ISSN: 2319-8753

International Journal of Innovative Research in Science, Engineering and Technology

*(An ISO 3297: 2007 Certified Organization)*

Vol. 3, Issue 2, February 2014

# A Study on Aging Behaviour of Well-Dispersed Alumina Suspensions by Varying the Particle Size using Poly vinyl Butyral as Binder

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**Abstract:** Understanding the influence of storage time on rheological properties of the alumina suspensions is very important in many applications and fields such as tape casting processing advance coating, ink-jet printing, ceramic engineering, forming process of nano-powders etc. A rheological study of the aging process of Alumina – polyvinyl butyral (Al-PVB) tape casting slurry has been carried out by means of a conventional couette device at constant low shear rate. The slurries taken for the experiment has shown that at low constant shear rate there exist viscosity profiles showing gradual increasing behavior with waiting time (age) variation. Moreover, interestingly in the beginning the raise of viscosity is seemed to be higher and the trend of the viscosity profile remained almost similar in both alumina powders taken for the experiment, however the rate and initial viscosity of the suspension A16SG is observed much more as compared to the suspension A17NE.

**Keywords:** Aging, suspension, alumina powder, aggregation, shear-induced diffusion.

## I. INTRODUCTION

The particle motion in the suspension and flow behavior of solid suspension have been found a great interest in the fields of industrial process and material development consisting high strength ceramics, rocket propellants and reinforced polymer composites [1-3]. Industrial materials such as suspensions, physical gel, foam, wet granular materials or emulsions of form network of interacting element in given condition have a significant importance It is highly desirable to understand and correlate the effect of aging to their microstructure and physical properties such as surface area, pore volume and size. It has been already demonstrated in the literature that rheological measurements can be useful in controlling and handling sol-gel processes [1–6]. The impact of aging on alumina sols and gels depend on the history of the gelation process and on the conditions of the aging such as pH, temperature, solvent etc. Some investigations on the effect of aging for a few hours in the aluminum-sec-butoxide water- isopropyl alcohol system were performed [7]. Based on viscosity measurements, they distinguished between polymeric gels obtained at high water and alcohol concentrations, and cluster like particulate gels obtained at low water to alkoxide molar ratio. Bye and Sing [8] investigated the aging behavior of aluminum hydroxides prepared by the hydrolysis of their benzene or ethyl benzene solutions with water and other solvents. They showed that phase transformation to pseudobohemite

ISSN: 2319-8753

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

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or bayerite occurs during aging at room temperature, causing changes in the surface area of the gels. Thus it is necessary in the Alumina system to study each gelation process with its specific procedure and materials. Furthermore aging phenomenon were investigated for a wide range of soft materials, including hard sphere, colloid- polymer mixture, pastes, multi lamellar vesicles, clays and nanocomposites [6,9,12]. The parameters that control the rheological behavior are particle size distribution, phase volume, shape, interaction with other particles, viscosity of the continuous phase and the type and time of deformation. In the present work we study the influence of storage time on rheological properties of alumina powders having its loading concentration 55% (w/w) by varying the particle size distribution using Poly vinyl Butyral as binder.

## II. EXPERIMENTAL

**A) Materials used:** In the present work, Alumina powder A16SG (ACC-Almatis) and A17NE (ACC-Almatis) was used. The composition of the powder according to the manufacturer's information is given in the below (table I).

**Table I:** Characteristics of A16SG and A17NE alumina powders taken for study

| ***Alumina powder*** | | ***A 16 SG*** | ***A 17 NE*** |
|---|---|---|---|
| ***Particle size*** | | $d_{50}$ = 0.5 $\mu m$<br>$d_{90}$ = 2.0 $\mu m$ | $d_{50}$ = 2.3 $\mu m$<br>$d_{90}$ = 7 $\mu m$ |
| ***Specific Surface area/BET (m²/g)*** | | 8.9 | 2.9 |
| ***Chemical Composition*** | $Al_2O_3$ | 99.8% | 99.81%, |
| | $Na_2O$ | 0.07% | 0.10%, |
| | $Fe_2O_3$ | 0.02% | 0.03%, |
| | MgO | 0.05% | 0.01%, |
| | $SiO_2$ | 0.03% | 0.03% |
| | CaO | 0.02% | 0.02% |

The binder used was Poly vinyl Butyral (PVB) of grade Maripol B-30 (Parekh Chemical). Solvents used were azeotropic mixture of 50 % (by weight) Methyl Ethyl Ketone; MEK (Merck) and 50% by weight) of 99.9 %Ethanol; EtOH, (ChangShu Yangyuan Chemical, China).

**Table II:** Composition of the Alumina Slurry and Formulation particulars used

| **Components** | **Function** | **Wt. % (vol. %)** |
|---|---|---|
| Polyethylene Glycol 400 (PEG) Merck, $[(C_2H_4O)_nH$ where n = 380-400 ] | Plasticizer | 6.08(8.29) |
| Butyl Benzyl Phthalate (BBP) Aldrich, $[2\text{-}(CH_3(CH_2)_3O_2C)C_6H_4CO_2CH_2\,C_6H_5]$ | Plasticizer | 1.38(1.90) |

ISSN: 2319-8753

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| | | |
|---|---|---|
| Mixture of ethanol & Methyl ketone | Solvent | 30.12(58.09) |
| Alumina | Powder | 55.29(21.77) |
| Poly vinyl Butyral (PVB) | Binder | 7.13 (9.95) |

**B) Preparation of suspended slurries:** To ensure a negligible moisture content of the powders, we prepared the slurries (Table I) by vacuum heating the powders at $100^0$ C for 7days prior to their use. In the first stage, to a portion (13.96%) of the total azeotropic solvent mixture utilized in the formulation, 6.07% by weight of PEG, 1.38% by wt BBP and 1.38% of the binder PVB was added. The resultant mixture was stirred and kept overnight. After the time period, 55.2% by wt of the heat treated powder was then weighed and poured into the above mixture containing solvent & plasticizers. The resultant slurry was subsequently ball milled at 73rpm for 10 h with 10mm alumina balls (138% by wt of the total formulation) as the grinding medium. In the second stage, the solution of 5.74 % by weight of (PVB) and 16.28% of solvent mixture (viscosity: 665 $\mp$ 5 mPa.s) was added to the slurry. The slurry was further ball milled for 14h. The weight of the container containing the slurry was measured before and after the ball milling process to rule out any solvent or material loss. The alumina suspension thus formed was poured into a container and was de-aired under slow stirring and in vacuum conditions (300 mm Hg) till no more bubbles were seen to form. The weight loss during the de-airing process was found to be nominal (0.2%). Graduated cylinders (Borosil) fitted with stoppers and sealed with Parafilm "M" (Pechiney Plastic Pakaging) were used to investigate the sediment nature. The graduated cylinders containing the slurry were placed in an oven fixed at $60^0$ C for 72 h before the sediment nature was investigated.

**C) Experimental set up:** A programmable Brookfield concentric cylinder Rheometer DV-III ULTRA was used to measure viscosity. This Rheometer was coupled with a small sample adaptor (SSA 13RP, Brookfield) with EZ-lock assembly and embedded RTD temperature probes. The data was gathered with the help of Rheocal program supplied by Brookfield at a time interval of 1 min. During the experiment the temperature of measurements was kept constant at $20^0$C $\mp$ 0.2 with the help of Brookfield water bath TC 502. Prior to any measurement, the slurries were kept at rest in the SSA till the required temperature was obtained. As the required temperature was reached, the suspensions were pre sheared ($\dot{\gamma} t$ = 1800) and after the pre shear stage the suspensions were left at rest for a period of 30 min, 120 min, 360 min and 720 min in order to let the system develop an initial structure level.

## III. RESULTS AND DISCUSSION

Powder loading of the alumina slurry prepared was taken 55% (w/w) (Table I). It is observed that suspended slurries taken for experiments were remained high turbid even on standing at accelerated weather condition ($60^0$C, 72h) [10]. Moreover, at the end of sedimentation tests it is found that the both the parent suspensions of alumina powder A16 SG and A17 NE remained very turbid. The high turbidity of the suspension gives significance that sufficient number of particles is well-dispersed. Furthermore, it was also observed that there was no any visible phase separation after four months of standing at ambient conditions in the suspension taken for experiment which ensure retained high turbidity. These observations pointed out that the suspension to be well dispersed. To ensure the systematical accuracy of the experiment, we utilize fresh suspensions for each of these measurements. Once the time period is elapsed, the suspension was sheared at 4 $sec^{-1}$ for a period of 2h.

*Aging behavior of well-dispersed A16SG alumina slurries:* After 30, 120, 360 and 720 minutes rest period before shearing depicted in figure 1 shows interesting rheological behaviors which are summarized as follows: (i) a gradual increase in viscosity with time was observed at applied constant shear rate. (ii) in beginning, the raise in viscosity is seemed to be much more for the suspension (iii) the change in viscosity follows the order 30-120 min<120-

ISSN: 2319-8753

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

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360 min<<360-720 min with application of successive constant shear and (iv) the trend in slope of viscosity curve of the suspension sheared at 4 $sec^{-1}$ almost similar till 720 min although the difference in viscosity drift is significant to be considered (v) an increase in wait time progressively increased the drift in viscosity.

In the colloidal suspensions there has been growing interest on the microstructures of the particle in the suspension since the material properties are largely determined by the microstructure developed through the migration of the particle in the suspension especially when consideration of aging is necessary. It is well known that in the colloidal dispersion, the suggest process is determined by the interaction forces between the particles, whenever there is a suitable balance between the attraction forces and the electrostatic and steric repulsion, a weak coagulation takes place [11-14].

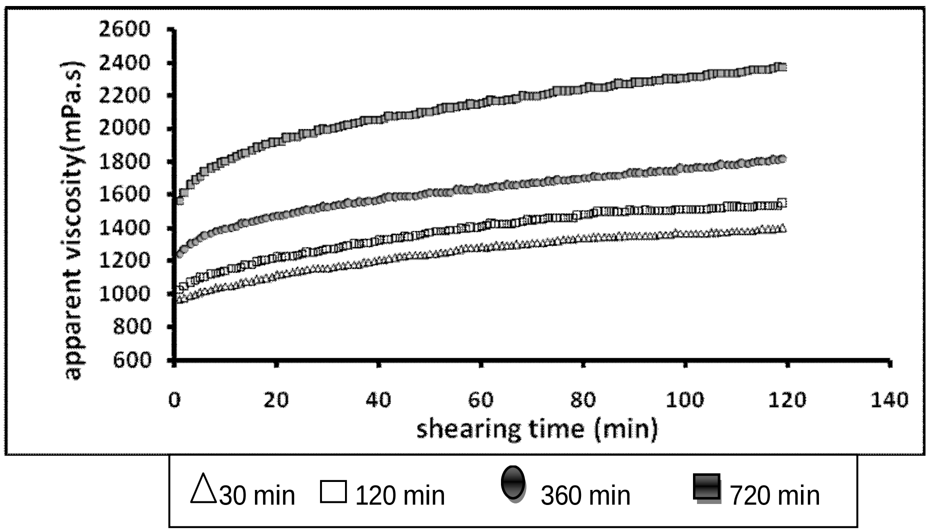


*Fig 1*: Aging behavior of well-dispersed A16SG alumina slurries at constant shear rate

Consequently there is the formation of isolated large flocs or of a single particulate structure throughout the whole material. The supportive evidence regarding the structural changes as well as the establishment of the relation between rheological characterization and the stability parameters have been already explained [15-20]. Binder et al. [23] has showed the existence of hydrodynamics lubrication forces by measuring rhelogy, turbidity flow small angle, neutron scattering and stress optical relationship the hydrodynamic cluster are composed of group of particles formed as shear forces derive them to contact and short range lubricant forces dominate the flow which comes to result in increase in viscosity. It is well known that a good dispersed fine particulate suspension may be unstable with time.

These suspensions usually have a tendency to form agglomerates with time resulting in flocs. For the present well dispersed suspensions, the overall observed viscosity curves is a consequent of two major competitive processes of shear induced hydrodynamic diffusion and orientation/agglomeration of the particles under shear. Furthermore, it may be pointed out that conducting experiments on the aging behavior of the suspension becomes significant in the light of results obtained from the sedimentation tests which showed very long time turbidity for suspensions without any phase separation. Hence, it is expected that while considering the aging behavior of the suspension, the resultant changes in viscosity profiles may be the outcome of agglomerates even to a small degree dependent on time and the applied shear stress.

*Aging behavior of well-dispersed A17NE alumina slurries:* To analyze the aging behavior of well dispersed alumina suspension *A17NE having* much wider particle size we conducted the experiment with the similar

ISSN: 2319-8753

International Journal of Innovative Research in Science, Engineering and Technology

*(An ISO 3297: 2007 Certified Organization)*

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waiting time. It is shown in the figure 2 that the trend in viscosity profile for suspension *A17NE* with waiting time (age) is just similar to the suspension A16SG. However the rate of increasing the viscosity at constant shear rate $4sec^{-1}$ for suspension *A17NE* is much lesser than corresponding suspension A16SG. The increase of viscosity with time may be attributed to formation of new bonds through condensation reactions. Since the viscosity is proportional to the number of touching particles in the dynamic network. Since as the rest period for the suspension before shearing is increased, there is more possibility for colloidal particles to interact with each other, hence the dynamic network of the particles consisting of more flocculated, coagulated and higher particles near the bottom end of viscometer.

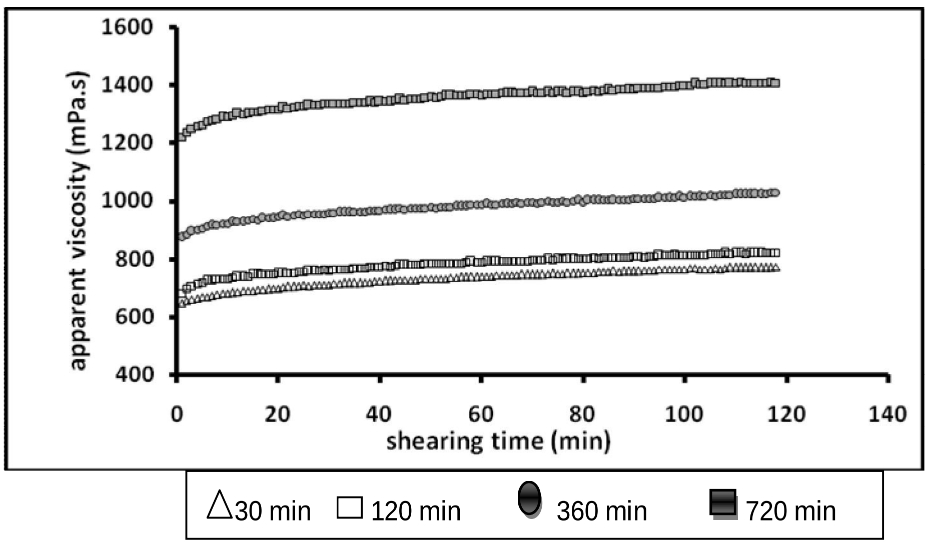


*Fig 2*: Aging behavior of well-dispersed A17NE alumina slurries at constant shear rate

When considering the formation of aggregates the inter-particle interaction forces are of central importance since these define the kinetics of aggregation and the strength of particle-particle bonds both of which ultimately influence aggregate structures [15-18]. The presence of attractive colloidal forces will give rise to structuring and de-structuring of the suspension microstructure in the flow field. On increasing the waiting time (age), more chance to develop high concentrated profile nearer the bottom end of viscometer. As the shear stress is applied, settled particles getting more chance to come out from bottom end to the upper end of the viscometer. This type of phenomenon is found in the literature as shear induced diffusion [19-22].

*A comparative analysis on aging behavior of alumina suspensions A16SG and A17NE:* Since both the suspension A16SG and A17NE have different particle size distribution and the polydispersity of the suspension A17NE is much high. Obviously, the effect of shear induced hydrodynamic diffusion on the observed viscosity curves will be nominal in suspension A16SG and the effects of particle orientation and deagglomeration in suspension A17NE will be more prominent. This is especially so when majority of the practical particulate systems contains particles which are irregular in shape, have rough surfaces and have conventional aspect ratios. Since the larger particle size fraction present in suspension A17NE are more difficult to pump out from the viscometer after establishing the aging viscosity profile while comparing with the suspension having smaller particle size fraction A16SG. Moreover for a polydisperse system, the size distribution trends to have an important influence on viscosity regardless of the volume fraction concerned. For a given volume fraction of a disperse species, having a size distribution tends to reduce the hydrodynamic resistance to flow which results the decrease in viscosity and maximum achievable dispersed phase

ISSN: 2319-8753

International Journal of Innovative Research in Science, Engineering and Technology

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Vol. 3, Issue 2, February 2014

volume fraction is increased. Consequently the resultant increase in the suspension depicted in table (III) during the experiment is much less than corresponding suspension A16SG.

**Table III:** A comparative study of aging behavior for the alumina suspension A17NE and A16SG

| ***Wait Time (min)*** | **30min** | **120min** | **360min** | **720min** |
|---|---|---|---|---|
| ***A16SG – PVB*** $\Delta\eta = \eta_{final} - \eta_{initial}$ ***(mPa.s)*** | +432 $\eta_{initial}$=940 | +521 $\eta_{initial}$=1022 | +611 $\eta_{initial}$=1204 | +806 $\eta_{initial}$=1565 |
| ***A17 NE – PVB*** $\Delta\eta = \eta_{final} - \eta_{initial}$ ***(mPa.s)*** | +126 $\eta_{initial}$= 646 | +141 $\eta_{initial}$= 680 | +154 $\eta_{initial}$= 873 | +186 $\eta_{initial}$= 1220 |

Hence, the progressive increase in viscosity for all the suspensions with time may be attributed with a process where particles approach each other due to the restructuring of the particles after thermal agitation and in the presence of appropriate additive forces stays together. It is noteworthy that after 720 min waiting time (age) in both suspensions A16SG and A17NE there is a higher positive drift in viscosity while on the other hand difference in initial viscosity and drift viscosity profile is not much during 30 min to 120 min. Furthermore, experimental work on well-defined colloids has shown that colloid stability increases, reaches a maximum and then decreases as the particle size increases [24]. Perhaps a sizeable fraction of particles still remains stable even on aging may be the most likely cause and these results in continued high turbidity of the suspension. When considering the properties of sediment beds, the strength of particle bonds and the number of bonds that have to be broken, which is determined by the network structure which is in turn related to the aggregate structures, are of critical concern. Hence, to optimize the basic solid-liquid separation processes, it is very necessary to lay emphasis on understanding behavior of what controls aggregate properties and how these proper ties impact on sediment bed properties especially when the consideration of aging is essential.

## IV. CONCLUSION

In this work, we studied the impact of well dispersed alumina suspension using Poly vinyl Butyral as binder in non aqueous solvent by varying the particle size distribution on the viscosity profile curve by considering waiting time (age). To understand the rheological properties (aging) of these suspensions A16SG and A17NE we systematically investigate and then compare the aging behavior by varying time period from 30-720 minutes. We found that in both the suspensions the trend in viscosity profile at constant continuous shearing for 2h remained somewhat similar to each other, however comparative initial viscosity for the suspension A17NE conducting aging experimental process remained lower and have less positive drift. Interestingly, it has been found that in the beginning of shear applied the raise in viscosity is much positive which is seen during all variation from 30-720 minutes. Thus, the observation for the aged suspension showed cumulative effect of shear induced hydrodynamic diffusion and aggregation developed.

## ACKNOWLEDGEMENT

This research work was funded by the DST, Government of India under the SERC Scheme (vide order no. SR/S1/PC-12/2009) as a major research project awarded to Dr. Amit Mukherjee. Deepak Sharma is associated with this project as a Project Fellow. The authors also acknowledge the authorities of Mody Institute of Technology and Science for providing space and other infrastructural support.

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