

RESPONSIVE BINDERS FOR CONTROLLING DISPERSION BEHAVIOR OF FINE- PARTICLE CLUSTERS

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Introduction

Agglomerates of fine particles are frequently encountered in a wide range of important chemical, biotechnical, medical and materials processing applications including pharmaceutical, polymer, mining, and food technologies. Often, the processing goal is the dispersion of the agglomerate into smaller clusters (or if possible, into its constituent particles) and distribution of these finely divided units throughout the suspending medium. In other industries, the processing of powders aims to achieve an opposite goal, namely the consolidation of particles into agglomerates or the compaction of existing agglomerates into denser units. The same set of fundamental forces that govern dispersion processes also control granulation processes. Hydrodynamic dispersion occurs when the cohesive forces that hold the particle assemblies together are overcome by fluid stresses that act to pull the agglomerate apart. Traditionally, dispersion has been controlled and enhanced by optimizing the factors that directly affect this counterbalance of forces [1-6].

This study focuses on a new approach to control particle processing behavior through manipulation of parameters which are not directly associated with the solid or dispersing fluid properties. This is achieved with the use of chemical additives that respond to external stimuli. By incorporating such additives within agglomerates, it is possible to adjust the degree of interparticle interaction by changing the variable to which the additive is responsive. In particular, this study involves the use of silica agglomerates incorporating Poly(N-Isopropyl Acrylamide), PNIPAM, a thermo-responsive polymer. PNIPAM shows a lower critical solution temperature (LCST) in aqueous solution at about 32°C. Below this temperature the polymer is soluble in water and hydrophilic interactions dominate. Above the LCST the polymer chains collapse and hydrophobic interactions become important. This study is aimed at evaluating whether changes in processing temperature lead to physical re-conformation of the PNIPAM chains, which alters the cohesion of the agglomerates and therefore, the mode and/or kinetics of the dispersion process.

Experimental

Experiments were conducted in a rotating cone-and-plate device [7]. PNIPAM-treated and untreated silica agglomerates, suspended in a processing fluid, were subjected to a constant shear stress. The dispersion kinetics of silica agglomerates was quantified by monitoring the fractional reduction in size of the parent agglomerate ($1-R(t)/R(0)$) with time, with $R(t)$ being the radius at time t of the residual parent agglomerate and $R(0)$ its initial size. Dispersion of hydrophobic and hydrophilic silica powders was evaluated at room and higher temperatures to capture the effect of the binder transition. In addition, the effects of the agglomerate packing density, water content, and PNIPAM concentration on dispersion behavior were tested.

Results

Effect of powder surface chemistry- Tests were conducted at a shear stress of 1050 Pa. Results of dispersion experiments performed on hydrophilic and hydrophobic agglomerates are shown in Figures 1a and b. While the hydrophilic agglomerates show no significant difference in the dispersion extent at both temperatures tested (Figure 1a), the temperature-sensitivity of the dispersion kinetics are more pronounced for the hydrophobic agglomerates (Figure 1b). The independence of dispersion on the processing temperature for the hydrophilic silica can be attributed to the strong hydrogen bonding between the hydroxyl groups of the particle surface and the PNIPAM carbonyl groups, which is expected to inhibit the thermal transition of the binder. Due to the surface treatment of the hydrophobic silica, its ability to hydrogen bond with PNIPAM is significantly reduced. This enables the binder transition to its hydrophobic configuration, which is manifested as a temperature sensitivity of the cohesivity of the agglomerate and its dispersion behavior. Dispersion of both types of silica agglomerates occurred by an erosion mechanism, involving detachment of small fragments from the outer surface of the agglomerate.

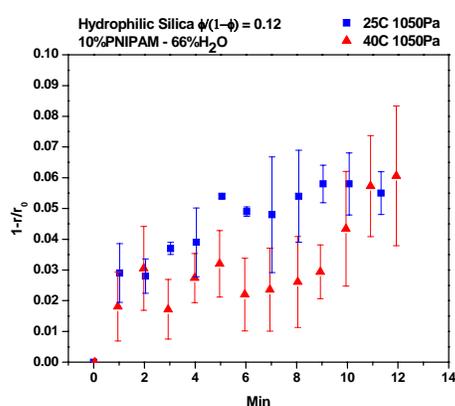


Figure 1a: Dispersion kinetics for agglomerates prepared with hydrophilic silica powder with 10 % PNIPAM and 66% H_2O at a reduced solid volume fraction of 0.12. The shear stress applied was 1050 Pa using PDMS of 10 Pa·sec. Changes in temperature do not lead to significantly different dispersion behavior.

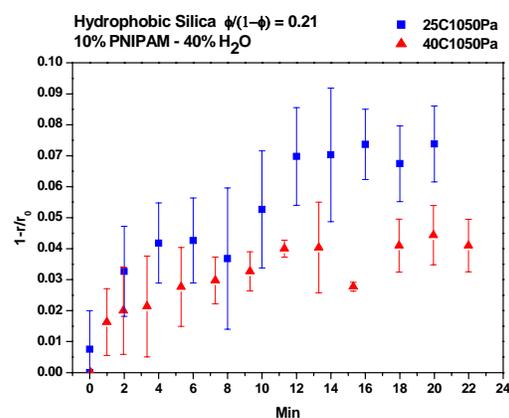


Figure 1b: Dispersion kinetics for agglomerates prepared with hydrophobic silica powder with 10% PNIPAM and 40% H_2O at a reduced solid volume fraction of 0.21. The shear stress applied was 1050 Pa using PDMS of 10 Pa·sec. Slower erosion is observed at 40°C.

Effect of powder surface treatment - Surface treatments with different PNIPAM and water contents were analyzed for the hydrophobic silica powder at a shear stress of 2100 Pa and a solid volume fraction of 0.29 (Figure 2a, b and c). Agglomerates made from hydrophobic silica powder treated with 10% PNIPAM and 40% H_2O show differences in erosion kinetics, whereas agglomerates prepared from powder treated with 20% PNIPAM and 50% H_2O show changes in the dispersion mechanism. No temperature sensitivity was observed for the powder with 20% PNIPAM and 130% H_2O . The results obtained for silica powders modified with 10% PNIPAM (Figure 2a) indicate a reduction in the erosion extent at 68°C, which can be explained in terms of an enhancement in the cohesivity of the agglomerate due to the strong PNIPAM-silica interactions at temperatures above the PNIPAM transition (both silica and PNIPAM have a hydrophobic nature). At room temperature the agglomerates show a significantly higher dispersibility as evidenced by the faster dispersion kinetics.

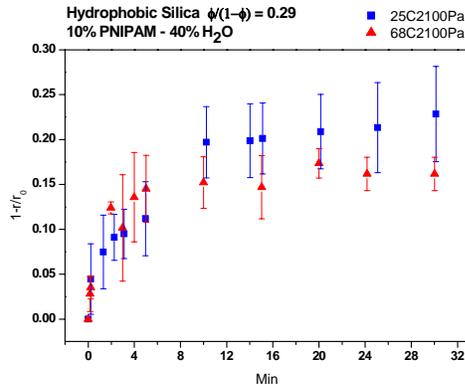


Figure 2a: Dispersion kinetics for agglomerates prepared with hydrophobic silica powder with 10% PNIPAM and 40% H₂O at a reduced solid volume fraction of 0.29. The shear stress applied was 2100 Pa using PDMS of 30 and 60 Pa-sec for the 25°C and 68°C test respectively. Slower erosion is observed at 68°C.

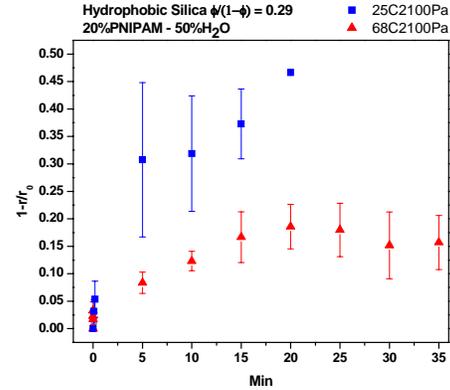


Figure 2b: Dispersion kinetics for agglomerates prepared with hydrophobic silica powder with 20% PNIPAM and 50% H₂O at a reduced solid volume fraction of 0.29. The shear stress applied was 2100 Pa using PDMS of 30 and 60 Pa-sec for the 25°C and 68°C test respectively. Changes in the dispersion mechanism are observed at room and high temperature: dispersion takes place through erosion at 68°C and through rupture at 25°C.

On the other hand, the results obtained in dispersion experiments using powders treated with 20% PNIPAM and 50% H₂O (Figure 2b) show a change in the dispersion mechanism [7] upon changing the temperature. At 68°C, dispersion occurs by erosion, involving detachment of small fragments from the outer surface of the agglomerate while at 25°C dispersion occurs by a rupture mechanism, which is characterized by breakage of the parent agglomerate into few large fragments. When rupture occurs, it is mainly caused by the presence of flaws in the agglomerate. Fragments produced by rupture can continue to disperse by either erosion or rupture. However, when the water concentration is increased to 130%, no evidence of temperature sensitivity was seen (Figure 2c). In this case, the presence of liquid

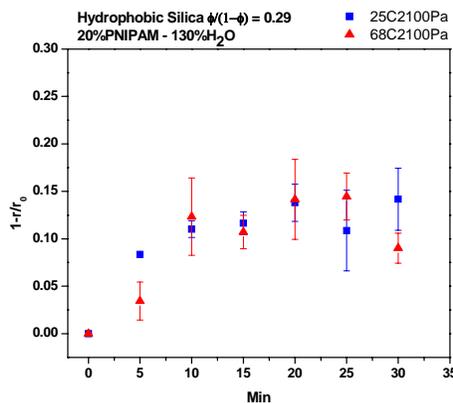


Figure 2c: Dispersion kinetics for agglomerates prepared with hydrophobic silica powder with 20% PNIPAM and 130% H₂O at a reduced solid volume fraction of 0.29. The shear stress applied was 2100 Pa using PDMS of 30 and 60 Pa-sec for the 25°C and 68°C test respectively. Changes in the dispersion mechanism are not observed due to saturation of the agglomerate, at both temperatures dispersions occurs by slow erosion.

bridges can result in an agglomerate with much higher cohesivity, one for which the binder transition has relatively minimal effect.

Effect of agglomerate porosity - The agglomerate solid volume fraction (Φ) has also an important effect on the agglomerate dispersibility. Results obtained for agglomerates prepared with hydrophobic silica powder with 20% PNIPAM and 130% H₂O at a lower reduced solid volume fraction of 0.21 (Figure 3b), indicate not only an increase in the dispersion extent (in comparison with the results shown in Figure 2c), but additional differences in the dispersion at high and room temperature. Similar results were obtained in dispersion experiments using agglomerates prepared from the powder treated with 20% PNIPAM and 80% H₂O (Figure 3a). In this case, due to a reduced amount of water (and lower likelihood for the formation of liquid bridges) there is no need to decrease the reduced solid volume fraction to very low levels; a solid volume fraction of 0.24 will allow the manifestation of different dispersion behavior at different temperatures.

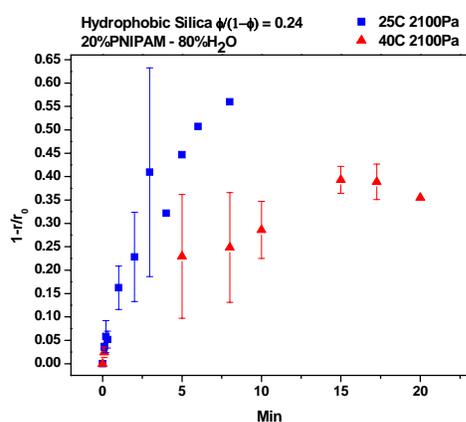


Figure 3a: Dispersion kinetics for agglomerates prepared with hydrophobic silica powder with 20% PNIPAM and 80% H₂O at a reduced solid volume fraction of 0.24. The shear stress applied was 2100 Pa using PDMS of 30 and 60 Pa-sec for the 25°C and 68°C test respectively. Changes in the dispersion mechanism are observed at room and high temperature: dispersion takes place through erosion at 68°C and through rupture at 25°C.

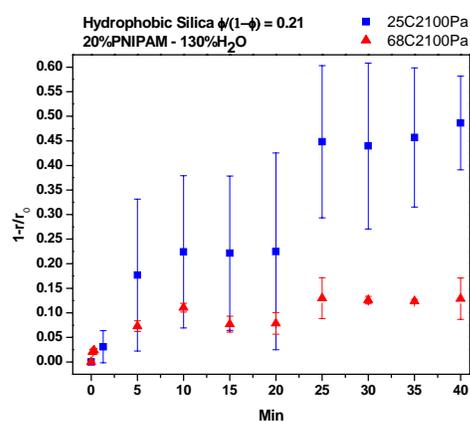


Figure 3b: Dispersion kinetics for agglomerates prepared with hydrophobic silica powder with 20% PNIPAM and 130% H₂O at a reduced solid volume fraction of 0.21. The shear stress applied was 2100 Pa. using PDMS of 30 and 60 Pa-sec for the 25°C and 68°C test respectively. Changes in the dispersion mechanism are observed at room and high temperature: dispersion takes place through erosion at 68°C and through rupture at 25°C.

Conclusions

The study shows that PNIPAM does act as a thermo-responsive binder enabling control of the dispersion behavior of hydrophobic silica agglomerates through the processing temperature. In addition, whereas the dispersion of agglomerates of hydrophilic silica incorporating PNIPAM seems to be temperature independent, dispersion of treated hydrophobic silica agglomerates shows evidence of temperature dependence through changes in the kinetics and mechanism of dispersion. The results of this study demonstrate that the water-to-binder ratios as well as the agglomerate solid volume fraction have an impact on the ability of the system to respond to temperature changes. Certain subsets of values

for binder and water content as well as solid volume fractions seem to optimize the temperature dependence effect at a given shear stress.

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