INTRODUCTION

Dispersive mixing of particulate clusters into liquids is an important step in a variety of materials and chemical processing applications. In dispersive mixing, mechanical forces, typically applied through hydrodynamic shear, are used to break the clusters into smaller size units or even down to the individual particle size. An understanding of the fundamental physical and chemical factors that govern hydrodynamic dispersion can lead to process optimization and ultimately better performance of the materials in which the particles are dispersed. It is common, however, that agglomerates encountered in practice exhibit a range of physical characteristics, even though they may be prepared under very controlled manufacturing conditions. Such variability makes determination and prediction of processing behavior difficult. In this paper, we describe characterization techniques that can provide information on the modes and kinetics of hydrodynamic dispersion of particle clusters, and how these dispersion characteristics are linked to processing history, even when the agglomerates being studied exhibit non-uniform properties.

In experimental studies of the dispersion of agglomerates of carbon black [1], two distinct breakup mechanisms were observed. One was denoted as “rupture” in which an abrupt fragmentation of the cluster into a small number of relatively large pieces takes place. The second breakup mode, termed “erosion,” is characterized by the continuous detachment of small fragments from the outer surface of the agglomerate. The erosion process typically initiates at a lower applied shear stress than does rupture.

Abstract

The processing characteristics of agglomerates of silica aerogel particles (surface treated to possess either hydrophilic or hydrophobic nature) have been examined. Although these agglomerates were purported to be highly uniform in terms of internal structure, fluid infiltration studies performed via direct visualization revealed significant heterogeneities. Dispersion studies performed under both steady and time-varying flow conditions, revealed additional non-uniformities among the population of agglomerates. Despite these difficulties, discernable trends linked to the duration of time the agglomerates were allowed to soak in the processing medium prior to the application of the shear flows were discovered. Additional experiments, in which the agglomerates were presoaked with a different, low viscosity fluid prior to shearing, revealed that dispersion could be promoted through this processing strategy. The experimental approaches and analyses presented in this study should be of interest to particle technologists faced with understanding and characterizing dispersion phenomena when the agglomerates being dispersed exhibit significant variability in properties.

Key words: Silica aerogels, agglomerates, dispersion, infiltration, wetting behavior
Boyer and Colwell [2] first proposed that dispersion occurs whenever hydrodynamic drag forces acting on the surface of the particle cluster induce internal stresses exceeding the cohesivity of the cluster. Therefore, the dispersion properties are affected by the cluster cohesivity and the geometry and intensity of the flow field.

Cluster cohesivity is related to both the strength of the interparticle forces between its constituent particles and the structural details of the particle packing within the cluster [3]. Since particle clusters are porous, capillary-pressure driven infiltration of liquid into the cluster can occur upon immersion of the cluster into the processing media. This infiltration may cause some rearrangement of the packing structure as well as alter the cohesive forces acting within the cluster. Additionally, the presence of fluid within the cluster can modify the manner in which hydrodynamic stress is transmitted from the external fluid to the cluster. Thus, knowledge of the extent of infiltration of the fluid medium, which is directly linked to the processing history, is an important factor in understanding the outcome of dispersion attempts.

The geometry and dynamics of the applied flow field is also expected to influence the dispersion kinetics of clusters. Many of the previous experimental studies on dispersion were performed under steady shear flow conditions. Dispersion in non-steady flows is more representative of the complex shear history experience by particle clusters in practical processing equipment [4].

In this study, we examine the synergies between fluid infiltration and flow conditions as they influence the dispersion of particle clusters. Specifically, we report on experiments to analyze the dispersion behavior of clusters of silica aerogels sheared within polydimethylsiloxane (PDMS) fluids. These particles were selected to represent a typical, non-ideal situation encountered in practice, namely one in which agglomerates with non-uniform structure and significant agglomerate-to-agglomerate variability are used. Still, we are able to discern trends in the dispersion results that can be interpreted in the context of fundamental chemical and physical concepts.

Different surface treatments applied to the aerogel particles, which modify the magnitude of the capillary pressure driving infiltration, enable some degree of control over the extent of fluid infiltration. In addition to using steady shear for dispersion, we report on experiments performed under oscillatory shear-flow conditions. Both the mode of dispersion and dispersion kinetics are reported, and these results can be linked to the extent of infiltration of the processing fluid.

**EXPERIMENTAL**

**Materials**

Two types of non-commercial silica aerogel particles, provided in the form of clusters by the Cabot Corporation, were used in this study. These clusters, carefully prepared using standard forming techniques, were nominally of high uniformity, both in terms of packing structure within an individual agglomerate, and in terms of consistency between different agglomerates. One type (grade P346) is reported by the manufacturer to be treated (in an unspecified manner) to make the agglomerate hydrophilic while the other (grade P597) was treated to result in a hydrophobic surface. Each cluster ranged from 1 to 2 mm in diameter and was composed of individual particles in the 10–100 µm range. The BET surface area was ~700 m²/g, which indicates a high degree of fine structure within these aerogels. Information on the composition and structure of the clusters is not available, and clusters were tested as received.

PDMS fluids of varying viscosities were used in the infiltration and shearing experiments. In the steady shear experiments, both 10 and 30 Pa·s PDMS were found to be effective in inducing dispersion. For the range of shear rates examined in the oscillatory shear experiments, the use of 60, 100, and 600 Pa·s PDMS fluids were necessary to cause dispersion. Before being used in the shearing experiments, fluids were placed under vacuum to aid the removal of entrapped air bubbles. In the range of shear rates employed in the experiments, these fluids exhibit Newtonian rheological behavior.

**Dispersion Experiments in Steady Shear Flow**

Figure 1 shows a schematic diagram of the cone-and-plate shearing device used for the steady shear experiments. The set-up procedure involved removing the transparent plate from the instrument and filling it with PDMS. A single agglomerate was submerged into the polymer and positioned within the plate. The plate was raised up under the cone, and the fluid slowly surrounded the cone. The motor was set to a particular speed \( \dot{N} \) (in rotations per minute) and turned on to start the application of shear. The time between submersion of the agglomerate and application of shear is called the presoaking time; the polymer infiltrated into the agglomerate during this time.

The steady shear rate \( \dot{\gamma}_{steady} \) that the agglomerate
experiences is related to the angular velocity of the cone $\Omega$ and the cone angle $\Psi_o$ according to the following equation:

$$\dot{\gamma}_{\text{steady}} = \frac{\Omega}{\Psi_o}$$  \hspace{1cm} (1)

Since the fluid exhibits Newtonian behavior in the range of shear rates used here, the nominal shear stress can be computed from the shear rate and viscosity:

$$\tau_{\text{steady}} = \mu \dot{\gamma}_{\text{steady}}$$  \hspace{1cm} (2)

The results of dispersion experiments were recorded with a video camera connected to a computer. The agglomerate moves with the flow and passes through the focal point of the camera once per orbit. Scion image software was used to measure the average radius of the agglomerate as a function of shearing time.

**Dispersion Experiments in a Non-Steady Shear Flow**

Dispersion experiments were also performed in an oscillatory shear flow device (OSD) illustrated in Figure 2. In preparation for an experiment, the transparent lower container was removed from the instrument and filled with PDMS. Then the agglomerate was submerged into the polymer and positioned laterally. The container was raised up under the oscillating plate, and the fluid surrounded the plate. The motor was set to a particular speed $N$ (in rotations per minute) and turned on to start the application of shear. The transmission mechanism results in the rotational motion of the motor being converted to an oscillatory motion of the moving plate. The maximum shear rate $\dot{\gamma}_o$ over one cycle of oscillation is related to the position of the transmission linkage on the motor ($A$), motor rotation rate $N$, and gap between plates $G$ according to the following equation:

$$\dot{\gamma}_o = \frac{2\pi A N}{G}$$  \hspace{1cm} (3)

From this equation the mean shear stress over a cycle $\dot{\gamma}_{\text{mean}}$ can be calculated:

$$\dot{\gamma}_{\text{mean}} = \frac{2}{\pi} \dot{\gamma}_o$$  \hspace{1cm} (4)

For the experiments reported here, we used $A=10$ mm, $G=4.83$ mm, and $N$ ranging from 100 to 1500 s$^{-1}$.

As in the steady shear experiments, the process of dispersion was viewed directly through the transparent plate and recorded with a VCR. Using the OSD, the entire dispersion process can be viewed continuously, unlike in the cone-and-plate device where the...
agglomerate only enters the field of view of the camera once per rotation.

Preparation Procedures for the Clusters of Hydrophilic Silica

Humidity present in the ambient air could alter the hydrophilic agglomerates and affect their dispersion behavior. Therefore, precautions were taken to ensure that these agglomerates were not exposed to air before they were used in infiltration and shearing experiments. The container of silica and a dish of PDMS were placed in a glove bag flushed with dry nitrogen. In this environment, the container of agglomerates was opened, and a single cluster was selected and submerged in the PDMS. Subsequently, this dish was removed from the glove bag and placed in the cone-and-plate (steady shear) device or oscillatory device.

Infiltration Experiments

As mentioned, infiltration of the polymeric fluid into the agglomerate has a large effect on its dispersion properties. Therefore, a study of infiltration can help explain dispersion properties. Furthermore, an infiltration study can be used to probe agglomerate structure since the most porous regions of an agglomerate tend to become infiltrated first.

Since the silica agglomerates and the PDMS fluids have nearly identical indices of refraction, direct visualization of infiltration is possible. A transparent container was filled with 10 Pa·s PDMS. The agglomerate was removed from the sample container and submerged in the fluid. A video camera was used to view and record the agglomerate through the wall of the container. The camera and VCR were attached to a computer, where periodic images of the agglomerate were captured and analyzed. The infiltrated portion of the agglomerate was assumed to be that which became transparent, while the dry portions remained opaque. The extent of infiltration was quantified by measuring the apparent area of the infiltrated region using the Scion Image software.

RESULTS AND DISCUSSION

Infiltration Study

Hydrophobic Silica Agglomerates

The extent of infiltration as a function of time is shown in Figure 3a for a representative set of eight different clusters. The extent of infiltration is reported as the fraction of the cross-sectional area of the cluster apparently occupied by infiltrated fluid. As shown, there is a large amount of scatter among the various agglomerates, even though they had ostensibly identical structures. The time for complete infiltration ranged from 15 min to approximately 1 hr. No strong correlation between cluster diameter and infiltration rate was observed. Figure 3b shows images of some
agglomerates as they were being infiltrated. In most cases, the infiltration did not occur uniformly from the outside surface to the inner core. For many agglomerates, fluid was observed to reach the center of the agglomerate long before the periphery was fully infiltrated. The infiltration patterns suggest a large degree of non-homogeneity in the structure of these clusters.

**Hydrophilic Silica Agglomerates**

The extent of infiltration as a function of time is shown in Figure 4a for representative sample of seven hydrophilic clusters. As with the hydrophobic agglomerates, there is a large amount of scatter among the samples. The total infiltration time ranged from 3 hr to several days. Figure 4b shows images of some agglomerates as they were being infiltrated. Unlike the hydrophobic agglomerates, these samples tended to infiltrate uniformly from the outer surface inward. This suggests a more homogeneous structure for the hydrophilic agglomerates by comparison with the hydrophobic ones.

Despite the large scatter in the observed infiltration behavior, some trends can still be discerned. For example, Figure 5 shows a comparison of the median and extreme infiltration rates observed for the hydrophobic and hydrophilic agglomerates. In all cases, the infiltration of PDMS into the hydrophilic agglomerates was much slower than that of hydrophobic agglomerates. This can be attributed to a combination of the higher packing density in the hydrophilic agglomerates which was revealed in the infiltration studies, plus the expected strong interaction expected between the hydrophobic agglomerates and the PDMS.

**Fig. 4a** Extent of infiltration as a function of time for the hydrophilic agglomerates. The diameter \( d \) of each agglomerate is indicated in the legend.

**Fig. 4b** View of the hydrophilic agglomerates as they become infiltrated. The time in seconds and minutes is indicated.

**Fig. 5** Comparison of observed infiltration rates among the two types of agglomerates studied.
Dispersion of Hydrophobic Silica Agglomerates

Steady Shear

Table 1 presents a statistical summary for the results of steady shear experiments for the dispersion of the hydrophobic aerogels. The agglomerates were allowed to presoak for various periods of time before shear was applied, and shear stresses necessary to initiate a dispersion event were observed. Shown are the relative frequencies of rupture, erosion, and “no dispersion” events observed at the various applied shear strengths. Although shear conditions were carefully controlled, the agglomerates show a range of dispersion behavior. Generally, rupture was more likely to occur at higher shear stresses, but there was no clearly identifiable threshold value above which rupture would occur. Extended infiltration tended to suppress dispersion, most likely due to reinforcement of powder through the formation of liquid bridges.

The erosion mechanism was rarely observed for the hydrophobic agglomerates. For those cases in which erosion did occur, a large variation in erosion rates was observed. Furthermore, there was no apparent correlation between the presoaking time and the observed dispersion kinetics.

Oscillatory Shear

Table 2 provides a statistical summary of the results of the oscillatory shear experiments for hydrophobic silica. Erosion was not observed in any case. Rupture was less likely to occur after a long pre-soaking time, suggesting that extended infiltration enhances agglomerate cohesivity. For experiments with a 1.5-minute presoak, 500 Pa appeared to be the threshold stress above which dispersion will occur. For longer infiltration times, no definite trends were observed.

Dispersion of Hydrophilic Silica Agglomerates

Steady Shear

Thirteen experiments were carried out in the cone-and-plate device using the hydrophilic agglomerates. Rupture was observed only once, and erosion was never observed. Even at shear stresses as high as 4500 Pa, no dispersion occurred. In the case of the hydrophobic agglomerates, dispersion occurred at stresses between 450–600 Pa. This indicates that the hydrophilic agglomerates are more cohesive than the hydrophobic agglomerates in PDMS fluids.

Because of experimental limitations, the presoaking time for these experiments was around four minutes. However, the extent of infiltration of 30,000-cSt PDMS in four minutes is not significant and is most likely not the reason for the resistance to erosion.

Oscillatory Shear

Table 3 summarizes the results of the oscillatory shear experiments for the hydrophilic aerogels. Erosion was not observed in any case. Rupture was more likely to occur after shorter presoaking times, again suggesting that infiltration impedes dispersion by

Table 1  Summary of the results of steady shear experiments with hydrophobic agglomerates. The relative frequency of the three possible dispersion outcomes are shown as a function of presoak time. Also shown are the ranges of shear stress used to achieve the dispersion events.

| Presoak Time | No Dispersion | Erosion | Rupture |
|--------------|---------------|---------|---------|
| 3–5 min      | 6 agglomerates | 3 agglomerates | 4 agglomerates |
|              | 100–600 Pa     | 600 Pa   | 450–600 Pa |
| 10 min       | 2 agglomerates | 2 agglomerates | 3 agglomerates |
|              | 600, 1000 Pa   | 1100 Pa  | 1000–1100 Pa |
| 15 min       | 9 agglomerates | 2 agglomerates | 4 agglomerates |
|              | 450–1200 Pa    | 800 Pa   | 450–800 Pa |

Table 2  Summary of the results of oscillatory shear experiments with hydrophobic agglomerates. The erosion mode of dispersion was never observed.

| Presoak Time | No Dispersion | Rupture |
|--------------|---------------|---------|
| 1.5 min      | 5 agglomerates | 15 agglomerates |
|              | ≤ 500 Pa      | ≥ 500 Pa |
| 2.0–2.5 min  | 5 agglomerates | 18 agglomerates |
|              | ≤ 4300 Pa     | ≥ 415 Pa |
| 3.0–6.0 min  | 5 agglomerates | 11 agglomerates |
|              | ≤ 4400 Pa     | ≥ 1725 Pa |

Table 3  Summary of the results of oscillatory shear experiments with hydrophilic agglomerates. The erosion mode of dispersion was never observed.

| Presoak Time | No Dispersion | Rupture |
|--------------|---------------|---------|
| 1.5–1.75 min | 4 agglomerates | 2 agglomerates |
|              | ≤ 3500 Pa     | ≥ 2600 Pa |
| 2.0–2.5 min  | 9 agglomerates | 5 agglomerates |
|              | ≤ 3800 Pa     | ≥ 2500 Pa |
| 3.0–6.0 min  | 11 agglomerates | 4 agglomerates |
|              | ≤ 7600 Pa     | 3150 Pa |
increasing cohesivity. Stresses of 2500 Pa or higher were required for rupture to occur, whereas only 500 to 2000 Pa was required in the case of the hydrophobic samples.

**Dispersion of Fully Infiltrated Agglomerates**

As is sometimes done in practice, low viscosity fluids can be used to impregnate agglomerates prior to dispersing them in high viscosity media. Presumably, the soaking of the agglomerates with the low viscosity fluids can result in a lower overall agglomerate cohesivity or provide additional compatibility with the intended dispersion media. To study the effect of saturating agglomerates with liquids on its dispersion behavior, we carried out additional experiments in the oscillatory shear device. Relatively low viscosity fluids were used to presoak the agglomerates prior to the application of shear. Hydrophobic agglomerates were soaked in hexane for 15 s (enough for complete infiltration) and then tested at different stress levels in PDMS. Hydrophilic agglomerates were soaked in water or glycerin for 5 min (enough for complete infiltration) and then tested in the same way. After soaking, the excess water was removed from around the hydrophilic agglomerates in one of two different ways: (1) by placing the agglomerate on a towel; or (2) by carefully removing the water with an eyedropper. More water remained in the hydrophilic agglomerates when the excess was removed with an eyedropper instead of a towel.

Table 4 displays a summary of the results of these experiments. Dispersion of soaked agglomerates contrast the previous results reported. For both the hydrophobic and hydrophilic agglomerates, complete fluid saturation seems to promote dispersion at lower shear stresses. These results are consistent with expectations.

**CONCLUSIONS**

Experimental observations in the infiltration and dispersion studies indicate a large degree of non-homogeneity for the agglomerates as received from the manufacturer. However, despite of this complication, useful observations regarding general trends of infiltration/dispersion behavior for these agglomerates could be made.

In the case of hydrophobic agglomerates, the infiltration patterns suggest a very non-uniform structure for the agglomerates. Such non-uniformity may be responsible for initiating rupture at the locus of weak, less dense spots in the cluster. Partial infiltration of these agglomerates seemed to suppress dispersion, most likely due to reinforcement of powder through the formation of liquid bridges.

In the case of hydrophilic agglomerates, infiltration studies suggest more dense and homogeneous agglomerates, which resist dispersion to a larger extent than their hydrophobic counterparts. Also, partial infiltration of these agglomerates seems to impede dispersion by increasing cluster cohesivity.

In contrast with the results obtained with partially infiltrated agglomerates, complete saturation of the agglomerates using low viscosity fluids that interact favorably with the constituent solids seems to reduce overall agglomerate cohesivity, thereby enhancing dispersion.

The experimental approaches outlined in this pa-

| Type of Agglomerates | Procedure | Lowest stress at which rupture occurred (Pa) | Highest stress at which no dispersion occurred (Pa) | Presoak time in PDMS prior to shear (min) | Number of tests run | Range of stresses tested (Pa) |
|----------------------|-----------|---------------------------------------------|---------------------------------------------------|------------------------------------------|-------------------|-----------------------------|
| Hydrophobic          | dry       | 414                                         | 4306                                              | 1–3                                      | 55                | 331–16500                   |
| Hydrophobic soaked in hexane for 15 s; excess hexane removed with eyedropper | 15 | 773 | 1.5–2 | 35 | 1–911 |
| Hydrophilic          | dry       | 2526                                        | 5963                                              | 1–6                                      | 35                | 1077–22360                  |
| Hydrophilic soaked in water for 5 min; excess water removed with towel | 1408 | 3975 | 2 | 19 | 538–6874 |
| Hydrophilic soaked in water for 5 min; excess water removed with towel | 311 | 828 | 2 | 28 | 75–2551 |
| Hydrophilic soaked in glycerin for 5 min; excess glycerin removed with eyedropper | 331 | 795 | 2 | 7 | 124–1284 |
provide a means of characterizing the behavior of particle agglomerates, even though there may be experimental difficulties associated with non-uniform agglomerate structures.

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NOMENCLATURE

$A$ amplitude of oscillation (m)

$G$ gap between parallel plates in the oscillating shear device

$N$ rotation speed of the motor (rotations/min)

Greek

$\gamma_{o}$ maximum shear rate over one cycle in the oscillating flow experiments (s$^{-1}$)

$\gamma_{steady}$ shear rate in the steady-flow experiments (s$^{-1}$)

$\gamma_{mean}$ mean shear rate over one cycle in the oscillating flow experiments (s$^{-1}$)

$\Omega$ rotation rate of the cone (s$^{-1}$)

$\Psi_{o}$ cone angle (radians)

$\mu$ fluid viscosity (Pa)

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