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# Enhancing Surface Properties of Fumed Silica via APTMS Functionalization: A Comprehensive Characterization Study

**Savita Meena**

Department of Chemistry, M.S.J. Government P.G. College, Bharatpur 321001, Rajasthan, India
Corresponding author Email: *savita.iitd[at]gmail.com*
Authors ORCID iD: https://orcid.org/0000-0003-1238-7946

**Abstract:** ***Surface modification of fumed silica was achieved by using condensation reaction between surface silanol groups and 3-aminopropyltrimethoxysilane (APTMS) in acetone, leading to enhanced particle dispersion and reduced agglomeration. The functionalization process introduced 3-aminopropyl groups onto the silica surface through a co-condensation mechanism in the presence of a solvent. The modified nanosilica exhibited improved stability in comparison to unmodified fumed silica, which contains only surface hydroxyl groups. Successful chemical functionalization and modifications in surface chemistry were confirmed by Fourier-transform infrared spectroscopy (FT-IR). Particle stability and dispersion behavior were evaluated using zeta potential measurements, atomic force microscopy (AFM), and scanning electron microscopy (SEM). The results demonstrated that APTMS modification effectively tailored the surface properties of nanosilica, contributing to better dispersion and reduced aggregation.***

**Keywords:** Fumed silica; 3-aminopropyltrimethoxysilane; FT-IR; AFM; SEM

## 1. Introduction

Fumed silica, a nanostructured form of silicon dioxide, has garnered significant attention as a multifunctional additive in various industrial applications due to its ultrafine particle size, high specific surface area, and high purity [1,2]. It is generally synthesized via flame hydrolysis of chlorosilanes, such as silicon tetrachloride, in a hydrogen-oxygen atmosphere, yielding in amorphous silica nanoparticles along with hydrogen chloride as a byproduct [3]. The resulting material exhibits unique physicochemical properties that make it a highly effective reinforcing agent in polymer matrices, particularly in applications demanding enhanced mechanical strength, thermal stability and tailored rheological behaviour [4].

Fumed silica is widely used across numerous industries such as adhesives, sealants, coatings, composites, epoxy resins, polyurethanes, acrylics, and cyanoacrylates [5]. Beyond these, nanosilica also plays an important role in areas like catalysis,[6] greenhouse application [7], flexible substrates [8], insulative materials [9] and emerging biomaterials [10]. However, the broader application of fumed silica in organic syntheses is limited by its inherently hydrophilic surface due to a high concentration of surface silanol groups. This hydrophilicity impairs dispersion in non-polar media and promotes particle agglomeration, ultimately diminishing the performance of resulting composite materials [11,12].

To address these challenges, surface modification has emerged as a critical strategy to enhance the compatibility of fumed silica with hydrophobic polymer matrices. Such modifications improve dispersion, suppress agglomeration and contribute to the overall enhancement of composite performance in non-polar environments [13-15]. A range of chemical treatments has been explored to modify the surface of fumed silica, including the application of alcohols [16], surfactants [17], titanates and silane coupling agents [18,19]. Among these, organofunctional silanes stand out for their effectiveness, attributed to their bifunctional design. One functional group reacts through condensation [20] with hydroxyl groups on the silica surface, while the other is engineered to interact with the surrounding polymer matrix. This dual functionality enhances interfacial compatibility and promotes better dispersion in hydrophobic systems.

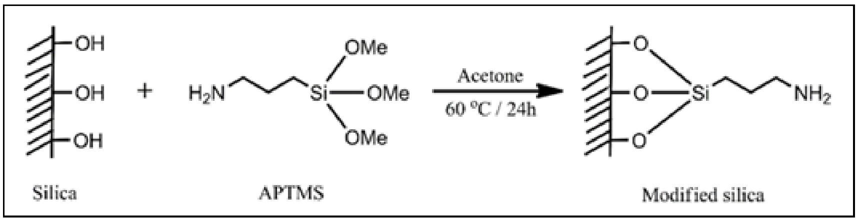
Organofunctional silanes are extensively used to tailor the surface properties of fillers, particularly those bearing hydroxyl groups. Among these, amino silane coupling agents are frequently utilized for effective surface modification. APTMS modifies the silica surface by forming stable Si–O–Si bonds in the presence of a polar medium like acetone, converting hydrophilic surfaces into hydrophobic ones [21]. This modification enhances silica dispersion in polymers, minimizes filler-filler interactions and introduces functional groups that facilitate covalent or physical interactions with matrix materials [22].

Additionally, such functionalized silica can be utilized in fluorescent tagging or as pigment-coupling agents, expanding its utility in specialty formulations [23]. In summary, surface modification of fumed silica is essential for enhancing its integration into silica-reinforced hydrophobic polymer systems. The performance improvements resulting from surface-modified silica have been well-documented in polymer composites [5, 24, 25].

In the present study, surface modification of nanosilica was carried out using APTMS through a condensation reaction with surface silanol groups in an acetone medium. Successful surface functionalization and chemical modification were confirmed by FT-IR. Additionally, AFM, SEM and zeta potential analysis were employed to evaluate morphological changes and dispersion behavior.

## 2. Experimental

### 2.1 Materials



**Scheme 1:** Chemical reaction of surface modification of silica

The solvents acetone was purified and dried or distilled using well known standard procedures [26] and kept in a glove-box for all chemical reactions. This study employs HDK N-20, hydrophilic fumed silica in the form of an odorless white powder. It possesses a particle size in the 100–500 nm range, along with high surface area and purity. The material exhibits a pH of 3–4.5, high melting (1700 °C) and boiling (2230 °C) points, and is insoluble in water. APTMS is silane coupling agent obtained from sigma Aldrich, Germany, having molecular weight of 179.29 and density of 1.027gm/ml.

### 2.2 General Measurements and Characterization

The silica dispersions obtained by the sol-gel method were investigated in order to determine the size of the particles, the stability and the film forming ability. Fourier transform infrared (FT-IR) spectra of fumed silica and modified silica particles were recorded on Thermo Scientific Nicolet 6700 FT-IR spectrometer in spectral range of 4000-450 $cm^{-1}$. Samples of unmodified silica and modified silica particles samples were dried at room temperature and characterized (by preparing disk with dried KBr) as powders. Surface morphology of unmodified and modified silica surface was investigated using scanning electron microscopy (SEM, Zeiss EVO-50) by preparing silica thin film in compression molding at 260°C. Dynamic Light Scattering (DLS) measurements were carried out using a Malvern Zetasizer Nano ZS25 instrument at 25 °C, with an equilibration time of 2 minutes. Measurements were performed in standard glass cuvettes. The zeta potential or overall surface charge of nanoparticle samples in solution (~1 mg/ mLin Millipore water) was determined using a Zeta Plus, zeta potential analyzer. For these measurements, siica nanoparticle suspensions were prepared in Millipore water at a concentration of approximately 1 mg/mL. Surface morphology of active layers (unmodified and modified silica surface) was investigated through atomic force microscopy (AFM) in tapping mode under ambient conditions using Nanoscope Bruker icon dimension with scan Asyst.

### 2.3 Surface Modification of Fumed Silica

The surface modification of silica was performed in the liquid phase using APTMS as a coupling agent, with concentrations ranging from 1 wt% to 4 wt% relative to the silica content. The process involved a condensation reaction between the silica nanoparticles and varying compositions of APTMS, carried out in a round-bottom flask fitted with a mechanical stirrer and a thermometer. A solution of APTMS in acetone was added dropwise to the silica nanoparticles under vigorous mechanical stirring, followed by reflux at 60 °C for 24 hours. During this process, the $Si(OMe)_3$ groups react with the silica surface, leading to its functionalization [27]. The modification reaction is illustrated in **Scheme 1**. Afterward, the resulting modified silica slurry was stored in desiccators for 2–3 days to allow complete removal of the acetone solvent. Following the surface modification of the silica nanoparticles, their chemical structure and the interactions of polar groups on the modified surface were examined using FT-IR spectroscopy, in agreement with reported literature [28]. The surface morphology was further evaluated through particle size analysis, SEM and AFM.

## 3. Result and Discussion

### 3.1 Fourier Transform Infrared Spectrometry (FT-IR)

The FT-IR spectroscopy was employed to characterize the surface chemistry of fumed silica before and after modification with APTMS. For analysis, the dried samples were mixed with KBr and compressed into thin pellets. **Figure 1** presents the FT-IR spectra of unmodified silica, APTMS silane coupling agent, and the APTMS modified silica.

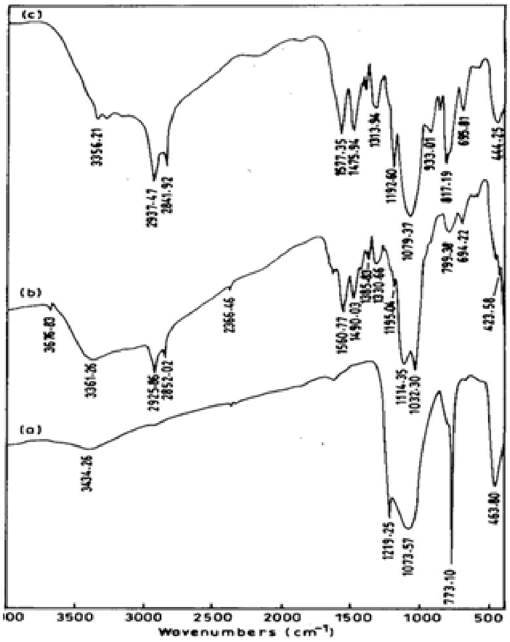


**Figure 1:** FT-IR spectra of (a) Unmodified silica (b) Modified silica (c) APTMS

A comparative analysis of these spectra verifies that the silica surface was successfully modified through covalent bonding with APTMS. The FT-IR spectrum of the APTMS functionalized silica nanoparticles exhibit characteristic absorption bands that confirm effective surface modification. The strong and broad band appearing in the range of 1022–1114 $cm^{-1}$ is associated with the asymmetric stretching vibrations of Si–O–Si, whereas the peak at 799 $cm^{-1}$ corresponds to the symmetric stretching mode of Si–O–Si [27]. Comparing the FT-IR spectra of both modified silica and unmodified silica alongside pure APTMS reveals the appearance of new absorption bands at 2925 and 2852 $cm^{-1}$, which suggest the successful amine functionalization of the nanoparticles. A prominent band at 2926.86 $cm^{-1}$ corresponds to the C–H stretching vibrations of the propyl chain, while the peak at 3361.26 $cm^{-1}$ is attributed to N–H stretching vibrations of the terminal amine ($-NH_2$) group. Additionally, a band at 1577.36 $cm^{-1}$ is assigned to N–H bending vibrations. These bands are absent in the spectrum of unmodified silica, confirming the presence of APTMS on the silica surface. The appearance of asymmetric and symmetric $-CH_2$ stretching vibrations on the modified silica surface further supports the grafting of aminopropyl groups from APTMS onto the silica nanoparticles. The presence of these characteristic vibrational bands confirms the covalent attachment of APTMS to the silica surface through condensation reactions with surface silanol groups. Surface modification incorporates amino and alkyl functional groups onto the silica, which play a key role in enabling further interactions and expanding the potential applications of the functionalized silica nanoparticles.

### 3.2 Particle Size Distribution and Stability Analysis

The particle size distribution of both unmodified and modified silica particles was determined using a Malvern Zetasizer based on dynamic light scattering. Measurements were carried out on aqueous dispersions, with each sample diluted in distilled water prior to analysis. The reported particle sizes correspond to the average values obtained from three independent measurements for each sample (**Table 1**). Unmodified silica particles showed a Z-average diameter of about 291 nm along with a high polydispersity index (PDI), indicating a broad size distribution and non-uniformity.

**Table 1:** Particle size distribution of unmodified and modified silica surface

| *S. No.* | Silica | PDI | Z-Average |
|---|---|---|---|
| 1 | Unmodified | 0.249 | 291 nm |
| 2 | APTMS Modified (1 wt%) | 0.554 | 1214 nm |
| 3 | APTMS Modified (4 wt%) | 0.574 | 6345 nm |

Dynamic light scattering analysis results for the modified silica particles revealed an increase in Z-average diameter band a higher intensity percentage, suggesting a narrow particle size distribution largely within the nanometer scale. Among the samples, silica particles functionalized with APTMS exhibited the highest Z-average and intensity values, implying that surface modification increases particle size, most likely due to agglomeration of silica aggregates, which in turn raises the overall hydrodynamic diameter [21]. Despite this increase, the narrow PDI suggests a uniform particle size distribution, confirming that the modified silica particles remain relatively monodisperse even after functionalization (**Figure 2**).

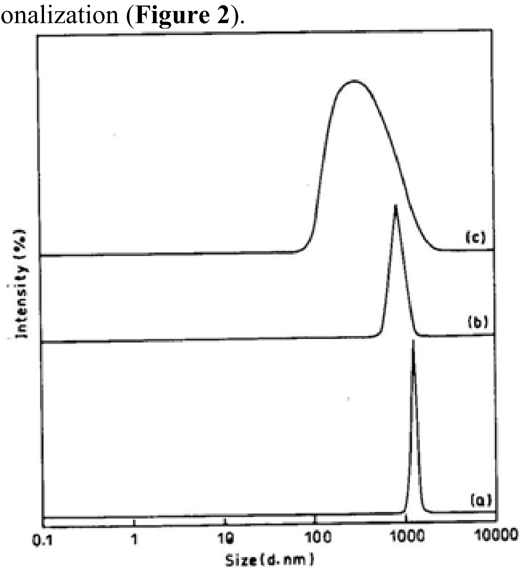


**Figure 2:** Silica particle distributions curve (a) silica modified by 4 wt% APTMS (b) Silica modified by 1 wt% APTMS (c) Unmodified silica

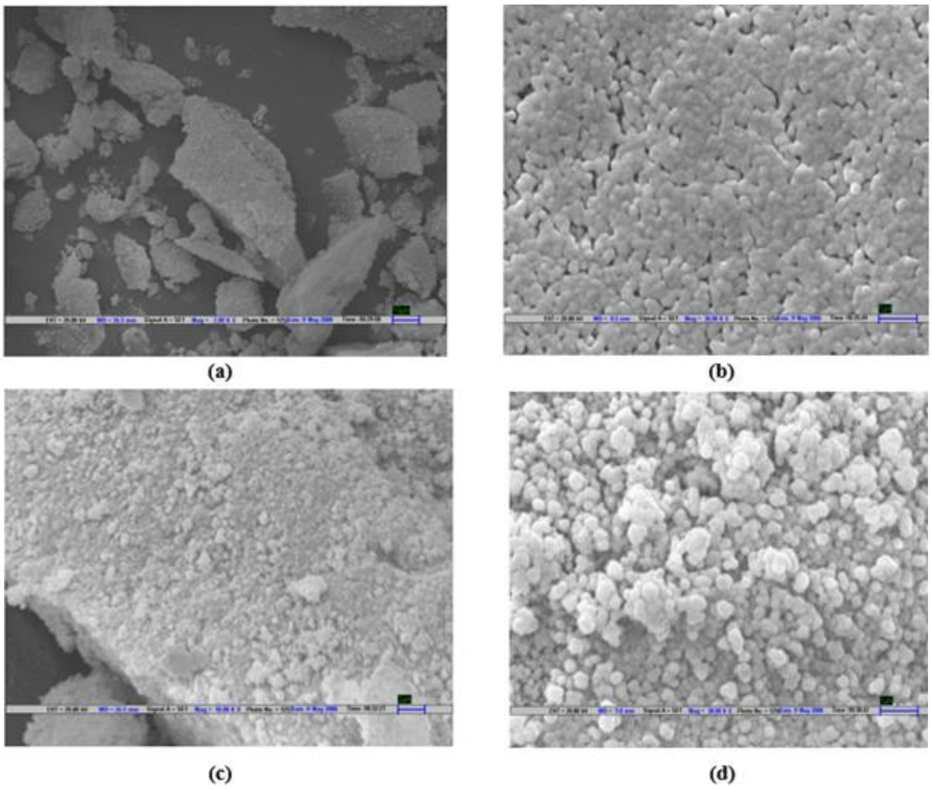
### 3.3 Scanning electron microscopy (SEM)

The SEM technique was employed to study the surface modification of both unmodified and APTMS modified silica nanoparticles in thin films. For SEM analysis, small pieces of the films were mounted onto carbon tape and allowed to dry before imaging under ambient conditions. The morphology of the silica nanoparticles, both before and after surface modification, was examined to verify successful functionalization. As shown in **Figure 3**, the unmodified silica nanoparticles are approximately 300 nm in diameter and exhibit a predominantly spherical shape with smooth surfaces and minimal agglomeration, suggesting good dispersion [20]. In contrast, the APTMS-modified silica particles exhibit increased average diameters of about 500 nm and show clear signs of agglomeration.

This agglomeration behaviour is attributed to the presence of aminopropyl groups from APTMS on the fumed silica surface, which facilitates hydrogen bonding and van der Waals forces between adjacent particles [21]. The formation of these aggregates is a strong indication of successful surface modification. The observed morphological differences between the unmodified and modified silica particles further confirm the occurrence of surface modification. Overall, the SEM analysis indicates that APTMS has been successfully grafted onto the silica surface, leading to altered particle interactions and dispersion behavior.

### 3.4 Atomic Force Microscopy (AFM)

The AFM analysis was used to examine the surface morphology of silica films deposited on glass substrates through spin-coating. **Figure 4 (a & b)** and **Figure 5 (a & b)** display the topographical and three-dimensional (3D) AFM images, respectively, for both unmodified and APTMS



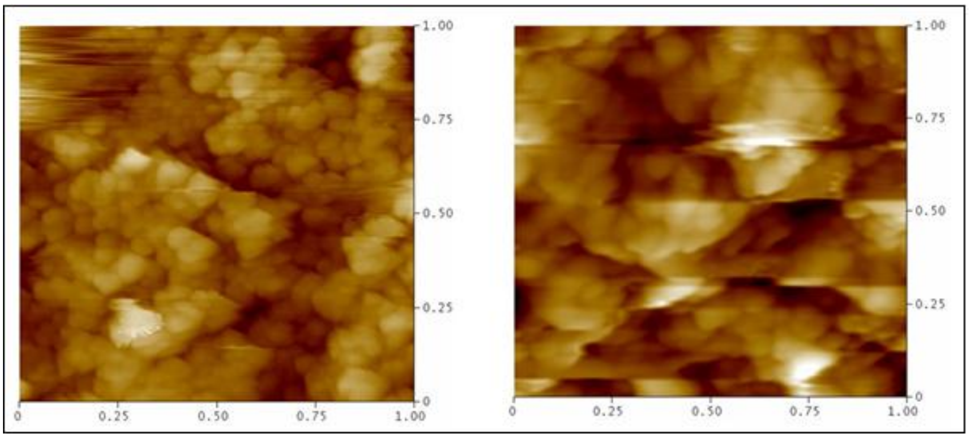
(a) (b) (c) (d)

**Figure 3:** Scanning electron micrograph of unmodified (a & b) and modified (c & d) silica surface by APTMS

modified silica surfaces. **Figure 4** illustrates the surface morphology and particle distribution, while **Figure 5** presents 3D surface profiles, clearly showing changes in surface roughness and texture after APTMS functionalization.

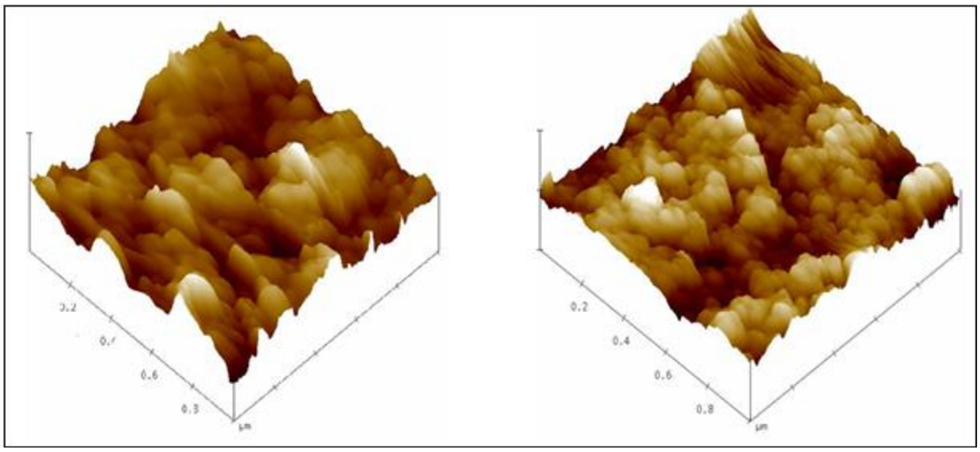
To evaluate the surface morphology in greater detail, high-resolution scans were performed over smaller areas, and the root mean square (RMS) surface roughness was measured. As shown in **Figure 4a**, the unmodified silica surface comprises of nanoscale particles that exhibit significant agglomeration while remaining uniformly distributed across the surface. The particles size is within the nanometer range, and their aggregation contributes to a relatively rough surface, with a measured RMS roughness of 48.77 nm. This roughness arises from the intrinsic tendency of unmodified silica nanoparticles to aggregate due to high surface energy and intermolecular interactions. In contrast, APTMS modified silica surface showed noticeable changes in surface topography. The AFM image of APTMS modified sample (**Figure 4b**) reveals an increase in surface roughness and particle size, indicating that surface modification alters the microstructure of the silica film. Notably, at a higher APTMS concentration (4 wt%), the surface roughness increased significantly to 59.99 nm. This pronounced rise in roughness indicates the formation of an organosilane layer on the silica surface, likely resulting from a condensation reaction between surface silanol groups and APTMS molecules [29]. Furthermore, the elevated roughness following APTMS treatment may be attributed to the formation of a monolayer or even a partial multilayer of the silane coupling agent. This structural modification supports the occurrence of a successful surface reaction, confirming the chemisorption of APTMS onto the silica surface. This modification not only alters the topography but also impacts the surface chemistry and potential functionality of the silica film. Quantitatively, the surface roughness of the APTMS-modified silica (4 wt%) is approximately 23% higher than that of the unmodified silica, demonstrating the effect of surface treatment on nanoscale morphology.

These observations are in agreement with previous reports on silane-functionalized silica surfaces [29], where the introduction of organosilanes leads to changes in both topography and surface chemistry. Overall, the AFM analysis confirms the successful surface modification of silica with APTMS, as evidenced by the increased surface roughness and changes in particle distribution and morphology, which indicate the formation of a silane layer through the condensation of APTMS molecules, thereby altering the nanostructure of the silica surface and potentially enhancing its interaction with surrounding media or matrix materials while providing a functionalized surface for further applications.



(a) (b)

**Figure 4:** AFM images of (a) unmodified silica surface (b) Silica surface modified by silane coupling agent



(A) (B)

**Figure 5:** AFM 3D image of (a) unmodified silica surface (b) Silica surface modified by silane coupling agent

## 4. Conclusion

Fumed silica was successfully functionalized using APTMS as a coupling agent, which was characterized by FT-IR spectrum. Their morphologies were studied by AFM, SEM and particle size distribution measurements. AFM images of both unmodified and modified silica particles reveal clear differences in particle size and surface roughness, with the modified silica exhibiting higher roughness and larger particle size. The use of APTMS as a coupling agent led to improved dispersion and reduced agglomeration of silica nanoparticles in the composites, resulting in enhanced overall properties. FT-IR analysis of the modified silica composite showed characteristic bands at 2925.86 cm$^{-1}$ (C–H stretching), 3361.26 cm$^{-1}$ (amine group), and 1560.77 cm$^{-1}$ (N–H bending), confirming successful surface functionalization. Furthermore, AFM and SEM analyses demonstrated that surface modification significantly improved particle stability and dispersion, while the increased roughness and particle size indicate the formation of a well-defined interphase layer, enhancing compatibility with the polymer matrix.

In conclusive, these results demonstrate that surface modification of silica using APTMS can significantly enhance the dispersion, morphology, and interfacial properties of polymer/silica composites, highlighting its potential to improve the performance of polymer nanocomposites in engineering applications.

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## References

[1] H. Barthel, L. Rösch, J. Weis, Fumed Silica - Production, Properties, and Applications, Organosilicon Chemistry Set, pp. 761-778, 2005.

[2] H. Barthel, M. Heinemann, M. Stintz, B. Wessely, "Particle Sizes of Fumed Silica," Particle & Particle Systems Characterization, 16, 169-176, 1999.

[3] F. Yan, J. Jiang, X. Chen, S. Tian, K. Li, "Synthesis and Characterization of Silica Nanoparticles Preparing by Low-Temperature Vapor-Phase Hydrolysis of $SiCl_4$," Industrial & Engineering Chemistry Research, 53, 11884-11890, 2014.

[4] J.G. Croissant, C.J. Brinker, Chapter Eight - Biodegradable Silica-Based Nanoparticles: Dissolution Kinetics and Selective Bond Cleavage, in: F. Tamanoi (Eds.), The Enzymes, Academic Press, pp. 181-214, 2018.

[5] K.-M. Kim, H. Kim, H.-J. Kim, "Enhancing Thermo-Mechanical Properties of Epoxy Composites Using Fumed Silica with Different Surface Treatment," Polymers, 13, 2691, 2021.

[6] Pratibha, J. K. Rajput, 10 - Application of silicon-based hybrid nanoparticles in catalysis, in: S. Thomas, T.A. Nguyen, M. Ahmadi, G. Yasin, N. Joshi (Eds.), Silicon-Based Hybrid Nanoparticles, Elsevier, pp. 199-246, 2022.

[7] M.A. Alghdeir, K. Mayya, M. Dib, Nanosilica Composite for Greenhouse Application, in: T.-D. Ngo (Eds.), Composite and Nanocomposite Materials - From Knowledge to Industrial Applications, IntechOpen, Rijeka, 2020.

[8] E. Radu, D. Panaitescu, L. Andrei, F. Ciuprina, C.-A. Nicolae, R. Gabor, R. Trusca, "Properties of Polysiloxane/Nanosilica Nanodielectrics for Wearable Electronic Devices," Nanomaterials, 12, 95, 2021.

[9] H.F. Gangåssæter, B.P. Jelle, S.A. Mofid, "Synthesis of Silica-Based Nano Insulation Materials for Potential Application in Low-Energy or Zero Emission Buildings," Energy Procedia, 122, 949-954, 2017.

[10] E. Bourgeat-Lami, P. Espiard, A. Guyot, "Poly(ethyl acrylate) latexes encapsulating nanoparticles of silica: 1. Functionalization and dispersion of silica," Polymer, 36, 4385-4389, 1995.

[11] C.P. Whitby, "Structuring Edible Oils With Fumed Silica Particles," Frontiers in Sustainable Food Systems, 4, 585160, 2020.

[12] A. Kawamura, C. Takai, M. Fuji, T. Shirai, "Effects of Water Adsorption on Dispersibility of Fumed Silica in Mixed Organic Solvents of Ethanol and Hexane," Journal of the Society of Powder Technology, Japan, 48, 755-760, 2011.

[13] A.Y. Fadeev, Y.V. Kazakevich, "Covalently Attached Monolayers of Oligo(dimethylsiloxane)s on Silica: A Siloxane Chemistry Approach for Surface Modification," Langmuir, 18, 2665-2672, 2002.

[14] I. Protsak, E. Pakhlov, V. Tertykh, Z.-C. Le, W. Dong, "A New Route for Preparation of Hydrophobic Silica Nanoparticles Using a Mixture of Poly(dimethylsiloxane) and Diethyl Carbonate," Polymers, 10, 116, 2018.

[15] W.A. Daoud, J.H. Xin, X. Tao, "Synthesis and characterization of hydrophobic silica nanocomposites," Applied Surface Science, 252, 5368-5371, 2006.

[16] T. Jesionowski, A. Krysztafkiewicz, "Properties of Highly Dispersed Silicas Precipitated in an Organic Medium," Journal of Dispersion Science and Technology, 20, 1609-1623, 1999.

[17] A. Krysztafkiewicz, B. Rager, "Hydrated silicas modified by nonsilane pro-adhesion compounds," Journal of Adhesion Science and Technology, 13, 393-415, 1999.

[18] K.L. Mittal, Silanes and Other Coupling Agents, Volume 4 (1st ed.), CRC Press, London, 2007.

[19] E.F. Vansant, P. Van Der Voort, K.C. Vrancken, Characterization and chemical modification of the silica surface, Elsevier Science, Volume 93 (1st ed.), 1995.

[20] B. Arkles, J. Steinmetz, J. Zazyczny, P. Mehta, "Factors Contributing to the Stability of Alkoxysilanes in Aqueous Solution," Journal of Adhesion Science and Technology, 6, 193-206, 1992.

[21] T. Kang, I. Jang, S.-G. Oh, "Surface modification of silica nanoparticles using phenyl trimethoxy silane and their dispersion stability in N-methyl-2-pyrrolidone," Colloids and Surfaces A: Physicochemical and Engineering Aspects, 501, 24-31, 2016.

[22] P.S. Chinthamanipeta, S. Kobukata, H. Nakata, D.A. Shipp, "Synthesis of poly (methyl methacrylate)–silica nanocomposites using methacrylate-functionalized silica nanoparticles and RAFT polymerization," Polymer, 49, 5636-5642, 2008.

[23] T. Kondo, W.J. Chen, G.S. Schlau-Cohen, "Single-molecule fluorescence spectroscopy of photosynthetic systems," Chemical Reviews, 117, 860-898, 2017.

[24] I. Mora-Barrantes, A. Rodríguez, L. Ibarra, L. González, J.L. Valentín, "Overcoming the disadvantages of fumed silica as filler in elastomer composites," Journal of Materials Chemistry, 21, 7381-7392, 2011.

[25] K. Rishi, L. Pallerla, G. Beaucage, A. Tang, "Dispersion of surface-modified, aggregated, fumed silica in polymer nanocomposites," Journal of Applied Physics, 127, 174702, 2020.

[26] B.S. Furniss, A.J.H. Hannaford, P.W.G. Smith, A.R. Tatchell, Vogel's Textbook of Practical Organic Chemistry, 5th ed., ELBS, Longman Group, London, 1989.

[27] H.-T. Lu, "Synthesis and characterization of amino-functionalized silica nanoparticles," Colloid Journal, 75, 311-318, 2013.

[28] S.S. Shafqat, A.A. Khan, M.N. Zafar, M.H. Alhaji, K. Sanaullah, S.R. Shafqat, S. Murtaza, S.C. Pang, "Development of amino-functionalized silica nanoparticles for efficient and rapid removal of COD from pre-treated palm oil effluent," Journal of Materials Research and Technology, 8, 385-395 2019.

[29] S.A. Kulkarni, S.B. Ogale, K.P. Vijayamohanan, "Tuning the hydrophobic properties of silica particles by surface silanization using mixed self-assembled monolayers," Journal of Colloid and Interface Science, 318, 372-379, 2008.