Collision-Induced Dispersion of Agglomerate Suspensions in a Shear Flow

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ABSTRACT: Agglomerates suspended in a polymer fluid have been known to disperse in a flow through two mechanisms—rupture and erosion. Using silica agglomerates, it is shown here that a third mechanism can occur, i.e., detachment of fragments due to agglomerate collision. This mechanism requires a much lower overall stress than erosion (and rupture, which occurs at even larger stresses than erosion). The fragment concentration produced by collision at a given time is proportional to the square of the applied shear rate. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 78: 1130–1133, 2000

Key words: agglomerate; dispersion; collision flow

INTRODUCTION

The process of dispersing and distributing agglomerates by a flow is central to the preparation of aggregate-filled polymers. Two general mechanisms of dispersion have been recognized. The first one is the simple rupture of the agglomerate when the hydrodynamic stress acting on the agglomerate exceeds its cohesion stress.[1] The second mechanism is erosion, where aggregates are pulled from the agglomerate surface. This second mechanism is less understood, and occurs at a lower stress than rupture.[2]

The objective of this work is to show that collisions between flowing agglomerates can also induce dispersion. This will be shown directly by observing collisions of silica agglomerates in a counterrotating transparent rheometer. An extensive study of the dispersion mechanisms with the system under consideration (silica agglomerates in a polyisobutylene fluid) showed that neither rupture nor erosion are active in the conditions of flow that were used in this article.[3]

EXPERIMENTAL

The silica agglomerates that were used are produced by Rhône-Poulenc. They have diameters in the range 100–500 μm. They were suspended in a polyisobutylene fluid of 1000 Pa · s viscosity. The use of silica instead of carbon black allows us to work with concentrated suspensions because they are transparent enough to visible light.

Suspensions up to 5% concentration were observed by optical microscopy while subjected to a shear, in the range 1–8 s^{-1}. The counter rotating optical rheometer consists of two 40-mm glass plates rotating in opposite directions. Each plate is independently driven by a motor. The suspension is filled between the plates. After the gap is set, one particle is selected, and will be followed during the whole shear history. The relative rotation velocity of the two plates must then be chosen to keep the particle immobile in the reference frame of the laboratory (only particle being exactly at the midplane in the gap will be immo-

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bile if the absolute velocities of the two plates are equal). A fine tuning of the rotation velocity of one plate allows for small vertical position variations of the particle, that would otherwise slowly draw the particle out of the field of view.

The observations were made with a Wild Leitz optical microscope fitted in the optical rheometer. The images are captured by a video camera, and stored on high-quality video tapes equipped with a frame counter giving a maximum time resolution of one 25th of a second.

The observations are performed in a plane containing the vorticity axis and the flow direction. The incident light beam is sent along the vorticity axis.

Owing to the use of such a counterrotating system, it is possible to observe a single agglomerate while it is flowing and colliding with other agglomerates that are passing around it. Objects detached from the test agglomerate can be observed only when they are larger than a few micrometers and their diameter was accurately measurable above 10 μm.

To estimate the concentration of fragments produced by these collisions, the turbidity T of the suspended fluid was measured, taking care to choose areas in the fluid where there was no agglomerate. T is classically given by

$$T = k \log \frac{V_0}{V_m} \qquad (1)$$

with k a constant, V_0 the voltage measured by the photodiode with the polymer only, and V_m the voltage measured with the polymer filled with the fragments. The fragment concentration is proportional to T.

The size of the fragments can be measured using Transmission Electron Microscopy (TEM) on microtomed samples. This technique consists of freezing the suspension and cutting a thin film of less than one micrometer thickness. The film is then observed by TEM. The TEM pictures are scanned and analyzed using an image analysis system that gives the size of the fragments.

RESULTS AND DISCUSSION

Collision-Induced Production of Fragments

The first result is rather obvious. When particles are suspended in a fluid and subjected to flow, they may collide. This collision can be easily studied with the use of a counterrotating device. The collision frequency C, calculated by Smoluchowski,[4] increases with concentration as

$$C = \frac{32}{3} \dot{\gamma} R^3 n \qquad (2)$$

where $\dot{\gamma}$ is the applied shear rate, R the radius of the agglomerate, and n the number of particles per unit volume. C is increasing with concentration and shear rate.

Figure 1 illustrates the collision between two agglomerates occurring at a shear rate of 5 s^{-1}. Such observations were performed in rather diluted suspensions so that the collision mechanisms can be easily seen. The two agglomerates collide because their centers of mass are not at the same depth in the gap, which gives them a relative velocity. The interesting point is that the collision generated a fragment. In Figure 1, the sequence of events is from Picture 1 to 6. In Picture 1, the two agglomerates that will collide are the large elongated agglomerate on the left-hand side, and the small agglomerate on the middle of the picture. Both are moving because neither is precisely in the immobile layer defined by the relative velocities of the two counterrotating plates. They are moving in opposite directions, as shown by the two arrows, because they are not placed in the same position along the shear gradient. In the pictures, the flow direction is horizontal (as shown by the arrows), and the vorticity axis is vertical. Note that the elongated agglomerate is oriented along the vorticity axis, as often seen for suspensions in visco-elastic fluids.[5] Impact occurs at Picture 3. The two agglomerates continue to move apart as is illustrated by the arrows in Picture 5. The fragment rotates around the particle from which it was detached. The fragment can be seen in Picture 6. As can be seen in Pictures 3 and 4, a collision that produces the detachment of a fragment from an agglomerate always leaves a dark spot that slowly vanishes. The origin of this phenomenon is unclear (a local propagation of cracks that is strongly scattering light?). The size of the fragments produced varies from a few tens of microns for the largest to sizes much smaller than one micron. This can be seen by observing that the matrix fluid becomes darker and darker with time. By transmission electron microscopy observations, we see that these fragments were parts of agglomerates of size below 1 μm (Fig. 2). The concentration of these fragments will be reported in the next paragraph.

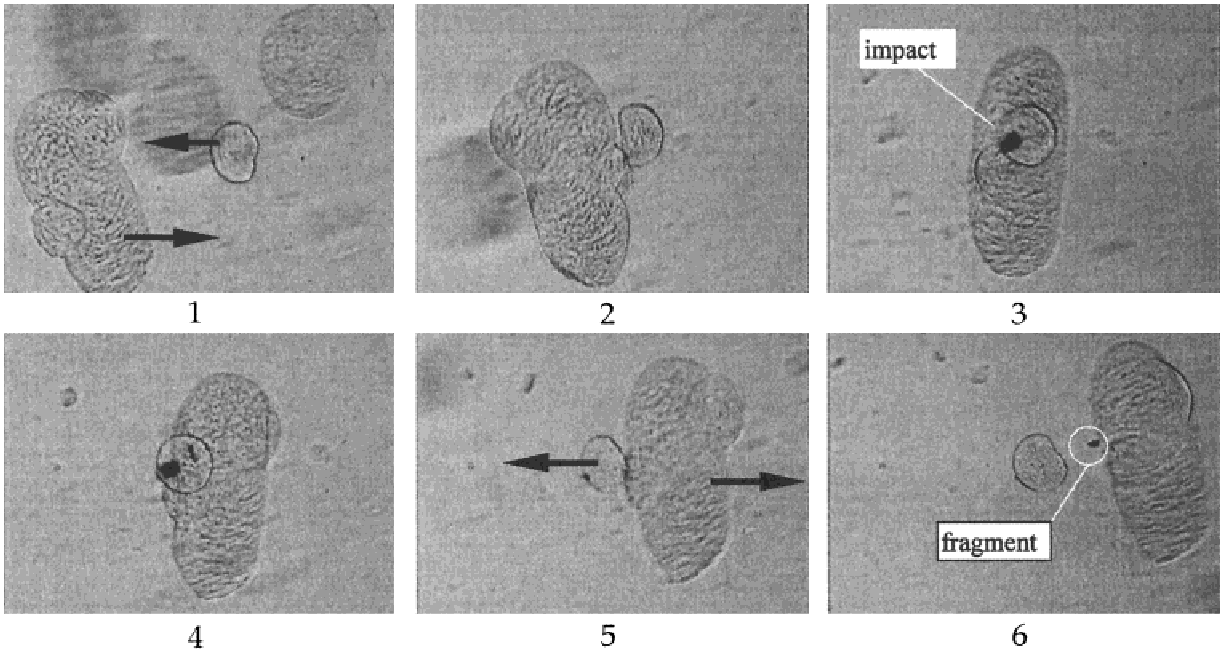

Figure 1 Collision between two silica agglomerates flowing in polyisobutylene. The shear rate is 5 s^{-1}.

Another interesting result is that, within the studied shear rate range, neither rupture nor erosion are occurring because the stress that is imposed on the agglomerate is much lower than the critical stress for rupture or erosion. This was carefully checked by observing that these mechanisms are not present on single agglomerates, and by measuring these stresses by destructive methods after flow in mixers.[3] This means that at shear stresses smaller than that required for erosion or rupture, there is nevertheless a dispersion mechanism that can be activated. This was not recognized before, as far as we are aware.

A sketch of what happens to the fragment after collision is shown in Figure 3. The detached fragment orbits around the agglomerate during a time t_s before leaving it. The time t_s is inversely proportional to the force tending to separate the two objects. It was shown by Tadmor[6] that the hydrodynamic forces acting to separate two spheres of radius R_1 and R_2 are proportional to the product R_1R_2:

$$F_h = -3\pi\eta\dot{\gamma}R_1R_2 \qquad (3)$$

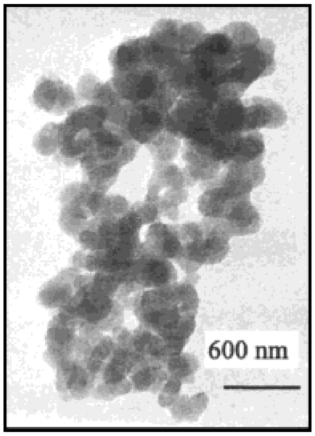

Figure 2 TEM observation of a fragment detached from an agglomerate.

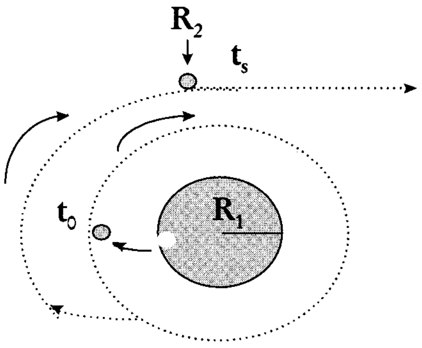

Figure 3 Schematic drawing of the relative motions of an agglomerate and a fragment detached by a collision.

with R_1 and R_2 being the radius of the two particles.

The larger the F_h, the quicker the two particles will be separated. Such a process is illustrated in Figure 4, where the time needed to separate the fragments from the agglomerate is shown to be inversely proportional to R_1R_2, for a series of radii of fragment and parent agglomerate.

Fragment Concentration

Using the turbidity measurements, it is possible to study how the concentration of fragments changes on varying the shear rate. Figure 5 gives the relative concentration of fragments produced by collisions as a function of the square of the shear rate, for a 30-min shearing of a 5% concentration suspension. The fragment concentration is linearly proportional to the square of the shear rate. This can be understood by considering that the fragment production is proportional to the collision frequency C and to the stress of the collision, E_c:

$$\text{concentration of fragments} \propto C \times E_c \qquad (4)$$

The collision frequency C is proportional to the shear rate and E_c is proportional to $\eta\dot{\gamma}$, so

$$\text{concentration of fragments} \propto \dot{\gamma}^2 \qquad (5)$$

Collision Stress

In principle, it could be possible to measure the stress that is required to produce a fragment. Knowing the size of the fragment, it should then be possible to evaluate the cohesion stress by estimating the kinematic energy. In reality, this is not an easy task, even if we know the kinematics and mass of the collision agglomerate. This is due to the fact that when agglomerates approach each other, a lot of energy is dissipated in the squeezing of the polymer film between the two agglomerates. In addition, energy is also dissipated during the propagation of the stress in the agglomerates. Neglecting these two effects, a (very) approximate upper bound for the collision stress for the studied silica is 40 kPa. This is about 30 times smaller than the stress necessary to break into two parts the same agglomerate.[3]

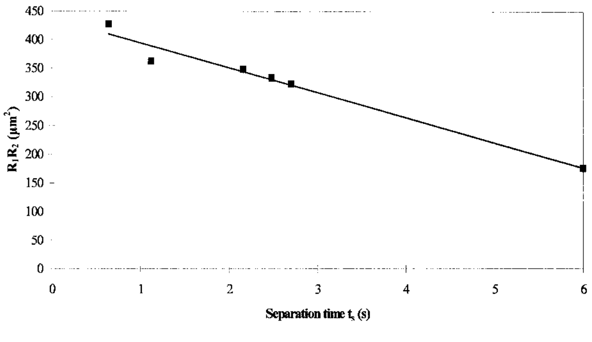

Figure 4 Product of the fragment and agglomerate radius vs. separation time t_s for a series of six experiments at a shear rate of 1 s^{-1}.

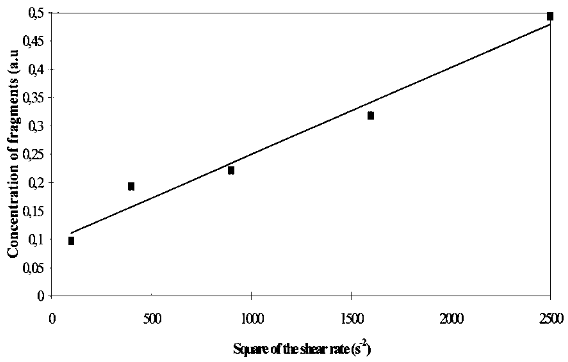

Figure 5 Concentration of fragments in arbitrary units as a function of the shear rate, after a shear of 30 min.

CONCLUSION

Collisions between agglomerates are shown to be an effective way to disperse concentrated suspensions. We showed that this occurs at a relatively low stress, and that the concentration of fragments scales with the square of the shear rate.

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