Controlling the Processing Behavior of Silica Agglomerates Using a Thermoresponsive Binder

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1. INTRODUCTION

Dispersion of agglomerates or assemblies of small particles is frequently encountered in a wide range of industries including material processing, pharmaceuticals, mining, and food technologies. Particulate fillers are used to modify product properties such as mechanical strength, chemical resistance, oxidative resistance or color. Effective dispersion of agglomerates is vitally important to the properties of the final material.

Dispersion, the break up of particle clusters flowing in a process stream, is generated by a competition between hydrodynamic forces acting to pull the agglomerate apart and the cohesive forces acting to hold it together. The systems studied here involve fine particle clusters within polymeric fluids.

Hydrodynamic forces are generally dependent upon the strength and the geometry of the flow field, whereas the cohesive strength of agglomerates is dependent upon the physical nature of its constituent particles, the packing density and morphology within the agglomerate, and the presence of any binder or processing aid [1, 2]. The purpose of this work is to explore the feasibility of using a new class of binders based on chemical systems that respond to external stimuli. We hypothesize that changes in the cohesion of a particle cluster can be triggered by changing the processing variable to which the binder is responsive. In particular, we explore this assumption using agglomerates of silica powder bound with Poly(N-Isopropyl Acrylamide), PNIPAM, a thermoresponsive polymer. Changes in temperature are expected to lead to physical changes in the conformation of the PNIPAM chains thereby altering the cohesion of the agglomerate and the kinetics of its dispersion.

2. BACKGROUND

Responsive polymers

Responsive polymers are those that under exposure to stimuli present an abrupt, reversible and predictable or controllable response. There are number of polymer systems that exhibit a response to environmental changes; this work focuses on Poly(N-Isopropyl Acrylamide) (PNIPAM). PNIPAM shows a mechanical response to a change in temperature. The hydrophilic and hydrophobic portions of this polymer are responsible for the thermoresponsive effect: at low temperatures, hydrogen bonding between the solvent (water) and the polymer is favored and the polymer is soluble. However, when the temperature is above its low critical solution temperature (LCST), the hydrophobic interaction of the polymer chains are preferred, water is expelled and the polymer chain contracts. This contraction results in aggregation of the individual chain molecules, precipitation occurs and mechanical work is produced (Figure 1). PNIPAM exhibits a LCST of about 31ºC. The fast PNIPAM transition in response to changes in temperature requires the presence of water. Changes in the transition temperature and in the sensitivity or sharpness of the transition should be expected when limited amount of moisture or other materials are present in the system.

Dispersion behavior associated with responsive binders

Binders are typically used to strengthen the force between particles constituting an agglomerate. This study of responsive binders intends to evaluate processing aids that can provide either a repulsive or attractive force to the particle system, and additionally can be manipulated using external triggers such as temperature. In this way, the cohesivity of the particle cluster becomes an externally controlled variable and consequently, it may be possible to actively control the dispersion behavior of particle clusters.

Since the influence of responsive materials on dispersion behavior has not been studied previously, full details of the mechanisms are not known. However, one can anticipate different scenarios of how the responsive binders may affect dispersion. In an extreme case, where the responsive material is capable of breaking particle-particle bonds, the responsive material itself may induce dispersion. Suppose the agglomerate has the responsive material

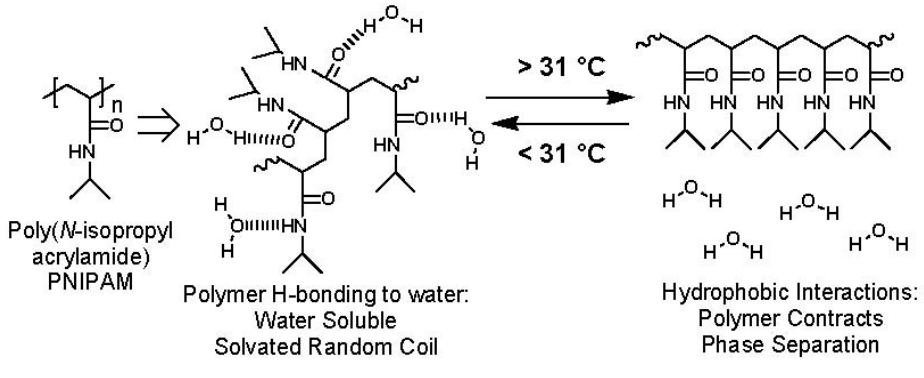

Figure1: representation of the thermal response of PNIPAM. Below the LCST the polymer is soluble in water and hydrophilic interactions dominate. Above the LCST the polymer chains collapse and hydrophobic interactions dominate

embedded throughout its structure. When the environmental trigger occurs, mechanical energy is produced, and breakage may occur on the scale of agglomerates or even its constituent units. In another case where the responsive material is not capable of producing forces large enough to break the agglomerate, the responsive material can act as a binder with variable strength. Under certain conditions the binder results in strong agglomerates while under others, the net strength of the agglomerate can be reduced.

2. EXPERIMENTAL

Two steps in evaluating the dispersion behavior of responsive binders are presented here; first, the evaluation of the dispersion kinetics of PNIPAM-silica-agglomerates at room and higher temperatures; and secondly, the evaluation of the PNIPAM transition temperature in water solution and in conditions mimicking the setting of the dispersion tests.

2.1. DISPERSION EXPERIMENTS

MATERIALS

Two different types of silica powder were used to make the agglomerates: hydrophilic Cab-o-sil LM 150D and hydrophobic Cab-o-sil TS 610; both provided by Cabot Corporation. Selected properties of the powders are listed in Table 1 The thermoresponsive polymer studied was Poly(N-Isopropyl Acrylamide) (PNIPAM) 20,000 MW and was supplied by Sigma-Aldrich. Polydimethyl siloxane (PDMS) of kinematic viscosity 10,000 cSt, 30,000 cSt and 60,000 cSt, were used as the dispersing fluid. The Dow Corning Corporation supplied the PDMS fluids.

Table 1: Silica powder characteristics

	Surface chemistry	BET Surface Area (m^2/g)
Powder A: LM150D Cab-O-Sil	Hydrophilic	160
Powder B: TS-610 Cab-o-sil	Hydrophobic	105-145

PROCEDURES

Powder treatment: Powders were coated with a PNIPAM-H_2O solution. Hydrophilic powders were treated in a commercial blender. An aqueous solution of the binder was micropipetted into the blender and mixed with the amount of powder required for the desired concentration. Hydrophobic silica powders were treated in a rotovap where the silica powder, binder-water solution and acetone were incorporated; the process was completed at room temperature until all the acetone evaporates. Water content was determined using TGA tests. Table 2 describes the characteristics of the treated solids.

Table 2: Surface treatment details

	Base silica powder	Binder content % wt. PNIPAM / wt. silica	Moisture content % wt. H2O / wt. silica
Powder A1	Hydrophilic	10	66
Powder B0	Hydrophilic	0	40
Powder B1	Hydrophobic	10	40
Powder B2	Hydrophobic	20	50

Agglomeration: Spherical agglomerates were made with the materials described above by unidirectional pressing the powder into a compact of a prescribed solid volume fraction (Φ), fracturing the compact into fragments, and then shaping the fragments into spheres of approximately 2 mm diameter.

Dispersion tests: Dispersion experiments were performed in a rotating cone-and-plate device described in reference [3] and shown in Figure 2. The agglomerate, suspended in the processing fluid, was subjected to a well-defined flow field at a constant shear stress. Experiments were performed at room temperature (25°C) and higher temperatures (40°C, 68°C) to capture the effect of the binder transition. The nominal values of shear stress (given by the product of the fluid viscosity ant the shear rate) were 1,050 Pa and 2,100 Pa. The dispersion process was recorded using a CCD camera and the reduction in size of the agglomerate was monitored using an image analysis system.

2.2. EVALUATION OF TRANSITION TEMPERATURE

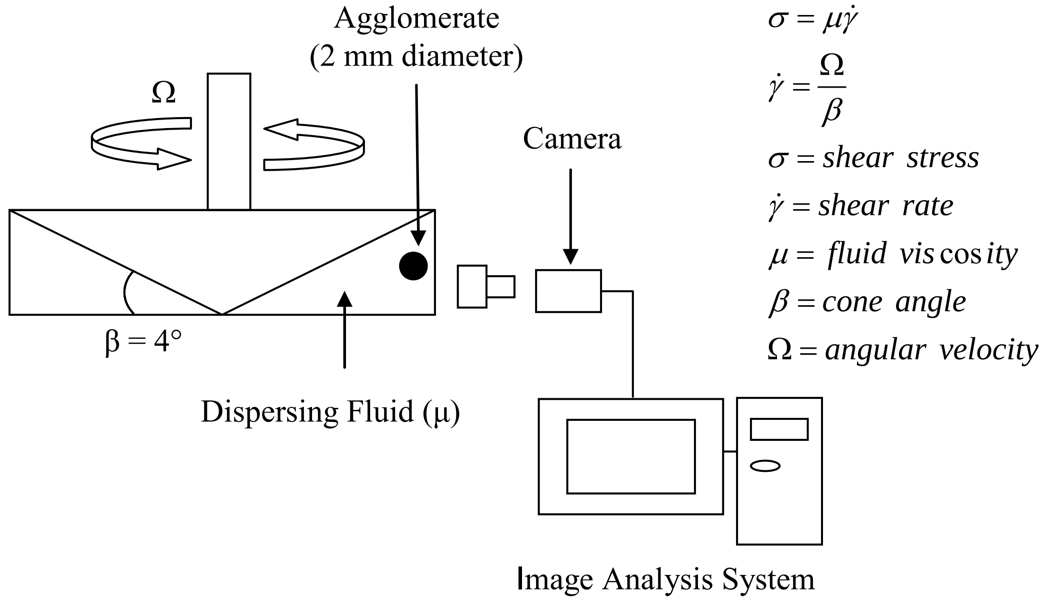

Figure 2: Schematic of the cone-and-plate device.

The LCST of the themo-responsive binder (PNIPAM) was evaluated in two different media:

1) Aqueous media: transmittance measurements of a PNIPAM aqueous solution in a UV Spectrometer.
2) Dispersion test media: visual inspection of the transition of the binder-treated powder in presence of PDMS (used as dispersing fluid in the experimental tests) to mimic the experimental environment under which dispersion experiments will be performed.

MATERIALS

Polydimethyl siloxane (PDMS) of kinematic viscosity 10 cSt, was used as the suspending solution of the treated powder.

PROCEDURES

UV Spectometer Measurements: Direct measurements of PNIPAM aqueous solution (0.0075M) were made in UV Spectrometer at 500nm.

Visual Inspection: Powder B0 and B1 were mixed separately in 10-cSt PDMS in test tubes. The test tubes were placed in an oven at 68ºC for 20 min. Images of the test tubes were taken before placing the tubes in the oven and after 20 min at 68ºC.

3. RESULTS AND DISCUSSION

3.1. DISPERSION EXPERIMENTS

Dispersion was quantified in terms of the erosion kinetics of prepared spherical agglomerates by monitoring the relative reduction in size ($1-r/r_0$) of the parent agglomerate with time when eroded in a controlled flow field. The tests were performed at low temperature (25ºC) and high temperatures (40ºC or 68ºC).

Effect of surface chemistry

Results of dispersion experiments performed on agglomerates of Powder A1 (hydrophilic) and B1 (hydrophobic) are shown in Figures 3 and 4 respectively. The dispersing fluid was PDMS 10 Pa·s and the shear stress applied was 1,050 Pa.

Hydrophilic powders at 25ºC are characterized by strong interparticle interactions due to hydrogen bonding between the PNIPAM and the silica hydroxyl surface groups. Upon increasing the temperature and if the binder transition occurs, the PNIPAM should adopt a hydrophobic configuration weakening the interparticle interaction and leading to changes in the agglomerate cohesivity. If the binder transition does not occur, the cohesivity of the agglomerate should be independent of the temperature. For the hydrophobic powders, the opposite behavior is expected (weak interactions at low temperatures and strong interaction at

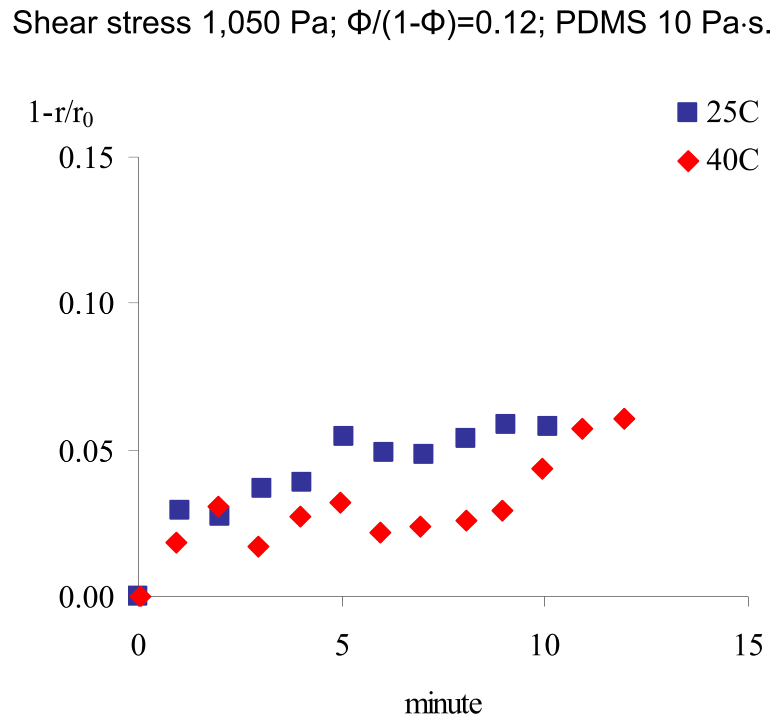

Figure 3: Erosion kinetics for silica agglomerates prepared from Powder A1 (10% wt PNIPAM/wt silica; 66% wt H_2O/wt silica).

high temperature). At 25ºC, the interparticle interaction is weak due to fewer hydroxyl groups available to hydrogen-bond with the silica surface groups. These interactions will facilitate the very likely transition of the binder which will adopt a hydrophobic configuration at high temperatures leading to the formation of a stronger agglomerate.

Powder A1 shows no significant difference in the dispersion extent at both tested temperatures. The binder transition may not occur due to strong PNIPAM-silica interaction, or may not be important enough to generate differences in the particle-binder interactions. Consequently, the cluster cohesivity and dispersion kinetics remained unchanged between the two temperatures. The results shown in Figure 3 may also indicate that the binder transition temperature in the presence of hydrophilic silica is above the LCST determined for the PNIPAM aqueous solution and may not be within the investigated temperature range (25ºC-40ºC).

As shown in Figures 3 and 4, dispersion differences between the two temperatures are more visible for Powder B1 (hydrophobic silica) than those observed for Powder A1. At low temperatures, silica-binder interactions for Powder B1 are weaker (due to the hydrophobic nature of the powder) and binder transition seems to be facilitated. The transition produces stronger agglomerates at higher temperatures when both silica and binder have a hydrophobic nature. The tested range of temperatures (25°C-40°C) seems to capture the binder transition which leads to differences in the agglomerate cohesivity and the extent of dispersion.

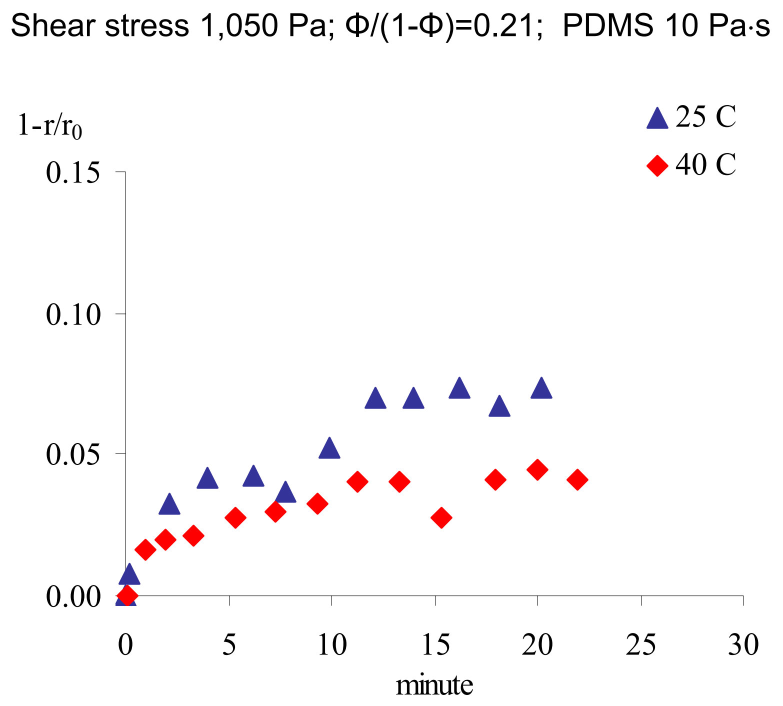

Figure 4: Erosion kinetics for silica agglomerates prepared from Powder B1 (10% wt PNIPAM/wt silica; 40% wt H_2O /wt silica).

Dispersion of both powders occurred mainly by an erosion mechanism, involving detachment of small fragments from the outer surface of the agglomerate. No alteration of the erosion mechanisms was observed at the different temperatures tested.

Effect of binder concentration

Results of dispersion experiments performed on agglomerates of hydrophobic Powder B1 (10%) and B2 (20%) are shown in Figure 5 and 6 respectively. The dispersing fluid was 30-Pa·s PDMS for the tests at room temperature (25ºC) and 60-Pa·s PDMS for the test at higher temperatures (68ºC), which has a viscosity close to 30 Pa·s at 68ºC. This allows the application of the same shear rate at both tested temperatures, and eliminates any effect of the shear rate and fluid viscosity. The shear stress applied was 2,100 Pa in both cases.

Increasing the concentration of responsive binder from 10% to 20% intensifies the sensitivity of dispersion kinetics with temperature.

The results presented in Figures 5 and 6 indicate a reduction in erosion extent (for both powders) at 68ºC, which can be explained in terms of the enhancement in the cohesivity of the agglomerate due to the strong PNIPAM-silica interactions at temperatures above the PNIPAM transition. At room temperatures, both powders show a significantly higher dispersability as evidenced by much faster erosion kinetics.

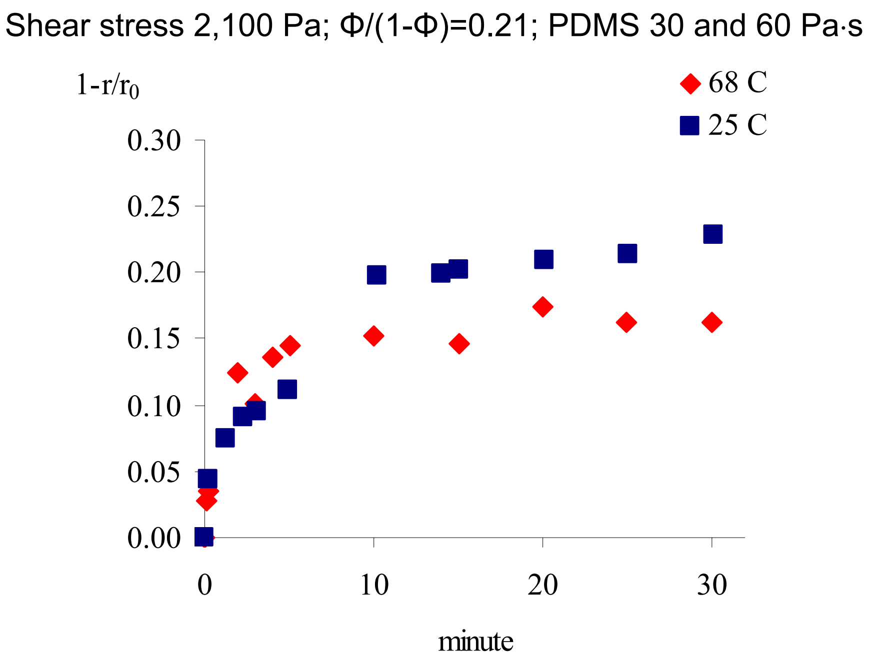

Figure 5: Erosion kinetics for silica agglomerates prepared from Powder B1 (10% wt PNIPAM/wt silica; 40% wt H_2O/wt silica).

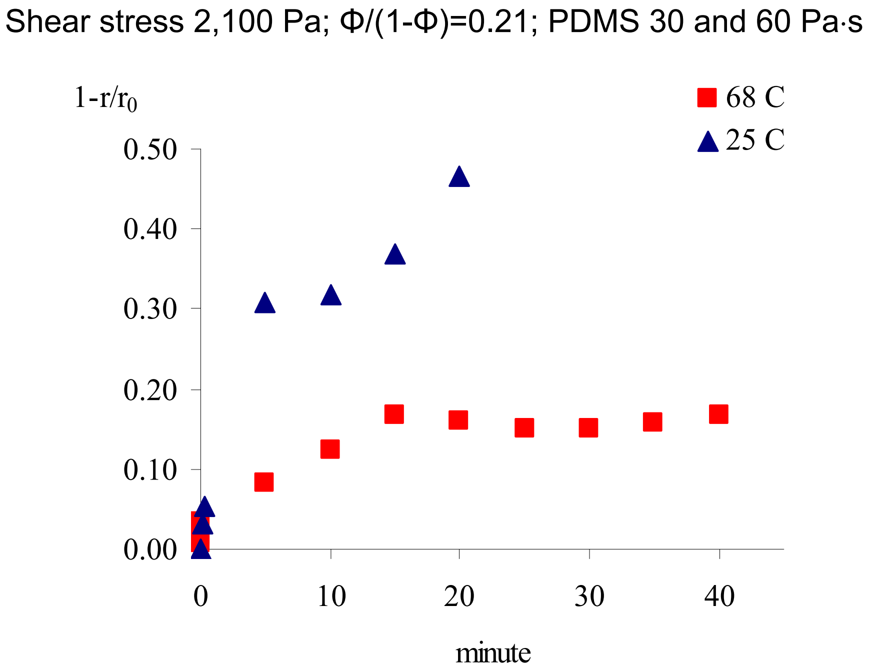

Figure 6: Erosion kinetics for silica agglomerates prepared from Powder B2 (20% wt PNIPAM/wt silica; 50% wt H_2O/wt silica).

Additionally, Powder B2 shows a change in the dispersion mechanisms upon changing the temperature. At 68ºC, dispersion occurs by erosion, involving detachment of small fragments from the outer surface of the agglomerate. At 25ºC dispersion occurs by a rupture mechanism, involving 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.

It is evident that the binder transition occurred in the range of temperatures tested (25ºC-68ºC) leading not only to differences in the dispersion extent (as observed for Powder B1), but also to alteration in the dispersion mode (as observed for Powder B2).

Effect of shear stress

Figure 4 and 5 show the expected trend in the dispersion kinetics when different shear stresses are applied. The degree of dispersion at 1,050 Pa (Figure 4) is lower than that observed at 2,100 Pa (Figure 5). It is also noticeable that the effect of temperature is more pronounced when higher degrees of dispersion are achieved.

3.2. EVALUATION OF TRANSITION TEMPERATURE

UV Spectrometer Measurements

Figure 7 shows the transmittance measurements for a PNIPAM solution in water (0.0075M). At low temperatures, the PNIPAM is soluble in water, the solution is transparent and the transmittance is high, whereas at higher temperatures when the polymer becomes insoluble, the solution is opaque and consequently, the transmittance measurements drop. The transition temperature or low critical solution temperature (LCST) measured is 32.9°C, this value is very close to the reported value in literature (31-32°C).

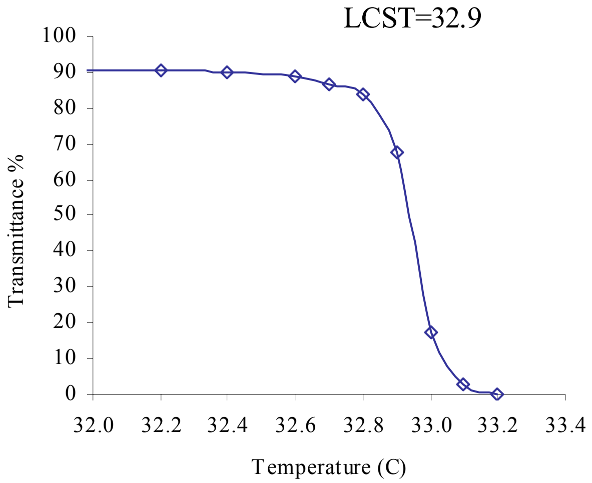

Figure 7: Transmittance (T%) measurements of a solution of PNIPAM in water at a wavelength of 500 nm. T% = I / I_0 x 100; I = transmitted power at a given wavelength; I_0= incident power at a given wavelength

Visual Observations

As mentioned previously, the rapid transition of the polymer solubility in response to changes in temperature requires the presence of water. We expect the sharpness of this response to be sensitive to the amount of moisture present in the system. The sources of water in the dispersion experiments come exclusively from the silica powder treatment. Thus, visual observation of the effects of the binder transition that may occur during the dispersion experiments (where the moisture content is limited) may be useful in interpreting the effect of the responsive binder on dispersion studies.

Powder B0 and B2 were dissolved separately in 10 cSt-PDMS in test tubes and placed in an oven at 68ºC. Figure 8 shows the pictures taken before placing the tubes in the oven (0 min) when the solutions were at 25ºC and after 20 min of keeping the solutions in the oven at approximately 68ºC. Figure 8 indicates that the binder solution becomes more opaque after 20 min in the oven, which provides some evidence that the binder transition takes place at a temperature between 25C and 68ºC. This also suggests that the binder transition during the dispersion test may occur in the same broad temperature range.

4. CONCLUSIONS

Using responsive materials to carry out powder dispersion is an interesting new area of research with many possible industrial applications. It was shown here that PNIPAM does act as a thermoresponsive binder enabling control of the dispersion behavior of (hydrophobic) silica agglomerates.

Using PNIPAM enables silica agglomerates to be relatively stronger at 25ºC and weaker at 68ºC. The dispersion studies at different temperatures not only show differences in the kinetics (faster dispersion is observed at 25ºC), but also changes in the mechanism of dispersion (rupture versus erosion).

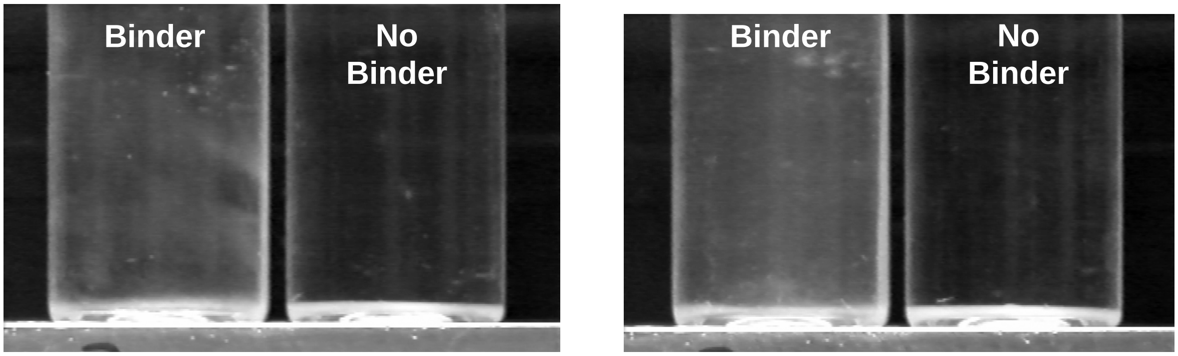

Figure 8: Photographs of PDMS solutions with and without binder at 25ºC (left) and at 68ºC (right).

5. ACKNOWLEDGEMENT

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6. REFERENCES

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