

SURFACE MODIFICATION OF NEUTRAL COLLOIDAL SILICA NANOPARTICLES

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ABSTRACT

The surface of neutral Colloidal Silica nanoparticles was modified by treating with Vinyltris(2-methoxyethoxy) silane coupling agent. The unmodified and modified SiO₂ particles were investigated. The particle size and particle size distribution were determined by Dynamic light scattering (Malvern Instruments Ltd.). The results showed increased particle size, increase in zeta potential and narrowed the particle size distribution of silane modified SiO₂ particles in comparison to unmodified SiO₂ particles. The results revealed homogenous dispersion stability of modified colloidal silica nanoparticles surface.

Keywords: Colloidal Silica, Silane, Vinyltris(2-methoxyethoxy) silane.

1. INTRODUCTION

The stable dispersions of amorphous silica have been commercially available¹. The main component of the crust of the earth is Silica. The SiO₂ particles being stable, nontoxic with high thermal resistant inorganic fillers made them available in many fields, such as rubbers, coatings, plastics, cosmetics and printings. In present technology it is used in variety of application areas like catalyst in oil refinery, fiber optics and microcircuits². There are still applications where many of the properties of colloidal silica could be put to good use but only with difficulty, because even the outstanding stability of modern silica sols is not high enough. The mechanical properties in polymers were improved by silica nanoparticles³⁻⁶. The weak compatibility leads to uneven dispersion of inorganic nanoparticles in the matrix. Due to hydrophilicity of hydroxyl group (-OH), dispersibility and agglomeration are difficult in the silica surface. Surface modification of nanoparticles is one of the mostly accepted methods to improve the dispersion stability of

nanoparticles in challenging conditions by making the particles to hydrophobic.

There are many techniques of surface modification as reported in the literature⁷⁻¹⁹ but Chemical modification of the silica surface with silane coupling agent creates a broad field of both industrial and analytical applications.

The Dispersion stability was increased by modification of colloidal silica particles by covalent grafting of silane molecular on inorganic surfaces²⁰⁻²¹. To obtain organo-functionalized silica nanoparticles to suit various purposes; organic compounds, PEG, polymers, organic isocyanates, PMHS and different silanes were adopted²²⁻²⁷. Fatemeh Ahangaran et al.²⁸ modified the Fe₃O₄@SiO₂ core-shell microsphere by vinyltriethoxysilane (VTES) for the removal of the silanol groups on the SiO₂ shell and found there was decrease in the agglomerations. In 2002 Kim et al.²⁹ found that modified silica with silane coupling agents had smaller agglomerate size and lower viscosity. Zhang et al.³⁰ modified silica nanoparticles by MPS and prepared monodispersed silica-

polymer core-shell nanospheres via emulsion polymerization.

The concentration effects of 3-methacryloxypropyltrimethoxysilane (MEMO) on the surface coverage extent, orientation, and structures of MEMO silane grafted onto the surface of SiO₂ particles were investigated by Hsing I. et al.³¹ and reported the enhanced steric hindrance and compatibility between the MEMO modified SiO₂ particles improved the dispersibility of nanosized SiO₂ in acrylate suspensions. Mahdavian et al.³² reported a method to prevent the aggregation of nanoparticles. The results by Wu et al.³³ demonstrated extra steric stabilization for the nanoparticles, which ensured satisfactory nano-scale dispersion in the final nanocomposites.

The objective of this study was to modify neutral colloidal silicananoparticles with Vinyltris(2-methoxyethoxy) silane and observe the dispersibility and change in the particle size.

2. EXPERIMENTAL

The materials required and the method of preparation of modified slurry that can be used in any manufacturing process is discussed.

2.1 Materials

Ultra-Sol® 3EX 30% Colloidal Silica by weight and pH 7.3, was procured from Eminess Technologies USA. Vinyltris(2-methoxyethoxy)silane >96%, obtained from Acros organics Switzerland. All the chemicals purchased were used as received without further purification. Purified water having a water resistivity 18 MΩ cm was used. All the sample preparations were done at room temperature.

2.2 Preparation of the modified Slurry

The slurry was prepared by rapidly mixing the neutral colloidal silica solutions and silane (VTMES) as modifier at room temperature. One ml of modifier is added slowly in 2 hrs under room temperature with vigorous stirring into a 100 ml of colloidal silica. The particles were then separated by centrifugation. The so-obtained product was kept under observation for 48 hours in temperature controlled clean room. Finally, the resulting modified nano-particles were dried at 80°C for 12 hours in vacuum oven.

The dried powder of one gram mixture was diluted by 100 ml of De-Ionized water in a container by stirring continuously. The solution was kept for 24 hours. The mixture was filtrated with a strainer to obtain slurry solution containing Modifier (Silane) and colloidal silica abrasive.

The clear solution thus obtained was used for characterization.

The same procedure was adopted even for acidic and basic colloidal silica modification³⁴

3. RESULTS AND DISCUSSION

The modified slurry is analysed to observe if it can be used as slurry in any of manufacturing process involving surface quality or material removal or both. Hence characterisation techniques for particle size and zeta potential was carried out. Zeta Nano sizer ZS90 was used.

3.1 Characterisation Technique

The size of nanoparticles in solution was characterized by Dynamic Light Scattering (DLS, Malvern). The light scattering from a laser that passes through a colloidal solution is analysed by the modulation of the scattered light intensity which is function of the hydrodynamic size of particles and agglomeration of particle. Larger particles will diffuse slower than smaller particles and the DLS instrument measures the scattered light that is time dependent and generates a correlation function that can be mathematically linked to a particle size³⁵.

The zeta potential is measured by Laser Doppler Micro-electrophoresis. This velocity measured by applying electric field to dispersion of particles using a laser interferometric technique called M3-Phase analysis Light Scattering and calculates the electrophoretic mobility and zeta potential³⁵.

3.1.1 Particle size

The particle size of neutral colloidal silica was found to be 21.86d nm. As the neutral colloidal silica were modified with vinyltris(2-methoxyethoxy)silane as per the procedure explained in experimental section, it was found that the average size of the modified particles increased to 131.2d nm almost six times greater than the unmodified silica particles.

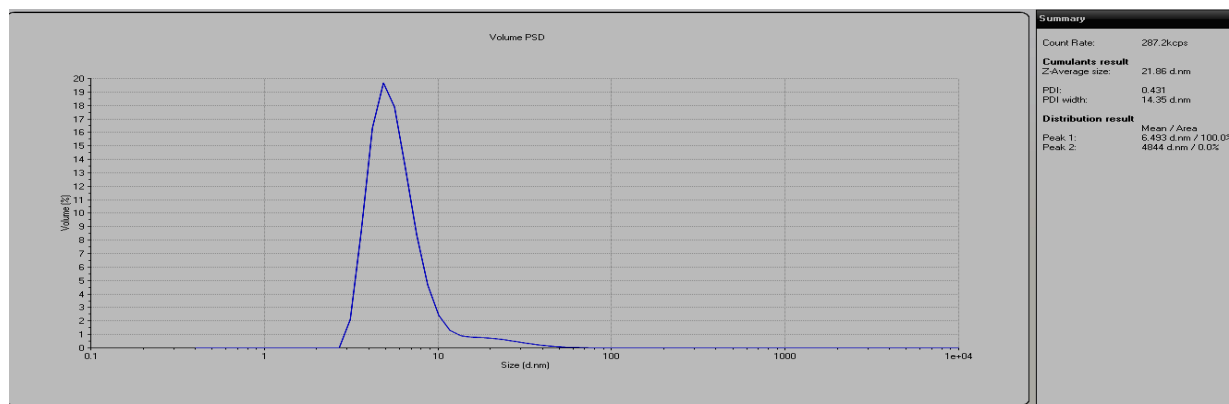


Fig. 1: Average Particle Size of Neutral Colloidal Silica

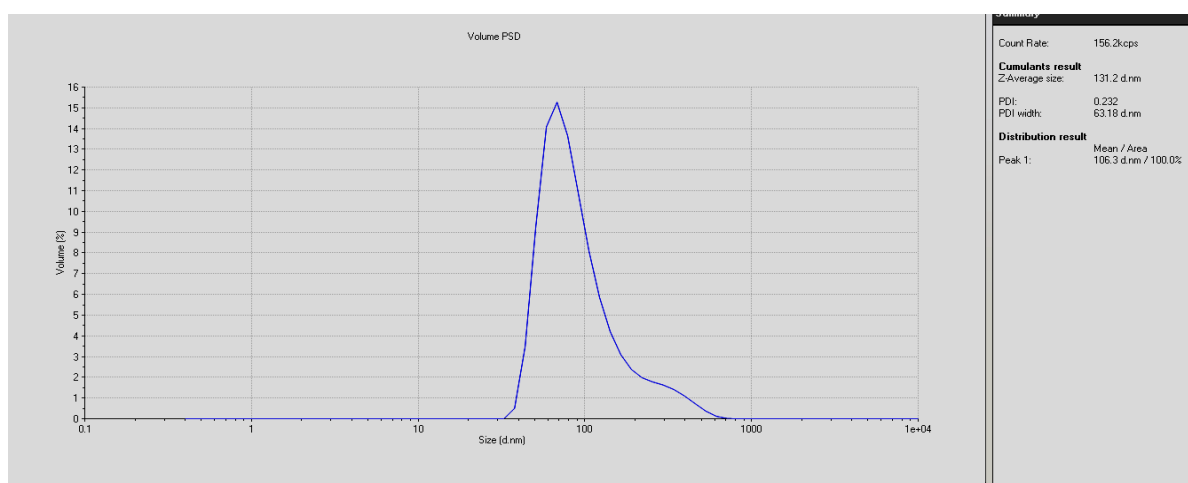


Fig. 2: Average Particle Size of Modified Neutral Colloidal Silica

3.1.2 Average Particle Size of Modified Neutral Colloidal Silica with VTMS

After modification, the average size of neutral silica sol increased due to hydrolysis of silane to produce silanol groups. After hydrolysis, the condensation follows: (1) Formation of oligomers (Small part of silane molecular react with each other). (2) Grafting of some silane molecules on to the surface of silica nanoparticles.

(3) Formation of large aggregates with several nanoparticles connected with silane as bridge due to reaction of silane molecules with each other and grafting to the surface of nanoparticles simultaneously.

Studies of particle interaction in model suspensions by scattering methods require narrow size distributions as well. The

polydispersity of sizes will cause an incoherent contribution which may become the main part of the measured scattering intensity at small angles. It was found that polydispersity index of modified neutral colloidal silica had 0.232 in comparison to unmodified colloidal silica particles with 0.432 showing a very wide distribution in pure colloidal silica particles.

3.1.3 Dispersion Stability of modified (Neutral Colloidal Silica + VTMS) Colloidal Silica:

The moisture or water is responsible for some hydroxyl groups on the surface in the conventional inorganic nanoparticles³⁶. VTMS being hydrophobic maintains a high degree of permeability reducing deterioration at the interface associated with entrapped water.



(Where R = -CH=CH₂)

As shown in the reaction 1, VTMES would be immobilized directly on the surface of neutral colloidal silica nanoparticles through silanization reaction with hydroxyl groups. Oligomers formed as a result of polymerization on VTMES surface produce steric hindrance between colloidal silica nanoparticles. It leads to the formation of homogenous dispersion of colloidal silica nanoparticles in aqueous medium. It maintains stability for a long period.

It was observed that VTMES being neutral has more affinity towards neutral colloidal silica surface thus reacting almost instantly. The increase in average diameter of modified colloidal silica slurry as compared to pure neutral colloidal silica slurry with wide size distribution of 0.432 and modified neutral colloidal silica particles with narrow size of 0.232, suggest a better dispersion by surface modified particles in spite of the aggregation. The coating on the surface of neutral colloidal silica particles prevents aggregation resulting in increasing of mean diameter of modified particles.

In order to investigate the dispersion mechanism, zeta potential was measured. Through grafting with silane, the negative surface charge of colloidal silica was increased. The higher the zeta potential is, the better is the dispersion stability. In other words, the dispersion stability of colloidal silica was improved by coating silane on the surfaces. The increasing of zeta potential may account for why the modified colloidal silica has better dispersibility than pure Colloidal silica. The improvement of surface qualities was due to the cushioning effect of its silane coating and reduction or the elimination of the agglomeration among modified colloidal silica particles. The slurries VTMES had better dispersibility, with zeta potential of -27mV more than the neutral colloidal silica.

4.0 CONCLUSION

The modification of colloidal silica nanoparticles with silane and considerable achievements on the surface have been reported by researchers yet further improvement in the compatibility of the inorganic nanoparticles with polymer matrix and to synthesize of novel functional materials with more excellent properties through more extensive and in-depth investigation is necessary. Fairly recent and important developed applications of colloidal silica, which have been studied in the present work, are the use of colloidal silica as polishing agents for

silicon wafers or glass substrates, to provide solid electrolytes in lead-acid batteries and as components in high quality coatings.

The Modified colloidal silica particles with VTMES solution prepared can be directly used in polishing of wafer or glass substrate thus leading to enhancement in surface finish.

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