

T.R.
EGE UNIVERSITY
Graduate School of Applied and Natural
Science

**ANTI-REFLECTIVE SiO₂, TiO₂, SiO₂/TiO₂ THIN
FILM COATINGS: SYNTHESIS,
CHARACTERIZATION AND APPLICATION TO
GLASSES IN AUTOMOTIVE INDUSTRY**

Pelin ÖZ

Supervisor : Prof. Dr. Şerife Şeref HELVACI

Chemical Engineering Department
Chemical Engineering Second Cycle Programme

İzmir
2021

EGE ÜNİVERSİTESİ FEN BİLİMLERİ ENSTİTÜSÜ

ETİK KURALLARA UYGUNLUK BEYANI

EÜ Lisansüstü Eğitim ve Öğretim Yönetmeliğinin ilgili hükümleri uyarınca Yüksek Lisans Tezi olarak sunduğum “ANTI-REFLECTIVE SiO₂, TiO₂, SiO₂/TiO₂ THIN FILM COATINGS: SYNTHESIS, CHARACTERIZATION AND APPLICATION TO GLASSES IN AUTOMOTIVE INDUSTRY/ YANSIMA ÖNLEYİCİ SiO₂, TiO₂, SiO₂/TiO₂ İNCE FİLM KAPLAMALARI: SENTEZİ, KARAKTERİZASYONU ve OTOMOTİV ENDÜSTRİSİNDEKİ CAMLARA UYGULAMA ÇALIŞMALARI” başlıklı bu tezin kendi çalışmam olduğunu, sunduğum tüm sonuç, döküman, bilgi ve belgeleri bizzat ve bu tez çalışması kapsamında elde ettiğimi, bu tez çalışmasıyla elde edilmeyen bütün bilgi ve yorumlara atıf yaptığımı ve bunları kaynaklar listesinde usulüne uygun olarak verdiğimi, tez çalışması ve yazımı sırasında patent ve telif haklarını ihlal edici bir davranışımın olmadığını, bu tezin herhangi bir bölümünü bu üniversite veya diğer bir üniversitede başka bir tez çalışması içinde sunmadığımı, bu tezin planlanmasından yazımına kadar bütün safhalarda bilimsel etik kurallarına uygun olarak davrandığımı ve aksinin ortaya çıkması durumunda her türlü yasal sonucu kabul edeceğimi beyan ederim.

28 / 09 / 2021

Pelin ÖZ

ÖZET

Yansıma Önleyici SiO₂, TiO₂, SiO₂/TiO₂ İnce Film Kaplamaları: Sentezi, Karakterizasyonu ve Otomotiv Endüstrisindeki Camlara Uygulama Çalışmaları

ÖZ, Pelin

Yüksek Lisans Tezi, Kimya Mühendisliği Bölümü

Tez Danışmanı: Prof. Dr. Şerife Şeref HELVACI

Eylül 2021, 79 sayfa

Bu tez çalışmasında yansıma önleyici, SiO₂, TiO₂, SiO₂/TiO₂ ince film kaplamalarının sentezi, karakterizasyonu ve otomotiv endüstrisindeki camlara uygulama çalışmaları yapılmıştır.

Yansıma önleyici özelliğin sağlanması amacıyla SiO₂ sentezi esnasında iki farklı polimerik şablon kullanılmıştır. Bunlar poliakrilik asitin homopolimeri (h-PAA) ve kopolimerleridir (c-PAA). Kaplamalarda uygulama kolaylığı sağlamak amacıyla SiO₂ sol (SS) olarak sentezlenmiş, tetraetil ortosilikat (TEOS) ve pirinç kabuğu külü (RHA) olmak üzere iki farklı kaynaktan sentez çalışmaları yapılmıştır. TEOS kullanılarak gerçekleştirilen sentez çalışmalarında sentez sırasındaki, karıştırma hızı (500 ve 800 rpm), polimerik şablon tipi (h-PAA ve c-PAA), polimerik şablon miktarı (0.4, 0.6 ve 0.8 g) ve TEOS miktarı (2.1, 3.2 ve 4.8 mL) üzerine parametrik çalışmalar gerçekleştirilmiştir. Elde edilen optimum koşullar ile pirinç kabuğu külünden elde edilen sodyum silikat (Na₂SiO₃) ile de 4.8 mL TEOS içerisindeki eşdeğer Si miktarında Na₂SiO₃ ile polimerik şablon tipi (h-PAA ve c-PAA) ve polimerik şablon miktarı (0.4, 0.6 ve 0.8 g) deneyleri gerçekleştirilmiştir. Ayrıca elde edilen SSler kullanılarak daldırma hızı (100mm/min ve 150 mm/min) ve kaplama sayısı (1 katman ve 2 katman) gibi parametreler ince film kaplamalar kapsamında incelenmiştir.

TEOS kullanılarak sentezlenen optimum koşuldaki SS ile yansıma önleme performansını artırmak için SiO₂/TiO₂ sol sentezi gerçekleştirilmiştir. SS ince film kaplamalarında elde edilen optimum kaplama koşulları ile SiO₂/TiO₂ sol kaplaması yapılmıştır. İstenilen düzeyde yansıma önleyici özelliğin SiO₂/TiO₂ sol

kaplamalarında elde edildiđi görölmüştür. Tez kapsamında ayrıca viniltrimetoksisilan (VTMO) ile $\text{SiO}_2/\text{TiO}_2$ kompozit solün modifikasyonu gerçekleştirilmiştir. Yapılan bu ön çalışma ile kaplamalara hidrofobik özellik kazandırılarak camların kendi kendini temizleme özelliđine sahip olması ileriki aşamalarda hedeflenmektedir. Ayrıca, 2 bileşenli cam boyası içerisinde modifiye kompozit sol farklı oranlarda kullanılarak, kaplama filminin yansıma önleyici, temas açısı ve film özellikleri tez kapsamında incelenmiştir. Elde edilen filmler, hidrofobik özellikte ve sert yapılar olup, yansıma önleyici özellikleri modifiye kompozit sol eklenmemiş boya filmine göre düşük bulunmuştur.

Anahtar Kelimeler: pirinç kabuđu külü, TEOS, silika, $\text{SiO}_2/\text{TiO}_2$ kompozit, yüzey modifikasyonu, kaplama, yansıma önleme.

ABSTRACT

Anti-Reflective SiO₂, TiO₂, SiO₂/TiO₂ Thin Film Coatings: Synthesis, Characterization and Application to Glasses in Automotive Industry

ÖZ, Pelin

Master Science Thesis, Chemical Engineering Department

Supervisor: Prof. Dr. Şerife Şeref HELVACI

September 2021, 79 pages

In this thesis, the synthesis and characterization of anti-reflective, SiO₂, TiO₂, SiO₂/TiO₂ thin film coatings and their application to glasses in the automotive industry were carried out.

Two different polymeric templates were used during the synthesis of SiO₂ in order to provide anti-reflective property. These are homopolymer (h-PAA) and copolymers (c-PAA) of polyacrylic acid. In order to provide ease of application in coatings, SiO₂ was synthesized as sol (SS), and synthesis studies were carried out from two different sources, tetraethyl orthosilicate (TEOS) and rice husk ash (RHA). In SiO₂ synthesis using TEOS as silica source, parametric studies were carried out. The investigated parameters during synthesis were the mixing speed (500 and 800 rpm), type of polymeric templates (h-PAA and c-PAA), amount of polymeric template (0.4 g, 0.6 g and 0.8 g) and amount of TEOS (2.1, 3.1 and 4.8 mL). Using these optimum conditions, sodium silicate (Na₂SiO₃) obtained from rice husk ash experiments were performed. In the experiments, Na₂SiO₃ in equivalent Si amount in 4.8 mL TEOS were used. Same type of polymeric templates (h-PAA and c-PAA) and amount of polymeric templates (0.4, 0.6 and 0.8 g) were carried out in the Na₂SiO₃ experiments. In addition, parameters such as withdrawal speed (100mm/min and 150 mm/min) and number of coating layers (1 layer and 2 layers) were investigated within the scope of thin film coatings by using the obtained SSs.

SiO₂/TiO₂ sol synthesis was carried out to increase the antireflection performance with SS at optimum condition synthesized using TEOS. SiO₂/TiO₂ sol coating was made with optimum coating conditions obtained in SS thin film

coatings. In addition, the modification of $\text{SiO}_2/\text{TiO}_2$ sol with vinyltrimethoxysilane (VTMO) was performed within the scope of the thesis. With this preliminary study, it is aimed to give the coatings a hydrophobic feature and to have the self-cleaning feature of the glasses. In addition, the anti-reflective, contact angle and film properties of the coating film were investigated within the scope of the thesis by using modified composite sol in different ratios in 2-component glass paint. The films obtained are hydrophobic and rigid structures, and their anti-reflective properties were found low with respect to the paint film that not containing modified composite sol.

Keywords: Rice husk ash, TEOS, silica, $\text{SiO}_2/\text{TiO}_2$ composite, surface modification, coating, anti-reflection.

PREFACE

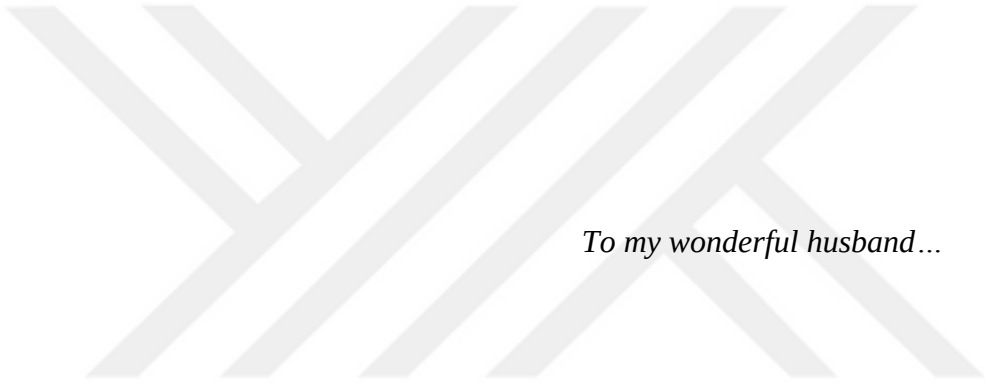
The subject of this thesis was determined according to research of the literature. In the study, SiO_2 sol was synthesized from two different sources which were tetraethyl orthosilicate, TEOS, and rice husk ash. Synthesis from tetraethyl orthosilicate was performed to prepare reference for the rice husk ash studies. $\text{SiO}_2/\text{TiO}_2$ and modified $\text{SiO}_2/\text{TiO}_2$ composites were synthesized to investigate the anti-reflection property. In this process, different parametric studies were performed to obtain optimum synthesis and application conditions. Two component, 2C glass paint application of modified composite sol was also performed from the point of view of industry.

I would like to thank my supervisor, Prof. Dr. Şerife Şeref HELVACI for her support and guidance throughout this thesis. Also, I would like to thank Erdoğanlar Food Industry for their supply of rice husk ash and Hayat Kimya for their supply of chemicals. I would like to thank Kansai Altan Paint Industry for providing me the opportunity to perform the industrial applications of my thesis.

İZMİR

28 / 09 / 2021

Pelin ÖZ



To my wonderful husband...

TABLE OF CONTENTS

	<u>Page</u>
ETİK KURALLARA UYGUNLUK BEYANI.....	v
ÖZET	i
ABSTRACT	iii
PREFACE.....	v
TABLE OF CONTENTS	vii
LIST OF FIGURES	x
LIST OF TABLES.....	xii
NOMENCLATURE	xiii
1. INTRODUCTION	1
2. GENERAL INFORMATION.....	3
2.1. Silica	3
2.2. Silica Sources.....	5
2.3. Silica Synthesis Methods in the Presence and Absence of Templates	6
2.4. Synthesis of Silica Sols from TEOS	11
2.5. Synthesis of Silica Sols from Rice Husk Ash.....	13
2.6. SiO ₂ /TiO ₂ Composites	19
2.7. Synthesis of SiO ₂ /TiO ₂ Composites in the Presence and Absence of the Templates	20
2.8. Surface Modification of SiO ₂ /TiO ₂ Composites.....	22
2.9. SiO ₂ /TiO ₂ Thin Film Coatings.....	23
2.10. Application of SiO ₂ /TiO ₂ Thin Film Coatings.....	24
2.11. Theory of Antireflection	25
2.12. Theory of Contact Angle and Surface Free Energy	25
3. EXPERIMENTAL STUDIES	27
3.1. Materials Used.....	27
3.1.1. Silica sol synthesis.....	27
3.1.2. SiO ₂ /TiO ₂ composite sol synthesis	27

3.1.3. Modified SiO ₂ /TiO ₂ composite sol synthesis	27
3.1.4. Thin film coating	28
3.2. Synthesis of SiO ₂ Sol from TEOS by Using Polymeric Templates	28
3.3. Synthesis of SS from Rice Husk Ash by Using Polymeric Templates.....	29
3.4. Synthesis of SiO ₂ /TiO ₂ Composite Sol from TEOS by Using Polymeric Templates	31
3.5. Synthesis of Modified SiO ₂ /TiO ₂ Composite Sol.....	32
3.6. Thin Film Coatings.....	34
3.7. Application of Glass Paints Containing Modified SiO ₂ /TiO ₂ Composite Sol.....	35
3.8. Characterization of SiO ₂ , SiO ₂ /TiO ₂ and Modified SiO ₂ /TiO ₂ Composite Sols.....	36
3.9. Characterization of SiO ₂ , SiO ₂ /TiO ₂ , Modified SiO ₂ /TiO ₂ Composite Thin Film Coatings.....	37
3.10. Characterization of Coatings Prepared by Glass Paints Containing Modified SiO ₂ /TiO ₂ Composite Sols.....	37
4. RESULTS.....	38
4.1. Parametric Study on Silica Sol Synthesis.....	38
4.1.1. Effect of stirring rate on the synthesis of silica sol.....	38
4.1.2. Effect of type of polymeric template on the synthesis of silica sol	40
4.1.3. Effect of amount of polymeric template on the synthesis of silica sol	42
4.1.4. Effect of amount of TEOS on the synthesis of silica sol	44
4.1.5. Effect of silica source on the synthesis of silica sol	45
4.2. Characterization of SiO ₂ /TiO ₂ Composite Sols	47
4.3. Characterization of Modified SiO ₂ /TiO ₂ Composite Sol.....	48
4.4. Characterization of Thin Film Coatings	52
4.5. Characterization of Glass Paints Containing Modified Composite Sols	62
5. DISCUSSION.....	68
6. CONCLUSIONS and RECOMMENDATIONS	71
REFERENCES	72
ACKNOWLEDGEMENTS	79
CV	80
APPENDIX	82

A1. SEM micrographs of SiO ₂ /TiO ₂ composite sol and modified composite sol	83
A2. SEM micrographs of h-PAA SSs.....	83
A3. SEM micrographs of c-PAA SSs.....	83



LIST OF FIGURES

<u>Figure</u>	<u>Page</u>
Figure 2.1. Structure of TEOS.....	6
Figure 3.1. Schematic representation of SS synthesis	28
Figure 3.2. Experimental set-up for the synthesis of SS.....	29
Figure 3.3. Rice husk ash.....	30
Figure 3.4. Schematic representation of synthesis of sodium silicate solution	30
Figure 3.5. Schematic representation of synthesis of silica gel	30
Figure 3.6. Schematic representation of synthesis of SS from rice husk ash	31
Figure 3.7. Experimental set-up of synthesized composite sol.....	32
Figure 3.8. Schematic representation of synthesis of SiO ₂ /TiO ₂ composite sol.	32
Figure 3.9. Schematic representation of synthesis of modified SiO ₂ /TiO ₂ composite sol.....	33
Figure 3.10. Experimental set-up of modified composite sol.....	33
Figure 3.11. Dip coating device.....	34
Figure 3.12. Procedure of thin film coatings	35
Figure 3.13. Experimental procedure of application of glass paints containing modified composite sol	36
Figure 3.14. Experimental set-up for process of glass paint.....	36
Figure 4.1. Particle size distribution of SS at different stirring rates.....	39
Figure 4.2. FTIR spectrum of h-PAA and c-PAA SS synthesized at 500 rpm and 800 rpm	40
Figure 4.3. Effect of type of polymer on silica sols' particle size	41
Figure 4.4. Effect of amount of c-PAA on silica sols' particle size	42
Figure 4.5. Effect of amount of h-PAA on silica sols' particle size	43
Figure 4.6. Effect of amount of TEOS on silica sols' particle size	45
Figure 4.7. Effect of silica source on silica sols' particle size.....	46
Figure 4.8. FTIR spectra of SSs synthesized from different silica sources	47
Figure 4.9. Particle size distribution of SiO ₂ /TiO ₂ composite sol	48
Figure 4.10. Particle size distributions of SS, composite sol and modified composite sol	49
Figure 4.11. XPS spectrums of SiO ₂ /TiO ₂ composite sol and modified SiO ₂ /TiO ₂ composite sol	51
Figure 4.12. FTIR spectra of unmodified, modified and calcined modified composite sols	52

Figure 4.13. SEM micrographs of SS prepared 6000 ppm h-PAA with different withdrawal speeds (100 mm/min and 150 mm/min), number of coatings (1 and 2 layers) and stirring rates (500 rpm and 800 rpm)	53
Figure 4.14. UV-Visible spectra of SS prepared 6000 ppm h-PAA with different withdrawal speeds (100 mm/min and 150 mm/min), number of coatings (1 and 2 layers) and stirring rates (500 rpm and 800 rpm)	54
Figure 4.15. SEM micrographs of SS prepared 6000 ppm c-PAA with different withdrawal speeds (100 mm/min and 150 mm/min) and number of coatings (1 and 2 layers) at 500 rpm	55
Figure 4.16. UV-Visible spectra of SS prepared 6000 ppm c-PAA with different withdrawal speeds (100 mm/min and 150 mm/min), number of coatings (1 and 2 layers)	56
Figure 4.17. SEM micrographs of SS synthesized with different amount of c-PAA at constant amount of TEOS (4.8 mL) rpm	57
Figure 4.18. UV-visible spectra of the coatings fabricated using 4000 ppm c-PAA, 6000 ppm c-PAA and 8000 ppm c-PAA at constant amount of TEOS.....	57
Figure 4.19. UV-visible spectra of the coatings fabricated using different amount of TEOS	58
Figure 4.20. SEM micrographs of the coatings fabricated using 6000 ppm c-PAA and 8000 ppm c-PAA at constant amount of TEOS and Na ₂ SiO ₃	59
Figure 4.21. UV-Visible spectra of the coatings fabricated using TEOS and Na ₂ SiO ₃ ...	60
Figure 4.22. SEM micrographs of coatings fabricated using SS, composite sol and modified composite	61
Figure 4.23. UV-visible spectra of the coatings fabricated using SS, composite sol and modified composite sol.....	62
Figure 4.24. Transmittance values of glass paints containing various amount of modified composite sol	64
Figure 4.25. Relation in between amount of modified composite sol and Tg-Network parameter	65
Figure 4.26. Relation in between amount of modified composite sol and storage-elastic modulus	66
Figure 4.27. Relation in between amount of modified composite sol and transmittance of the coatings	66
Figure 4.28. Relation in between amount of modified composite sol and water contact angle-surface free energy.....	67

LIST OF TABLES

<u>Table</u>	<u>Page</u>
Table 2.1. Synthesis methods and parameters of SiO ₂	8
Table 2.2. Synthesis methods and parameters of SiO ₂ (continued)	9
Table 2.3. Synthesis methods and parameters of SiO ₂ (continued)	10
Table 2.4. Synthesis of silica sols by sol-gel method at the presence and absence of template	15
Table 2.5. Synthesis of silica sols by sol-gel method at the presence and absence of template (continued)	16
Table 2.6. Synthesis of silica from agricultural waste rice husk.....	17
Table 2.7. Synthesis of silica from agricultural waste rice husk (continued)	18
Table 2.8. Synthesis of silica from agricultural waste rice husk.....	18
Table 2.9. SiO ₂ /TiO ₂ thin film coatings	24
Table 4.1. XPS results of SiO ₂ /TiO ₂ composite sol and modified SiO ₂ /TiO ₂ composite sol	50
Table 4.2. Results of contact angle and surface free energy of coatings fabricated with glass paints containing different amount of modified composite sol	62
Table 4.3. DMA results of glass paints containing various amount of modified composite sol	65

NOMENCLATURE

ARC	Antireflective coating
AVT	Ammonia vapor treatment
CVD	Chemical vapor deposition
c-PAA	Copolymer of polyacrylic acid
h-PAA	homopolymer of polyacrylic acid
HDTMOS	Hexadecyltrimethoxysilane
HMDS	hexamethyldisilazane
MTES	Methyltriethoxysilane
PAA	Polyacrylic acid
PMHS	Polymethylhydrosiloxane
RH	Rice Husk
RHA	Rice husk ash
rpm	rev/min
SS	Silica sol
T	temperature [°C]
t	time [min]
TBOT	Tetrabutylorthotitanate
TEOS	Tetraethylorthosilicate

NOMENCLATURE (*continued*)

TTIP Titaniumtetraisopropoxide

VTMO Vinyltrimethoxysilane



1. INTRODUCTION

In recent years, smart materials are popular in scientific world such as self-healing, self cleaning, antireflective, thermochromic, photochromic, shape memory materials etc. The reason of this is the need of the industry and indirectly customer needs. For example, companies that produce self-cleaning paints stand out in the sector, however, they provide customer satisfaction by meeting the needs of the customers. In the smart material, self-cleaning has a long history and it is one of the most desired characteristic. In the Lotus leaves, self cleaning effect can be seen and it depends on the hydrophobicity of the surface. Because of the hydrophobic effect contaminants such as solid particles and liquids slides on the surface of leafs. The mechanism can be explained by water droplets. In hydrophobic surfaces, water droplets has spherical shape and because of the hydrophobicity of the surface water droplets rolled over the surface by removing the solid particles or liquids. In general, self-cleaning materials is obtained by after different processes such as roughing the surface by using low surface energy compounds or by doing modification with low surface energy materials (Rosales and Esquivel, 2020). At this point, surface modification agents are used to make the surface hydrophobic.

Anti-reflection materials are materials that are transmit the all light coming the surface. It is desired mostly in automotive glasses and solar cells. In automotive glasses, the reflection is an unwanted phenomena because it obstructs the vision and it can cause accidents. In solar cells, the reflection of the sun light on the panel decreases the efficiency of the cell. It is undesired because solar cells are converted the sun light to the energy. SiO_2 and TiO_2 are generally used in the synthesis of antireflection coatings because SiO_2 has low refractive index and TiO_2 can degrade the organic and inorganic pollutants. There are different studies in the literature but the most preferable option is the template method for the synthesis. The particles surround the template and after the coating process, the film coatings are calcined. The purpose of doing this is to construct a void in the spherical particles. By this void the refraction of the surface is decreased and transmittance is increased.

In this thesis, synthesis of SiO_2 sols by using polymeric templates and different silica sources were performed. Parametric study were done on the synthesis parameters such as stirring rate, effect of type of the template, amount of template, concentration of TEOS and type of silica source. Finding the optimum conditions, $\text{SiO}_2/\text{TiO}_2$ composite sol and modified $\text{SiO}_2/\text{TiO}_2$ composite sol were synthesized. Modification had been done to obtain hydrophobic surface. Synthesized sols were characterized by particles size distribution and chemical structure. The synthesized sols were used to fabricate the thin film coatings in order to indicate the anti-reflection property. They fabricated by using dip-coating method and also parametric study were performed on withdrawal speed and number of coating layer. Modified $\text{SiO}_2/\text{TiO}_2$ composite sol was added to the 2-components glass paint in different ratios and hydrophobicity, antireflection and film properties were investigated.

2. GENERAL INFORMATION

2.1. Silica

In the Earth, one of the most plentiful element is silicon and the most occupied mineral is crystalline silica in the form of quartz in the Earth's crust (Mebert et al., 2017). Quartzite, tridymite, metamorphic rock, cristobalite and minerals such as polymorphs of silica are known as silica minerals. Silicate is consists of combination of silicon and oxygen, and silicate minerals exist in the ratio of 90% in the Earth's crust. There are different usage of silica and silicate minerals such as making Portland cement in building mortar and modern stucco. The main ingredient of the concrete, a major building material, is silicates that contains silica sand. Silicone based materials are used to fabricate different products such as mold-release agents, molding compounds, pigments, steel industry products, solar cells, antireflection thin-film coatings, thermal control paints, waxes, waterproofing treatments, absorbents, mechanical seals and high-temperature greases etc (Soltani, 2015, Kayhan, 2012, Liang, 2018, Guldin, 2013, Prabha, 2020). Silica has featured properties that make stand out from other materials such as low density, large specific surface area, high level of wettability, high mechanical and thermal stability and easy structural regulation. Different studies exist in the synthesis of silica based materials with different sizes and shapes to achieve the applications' different requirements. In the synthesis of silica based materials two different method generally used which are template and template-free methods. In the template-free method, the synthesis of silica particle is generally based on some the mechanisms such as the nucleation and growth of pores. The template method has opportunity to synthesize silica based materials with narrow-size distribution and a wide range of well-defined shapes. Generally, template materials consists of emulsion droplets, inorganic nanoparticles, polymers and micelles of surfactants- (Jong-Hong et al., 2014).

Silica nanoparticles are used in the aselectronic devices, insulator, catalysis or pharmaceuticals. SiO₂ nanoparticles have better electrical, optical and magnetic properties than the other oxide nanoparticles. Silica nanoparticles have also applications such as catalysis, pharmaceuticals, drug delivery and pigments. In order to produce electronic substrates, thin film substrates, electrical insulators,

thermal insulators and humidity sensors amorphous SiO_2 nano-particles are used. These applications take advantage of the very different properties of silica particles. In the quality of these materials, size, size distribution and surface area of the silica particles have high importance (Dubey et al., 2015).

Clean and sustainable energy activities, which have become more widespread in recent years, have also increased the importance of material studies to be developed in these areas. Solar panels are the best examples of this. The conversion of the energy of the sun's rays into electrical energy without any loss is a clear indication that the surfaces of the panels should be covered with special coatings. These coatings, which reduce the reflection of light and increase the permeability, are called anti-reflection coatings. Anti-reflection coatings (ARCs) are widely used in energy-related applications, including high-power laser optical devices, lenses, goggles, exterior surfaces of tall buildings, and solar cells; there are a lot of researches on this subject (Mehmood et al., 2016, Xu et al., 2014, Zou et al., 2018).

The visible transmittance of the glass plates (with a refractive index at around 1.5) is approximately 92%. However, the surface of these glass plates may be coated by an antireflection film to upgrade transmittance. Transmittance in the range of visible wavelength (400-700 nm) is classified as high (> 95%), super high (> 97%) and excellent (> 98%). In anti-reflective glasses, the absorption of visible light in ultra-transparent substrate layers should be suppressed to a negligible level. The adhesion, transmittance and reflection properties of the interfaces are effective on refractive index in thin glass films. For this reason, it is very important to optimize the properties specified in the production of anti-reflective glass (Jong-Hong et al., 2014).

In the glass of the solar cells in order to increase the transmittance of the light SiO_2 based antireflection films are widely used. By increasing the transmittance of the light, energy generation increases. The high porosity and having hydroxyl group on the surface of silica films, has disadvantage because they affected by the pollutants such as organic compounds, water vapor around the environment. It increases the refractive index of the film and, the efficiency of the solar cell is decreased with respect to decreasing transmittance. There is no strong chemical bond in between silica nanoparticles. So that, the mechanical properties of the silica films are low. This cause a problem in the practical

applications so different studies were performed in order to develop chemical bonding. In the literature, most of the studies are relevant with the vapor treatment and silane modification. Belleville and coworkers (1994) has study in order to increase mechanical strength of the film by using ammonia vapor treating (AVT). Another method is the silane modification with modification agents such as hexamethyldisilazane (HMDS) (Cecilia et al., 2019, Qu et al., 2021, Tao et al., 2016a, Zhang and Xu, 2020, Zhang et al., 2020), methyltriethoxysilane (MTES) (Purcar et al., 2012), and polymethylhydrosiloxane (PMHS) (Yuan et al., 2016). In the modification, the hydroxyl groups in the film switch with methyl groups and the modified surface become superhydrophobic depending on the modification agent (water contact angle over 150° and a slide angle lower than 10°). In these type of surface, the dust on the surface of film was carried away by rainwater, indicating a good self-cleaning performance (Zhang et al., 2021).

2.2. Silica Sources

Si is one of the easy to reach structure in the world. In recent years, it is important to use the agricultural waste in order to produce valuable materials. There are different silica sources such as, rice husk (RH), bamboo leaves, groundnut shell, and sugarcane bagasse and they are considered as a waste material. During the harvest, these waste materials are burnt to release nutrients for the next growing season and to get rid of the huge quantity of it. In the burning process, carbon, oxygen and hydrogen elements which are exist in these wastes that depend on the soil characteristics are converted into flammable gases such as carbon is a major agricultural waste which can be used as a fuel. Some agricultural wastes have elevated mineral ingredient compared to other. In the 20% of the rice husk (RH) is silica. After burning rice husk, rice husk ash (RHA) was obtained and the RHA usually contains more than 60% of silica (SiO_2), 10-40% of carbon and other minor mineral composition. Therefore, it is convenient to use RHA in order to synthesize silica based materials. By this way, an agricultural waste recycle in valuable product (Vaibhav et al., 2015). The rice husk ash is used to get sodium silicate solution which contains high amount of silica and by this way natural based silica materials could be produce by mass.

Generally, in the industries commercial silica sources are used and the most featured one is the tetraethylorthosilicate (TEOS). TEOS is a slightly odorless and colorless liquid at room temperature, which is often used as a synthetic material of organic intermediates and is often used to prepare silica film for desalination of seawater (Rahman et al., 2020). TEOS is also added to organic or inorganic materials to form three dimensional network structure of Si-O-Si. (Wang et al., 2021). Especially in paint industry silica is important material and TEOS is used. Figure 2.1 shows the structure of TEOS.

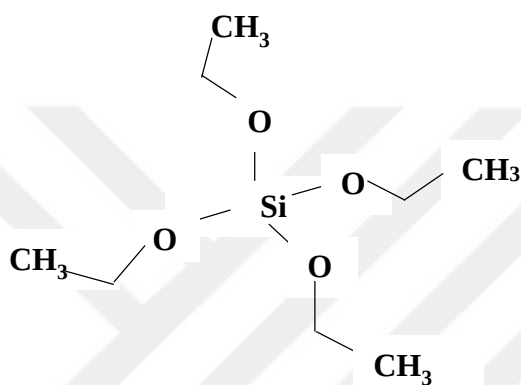


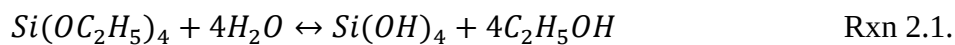
Figure 2.1. Structure of TEOS

2.3. Silica Synthesis Methods in the Presence and Absence of Templates

Silica is synthesized with different methods such as microemulsion processing, chemical vapor deposition, combustion synthesis, hydrothermal techniques, plasma synthesis and sol-gel processing etc. There are three important points in the synthesis of silica which are controlling of particle diameter, particle surface reactivity and morphology. In this study the silica is synthesized in sol form but it is important to understand the effect of the synthesis methods on the particle formation. In Table 2.1, synthesis methods and parameters affecting the SiO₂ synthesis were given.

The most popular process to produce silica nanoparticles is a sol-gel technique which consists of the synchronous hydrolysis and condensation reaction of the metal alkoxide. Generally, TEOS is one of the most used silica source in the

sol gel and in Rxn 2.1. and Rxn 2.2. show the hydrolysis and condensation reactions for the synthesis of SiO₂, respectively.



The hydrolysis reaction with only water is very slow so that either an acid or a base catalyst is used such as ammonia. In the usage of alkaline solutions, internal condensation and crosslinking take place and as a conclusion of this yielding particles whose interior consists of four silicon-oxygen bonds and in which the hydroxyl groups are only oriented on the surface of the particles (Darbandi et al., 2005).

Another method is microemulsion method. In this method, thermodynamically stable transparent, isotropic dispersion of two immiscible liquids such as water and oil stabilized by surfactant molecules at the water/oil interface. Water droplets are dispersed in the continuous phase in water-in-oil microemulsions. These water droplets are surrounded with the surfactant molecules at the interface. Microemulsion techniques allow to synthesize nanosized particles with minimum agglomeration, since the reactions (Rxn 2.1. and Rxn 2.2.) take place in dispersed phase in nanosized scale. (Finnie et al., 2007).

Table 2.1. Synthesis methods and parameters of SiO₂

Reference	Method	Temperature (°C)	Reaction time (h)	Si sources	Solvents	Other Chemicals	Characterization	Particle size (nm)
Stöber et al., 1968	Sol-gel	25	2	Tetraalkylsilicates Silicon tetrachloride	Methanol Ethanol n-propanol n-butanol	Ammonia (NH ₃) Sodium hydroxide (NaOH)	Particle size	50-2000
Zhang et al., 2021	Sol-gel	25	3	Tetraethyl orthosilicate (TEOS)	Ethanol	Ammonia (NH ₃) Water (H ₂ O)	Particle size	10-27 nm
Rahman et al., 2019	Sol-gel	50	3	ES40 – P123	Ethanol	Ammonia (NH ₃) Nitric acid (HNO ₃)	FTIR	-
Shokuhfar et al., 2012	Sol-gel	27	3	Tetraethyl orthosilicate (TEOS)	Ethanol	Water (H ₂ O)	Particle size	19-42
Xu et al., 2014	Sol-gel	25	4	Tetraethyl orthosilicate (TEOS)	Ethanol	Poly acrylic acid (PAA) Ammonia (NH ₃) Water (H ₂ O)	Particle size	45
Xu et al., 2014	Sol-gel	25	4.5	Tetraethyl orthosilicate (TEOS)	Water (H ₂ O)	Cetyltrimethylammonium bromide (CTAB) Ammonia (NH ₃) Ethyl ether	Particle size	-
Zou et al., 2018	Sol-gel	25	5	Tetraethyl orthosilicate (TEOS)	Ethanol	Poly acrylic acid (PAA) Ammonia (NH ₃)	Particle size	50
Jiang et al., 2021	Sol-gel	25	3	Tetraethyl orthosilicate (TEOS)	Ethanol	Water (H ₂ O) Hydrochloric acid (HCl)	UV-vis spectrophotometer	-
Jiang et al., 2021	Sol-gel	25	3	Tetraethyl orthosilicate (TEOS)	Ethanol	Water (H ₂ O) Hydrochloric acid (HCl) Triton-X	UV-vis spectrophotometer	-

Table 2.2. Synthesis methods and parameters of SiO₂ (continued)

Reference	Method	Temperature (°C)	Reaction time (h)	Si sources	Solvents	Other Chemicals	Characterization	Particle size (nm)
Finnie et al., 2007	Microemulsion	25	-	Tetraethyl orthosilicate (TMOS)	Cyclohexane	Acetonitrile Polyoxyethylene (5) nonylphenyl ether Nitric acid (HNO ₃) Ammonia (NH ₃) Sodium Fluoride	FTIR N ₂ adsorption-desorption XRD	-
Greasley et al., 2016	Sol-gel	25	24	Tetraethyl orthosilicate (TEOS)	Ethanol	Ammonia (NH ₃) Water (H ₂ O)	Particle size	20-825
Dubey et al., 2015	Sol-gel	25	1.5	Tetraethyl orthosilicate (TEOS)	Ethanol	Acetic acid Polyvinylpyrrolidone (PVP)	TEM XRD FTIR UV-visible	25
Kozlecki et al., 2016	Microemulsion	25	24	Tetraethyl orthosilicate (TEOS)	n-heptane Ethanol Acetone	Hydroxyethylcellulose (HEC) Tween-85 β -cyclodextrin Ammonia (NH ₃)	Particle size Electrokinetic potential XRD N ₂ adsorption-desorption	130-430
Bagwe et al., 2004	Microemulsion	25	24	Tetraethyl orthosilicate (TEOS)	heptane	Ammonia (NH ₃) Water (H ₂ O) Triton X-100 Sodium dodecyl sulphate (SDS) Dioctyl sulfosuccinate (Aerosol AOT) Hexanol cyclohexane	TEM	14-130

Table 2.3. Synthesis methods and parameters of SiO₂ (continued)

Reference	Method	Temperature (°C)	Reaction time (h)	Si sources	Solvents	Other Chemicals	Characterization	Particle size (nm)
Darbandi et al., 2005	Microemulsion	25	24	Tetraethyl (TEOS)	Cyclohexane	poly(ethylene glycol) nonylphenyl ether Ammonia (NH ₃) 1-butanol 1-propanol Acetone Ethanol Water (H ₂ O)	TEM	20-50
Park et al., 2011	Chemical vapor deposition	25	-	bis(ethylmethlamino)silane (BEMAS)	Water (H ₂ O)	-	Particle size XRD FTIR	60-80
Rezaei et al., 2014	Chemical vapor deposition	25, 30, 35, 40	3	Tetraethyl (TEOS) Vinyltrimethoxysilane (VTMS)	Ethanol	Ammonia (NH ₃) Water (H ₂ O)	TEM FTIR Water contact angle	18-70

Chemical vapor deposition (CVD) is a field that interesting scientific studies are performed. CVD is a method used to deposit a solid material such as silica onto a substrate with a gas phase or surface reaction. There are different forms of CVD each of them has distinct reaction routes. Generally, the first thing have to be done is vaporization of the precursors. Vaporization could be done by sonic action on a solution, thermal heating and reduction of pressure. After vaporization the reactants may require some activation to react, in this part commonly heating is used but electromagnetic radiation and plasma activation also used. CVD of hydrophobic films is a difficult process. At the beginning, the general mechanism for CVD tends to result in flat and chemically homogenous films. For this reason precursors must have surface roughness before the CVD if it does not exist this property should supply to the particles. Secondly, for the synthesis of silica coating, the surface film has to be modified using post treatment. In silica based materials, hydroxyl (silanol) groups exist on their surfaces. These groups want to interact with water and hydrogen bond is formed. It causes the hydrophilic silica films. In order to synthesize hydrophobic silica, surface energy should be lowered or the interaction and by this way lowering the extent of interaction with water (Rezaei et al., 2014).

2.4. Synthesis of Silica Sols from TEOS

In the synthesis of silica sol, sol-gel method has advantages because it permits the low temperature synthesis and control of reaction mechanism by varying the composition of components. But also there are challenging parts, sol gel process is high sensitivity to the temperature, pH and reactant concentrations. They affected reproducibility and consistent trends (Greasley et al., 2016). According to Stober et al., by using sol-gel method, SiO_2 particles was obtained of $1\mu\text{m}$. In recent years, nanoparticles of few hundred nanometers to several micrometers size are synthesized with respect to hydrolysis of TEOS in ethanol. The size and shape of silica nanoparticles are controllable with electrolytes, surfactants and organic acids etc. In similar manner, silica nanoparticles were reported by using electrolyte, sodium iodide, whereas control mechanism of particle size was reported by using ammonium bromide.

There are SiO₂ synthesis methods with template and template free. In the synthesis of SiO₂ with template methods, the Si covers the template and in the middle there is a space which allows the antireflection property. In template free methods, solid SiO₂ nanoparticles are obtained. In Table 2., the literature studies about synthesis of silica sols by sol-gel method at the presence and absence of template were given. In this thesis, synthesis were performed by using template so that the studies in the literature were explained in detail.

Zou and coworkers (2018) studied on the synthesis of ultralow refractive index porous coatings with mulberry like hollow silica nanostructures. In the synthesis, TEOS was used as silica source and PAA ($M_w=3000$) used as a template. The synthesis was performed based on Stöber method. 1H, 1H, 2H, 2H-perfluorooctyltrimethoxysilane (POTS) was used as co-precursor. Dip coating procedure was performed in 500 mm/min withdrawal speed. Parametric study performed on POTS/TEOS ratio in the range of 0, 0.005, 0.01, 0.02, 0.04, 0.06, 0.08 and 0.1. In FTIR spectrum, six absorption bands was observed at 1738 cm⁻¹ (C=O stretching), 1452 cm⁻¹ (-CH₂- bending), and 1402 cm⁻¹ (C-OH bending), 1089 cm⁻¹ (Si-O-Si asymmetric stretching), 968 cm⁻¹ (Si-OH stretching vibration), 804 cm⁻¹ (Si-O-Si vibration). In TEM micrographs, air voids in the particles decreased when the POTS/TEOS increased to 0.1. The shape of the silica nanoparticles were became irregular. The refractive index was also decreased 1.17 to 1.08 by increasing POTS/TEOS. In the parallel, the porosity of the structure were increased. The water contact angles of coatings were measured and hydrophobic coatings were get by increasing POTS/TEOS ratio.

Tao and coworkers (2016a) studied on the synthesis of shape controlled hollow silica nanostructures with a simple soft templating method and their application as superhydrophobic antireflective coatings with ultralow refractive indices. TEOS WAS used as silica source and PAA ($M_w=3000$) was used as a template. Shape controlled silica nanoparticles were synthesized by changing the amount of the template (0.04 g, 0.08 g and 0.15 g indicates 0.213g/L, 0.426 g/L and 0.798 g/L) and amount of TEOS. Dip coating procedure was applied with 1000 mm/min withdrawal speed, 5 minutes retention time. Coatings were calcined at 300-450°C for 1 hour. Hydrophobic modification was performed by chemical

vapor deposition of POTS. Decreasing concentration of TEOS was decreased the shell thickness of the nanoparticle from 15.5 nm to 5.9 nm. In the TEM images the hollow silica nanoparticles were seen and worm like hollow silica nanoparticles are obtained in the low concentration of PAA, 0.213 g/L. The hollow silica nanoparticles prepared with high proportions of PAA, uniform nanoparticles obtained. The transmittance values were increased from 92%, 96.3%, 97.3% and 97.1% by increasing amount of PAA before the calcination and hydrophobic modification. After the calcination and hydrophobic modification, transmittance values were decreased considering the transmittance values before the calcination and hydrophobic modification. But after the calcination and hydrophobic modification transmittance were increased until PAA concentration reach the value of 0.426 g/L and decreased after this concentration. The refractive index of coatings for 0.213g/L, 0.426 g/L and 0.798 g/L PAA concentration were obtained as 1.14, 1.15 and 1.15, respectively. So that increasing amount of PAA did not affect the refractive index of the film coatings.

In another work is belonged to Jia and coworkers (2014), it is about the preparation and properties of five-layer graded refractive index antireflection coating nanostructured by solid and hollow silica particles. TEOS (0. 2-2 mL) was used again as silica source and different amounts of PAA ($M_w=5000$, 0.12-0.22 g) were used. Synthesis procedure was one-step wet synthesis method. When the PAA ratio increases and TEOS ratio decreases, the hollow nanoparticles become bigger and the thickness of the nanoparticles becomes thinner. Increasing the amount of PAA increases the cavity in the middle of the particle and the refractive index were decreased from 1.44 to 1.27.

2.5. Synthesis of Silica Sols from Rice Husk Ash

Rice husk has high silica content and it is an agricultural waste that has to be deal with it. Converting the agricultural waste in a valuable product has high importance for environment and industry. For this reason, in recent years studies in the worldwide are increased about the evaluating the agricultural wastes. In Turkey, rice husk is also a problem, for this reason in this thesis preliminary studies are performed in order to fabricate antireflective film coatings from rice

husk based silica. Le and coworkers (2013) has a study about synthesis of sodium silicate from rice husk by using sol gel method. Firstly, rice husk was pretreated by % 10 by weight hydrochloric acid and %30 by weight sulfuric acid solution. Then, suspension was burned in muffle furnace at 600°C for 4 hours. After that, the rice husk ash was introduced with acid washing in order to extract the silica from the rice husk ash under reflux. Then, the slurry was filtered and washed with distilled water until neutral pH. The obtained product was boiled with 3.5 M sodium hydroxide solution under reflux to dissolve the silica particles into the solution. After the boiling, the solution was filtered and washed with boiling distilled water. The final form of the product is a solid and that is cooled in room conditions. The silica particles were synthesized by sol gel method. To synthesize the silica particles sulfuric acid was added drop by drop into the sodium silicate until the pH of the solution 4 in order to start hydrolysis-condensation reactions. The resulting product which is in gel form was aged at 60°C for 8 hours. After this step, silica gel was dispersed in butanol then washed with water. After the calcination, solid form of silica obtained.

Tufaner and coworkers (2019) studied on the synthesis of silica particles from rice husk and rice husk ash. Thermal, Stöber and precipitation methods were investigated. Sodium silicate was synthesized from rice husk ash by using Stöber method. 20 g RHA was mixed with 2.5 M 160 mL, 250 mL, 634 mL NaOH aqueous solutions under reflux at 120 °C and 3 hours. Then, it was filtered and sodium silicate solution was obtained. After this step, 2.5 M H₂SO₄ aqueous solution were added into sodium silicate solution until pH was 2. Then NH₃ was added to the system in order to get neutral pH silica gel. In the study, APTES and MEMO was used as modification agent to obtain hydrophobic silica particles.

Table 2.4. Synthesis of silica sols by sol-gel method at the presence and absence of template

Reference	Temperature (°C)	Reaction time (h)	Si sources	Amount of Si source (mL)	Template	M _w of template	Amount of template (g)	Other Chemicals	Characterization	Particle size (nm)
Xu et al., 2014	25	4	Tetraethyl orthosilicate (TEOS)	1.8	Poly acrylic acid (PAA)	5000	0.4	Ethanol Ammonia (NH ₃) Water (H ₂ O)	Particle size	45
Zou et al., 2018	25	5	Tetraethyl orthosilicate (TEOS)	1	Poly acrylic acid (PAA)	3000	0.15	Ethanol Ammonia (NH ₃)	Particle size	50
Aghaei et al., 2018	25	25	Tetraethyl orthosilicate (TEOS)	2.5	Poly acrylic acid (PAA)	5000	0.3	Ethanol Ammonia (NH ₃)	Particle size XRD UV-Visible FTIR XPS	120
Tao et al., 2016a	25	15, 48	Tetraethyl orthosilicate (TEOS)	1	Poly acrylic acid (PAA)	3000	0.04, 0.08, 0.15	Ethanol Ammonia (NH ₃)	Particle size	45
Jia et al., 2017	25	10	Tetraethyl orthosilicate (TEOS)	0.2-2	Poly acrylic acid (PAA)	5000	0.12-0.22	Ethanol Ammonia (NH ₃)	Particle size	50
Xiao et al., 2016	25	12	Tetraethyl orthosilicate (TEOS)	1-4	Poly acrylic acid (PAA)	3000	0.36	Ethanol Ammonia (NH ₃)	Particle size	10-100
Xu et al., 2012	25	15	Tetraethyl orthosilicate (TEOS)	1.8	Poly acrylic acid (PAA)	5000	0.4	Ethanol Ammonia (NH ₃) Water (H ₂ O)	Particle size	45

Table 2.5. Synthesis of silica sols by sol-gel method at the presence and absence of template (continued)

Reference	Temperature (°C)	Reaction time (h)	Si sources	Template	M _w of template	Amount of template (g)	Other Chemicals	Characterization	Particle size (nm)
Yao et al., 2015	25	12	Tetraethyl orthosilicate (TEOS)	Poly acrylic acid (PAA)	5000	0.1-0.5	Ethanol Ammonia (NH ₃)	Particle size	10-60
Wu et al., 2018	25	12	Tetraethyl orthosilicate (TEOS)	Poly acrylic acid (PAA)	5000	0.48	Ethanol Ammonia (NH ₃)	Particle size	110
Shokuhfar et al., 2007	27	3	Tetraethyl orthosilicate (TEOS)	-	-	-	Ethanol Water (H ₂ O)	Particle size	19-42
Stöber et al., 1968	25	2	Tetraalkylsilicates Silicon tetrachloride	-	-	-	Ethanol Ammonia (NH ₃) Methanol n-propanol m-butanol Sodium hydroxide (NaOH)	Particle size	5-2000
Dubey et al., 2015	25	1.5	Tetraethyl orthosilicate (TEOS)	-	-	-	Ethanol Acetic acid Polyvinylpyrrolidone (PVP)	Particle size	45
Greasley et al., 2016	25	24	Tetraethyl orthosilicate (TEOS)	-	-	-	Ethanol Ammonia (NH ₃) Water (H ₂ O)	Particle size	20-825
Zhang et al., 2021	25	3	Tetraethyl orthosilicate (TEOS)	-	-	-	Ethanol Ammonia (NH ₃) Water (H ₂ O)	Particle size	10-27 nm

Table 2.6. Synthesis of silica from agricultural waste rice husk

Reference	Silica source	Washing and drying conditions	Acid treatment conditions	Thermal treatment conditions	Silica extraction	Nanosilica preparation
Nguyen et al., 2019	Rice husk	Water, 110°C, 24 h air	60 mL, 1 N HCl	500 °C, 700°C, 1000 °C, 6 h	2.5g RHA, 250mL 2.5 N NaOH aqueous solution	1. Addition of HCl until neutral pH 2. Precipitate silica washing with water 3. Centrifuged with 5000 rpm, 10 min, 3 times 4. Dried 110 °C for 24 hours 5. Calcination muffle furnace 450°C 1 hour
Wittayakun et al., 2008	Rice husk	Water, 100°C, 24 h air	3 M HCl, 3 h	-	-	1. Filtering and washing the precipitate until neutral pH 2. Drying 100°C for 24 h. 3. Calcination in muffle furnace at 550 °C, 6 hours.
Zulkifli et al., 2013	Rice husk	-	HCl, 75°C, 4 h 1. Filtering and washing the precipitate until neutral pH 2. Drying 110°C for 12 h.	-	10wt% NaOH aqueous solution, 90°C, 1 h	1. Ethanol mixed with sodium silicate 2. Water added and stirred 10 minutes 3. 3 M H ₃ PO ₄ added until gel was formed. 4. Gel was centrifuged at 7000 rpm and washed with hot water 5. Dried in freeze dryer (24 h) and calcination (550 °C, 30 min) in furnace
Yener and Helvacı, 2015	Rice husk ash	-	-	-	2.5 M NaOH aqueous solution, 25°C, 30 min	1. Pretreated RHA was boiled with 2.5 M NaOH aqueous solution under 120°C, 3 h 2. Filtering and washing with boiling water 3. Addition of 2.5 M H ₂ SO ₄ until pH 2 4. Addition of NH ₄ OH until neutral pH 5. Drying at 120°C 15 h 6. Washing to remove sulphate and sodium ions, drying 60°C for 2 days

Table 2.7. Synthesis of silica from agricultural waste rice husk (continued)

Reference	Silica source	Washing and drying conditions	Acid treatment conditions	Thermal treatment conditions	Silica extraction	Nanosilica preparation
Wang et al., 2012	Rice husk ash	-	1. Boiled with 10 wt% HCl for 2 h 2. Rinsed with water and dried at 100°C for 24 h	700°C, 2 hours	-	1. Ultrasonication with 0.2, 0.5 M KNO ₃ 2. Stirring 1 h 3. Filtered and drying at 105°C, for 4 hours 4. Calcination at 800°C for 2 h, 4 h and 8 h
Setyawan et al., 2019	Rice husk ash	-	-	-	-	1. 25 g RHA was mixed with 0.5 N, 0.75 N and 1 N NaOH solution, heated at 80°C for 1 h 2. Filtered and titrated 1 N HCl until pH 7 3. Gel aged for 24 h 4. Washed with water 4 times 5. Dried at 70 °C for 22 h
Elamawi et al., 2020	Rice husk	Water, 100°C, 24 h	1. 20 g RH mixed with 100 mL 1 N HCl for 2 h 2. Rinsed with water and dried at 100°C for 24 h 3. Filtered	700°C, 3 hours	-	-
Elamawi et al., 2020	Rice husk	Water, drying 100°C, 24 h	1. 20 g RH mixed with 100 mL 1 N HCl for 2 h 2. Rinsed with water and dried at 100°C for 24 h 3. Filtered	700°C, 3 hours	-	-
Rojas et al., 2019	Rice husk	Water, drying 100°C, 3 h	-	550°C, 1 hour 700°C, 1 hour	-	1. 15 g RHA, 1 mL HNO ₃ mixed at 90°C for 1 h. 2. Washing, filtered, dried at 100°C for 3 h.

2.6. SiO₂/TiO₂ Composites

Silicon dioxide (SiO₂) has different properties such as, semiconductor, low toxicity, high thermal stability, and has both an amorphous and crystalline structure. These different characters have been used in electronics, photo-tonic, chemicals, environmental, electrochemistry, and biomedical fields.

In pharmaceutical, make up, environmental remediation, biomedical applications, TiO₂ is one of the most used material. It has chemical stability low toxicity and easy to reach character. So that, these properties provide advantage to TiO₂. Also, due to these characteristics, TiO₂ is one of the most employed photocatalyst. TiO₂ has ability to degrade of inorganic and organic pollutants. The photocatalytic properties are exhibited under irradiation with UV light, due to the band gap value of 3.2 eV, limiting the application. The SiO₂/TiO₂ composite provide the properties of both, where the SiO₂ is a support for the TiO₂ particles, with chemical, electronic and hydrophobic properties (Rosales and Esquivel, 2020).

Kwon and coworkers (2003), synthesize SiO₂/TiO₂ composite by sol-gel method using titanium and silicon alkoxides as precursors. They investigated photocatalytic activity of the composite thin film coatings for the decomposition of methylene blue.

Lin and coworkers (2018) studied on the sol-gel preparation of self cleaning SiO₂-TiO₂/SiO₂-TiO₂ double layer antireflective coating. Antireflective coatings generally used in optical devices and energy related applications in order to decrease the transmission losses. Photovoltaic (PV) power is a type of renewable energy, and it is an area that continues to develop day by day. PV installations were set up outdoors and even in the deserts. So that, glass covers are important and necessary in order to prevent PV cells from samage of physical shock and corrosion. The glass covers had a refractive index approximately 1.52. The difference between air and glass cover results in about 8% reflection on the surfaces of cover glass. The reflection of the light decreased the efficiency of the PV cells. It is desired for an ideal antireflective coating has 100% transmittance at a specific wavelength when its refractive index is equal to $(n_a n_s)^{1/2}$, where n_a and

n_s are the refractive indices of air and substrate, respectively. The refractive index of AR coating for cover glass should be about 1.22 according to equation.

2.7. Synthesis of SiO₂/TiO₂ Composites in the Presence and Absence of the Templates

In the literature, synthesis methods SiO₂/TiO₂ varies but the sol gel method is the most used method in the synthesis. Considering the usage area of the composite the synthesis mechanisms can be changed. In order to reach low reflectance and hollow spherical particles, templates are used. If different properties are expected, the synthesis mechanisms can be changed. Zhang and coworkers (2021) synthesized SiO₂/TiO₂ complex colloidal sol in order to have good mechanical property and antireflection. They used TEOS as a silica source, ammonia as catalyst, ethanol as continuous phase. The reaction takes place in room conditions and the reaction time was determined as 3 hours. The silica sol was aged for 5 days and refluxed at 30 hours to 80°C. This obtained was called as SiO₂ sol. Secondly, TiO₂ sol was prepared by using tetrabutylorthotitanate as Ti source. HCl used as catalyst, ethanol used as a solvent. This reaction continues for 3 hours and then aged. The TiO₂ sol obtained. The SiO₂/TiO₂ composite sol was obtained by adding the TiO₂ sol into the SiO₂ under stirring 3 hours.

Halin and coworkers (2017) studied on the synthesis of SiO₂/TiO₂ composite sol by using TEOS and tetra-n-butyl orthotitanate (TBOT), were used as the sources of SiO₂ and TiO₂, respectively. to prepare the solutions of SiO₂ solutions and TiO₂ solutions. Firstly, TiO₂ sol was prepared from TBOT and HCl which is used as catalyst. HCl was added drop by drop into the TBOT. The solution was mixed for 1 hour. After 1 hour, a clear solution was obtained and TEOS was added to the solution under mixing. The solution (TBOT:TEOS=1:1) was mixed at 45 °C for 30 minutes. The final solution was obtained after aging process for 24 hours. Prepared composite sol were coated on glass substrates by spin coating with speed at 1000 rpm for 30 s. Then, coatings were annealed at three different temperature 300°C, 400°C and 500°C in air for 3 hours by using muffle furnace. SEM micrographs showed the large flake shaped

particles. Transmittance values were low in the visible region because of the insufficient coating of the layer which was seen in the SEM micrographs.

In the study of Wu and coworkers (2018), firstly SiO_2 sol was prepared. 0.48 g of PAA was dissolved in 12 mL of aqueous ammonia then, 240 mL of absolute ethanol was added slowly, and the injection of five TEOS aliquots totaling 4 mL under vigorously magnetic stirring at 25°C for 10 minutes. After 12 h, the solution were centrifuged at 10000 rpm for 10 min and washed with deionized water and absolute ethanol to remove the PAA template. The obtained hollow SiO_2 nanospheres (ca. 100 nm in diameter) with an inner-cavity size of around 60 nm were re-dispersed in 80 mL of deionized water. The inner-cavity size of hollow SiO_2 nanospheres was 90 nm when 2 mL of TEOS and 0.72 g of PAA were added under the same experimental conditions. The synthesized hollow SiO_2 sol were mixed with different amount of TBOT (0.24, 0.12, 0.06, 0.03 ml). The mixture was stirred for 12 hours at room temperature. Then, centrifuged (10000 rpm, 5 min) and redispersed the solid in 20 mL ethanol. The transmittance values for the composite films were between in 95.64% to 99.04%. Particle sizes of the composite sols were around 100 nm.

Yao and coworkers (2015), synthesize SiO_2 / TiO_2 double shelled nanosphere sol. Firstly, 0.1–0.5 g of PAA dissolved in 3–5 mL aqueous ammonia was added into the 90 mL of absolute ethanol. This was followed by the injection of 0.5–4.0 mL TEOS under vigorous magnetic stirring at 25°C . After 12 h, 45 nm SiO_2 hollow nanoparticle sols were formed. Ammonia (NH_3) was removed by stirring the sol in a ventilating cabinet. In the second step, hydroxypropyl cellulose (HPC, 0.1–0.4 g) was dissolved in the SiO_2 hollow nanoparticle sols. After that, 0.5–2.0 mL titanium (IV) n-butoxide (TNBT) mixed with 7.5 mL ethanol was injected slowly. After the injection, the temperature was increased to 90°C under vigorous stirring, and refluxed for 3 h. The sol was then cooled to room temperature, and was aged at room temperature for 7–30 days. Thin film coatings fabricated 50-200 mm/min, 2 layers by dip coating method. Calcination was performed at 550°C for 3 hours. The transmittance values were obtained in the range of 97.5%-98.6%.

2.8. Surface Modification of SiO₂/TiO₂ Composites

Due to the electrostatic forces nanoparticles want to build agglomerate. To prevent the agglomeration of this particles chemical and physical modification is usually applied. With respect to this action nanoparticles do not agglomerate and can be more uniformly distributed. In conclusion, mechanical or surface properties are developed of resulting nanocomposite. Surface modification of SiO₂ or TiO₂ nanoparticles can be applied by chemical or physical process. In the chemical methods, different organic or inorganic compounds of low molecular weights are used or polymer grafting is applied. The most common modification agents are silanes with functional groups capable to hydrolysis. The general structure of these type of silanes as RSiX₃, where X is a hydrolyzable group, i.e. chloric, ethoxyl or methoxyl, while R is an organic group of different functionality. The X group react with hydroxyl groups from silica or titanium surface, while alkylene residue can react with polymer matrix. Due to this, hydrophilic surface of nanoparticles exchange with hydrophobic nanoparticles. The hydroxyl group on silica surface permit to bond covalently different trialkoxyorganosilanes functionalized with amine (–NH₂) or mercaptyl (–SH) groups. High performance and homogeneous distribution of nanoparticles can be produce by amine surface modification. The amine group can change into carboxylic group. Surface grafting with polymers is another popular method for the surface modification (Gradzik et al., 2011).

Another method of surface modification is physical modification which is applied by using surfactants or macromolecules adsorbed on the surface of SiO₂ or TiO₂ nanoparticles. The hydrophilic head of surfactants are adsorbed on the nanoparticle surface due to electrostatic interactions. Surfactants have capable of the lower the particle-particle interactions thus the agglomerates formation decreases (Gradzik et al., 2011).

In some studies, the hydrophobic modification was applied by chemical vapor deposition. Wu and coworkers (2018) were fabricated SiO₂/TiO₂ composite thin film coatings with 140 mm/min withdrawal speed, dried 80°C for 30 minutes and calcined at 550°C for 2 hours. After the calcination, the coated glass were put

into autoclave. Hexadecyltrimethoxysilane (HDTMOS) was dropped into the bottom of the autoclave and autoclave was put into the oven at 120°C for 2 hours. After the process, autoclave was opened and put into oven at 140°C to remove unreacted HDTMOS.

In another study, Rezaei and coworkers (2014) studied on the modification of silica nanoparticles with vinyltrimethoxysilane (VTMS). In the synthesis of vinyl modified silica nanoparticles a solution consisting of NH_4OH (0.9 M) and water (9.5 M) in 100 ml of EtOH was prepared. At 40 °C, a 1:1 (w/w) solution of TEOS in EtOH was added suddenly with vigorous stirring. Stirring was continued for 30 min. During this time, VTMS was added after the reaction mixture started to become turbid (after about 5 min). After 30 min, stirring was stopped and the reaction continued for the next two hours. The size of the particles were around 72 nm. Water contact angle was measured as 158 ° which indicates the hydrophobivity of the surface.

2.9. $\text{SiO}_2/\text{TiO}_2$ Thin Film Coatings

$\text{SiO}_2/\text{TiO}_2$ thin film coatings have wide application area. Zhang and coworkers (2020) synthesize $\text{SiO}_2/\text{TiO}_2$ composite sol and they fabricate the thin film coatings by using dip coating method. The withdrawal speed was 120 mm/min and impregnation time was 90 s. The coated film was heated to 80°C for 15 min. After the heating, thin film coatings were calcined in muffle furnace for 2 hours. During the calcination ammonia vapor was applied in order to increase mechanical strength of the composite film. The particle size on the film was in the range of 10-27 nm.

Different studies have been performed for the $\text{SiO}_2/\text{TiO}_2$ thin film coatings and conditions and transmittance values of thin film coatings for the thin film coatings were tabulated in Table 2.4.

Table 2.9. SiO₂/TiO₂ thin film coatings

Reference	Fabrication of coatings		Drying		Calcination		T (%)
	Withdrawal Speed (mm/min)	Number of layer	T (°C)	t (min)	T (°C)	t (h)	
Aghaei et al., 2018	180	2	25	10	450	1	98.4 (@ 550 nm)
Jia et al., 2017	120	2	80	30	550	2	99.04 (@ 503 nm)
Jiang et al., 2021	420	1	-	-	400	1	94.5-93.7 (400-760 nm)
Lin et al., 2018	150 and 120	2	-	-	500	2	98.8 (@ 550 nm)
Tao et al., 2016b	1000	1	-	-	300-450	1	96.3, 97.3, 97.1
Tao et al., 2016c	1000	1	-	-	-	-	97 (@400-1200 nm)
Wu et al., 2018	140	1	80	30	550	2	99.04 (@400-800 nm)
Xiao et al., 2016	1-5	1	25	2	450	1	98.21 (@550-680 nm)
Xu et al., 2012	80	4	25	2	150	1.5	92.6 (@ 690 nm)
Yao et al., 2015	150	2	25	2	550	3	97.5-98.6 (@380-1100 nm)
Zhang et al., 2021	120	1	80	15	500	2	94.4 (@ 450-700 nm)
Zou et al., 2018	500	1	-	2	-	-	95.6 (@400-1200 nm)

2.10. Application of SiO₂/TiO₂ Thin Film Coatings

There are various applications of SiO₂/TiO₂ thin film coatings but according to this thesis, the important applications are automotive and anti-reflection applications. Shokuhfar and coworkers (2012) are synthesized SiO₂/TiO₂ composite film in order to use in automotive windshields. They investigate the photocatalytic activity of the composite and found that increasing calcination temperature is decreased the photocatalytic activity. But, applying at high calcination temperature, formed more hydrophobic character under UV light.

Zou and coworkers (2018) studied on the hollow silica nanoparticles and their thin film coatings. Optical measurements light transmittance, water contact angle measurements, mechanical stability and mechanical flexibility tests, acid resistant test, thermal stability and antifogging test were performed.

2.11. Theory of Antireflection

Antireflection is a property of the light reflectance is minimum. Antireflective coatings have maximum light transmittance. They are type of coatings that are used to minimize the reflection of light. They have many applications such as optical instruments containing high power lasers and outdoor applications and surfaces affected from materials such as glass windows and modules of solar cells. Fundamentally, these coatings are used to enhance the transmittance of incoming light. Light is always reflected when it travels from one medium to another medium due to the differences in refractive indices of the two media. When the difference is high, the reflectance is high and valid for vice versa. Reflection from surfaces can be described with Fresnel equation. The refractive index is the main property which determines the transmission of light in a medium. Fresnel equation is the basic mathematical model describing reflection and refraction. It depends on the two assumptions for single-layer coatings. One of them is all reflected waves have the same intensity and one wave is reflected per interface. The other one is other scattering, absorption, etc. are neglected. If there is destructive interference between the light reflected from the coating-substrate interface and the air-coating interface, light will not be reflected from the surface (Mehmood et al., 2016)

When the light comes to the material, three possibilities exist which are transmittance, absorbance and reflectance. If the light passes through into the materials, it defined as transmittance. If the light comes to the material and atoms of the material absorbs the light, it defined as absorbance. Finally, if the light comes to the surface and reflected from the surface considering to refractive index of the material. For materials, sum of the reflectance, transmittance and absorbance equals to 100. Therefore, for antireflective materials when transmittance increases, reflectance decreases.

2.12. Theory of Contact Angle and Surface Free Energy

The wettability or non-wettability of a solid is based on the contact angle, which is the angle that a water droplet dropped on the surface of that solid makes

with the surface. If the surface has a hydrophilic character, the interaction in between surface and water (adhesion forces) is higher than the interaction in water molecules itself (cohesion forces). By this way, surface molecules attract with water molecules and contact angle lowers. For hydrophilic character, contact angle is lower than 90° . In the case of hydrophobic character, the cohesive forces in between water molecules are higher than adhesive forces in between water and surface molecules. So that the water drop is collected by moving away from the surface. If the contact angle is in between 90° and over 150° , the surface is called as hydrophobic, is it is higher than 150° , the surface has superhydrophobic character.

Contact angle measurements firstly defined by Thomas Young are still one of the simplest and most accurate methods for characterizing the surface properties of solids such as wettability and surface energy, and for determining the liquid-solid interface and solid surface energy at minimum equilibrium distances. Eq. 1 is the Young's equation and it express the contact angle with respect to surface and interface energies. γ_{LT} , γ_{SG} , γ_{SL} and θ indicate the liquid surface tension, solid surface free energy, solid-liquid interfacial tension and contact angle respectively.

$$\gamma_{LT} \cos \theta = \gamma_{SG} - \gamma_{SL} \quad \text{Eq.1.}$$

The atoms on the surface always contain unbalanced forces compared to the atoms in the interior of the material, which is due to broken or weakened chemical bonds on the surface. For all this reason, it causes an excess of energy on the material, which is called the free surface energy of the solid. Materials can be divided into two groups as low and high surface energy. The materials have hydrophobic character has low surface energy and energies are generally below 100 mN/m. On the other hand, hydrophilic materials have high surface energy in between 500-5000 mN/m. The relationship between surface energy and hydrophobicity is generally as hydrophobicity increases, surface energy decreases, and vice versa, as hydrophobicity decreases, surface energy increases (Evcin et al., 2018).

3. EXPERIMENTAL STUDIES

3.1. Materials Used

3.1.1. Silica sol synthesis

Two different silica sources were used in the study which are rice husk ash (RHA) and tetraethyl orthosilicate (TEOS). Rice husk ash was supplied from ERDOĞANLAR Food Industry Trade and Limited Company. Rice husk was burnt at 700°C, 1 atm for 6 hours by the company and RHA was obtained. RHA is an agricultural waste. TEOS (Evonik Dynasylan A) was used as commercial silica source. Copolymer (BASF Sokalan® CP 5) and homopolymer (BASF Sokalan® PA 30 CL) of polyacrylic acid were used as templates. Ammonia solution (NH₄OH, MERCK, %25) was used as catalyst. Ethanol (C₂H₅OH, MERCK, %99) was used as a solvent in the synthesis. Also, the other chemicals used were sulfuric acid (H₂SO₄, TEKKİM, 95-98%), sodium hydroxide (NaOH, pellets for analysis). The conductivity and pH of the double distilled water were 1.1 µS cm⁻¹ and 6, respectively were used in the synthesis of silica sol from Na₂SiO₃.

3.1.2. SiO₂/TiO₂ composite sol synthesis

In the synthesis of SiO₂/TiO₂ composite sol, titanium (IV) isopropoxide (Ti[OCH(CH₃)₂]₄, Sigma Aldrich, ≥97%), (TTIP) was used as TiO₂ source. Hydrochloric acid (HCl, Merck, 37%) was used as catalyst.

3.1.3. Modified SiO₂/TiO₂ composite sol synthesis

In the modified SiO₂/TiO₂ composite sol, vinyltrimethoxysilane (VTMO, Evonik Dynasylan VTMO) was modification agent in the synthesis.

3.1.4. Thin film coating

1 cm x 4 cm glass substrates were used for the fabrication of thin film coatings. For the cleaning of the substrates chromic acid which is prepared in the laboratory, ethanol and double distilled water were used.

3.2. Synthesis of SiO₂ Sol from TEOS by Using Polymeric Templates

In the preparation of silica sol (SS), Stöber method was applied at room temperature using TEOS as silica source. A summary of the experimental procedure was given in Figure 3.1. Firstly, PAA (h-PAA or c-PAA) was dissolved in 5 mL aqueous ammonia and 90 mL ethanol was added under mixing at a rate of 500 or 800 rpm. Then, TEOS was injected with a total volume of 4.8 mL at equal intervals of 6 hours under vigorous magnetic stirring and reflux. After the last TEOS injection, the sol was continued to mix at room temperature for 12 hours. Then, silica sols were aged 5 days for complete reaction and for the removal of ammonia. Parametric studies had been performed on the mixing rate (500 and 800 rpm), type of polymeric template (h-PAA and c-PAA), amount of polymeric template (0.4 g, 0.6 g and 0.8 g) and amount of TEOS (2.1 mL, 3.1 mL and 4.8 mL). Amount of polymeric template and TEOS are determined with respect to literature studies which are given in Table 2.2. Figure 3.2 shows the experimental set-up for the silica sol synthesis.

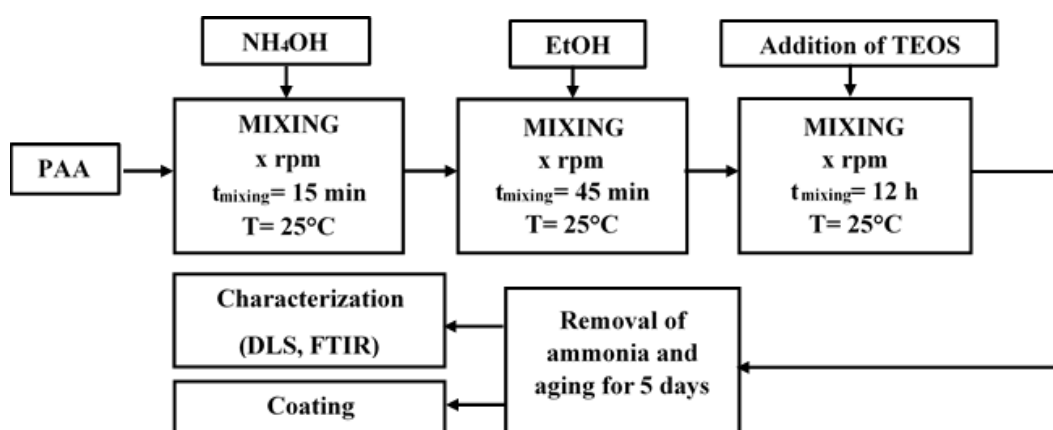


Figure 3.1. Schematic representation of SS synthesis



Figure 3.2. Experimental set-up for the synthesis of SS

3.3. Synthesis of SS from Rice Husk Ash by Using Polymeric Templates

In order to synthesize SS from rice husk ash, firstly sodium silicate (Na_2SiO_3) solution must be obtained. Figure 3.3 shows the schematic representation of experimental procedure. 20 g rice husk ash (Figure 3.4) was grinded to increase surface area. Then, 160 mL, 2.5 M sodium hydroxide aqueous solution was added to the suspension and mixing was started at 550 rpm for 0.5 h. After the pre-mixing, temperature was set at 120°C . The suspension was boiled under reflux for 3 hours at a constant stirring rate, 450 rpm. During this period, the silica in the rice husk ash was extracted. At the end of the 3 hours boiling, the suspension was filtered to obtain a silica-rich filtrate and a carbon-rich residue. Silica rich filtrate was named as sodium silicate solution. Next step obtaining silica gel from sodium silicate solution, the procedure was shown in Figure 3.5 . 56.5 mL 2.5 M H_2SO_4 aqueous solution was added to 160 mL sodium silicate drop by drop until sodium silicate gel formation. Then, addition of 2.5 M H_2SO_4 aqueous solution was continued until pH of the solution was at 2. After this step,

addition of NH_3 was started and continued until pH 7. Totally 3.4 mL NH_3 was added to the solution. There were two washing steps obtaining for the silica gel. The first one was the double distilled water washing. At this step, 300 mL double distilled water was added to the gel and stirred at 750 rpm for 1 hour, solution was aged 1 day. After 1 day, top of the solution was taken and again 300 mL water added to the solution and stirred. This procedure was continued for 15 days. At the end of the 15 days, ethanol washing was started. After the taken 15th washing water, 250 mL ethanol was added. Temperature was set at 140 °C, the solution was stirred 750 rpm under reflux for 8 hours. After 1 day aging, obtained gel was ready for the silica sol synthesis experiments.



Figure 3.3. Rice husk ash

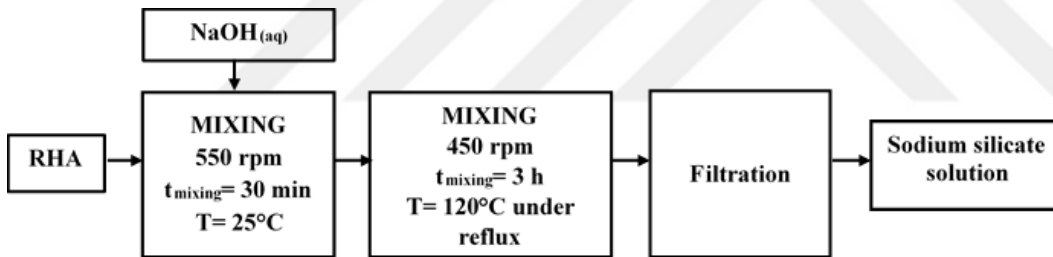


Figure 3.4. Schematic representation of synthesis of sodium silicate solution

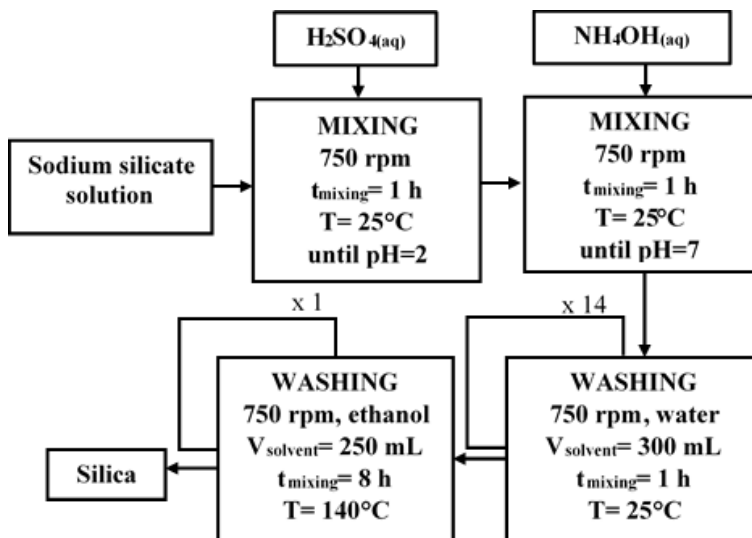


Figure 3.5. Schematic representation of synthesis of silica gel

SS synthesis procedure from rice husk ash (Figure 3.6) was similar with the synthesis procedure from TEOS. Firstly, PAA (h-PAA or c-PAA) was dissolved in 5 mL aqueous ammonia and 35.15 mL ethanol was added under mixing at a rate of 500 rpm. Then, 12.4 g silica gel was dissolved in 54.85 mL ethanol under mixing until obtaining homogenous solution. Silica gel-ethanol solution was added at equal intervals of 6 hours. After the last silica gel-ethanol solution injection, the sol was continued to mix at room temperature for 12 hours under reflux. Then, silica sols were aged 5 days for complete reaction and for the removal of ammonia. Parametric studies had been performed on the type of polymeric template (h-PAA and c-PAA) and amount of polymeric template (0.4 g, 0.6 g and 0.8 g).

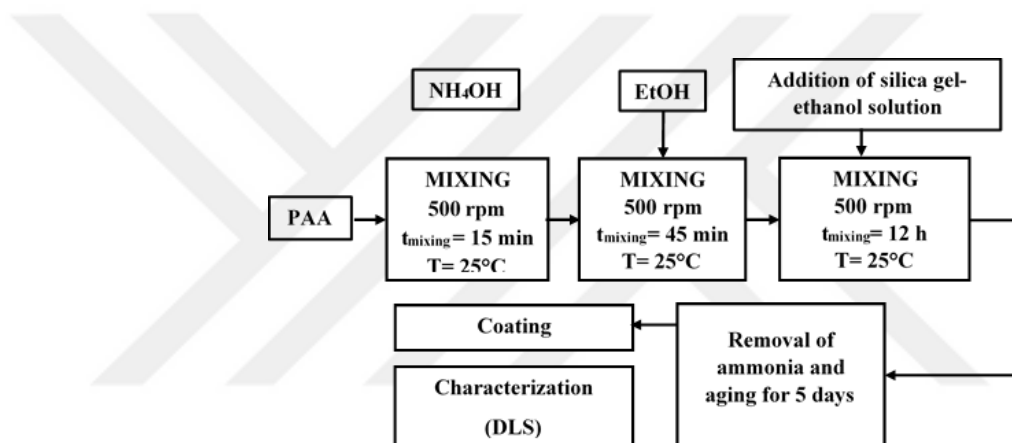


Figure 3.6. Schematic representation of synthesis of SS from rice husk ash

3.4. Synthesis of SiO₂/TiO₂ Composite Sol from TEOS by Using Polymeric Templates

SiO₂/TiO₂ composite sol was synthesized from SiO₂ sol which was synthesized under optimum conditions (0.6 g c-PAA, 4.8 mL TEOS), and titania source which was TTIP. First of all, SS was synthesized according to Section 3.2. Experimental set-up was shown in Figure 3.7. This procedure based on Halin and coworkers (2017) study. After 5 days aging, composite sol synthesis was performed. 40 mL SS was taken in a reactor and the reaction temperature was set at 45 °C. Figure shows the experimental set up for the synthesis of composite sol. Solution of 0.262 M TTIP and ethanol was prepared for the synthesis. After the temperature was reached the desired value, 6.6 mL TTIP and ethanol mixture was

added to the reactor under reflux and continuous stirring for 30 minutes. The reaction was finished after 30 minutes. Figure 3.8 shows the schematic representation of synthesis.



Figure 3.7. Experimental set-up of synthesized composite sol

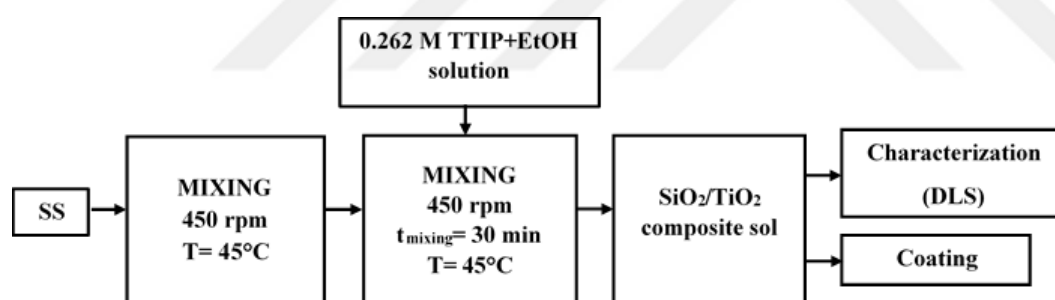


Figure 3.8. Schematic representation of synthesis of SiO₂/TiO₂ composite sol.

3.5. Synthesis of Modified SiO₂/TiO₂ Composite Sol

SiO₂/TiO₂ composite sol was modified with vinyltrimethoxysilane. In the synthesis the SiO₂ to VTMO ratio was selected as 0.25 depending on the literature. Firstly, SiO₂/TiO₂ composite sol was prepared with respect to Section 3.4. Figure 3.9 shows the schematic representation of modified composite sol synthesis.

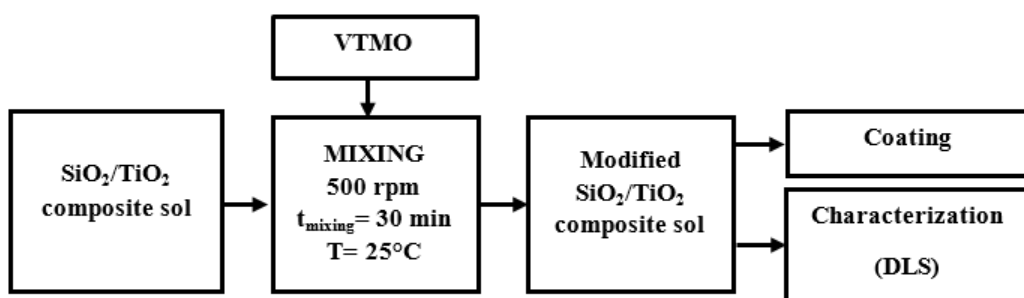


Figure 3.9. Schematic representation of synthesis of modified $\text{SiO}_2/\text{TiO}_2$ composite sol

Synthesis was performed at 25°C , under continuous stirring (500 rpm) and reflux. VTMO was added drop by drop into the reactor. When the addition of the VTMO was completed, the solution was mixed for 30 minutes. After this time, the modified composite sol was obtained. Figure 3.10 shows the experimental set up of this synthesis.



Figure 3.10. Experimental set-up of modified composite sol

3.6. Thin Film Coatings

Thin film coatings were fabricated by using dip-coating device which is shown in Figure 3.11. The dip coating device ensures that the surfaces to be coated are immersed in the solution at a constant speed. Schematic representation was given in Figure 3.12. After the surface was hold in solution for a defined time, 30 seconds, it was removed at a constant rate. In the literature the glass substrates are washed with water and ethanol for cleaning (Zou et al., 2018). In the first step, cleaning of glasses, the glass substrates (1 cm x 4 cm) were held in a chromic acid for 1 day, then washed with distilled water. Then, they were held in an ultrasonic bath putting them in pure water for 10 minutes at 35 kHz, and they were finally washed with ethanol and dried in an oven at 80 °C, 6 hours. The cleaned glass substrates were dipped into the sol using dip coating device with two different withdrawal speeds, 100 mm/min and 150 mm/min. They were held in the sol for 30 s and withdrew with the same speed. After the coating, the coated glasses were dried in an oven at 80 °C for 30 minutes. The last step was calcination, the coated glasses were calcined in muffle furnace (Protherm PLF130/9) at 550 °C for 2 hours with a heating rate 10 °C/min.



Figure 3.11. Dip coating device

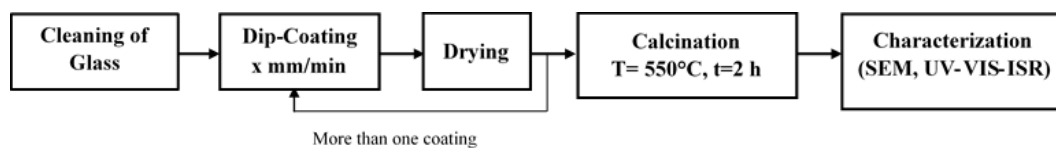


Figure 3.12. Procedure of thin film coatings

3.7. Application of Glass Paints Containing Modified $\text{SiO}_2/\text{TiO}_2$ Composite Sol

In this thesis, effect of modified composite sol in two component glass paint was investigated. The aim of this was to analyze the hydrophobicity, antireflection and mechanism of film forming depending on the variable amount of composite sol. 0.5, 1.25, 2.25 and 5 weight percent of modified composite sol were used in the clear solution. Also, the glass paint was prepared without adding modified composite sol to fabricate the standard panel. In Figure 3.13 show the procedure of fabrication of glass paint films containing different amount of modified composite sol. First of all, clear solution was prepared by adding determined amount of modified composite sol under mixing (Figure 3.14) at a rate of 750 rpm of 5 min. Then, hardener was added to the system under same mixing conditions. After that, the glass paints were applied by bar applicator (BYK Four sided bar applicator 30-60-90-120 μm , film width: 6 cm) and spray machine (RX20-D Spray Machine). After the application, flash of was applied to the films at 25°C for 30 minuteS. Then, films were dried at 80°C for 30 minutes to reach the dry film thicknesses in between 30-40 μm .

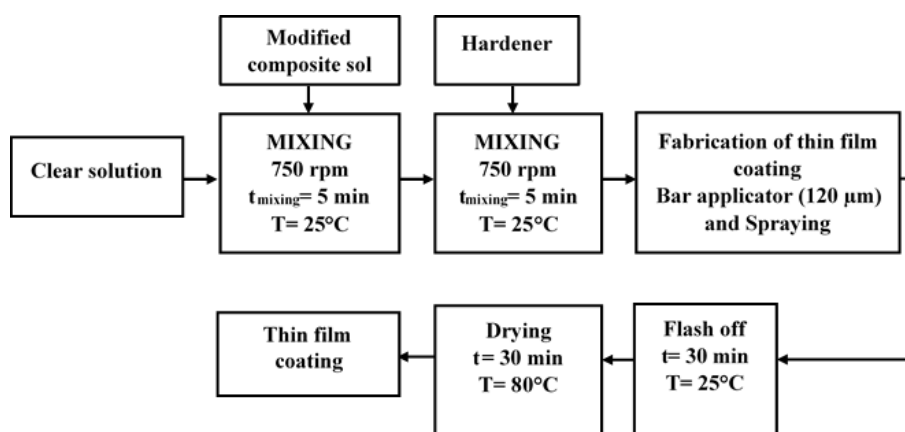


Figure 3.13. Experimental procedure of application of glass paints containing modified composite sol



Figure 3.14. Experimental set-up for process of glass paint

3.8. Characterization of SiO_2 , $\text{SiO}_2/\text{TiO}_2$ and Modified $\text{SiO}_2/\text{TiO}_2$ Composite Sols

At the beginning of the study, parametric studies had been performed in order to find optimum synthesis conditions such as type of template, amount of template and amount of Si source (TEOS). After these different SS synthesis, Fourier Transform Infrared Spectroscopy attached with ATR (ATR-FTIR Perkin Elmer Spectrum 100, Diamond/ZnSe crystal) was used to indicate the chemical structures of the silica sols. Particle distribution of silica sols were analyzed by dynamic light scattering (MALVERN Zetasizer NanoZS). $\text{SiO}_2/\text{TiO}_2$ and

modified $\text{SiO}_2/\text{TiO}_2$ composite sols also were characterized with dynamic light scattering. In order to indicate the modification of $\text{SiO}_2/\text{TiO}_2$ composite sols, both $\text{SiO}_2/\text{TiO}_2$ composite sols and modified $\text{SiO}_2/\text{TiO}_2$ composite sols were analyzed with X-Ray Photoelectron Spectroscopy (XPS, Thermo Scientific K-Alpha).

3.9. Characterization of SiO_2 , $\text{SiO}_2/\text{TiO}_2$, Modified $\text{SiO}_2/\text{TiO}_2$ Composite Thin Film Coatings

Synthesized all SiO_2 , $\text{SiO}_2/\text{TiO}_2$ composite and modified $\text{SiO}_2/\text{TiO}_2$ composite sols were coated on a glass substrates. The morphology and porosity of the samples were analyzed by scanning electron microscopes (SEM, Thermo Scientific, Apreo S and FEI QUANTA 250 FEG). For the determination of antireflection characteristics of the thin film coatings, UV-visible spectrophotometer (UV-vis, Shimadzu UV-Vis-ISR 2600) was used in order to determine the visible light transmittance spectra of the film coatings.

3.10. Characterization of Coatings Prepared by Glass Paints Containing Modified $\text{SiO}_2/\text{TiO}_2$ Composite Sols

The glass paints were applied to the glass and polypropylene surfaces for the analysis of water contact angle, antireflection and dynamic mechanical analysis. Water contact angle indicated the hydrophobicity of the coatings and it was aim to analyze the effect of addition. Water contact angle and surface free energy was analyzed with the Krüss DSA100 by using water and diiodomethane. The antireflection property of coatings were analyzed by using UV-visible spectrophotometer (UV-vis, Shimadzu UV 3600i Plus) in the range of 190-1100 nm. The properties of coatings were searched by using dynamic mechanical analysis (DMA), TA Instruments Q800 was used for the analysis. The analysis were perform at 90°C, 120°C and 140 °C. The films were burned at 120°C and 140 °C so 90 °C results were given for this thesis.

4. RESULTS

4.1. Parametric Study on Silica Sol Synthesis

In this section the results of different silica sol synthesis parameters were shown. Effect of stirring rate (500 rpm and 800 rpm), type of polymeric template (h-PAA and c-PAA), amount of polymeric template (0.4 g (4000 ppm), 0.6 g (6000 ppm) and 0.8 g (8000 ppm)), amount of TEOS (2.1 mL, 3.1 mL and 4.8 mL) and type of silica source (TEOS and Na_2SiO_3) were investigated.

4.1.1. Effect of stirring rate on the synthesis of silica sol

When looking at the purpose of the stirring, it provides homogeneous mixture of the components and it increases the reaction rate by colliding the components in the solution. Whether the components interact with each other, the reaction rate increases. Depending on this general rule, in the study two different stirring rates were chosen to apply the system which were 500 rpm and 800 rpm. 800 rpm is much more vigorous than 500 rpm and it allowed the components to interact with each other more. So that, the size of SS particles synthesized at 800 rpm was bigger than 500 rpm. The experiments were performed under room conditions with two different polymeric templates (h-PAA and c-PAA) which were used as amount of 0.6 g (6000 ppm) and the other all process parameters were kept constant (4.8 mL TEOS, 5 mL NH_3 , 90 mL EtOH) at same conditions. Figure 4.1 shows the particle size distribution of two different stirring rates. According to h-PAA particle size distributions, 500 rpm stirring rate gave smaller particle size than 800 rpm stirring rate. Similarly, in the c-PAA experiments 500 rpm stirring rate. When the c-PAA and h-PAA experiments were compared at the same stirring rate at 500 rpm, it was observed that the particle sizes in the c-PAA experiments were smaller than h-PAA experiments. Both polydispersity index values (PDI) were smaller than 1 which are 0.064 for c-PAA (500 rpm) and 0.232 h-PAA (500 rpm). Optimum stirring rate was chosen as 500 rpm for other SS experiments.

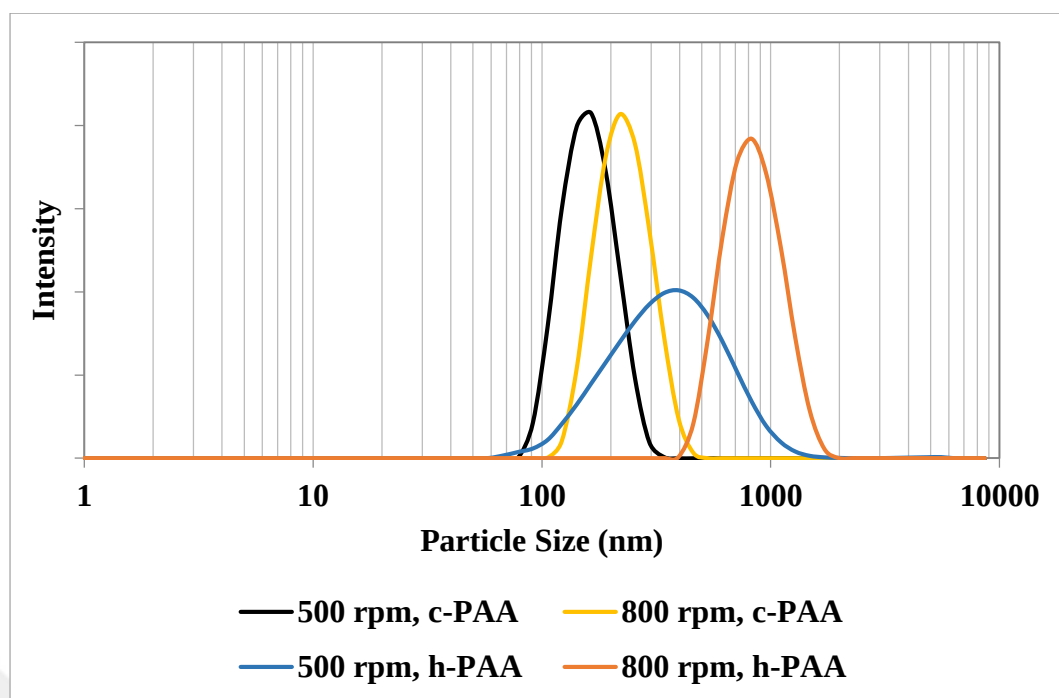


Figure 4.1. Particle size distribution of SS at different stirring rates

In the literature stirring rate of the solution did not indicate, the term vigorous was used in order to define stirring rate. Therefore, two different stirring rates were studied and the particle size distribution was close to each other but 500 rpm were chosen as an optimum stirring rate depending on the small particle size.

The chemical structure of the silica sols were characterized by FTIR spectroscopy attached with ATR, and their spectra were given in Figure 4.2. All silica sols showed similar absorption bands. Seven absorption bands observed and they were at 3325 cm^{-1} (OH-stretching), 2970 cm^{-1} (C=H stretching), 1547 cm^{-1} (C=C stretching), 1377 cm^{-1} (C-H bending), 1043 cm^{-1} (asymmetric Si-O-Si stretching) and 880 cm^{-1} (symmetric Si-O-Si vibration) (Zou et al., 2018). When FTIR spectra of silica sols compared with TEOS, h-PAA and c-PAA spectra, it was seen that the spectra of h-PAA SS and c-PAA SS synthesized at 500 and 800 rpm were identical with TEOS spectrum. This can be concluded that PAA molecules were surrounded with silica molecules and it was the evidence of synthesis of silica.

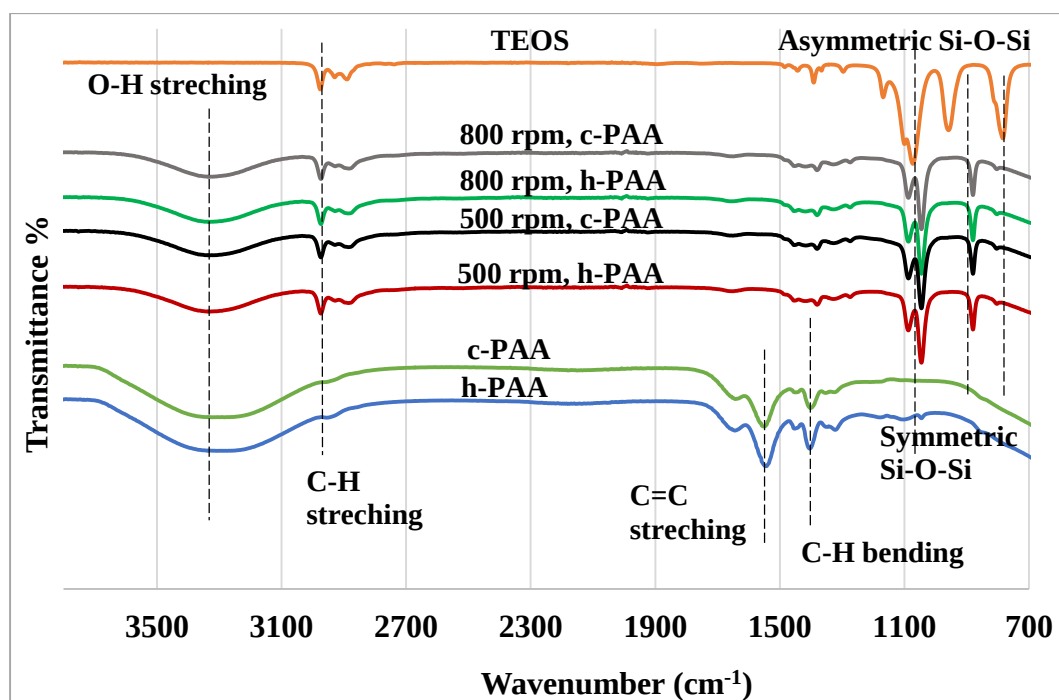


Figure 4.2. FTIR spectrum of h-PAA and c-PAA SS synthesized at 500 rpm and 800 rpm

4.1.2. Effect of type of polymeric template on the synthesis of silica sol

Throughout the experiment, two different polymeric template was used which were h-PAA and c-PAA. Both of them are polymers of polyacrylic acid. These polymers were used as a template for the silica particles. Templates were surrounded by silica particles to obtain spherical-hollow particles. Takai-Yamashita and coworkers worked on hollow silica nanoparticles supported by VO₂ to get thermochromic property and polymeric template was also used polyacrylic acid. In another study, polyacrylic acid was used as a template to get antireflective coatings (Xu, et al., 2014). The molecular weight of h-PAA was 8000 g/mol and it is based on sodium polyacrylate structure. The molecular weight of c-PAA was 70000 g/mol and it consists of maleic acid-acrylic acid copolymer base. In the literature, generally polymeric templates had molecular weight of 3000 and 5000 are used (Yao et al., 2015, Zou, et al., 2018)

In the parametric study of comparing these two polymeric template, again other conditions kept constant and 0.6 g (6000 ppm) polymer, 4.8 mL TEOS, 5

mL NH_3 and 90 mL EtOH were used. Figure 4.3 shows the particle size distribution of h-PAA and c-PAA based silica sols.

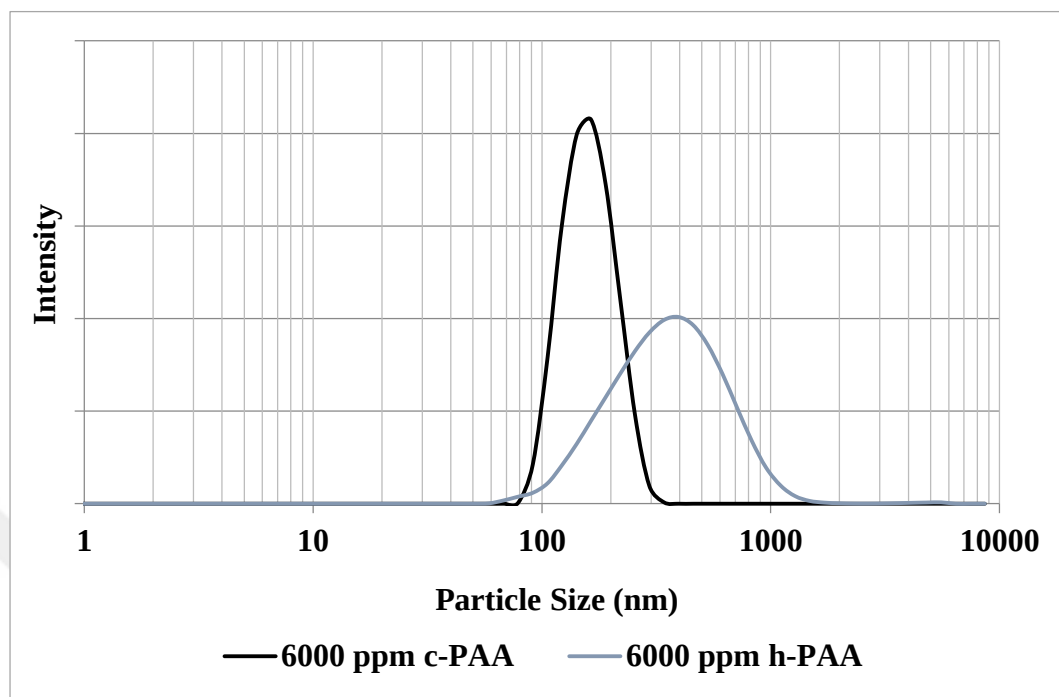


Figure 4.3. Effect of type of polymer on silica sols' particle size

When the Figure 4.3 evaluated, the particle size of the SS obtained by using c-PAA was smaller than h-PAA. The reason of this result could be the interaction of the functional groups of the c-PAA with TEOS higher than the interaction with h-PAA with TEOS. As a result of this strong interaction, silica particles that are better oriented around c-PAA result in smaller particles. Considering literature particle size, prepared silica sols' particle size were a little bit bigger than literature values (Wu et al., 2018, Xiao et al., 2016).

Figure 4.2 shows the FTIR spectrums of SS by using h-PAA and c-PAA as polymeric templates. There is no difference between spectrums and both SS have silica vibration bands in the range of 1043 cm^{-1} (asymmetric Si-O-Si stretching) and 880 cm^{-1} (symmetric Si-O-Si vibration) (Zou et al., 2018).

4.1.3. Effect of amount of polymeric template on the synthesis of silica sol

In this section, the effect of amount of polymeric template was investigated. Three different amount of polymeric templates were used which were 0.4 g (4000 ppm), 0.6 g (6000 ppm) and 0.8 g (8000 ppm) for both polymer type. Figure 4.4 and Figure 4.5 shows the effect of the amount on the SS particles for both polymeric template usages.

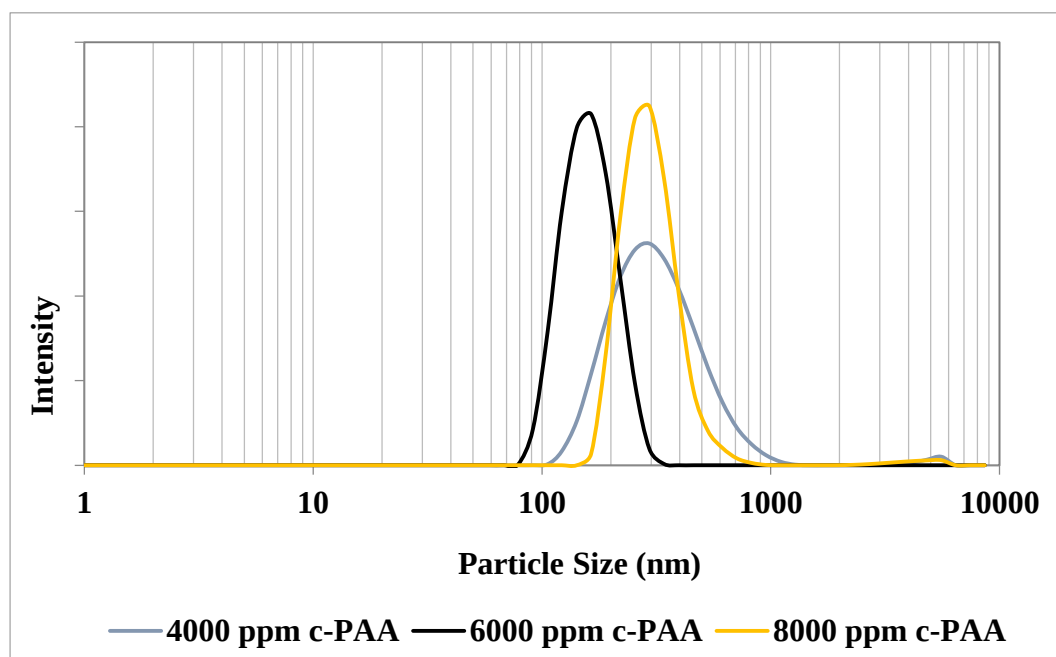


Figure 4.4. Effect of amount of c-PAA on silica sols' particle size

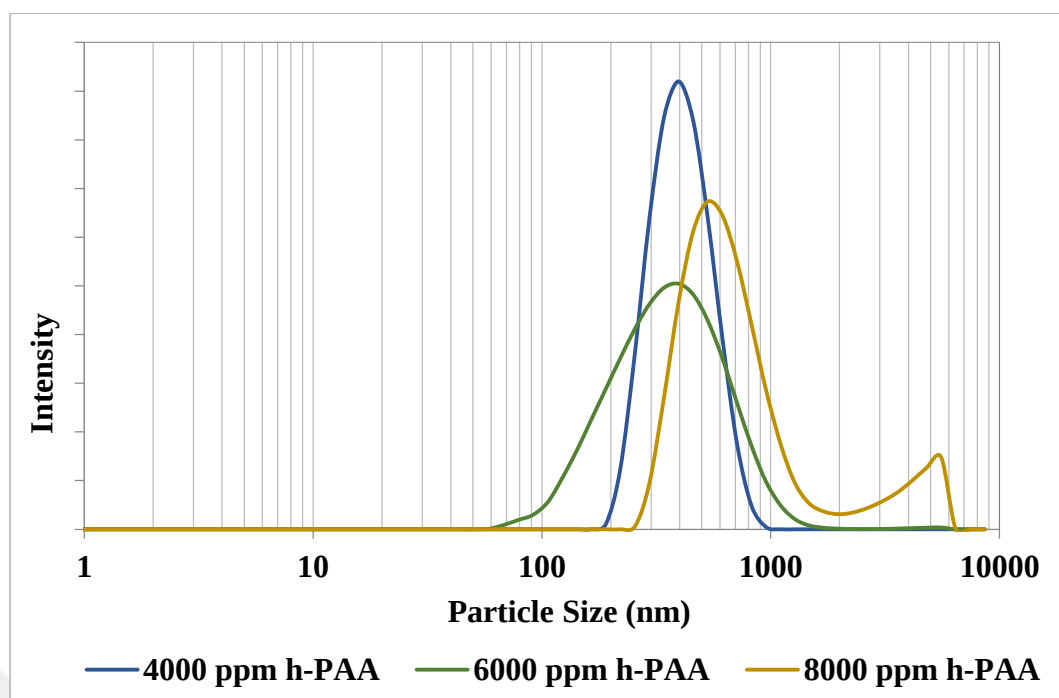


Figure 4.5. Effect of amount of h-PAA on silica sols' particle size

The experiments performed by using c-PAA as a polymeric template, the smallest particle size was obtained with the 0.6 g c-PAA usage. Using amounts of polymeric templates of 0.4 g and 0.8 g were get higher particles size than 0.6 g experiment. The particle sizes of these two experiment were close to the each other. The reason of this could be the loading capacity of the template. The amount of TEOS was constant so it was needed definite number of functional groups. So that the amount of functional groups around the polymer in the 0.4 g experiment could be insufficient to silica particles oriented on the template. So, silica particles accumulate around the template and were occurred high particle size. In the 0.6 g experiment, the particle size decreased with respect to 0.4 g experiment. The functional groups of the template were surrounded by the silica particles as a thin layer. On the other hand 0.8 g experiments' particles size got higher than 0.6 g experiments. Since the amount of polymeric template is higher than the amount of silica, the interactions in the polymer are higher than the interaction of the polymer with silica. For this reason, polymers that cannot interact with silica in sufficient quantity on the surface cause an increase in particle size by accumulating in the middle of the particle.

Similar results were obtained by using h-PAA in the synthesis. 0.4 g and 0.6 g experiments' particle sizes were close to the each other but, 0.6 g experiment was get smallest particle size. Considering both cases in h-PAA and c-PAA, 0.6 g was found as optimum amount of polymeric template for the particle size.

Jia and coworkers (2017), performed a study by changing amount of both PAA and TEOS. They concluded their result, as the PAA ratio increases and TEOS ratio decreases, the hollow nanoparticles become bigger and the thickness of the nanoparticles becomes thinner. If the ratio of TEOS was kept constant the hollow silica nanoparticles become bigger by increasing PAA ratio. Considering the particle distribution of 0.4 g, 0.6 g and 0.8 g PAA synthesized SS, results were agreed with Jia and coworkers study.

4.1.4. Effect of amount of TEOS on the synthesis of silica sol

The silica source of the SS was used as TEOS. At the beginning of this study, all experiments were performed at 4.8 mL TEOS because in the literature the maximum value was 4 mL (Xiao et al., 2016) and with this thesis it was desired to see the effect of high amount of TEOS. In order to see the effect of amount of TEOS, two more sets experiment were done for 2.1 mL and 3.1 mL TEOS. These experiments were performed with the amount of 0.6 g c-PAA. The amount of TEOS was affect the particle size directly because polymeric template in the solution was surrounded by TEOS. Increasing the amount of TEOS increased the thickness of the layer around the polymer. Figure 4.6 shows the effect of the amount of the TEOS on particle size. When the amount of TEOS decreased from 4.8 mL to 3.1 mL, particle size was decreased from 155 nm to 116 nm. A little change in the amount of the TEOS from 3.1 to 2.1 had also effect, particle size decreased from 116 nm to 110 nm. In similar trend were seen in Tao and coworkers (2016b) study, the increasing amount of TEOS from 1.99 g/L to 3.98 g/L resulted in the increase of the thickness of the shell from 5.9 to 15.5 nm.

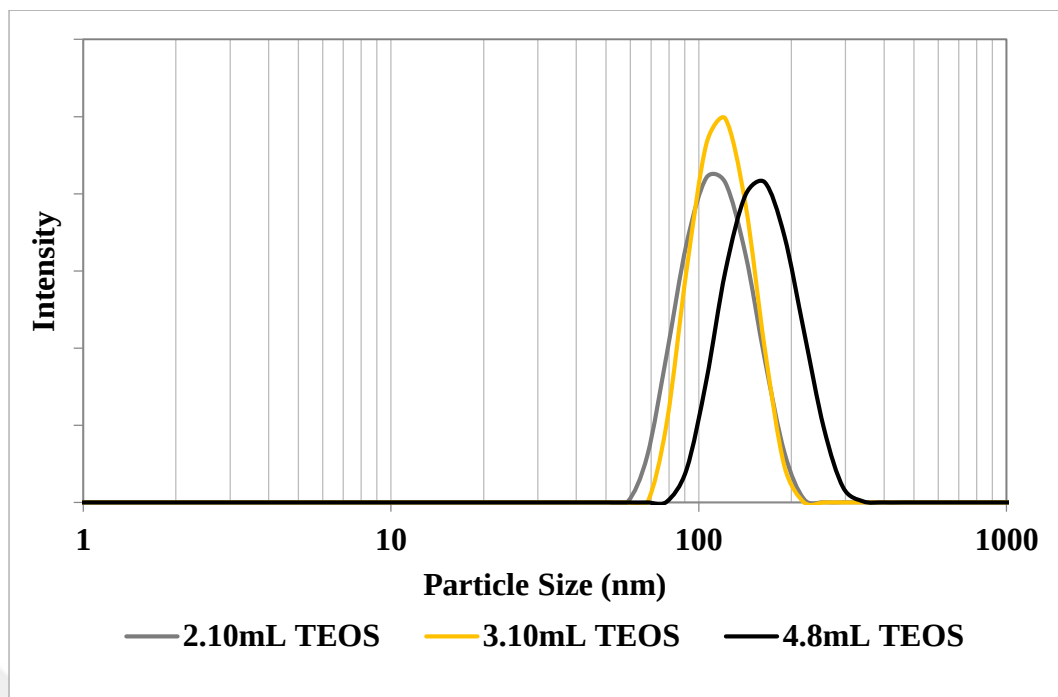


Figure 4.6. Effect of amount of TEOS on silica sols' particle size

4.1.5. Effect of silica source on the synthesis of silica sol

In this section, silica sols were synthesized from TEOS and sodium silicate. The main purpose of this section was to evaluate the agricultural waste, rice husk ash, in the synthesis of SS and comparing its results with SS synthesized from commercial silica source which is TEOS. In all experiments, the amount of silica was kept constant, equivalent to the amount of silica in 4.8 mL of TEOS. Figure 4.7 shows the particles size distribution of SSs' from different silica sources. At constant c-PAA amount for both 6000 (0.6 g) and 8000 ppm (0.8 g), the particle size was higher for the SS synthesized from sodium silicate than TEOS. The reason of this could be the functional groups on the silica source surface. If the SSs' surface synthesized by using sodium silicate changed by using modification, the interaction in between polymer and silica could be increased.

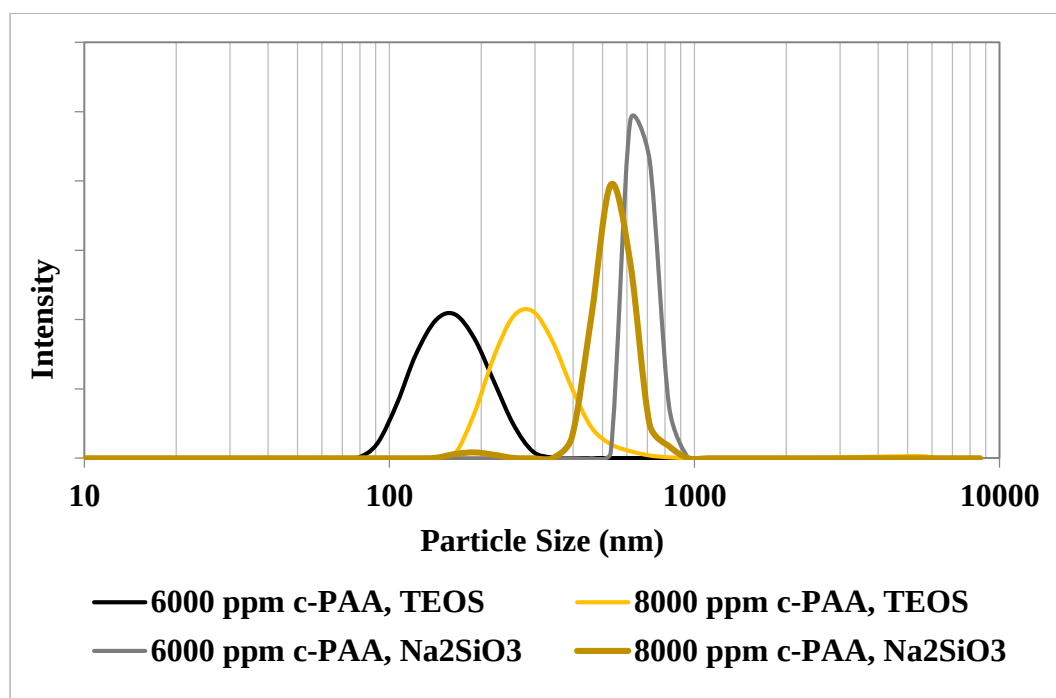


Figure 4.7. Effect of silica source on silica sols' particle size

FTIR spectrums of the SS synthesized from TEOS and sodium silicate were given in Figure 4.8. In the both TEOS and sodium silicate spectrums the existence of Si were seen at 1043 cm^{-1} (asymmetric Si-O-Si stretching). SS synthesized from TEOS and sodium silicate had similar absorption bands at 1043 cm^{-1} (asymmetric Si-O-Si stretching) and 880 cm^{-1} (symmetric Si-O-Si vibration) (Zou et al., 2018). That indicates the existence of Si in the structure.

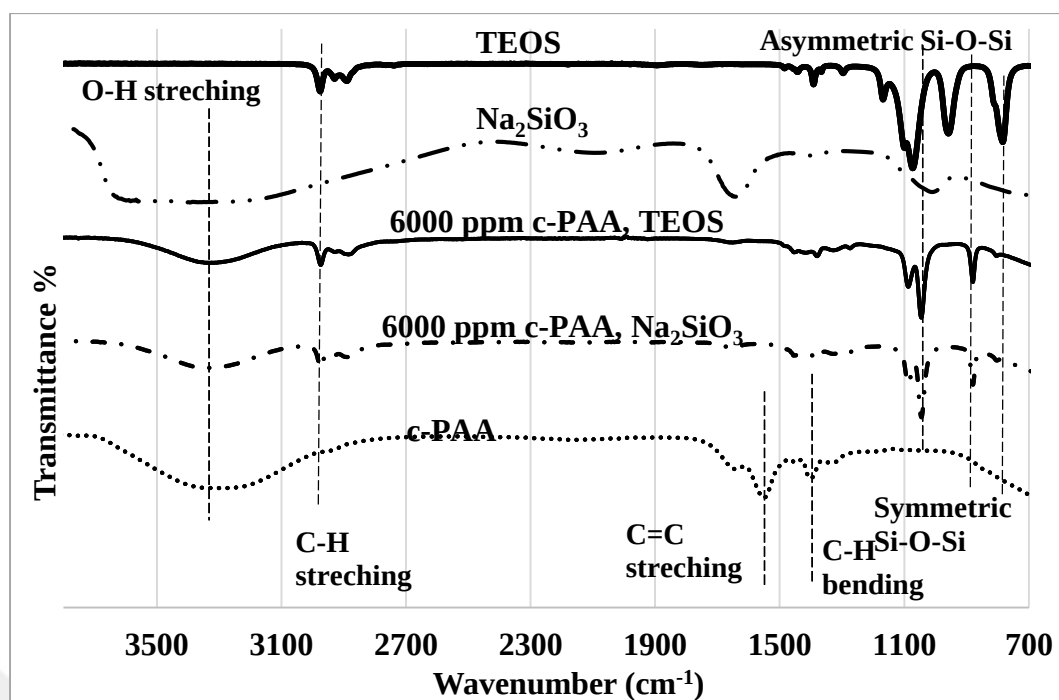


Figure 4.8. FTIR spectra of SSs synthesized from different silica sources

4.2. Characterization of SiO₂/TiO₂ Composite Sols

The composite sol was synthesized by the procedure which was explained in Section 3.4. This composite synthesis was carried out by using 0.6 g c-PAA, 4.8 mL SS because with these parameters particle size of the SS minimized. Figure 4.9 shows the particle size distribution. Addition of TTIP was increased the particle size from 155 nm to 280 nm as expected because silica layer was surrounded by TiO₂. Also, the aging was affected the particle size in increasing way from 280 nm to 360 nm. This result occurred because of the agglomeration in the solution. The obtained composite sol nanoparticle size was bigger than the Wu and coworkers (2018) study which was maximum value 100 nm.

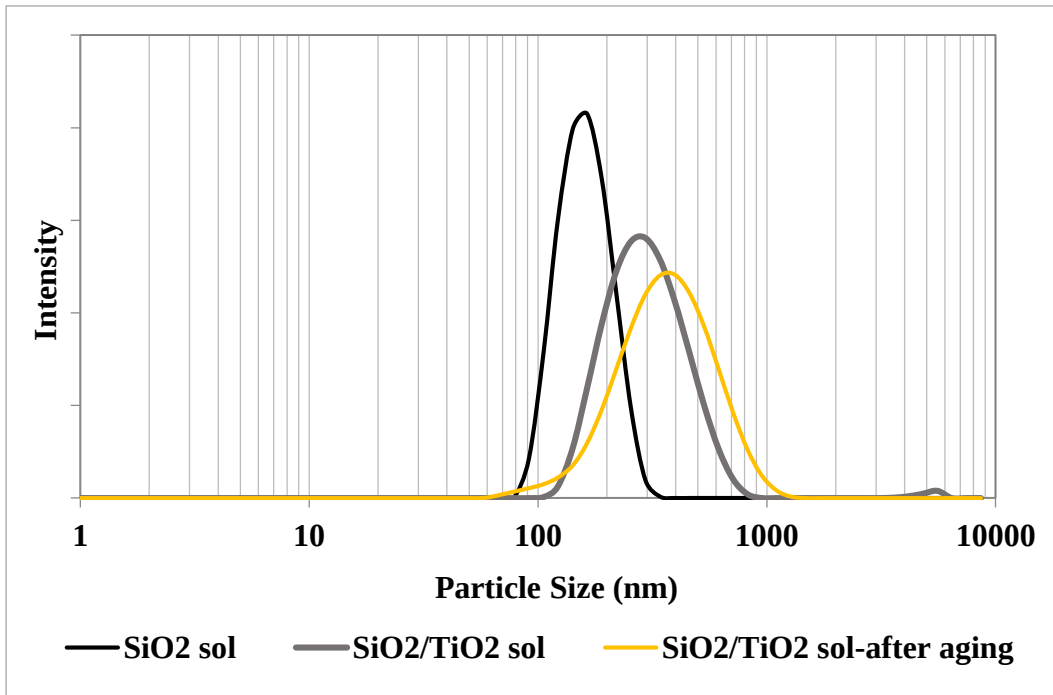


Figure 4.9. Particle size distribution of $\text{SiO}_2/\text{TiO}_2$ composite sol

4.3. Characterization of Modified $\text{SiO}_2/\text{TiO}_2$ Composite Sol

Modified $\text{SiO}_2/\text{TiO}_2$ composite sol was synthesized by using vinyltrimethoxysilane (VTMO) as a modification agent. Procedure was explained in the Section 3.5. In Figure 4.10 particle size distributions of SS, composite sol, composite sol during modification and modified composite sol were shown. Depending on the addition of the new compositions into the SS particle size increases. Firstly, during the synthesis of composite sol from the SS, particles of TiO_2 were increased the particles size of the structure. Then, the aging of composite sol was also increased the particle size and addition of modification agent a little bit change were observed.

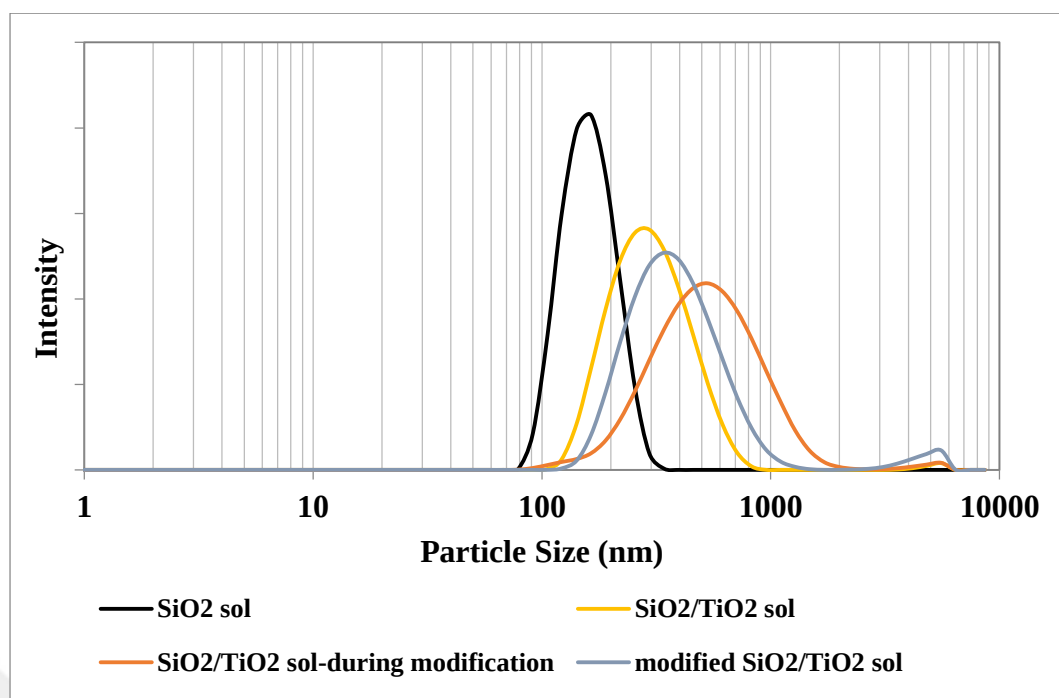


Figure 4.10. Particle size distributions of SS, composite sol and modified composite sol

X-Ray photoelectron spectroscopy (XPS) was performed for the investigation of surface chemistry of the $\text{SiO}_2/\text{TiO}_2$ composite and modified $\text{SiO}_2/\text{TiO}_2$ composite. In the XPS analysis, the binding energy is a characteristic of the elements and it changes with the electron density. If the binding energy increases, electron density decreases. For the analysis, composite and modified composite sols were dried at vacuum oven under 80°C , -0.5 atm for 24 hours in order to evaporate volatile components. In Table 4.1 atomic percentages and characteristic peaks of elements were tabulated. Bare composite sol had three O1s peaks at 530.09 eV, 532.92 eV and 531.45 eV that indicates the O^{2-} ions and absorbed oxygen chemically at the surface. At 530.09 eV signal corresponds to O1s of TiO_2 , 532.92 eV signal belongs to O1s of SiO_2 . 531.45 eV signal could carbon based impurities or water from outside. There was a peak at 458.54 eV which probably belongs to Ti-O-Si bond in the composite structure. There were C1s peaks at 284.56 eV, 286.13 eV, 288.61 eV and 286.94 eV. They are evidence of the C-C, C-H, C-O and -C-Si- bonds, respectively (Aghaei et al., 2018 and Milosev et al., 2012). In the Si2p3 peaks, which were at 101.2 eV and 103.39 eV probably belong to Si-O-Ti and Si-O-Si bonds respectively. Si-O-Ti bond has lower binding energy than Si-O-Si bond. In Si-O-Ti bond Ti is supplied more

electrons than Si to O, so it increases the electron density of the on Si atoms and lowers the binding energy of Si-O-Ti bond.

Table 4.1. XPS results of SiO₂/TiO₂ composite sol and modified SiO₂/TiO₂ composite sol

Sample	Peak Name	Peak BE	Atomic %
Modified SiO₂/TiO₂ composite	Si2p3 Scan A	102.01	21.33
	C1s Scan A	284.63	38.16
	C1s Scan B	286.47	2.81
	C1s Scan C	292.61	1.19
			42.16
	Ti2p3 Scan A	459.03	2.39
	Ti2p3 Scan B	458.06	0.38
	O1s Scan A	530.45	4.64
	O1s Scan B	532.19	29.09
SiO₂/TiO₂ composite	Si2p3 Scan A	101.2	1.48
	Si2p3 Scan B	103.39	6.1
	C1s Scan A	284.56	22.17
	C1s Scan B	286.13	5.55
	C1s Scan C	288.61	2.15
	C1s Scan D	286.94	1.41
			31.28
	Ti2p3 Scan A	458.54	14.55
	O1s Scan A	530.09	24.46
	O1s Scan B	532.92	8.38
	O1s Scan C	531.45	13.75

In Figure 4.11 XPS spectrums were shown for both composite sol and modified composite sols. In similar peaks were observed in the modified composite sol. The composite sol had two O1s peaks at 530.45 eV and 532.19 which correspond to O1s of TiO₂, and O1s of SiO₂, respectively. The atomic percentage of the O1s was decreased after modification from 46.59% to 34.54%. This could be the consequences of the settlement of the silanol groups in the place of the oxygen at the surface. The peaks at 459.03 eV and 458.06 eV indicate the Ti⁴⁺ belongs to Ti-O-Ti or Ti-O-Si bond in the composite structure. There are C1s peaks at 284.63 eV, 286.147 eV and 292.61 eV. They are evidence of the C-C, C-H, C-O and -C-Si- bonds, respectively (Aghaei et al., 2018 and Milosev et al., 2012). In the Si2p3 peak, which were at 102.01 probably belongs to Si-O-Si bonds respectively. After the modification, C atomic percentage increased from 31.28 to 42.16. This is the evidence of the modification and the hydrophobicity of the surface was increased with the attached carbon bonds.

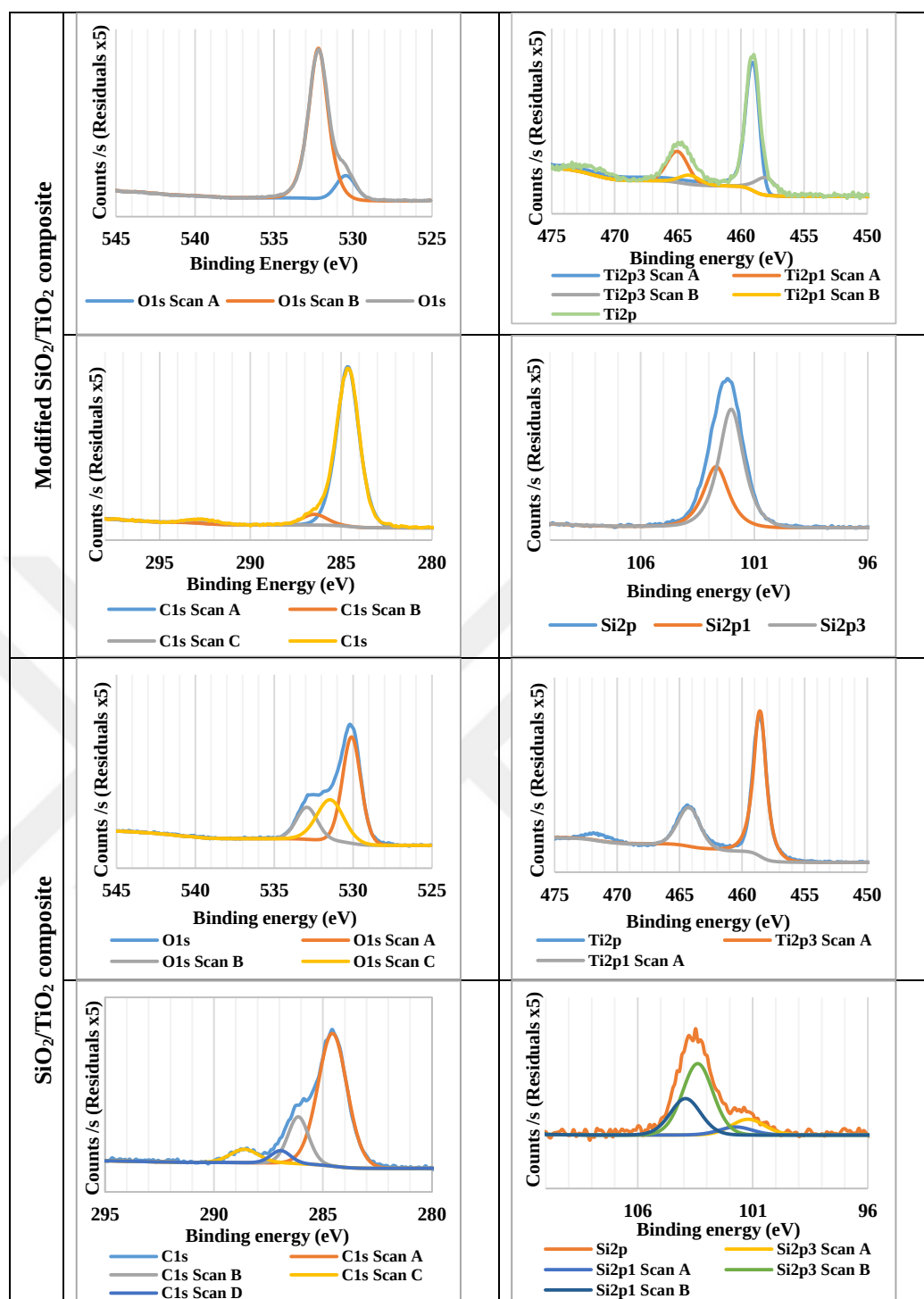


Figure 4.11. XPS spectrums of $\text{SiO}_2/\text{TiO}_2$ composite sol and modified $\text{SiO}_2/\text{TiO}_2$ composite sol

The FTIR spectra of unmodified and modified composite sols were given in Figure 4.12. The absorption band at 1091 cm^{-1} indicates the Si-O-Si group in the structure, around 700 cm^{-1} peak indicates the existence of Ti-O and Ti-O-Ti bonds and 960 cm^{-1} is attributed to Si-C bonding which indicates the modification for modified composite sol (Gradzik et al., 2011, Rahman et al., 2020 and Zou et al.,

2018). When FTIR spectra of composite sol were analyzed, there are peaks at around 1090 cm^{-1} and 700 cm^{-1} which are indicates the Si-O-Si and Ti-O groups in the structure. When calcined- and modified- composite sol FTIR spectra were analyzed, all C content was burned and only Si-O-Si and Ti-O bonds were in the structure.

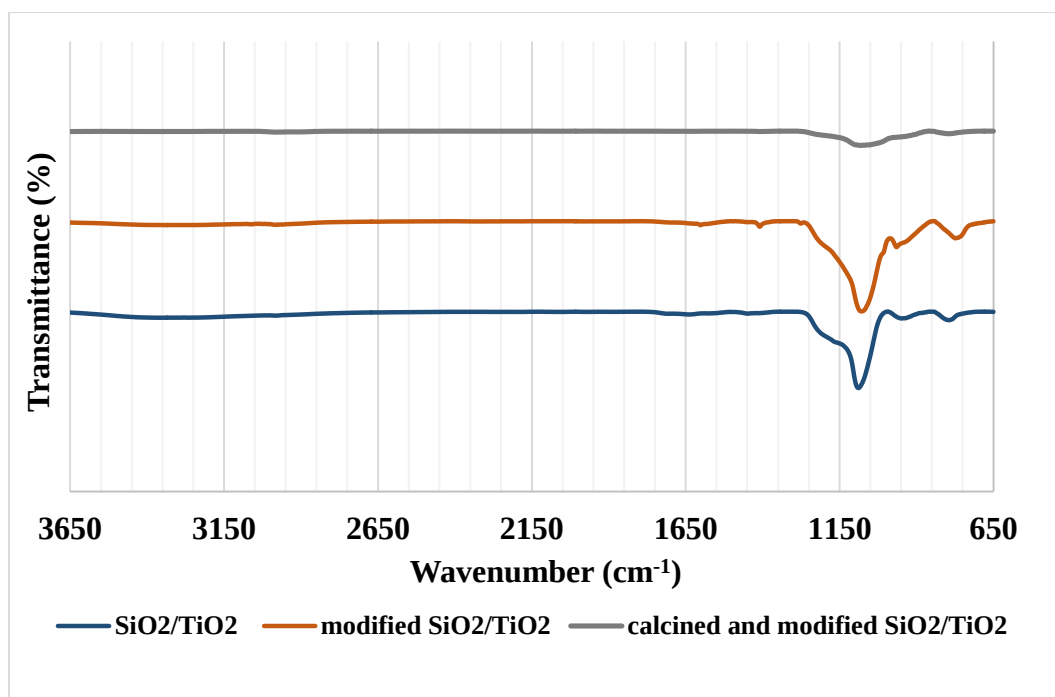


Figure 4.12. FTIR spectra of unmodified, modified and calcined modified composite sols

4.4. Characterization of Thin Film Coatings

The prepared silica sols were used in the fabrication of thin film coatings. In this step, different parametric studies were performed. In the first step the effect of withdrawal speed, number of coating layer and effect of stirring rate in the synthesis were investigated for h-PAA and c-PAA under the conditions of 6000 ppm polymeric template, 4.8 mL TEOS. Thin film coatings were characterized by scanning electron microscopy and UV-visible spectrophotometer.

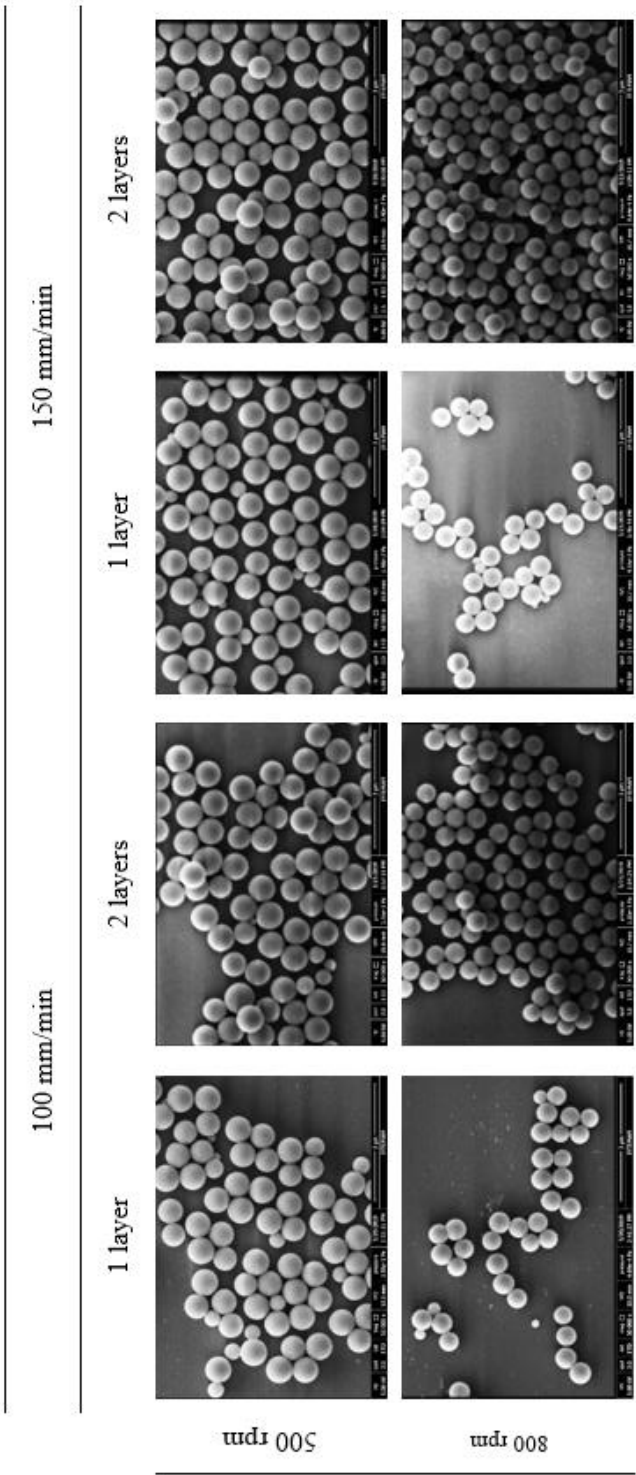


Figure 4.13. SEM micrographs of SS prepared 6000 ppm h-PAA with different withdrawal speeds (100 mm/min and 150 mm/min), number of coatings (1 and 2 layers) and stirring rates (500 rpm and 800 rpm)

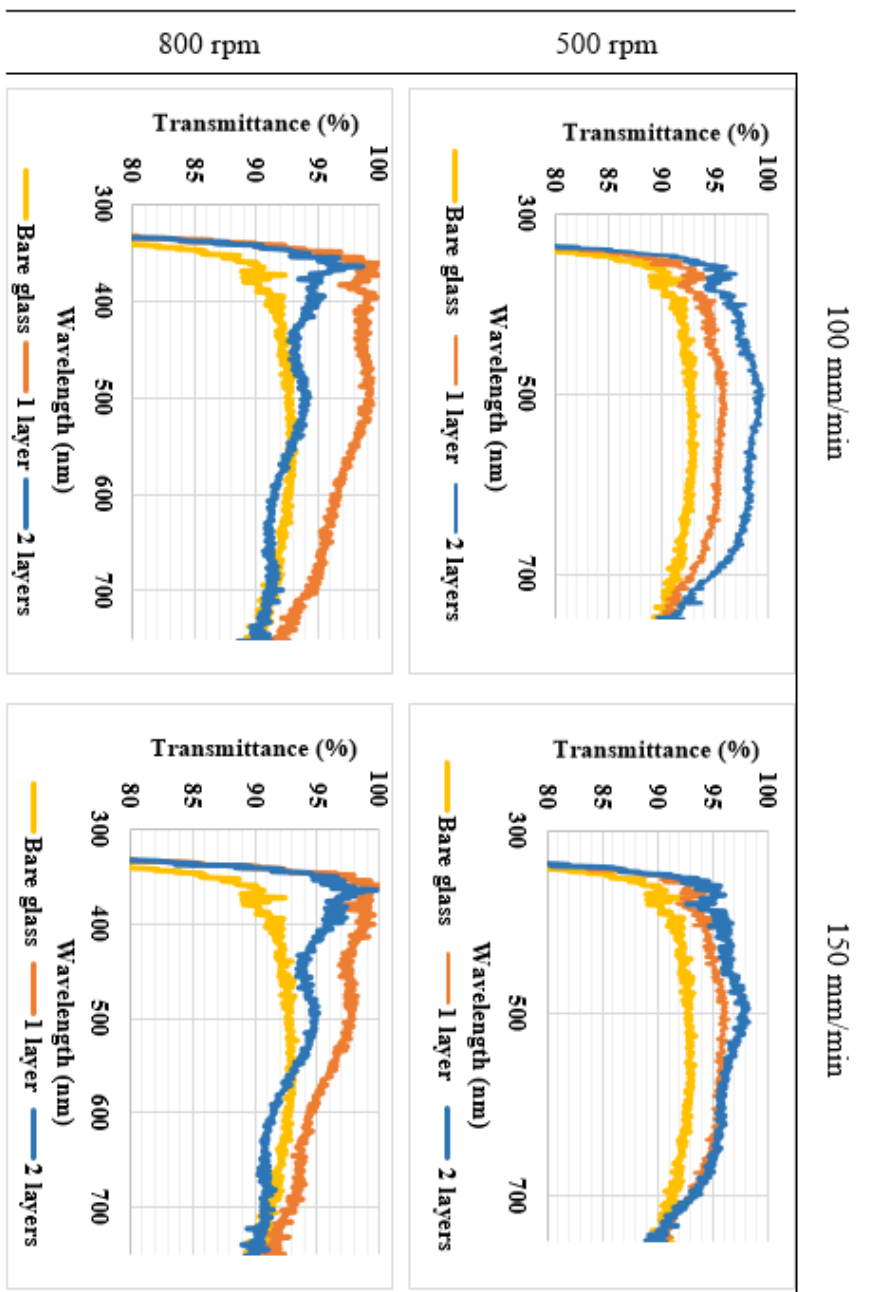


Figure 4.14. UV-Visible spectra of SS prepared 6000 ppm h-PAA with different withdrawal speeds (100 mm/min and 150 mm/min), number of coatings (1 and 2 layers) and stirring rates (500 rpm and 800 rpm)

In Figure 4.13 SEM micrographs of SS prepared by using 6000 ppm h-PAA as a polymeric template and they were synthesized two different stirring rate; 500 rpm and 800 rpm. Comparing SEM micrographs for 500 rpm and 800 rpm at 100 mm/min and 1 layer, it has been observed that the SS synthesized at 500 rpm had more adhesion to the surface. In the Figure 4.14, UV-visible spectrophotometer values were showed of the h-PAA coatings. At 800 rpm, the transmittance of the 1 layer coatings was greater than 2 layer. This was probably result of improper coatings of the surface. At 500 rpm, 100 mm/min, 2 layers showed better orientation in the micrograph than 1 layer. Its spectrometer results were convenient with the SEM micrograph. For the 800 rpm results of SEM, the coating for 1 layer was insufficient, 2 layers coatings had more than two layer and there was accumulation on the surface. Because of this and considering particle size distribution, 800 rpm was determined to be unsuitable for the stirring rate. For 150 mm/min 2 layers coating gave better transmittance values (max %95) so for coating with h-PAA, the best condition were chosen as 150 mm/min 2 layers at 500 rpm.

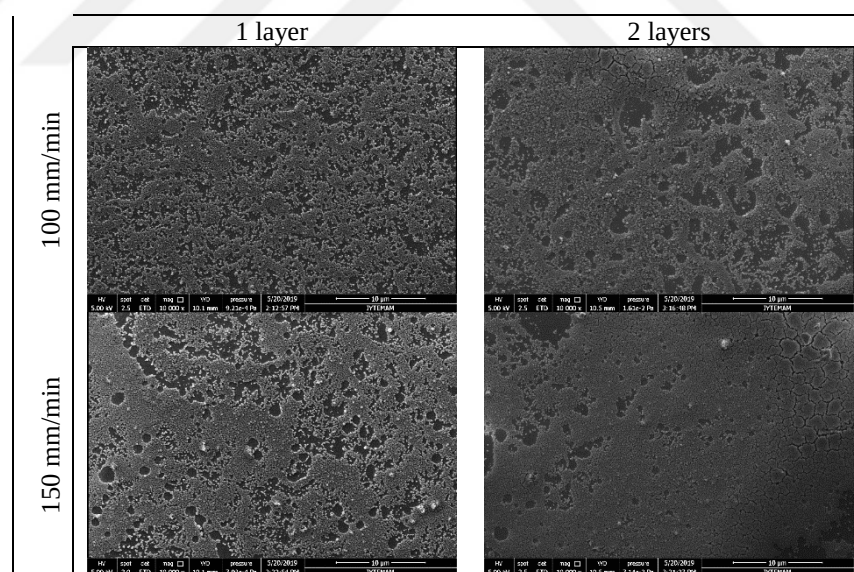


Figure 4.15. SEM micrographs of SS prepared 6000 ppm c-PAA with different withdrawal speeds (100 mm/min and 150 mm/min) and number of coatings (1 and 2 layers) at 500 rpm

In Figure 4.15 SEM micrographs of SS prepared by using 6000 ppm c-PAA as a polymeric template and synthesized at 500 rpm stirring rate. When SEM micrographs of 100 mm/min and 150 mm/min for 2 layers, coatings prepared with 150 mm/min 2 layers had better view than 100 mm/min, 2 layer. This was also

valid for 1 layer coatings. So that 150 mm/min was found optimum withdrawal speed. In order to find optimum number of layer of the coatings, fabricated coatings with 150 mm/min withdrawal speed 1 layer and 2 layers were compared. In 2 layers coating, there were more than 2 coating layers seen in the micrograph and this could be lower the transmittance of the surface. For 1 layer coatings the surface was nearly coated except in the center of the void. At this point the optimum layers only determined with respect to UV-visible spectrometer results. The UV-visible results investigated 1 layer coatings had %96 transmittance in between 450 and 550 nm. 2 layer coatings transmittance values were lower than 1 layer because there were more than 2 layers exist which was seen in Figure 4.16.

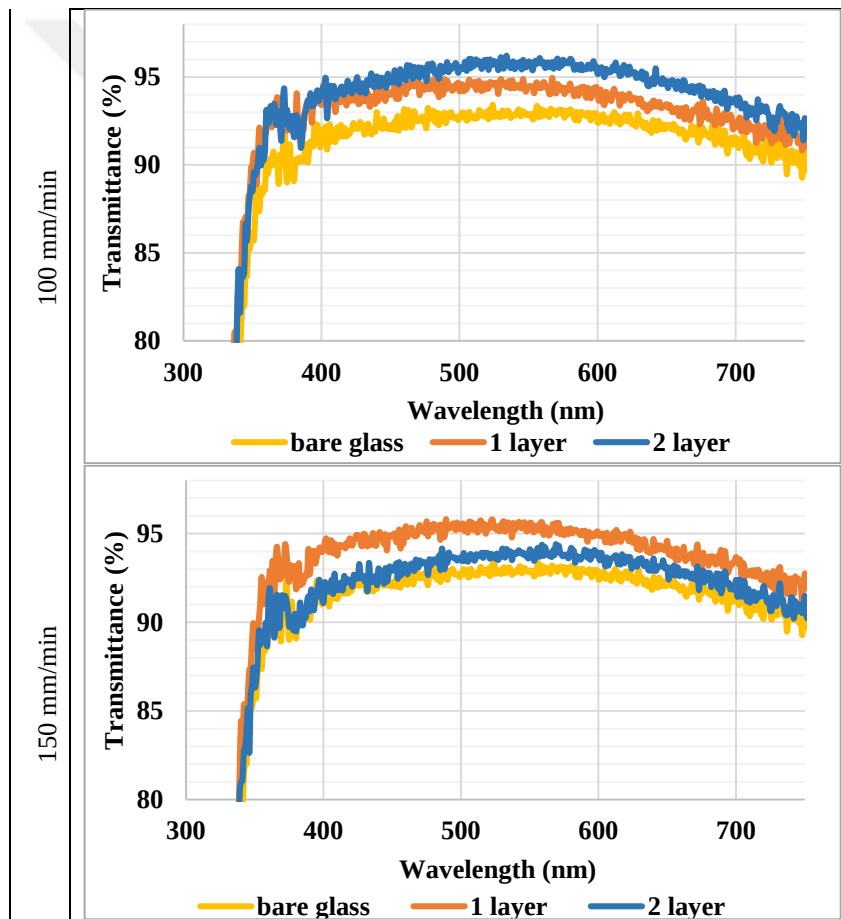


Figure 4.16. UV-Visible spectra of SS prepared 6000 ppm c-PAA with different withdrawal speeds (100 mm/min and 150 mm/min), number of coatings (1 and 2 layers)

The SEM micrographs of coatings of SSs synthesized by using different amount of c-PAA which was chosen as optimum polymer type were given in

Figure 4.17. The coating that was fabricate by using SS prepared by using 4000 ppm c-PAA had empty regions on the substrate and that was undesired. For 6000 ppm c-PAA coating, almost all over the surface coated with the sol and 8000 ppm c-PAA coatings' surface was covered with SSs but there were some empty regions. In conclusion, the best coverage of the surface was gained by SS synthesized by using 6000 ppm c-PAA.

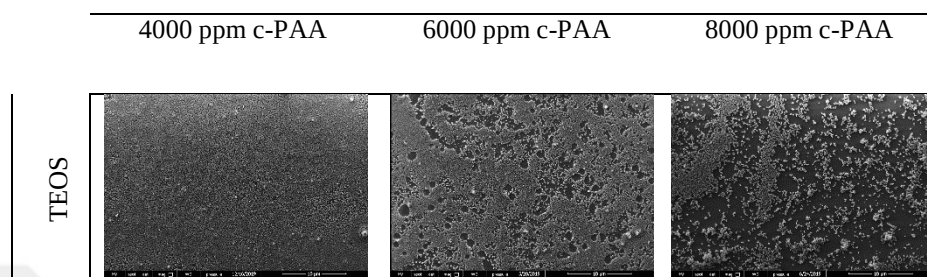


Figure 4.17. SEM micrographs of SS synthesized with different amount of c-PAA at constant amount of TEOS (4.8 mL) rpm

Figure 4.18 shows the UV-visible spectra of the coatings fabricated using 4000 ppm c-PAA, 6000 ppm c-PAA and 8000 ppm c-PAA. When the UV-visible spectra was examined, high transmittance value 95.80 %, was achieved with the 6000 ppm c-PAA coating. The other coatings had lower transmittance values and the SEM micrographs were supported this result.

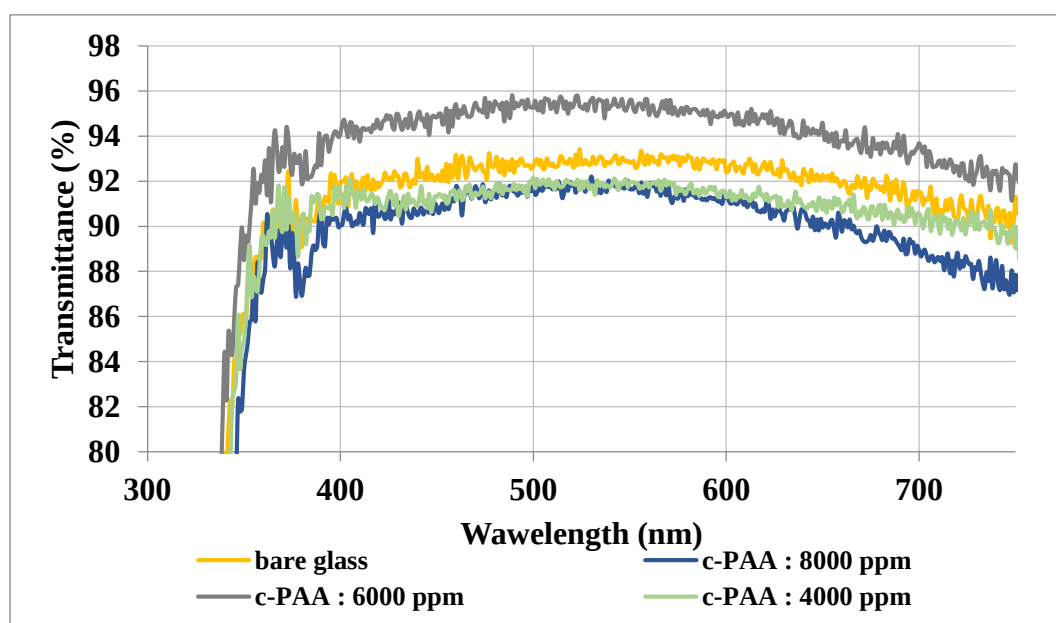


Figure 4.18. UV-visible spectra of the coatings fabricated using 4000 ppm c-PAA, 6000 ppm c-PAA and 8000 ppm c-PAA at constant amount of TEOS

Figure 4.19 shows the UV-visible spectra of coatings that fabricated different amount of TEOS. The best transmittance result was obtain with 3.1 mL TEOS with the value of 96.75%. At this point the orientation and surface coverage of the sol is important to reach the optimum amount of TEOS.

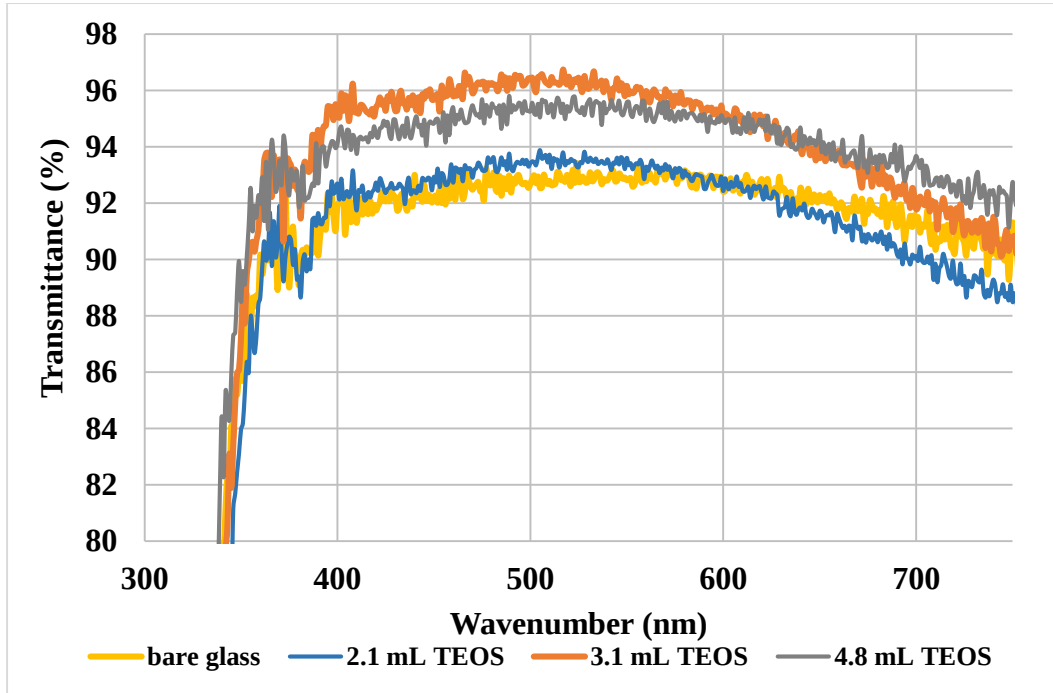


Figure 4.19. UV-visible spectra of the coatings fabricated using different amount of TEOS

In order to compare structure and orientation of SSs synthesized from different type of silica source, SEM micrographs were given in Figure 4.20. It was seen that coatings fabricated from TEOS had spherical particles and the size distribution of particles nearly equal. For the Na_2SiO_3 coatings there were particle distribution but all of the surface was cover with the particles and this was a good result for the preliminary study of this synthesis. In the SEM micrographs, it was seen that the coatings' particle size that was fabricate 6000 ppm c-PAA and Na_2SiO_3 was bigger than 8000 ppm c-PAA and Na_2SiO_3 . The particle size distribution was also supported this result in Figure 4.7.

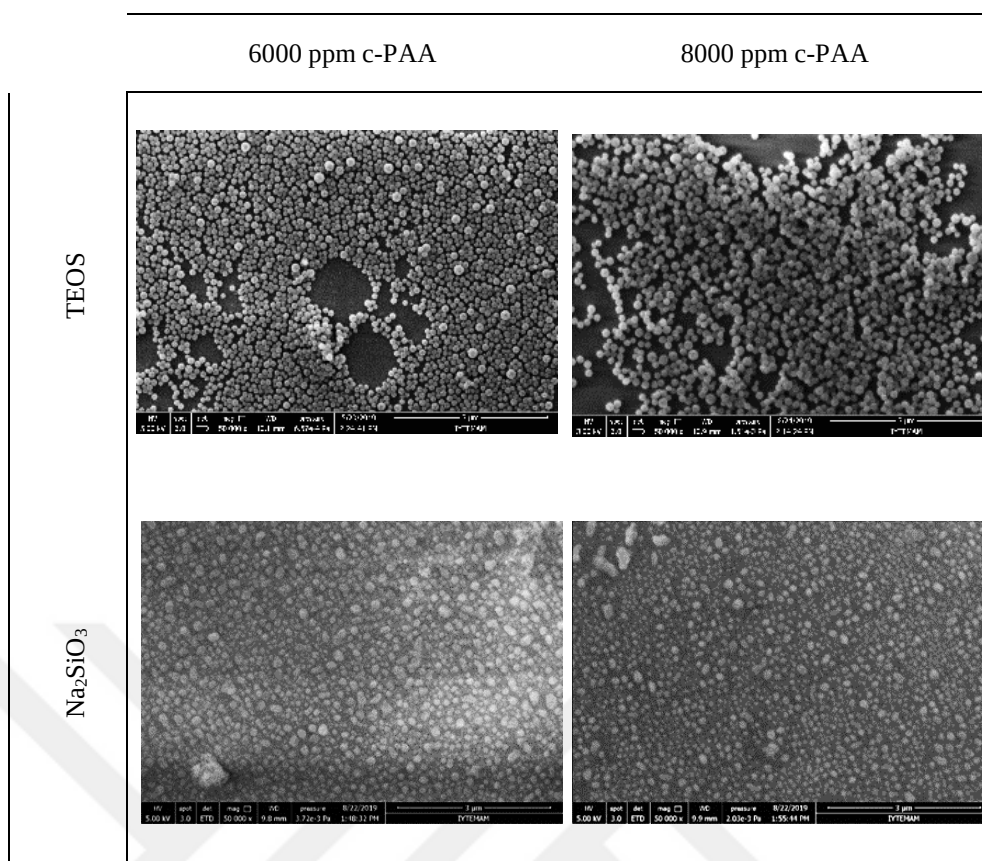


Figure 4.20. SEM micrographs of the coatings fabricated using 6000 ppm c-PAA and 8000 ppm c-PAA at constant amount of TEOS and Na₂SiO₃

The UV-visible spectra of SSs synthesized from different type of silica source was given in Figure 4.21. The best transmittance value was obtained with coating SS synthesized by using 6000 ppm c-PAA and TEOS. The surface coverage of Na₂SiO₃ coatings were similar but probably depending on the particle size of the 8000 ppm c-PAA, Na₂SiO₃ coating, transmittance value was higher than 6000 ppm c-PAA, Na₂SiO₃ in the range of 450-550 nm. When 8000 ppm c-PAA results compared, Na₂SiO₃ had higher performance than TEOS.

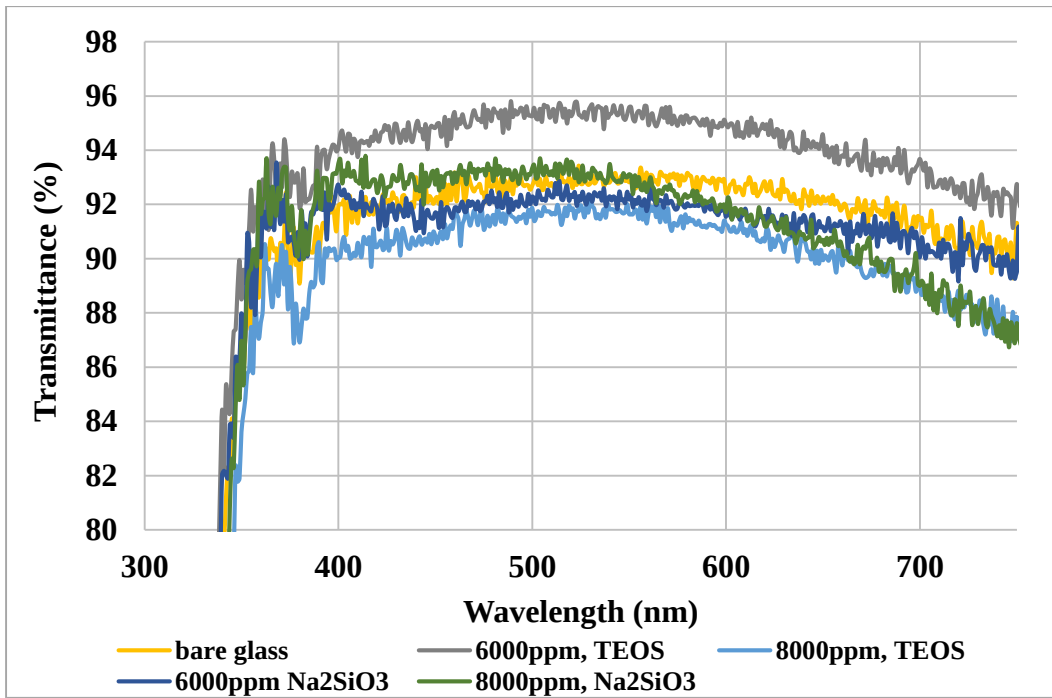


Figure 4.21. UV-Visible spectra of the coatings fabricated using TEOS and Na₂SiO₃

In Figure 4.22 shows SEM micrographs of the coatings fabricated using SS, composite sol and modified composite sol. In SiO₂/TiO₂ sol composite sol micrograph, there were network structures in between SiO₂ nanoparticles and there were a layer structure around the SiO₂ particles. These structures were TiO₂. The all surface of substrate was covered with the nanoparticles. It is also seen that there are two-layered structures in some places. The SEM micrograph of coating that belongs to modified SiO₂/TiO₂ sol, there were network structure and the spaces between the particles were increased. The reason of this result could be the interaction of the modified nanoparticles.

In Figure 4.23 shows the UV-visible spectra of coatings fabricated with SS, SiO₂/TiO₂ sol and modified SiO₂/TiO₂ sol. The highest transmittance value was get with the modified SiO₂/TiO₂ sol coating. SS is also close to the modified SiO₂/TiO₂ sol. SiO₂/TiO₂ sol has the lowest transmittance value and the reason of this could be the addition 2 layers structures on the substrate or the incomplete reaction of the SiO₂/TiO₂ sol because this coating was fabricated at the end of the synthesis experiment and the evidence of this could be the high transmittance value of the modified SiO₂/TiO₂ sol.

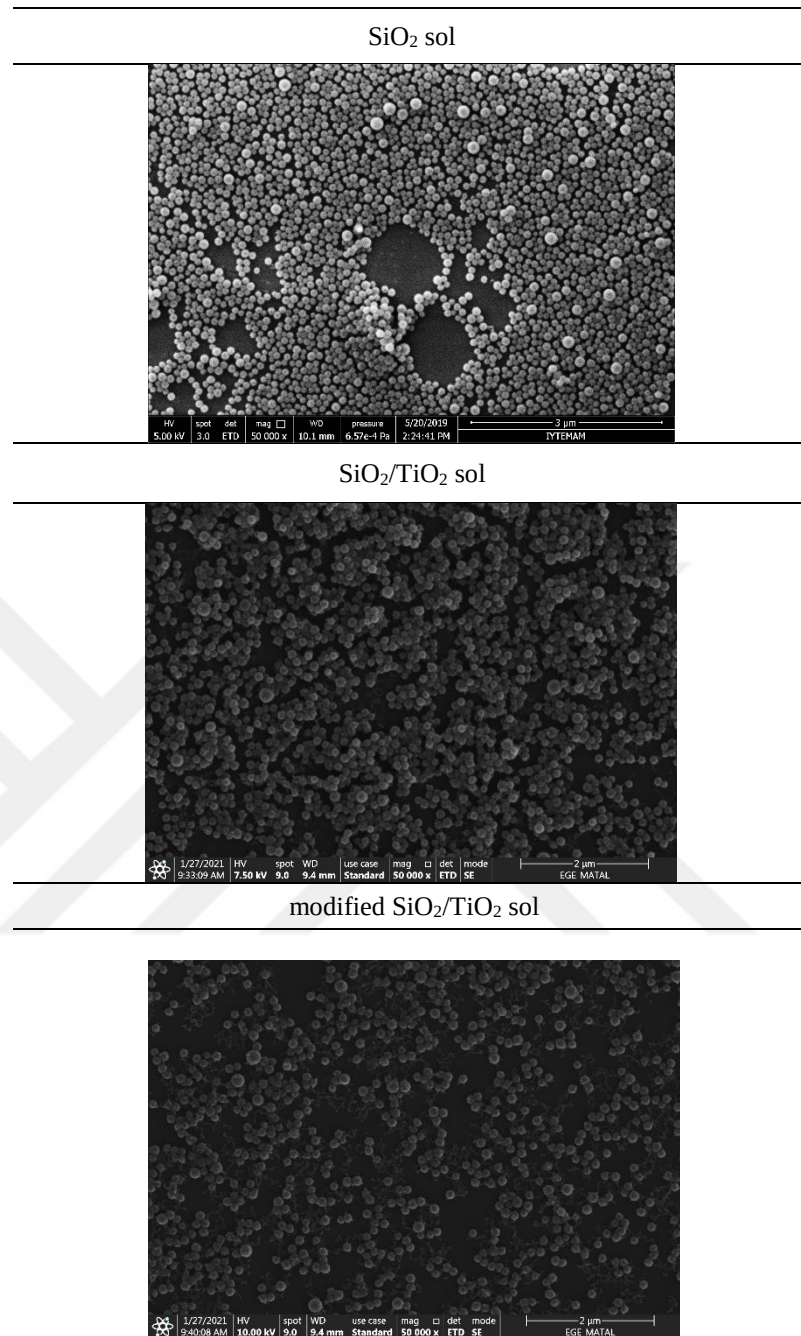


Figure 4.22. SEM micrographs of coatings fabricated using SS, composite sol and modified composite

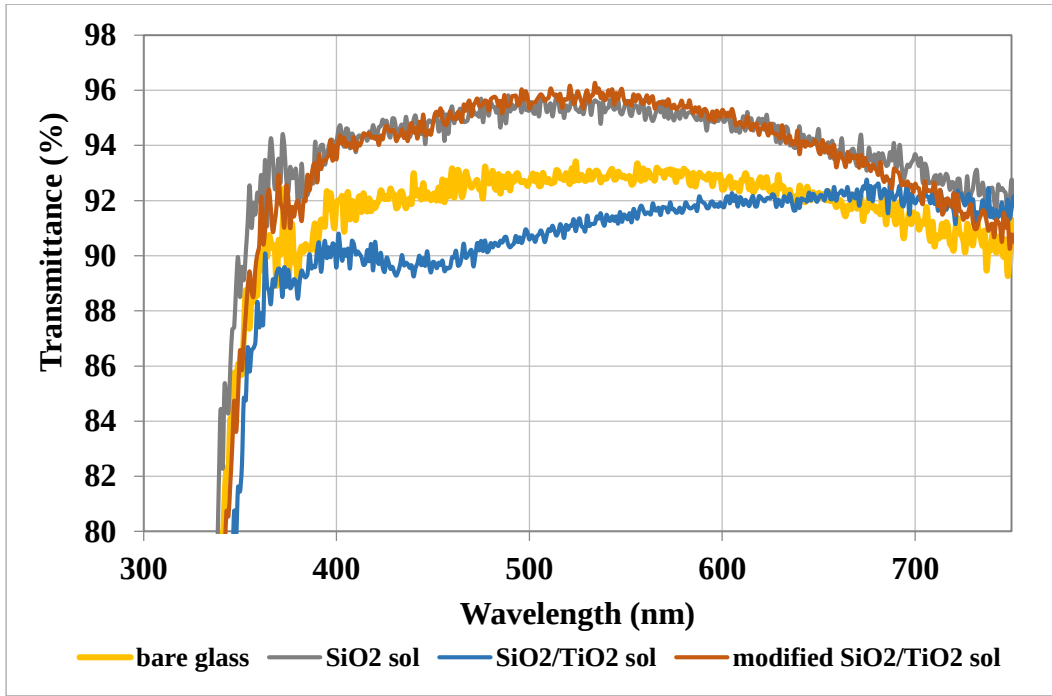


Figure 4.23. UV-visible spectra of the coatings fabricated using SS, composite sol and modified composite sol

4.5. Characterization of Glass Paints Containing Modified Composite Sols

In this section, the coatings fabricated with glass paints containing different amount of modified composite sol were investigated. The water contact angle indicates the hydrophobicity of the coatings and performance of the modification of sols. In Table 4.2, contact angle with respect to water and diiodomethane, surface free energy with respect to water were given. Water is a polar and diiodomethane is an apolar molecules.

Table 4.2. Results of contact angle and surface free energy of coatings fabricated with glass paints containing different amount of modified composite sol

Amount of modified composite sol (wt%)	0	0.5	1.25	2.25	5
Water contact angle , WCA (°)	94.69±1.45	92.35±0.49	125.26±2.34	89.36±1.08	93.41±0.72
Diiodomethane contact angle(°)	59.92±2.68	61.33±2.44	58.84±1.94	59.86±1.91	60.17±0.71
Surface free energy (mN/m)	30.02±1.92	29.88±1.68	31.15±1.62	31.39±1.48	30.18±0.59

The reason of analysis for both diiodomethane and water was to ensure the hydrophobicity of the surface because for polar and apolar molecules the contact angle should be in between 80-102 and 58, respectively (Evcin et al., 2018).

All coating films were in hydrophobic character considering the water contact angle which is bigger than 90°. It is seen that, until the 1.25 wt% the water contact angle increases when the deviation were considered. At 1.25 wt%, the highest water contact angle was obtained which is 125.26 ± 2.34 . It was expected the increase in water contact angle with respect to increasing amount of modified composite sol because the hydrophobic structures in the paints were increased by increasing amount. However, after the 1.25 wt%, increasing amount of composite sol decreases the water contact angle. The reason of this could be the impurity of the coating surfaces. In the literature, there is no data about increasing the superhydrophobicity of glass paints by adding modified composite sol but, there are studies that coatings fabricated by using POTS modified hollow silica nanoparticles. The water contact angle obtained as 162° (Zou et al., 2018).

In Figure 4.24, UV spectra of coatings fabricated from glass paints containing different amount of modified composite sol. It was seen that all transmittance values of coatings in between 450 to 600 nm are lower than bare glass. This result was undesired because it was expected the antireflection property of coatings have higher than bare glass. However, considering bare glass and coating without addition of composite sol, it was seen that the coating lowers the transmittance value. It was probably occurred for the nature of glass paint. By adding modified composite sol until 2.25 wt%, the decreasing of transmittance values continued. In the addition of 5 wt% modified composite sol transmittance values started to increase but again they are lower than bare glass.

The properties of films were investigated by using dynamic mechanical analysis (DMA). Table 4.3 shows the glass transition temperature (T_g), network parameter (M_c), storage modulus (E') and elastic modulus (E''). The curing temperature should be lower than glass transition temperature in order to obtain tough films. By this way, the coating wasn't affected from outside conditions. The network parameter defines the amount of crosslink in the coating. Storage and

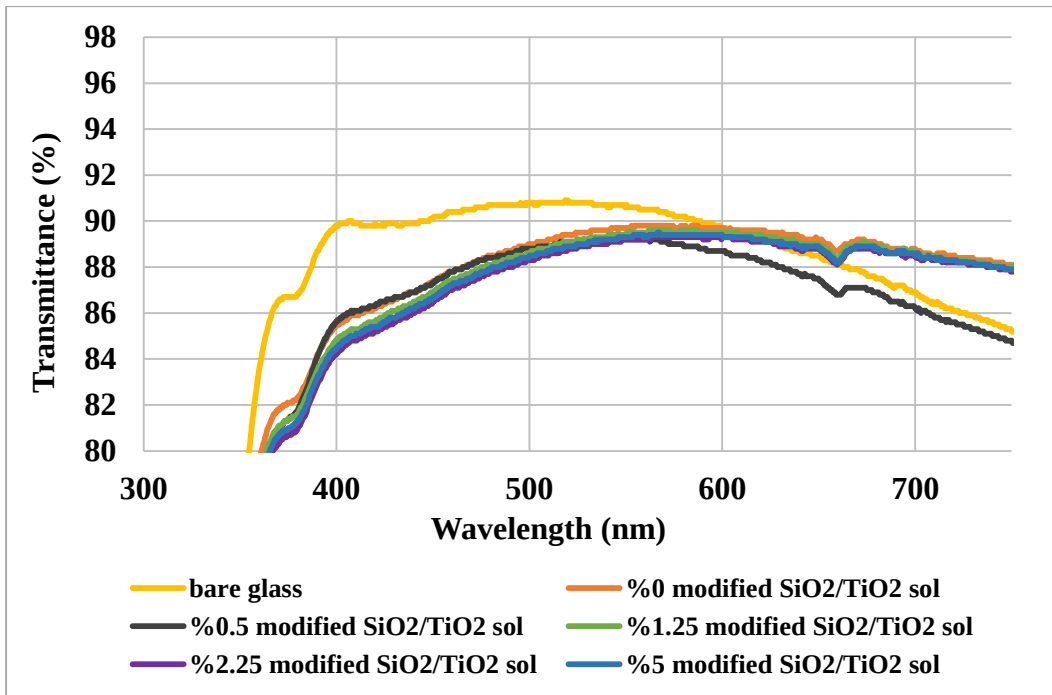


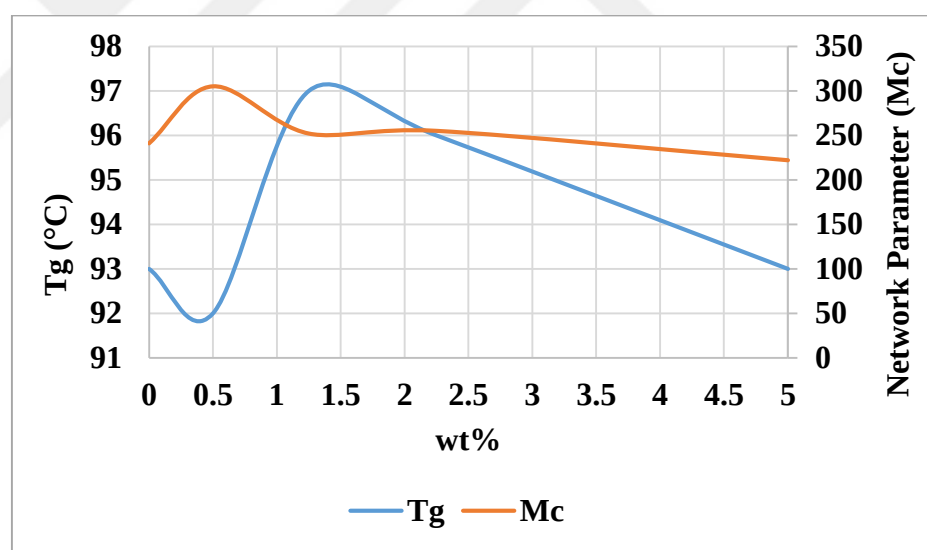
Figure 4.24. Transmittance values of glass paints containing various amount of modified composite sol

elastic modulus actually define the behavior of rigidity and elasticity of the coatings. Solid behavior of coating increases with an increase in the storage modulus. The glass transition temperatures of the films are similar for all amounts of modified composite sols and higher than curing temperature which was 80°C. This could be concluded that the though films were obtained. Storage modulus of films were also confirmed this result. They are higher than elastic modulus for all amount of composite sol but more rigid film were obtained in the usage of amount of composite sol 1.25 % which has storage modulus 1951 MPa. When looking at network parameter, except addition 5% modified composite sol result, all values are higher than in the cases of no addition of modified composite sol. The crosslink structure increases by increasing network parameter and it forms rigid films.

Table 4.3. DMA results of glass paints containing various amount of modified composite sol

Sample	0% modified SiO ₂ /TiO ₂	0.5% modified SiO ₂ /TiO ₂	1.25% modified SiO ₂ /TiO ₂	2.25% modified SiO ₂ /TiO ₂	5% modified SiO ₂ /TiO ₂
T _g [°C]	93	92	97	96	93
M _c	241	305	252	255	222
E' [MPa]	1870	1494	1951	1414	1378
E'' [MPa]	142	111	156	110	95

To sum up, the Figure 4.25., Figure 4.26, Figure 4.27 and Figure 4.28 show the relation in between amount of modified composite sol and glass transition temperature/network parameter, storage and elastic modulus, transmittance and water contact angle-surface free energy of the coatings, respectively. All graphs show the optimum amount of modified composite sol as in between 0.5 and 1.5.

**Figure 4.25.** Relation in between amount of modified composite sol and Tg-Network parameter

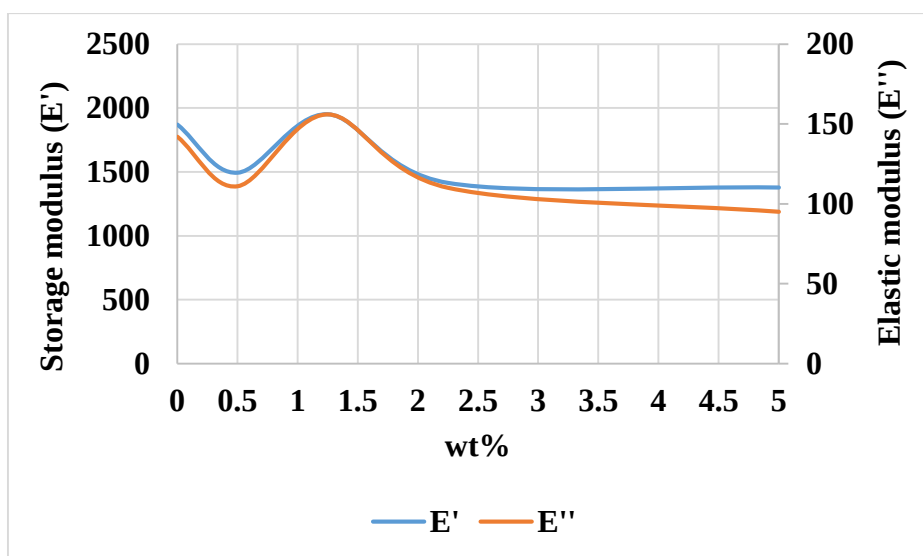


Figure 4.26. Relation in between amount of modified composite sol and storage-elastic modulus

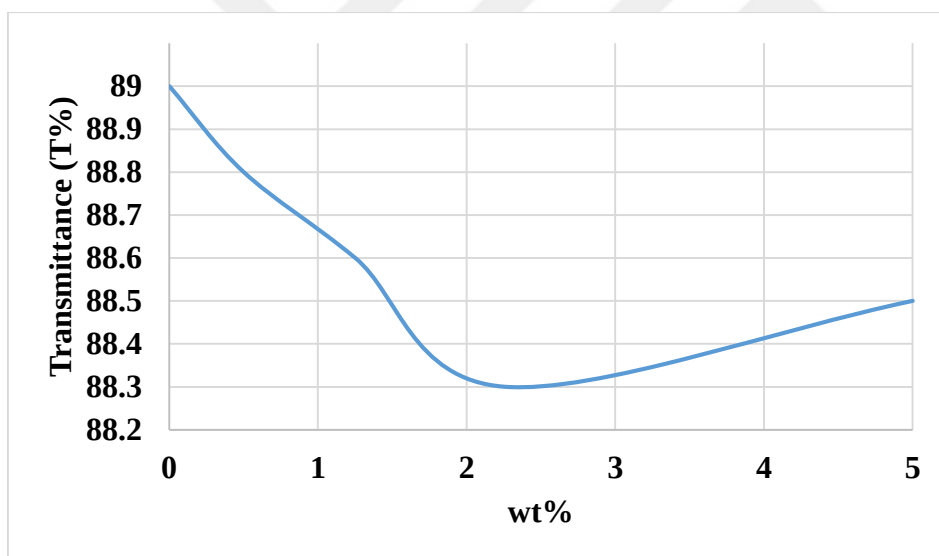


Figure 4.27. Relation in between amount of modified composite sol and transmittance of the coatings

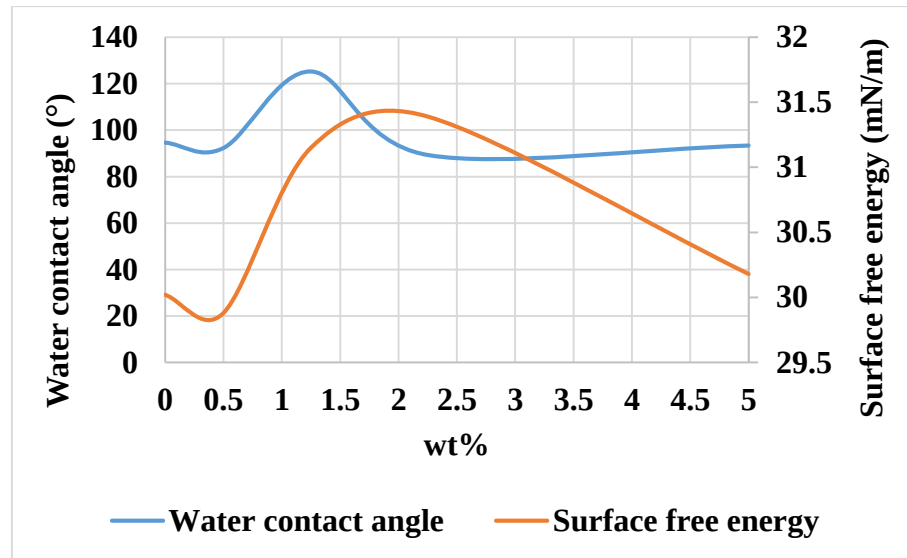


Figure 4.28. Relation in between amount of modified composite sol and water contact angle-surface free energy

5. DISCUSSION

In the synthesis of SS different parameters were investigated. After the synthesis, the application of thin film coatings, fabricated by using different SSs were examined. Firstly, the synthesis parameter of *stirring rate* was investigated for two different polymeric templates which are h-PAA and c-PAA. The particle size of SS was the best in the synthesis by using c-PAA as polymeric template and 500 rpm stirring rate. The reason of this could be the interaction in between the molecules. In the 800 rpm stirring rate the particles in the solution moves faster than 500 rpm and this could be result in agglomeration of SS particles. SEM micrographs and UV-visible spectra were also supported this result.

Another investigated parameter was *the type of polymeric template* in the synthesis. Two different polymeric templates were used as a template in the synthesis. One of them was h-PAA, the other one was c-PAA. Their molecular weights and monomers were different so that their behavior in the structure was observed differently. The SSs synthesized with h-PAA had higher particle size than c-PAA which was undesired. The c-PAA had smaller particle size because interaction in between c-PAA and SiO₂ molecules were better than h-PAA. When SEM micrographs were examined, it was seen that the coatings fabricated with c-PAA were more homogeneous than h-PAA. Also, the transmittance values are higher than h-PAA. Considering the literature particles sizes which was lower than 100 nm generally shown in Table 2.2, the particle size of our experiments are higher than the literature (Aghaei et al., 2018, Tao et al., 2016a, Zhang et al., 2021 and Zou et al, 2018). There can be more than one reasons such as types of polymeric template, amounts of polymeric templates, addition rate of ethanol in the reaction medium and addition rate and period of dosage.

The *effect of amount of polymeric template* was investigated for the synthesis of SS. Three different amounts were examined as 4000 ppm, 6000 ppm and 8000 ppm. The synthesis with 6000 ppm c-PAA was given the minimum particle size distribution. This could be the optimum interaction in between SiO₂ and c-PAA surface active in 6000 ppm. Also, in the SEM micrographs homogeneous coating was obtained in 6000 ppm and with respect to UV-visible

spectra also was supported this result. The particle size distribution a little bit greater than the literature value, the reason of this could be the molecular weight of the polymeric template. In the literature, molecular weight of polymeric template was around 3000 and 5000 (Xu et al., 2014, Tao et al, 2016a).

In the synthesis of SS, the effect of amounts of TEOS was investigated for 2.1 mL, 3.1 mL and 4.8 mL. When the amount of TEOS increased, the particle size of the SS increased because the layer around the template became thicker with respect to the high amount of the TEOS. Tao and coworkers (2016b) study, shows that the increasing amount of TEOS from 1.99 g/L to 3.98 g/L resulted in the increase of the thickness of the shell from 5.9 to 15.5 nm. The experimental results were appropriate with the literature. But in the coating step, the highest transmittance value was obtained in 3.1 mL TEOS. At this point the orientation in the coating was important.

Type of silica source was important in the synthesis because the synthesis method were different. Two different types of silica source was used the first one was commercial source TEOS, the other one was an agricultural waste rice husk ash. The rice husk ash was preferred because of its environmental unsolved problem in Turkey. The low density rice husk was burnt at high temperatures and it was converted to rice husk ash. The storage of rice husk ash is difficult so large amount of silica in its structure was preferred for this study. The particle size was moderate for the SSs from rice husk ash.

For the fabrication of thin film coatings, withdrawal speed which is 100 mm/min and 150 mm/min, and number of layer 1 layer and 2 layers were investigated. All of the coatings had better orientation at 150 mm/min withdrawal speed. In 1 layer coatings some of the SS had empty regions in the coated surface but some of the SS had homogeneous surface. In 2 layers coating, there were accumulation in some substrates and this was unacceptable for the UV-visible spectra because it was decreased the transmittance of the substrate, generally. Considering the Table 2.4, the transmittance values of experimental results are closed to literature but need some improvement. In the optimum condition the

transmittance value was found as 96.75 % for 6000 ppm c-PAA, 4.8 mL TEOS, 150 mm/min, 1 layer coating.

In the synthesis of composite sol, 6000 ppm c-PAA, 4.8 mL TEOS were used as the SS. The particle size distribution of composite sol was higher than SS as expected because a new layer added to the SiO₂ nanoparticles. The new structures also were seen in SEM micrographs. The particle size of the modified composite sol was larger than composite sol. The transmittance value of the modified composite sol was obtained higher than the other values which were desired for the study. But it is a little bit low considering the literature values Table 2.4 (Jia et al., 2017, Lin et al., 2018, Tao et al., 2016c and Wu et al., 2018).

The industrial application of modified composite sol was performed in 2C component glass paint. Four different weight ratios were added to the paint and all surfaces have to be found in hydrophobic character (WCA>90°) which was expected. Dynamic mechanical analysis results showed that the film has rigid characteristic and glass transition temperature are higher than curing temperature. When the amount of modified composite sol and its effects on coatings are considered such as glass transition temperature, network parameter, storage and elastic modulus, transmittance, water contact angle and surface free energy, the optimum weight percent of modified composite sol added to the glass paint was determined in the range of 0.5-1.5 wt%.

6. CONCLUSIONS and RECOMMENDATIONS

In this study, the synthesis of SSs, composite sol and modified composite sol were studied. At this time in order to reach the optimum conditions parametric study were performed for stirring rate of the synthesis (500 rpm and 800 rpm), type of polymeric template (h-PAA and c-PAA), amount of polymeric template (4000 ppm, 6000 ppm and 8000 ppm), amount of TEOS (2.1 mL, 3.1 mL and 4.8 mL) and silica source (TEOS and rice husk ash) were investigated. Also, in the fabrication of thin film coatings withdrawal speed (100 mm/min and 150 mm/min) and number of layers (1 layer and 2 layers) were investigated. The optimum conditions were satisfied under the conditions of 500 rpm stirring rate, in the usage of c-PAA as polymeric template with the amount of 6000 ppm, 4.8 mL TEOS. After this optimum condition, composite sol and modified composite sol were synthesized depending on these parameters. In the fabrication of thin film coatings, 150 mm/min and 1 layer was determined as optimum parameters and with respect to this composite sols coatings fabricated. In the application of glass paint, the antireflection property of coatings was lower than bare glass and which was undesired. The reason of this could be the compatibility of the paints' components and modified composite sol.

In future research, the optimum parameters for rice husk ash could be investigated. Transmission electron microscopy could be used to analyze the inner structure of the template silica sols. Lower molecular weight of polymeric template can be used. The application of self cleaning under UV light can be observed or the self cleaning due to the hydrophobicity can be examined by measuring water contact angle. Different type of modification agent could be used. New parametric study can be performed in synthesis due to the narrower region considering the amount of TEOS. The modification of nanoparticles can be performed after the fabrication of coatings by using chemical vapor deposition because of the loss of the modification agent at high calcination temperatures.

REFERENCES

- Aghaei, R., Eshaghi, A., Aghaei, A.,** (2018). Durable transparent super-hydrophilic hollow SiO₂-SiO₂ nanocomposite thin film. *Materials Chemistry and Physics*. vol. 219, p. 347-360.
- Bagwe, R.P., Yang, C., Hilliard, L.R., Tan, W.** (2004) Optimization of Dye-Doped Silica Nanoparticles Prepared Using a Reverse Microemulsion Method. *Langmuir*. vol. 20, p. 8336–8342.
- Belleville, P.F. and Floch, H.G.** (1994). Ammonia hardening of porous silica antireflective coatings. *Advances in Optics and Photonics*. vol. 2288, p. 25–32.
- Cecilia, A.S., Machado, M., Zubillaga, O., Tercjak, A.** (2019). Hydrophobic and spectrally broadband antireflective methyl-silylated silica coatings with high performance stability for concentrated solar applications. *Solar Energy Materials & Solar Cells*. vol. 200, p. 109962
- Chen, H., Wang, W., Martin, J.C., Oliphant, A.J., Doerr, P.A., Xu, J.F., DeBorn, K.M., Chen, C., Sun, L.** (2013). Extraction of Lignocellulose and Synthesis of Porous Silica Nanoparticles from Rice Husks: A Comprehensive Utilization of Rice Husk Biomass. *ACS Sustainable Chem. Eng.* vol. 1, p. 254–259.
- Darbandi, M., Thomann, R., Nann, T.** (2005). Single Quantum Dots in Silica Spheres by Microemulsion Synthesis. *Chem. Mater.* vol. 17, p. 5720–5725.
- Dubey, R.S., Rajesh, Y.B.R.D., More, M.A.** (2015). Synthesis and Characterization of SiO₂ Nanoparticles via Sol-gel Method for Industrial Applications. *Materials Today: Proceedings* vol. 2, p. 3575-3579.
- Elamawi, R.M., Tahoon, A.M., Elsharnoby, D.E., El-Shafey, R.A.** (2020). Bio-production of silica nanoparticles from rice husk and their impact on rice bakanae disease and grain yield. *Archives of Phytopathology and Plant Protection*. vol. 53, p. 459–478.
- Evcin, A., Ersoy, B., Uygunoğlu, T., Güneş, İ.** (2018). Farklı mineral katkıların epoksi zemin kaplama malzemesinin ıslanmazlığına ve yüzey enerjisine etkisi. *Journal of the Faculty of Engineering and Architecture of Gazi University*. vol. 33:2, p. 581-590.

- Finnie, K.S., Bartlett, J.R., Barbe, C.J.A., Kong, L.** (2007). Formation of Silica Nanoparticles in Microemulsions. *Langmuir*. vol. 23, p. 3017-3024.
- Gradzik, B., El Fray, M., Wisniewska, E.** (2011). Surface modification of TiO₂ and SiO₂ nanoparticles for application in polymeric composites. *Chemik*. vol. 65, p. 621-626.
- Greasley, S.,L., Page, S.J., Sirovica, S., Chen, S., Martin, R.A., Riveiro, A., Hanna, J.V., Porter, A.E., Jones, J.R.** (2016), Controlling particle size in the Stöber process and incorporation of calcium. *Journal of Colloid and Interface Science*. vol. 469, p. 213-223.
- Guldin, S., Kohn, P., Stefik, M., Song, J., Divitini, G., Ecarla F., Ducati, C., Wiesner, U., Steiner, U.** (2013). Self-Cleaning antireflective optical coatings. *Nano Letters*. vol. 13, p. 5329-35.
- Halin, D.S.C., Abdullah, M.M.A.B., Mahmed, N., Abdul Malek, S.N.A., Vizureanu, P., Azhari A.W.** (2017). Synthesis and characterization of TiO₂/SiO₂ thin film via sol-gel method. *IOP Conf. Series: Materials Science and Engineering*. vol. 209, 012002.
- Jia, G., Ji, Z., Wang, H., Chen, R.,** (2017). Preparation and properties of five-layer graded-refractive-index antireflection coating nanostructured by solid and hollow silica particles. *Thin Solid Film*. vol. 642, p. 174-181.
- Jong-Hong, L., Jen-Wei, L., Shiou-Ruei, C., Bo-Ying, C.** (2014). Antireflection coatings with SiO_x –TiO₂ multilayer structures. *Japanese Journal of Applied Physics*. vol.53, p. 11RA06-1-5.
- Kayhan, N., Razavi, R.S., Choopani, S.** (2012). Evaluation of two new white silicone thermal control paints under atomic oxygen. *Progress in Organic Coatings*. vol. 74, p. 603-607.
- Koźlecki, T., Polowczyk, I., Bastrzyk, A., Sawiński, W.** (2016). Improved Synthesis of Nanosized Silica in Water-in-Oil Microemulsions. *Journal of Nanoparticles*. vol. 2016, p. 1–9.
- Kwon, C.H., Kim, J.H., Jung, I.S., Shin, H., Yoon, K.H.** (2003). Preparation and characterization of TiO₂–SiO₂ nano-composite thin films. *Ceramics International*. vol. 29, p. 851–856.

- Le, V. H., Thuc, C.N.H., Thuc, H.H.** (2013). Synthesis of silica nanoparticles from Vietnamese rice husk by sol–gel method. *Nanoscale Research Letters*. vol.8, p. 58.
- Li, X. and He, J.** (2013). Synthesis of Raspberry-Like SiO₂–TiO₂ Nanoparticles toward Antireflective and Self-Cleaning Coatings. *ACS Applied Material Interfaces*. vol. 5, p. 5282–5290.
- Liang, G., Lan, H., Fan, P., Lan, C., Zheng, Z., Peng, H., Luo, J.** (2018). Highly uniform large area (100m²) perovskite CH₃NH₃PbI₃ Thin-films prepared by single source thermal evaporation. *Coatings*. vol. 8, p. 256-267.
- Lin, W., Zheng, J., Yan, L., Zhang, X.** (2018). Sol-gel preparation of self-cleaning SiO₂-TiO₂/SiO₂-TiO₂ double layer antireflective coating for solar glass. *Results in Physics*. vol. 8, p. 532-536.
- Mebert, A. M., Baglole C.J., Desimone, M.F., Maysinger, D.** (2017). Nanoengineered silica: Properties, applications and toxicity, *Food and Chemical Toxicology*, vol. 109, p. 753-770.
- Mehmood, U., Al-Sulaiman, F.A., Yilbas, B.S., Salhi, B., Ahmed, S.H.A., Hossain, M.K.** (2016). Superhydrophobic surfaces with antireflection properties for solar applications: A critical review. *Sol Energy Mater Sol Cells*. vol. 157, p. 604–623.
- Milosev, I., Jovanovic, Z., Bajat, J.B., Jancic-Heinemann, R., Miskovic-Stankovic, V.B.** (2012). Surface analysis and electrochemical behavior of Aluminum pretreated by vinyltriethoxysilane films in mild NaCl solution. *Journal of the Electrochemical Society*, vol. 159, p. 303-311.
- Nguyen, H.X., Dao, N.T.T., Nguyen, H.T.T., Le, A.Q.T.** (2019). Nanosilica synthesis from rice husk and application for soaking seeds. *IOP Conference Series: Earth and Environmental Science*. vol. 266, 012007.
- Park, S., Heo, J., Kim, H.J.** (2011). A Novel Route to the Synthesis of Silica Nanowires without a Metal Catalyst at Room Temperature by Chemical Vapor Deposition. *Nano Letters*. vol. 11, 2, p. 740–745.
- Prabha, S., Durgalakshmi, D., Rajendran, S., Lichfouse, E.,** (2021). Plant-derived silica nanoparticles and composites for biosensors, bioimaging, drug delivery and supercapacitors: a review. *Environmental Chemistry Letters*, vol. 19, p. 1667-1691.

- Purcar, V., Stamatin, I., Cinteza, O., Petcu C., Raditoui, V., Ghiurea, M., Miclaus, T., Andronie, A.** (2012). Fabrication of hydrophobic and antireflective coatings based on hybrid silica films by sol-gel process. *Surface Coating Technology*. vol. 206, p. 4449-4454.
- Qu, L.J., Rahimi, S., Qian, J., He, L.X., He, Z.B., Yi, S.L.** (2021). Preparation and characterization of hydrophobic coatings on wood surfaces by a sol-gel method and post-aging heat treatment. *Polymer Degradation and Stability*. vol. 183 p. 109429.
- Rahman, S.K., Maimunawaro, Rahma, A., Syauqiah, I., Elma, M.** (2020). Functionalization of hybrid organosilica based membranes for water desalination- Preparation using Ethyl Silicate 40 and P123. *Materials Today:Proceedings*.
- Razaei, S., Manoucheri, I., Moradian, R., Pourabbas, B.,** (2014), One-step chemical vapor deposition and modification of silica nanoparticles at the lowest possible temperature and superhydrophobic surface fabrication. *Journal of Chemical Engineering*, vol. 252, p. 11-16.
- Rojas, D.F.H., Gómez, P.P., Rivera, A.R.** (2019). Production and characterization of silica nanoparticles from rice husk. *Advanced Materials Letters*. vol. 10, p. 67–73.
- Rosales, A. and Esquivel, K.** (2020). SiO₂@TiO₂ Composite Synthesis and Its Hydrophobic Applications: A Review. *Catalysts*. vol.10, p. 171.
- Setyawan, N., Hoerudin, H., Wulanawati, A.** (2019). Simple extraction of silica nanoparticles from rice husk using technical grade solvent: effect of volume and concentration. *IOP Conference Series:Earth and Environmental Science*. vol. 309, 012032.
- Shokuhfar, A., Alzamani, M., Eghdam, E., Karimi, M., Mastali, S.** (2012). SiO₂-TiO₂ Nanostructure Films on Windshields Prepared by Sol-Gel Dip-Coating Technique for Self-Cleaning and Photocatalytic Applications. *Nanoscience and Nanotechnology*. vol. 2(1), p. 16-21.
- Soltani, N., Bahrami, A., Pech-Canul, M. I., González, L. A.** (2015). Review on the physicochemical treatments of rice husk for production of advanced materials. *Chemical Engineering Journal*. vol. 264, p. 899.
- Stober, W.,** (1968), Controlled growth of monodisperse silica spheres in micron size range. *Colloid Interface Science*. vol. 26, p. 62.

- Tao, C.Y., Yan, H.W., Yuan, X.D., Yin, Q., Zhu, J.Y., Ni, W., Yan, L.H., Zhang, L.,** (2016a). Detailed analysis and formation mechanism of superhydrophobic antireflective coatings with adjustable refractive index from trimethylsilanized silica nanoparticles. *Journal of Sol-Gel Science Technology*. vol. 80, p. 10–18.
- Tao, C., Yan, H., Yuan, X., Yao, C., Yin, Q., Zhu, J., Ni, W., Yan, L., Zhang, L.,** (2016b). Synthesis of shape-controlled hollow silica nanostructures with a simple soft-templating method and their application as superhydrophobic antireflective coatings with ultralow refractive indices. *Colloids and Surfaces A: Physicochem. Eng. Aspects*. vol. 501, p. 17–23.
- Tao, C., Yan, H., Yuan, X., Yin, Q., Zhu, J., Ni, W., Yan, L., Zhang, L.** (2016c). Hydrophobic antireflective coatings with ultralow refractive index synthesized by deposition of methylated hollow silica nanoparticles. *Materials Letters*. vol. 183, p. 374–377.
- Tufaner, G. and Helvacı, Ş.Ş.,** 2019, Synthesis of silica particles from ricehusk ash and their hydrophilic and hydrophobic surface modifications, MSc Thesis, Ege University, 187p (unpublished).
- Vaibhav, V., Vijayalakshmi, U., Roopan, S.M.** (2015). Agricultural waste as a source for the production of silica nanoparticles. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*. vol. 139, p. 515–520.
- Wang, W., Martin, J.C., Fan, X., Han, A., Luo, Z., Sun, L.** (2012). Silica Nanoparticles and Frameworks from Rice Husk Biomass. *ACS Applied Material Interfaces*. vol. 4, p. 977–981.
- Wang, Z., Xu, X., Wang, X., Jinyang, H., Guo, H., Yang, B.** (2021). Performance of modified asphalt of rubber powder through tetraethyl orthosilicate (TEOS). *Construction and Building Materials*. vol. 267, 111557.
- Wittayakun, J., Khemthong, P., Prayoonpokarach, S.** (2008). Synthesis and characterization of zeolite NaY from rice husk silica. *Korean J. Chem. Eng.* vol. 25, 4, p. 861–864.
- Wu, J., Wang, H., Bao, L., Zhong, J., Chen, R., Sun, L.** (2018). Novel raspberry-like hollow $\text{SiO}_2@\text{TiO}_2$ nanocomposites with improved photocatalytic self-cleaning properties: Towards antireflective coatings. *Thin Solid Films*. vol. 651, p. 48–55.

- Xiao, Y., Ma, R., Wang, C., Chen, X., Qiao, X., Fan, X.** (2016), High performance hierarchical nanoporous antireflective films by a facile sol-gel process. *Royal Society of Chemistry Advances*. vol. 6, p. 113911–113918.
- Xu, L., Gao, L., He, J.** (2012) Fabrication of visible/near-IR antireflective and superhydrophobic coatings from hydrophobically modified hollow silica nanoparticles and poly(methyl methacrylate). *Royal Society of Chemistry Advances*. vol. 2, p. 12764-12769.
- Xu, L., Geng, Z., He, J., Zhou, G.** (2014). Mechanically robust, thermally stable, broadband antireflective, and superhydrophobic thin films on glass substrates. *ACS Applied Material Interfaces*. vol. 6, p. 9029–9035.
- Yao, L., He, J., Geng, Z., Ren, T.** (2015). Fabrication of mechanically robust, self-cleaning and optically high-performance hybrid thin films by SiO₂&TiO₂ double-shelled hollow nanospheres. *Nanoscale*. vol. 7, 13125.
- Yener, H.B. and Helvacı, Ş.Ş.** (2015). Effect of synthesis temperature on the structural properties and photocatalytic activity of TiO₂/SiO₂ composites synthesized using rice husk ash as a SiO₂ source. *Separation and Purification Technology*. vol. 140, p. 84–93.
- Yuan, Y., Yan, G.H., Huang, S.H., Hong, R.J.** (2016). Preparation of hydrophobic SiO₂/PMHS sol and ORMOSIL antireflective films for solar glass cover. *Solar Energy*. vol.130, p. 1-9.
- Zhang, M., Liu, Q., Tian, S., Zhou, X., Liu, B., Zhao, X., Tang, G., Pang, A.** (2021). Facile synthesis of silica composite films with good mechanical property for spectrally broadband antireflection coatings. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. vol. 628, p. 127255.
- Zhang, S.M., Xiao, P.W., Wang, P.M., Luo, J.H., Jiang, B.,** (2020). Spherical-chain silica with super-hydrophobic surface and ultra-low refractive index for multi-functional broadband antireflective coatings. *Solar Energy*. vol. 207, p. 1222–1230.
- Zhang, C. and Xu, Y.** (2020). Transparent and hydrophobic hexylene-bridged polymethylsiloxane/SiO₂ composite coating with tunable refractive index and its application for broadband antireflection. *Thin Solid Films*. Vol. 701, p. 137944.
- Zou, X., Tao C., Yang K., Yang F., Lv H., Yan L.** (2018). Rational design and fabrication of highly transparent, flexible, and thermally stable

superhydrophobic coatings from raspberry-like hollow silica nanoparticles. *Applied Surface Science*. vol. 440, p. 700–711.

Zulkifli, N.S.C., Rahman, I.A., Mohamad, D., Husein, A. (2013). A green sol–gel route for the synthesis of structurally controlled silica particles from rice husk for dental composite filler. *Ceramics International*. vol. 39, p. 4559–4567.



ACKNOWLEDGEMENTS

I would like to thank my supervisor Prof. Dr. Şerife Şeref HELVACI for their kind suggestions, guidance and support.

Also, I would like to thank ERDOĞANLAR Food Industry for their supply of rice husk ash, also HAYAT KİMYA and KANSAI ALTAN Paint Industry for their chemical supply during the synthesis.

I appreciate Selim YETİŞ, Özlem ÜNLÜ IŞIK, Ediz DURMAZ, Dilek ŞANLIER Necati GÜDÜMCÜOĞLU and Mehmet ÜSTÜNDAŞ for their supports and comments in the application of glass paints. Also, I would like to thank Hakkı AK, Hasan KURT and Caner UMSULU for their help in the procedure of the coatings.

In addition, I would like to thank my laboratory colleague, Açelya ÇALIŞKAN and Gizem TUFANER for their suggestions, brain stormings and comments, the undergraduate students who worked with me in this project under my supervision, Seda Nur BİLGİLİBAŞLAR, Arda ALTILI and Sadi Atıl TÜRKYILMAZ.

Finally, I would like to thank my dear mother Seyhan ÖZ and my father Bahri ÖZ for all motivation, support, encouragement and efforts. Also, my lovely brother İsmail Berk ÖZ deserves a thank you for his enormous encouragement during the writing of the thesis. I would like to thank my mother-in-law Huri KINALI and my father-in-law Hikmet KINALI for their supports and comments. Also, I would like to thank my brother-in-law Özcan KINALI, my sister-in-law Ayşen KINALI and my nephew Atilla KINALI for their supports. I have special thanks to my dear husband Orhan KINALI for all support, love, encouragement, knowledge, guidance, suggestions and comments.

28 / 09 / 2021

Pelin ÖZ

CV

PELİN KINALI

PERSONAL INFORMATION

Sex :
 Date of Birth :
 Marital Status :
 Driving License :

EDUCATION

Master	Ege University – Izmir Chemical Engineering 09/2017 – (ongoing)	GPA : 3.65/4.00
Bachelor	Ege University – Izmir Chemical Engineering 09/2012 – 06/2017	GPA : 3.62/4.00
High School	Balçova Anadolu Lisesi– Izmir 06/2012	GPA : 84.29/100

WORK EXPERIENCE

07/2021-	Project Engineer	Kansai Altan Paint Inc.
03/2020 - 11/2020	Product Application Leader	MOLKİM Industrial Products
10/2019 - 03/2020	R&D Engineer	MOLKİM Industrial Products
08/2016 - 09/2016	Summer Training	TÜPRAŞ İzmir Refinery – Crude Oil Distillation Unit
07/2015 - 08/2015	Summer Training	Izmir Water and Sewer Authority Water Treatment Department Management of Water Treatment Tahtalı Drinking Water Treatment Plant

PROJECTS & CONGRESS

01/2020	TUBITAK–2209-B Industry Based Undergraduate Research Projects Support Program (Supervisor) <i>Synthesis of sodium silicate from agricultural wastes and its usage of preparation of hydrophobic silica sols</i>
11/2019	6th Symposium on Membrane Technologies and Applications (MEMTEK 2019)
06/2019	2 nd International Eurasian Conference on Biological and Chemical Sciences <i>Preparation of silica-sols and antireflective silica films-Parameters affecting the sol synthesis and film coating (Oral Presentation)</i> <i>Synthesis of silica particles using aqueous polymeric solution templates (Poster Presentation)</i>
03/2019	TUBITAK–2209-B Industry Based Undergraduate Research Projects Support Program (Supervisor) <i>Synthesis of silica particles from rice husk ash using aqueous polymeric solution templates</i>

11/2018	30 th National Chemistry Congress <i>A green technology for the synthesis of activated carbon and TiO₂ doped activated carbon composites from rice husk (Oral Presentation)</i>
09/2018	Masters' Thesis <i>Anti-reflective SiO₂, TiO₂, SiO₂/TiO₂ thin film coatings: Synthesis, characterization and application to glasses in automotive industry</i>
05/2017	TUBITAK-2209-B Industry Based Undergraduate Research Projects Support Program (Executive) <i>Production of activated carbon from rice husk ash</i>
09/2016	Undergraduate Thesis <i>Production of activated carbon from rice husk by using alkaline carbonates as activating agents</i>

ADDITIONAL EDUCATION & CERTIFICATES

10/2018	Multidisciplinary / Applied Infrared Spectroscopy Education EGE MATAI (Ege University, Central Research Test and Analysis Laboratory Application and Research Center)
05/2018	Analiz Hayatın Her Anında / Günlük Yaşam ve İleri Analitik Teknikler Semineri –ANT TEKNİK
05/2018	Determination of Particle Size Seminar / ANTON PAAR
03/2018	Material Safety Data Sheet Preparation Seminar (GBF/SDS) / TMMOB Kimya Mühendisleri Odası, Ege Bölge Şubesi
11/2017	Rheology Seminar / ANTON PAAR
09/2016	UniEndüstri – POLİNAS
02/2015	4 th UKMOP – İYTE
12/2013	İş Güvenliği Semineri- ÇASGEM

COMPUTER SKILLS

CANIAS ERP, MS Office 2013, Minitab 18.1, Autocad 2018, MathWorks MATLAB 2018, Curve Expert Professional, POLYMATH Professional, Aspen Plus 2006

INSTRUMENT SKILLS

UV-visible Spectrophotometer Shimadzu UV 2600
Dynamic Light Scattering and Zeta Potential Device Malvern Zetasizer Nano ZS

LANGUAGE SKILLS

English Reading: Good Writing: Good Speaking: Good
German Reading: Elementary Writing: Elementary

AWARDS & FELLOWSHIPS

Ege University – Faculty of Engineering
Chemical Engineering Department Graduated as 2nd of the department

SOCIAL ACTIVITIES

Tennis, Badminton, Theatre, Ballet, Swimming, Novels

CLUB & ASSOCIATION MEMBERSHIPS

TMMOB Kimya Mühendisleri Odası

REFERENCE

APPENDIX

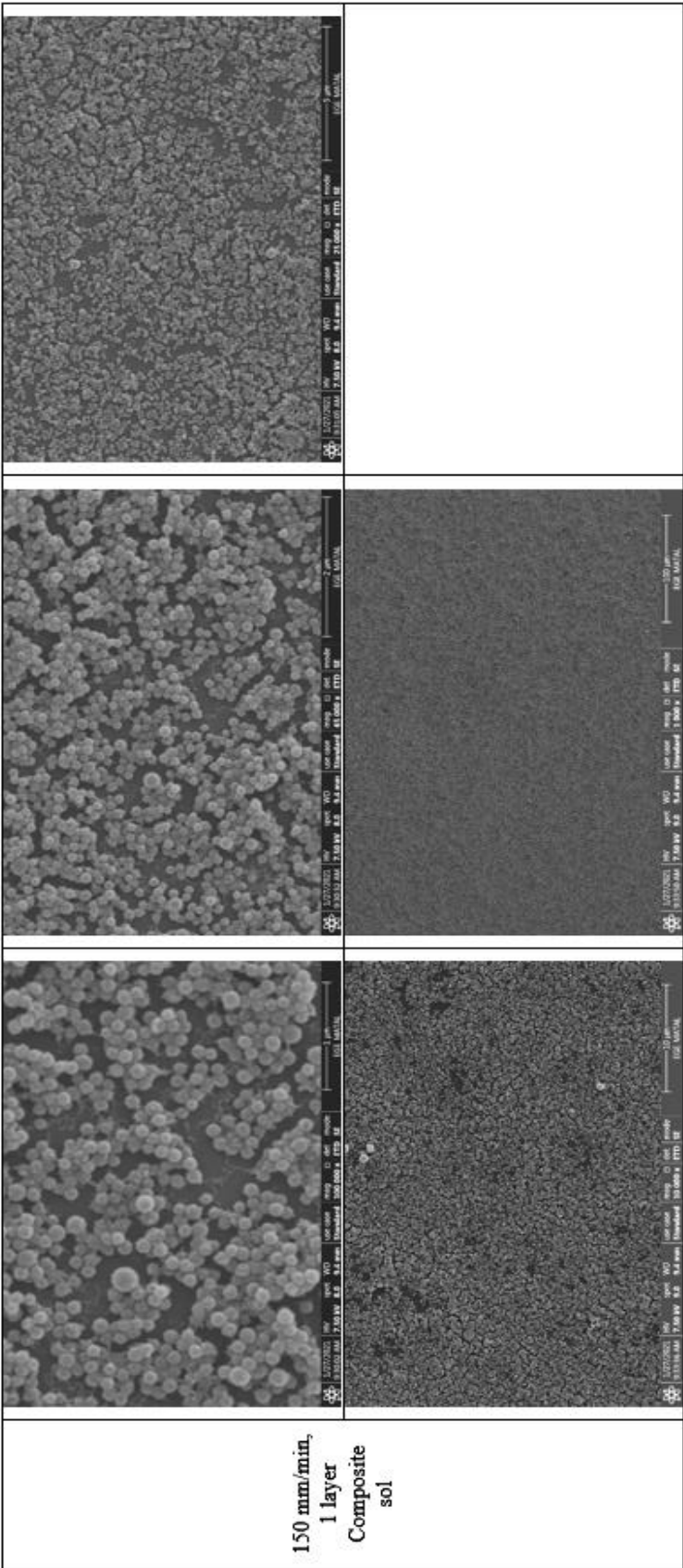
A1: SEM micrographs of SiO₂/TiO₂ composite sol and modified composite sol

A2: SEM micrographs of h-PAA SS

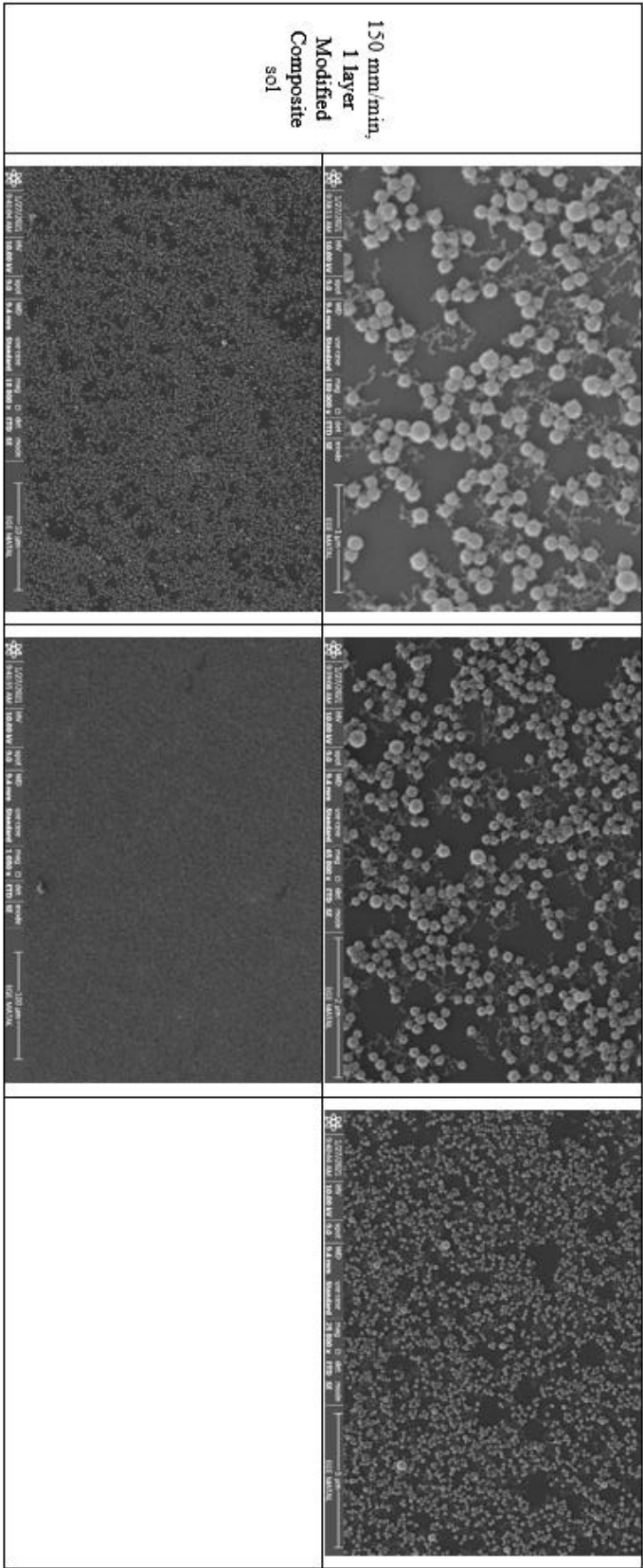
A3: SEM micrographs of c-PAA SS



A1. SEM micrographs of SiO₂/TiO₂ composite sol and modified composite sol



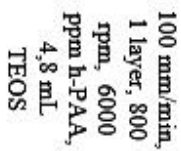
A1. SEM micrographs of SiO₂/TiO₂ composite sol and modified composite sol (continued)



A2. SEM micrographs of h-PAA SSs

100 mm/min,
1 layer, 500
rpm, 6000
ppm h-PAA,
4.8 mL
TEOS

A2. SEM micrographs



A2. SEM micrographs of h-PAA SSs (continued)

100 mm/min,
2 layers, 500
rpm, 6000
ppm h-PAA,
4.8 mL
TEOS

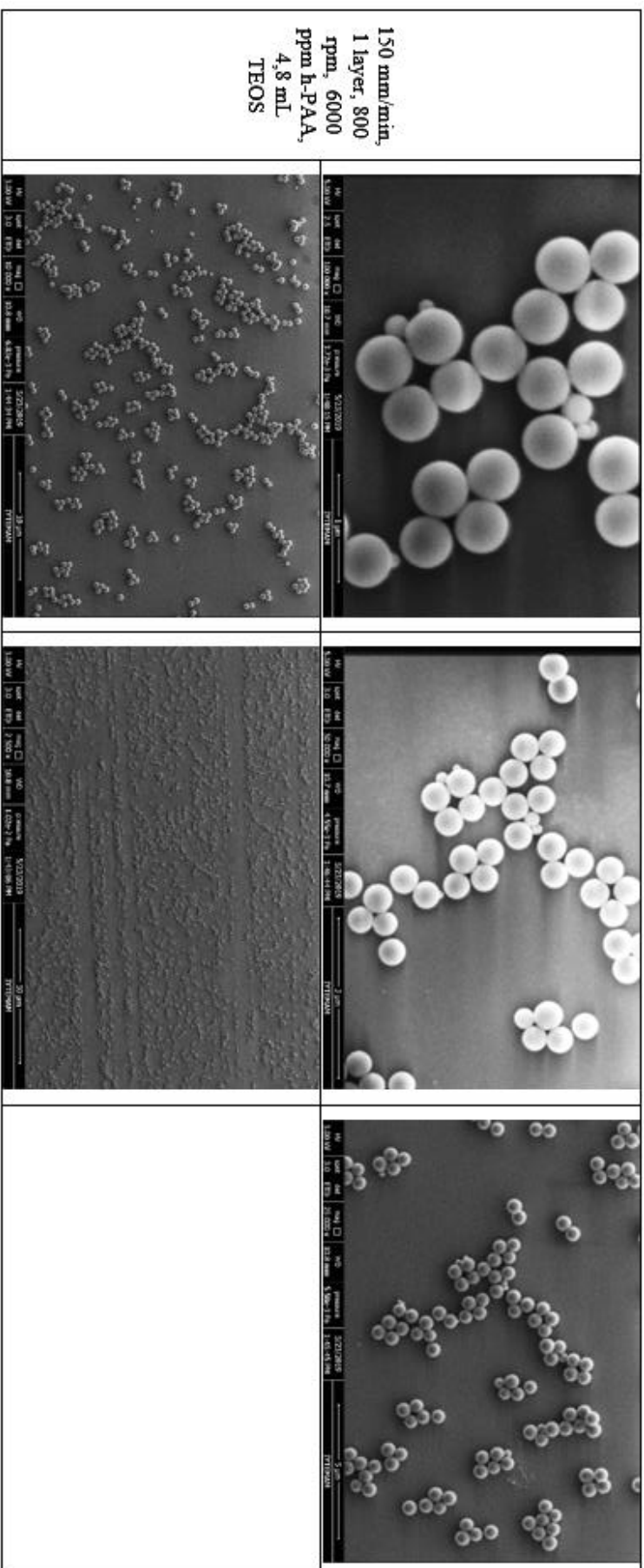
[illegible]

A2. SEM micrographs of h-PAA SSs (continued)

[illegible]

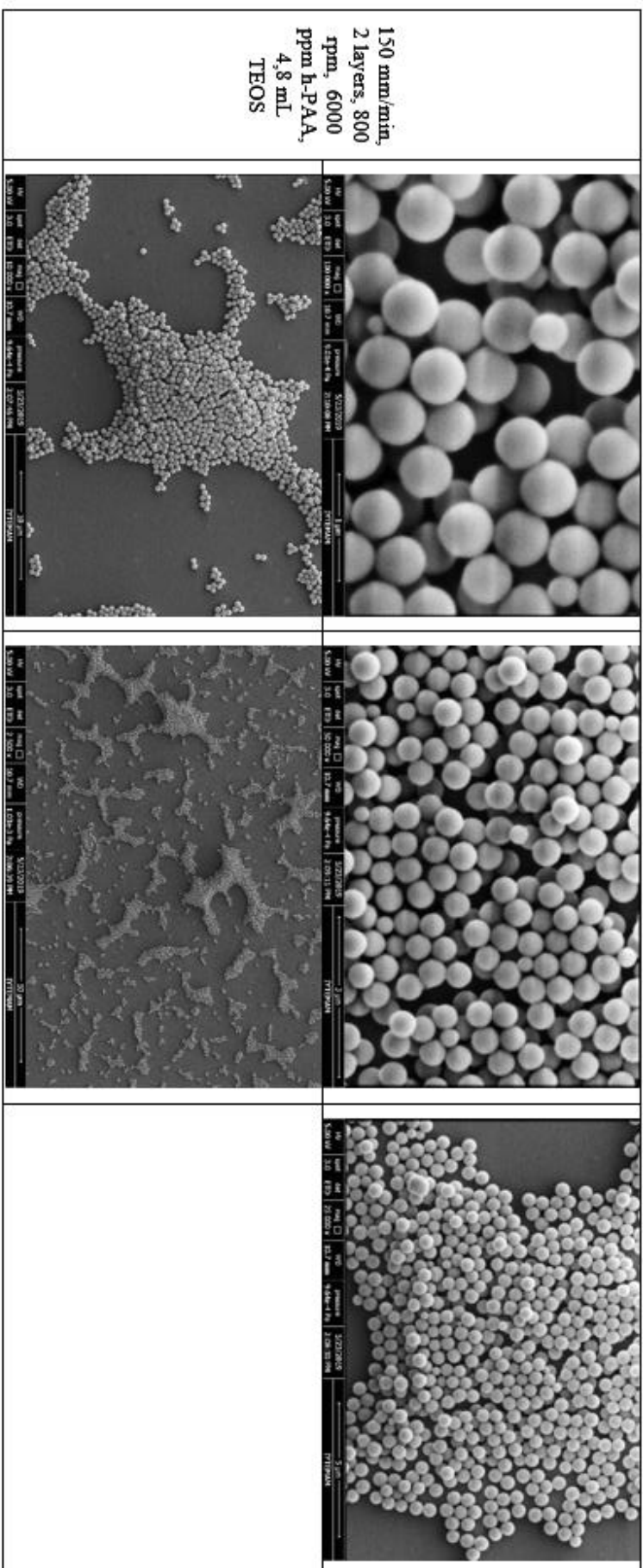
150 mm/min,
1 layer, 500
rpm, 6000
ppm h-PAA,
4,8 mL
TEOS

A2. SEM micrographs of h-PAA SSs (continued)

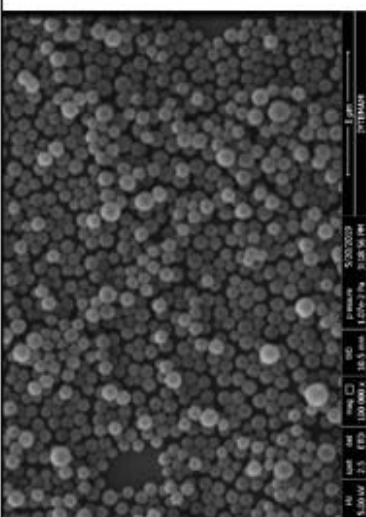
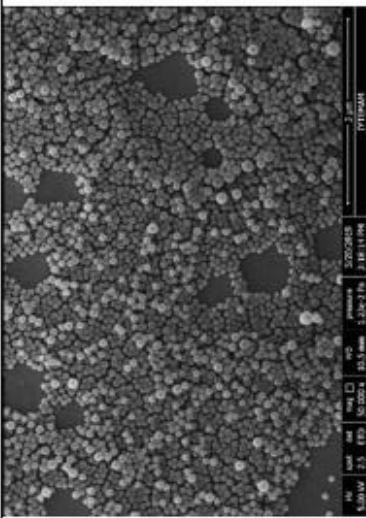
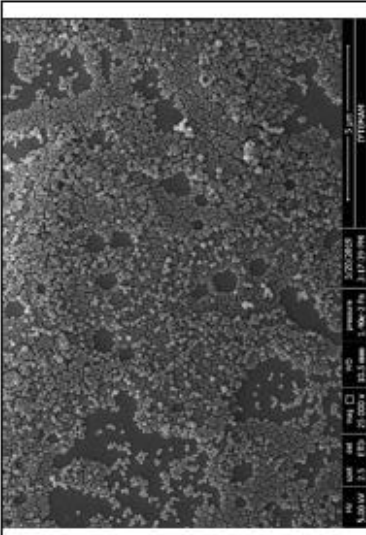
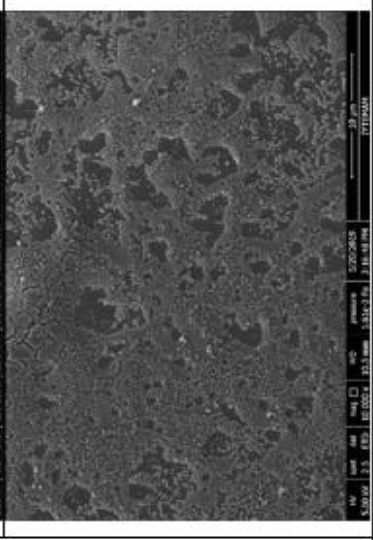
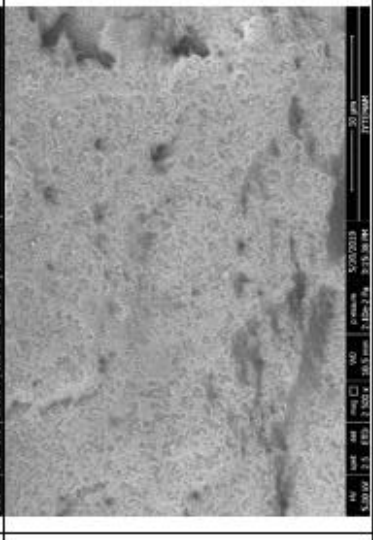
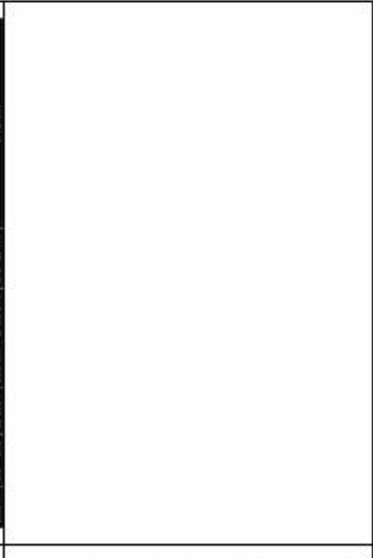


A2. SEM micrographs of h-PAA SSs (continued)

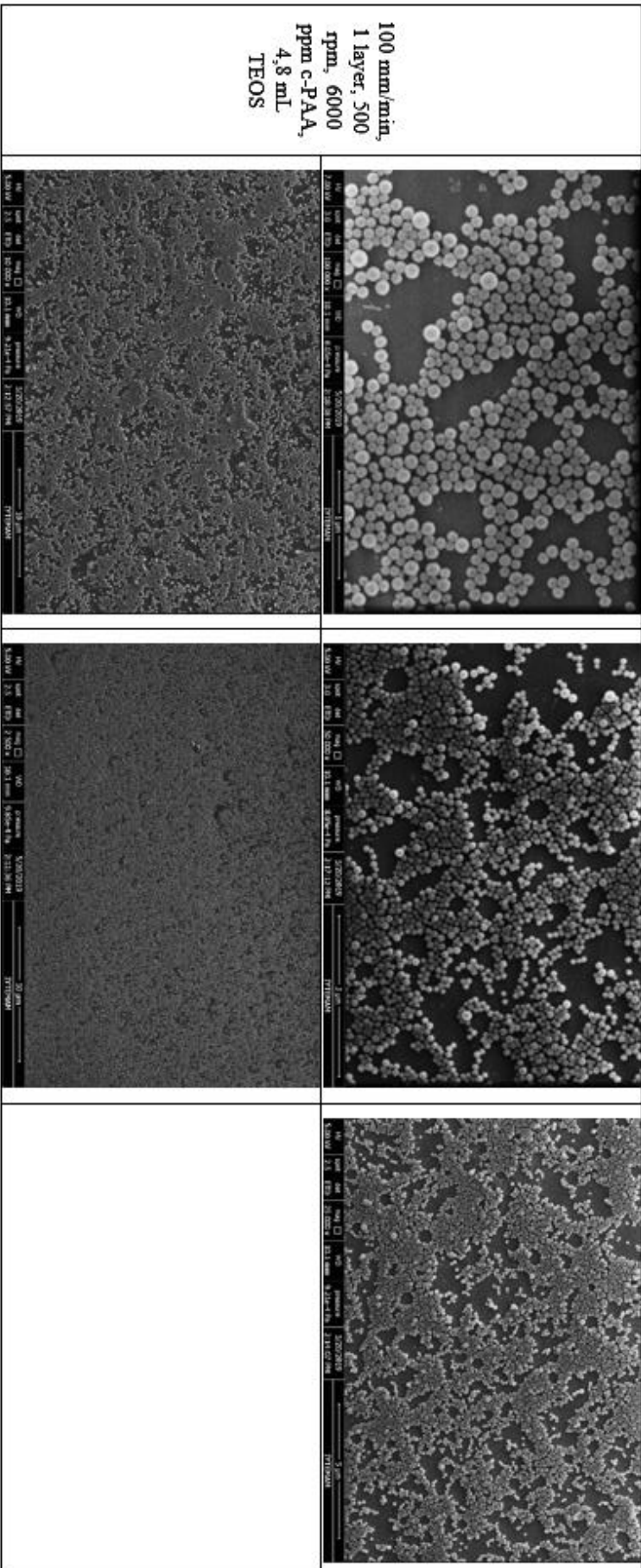
150 mm/min,
2 layers, 500
rpm, 6000
ppm h-PAA,
4.8 mL
TEOS



A3. SEM micrographs of c-PAA SSSs

100 mm/min, 2 layers, 500 rpm, 6000 ppm c-PAA, 4,8 mL TEOS	 100 mm/min, 2 layers, 500 rpm, 6000 ppm c-PAA, 4,8 mL TEOS	 100 mm/min, 2 layers, 500 rpm, 6000 ppm c-PAA, 4,8 mL TEOS	 100 mm/min, 2 layers, 500 rpm, 6000 ppm c-PAA, 4,8 mL TEOS	 100 mm/min, 2 layers, 500 rpm, 6000 ppm c-PAA, 4,8 mL TEOS	 100 mm/min, 2 layers, 500 rpm, 6000 ppm c-PAA, 4,8 mL TEOS	 100 mm/min, 2 layers, 500 rpm, 6000 ppm c-PAA, 4,8 mL TEOS	 100 mm/min, 2 layers, 500 rpm, 6000 ppm c-PAA, 4,8 mL TEOS
---	--	---	--	---	---	--	---

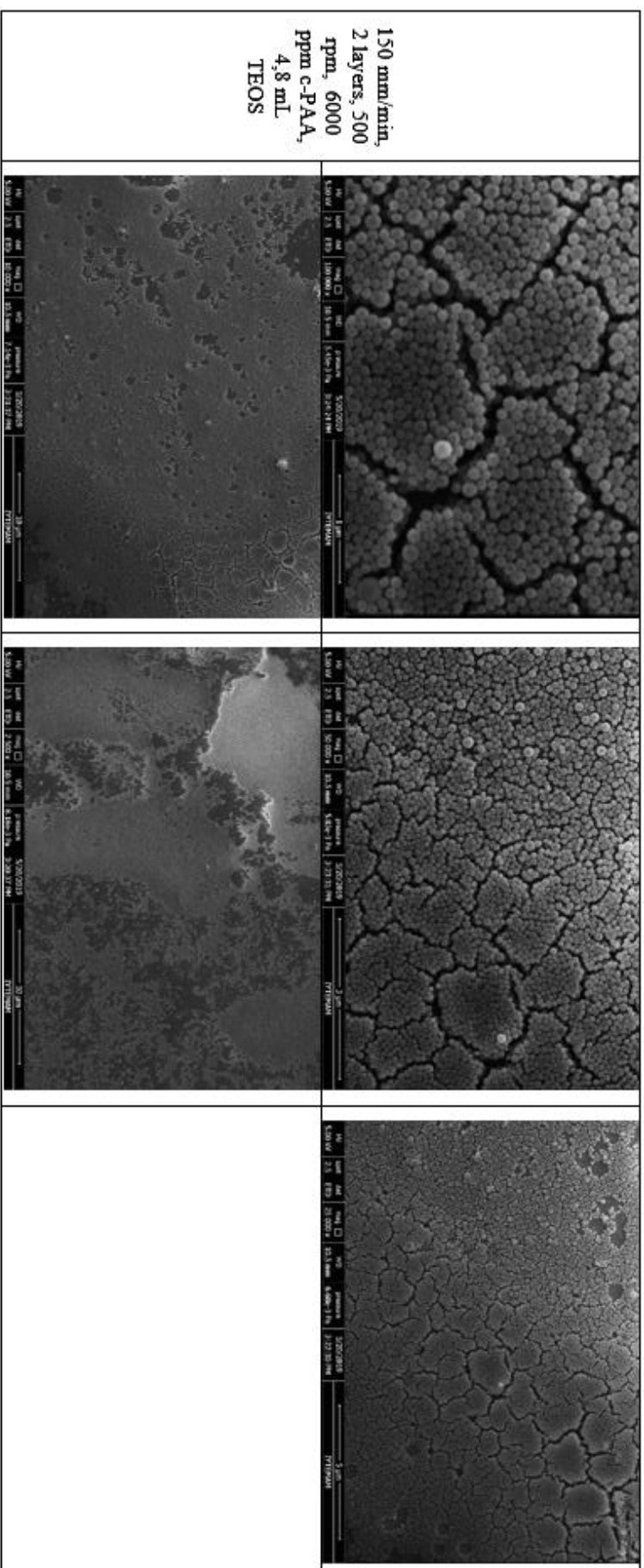
A.3. SEM micrographs of c-PAA SSs (continued)



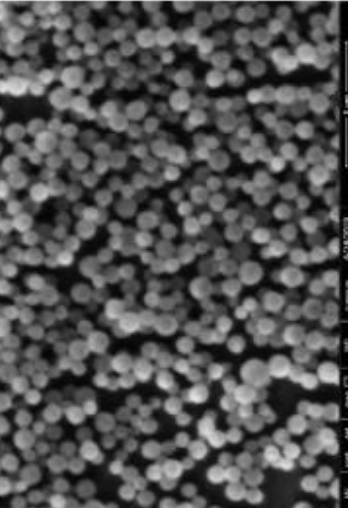
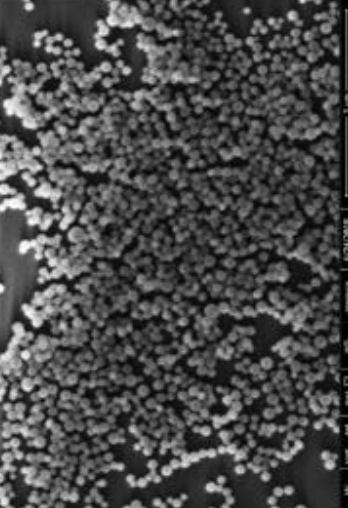
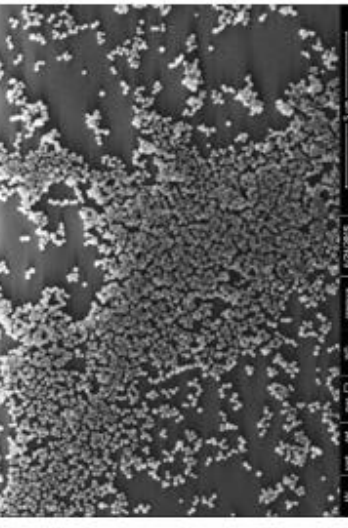
A3. SEM micrographs of c-PAA SSs (continued)

150 mm/min,
1 layer, 500
rpm, 6000
ppm c-PAA,
4,8 mL
TEOS

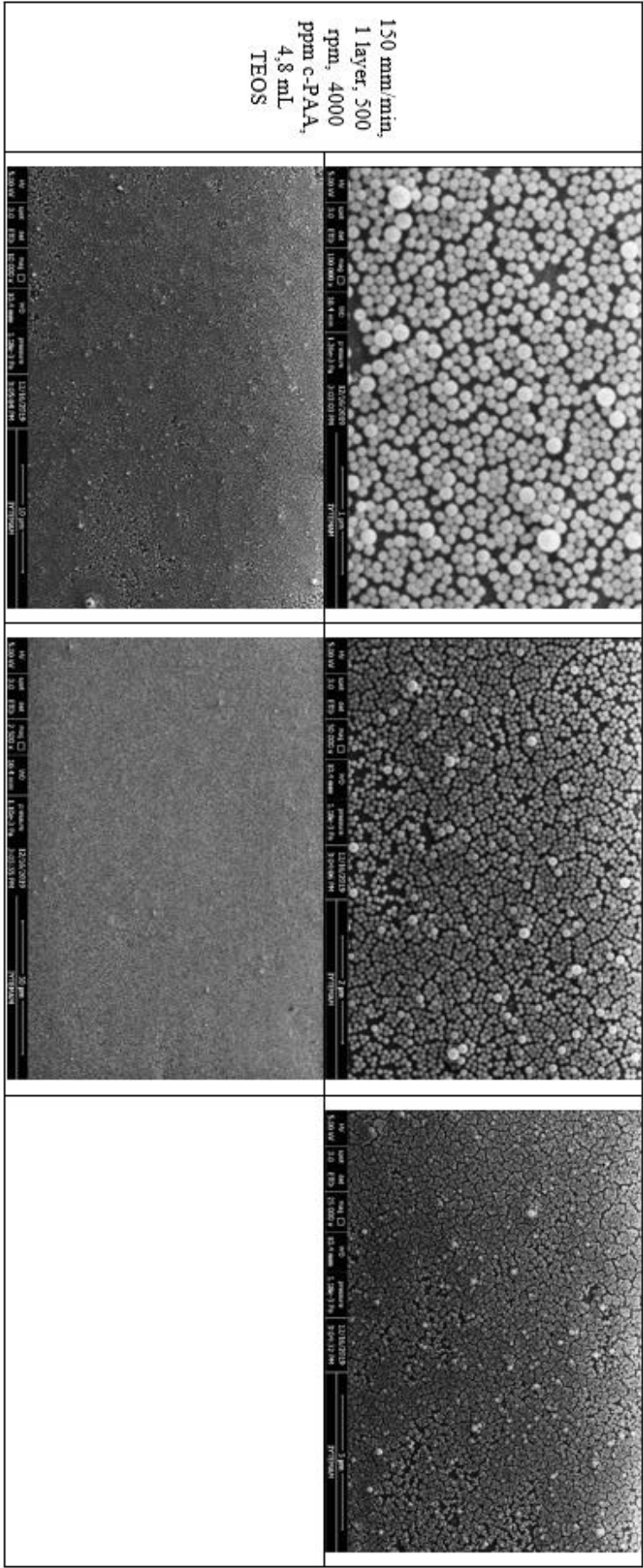
A3. SEM micrographs of c-PAA SSs (continued)



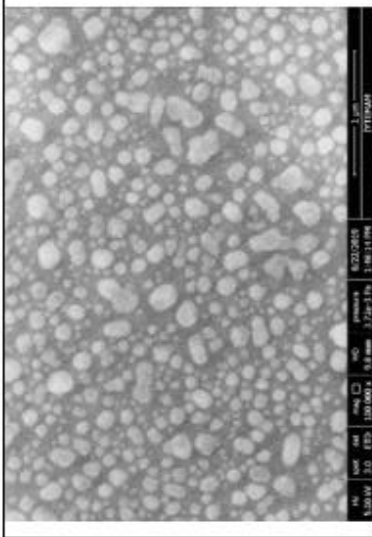
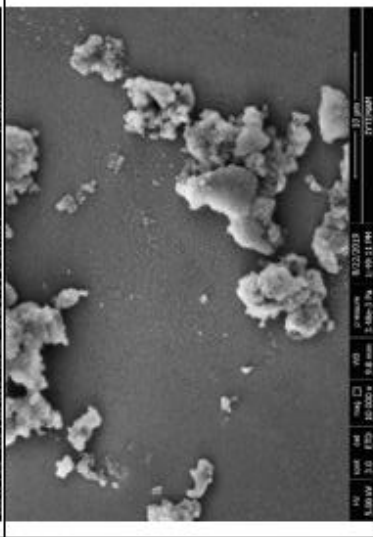
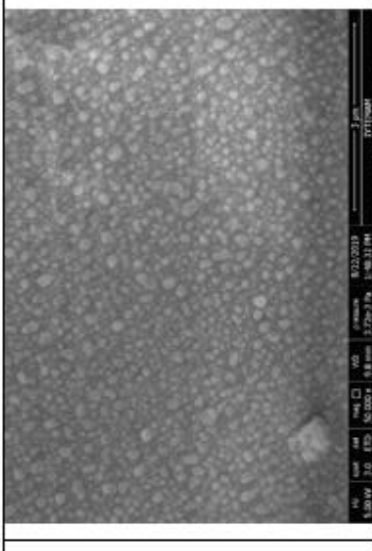
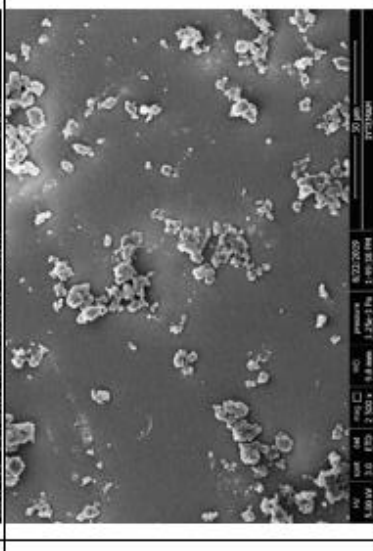
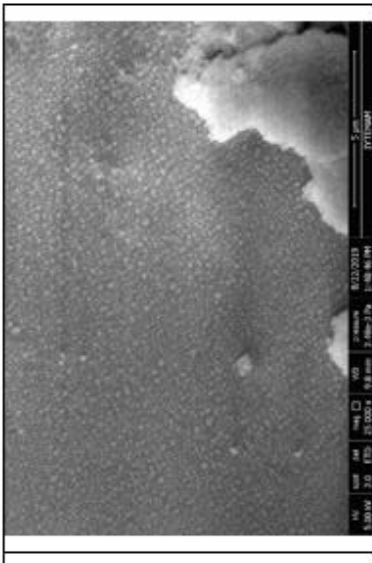
A3. SEM micrographs of c-PAA SSs (continued)

150 mm/min, 1 layer, 500 rpm, 8000 ppm c-PAA, 4,8 mL TEOS	 150 kV 3.00 kV 5.0 EDS 100.000x 16.8 mm 1.50um 1.19um 6/24/2013 2:05:50 PM PTF190426	 150 kV 3.00 kV 5.0 EDS 50.000x 15.9 mm 1.50um 1.19um 6/24/2013 2:06:50 PM PTF190426	 150 kV 3.00 kV 5.0 EDS 50.000x 15.9 mm 1.50um 1.19um 6/24/2013 2:11:10 PM PTF190426
--	--	--	---

A3. SEM micrographs of c-PAA SSs (continued)



A3. SEM micrographs of c-PAA SSs (continued)

150 mm/min, 1 layer, 500 rpm, 6000 ppm c-PAA, Na₂SiO₃	 1.0 μm 15.00 kV 3.00 kPa 100.000 μm 6.8 mm 3.77 μm 2.1 Pa 1.00 14.094 8/22/2019 8:23:08 PM EHT15000 150.000 μm	 1.0 μm 15.00 kV 3.00 kPa 100.000 μm 6.8 mm 3.77 μm 2.1 Pa 1.00 14.094 8/22/2019 8:23:08 PM EHT15000 150.000 μm	
 1.0 μm 15.00 kV 3.00 kPa 100.000 μm 6.8 mm 3.77 μm 2.1 Pa 1.00 14.094 8/22/2019 8:23:08 PM EHT15000 150.000 μm	 1.0 μm 15.00 kV 3.00 kPa 100.000 μm 6.8 mm 3.77 μm 2.1 Pa 1.00 14.094 8/22/2019 8:23:08 PM EHT15000 150.000 μm	 1.0 μm 15.00 kV 3.00 kPa 100.000 μm 6.8 mm 3.77 μm 2.1 Pa 1.00 14.094 8/22/2019 8:23:08 PM EHT15000 150.000 μm	 1.0 μm 15.00 kV 3.00 kPa 100.000 μm 6.8 mm 3.77 μm 2.1 Pa 1.00 14.094 8/22/2019 8:23:08 PM EHT15000 150.000 μm

A3. SEM micrographs of c-PAA SSs (continued)

