_{crit} with increasing elasticity for almost all values of the viscosity ratio p .

APPENDIX

The following calculation may serve as an illustration how to use the results from the above sections. The problem concerns the dispersion of an isolated droplet in a single screw extruder. The extruder geometry and the flow field are represented as simple as possible.

Consider an extruder, with dimensions:

diameter	$D = 25 \text{ mm}$
flight clearance	$\delta = 0.25 \text{ mm}$
tip width	$b = 2 \text{ mm}$
length	$L/D = 5$
channel depth	$H = 2.5 \text{ mm}$
pitch angle	$\varphi = 20^\circ$
relative flight width e	$e = b/(\pi D \sin \varphi) \approx 0.075$

and further:

throughput	$Q = 50 \text{ g/min}$
screw speed	$N = 200 \text{ rpm}$
density	$\rho = 800 \text{ kg/m}^3$

It is assumed that the material makes one pass through the nip between screw flight (or barrier flight, as in Maddock-type of screw elements) and barrel wall. The material is then transported towards the die by the drag flow in the screw channel.

The shear rate over the flight is:

$$\dot{\gamma} \approx V/\delta = \pi DN/(60 \delta) \approx 1000 \text{ s}^{-1} \quad (6)$$

Polystyrene (PS), which has a viscosity $\eta_d = 100 \text{ Pa.s}$ at this shear rate, is dispersed in high-density polyethylene (HDPE) with corresponding viscosity $\eta_c = 150 \text{ Pa.s}$. Hence, the viscosity ratio $p = 0.7$. The interfacial tension is about 5 mN.m^{-1} , so for droplets having a radius $R_0 = 1 \text{ }\mu\text{m}$ the local capillary number Ca can be calculated:

$$Ca = (\eta_c \dot{\gamma} R)/\sigma = 30 \quad (7)$$

This capillary number exceeds Ca_{crit} , required for breakup, by a factor 60 ($Ca_{\text{crit}} = 0.5$, (Grace, 1982)). However, the residence time in the clearance is very short:

$$t = B/V \approx 0.015 \text{ s}. \quad (8)$$

This yields a dimensionless time t^* :

$$t^* = t \cdot (\sigma/\eta_c R_0) \approx 0.5 \quad (9)$$

which is too short for the droplet to break up (compare Fig. 5, where a dimensionless time $t^* \geq 9$ is required (at $p = 0.7$) for droplet breakup at $Ca/Ca_{\text{crit}} \approx 60$). Because of the large capillary number, the droplet will deform affinely into an extended thread. Its dimensions follow from the total shear over the flight: $\gamma = \dot{\gamma} \cdot t \approx 15$, hence the elongation ratio $L/2R_0 \approx 15$ (with Eq 1).

After passing through the nip, the droplet will be subjected to much lower shear stresses in the extruder channel. The shear rate becomes (Eq 6) $\dot{\gamma} = 100 \text{ s}^{-1}$, and the capillary number (with a matrix viscosity $\eta_c = 700 \text{ Pa.s}$) ≈ 14 , which is high enough to keep the droplet extended. In this case, the value $Ca/Ca_{\text{crit}} = 14/0.5 = 28$. The dimensionless time t^* for

breakup is about 100, see Fig. 5.

At a throughput $Q = 1.10^{-6} \text{ m}^3 \cdot \text{s}^{-1}$, the average residence time in the extruder amounts to

$$t = \pi DLH/Q \approx 24 \text{ s, hence } t^* \approx 170 \quad (10)$$

The time available is of the same order of magnitude as the time required, allowing for interfacial tension-driven disturbances to cause breakup.

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