

## Modification of the surface of silica nanoparticles; studying its structure and thermal properties in order to strengthen it in preparing Nano composites

Naser Gharehbash<sup>1</sup>, Alireza Shakeri<sup>2</sup>

PhD Student, Academy sciences of Tajikistan<sup>1</sup>

<sup>2</sup>Faculty of Chemistry, University College of Science, University of Tehran, Tehran, Iran

<sup>1</sup> Corresponding authors: E-mail: [d.gha.5na@gmail.com](mailto:d.gha.5na@gmail.com)

**Abstract:** The surface of silica nanoparticles was modified with acid derivations derived from silica; propyl trimethyl Silane ( $C_6H_{16}O_3Si$ ); vinyl tries; 2-methoxy; ethoxy Silane ( $C_{11}H_{24}O_6S$ ) and  $\delta$ -amino propyl trimethyl Silane ( $C_6H_{17}O_3N$ ). The purpose of the present study is to modify the surface of hydrophilic in silica nanoparticles by organo silanolic compounds of acid derivations derived from silica so as to be consistent with hydrophobic polyolefin and improve the properties of new Nano composite materials by using organosilanic compounds of acid derivations derived from silica; Silica nanoparticles were prepared by using mechanical crusher by 120 mesh size. Changes in the structure of silica nanoparticles after surface modification by the use of electron microscopy (TEM); x-ray diffraction (XRD); infrared spectroscopy (FT-IR); and differential thermal analysis (DTA) were investigated. Results show that the samples of the modified hydrophobic surface and water absorption capacity have been reduced. Reinforced silica nanoparticles (which retained their main structure) are ready to get linked to polymers like polyolefin including polypropylene in order to prepare Nano composite.

[Naser Gharehbash, Alireza Shakeri. **Modification of the surface of silica nanoparticles; studying its structure and thermal properties in order to strengthen it in preparing Nano composites.** *J Am Sci* 2013;9(4):602-606]. (ISSN: 1545-1003). <http://www.jofamericanscience.org>. 66

**Keywords:** Nano silica; organo Silanolic; hydrophilic surface; polyolefin; Nano composite.

### INTRODUCTION:

Today the importance of using polymer Nano composites is evident to anybody. these material shaving unique properties have attracted the attention of many scientists and artisans[1]. polymer Nano composites are prepared from nanoparticles diffraction in the polymer matrix the more the compatibility and interaction between nanoparticles and the polymer is; the better properties are gained from Nano composite[2].

Polymer Nano composites are a group of materials in which the organic nanoparticles with a plate or spherical structure are dispersed in a polymer matrix. Compared to pure polymers; polymer nanocomposites have different physical and mechanical characteristics including modulus; strength; hardness; flammability; dimensional stability; electrical conductivity; thermal resistance; and moisture absorption-depending on type and amount of nanoparticles used[3-8]. Silica particles with a tiny size and a large contact area have a high application in polymer industries and surface coats. the surface of these particles has 3 chemical groups of hydroxyl; hydrogen; bound to hydroxyl groups; and Silane groups. therefore; the particles are hydrophilic. Though Silane groups. therefore; the particles are hydrophilic. though Silane groups; alone are hydrophobic; it is hydrophobic the surfaces of silica particles by using hydrophobic materials such as dimethyl Silane (DMS) and hexamethyldisilane

[9]. many studies have been done on the application of silica particles onto various polymers[10-13]. researchers found that silica particles can improve the strength; hardness; modulus; crystallization; viscosity; resistance against intra-structural creep and Cohesion in polyethylene; polypropylene; and thermoplastic elastomers-depending on surface properties of nan silica particles[14-17]. interaction between hydrophilic nan silica particles is mainly faced with challenges in the surface of hydrophobic polymers to prepare nan composites; in other words; modified silica Nano particles are more likely to remain in the matrix of a hydrophobic polymer; compared to the unmodified types. so; given the particular importance of the issue; in this study; we have tried to modify nan silica surface with 3 organosilanic composites derived from silicic acid and also by using necessary techniques; we have attempted to identify and convince linked groups in the surface of Nano silica particles with silicic acid derivation and creating a hydrophobic coat on the obtained nanoparticles so as to be consistent with non-polar polymers such as polypropylene for preparing Nano composites and improving their physical and mechanical properties.

### Materials and Methods

Materials: silica gel 11220k produced by (Mark) company; hydrochloric acid %37 sodium hydroxide %99; sulfuric acid %98; toluene and sodium

chloride produced by ((Aldrich))company silicic acid derivations (propyl trim ethyl Silone)%97 ( $C_6H_{16}O_3Si$ ) with 143 °c boiling point; vinyltri (2methoxyethoxy) Silone ( $C_{11}H_{24}O_6Si$ ) with 133 °c boiling point; and  $\delta$  -amino propyl trim ethyl Silone( $C_6H_{17}O_3N$ )%100 with 103 °c boiling point; a product of (Fuloka) company.

#### Equipment and devices:

Vacuum oven; and ultrasonic devices made by (Philips) company transmission electron microscopy (TEM) made by (Philips) (A German company); X-ray device (XRD) made by (Philips co); (TGA) device Made by (Prkinelmer co); spectrometer made by (per inelmer co).

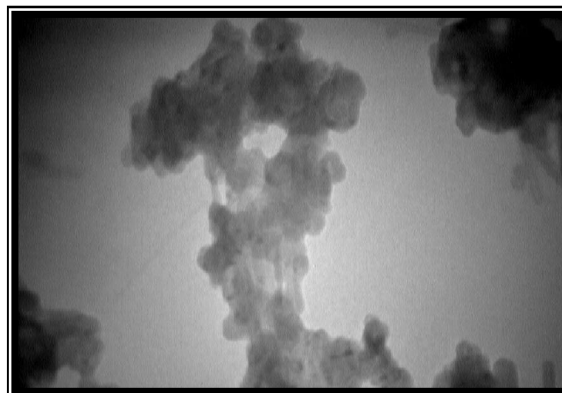
#### METHODS:

Sun these are and modification of the surface of Nano silica particles is as follows:600g silica gel was sieved by 100 and 200 mesh with a mechanical sieve; and 400g silica was obtained.

Then using 6 normal hydrochloric acid; it was refluxed by stirring for 5 hours; and after that; it was rinsed with hot water several times so as to remove the acid. Then using a mechanical mill the silica gel changed into powder once more. mixed with 2 normal sodium hydroxide; it was stirred continuously for two days with a constant magnetic stirrer. The mixture; then; changed into a solution. following complete dissolution of silica; sulfuric acid was added to it Drop by drop in order to neutralize it. as a result; silica gel was rinsed by distilled hot water again and again. rinsing continued non-stop for 12 days; and then the product was completely dried in vacuum oven at 60 c for 4 days. the prepared silica was crushed by 120 mesh with a mechanical mill and then it was collected. Sealed in a container to be used.to modifies the surface;10g Nano silica particles were mixed with 10 ml of each silica acid derivations separately and then;100 ml dried to loin was added to the mixture. They were mixed using a magnetic stirrer for half an hour. then the product formed was centrifuged for 30 minutes. These products were rinsed by dried to loin 3 times and the resulting sediment was dried in vacuum oven at 160 c for 10 hours. the products are modified Nano silica.

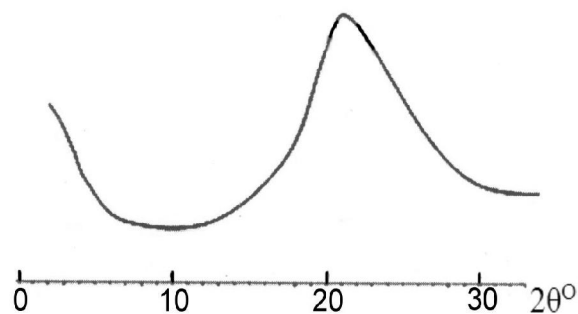
#### Conclusions and Discussions:

To investigate the size of Nano silica particles; transmitting electron microscopy (**TEM**) was used.fig.1 shows the picture of Nano silica particles tem. You can see that Nano silica particles are uniform and spherical; and their dimensions' are less than 60 nanometers. The obtained density(p)was  $1.2g/cm^3$  While its initial density was  $0.7g/cm^3$ .



**Fig.1 - Picture of a Nano silica particles tem (1cm=60nm).**

In order to determine the geometry and size of Nano silica particles crystals;(XRD)technique was used. in (fig.2);the diffraction model of silica nanoparticles is displayed.(XRD)spectrum was investigated using nickel filter and (cuka) radiation (with  $\lambda=1.5418$ )and with 50 KV and 40 ma and with step increase by 20 at %2 degree. Given the index of the variable coefficients( $H=2;K=0;L=3$ );peak width at half height (FWHM = $3/14$ );diffraction angle of 2 degrees; and using shrayder equation; the distance between the crystal plates of silica particles( $4/08$ )angstrom; its Nano crystal size ( $2/6$  nm)is obtained.

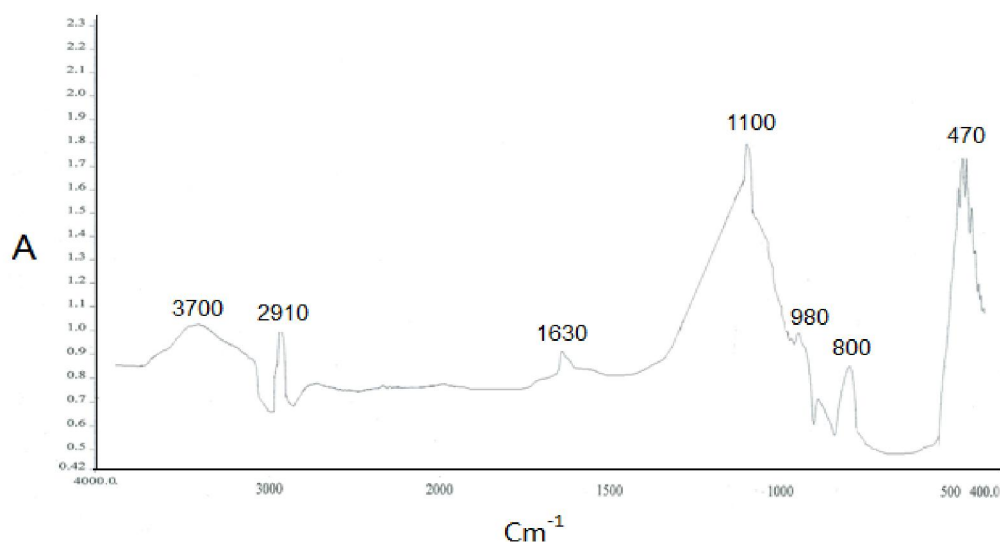


**Fig. 2 -x-ray diffraction (XRD) spectrum of a Nano silica sample**

OH groups available in Nano silica are polar; on the other hands; since most polymer composites are non-polar groups; in order to adjust Nano silica onto the polymers and composites; first of all the Nano silica surface was modified with silanolic groups (pairing up). Then the modified Nano silica which has nearly taken a non-polar from can be adjusted with non-polar polymer composites. To identify the binds of OH groups of the surface of Nano silica in clouding propyl trim ethyl Silone; vinyltrise; 2-methoxyethoxysilane and  $\delta$  -amino propyl trime

thoxysilane; (FT-IR) spectroscopy was used. Checking out the (FT-IR)spectroscopy of Nano silica sample in (fig. 3) shows that out of  $4000\text{ cm}^{-1}$ ;  $3000$  is related to hydroxyl groups. it shows the bending vibration of (Si-O-Si) at  $\text{cm}^{-1}$ ;  $470$ ; the stretching vibration of (Si-O-Si) and (Si-OH) with sharp and wide peaks in  $800$  and  $1100\text{ cm}^{-1}$ . studying the spectrum of Nano silica modified with derivation of

silica acid shows the following vibrations: C-H ( $1390$ ;  $3460\text{ cm}^{-1}$ ); N-H ( $1650\text{ cm}^{-1}$ ); C=C ( $3710$ ;  $1720\text{ cm}^{-1}$ ). By Analyzing the spectroscopy obtained we can make sure that amino silanole groups are bound to unsaturated vinyl group and silica acid derivations.



**Fig. 3-(FT-IR)spectrum of the Nano silica sample.**

All the groups selected for modification of Nano silica surface have the following two specific characteristics:

- 1- they have a (Si-O) covalent group in their hybrid structure which shows more readiness to form Si-O-Si hybrids.
- 2- the other side of silanolic groups selected is almost polar and these groups while pairing up on Nano silica; produce a matter which is consistent with polymer compounds (usually non-polar) and composites. the mechanism of the modifying linkage can be seen in fig 4.

Fig. 5 shows the results of differential thermogravimetric analysis (TGA) of Nano silica before and after the linkage. The initial weight loss between  $100$  and  $150\text{ }^{\circ}\text{C}$  is related to the loss of the absorbed moisture by Nano silica particles; which are  $5\%$  for the initial Nano silica; however it is  $2-3\%$  percent for bound Nano silica. Since these particles are Nano-sized; they have a large contact area; so they easily absorb the moisture of their environment. As it is seen in (fig.5); the bound Nano silica tends to absorb less moisture compared to unbound Nano silica; which may indicate the fact that Nano silica surface hydroxyl are bound by silanole groups (acid silicic derivations). thus; they have less tendency to absorb moisture. another weight loss can be seen at  $310-550\text{ }^{\circ}\text{C}$  which is related to the decomposition and destruction of the organic materials bound onto Nano silica particles. There can be seen little difference in decomposition start point due to the changes in the structure of linked (hybrid) matters. above  $520$  to  $600\text{ }^{\circ}\text{C}$ ; weight loss is not seen; in other words; above  $520\text{ }^{\circ}\text{C}$  the compound would lose its whole organic sample and only the mineral matter is left.

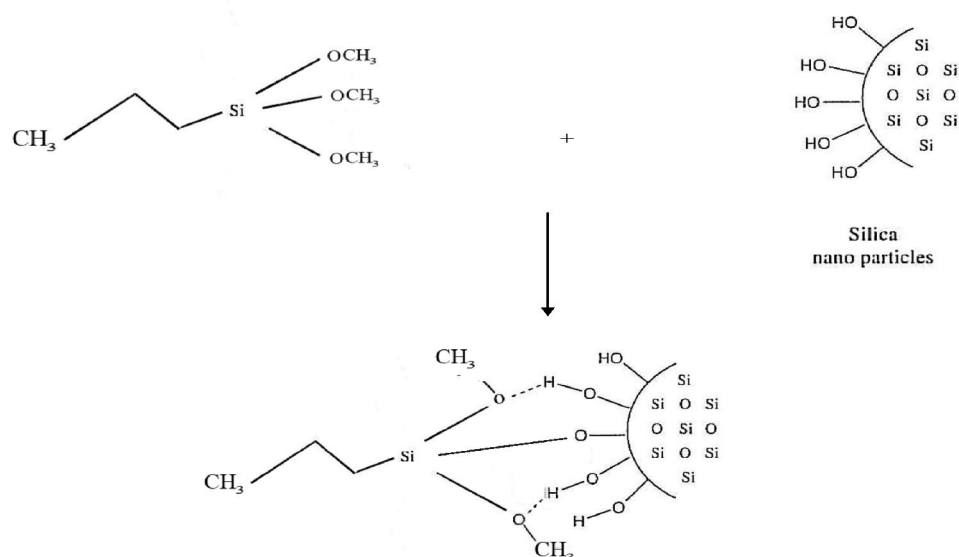
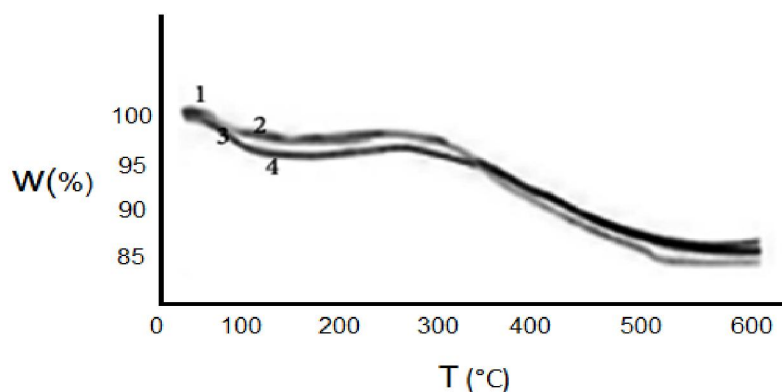


Fig. 4 - The mechanism of modifying propyl trim methoxysilane linkage on Nano silica.



- 1-nanosilica modified with  $\delta$ - amino propyl trim ethoxysilane
- 2-nanosilica modified with vinyltri (2-methoxyethoxy) silane
- 3-nanosilica modified with propyl trim ethoxysilane
- 4-unmodified Nano silica

Fig. 5-Investigating differential thermo gravimetric analysis (TGA) of modified and unmodified Nano silica

### Conclusion

Nano silica by sol-gel technique was prepared with high efficiency and nearly-uniform spherical Particles in demotions less then 60nm.its physical properties were studied using transmission elect on microscopy (TEM) and X-ray diffraction (XRD).the

surface of these no particles was modified with 3 types of paring up silanolic factors derived from silicic acid propyl etrimethoxysilane (C<sub>6</sub>H<sub>16</sub>O<sub>3</sub>Si), vinyltris 2-methoxyethoxysilane (C<sub>6</sub>H<sub>17</sub>O<sub>3</sub>N),  $\delta$ -amino propyl trim ethylSilane (C<sub>6</sub>H<sub>17</sub>O<sub>3</sub>N)the studies on (FT-IR) spectroscopy and Tga thermal analysis confirms the

linkage of silanolic compounds on the surface of Nano silica particles. And hydrophilic surface of silica nanoparticles was modified to be consistent enough with hydrophobic polymers such as olefins; and can prepare a Nano composite having better physical and mechanical properties.

#### References:

1. Pavlidou S. and Papaspyrides C.D., A Review on Polymer-layered Silicate anocomposites, *Prog. Polym. Sci.*, **33**, 1119–1198, 2008.
2. Choi Y., Lee S., and Ryu S., Effect of Silane Functionalization of Montmorillonite on Epoxy/Montmorillonite Nanocomposite, *Polym. Bull.*, **63**, 47–55, 2009.
3. Soon K., Jones E.H., Rajeev R.S., Menary G., Martin P.J., and Armstrong C.G., Morphology, Barrier, and Mechanical Properties of Biaxially Deformed Poly(ethylene terephthalate)-Mica Nanocomposites, *Polym. Eng. Sci.*, **52**, 532–548, 2012.
4. Leszczyńska A., Njuguna J., Pielichowski K., and Banerjee J.R., Polymer/Montmorillonite Nanocomposites with Improved Thermal Properties: Part I. Factors Influencing Thermal Stability and Mechanisms of Thermal Stability Improvement, *Thermochim. Acta*, **453**, 75–96, 2007.
5. Leszczyńska A., Njuguna J., Pielichowski K., and Banerjee J.R., Polymer/Montmorillonite Nanocomposites with Improved Thermal Properties: Part II. Thermal Stability of Montmorillonite Nanocomposites based on Different Polymeric Matrixes, *Thermochim. Acta*, **454**, 1–22, 2007.
6. Pesetskii S.S., Bogdanovich S.P., and Myshkin N.K., Tribological Behavior of Nanocomposites Produced by the Dispersion of Nanofillers in Polymer Melts, *J. Fric. Wear*, **28**, 457–475, 2007.
7. Bhat G., Hegde R.R., Kamath M.G., and Deshpande B., Nanoclay Reinforced Fibers and Nonwovens, *J. Eng. Fiber Fabric*, **3**, 22–34, 2008.
8. Njuguna J., Pielichowski K., and Desai S., Nanofiller-Reinforced Polymer Nanocomposites, *Polym. Adv. Technol.*, **19**, 947–959, 2008.
9. Xanthos M., *Functional Fillers for Plastics*, Wiley, Weinheim, 2005.
10. Chung S.C., Hahn W.G., and Im S.S., Poly(ethylene terephthalate) (PET) Nanocomposites Filled with Fumed Silicas by Melt Compounding, *Macromol. Res.*, **10**, 221–229, 2002.
11. Zhang X., Tian X., Zheng J., Yao X., Liu W., Cui P., and Li Y., Relationship between Microstructure and Tensile Properties of PET/Silica Nanocomposite Fibers, *J. Macromol. Sci. Phys.*, **47**, 368–377, 2008.
12. Zhang M.Q., Rong M.Z., Zhang H.B., and Rich K.F., Mechanical Properties of Low Nano-Silica Filled High Density Polyethylene Composites, *Polym. Eng. Sci.*, **43**, 490–500, 2003.
13. Aso O., Eguiazabal J.I., and Naza'bal J., The Influence of Surface Modification on the Structure and Properties of a Nanosilica Filled Thermoplastic Elastomer, *Compos. Sci. Technol.*, **67**, 2854–2863, 2007.
14. Zhang L., Tam K.C., Gan L.H., Yue C.Y., Lam Y.C., and Hu X., Effect of Nano-Silica Filler on the Rheological and Morphological Properties of Polypropylene/Liquid-Crystalline Polymer Blends, *J. Appl. Polym. Sci.*, **87**, 1484–1492, 2003.
15. Rong M.Z., Zhang M.Q., Pan S.L., Lehmann B., and Friedrich K., Analysis of the Interfacial Interactions in Polypropylene/Silica Nanocomposites, *Polym. Int.*, **53**, 176–183, 2004.
16. Parvinzadeh M., Moradian S., Rashidi A., and Yazdanshenas M.E., Surface Characterization of Polyethylene Terephthalate/Silica Nanocomposites, *Appl. Surf. Sci.*, **256**, 2792–2802, 2010.
17. Guyard A., Persello J., Boisvert J.P., and Cabane B., Relationship between the Polymer/Silica Interaction and Properties of Silica Composite Materials, *J. Polym. Sci., Polym. Phys.*, **44**, 1134–1146, 2006.

3/2/2014