

Investigation on Silane Concentration of SiO₂ Nanoparticle: FTIR Analysis

Huei Ruey Ong^{a,*}, Wan Mohd Eqhwan Iskandar^a, Jason Chong^a, Md. Maksudur Rahman Khan^b, Thai Kiat Ong^c, Beng Kooi Chua^d

^aFaculty of Engineering & Technology, DRB-HICOM University of Automotive Malaysia, Peramu Jaya Industrial Area, 26607, Pekan, Pahang, Malaysia

^bPetroleum and Chemical Engineering Programme area, Universiti Teknologi Brunei, Gadong, Brunei Darussalam

^cFaculty of Engineering and Technology, Tunku Abdul Rahman University of Management and Technology, Jalan Genting Kelang, Setapak, P.O. Box 10979, 50932, Kuala Lumpur, Malaysia

^dOperation Department, Mr. Packaging Sdn. Bhd., Lot PTD 10633 HS(D) 33688 Jalan Kempas 1, Off Kempas 5, Kawasan Perindustrian Bukit Bakri, 84200 Muar, Johor, Malaysia
roi_rui86@hotmail.com

Conventionally, silica (SiO₂) nanoparticle having a great potential as filler in many composites especially in plastic making. However, SiO₂ nanoparticle is not suitable to be mixed with the plastic due to its hydrophilic properties. Surface functionalization of nanoparticle would become a great potential to overcome the issue by proposing triethoxyvinylsilane (TVS) as a silane coupling agent to functionalize the surface of SiO₂. TVS can assist in tailoring the hydrophilic properties into hydrophobic which can further enhance SiO₂ properties. In this study, TVS has been prepared with various concentration to functionalize the surface of SiO₂ nanoparticle. SEM and FTIR has been conducted to study the morphology and determine the functional group of the SiO₂ nanoparticle. Findings shows that the size SiO₂ nanoparticle were in range the range of 100 nm and visualize the hierarchical microstructure showing the silane has successfully embedded on the surface of nanoparticle. Apart from that, new peak appearance at peak 2,975 cm⁻¹ and 1,089 cm⁻¹ confirms the successful grafting of TVS on the surface of SiO₂ nanoparticle. Furthermore, FTIR peak shift was investigated and found that the SiO₂ with 5 % TVS exhibit highest peak shift at 1,141 cm⁻¹ with respect to SiO₂ as spectrum at 1,089 cm⁻¹. These findings address the problem statement by demonstrating the successful surface modification of SiO₂ nanoparticle using TVS to tailor its hydrophilic properties to be hydrophobic.

1. Introduction

Inorganic and/or organic components are combined to form ultrafine particles known as nanoparticles, with a nano-sized ranging from 10 to 500 nm (Jeevanandam et al., 2018). Due to their distinctive characteristics, extensive study have been made and found useful in various applications such as automotive industries, chemistry materials and environmental testing, electronics industry including semiconductor, energy and biotechnology (Rudramurthy and Swamy, 2018). Among numerous types of nanoparticles, silica (SiO₂) nanoparticle has been widely used in many sectors such as biomedical (Singh et al., 2019), automotive (Bhattacharya et al., 2020), constructions (Lushinga et al., 2022) and supercapacitor applications (Li et al., 2018). However, synthesized nanoparticle normally will encounter common obstacle oxidation and rapid agglomeration that will limits of broadening their applications within some industries. To remedy this situation, surface functionalization of nanoparticle could enhance and prevents the addressed problems. The surface of the nanoparticle can be modified by adding a chemical functional group, which promotes self-organization, compatibility, and the potential for a wide range of applications (Kim, 2014). Atoms of chosen metals or metal oxides can have their surfaces modified by both organic and inorganic functional groups. This method not only stops nanoparticles from rusting and clumping together but also enables improved functionalization (Sun et al., 2014). By attaching to the surfaces of other molecules, solids, or nanoparticles, simple organic molecules or

groups provide sufficient potential defence for nanoparticles against agglomeration (Neouze and Schubert, 2008).

Recent nanoparticles were functionalized with the presence of silanes. The bonding between organic and inorganic materials can be strengthened by silane coupling agents. Extensive research has caught numerous of researcher to understand the bonding mechanism between silane coupling agent and the metal surface (Lambiase and Liu, 2022). Silanes are most commonly used to functionalize nanoparticles due to its advantages specifically in automotive applications (Vinodhini and Xavier, 2022). To the best of author's knowledge, there are limited studies on utilizing TVS silane coupling agent to functionalize the surface of SiO₂ nanoparticle. Hence, this study highlights the usage of TVS as a silane coupling agent to functionalize the surface of SiO₂ nanoparticle and to investigate the properties of the resulting composite. This study aims to enhance the properties of composites by tailoring the hydrophilic properties of SiO₂ nanoparticle into hydrophobic. The surface morphology, functional groups, and peak shift of the functionalized SiO₂ nanoparticle were evaluated using Scanning electron microscopy (SEM) and Fourier Transform Infrared Spectroscopy (FTIR).

2. Methodology

2.1 Materials

The SiO₂ were purchased from local supplier with a 99.8 % of purity. The coupling agent, Triethoxyvinylsilane (TVS) with a purity of 97% and all other chemical with analytical grade were purchased from PERMULA Chem. Sdn. Bhd.

2.2 Preparation of SiO₂ surface functionalized by TVS

A 100 mL of ethanol was adjusted by adding 0.1 vol% of acetic acid until pH 4 was achieved. Afterwards, different concentrations of TVS silane were prepared by adding various amounts of the silane to the ethanol-acetic acid solution with stirring at 500 rpm and heated at 30 °C for 90 mins using a magnetic stirrer hot plate. The concentration range used was 0-5 wt% with respect to the TVS silane concentration, while a fixed amount of 0.455 g of SiO₂ was added into the solution. The stirred samples were filtered by using 90 mm filter paper and washed with ethanol. Each of the samples were vacuum dried overnight at 65 °C to obtain functionalized SiO₂ nanoparticle. Table 1 provides information about the prepared samples.

Table 1: Details of samples for functionalized SiO₂ nanoparticle

Samples	SiO ₂ content (g)	NTVS content (g)
NTVS 0.5	0.455	0.5
NTVS 1.0	0.455	1
NTVS 1.5	0.455	1.5
NTVS 2.0	0.455	2
NTVS 2.5	0.455	2.5
NTVS 3.0	0.455	3
NTVS 3.5	0.455	3.5
NTVS 4.0	0.455	4
NTVS 4.5	0.455	4.5
NTVS 5.0	0.455	5

2.3 Samples characterization

Surface morphologies of the samples were characterized by using scanning electron microscopy (SEM). The platinum was coated on the samples using a sputter coater before conducted under SEM instrument. Fourier transform infrared spectroscopy (FTIR) (Model-Thermo scientific Nicolet 6700, Germany) were used to investigate the bonding structure, trends and peak shift involves in the samples. Bonding structure of the samples was analysed through FTIR analysis (Model-Thermo scientific Nicolet 6700, Germany). The wavenumber for testing were in the range of 4,000-400 cm⁻¹ and in accordance to standard potassium bromide pellet (KBr) method.

3. Results and discussions

3.1 Surface morphological study by SEM

Figure 1(a) reveals that the non-treated SiO₂ having the range size of approximately around 20 to 30 nm and are evenly distributed forming a smooth surface layer. The coating surface of non-treated SiO₂ reveals a porous silica nanoparticle and a lot of nanopores were visible on the surface structure. Meanwhile, Figure 1(b) showing

the TVS treated SiO₂ (NTVS) which reveals the modification of TVS grafted on the surface coating a complex hierarchical microstructure and showing a micro sponge shape. These microstructures formed on the surface comprise of huge nano pellets number with 100 nm of average diameter. The morphological structure is composed of a large number of interconnecting micro-domains that have nanoparticles agglomerated on them. Due to the formation of a porous micro-network with pore sizes between 500 nm and 2 μm as a result of this hierarchical microstructure, a significant volume of air can be trapped in the interspace. Hence, this observation suggests that NTVS has a high potential as a candidate for applications that require a material with high porosity and surface area. The formation of this hierarchical microstructure is attributed to the phase separation between SiO₂ and ethanol. As reported by Fujiwara et al. (2010) in their study on the preparation of hierarchical architectures of silica particles, ethanol acts as a bridging agent that induces phase separation between silica particles and creates a microphase-separated structure. During the TVS treatment process, the hydrophobic TVS molecules are grafted onto the surface of the SiO₂ particles, which further induces phase separation due to the repulsion between the hydrophobic TVS and the ethanol solvent. This phase separation results in the formation of the observed hierarchical microstructure in NTVS. Therefore, it is hypothesized that the phase separation between SiO₂ and ethanol plays a major role in the formation of the hierarchical microstructure observed in NTVS.

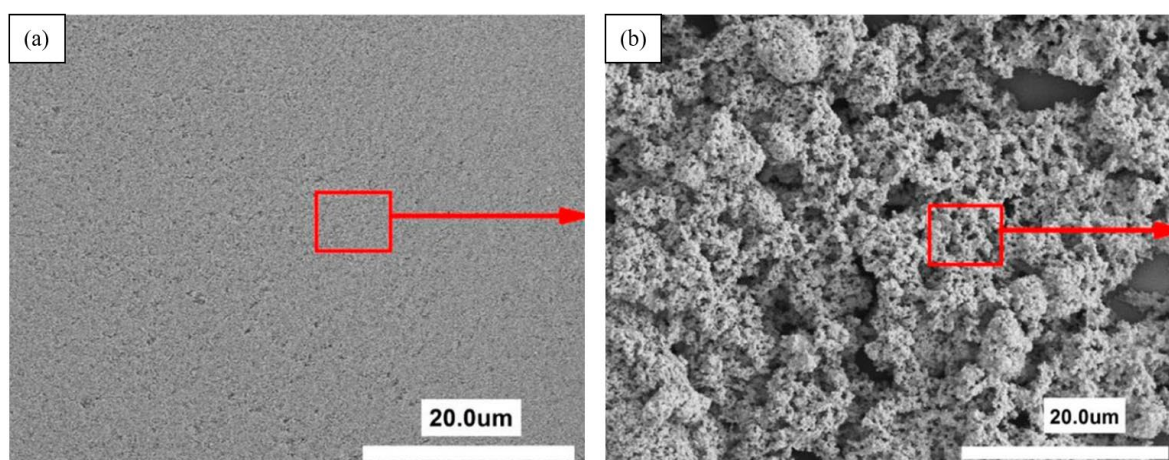


Figure 1: SEM images of the coating surface at low magnification: (a) non-treated SiO₂; (b) treated SiO₂ (NTVS)

3.2 FTIR analysis

Figure 2 shows the FTIR analysis of SiO₂, TVS and NTVS. Spectra band at 2,975, 1,390, 544 and 470 cm⁻¹ were referred to the symmetric stretching vibration of =CH₂, asymmetric deformation vibration of C-CH₃ (Xu et al., 2020), asymmetric deformation vibration of C-CH₃ and C-H (Xu et al., 2020), and deformation vibration of CH₃-CH₂ (Ong et al., 2012). Waveband 3,480 and 1,630 cm⁻¹ represents the presence of Si-OH and O-H stretching in SiO₂ spectrum (Lu, 2013). Furthermore band at 1,089 to 1,141 cm⁻¹ corresponds to Si-O-Si vibration network in SiO₂ and different amount of NTVS (Ong et al., 2015). TVS was successfully grafted onto the surface of SiO₂ as evidenced by the emergence of the typical absorption peaks at band 2,975 cm⁻¹ as well as 1,089 cm⁻¹ (Karnati et al., 2019). Furthermore, spectra band at 3,400 cm⁻¹, 1,630 cm⁻¹, and 544 cm⁻¹ were eliminated (Ong et al., 2018). Thus, proves that the SiO₂ were successfully functionalized by TVS silane coupling agent. Nevertheless, several changes were noted that resulted from interactions between the functional groupings. In contrast to intermolecular hydrogen bonding interactions, which depend on the concentration of the functional groups, intramolecular hydrogen bonding interactions are known to be independent of concentration. The intramolecular hydrogen bonding interactions occur within a molecule, in which hydrogen bonds are formed between functional groups of the same molecule. In this study, changes in the FTIR spectra of SiO₂, TVS, and NTVS, which indicated the occurrence of intermolecular and intramolecular hydrogen bonding interactions between the functional groups.

The relationship between the Si-O-Si frequency peak shift and the TVS concentration is shown in Figure 3 using the SiO₂ spectrum as a reference (Si-O-Si peak at 1,089 cm⁻¹). The highest peak shift was observed at 5% TVS concentration, indicating the occurrence of intermolecular hydrogen bonding interactions between the functional groups of SiO₂ and TVS molecules. These interactions were less pronounced at lower TVS concentrations (lower than 4 wt% of TVS concentration), where the functional groups of SiO₂ and TVS molecules displayed less interaction with their individual identity peaks, displaying overlap. However, as the TVS concentration

increased to 4 wt%, it appeared that the Si-O-Si group of SiO₂ also played a role in the interactions by providing the essential orientation for the same type of interaction (Ong et al., 2018). This suggested that both Si-O-Si and O-H groups interact effectively in the sample containing 5% TVS concentrations.

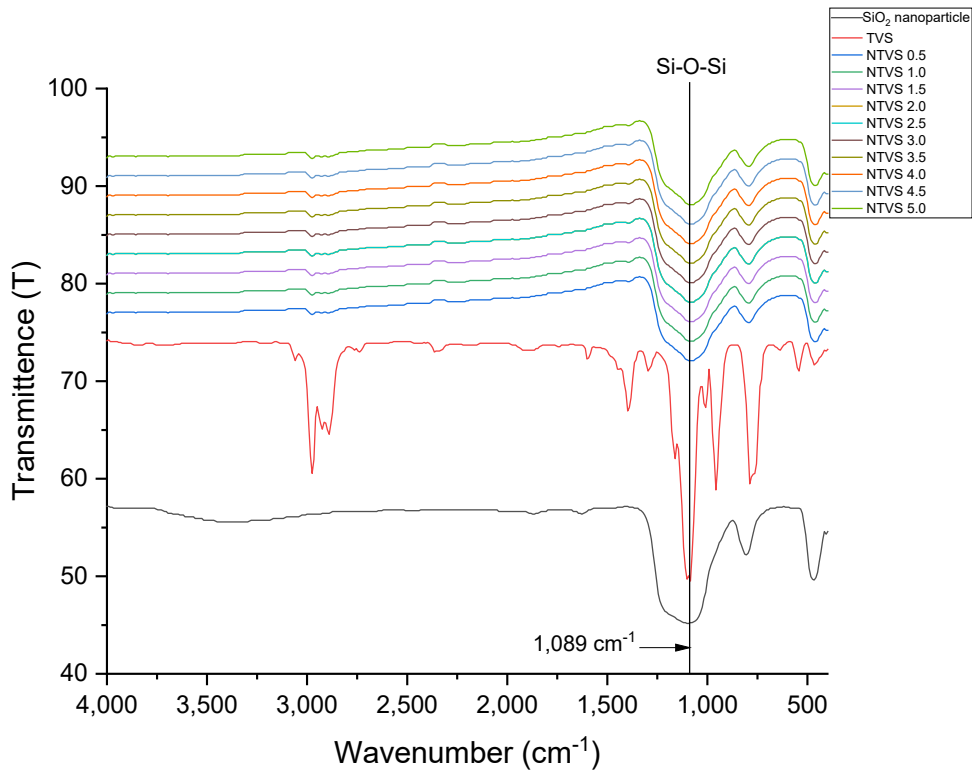


Figure 2: FTIR spectra of SiO₂, TVS and various concentration of NTVS

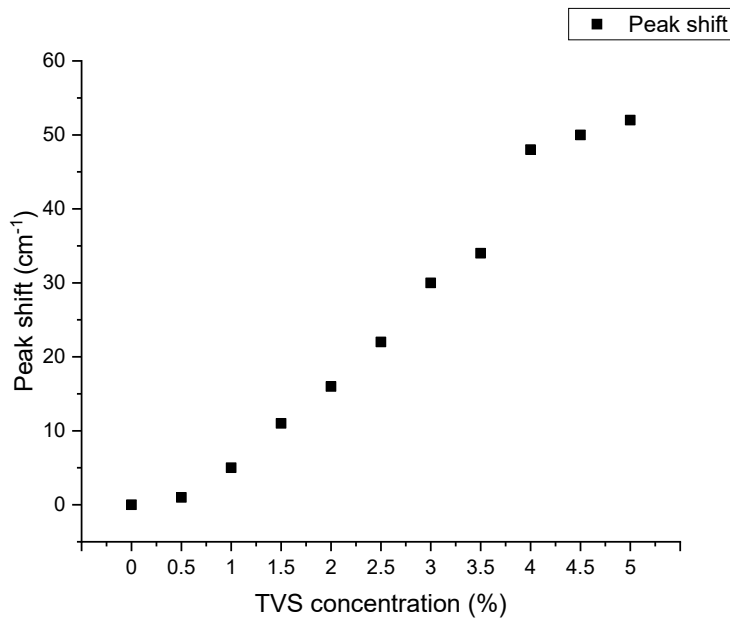


Figure 3: Peak at frequency (1,089 cm⁻¹) shift of FTIR with respect to different TVS concentration

From these results, it can be inferred that the Si-O-Si and O-H groups interact effectively in the sample containing 5 % TVS concentrations as opposed to 0 % TVS concentrations. In summary, the observed FTIR results indicate the occurrence of intermolecular and intramolecular hydrogen bonding interactions between the functional groups of SiO₂ and TVS molecules. The findings suggest that the TVS concentration plays a critical role in determining the extent of intermolecular hydrogen bonding interactions, which can be useful in designing and developing functional materials. Furthermore, the findings of this study provide a basis for further investigation into the role of functional groups in determining the properties of materials. By studying the interactions between different functional groups, it may be possible to design novel materials with unique properties and applications. For instances, by modifying the functional groups of SiO₂ and TVS molecules, it may be possible to develop materials with enhanced properties, such as improved adhesion, durability, and chemical resistance.

Additionally, SiO₂ and TVS hydrogen bonding interactions could be used in drug delivery application. The ability to control and modify the functional groups of nanoparticles can lead to the development of materials with improved drug encapsulation and release properties. By designing nanoparticles with specific functional groups, it may be possible to target drugs to specific cells or tissues, increasing the efficiency of drug delivery while minimizing harmful side effects.

Subsequently, the intermolecular and intramolecular hydrogen bonding interactions observed between SiO₂ and TVS molecules can also be utilized to develop biosensors with enhanced sensitivity and selectivity. By incorporating functionalized nanoparticles into biosensors, it is possible to develop sensors with improved interactions between the sensing elements and the target analytes. Additionally, the intermolecular and intramolecular hydrogen bonding interactions between the functional groups of SiO₂ and TVS molecules can lead to the development of biosensors with enhanced stability and reproducibility, leading to improved accuracy and precision in sensing applications.

The findings of this study can be extended to the field of catalysis, where functionalized nanoparticles can be utilized as catalysts in various chemical reactions. The intermolecular and intramolecular hydrogen bonding interactions between the functional groups of SiO₂ and TVS molecules can lead to the development of catalytic materials with enhanced activity, selectivity, and stability. The catalytic activity can be improved by modifying the functional groups of SiO₂ and TVS molecules to enhance the interactions between the catalyst and reactants.

On the other hand, the FTIR analysis can be utilized to investigate the behavior of functionalized nanoparticles under different environmental conditions, such as temperature and pressure. The intermolecular and intramolecular hydrogen bonding interactions can be studied under different conditions to investigate their effect on the structure and properties of the functionalized nanoparticles. This can lead to the development of materials with tailored properties for specific applications, such as high-temperature-resistant materials and pressure-sensitive materials.

In addition, further characterization methods including X-ray diffraction, transmission electron microscopy, and surface area analysis can be used in conjunction with the FTIR study to provide a comprehensive understanding of the structure and characteristics of the functionalized nanoparticles.

The results of this study provide valuable insights into the nature of intermolecular and intramolecular hydrogen bonding interactions between SiO₂ and TVS molecules. The observed peak shift at NTVS 5.0 suggests that the Si-O-Si and O-H groups play important roles in determining the properties of these materials. By understanding the nature of these interactions, it may be possible to develop functional materials with enhanced properties and unique applications.

4. Conclusions

In summary, the results of this study have demonstrated the successful modification of SiO₂ nanoparticles with TVS, which led to the formation of a hierarchical microstructure with increased roughness on the surface. The SEM analysis provided evidence of the formation of a rough surface, which could be useful in developing functional materials that require high surface area and reactivity. Furthermore, the FTIR analysis indicated that TVS molecules were effectively embedded onto the surface of SiO₂ nanoparticles, as evidenced by the emergence of new peaks and disappearance of existing peaks. The Si-O-Si peak shift was observed to increase with increasing TVS concentration up to 5 %, suggesting the occurrence of intermolecular hydrogen bonding interactions between the functional groups of SiO₂ and TVS molecules. These findings have implications for the design and development of functional materials, as intermolecular hydrogen bonding interactions can be utilized to control the surface properties and reactivity of nanoparticles.

However, further optimization is required to determine the optimal concentration of TVS on the surface of SiO₂ nanoparticles for specific applications. In addition, the characterization techniques employed in this study could be further expanded to include other analytical methods, such as X-ray diffraction or surface area analysis, to

gain a more comprehensive understanding of the modified nanoparticles. Overall, this study provides a valuable contribution to the field of materials science and highlights the potential of surface functionalization techniques for the development of advanced functional materials.

Acknowledgments

The author would like to express his gratitude to DRB-HICOM University for the contribution and continuous support for this project.

References

- Bhattacharya A.B., Raju A T., Chatterjee T., Naskar K., 2020, Development and characterizations of ultra-high molecular weight EPDM/PP based TPV nanocomposites for automotive applications, *Polymer Composites*, 41(12), 4950–4962.
- Fujiwara M., Shiokawa K., Sakakura I., Nakahara Y., 2010, Preparation of hierarchical architectures of silica particles with hollow structure and nanoparticle shells: a material for the high reflectivity of UV and visible light, *Langmuir*, 26(9), 6561–6567.
- Jeevanandam J., Barhoum A., Chan Y.S., Dufresne A., Danquah M.K., 2018, Review on nanoparticles and nanostructured materials: history, sources, toxicity and regulations, *Beilstein journal of nanotechnology*, 9(1), 1050-1074.
- Karnati S.R., Oldham D., Fini E.H., Zhang L., 2019, Surface functionalization of silica nanoparticles to enhance aging resistance of asphalt binder, *Construction and Building Materials*, 211, 1065-1072.
- Kim K.S., 2014, Functionalization of magnetic nanoparticles for biomedical applications, *Korean Journal of Chemical Engineering*, 31(8), 1289–1305.
- Lambiase F., Liu F., 2022, Recent advances in metal-polymer joining processes, *Joining Processes for Dissimilar and Advanced Materials*, 123–151.
- Li P., Zhang D., Xu Y., Ni C., Shi G., Sang X., Cong H., 2018, Hierarchical porous polyaniline supercapacitor electrode from polyaniline/silica self-aggregates, *Polymer International*, 67(12), 1670–1676.
- Lu H.T., 2013, Synthesis and characterization of amino-functionalized silica nanoparticles, *Colloid Journal*, 75(3), 311–318.
- Lushinga N., Dong Z., Cao L., Yang C., Ullah S., 2022, Fatigue characteristics and environmental sustainability of rubber asphalt composite modified asphalt mixtures incorporating nanosilica, *Construction and Building Materials*, 346, 128382.
- Neouze M.A., Schubert U., 2008, Surface modification and functionalization of metal and metal oxide nanoparticles by organic ligands, *Monatshefte für Chemie-Chemical Monthly*, 139(3), 183–195.
- Ong H.R., Khan M.M.R., Prasad D.R., Yousuf A., Chowdhury M., 2018, Palm kernel meal as a melamine urea formaldehyde adhesive filler for plywood applications, *International Journal of Adhesion and Adhesives*, 85, 8–14.
- Ong H.R., Khan M.R., Yousuf A., Jeyaratnam N., Prasad D.R., 2015, Effect of waste rubber powder as filler for plywood application, *Polish Journal of Chemical Technology*, 17(1), 41–47.
- Ong H.R., Prasad R., Rahman Khan M., Chowdhury M., Kabir N., 2012, Effect of palm kernel meal as melamine urea formaldehyde adhesive extender for plywood application: Using a Fourier transform infrared spectroscopy (FTIR) study, *Applied Mechanics and Materials*, 493–498
- Rudramurthy G.R., Swamy M K., 2018, Potential applications of engineered nanoparticles in medicine and biology: An update, *JBIC Journal of Biological Inorganic Chemistry*, 23(8), 1185–1204.
- Singh P., Srivastava S., Singh S.K., 2019, Nanosilica: recent progress in synthesis, functionalization, biocompatibility, and biomedical applications, *ACS Biomaterials Science & Engineering*, 5(10), 4882–4898.
- Sun S.N., Wei C., Zhu Z.Z., Hou Y.L., Venkatraman S. S., Xu Z.C., 2014, Magnetic iron oxide nanoparticles: Synthesis and surface coating techniques for biomedical applications, *Chinese Physics B*, 23(3), 037503.
- Vinodhini S., Xavier J.R., 2022, Effect of graphene oxide wrapped functional silicon carbide on structural, surface protection, water repellent, and mechanical properties of epoxy matrix for automotive structural components, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 639, 128300.
- Xu X., Tian F., Li X., 2020, Regenerated waste tire powders as fillers for wood fiber composites, *BioResources*, 15(2), 3029–3040.