EFFECT OF SOLVENT ON MELTING GEL BEHAVIOR

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ABSTRACT OF THE THESIS

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Melting gel and hybrid glass are organic-inorganic materials derived from sol gel processing. The behavior of the melting gel is that it is a solid at room temperature, but when the melting gel is reheated to 110°C (T_1) it becomes fluid. The melting gel has reversible behavior due to incomplete crosslinking between polysiloxane chains. When the melting gel is heated to its consolidation temperature of 150°C (T_2) the gel no longer softens ($T_2 > T_1$), because crosslinking is completed. The melting gel at the consolidation temperature becomes hybrid glass.

Melting gel coatings were applied to titanium alloy substrates. Melting gels were prepared containing phenyl substitutions with 1.0 mole Phenyltrimethoxysilane (PhTMS) in ratio to 0.25 moles of Diphenyldimethoxysilane (DPhDMS). The methanol to DPhDMS ratio was varied to change the thickness of the coatings. The coatings were inspected visually to see that there is good adhesion between the coating and the substrate. Nanoindenter tests were performed to determine hardness. The coated samples were placed in an oven and heated to 150ºC for 24, 48 or 96 hours before cooling back to room temperature, which took about 4 hours. The measurements of the hardness on samples containing 3 levels of solvent and heat treatment were collected by indentation

technique. The best combination of solvent and temperature was 1:8 PhTMS:MeOH for all temperatures.

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CHAPTER 1

1.0 Introduction

Preparation of hybrid glass using organic-inorganic precursors is known as the sol-gel process. Recently, there has been growing interest and intensive studies in the field of hybrid coating materials. During the sol-gel processing, there are two main reactions that can occur: hydrolysis and polycondensation [1-3]. The two reactions can occur at the same time during the sol-gel process. Spectroscope studies show that the two reactions go simultaneously when hydrochloric acid is added as catalyst [4]. During the process, water and alcohol are added to the organic-inorganic precursors; pH and temperature are calibrated and controlled in the experiment. When the reactions take place, the viscosity start to increase, and a rigid gel is formed as a result. To reach the glassy state, the gel is dried by increasing the temperature. Alcohol, water and residual organic materials are eliminated by controlling the heat [5]. When the gel becomes glassy, it has similar properties and structure of conventional glass materials.

Glass and ceramics are types of inorganic materials. Glass and ceramics both have high hardness, stiffness, and thermal resistance but they are difficult to apply as coatings or to be extruded into shapes [6]. In general, organic materials are more flexible than inorganic materials [7]. Organic material are include polymers and elastomers [8]. They are lightweight, soft, form at low temperature and have poor electrical and optical properties [9]. Over the past decades, many experiments have been done to synthesize hybrid organic-inorganic materials that contain both properties of organic and inorganic materials [10]. When the two organic and inorganic materials are combined together, it

results in hybrid coatings. The hybrid coatings have properties of both organic and inorganic materials [11].

In this chemical formation, the gel derived glass has some advantages compared to ordinary glass [12]. The hybrid glass has the purity from the alkoxide [13]. Alkoxide has been used during the process as precursor [14]. During the preparations of the melting gel, the chemical compounds are in molecular level [15]. Moreover, fundamental investigation shows that during the process sol-gel chemical material is homogeneous [15].

Sol-gel can be used in several applications; for example protective coatings, thin films, substrates, fibers and nanoscale powders. The melting gel can be formed as a single or multi-component [16]. The studies of sol-gel have shown excellent protective coatings and chemical stability [17]. Sol-gel coatings change and improve the surface of the metals. Nanocomposite materials coat the surface of the metals. The benefit of the hybrid coating can be used as corrosion resistance, protective layer and thermal isolation [18].

Melting gels have been prepared from combinations of mono-substituted and di-substituted alkoxysilanes. The state of the melting gel is solid at room temperature and flexible for softening and re-softening at temperature around 110°C. This happens when the crosslinking is incomplete between inorganic portions, Si – 0 – Si, in the gel [19]. Matsuda studied the softening behavior of melting gel in 2001 [20]. This phenomenon of the melting gel indicates a reversible network. After reaching the consolidation temperature when the temperature is higher than 150°C, the gel cannot re-soften again. It

becomes an irreversible solid. The consolidation temperature depends on the chemical compositions [20]. Melting gels are investigated and developed to substitute for low melting glasses [19].

The focus of this investigation is to produce uncracked hybrid glass. Several components can play an important rule to change the behavior of the melting gel such as immiscibility, precursors, catalyst, heat treatment and chemical compositions. Hybrid glass were produced containing 1 moles phenyltrimethoxysilane (PhTMS), 0.25 mole diphenyldimethoxysilane (DPhDMS), 1.5 mole water (H_2O) with hydrochloric acid (HCl). The pH of the water is 2.5, adjusted by hydrochloric acid. The moles of methanol are 4, 8, and 16 mole to study the effect on gel behavior. This dissertation investigates effects of solvents on the melting gel and hybrid glass behaviors. Chemical, physical and mechanical properties are analyzed of various melting gel and hybrid glass, especially of the effect temperature and the time of heat treatment on the hardness of the hybrid glass.

CHAPTER 2

2.0 Scientific Background and Motivation of the Study

This section presents the scientific background leading to the study of the sol-gel process. General properties of the gel, synthesis, chemical reactions, alkoxides, catalysts and precursors are presented as constituting the backbone of this dissertation.

2.1 History of the Sol Gel Process

The Sol Gel process was investigated in 1844 by Ebelmen. Ebelmen prepared the sol gel by using the ethylorthosilicate (alkoxide) from $SiCl_4$ with alcohol [21]. He observed that the chemical components of the alkoxide and alcohol become a glassy gel at room temperature due to the slow hydrolysis with the humidity of the environment. This phenomenon attracted the chemists for one hundred years.

In 1939, Geffcken and Berger investigated oxide thin films [22]. The oxide thin films contained ethylorthosilicate alkoxide.

In 1950, the sol gel coating materials was studied by a German firm. Schott Glass Company. The preparations were focused on SiO_2 or TiO_2 mixed with other oxide materials. This process was explored too by Schroeder [23].

For many years scientists, tried to define the gel structure. Graham discovered the theory of the gel. The theory mentioned that the gel contain a continuous solid network and had continuous porosity [24]. In other theories, the structures of the gel are coagulated sol with particles. A layer of bonding water surrounds those particles [24]. Hurd proved that the gels structure contain chains of polymeric silica, and that the liquid

phase and solid phase of the gel are continuous [25]. Kistler in 1932 showed the skeleton structure of gel. In the aerogels products during the drying technique [26].

In 1956, Roy discovered the homogeneous powder by sol gel process. His contributions led to expanded attention for the sol gel process [27, 28].

In 1987, a lot of factories they start to fabricate the ceramic fiber by using metal-organic precursors [29, 30]. Yamane and Yoldas they discover the monoliths by using drying technique [30-31].

2.2 Acid Base Catalysts

Catalysts can accelerate the reaction rate by adding an acid or a base, where either acid or base is not consumed in the chemical reaction. In addition, catalysts are able to make the reaction proceed at low temperatures and pressures [32]. The catalyzed reactions can occur as acid or base catalysis. Several reactions can occur with both the acids and bases catalysts [33].

Brønsted–Lowry explained the acid and base mechanism in terms of catalyzed reactions under the title of Brønsted–Lowry concept [34]. Lewis discovered the reaction between the sharing of an electron pair where a base catalyst donates or the acid catalyst accepts; this phenomenon is known as Lewis theory [35]. Moreover, the chemical reactions can be homogeneous, when base catalyzed during hydrolysis or alcoholysis [36].

2.3 Alkoxides

Sol-gel processing utilizes molecular precursors. The molecular precursors play an important role in the polymerization reactions during the process. The molecular precursors are known as metal alkoxides [37]. Alkoxides are written as RO−, where R is an organic substituent and O− is an oxygen atom that has negative charge [38]. Alkoxides are synthesized by the reaction between a metal or metals and alcohol [39]. Alkoxide can be investigated by using elements such as alkali and alkaline earths [40-41]. Alkali and alkaline earth elements combined with appropriate alcohol can produce the alkoxide [42]. Silicon alkoxides can be produced by chemical reaction. The chemical reaction contains silicon alkoxides, water with appropriate alcohol and catalyst must be used during the reaction as acid or base [43]. Silicon alkoxides are sources of silica and the water can help the alkoxides molecule mix [43]. Silicon alkoxides show good adhesion between the metallic substrate and the hybrid coating [44].

2.4 Organo-alkoxysilane

Organo-alkoxysilanes are chemical precursors, of which the most common one is organo-alkoxysilanes. The general formula of organo-alkoxysilanes are "$R_n` - Si(OR)_{4-n}$ where n=1, 2, or 3 and R` is $-CH_3$, $-C_6H_5$, and $-CH=CH_2$," together [45]. Hybrid nanocomposites in nanoscale can form by using organo-alkoxysilanes. The organo-alkoxysilanes can form strong covalent bonds between the particles of the organic and the inorganic materials by the sol gel process [46]. Organo-alkoxysilanes are classified as network modifiers by Schmidt in 1984 [47-48]. The example of R` is methyl or phenyl according to Schmidt [47]. The example of the stable state of the chemical reaction or

formation of the network of the modifiers is vinyl or methacryl [48]. Phenyltriethoxysilane (PhTES) and methyltriethoxysilane (MTES) are two common type of organo-alkoxysilanes precursor. They can act as network modifiers [49, 50].

2.5 Definition of the Sol gel Process

The name sol gel comes from two words: sol meaning fine particles, and the gel meaning materials between the solid and the liquid [45-46]. Alkoxide solutions are clear solutions and do not contain any particulate suspensions. The alkoxide solutions have long chains of molecules. These long chains can crosslink together and form the network structure of the substance. The network structure is formed during the polymerization reaction. The hybrid materials that reduce their volume by evaporation of the solvent are known as xerogels [53]. When the gel is dried by hypercritical evacuation, it is known as aerogels [54].

2.6 Sol-gel Chemical Reactions

During the sol gel process, there are two main reactions which are hydrolysis and polycondensation [45]. This happens before the melting gel is formed. The mono- and disubstituted alkoxysilanes are combined with water, alcohol, and the catalyst [55-56]. The two reactions take place and the substance transforms from liquid to gel [55-56]. The mechanism of the first reaction is the hydrolysis. Hydrolysis reaction is shown as:

$$Si - OR + H_2O \Rightarrow Si - OH + R - OH \quad (1)$$

In hydrolysis reaction the hydroxyl group (OH) replaces the alkoxide group (OR) [57].

The second mechanism is polycondensation. The polycondensation reaction include two forms producing condensation alcohol and water.

The alcohol producing reaction is:

$$Si - OR + HO - Si = Si - O - Si + ROH \quad (2)$$

The water producing reaction is:

$$Si - OH + HO - Si = Si - O - Si + H_2O \quad (3)$$

In polycondensation, the chemical reaction includes the silanol groups. The silanol group produces the siloxane bonds known as (Si-O-Si). Alkoxide components have Si - O bonds. This bond makes alkoxide components the preferred the precursors.

2.6.1 Effect of Water on the Chemical Reactions

Water quantity can play an important role affecting the reaction rates of the hydrolysis and polycondensation. For example, for less amount of water the hydrolysis reaction will become slower so that the polycondensation reaction will become faster than the hydrolysis reaction. The slow hydrolysis reaction is due to the shortage of the

water molecules. The water molecules are necessary to replace the alkoxy group during the hydrolysis reaction. The shortage in water molecules can form short chains during the polycondensation reactions. The solution becomes denser due to small cross-linking chains [58].

When the quantity of water becomes higher than the required amounts, the hydrolysis reaction increases and the polycondensation reaction increases. Both of the reactions become faster due to the availability of the bonding of the water. The bonding allows the chains to become longer and condense [58]. Sakka and Kamiya established that a deficit of water is good to produce thin films and fibers [59]. Klein and Garvey established the optimum ratio of water to alkoxide ions to produce 16 monolithic gels [60].

2.6.2 Effect of Alkoxides on the Chemical Reactions

Alkoxide reactivity depends on the size and the type of the alkoxy group. There are several types of alkoxide groups, for example methoxy, ethoxy, butoxy or amyloxy groups. In general, the hydrolysis reactions for the methoxy or ethoxy groups are more rapidly than butoxy or amyloxy groups [39, 55].

2.6.3 Effect of the Alcohol on the Chemical Reactions

Water usually mixes with the alkoxides in the sol gel processing. Alcohol acts on the alkoxide solution as a solvent to produce a homogeneous solution. An excessive amount of alcohol acts as diluting in the solution. An excessive quantity of alcohol can affect the hydrolysis reaction. The hydrolysis reaction will become more rapid due to the

addition of alcohol [61]. Alcohol interferes with hydrolysis and the polycondensation reactions. In addition, this excessive quantity of alcohol makes the sol gel process take longer time to form the melting gel.

2.6.4 Effect of Temperature on the Chemical Reactions

In the sol gel process the alkoxide solutions have low chemical reactivity. The chemical reactivity of the alkoxides can be activated by increasing the temperature. The common temperature to form the gel is between 50 and 75°C. Without the temperature increase, the solution could take weeks to form a melting gel at room temperature [62].

2.7 Sol gel Classification

There are two classes of bonds in the melting gel. Class I refers to the weak bonds between the organic and inorganic components. The example of the class I are hydrogen bonds or van der Waals bonds. Class II refers to the bonds between the organic and inorganic components and refers to the strong bonds. The example of the strong bonds in the melting gel are the covalent bonds [45]. The products in the polycondensation reactions can be alcohol or water as shown in chemical equation 2 and 3 [57].

2.8 The Advantages of the Hybrid Materials

There are several advantages of the sol gel process containing silica, such as chemical compositions are easier to control, and processing techniques are less complicated at low temperature and pressure. Melting gels show high purity in the final stage. The sol gel process can be done at low temperature. This working temperature

gives advantage to reduce the air pollution and phase separation [63]. This technique allows us to investigate new materials in the nano materials field.

The process of the sol gel involves liquid solution in the beginning. It can be used easily as coating material. The hybrid materials can be applied as thin films. The thin film is easier to form without the need of any machining or melting process. In addition, the hybrid materials can be used for larges areas for the coating technique. Hybrid materials can be applied at room temperature to certain applications.

On the other hand, the hybrid materials have some disadvantages. For example: some organic-inorganic precursors are costly materials and hence the volume of the sample used has to be reduced. The main reason for the reduction the volume is the evaporation of the solvent. Some organic solvents have some hazardous behavior and require proper ventilation. The sol gel process may take days to weeks.

2.9 Sol gel Applications

Several application are considered to use the sol gel materials. Sol gel materials can produce monolithic glass. Several applications of monoliths are considered, for examples: lenses, filters in optical applications, sensors, and membranes to separate and filter substances. In the area of ceramics, sol gel process can produce polycrystalline ceramic materials. These forms can be applied to thermal insulation and electronics devices for example in the electronics memory, IR devices and capacitors. Sol gel can be used as antireflection coatings in the automotive field [54]. Coating technique are one of the main topic in the field of sol gel. The industrial field are interested in the development of the sol gel materials. This development includes the behavior of thin films in different

environments, and the mechanical, chemical and physical properties. There are several coating techniques. For example: spraying, dipping, and pouring. Pouring is the method studied in depth in this thesis.

2.10 Coating Techniques

Sol gel technique has several methods for applying coatings onto the substrate. Each process has advantages and disadvantages. The coating properties are dependents on the coating technique [64].

2.10.1 Spraying Coating Technique

This technique is by using the nozzle to spray the coating materials onto the substrate. The coating materials are sprayed as fine droplets onto the substrate. The fine particles stick onto the substrate. The temperature of the substrate is an important factor in this technique because of the deposition rate [65].

The liquid of the coating materials in this technique has high dispersive behavior and depends on the carrier gas. The most used gas in this technique is air [66]. One side of the sample can be coated by this technique. To do coating on both sides can be done, but it is difficult to do.

2.10.2 Spinning Coating Technique

This technique can inject the coating solution materials onto the substrate. The substrate is installed on the spinning turntable. The rotational speed and the spin acceleration are controlled by the control panel. When the speed is adjusted, the solution

can be dripped into the rotating die. The machine starts to create the centrifugal force. The centrifugal force spreads the coating materials onto the substrate. The coating is formed as a thin film in this technique [67]. This technique gives a uniform coating surface and the thickness can be controlled before the coating process. However, the machine can coat only one side.

2.10.3 Pouring Coating Technique

In this technique, the solution of the coating materials is poured onto the substrate. The coating can be used to cover large substrate areas and complex shapes can be formed in this way. The thickness of the coating can be controlled by the angle of inclination. The process achieves homogeneous coatings on the surface of the substrate.

2.10.4 Dipping Coating Technique

This coating technique can be applied onto the substrate in two ways. First, the substrate can be submerged into the solution, and then the substrate is left inside the solution for a period. Second, by using a dip coating machine. The speed of dipping can be controlled. The substrate can be dipped into the solution at constant speed. This technique can form thin film coating materials.

Dipping technique has several advantages, such as good homogeneity, stability of the coating, great for large substrate without any limit, cheap process for the large substrate per unit area and can coat the two side of the substrate. The disadvantage of this technique such as expensive initial setup and coating contain a lot of porosity [65, 68].

2.11 Indentation Technique in the Sol gel Processing

Martens was the first scientist who invented the indentation device and the machine developed by Pethica in 1980 [69]. The study mentions that it is very difficult to evaluate the stress field under the tip and this is the reason the data is very difficult to collect. Oliver and Pharr discovered a method to analyze hardness and elastic modulus of the materials [69]. Tucci and Esposito, discovered a relationship between the hardness test and corrosion resistance test [70]. These techniques can determine the surface properties of the materials. In general, hard materials are more homogeneous higher density. Hardness tests can determine the surface morphology of the coating materials. Carani, discovered a relationship between the thickness and the hardness. The study found when the thickness is small the value of the hardness become smaller [71].

CHAPTER 3

3.0 Effect of Solvent on Melting Gel Properties

In this study, melting gels were prepared with 3 different molar ratios of the solvents. There are several reasons to change the molar ratio of the solvent. The solvent can act to dilute, delaying the cross-linking during the reaction, facilitating the condensation, controlling the glass transition temperature, controlling the thickness of the coating during the coating process, or improving the surface of the coating and making it crack-free. The main goals of this dissertation are to produce melting gels with desirable properties, such as optimum softening (non-porous materials), adhering to steel, stainless steel and titanium alloy, and pouring easily onto the substrate. There are two main chemical components that form the melting gel in this study: First is mono-substituted siloxane and second di-substituted siloxane. For the mono-substituted siloxane the chemical used is phenyltrimethoxysilane (PhTMS) and the disubstituted siloxane used is diphenyldimethoxysilane (DPhDMS). Figures1 and 2 show the chemical structures of the mono-substituted siloxane and di-substituted siloxane.

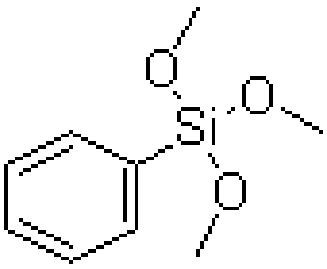


Figure 1 Phenyltrimethoxysilane (PhTMS).

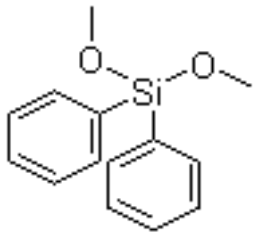


Figure 2 Diphenyldimethoxysilane (DPhDMS).

The molecular formula of phenyltrimethoxysilane is $C_9H_{14}O_3Si$ and the molecular formula of diphenyldimethoxysilane is $C_{14}H_{16}O_2Si$.

Melting gel was synthesized by changing the molar ratio of the solvent. The solvent that was used in the experiment is methanol. The original synthesis done by Jitanu et al contains four moles of methanol [45]. In this study, the molar ratio was 4, 8 or 16 moles. The thermal behavior of the melting gel was study by using Differential Thermal Analysis (DTA) and Thermal Gravimetric Analysis (TGA) to determine the rate of the reaction and the weight loss of the melting gel. The surface morphology, fracture surfaces and the microstructural change of the hybrid glass was study by using Scanning Electron Microscope (SEM) and Energy-dispersive X-ray Spectroscopy (EDS) to determine the elemental analysis. The hardness of the hybrid glass was measured by nano-indentation testing. The hardness of the coating can describe the abrasion resistance of the coating materials [72]. The roughness of the hybrid glass was measure by using Atomic Force Microscopy (AFM). The roughness tells how smooth the coatings are. The percentage of the organic-inorganic materials on the hybrid glass was study by Fourier Transform Infrared Spectroscopy (FT-IR).

In this study, the chemical composition of mono-substituted siloxane and di-substituted siloxane are constant. The molar ratio of the mono-substituted siloxane is 1.0 mole and the di-substituted siloxane is 0.25 mole. The coating technique in this study is pouring.

CHAPTER 4

4.0 Experimental Methods

4.1 Chemical Raw Materials

In this study, the sol-gel process followed the experiment of Jitianu et al [45]. The silica melting gel contains; phenyltrimethoxysilane (PhTMS), diphenyldimethoxysilane (DPhDMS) which both contain silica. Methanol was the solvent. Distilled deionized water was used for hydrolysis and hydrochloric acid was the catalyst.

The raw materials in the experiment are, phenyltrimethoxysilane (PhTMS) $C_9H_{14}O_3Si$ with molecular weight 198.29 grams/mole manufactured log Gelest Inc., Morrisville, PA, diphenyldimethoxysilane (DPhDMS) $C_{14}H_{16}O_2Si$ with molecular weight 244.36 grams/mole, also Gelest Inc., anhydrous methanol (CH_3OH) with molecular weight 32.0419 grams/mole, manufactured is by Sigma-Aldrich, distilled water (H_2O) with molecular weight 18.015 grams/mole and Hydrochloric acid (HCl) from Fisher Scientific, Atlanta, GA.

In this study, three different synthesis of melting gels was investigated with different solvent quantity. Each sample was created by using constant heat treatment from 70°C to 110°C and by using electric furnace for 1 to 8 hours. Melting gel was poured onto the substrate.

The substrate in this study was titanium alloy. The titanium alloy is selected because it is widely used in the manufacturing and industrial applications. The thickness of the substrate is 1.65 to 1.7 mm.

4.2 Melting Gel Preparation

The molar ratio of the PhTMS was 1.0 and for the DPhDMS 0.25. The pH of the water was adjusted by adding some droplets of the hydrochloric acid. The pH of the water was 2.5 measured by pH measurement device. The molar ratio of the water was 1.5 to 1 mole of PhTMS. The solvent used in the experiment was anhydrous methanol. The molar ratio of the anhydrous methanol was 4, 8 or 16. Table 1 presents the molar ratio of the chemical components and consolidation temperature, in the experiment.

Table 1. The chemical composition of the elements.

Chemical composition by moles				**pH of H_2O + HCl**	**Consolidation Temperature**
PhTMS	**DPhDMS**	**HCl+H2O**	**MeOH**	**Unit less**	**(°C)**
1	0.25	1.5	4	2.5	150
1	0.25	1.5	8	2.5	150
1	0.25	1.5	16	2.5	150

Figure 3 shows the flow chart of the synthesis route of PhTMS and DPhDMS in the experiment.

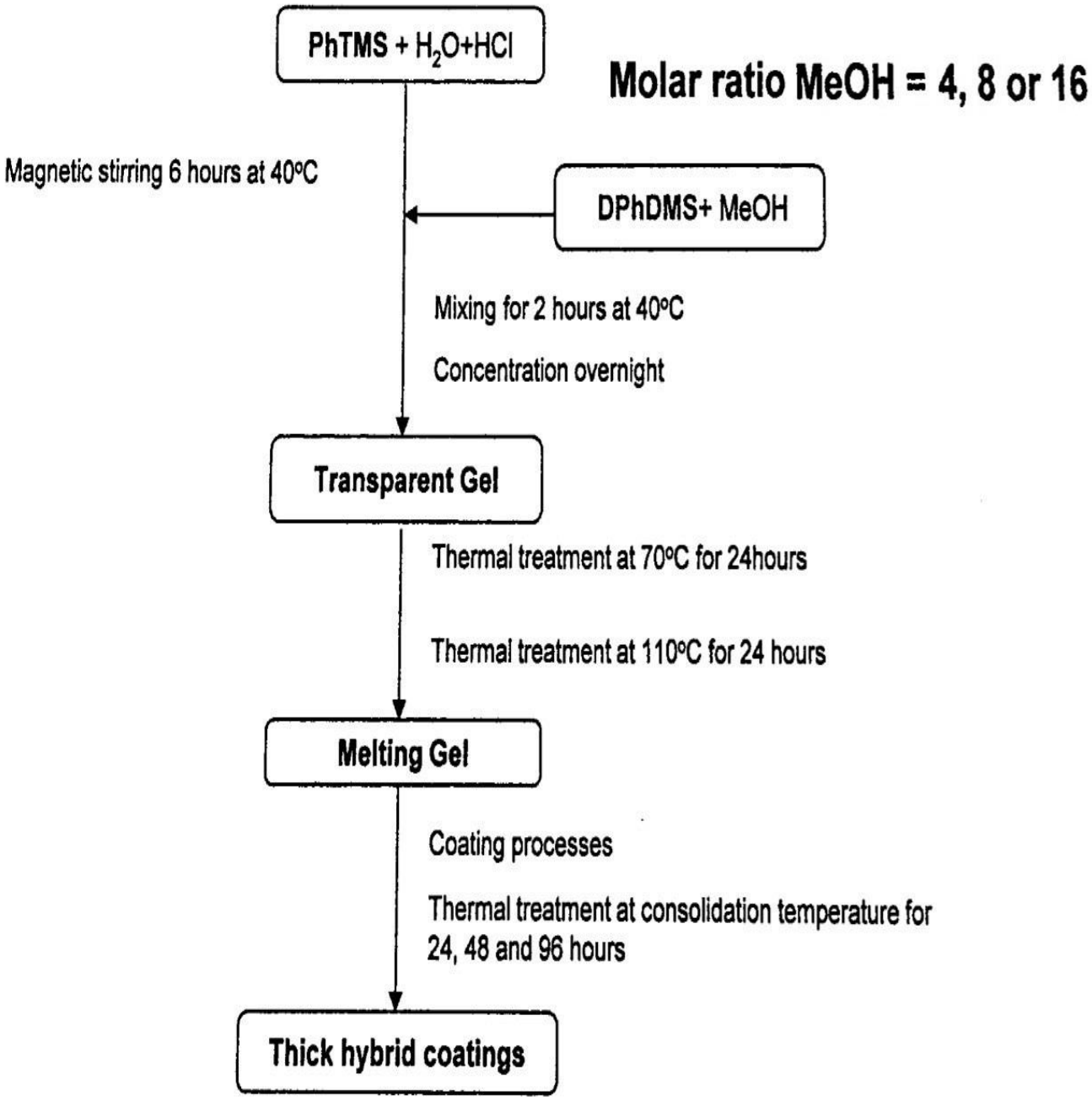


Figure 3 Flow chart for preparation of Melting Gel mole ratio 1.0 PhTMS-0.25 DPhDMS (80 mol% PhTMS-20 mole% DPhDMS).

In the beginning, monosubstituted alkoxide (PhTMS) and water (H_2O+HCl) were mixed together at 40°C inside the furnace by using magnetic stirrer in a closed beaker. The solution did not showed homogeneity at first. After 30 minutes of stirring, the solution became clear and homogeneous. The solution was mixed for 6 hours.

In the second step of the experiment, disubstituted alkoxide (DPhDMS) was diluted with alcohol (MeOH). The molar ratio of DPhDMS 0.25 and MeOH 4, 8 or 16 (0.25:4, 8 or 16) mol. The solution of disubstituted alkoxide with alcohol was added to the solution of monosubstituted alkoxide with water drop by drop. This took about 10 minutes. The two solutions were mixed together at 40°C in a closed beaker for two hours. The total time of the stirring was 8 hours. After 8 hours, the solution was cooled to room temperature. The solution was kept in an open beaker and stirred overnight until gelation occurred.

In the final step, the gel was heat treated. First, the gel was dried at 70°C for 24 hours followed by 110°C for 24 hours. The total treatment was 48 hours. The melting gel was solid at room temperature after the treatments.

However, the melting gel became soft at 110°C and when cooled down it became solid. This behavior is reversible for the melting gel.

4.3 Preparation of the Substrate

In this study, a titanium alloy substrate was used. The titanium alloy substrates were polished surfaces.

The substrate samples were cut by using lab electric saw. The size of the sample was cut as the desired dimension was needed. The sharp edges were removed by using a file.

The substrate surface was polished by using sandpaper. The sandpaper used was silicon carbide polishing paper and its grit was P2400. The manufacturer of the sandpaper was MICROCUT. The substrate was cleansed by using ultrasonic bath after the polishing. The sample was put into Isopropanol. The ultrasonic cleaner was operated for twenty-five minutes to clean the surface of the substrate. Afterwards, the substrate was dried inside the furnace at 150°C for one hour. This technique enhances the adhesion between the substrate and the hybrid coating.

4.4 Preparation of the Coating by Pouring

In the coating technique, the gel is heated up until it become fluid at 110°C. The fluid was poured onto the substrate inside the furnace at 110°C. After that, the temperature was increased to 150°C. At 150°C, the melting gel cannot be re-softened again and the hybrid glass is consolidated.

4.5 Characterizations Techniques

The main goal of the characterization studies is to get information about structural characterization of the melting gel and the hybrid glass. The Differential Thermal Analysis (DTA) and Differential Scanning Calorimetry (DSC) techniques were used to measure the thermal properties of the melting gel. The mechanical properties were measured by using Nano-indentation and Atomic Force Microscopy (AFM) techniques. The surface analysis and morphology of the hybrid coating materials were studied by using Fourier Transform Infrared Spectroscopy (FT-IR), Scanning Electron Microscope (SEM) and Energy-dispersive X-ray spectroscopy (EDS). The samples were stored in closed petri dishes to avoid contamination.

4.5.1 Thermal Analysis – DTA - DSC

The energy liberated, reaction types (exothermic or endothermic) and weight loss of the melting gel were studied and measured using a Seiko EXTAR TGA/DTA 6200 thermal analyzer using platinum crucibles and DSC TA-Q-20. The DTA device was operated and recorded using heating rate of 5 °C/min and temperature range between 50 to 1000 °C under continuous flow of dry air at flow rate of 100 mL/min. The DSC instrument was run using heating rate of 5 °C/min and temperature range between -90 to 500 °C under nitrogen flow rate of 20 mL/min.

4.5.2 Mechanical Testing Analysis – Nanoindenter - AFM

The hardness and elastic modulus of the hybrid glass were measured using Nanoindentation testing. The nanoindenter is Hysitron nanoindenter, lab model Triboindenter with Berkovich tip with a roughly 100 nm tip radius. Since it is a Nanoindenter, it is instrumented (unlike regular Vickers or other indenters). This allows for continuous measurement of both depth and load, while observing loading phenomena (such as pop-in events) and unloading phenomena (including plastic-elastic transitions). The hybrid glass indent and it is a pointy pyramid (Berkovich tip) and measure the load and depth of the sample. The indent loading conditions were 1 mN or 3 mN and loading rate of 10 sec load, 10 sec unload, and for 20 sec total for both loading and unloading rates.

The roughness of the hybrid glass was measured using Atomic Force Microscopy (AFM). Nanoscope IV Digital instruments was used for AFM with constant force 40 N/m and frequency ~325 KHz. The images were verified by tapping mode to obtain roughness measurements.

4.5.3 Surface Analysis and Morphology – FT-IR – SEM – EDS

The compositions of organic-inorganic materials of the hybrid glass was studied using Fourier transform infrared spectroscopy (FT-IR). Nicolet FT-IR IS10 spectrometer (Thermo Scientific) was used for FT-IR with resolution 4 cm^{-1}. The FT-IR spectra was recorded between 400 to 4000 cm^{-1}. The hybrid glass contains 80 mol % PhTMS and 20 mol % DPhDMS.

The surface topography of the hybrid glass was examined under Scanning Electron Microscope (SEM). Zeiss Σigma (Sigma) was used to study the SEM. The Zeiss Σigma SEM operates at low voltage for backscatter, with inlens, electron backscatter diffraction (EBSD) and energy dispersive spectroscopy (EDS) detectors. Different magnification were used during the test, for example 500, 1000, 5000, 10,000, 30,000, 50,000 times magnifications. The hybrid glass coating material was coated by gold layer to prevent the charging on the surface, using EMS150R-ES rotary coater. The thickness of the gold layer coating was 10 nm.

The elemental analysis of the surface of the hybrid glass coating was studied using Energy-dispersive X-ray spectroscopy (EDS). To get higher intensity the EDS device was operate at 10 kV voltage and area scan 10 micron.

CHAPTER 5

5.0 Results and Discussion

5.1 Introduction

This chapter presents results and discussions of the melting gel and the hybrid glass. It includes results of thermal analysis, mechanical testing analysis and surface analysis.

5.2 Melting Gel

Three types of melting gels were investigated with mole ratio 1.0 PhTMS, 0.25 DPhDMS, and 4, 8, 16 MeOH. The changing solvent ratio acts as dilution, delays cross-linking, facilitates condensation, prevents cracking, adjusts glass transition temperature and helps control the thickness of coating in dipping or pouring.

In the first step of the experiment, when acidified water (H_2O+HCl) was added to PhTMS the solution became inhomogeneous. The phase separation happens due to immiscibility between PhTMS and H_2O. During the stirring process at 40°C, the solution becomes clear (transparent) which means the hydrolysis and polycondensation reactions have occurred. When the methoxy groups reacted with water to produce hydroxyls, methanol was released. The solution cleared in 30 minutes [45].

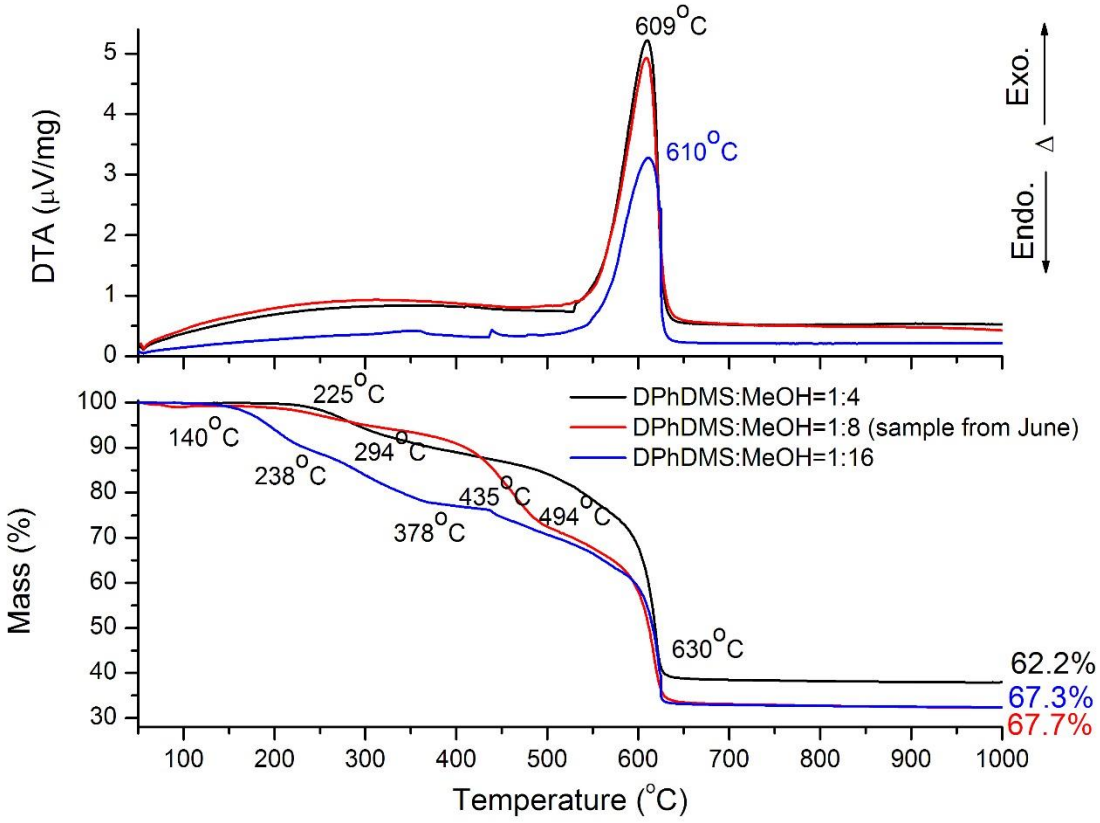
In the second step of the experiment, DPhDMS is diluted in MeOH. The MeOH was added to DPhDMS. After 8 hours of mixing a gel was formed. Then samples were given heat treatments. The main purpose of the heat treatment is to eliminate alcohol and water. At 70°C the alcohol was eliminated and at 110°C and water was removed from the surface of the samples. The melting gel became rigid at room temperature and re-softened

at 110°C. The re-softening could be repeated many times. The consolidation temperature was determined at 150°C by increasing and decreasing the temperature until the gel become glassy and no longer re-softened [45].

5.3 Characterizations Techniques

5.3.1 Thermal Analysis

Figures 4 gives the DTA and TGA curves for the samples of 1.0 mole PhTMS and 0.25 mole DPhDMS with different molar ratio of the MeOH.



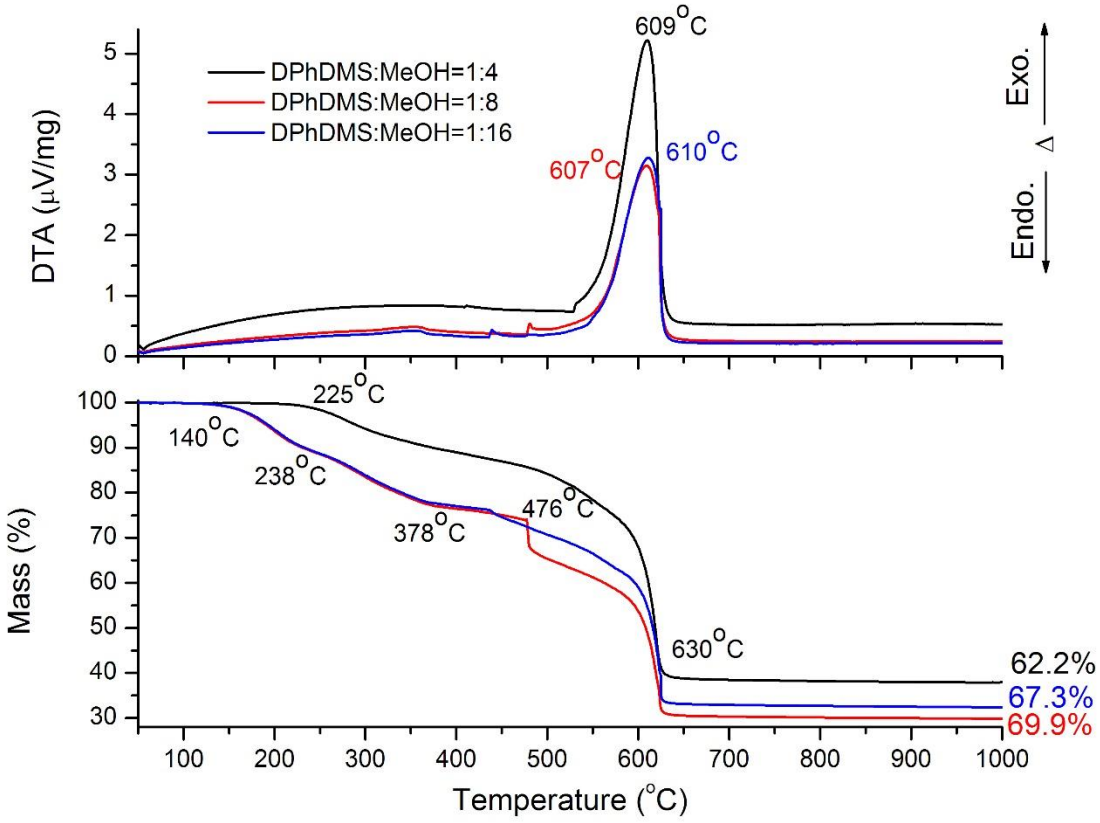


Figure 4 DTA and TGA curves of the samples contain PhTMS:DPhDMS = 1.0:0.25 and MeOH 4, 8, 16 mole.

The TGA experiments showed two weight loss regions. First region was between 140°C to 400°C, where the methanol group was changing in the region and was eliminated in the solution. Second region was between 550°C to 600°C, where the phenyl group was removed. The heating rate was 5°C/min. The DTA curve shows an exothermic peak at 360°C. The combustion of the organic group provides a high peak (exothermic peak), associated with burning of the phenyl groups. The exothermic peak occurs on all samples ~600°C.

DSC provided information about the location of the glass transition (T_g) of the melting gel. Glass transition behavior occurs in melting gel below the consolidation temperature. Figure 5 shows T_g for each sample. Table 2 presents the glass transition, weight loss and exothermic peak for each sample.

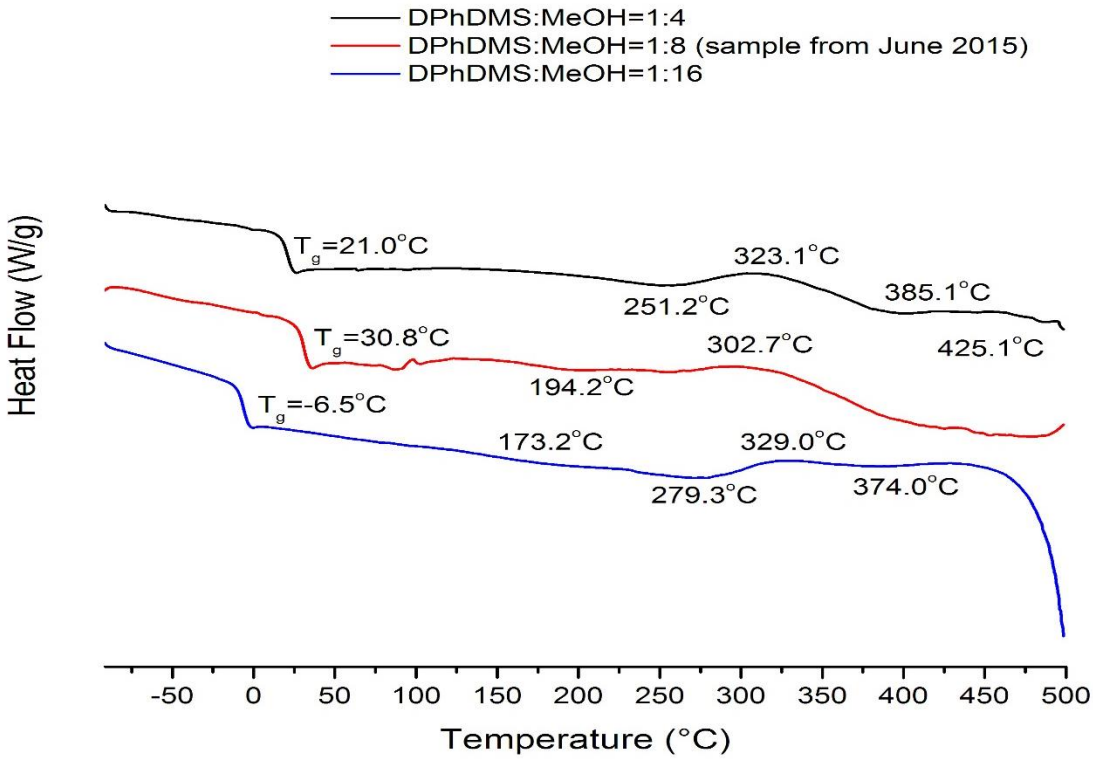


Figure 5 DSC results for each samples

Table 2. The data of the thermal analysis.

Chemical composition by moles			**Glass Transition (Tg)**	**Total loss**	**Exothermic Peak**
PhTMS	**DPhDMS**	**MeOH**	**(°C)**	**(%)**	**(°C)**
1	0.25	4	21.00	64	609
1	0.25	8	30.08	60.5	609.2
1	0.25	16	- 6.50	60	610

The glass transition increases from molar ratio 4 to 8 for MeOH but molar ratio 16 presents a lower glass transition for both of the systems. The weight losses were decreased with increasing amount of solvent. The exothermic peak was increased with increasing amount of solvent.

Table 3 presents the weight loss after the process of heat treatment at 150°C on the coating material (hybrid glass).

Chemical composition			**Weight of the hybrid glass at**		
mole			**150°C for 24 hrs**	**150°C for 48 hrs**	**150°C for 96 hrs**
PhTMS	**DPhDMS**	**MeOH**	**(g)**	**(g)**	**(g)**
1	0.25	4	0.923	0.891	0.882
1	0.25	8	0.86	0.842	0.835
1	0.25	16	0.739	0.727	0.724

Table 4 presents the weight loss after the process of heat treatment at 200°C on the coating material (hybrid glass).

Chemical composition			**Weight of the hybrid glass at**	
mole			**150°C for 24 hrs**	**200°C for 24 hrs**
PhTMS	**DPhDMS**	**MeOH**	**(g)**	**(g)**
1	0.25	4	0.575	0.535
1	0.25	8	1.078	1.032
1	0.25	16	0.526	0.488

From Table 3 and 4 the hybrid glass materials was seen to lose weight during the process of the heat treatment with increasing time of the treatment.

5.3.1.1 Coatings Thickness

Coatings poured onto the titanium alloy substrates were continuous and smooth. The thickness of the coating was between 0.9-1.16 mm. Tables 5 and 6 present the behavior of the coating thickness with changing treatment time.

Table 5 presents the value of the thickness after the process of heat treatment at 150°C

Chemical composition			**Thickness of the hybrid glass at**					
mole			**150°C for 24 hrs**		**150°C for 48 hrs**		**150°C for 96 hrs**	
PhTMS	**DPhDMS**	**MeOH**	**(mm)**	**Crack**	**(mm)**	**Crack**	**(mm)**	**Crack**
1	0.25	4	0.95	No	0.92	No	0.92	Yes
1	0.25	8	1.16	No	0.90	Yes	0.90	Yes
1	0.25	16	0.97	No	0.82	No	0.82	Yes

Table 6 presents the value of the thickness after the process of heat treatment at 200°C

Chemical composition			**Thickness of the hybrid glass at**			
mole			**150°C for 24 hrs**		**200°C for 24 hrs**	
PhTMS	**DPhDMS**	**MeOH**	**(mm)**	**Crack**	**(mm)**	**Crack**
1	0.25	4	0.95	No	0.3	Yes
1	0.25	8	1.3	No	0.2	Yes
1	0.25	16	1.05	No	0.2	Yes

In Table 5, after the samples was treated for 48 hours the thickness of the coating did not decrease any more with increasing the time of the treatment. In general, tables 5 and 6, show that the thickness increases with increasing amount of the solvent but synthesis PhTMS:MeOH 1:8 showed highest thickness compared to other synthesis. The crack problem was solved by using heat treatment for 1 day at 150°C and followed by 6

days at 110°C and 4 hour furnace-cooled to room temperature. A typical sample is shown in Figure 8 (a).

5.3.2 Mechanical Testing Analysis

Hardness defines how difficult or easy a material can be penetrated or scratched. There are several ways to measure hardness, for example, Scratch resistance test, Vickers hardness test, Rockwell hardness test, Brinell hardness test and Nano-microhardness indentation test. Nano-indentation testing was used in the experiment because the hybrid glass material is a soft material. The hybrid glass was cracked under the Vickers tip in high load condition. Figure 6 showed how the hybrid glass was cracked under high load.

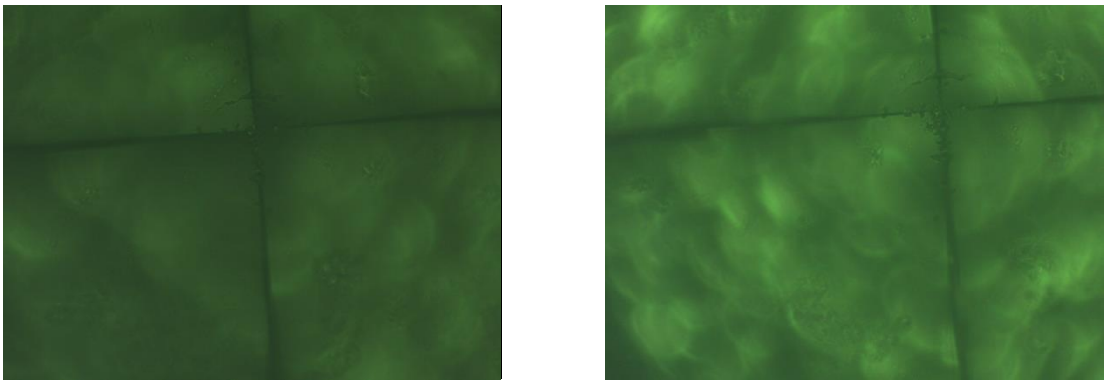


Figure 6 Hybrid glass tested under 2 Kg load by Vickers tip

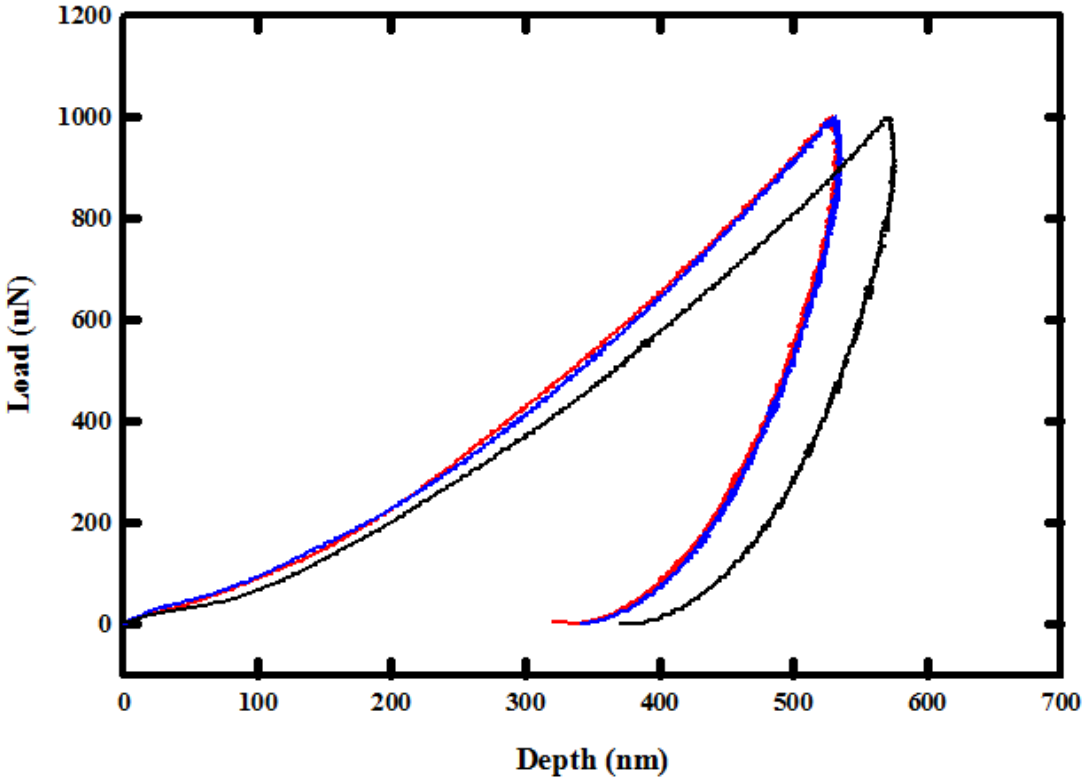
In Figure 6 the ellipse mark was bigger than the image under the microscope. In this case, the hardness cannot be measured by Vickers hardness test.

Nano-indentation testing was used to measure the hardness for each samples. Each sample had different thermal treatment. Table 7 presents the value of the hardness under different loading condition.

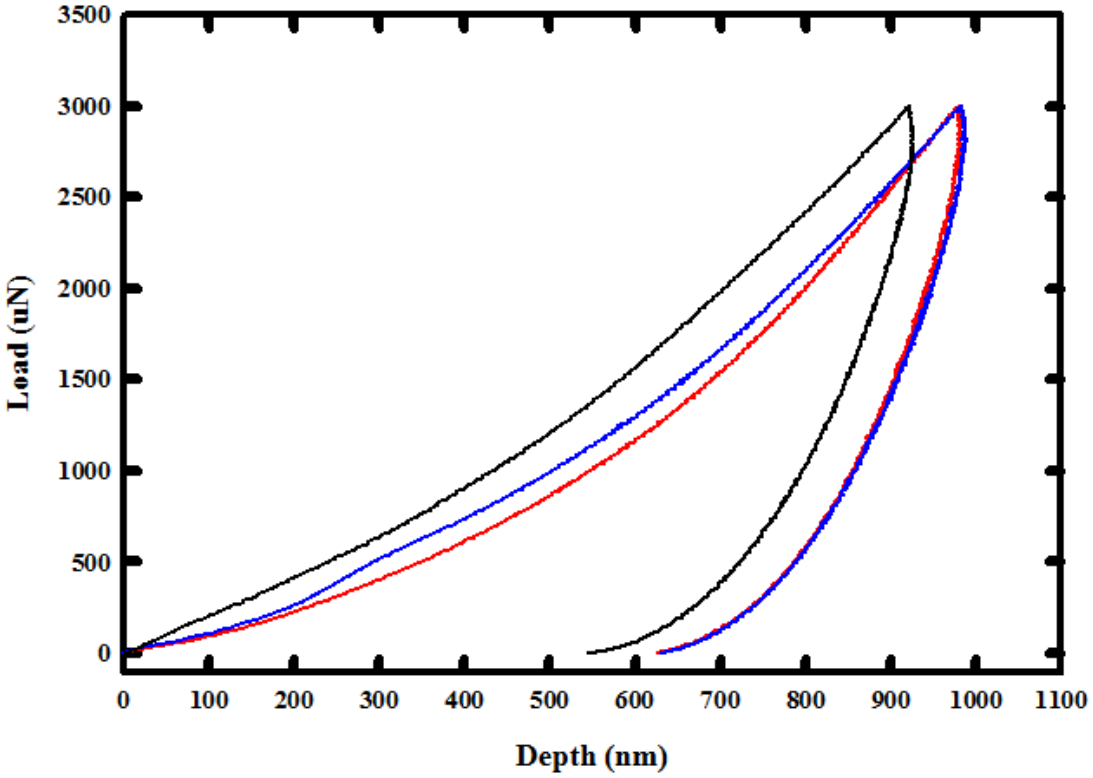
Table 7 presents the value of the hardness under loading 1, 3 mN

Molar Ratio %			Heat Treatment	Time	Hardness 1mN	Hardness 3mN	Crack
PhTMS	DPhTMS	MeOH	Temp. [C°]	[hrs.]	H [MPa]	H [MPa]	Yes OR No
1	0.25	4	150	48	169 ± 1.2	170 ± 0.9	No
1	0.25	8	150	48	211 ± 5.8	220 ± 3.0	Yes
1	0.25	16	150	48	113 ± 0.8	121 ± 0.8	No
1	0.25	4	150	96	255 ± 59.0	192 ± 5.3	No
1	0.25	8	150	96	207 ± 3.6	211 ± 1.8	Yes
1	0.25	16	150	96	164 ± 0.2	169 ± 4.6	No
1	0.25	4	200	24	165 ± 4.3	150 ± 17.7	Yes
1	0.25	8	200	24	214 ± 8.8	221 ± 5.4	Yes
1	0.25	16	200	24	144 ± 2.8	-	Yes

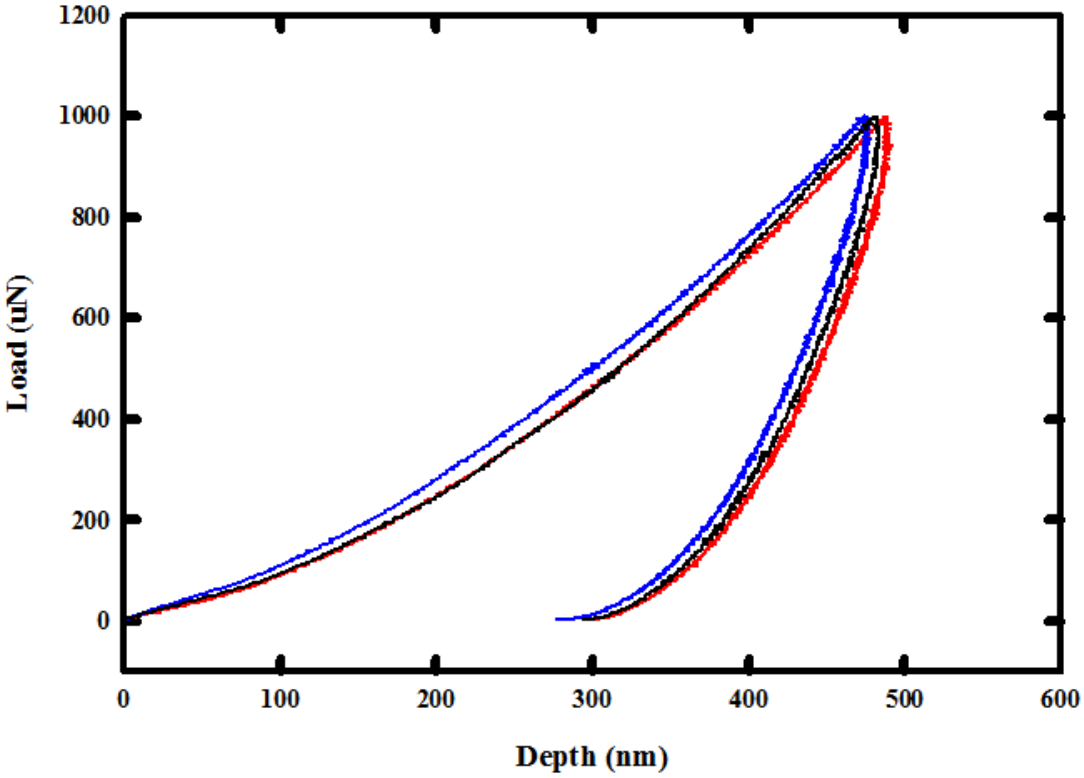
From the Table 5 synthesis, PhTMS:MeOH 1:8 showed the highest hardness in both loading conditions and treatment conditions. For the three systems, the optimum hardness was present in synthesis 1:8 PhTMS:MeOH. The higher hardness in samples 1:8 PhTMS:MeOH reflect that the crosslinking and chemical reactivity were more than in the other synthesis. For the samples PhTMS:DPhTMS:MeOH 1:0.25:4, 8, 16 which underwent treatment for 24 hours at 150°C, the hardness could not be measured because the samples were sticky. Figure 7 provides the loading and unloading curve for some sample under different loading condition 1mN and 3mN.



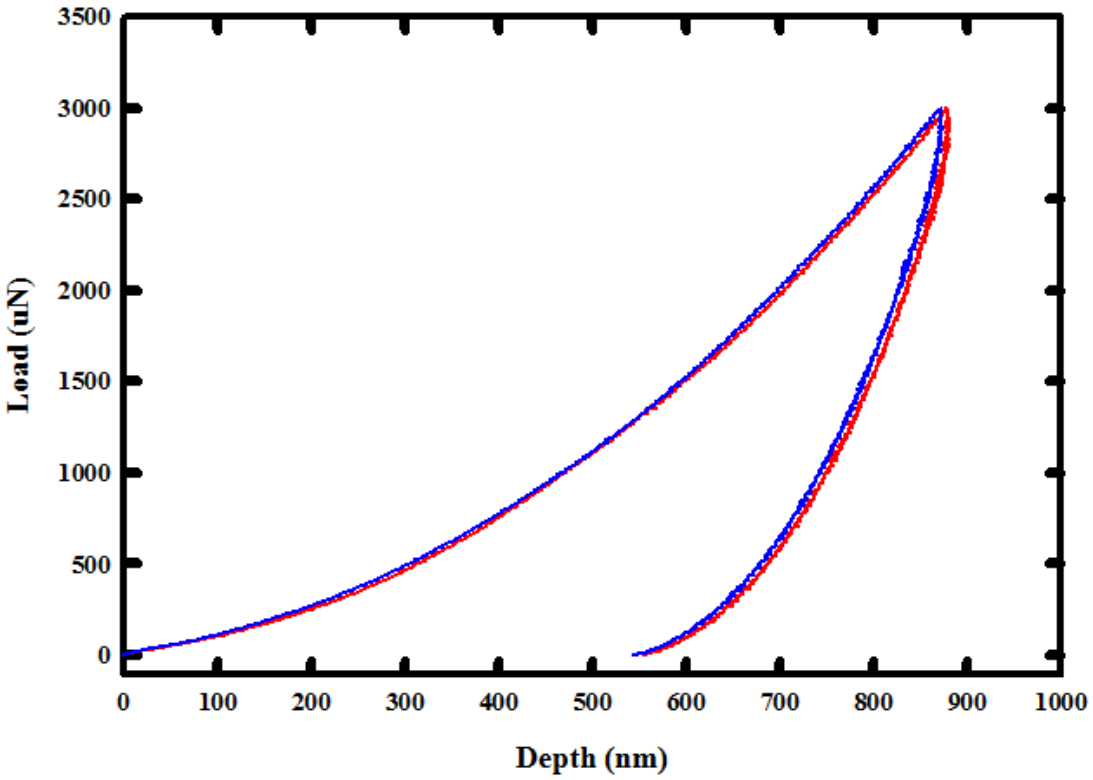
Sample: 1 to 4 at 150°C for 48hr with 1mN



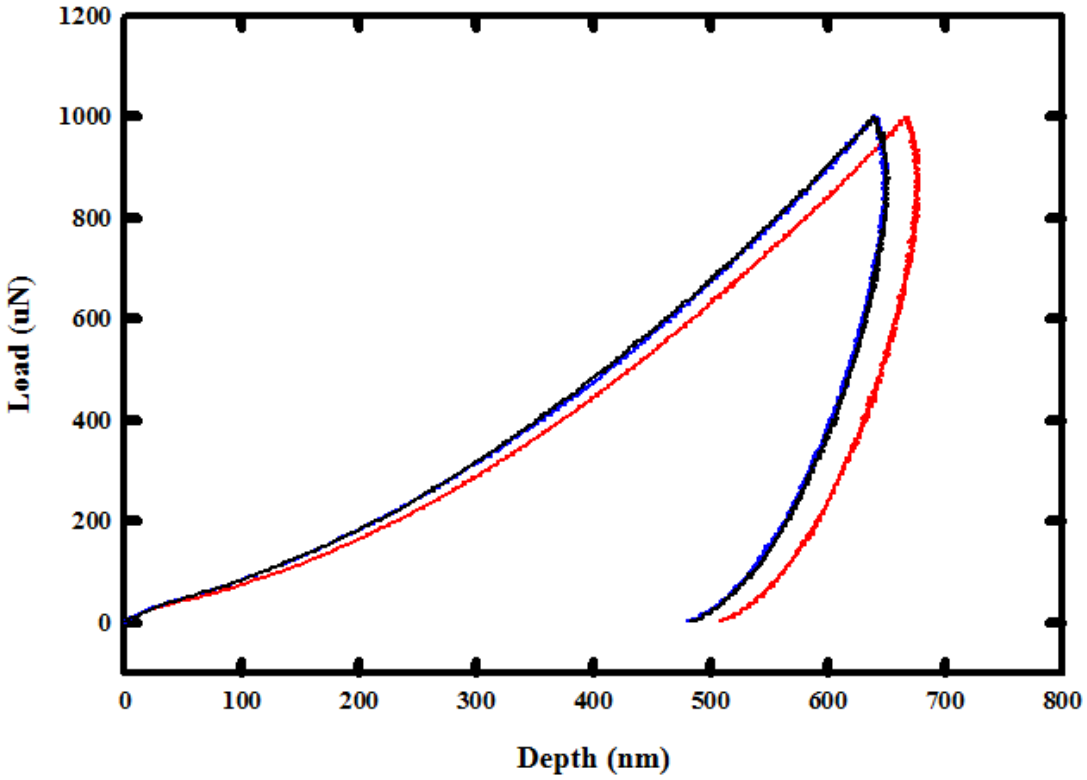
Sample: 1 to 4 at 150°C for 48hr with 3mN



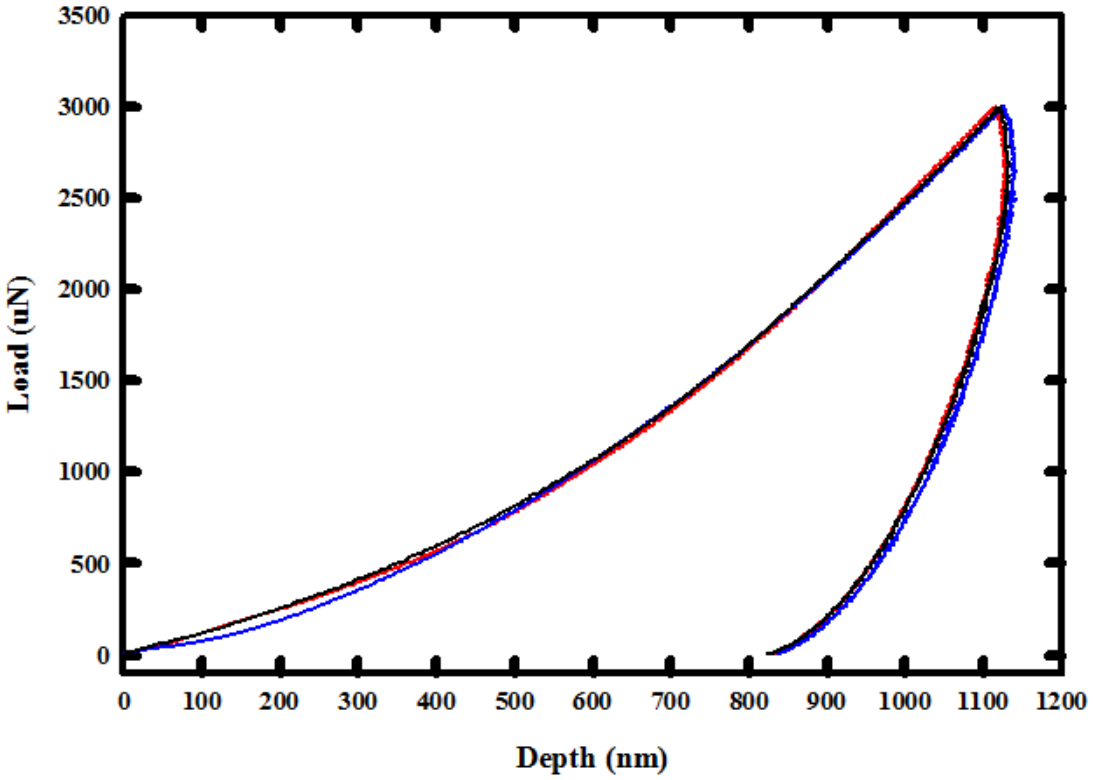
Sample: 1 to 8 at 150°C for 48hr with 1mN



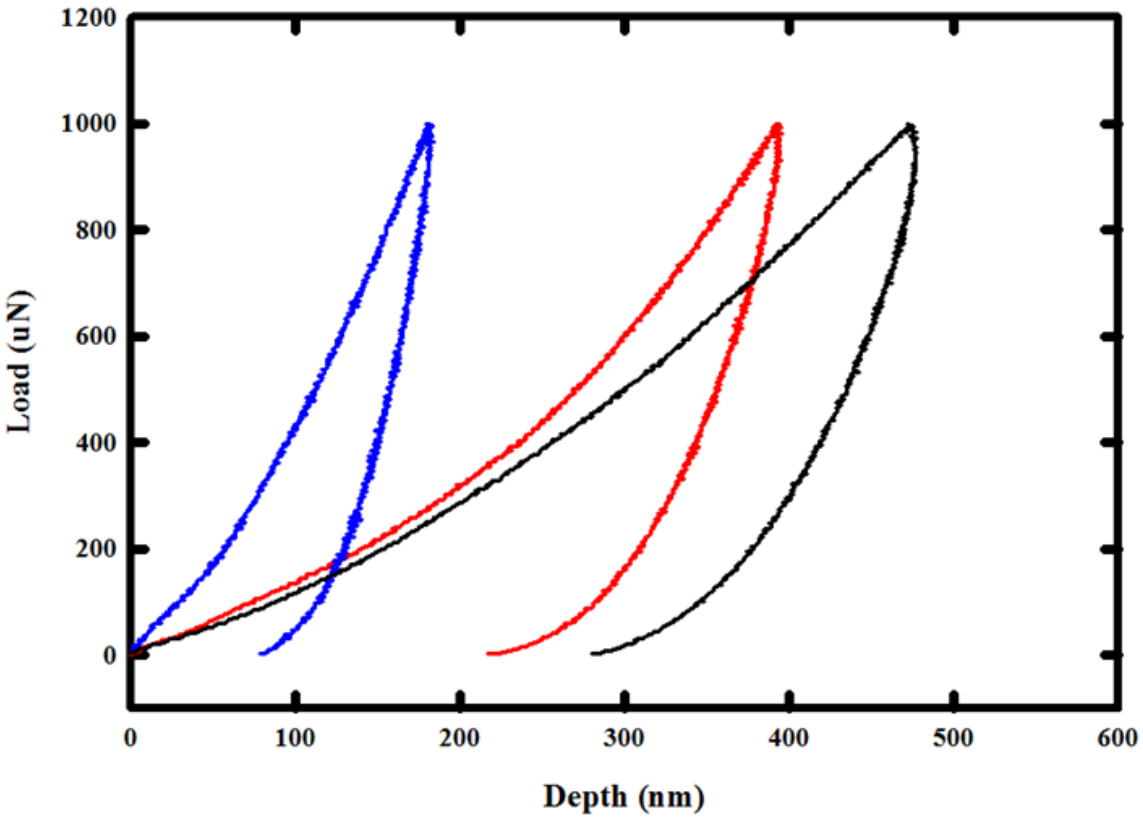
Sample: 1 to 8 at 150°C for 48hr with 3mN



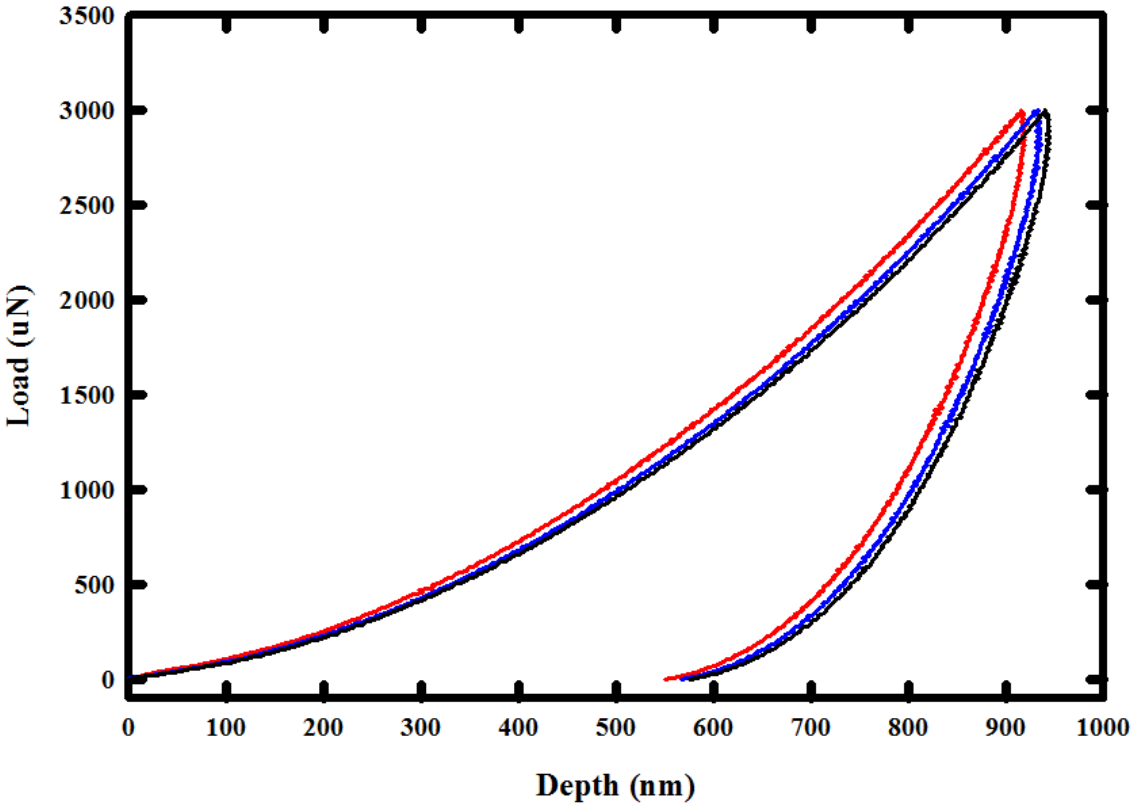
Sample: 1 to 16 at 150°C for 48hr with 1mN



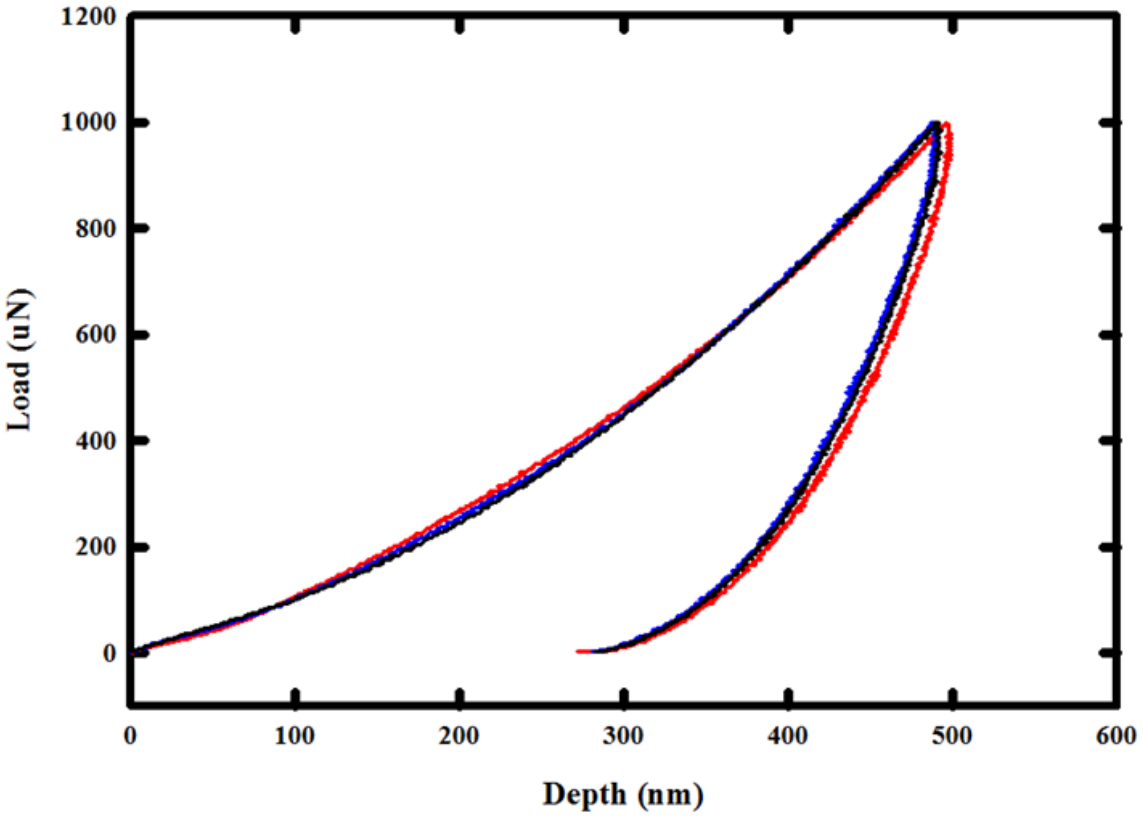
Sample: 1 to 16 at 150°C for 48hr with 3mN



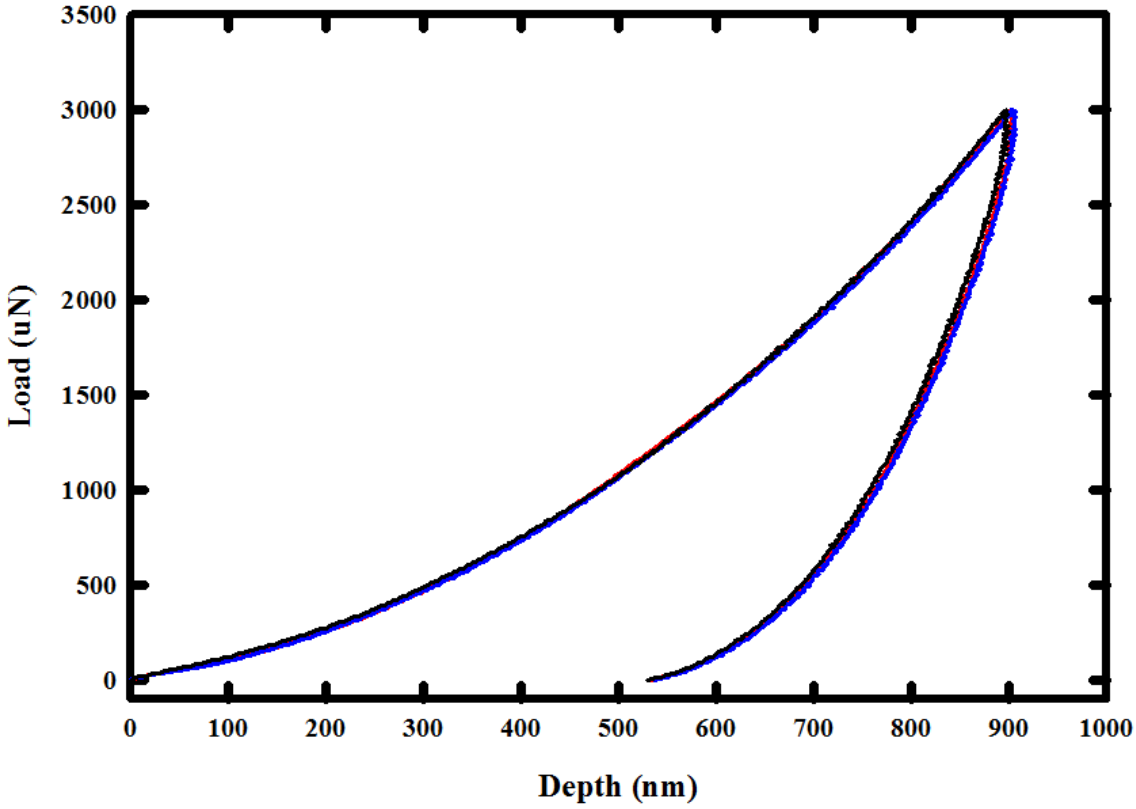
Sample: 1 to 4 at 150°C for 96hr with 1mN



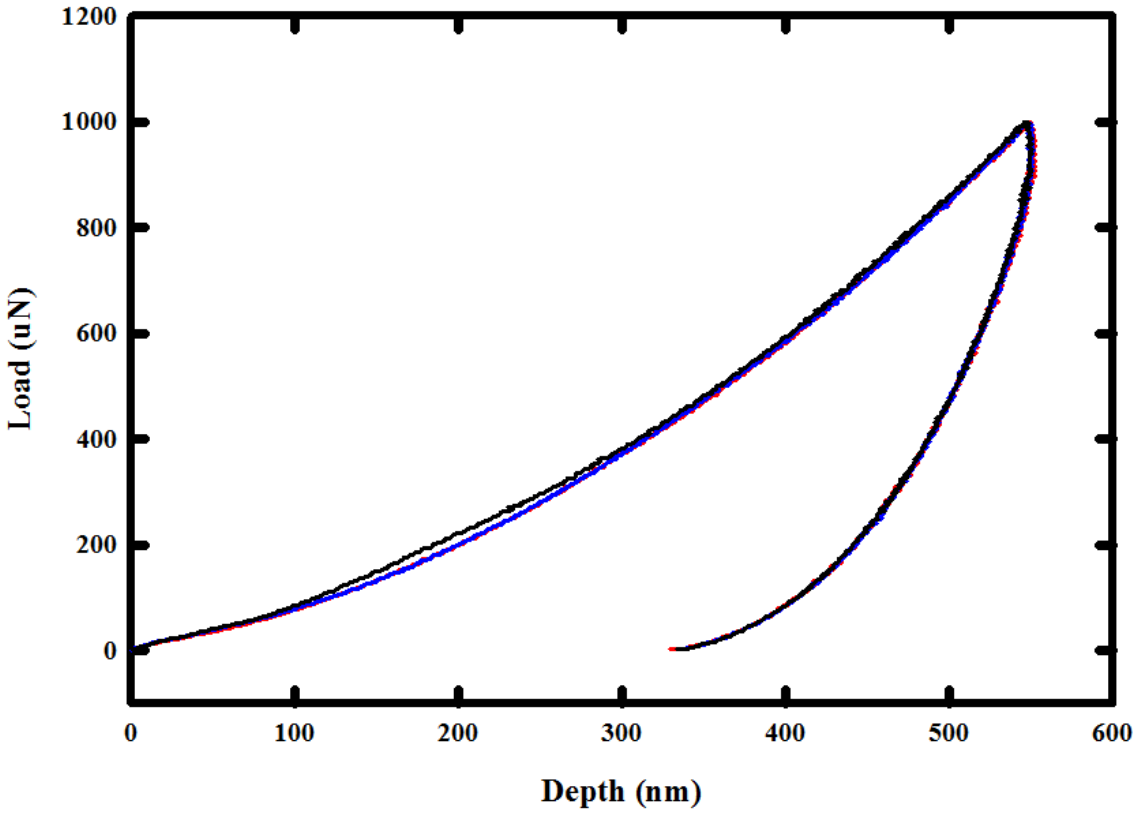
Sample: 1 to 4 at 150°C for 96hr with 3mN



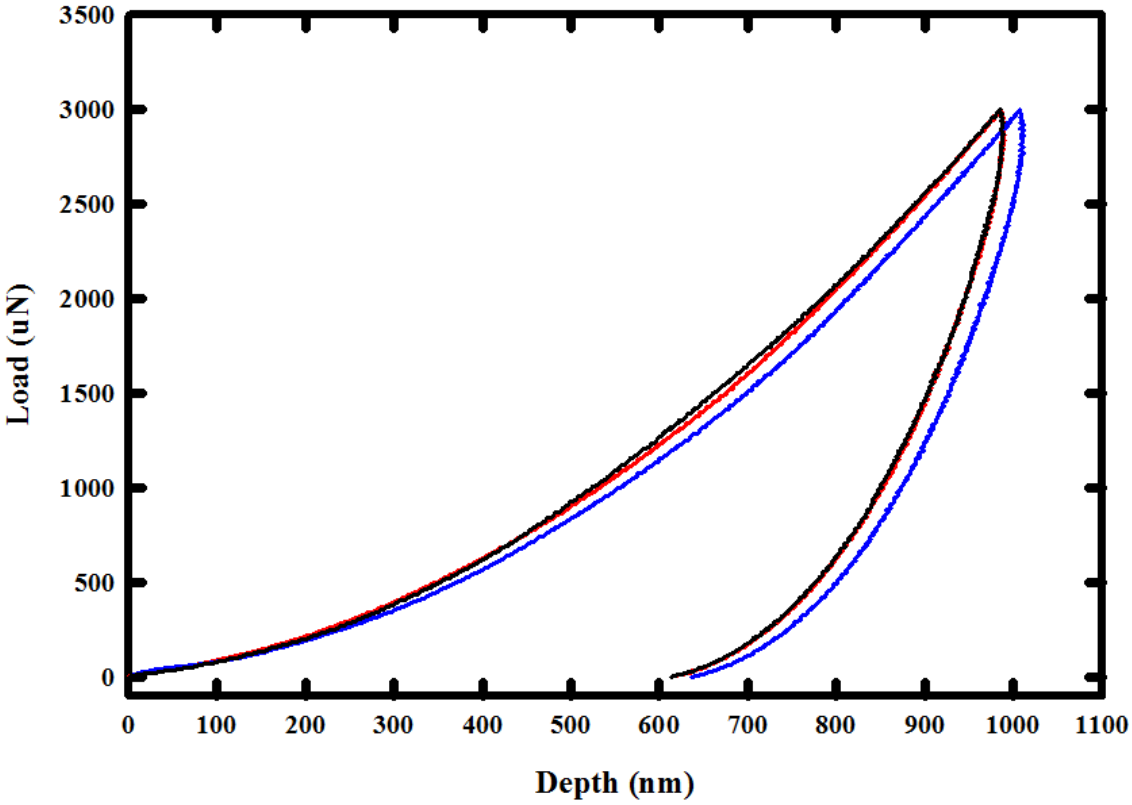
Sample: 1 to 8 at 150°C for 96hr with 1mN



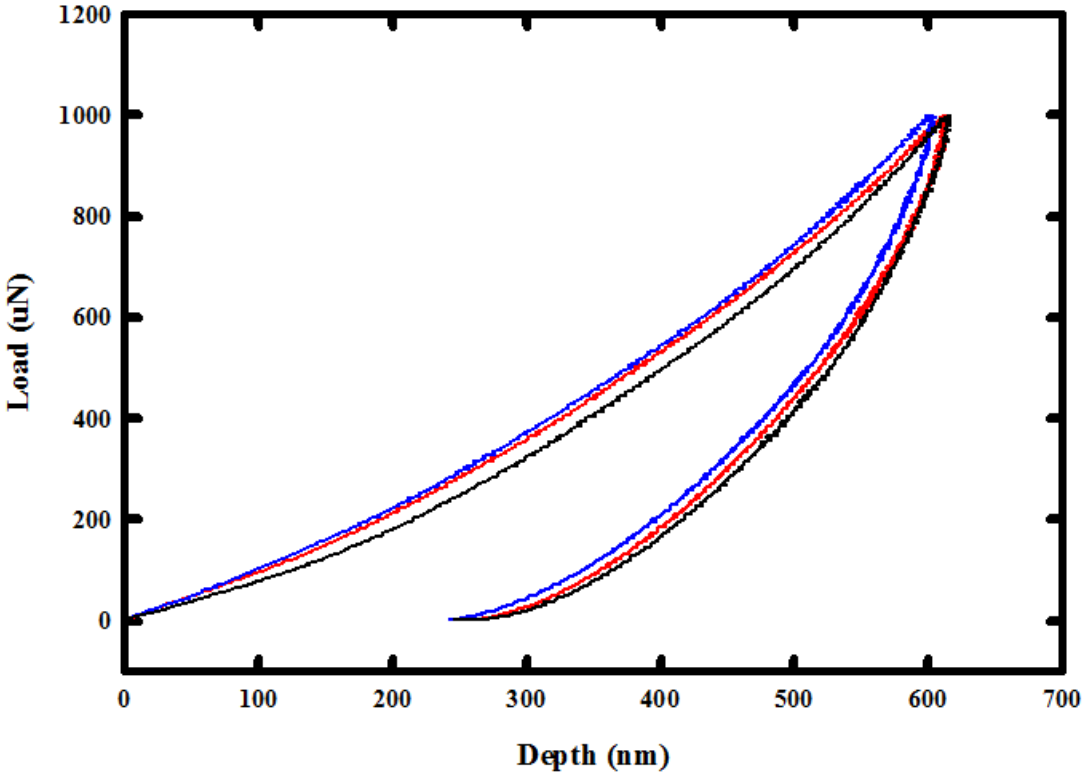
Sample: 1 to 8 at 150°C for 96hr with 3mN



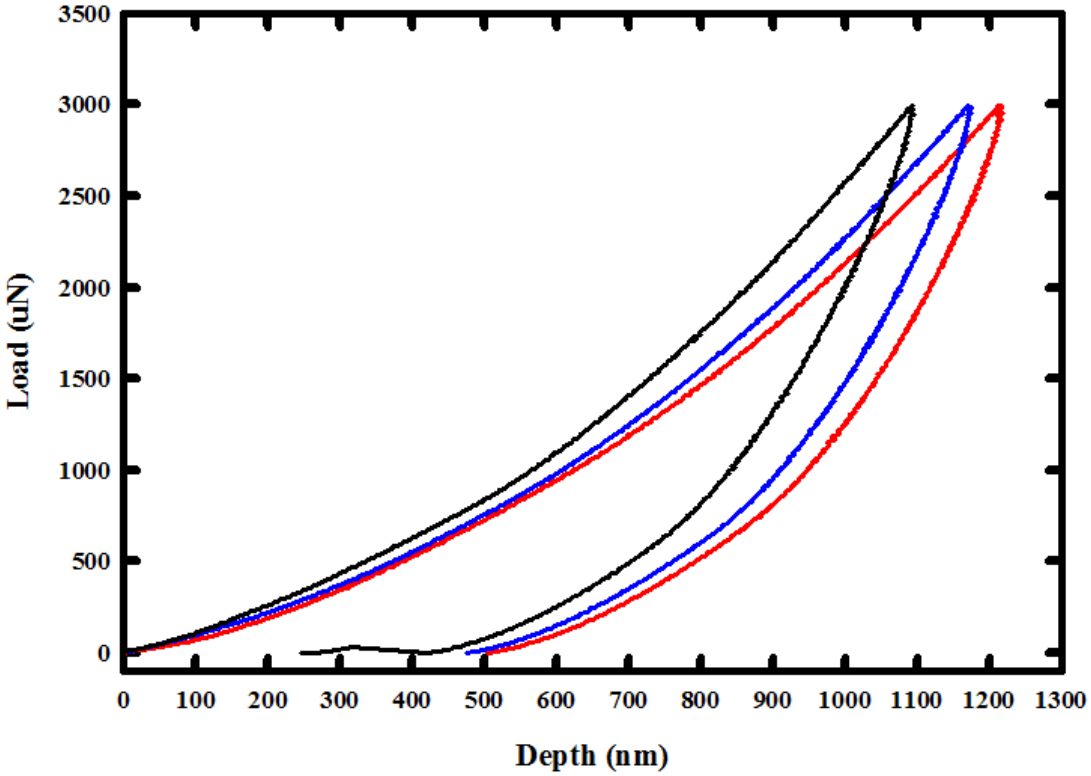
Sample: 1 to 16 at 150°C for 96hr with 1mN



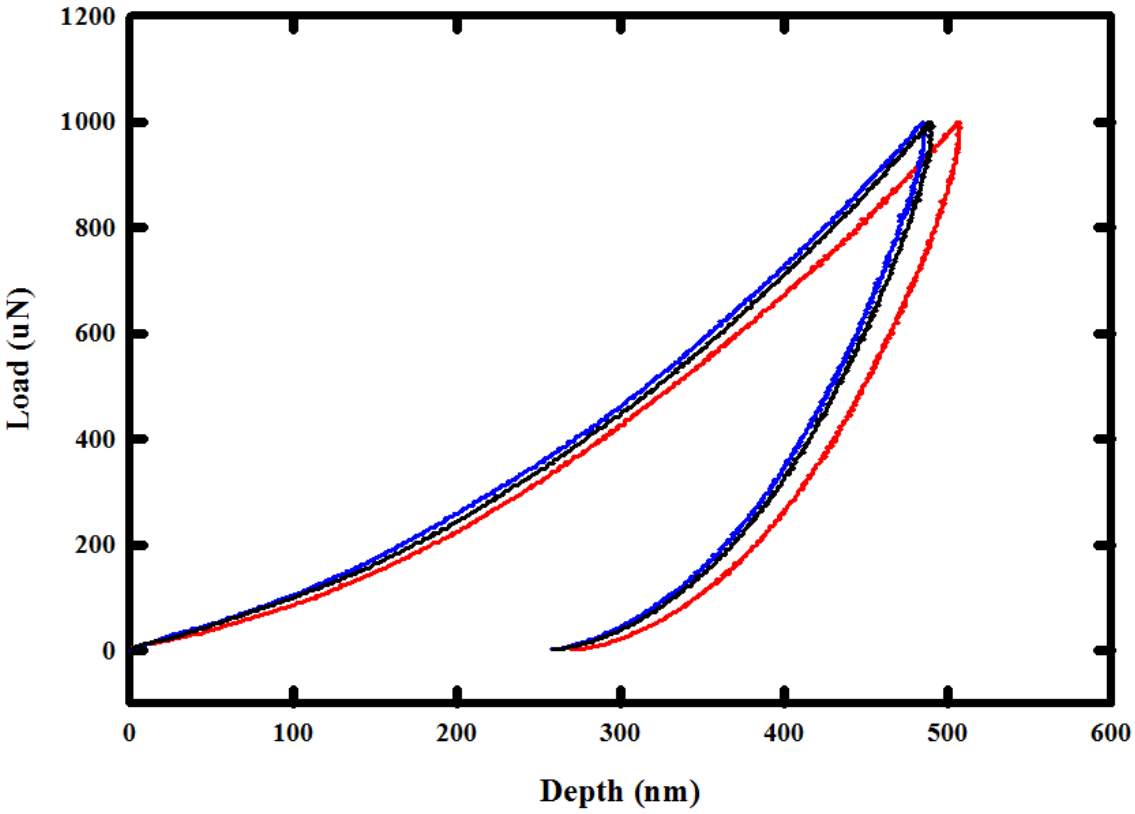
Sample: 1 to 16 at 150°C for 96hr with 3mN



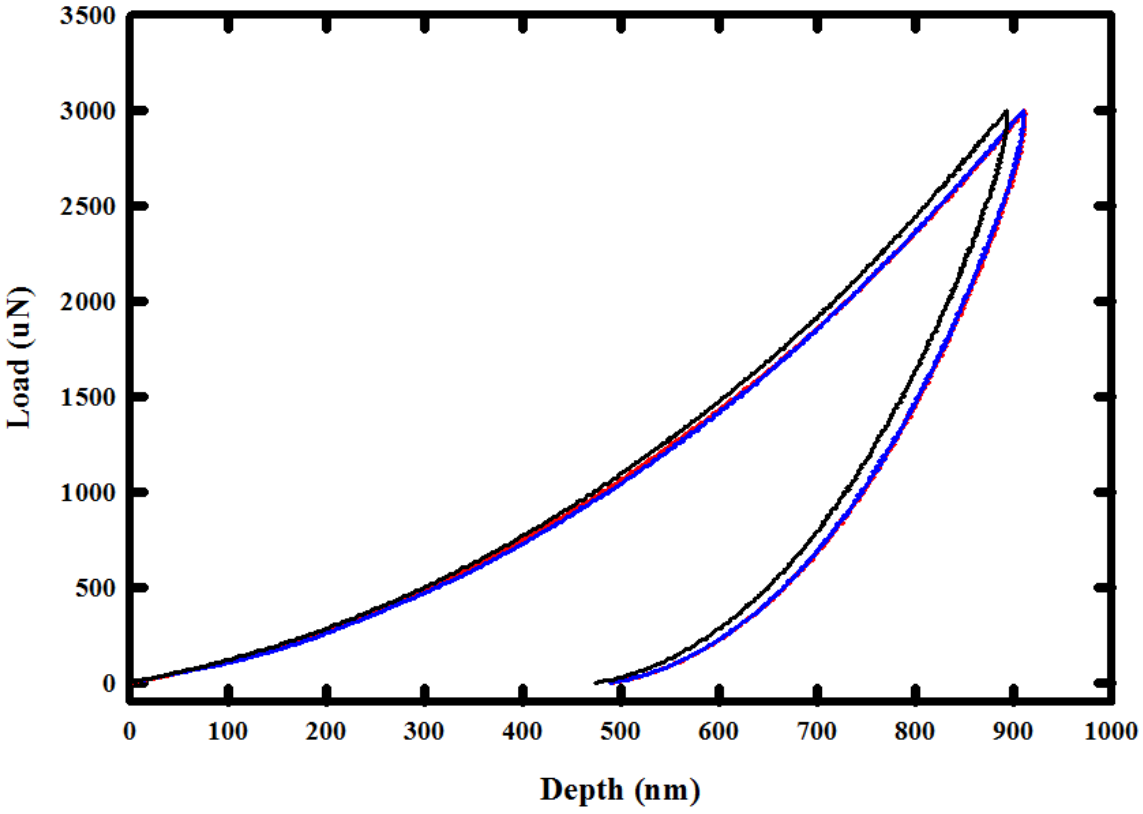
Sample: 1 to 4 at 200°C for 24hr with 1mN



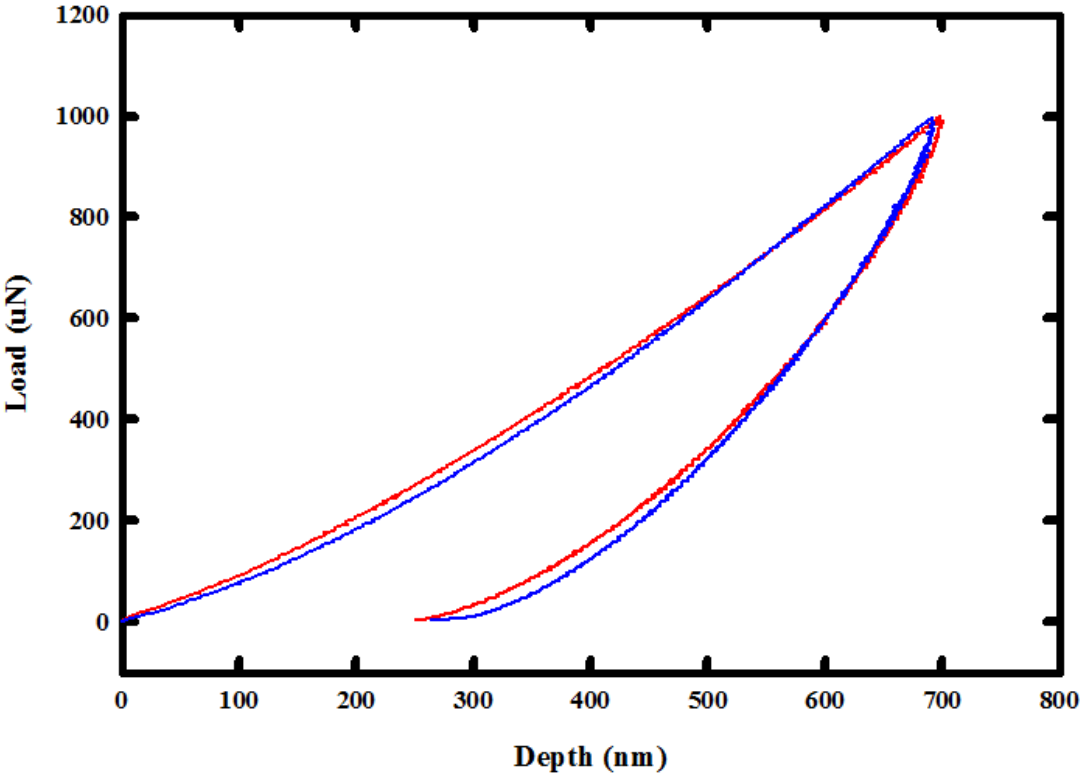
Sample: 1 to 4 at 200°C for 24hr with 3mN



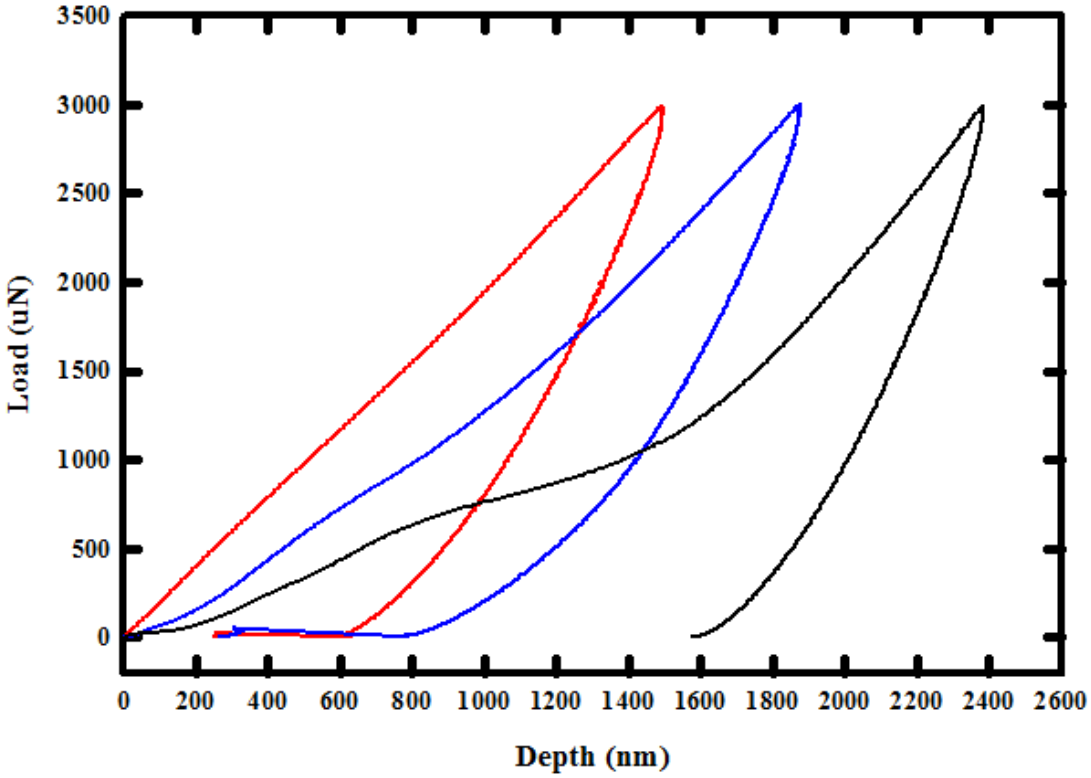
Sample: 1 to 8 at 200°C for 24hr with 1mN



Sample: 1 to 8 at 200°C for 24hr with 3mN



Sample: 1 to 16 at 200°C for 24hr with 1mN



Sample: 1 to 16 at 200°C for 24hr with 3mN

Figure 7 Loading and unloading curves for different synthesis and treatment of the hybrid glass

Doubling the time from 48 hrs. to 96 hrs. at 150ºC increased the hardness somewhat. Doubling the methanol made the gel more fluid for pouring, but harder when consolidated. The samples with 8 moles of methanol were found to be cracked. Increasing methanol to 16 moles introduced surface "stickiness", but these samples were less likely to crack than at 8 moles.

The best crack-free coatings were formed using a treatment of 1 day at 150º, followed by treatment for 6 days at 110ºC and a 4 hour furnace-cooled to room temperature. To see the benefit of the coating, compare the samples side by side in

Figure 8. The coated side of the sample (a) is still shiny, while the uncoated side of the sample (b) is showing serious corrosion damage after 6 months.

Figure 8 Comparison of the coated side (a) and the uncoated side (b) and stored inside plastic container for 6 months

The average roughness was measured using AFM. Table 8 presents the value of the average roughness for samples PhTMS:MeOH 1:4, 8, 16 moles with scanning area 1μm² . The samples were treated for 1 day at 150ºC, followed by 6 days at 110ºC and a 4 hour furnace-cooling to room temperature. The surface of the coatings were seen to be crack free. A typical sample is shown in Figure 9.

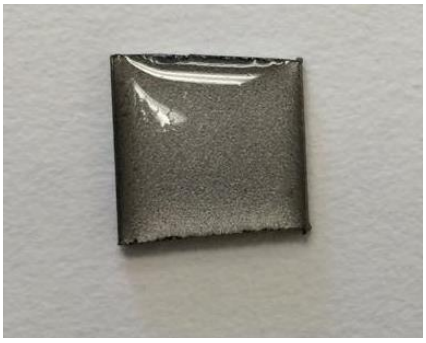


Figure 9 Sample PhTMS:MeOH 1:4 with heat treatment 1 day at 150º, followed by 6 days at 110^{o}C

Table 8 lists the values of the average roughness

Chemical composition			**Heat Treatment for 1 day at 150º, followed by 6 days at 110ºC**
mole			**average roughness (Ra) under scanning area 1 μm^2**
PhTMS	**DPhDMS**	**MeOH**	**(nm)**
1	0.25	4	0.89
1	0.25	8	0.453
1	0.25	16	3.41

From Table 8 sample 1:8 PhTMS:MeOH had lower roughness. The lower roughness indicates that sample 1:8 PhTMS:MeOH had higher crosslinking and more complete chemical reactions than other synthesis. All the samples presented on Table 8 were smooth. When the surface of the hybrid glass is smooth that means the surface of

the sample is nonporous. The smoothness gives advantage to the corrosion resistance. Figures 10, 11, 12 present the images of the AFM with different quantity of MeOH.

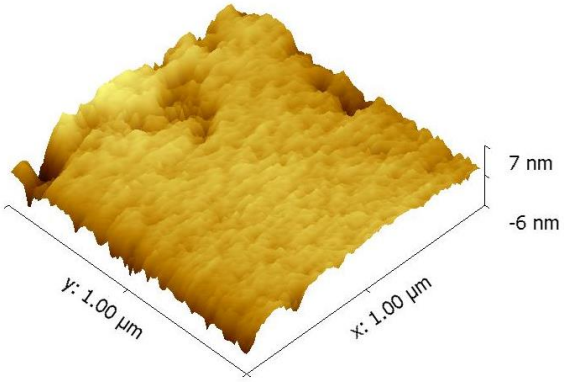


Figure 10 The AFM image for synthesis 1:4 PhTMS:MeOH

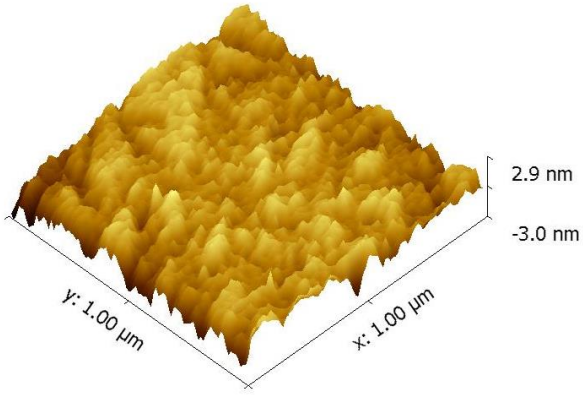


Figure 11 The AFM image for synthesis 1:8 PhTMS:MeOH

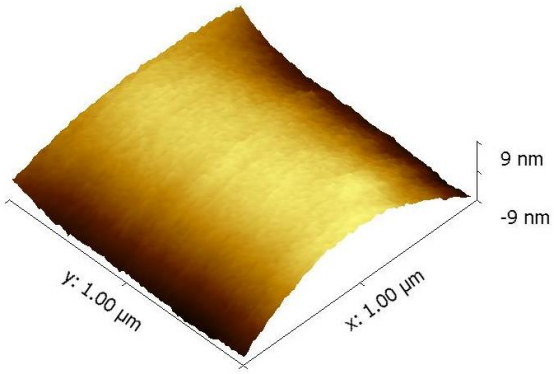


Figure 12 The AFM image for synthesis 1:16 PhTMS:MeOH

The scanning area for all the samples were 1 µm² with constant force 40 N/m and frequency ~325 KHz. The surface of all samples were crack-free.

5.3.3 Surface Analysis

Figure 13 shows the FT-IR spectra of the samples which contain PhTMS:DPhDMS:MeOH 1:0.25:4, 8, 16 moles and with heat treatment for 1 day at 150ºC, followed by 6 days at 110ºC and a 4 hour furnace cooling to room temperature. A typical sample of PhTMS:MeOH 1:4 is shown in Figure 9. All three samples gave spectra that were indistinguishable.

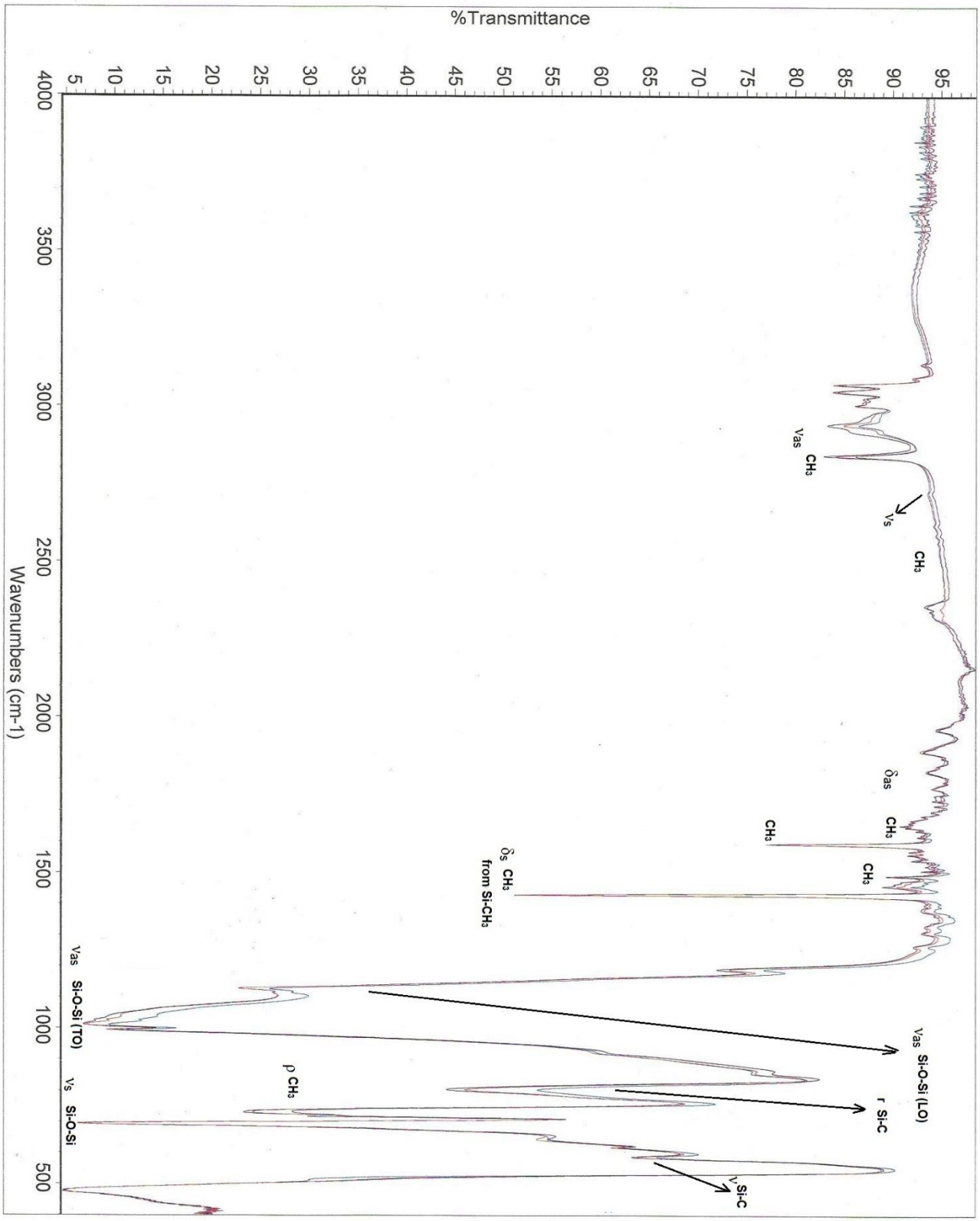
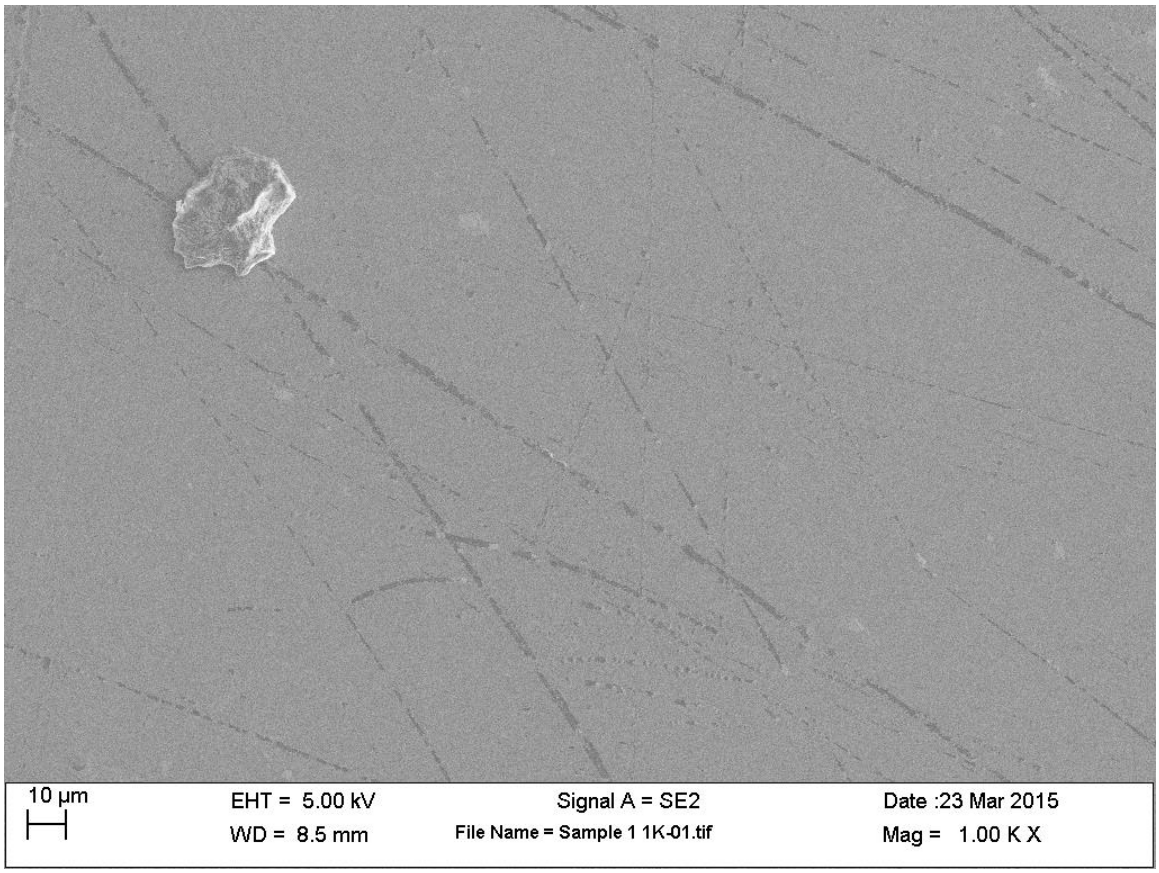


Figure 13 FT-IR spectrum of the samples with mole ratio 1.0 PhTMS-0.25 DPhDMS

For the 700 cm^{-1} peak the characteristic vibration of Si-O-Si bonds is labeled as ν_s Si-O-Si, the 600 cm^{-1} vibration is labeled as ν Si-O (H), the 1150 cm^{-1} vibration is labeled as ν_{as} Si-O-Si (TO) and the 1100 cm^{-1} vibration is labeled as ν_{as} Si-O-Si (LO) [73]. The FT-IR spectrum provide the characteristic absorbance of the methyl group, the 722 cm^{-1} vibration is labeled as ρ CH_3, the 1400 cm^{-1} vibration is labeled as δ_s CH_3 (from Si- CH_3), the 1510 cm^{-1} vibration is labeled as δ_{as} CH_3, the 2820 cm^{-1} vibration is labeled as ν_s CH_3, and the 2860 cm^{-1} vibration is labeled as ν_{as} CH_3 [73]. The sign of Si-C bonds at vibration peaks 600 cm^{-1} vibration is labeled as ν Si-C and the 700 cm^{-1} vibration is labeled as r Si-C. The results of the FT-IR shows the formation of Si-O-Si bonds and stable Si-C bonds following hydrolysis, polycondensation reactions and gelation.

The surface morphology of the hybrid glass coatings materials was examined in the Scanning electron microscope. All samples were crack-free with heat treatment for 1 day at 150ºC, followed by 6 days at 110ºC and a 4 hour furnace cooled to room temperature. In addition, all samples were coated with gold layer. Figure 14, 15, 16 showed that the hybrid glass coating materials had smooth and uniform surfaces.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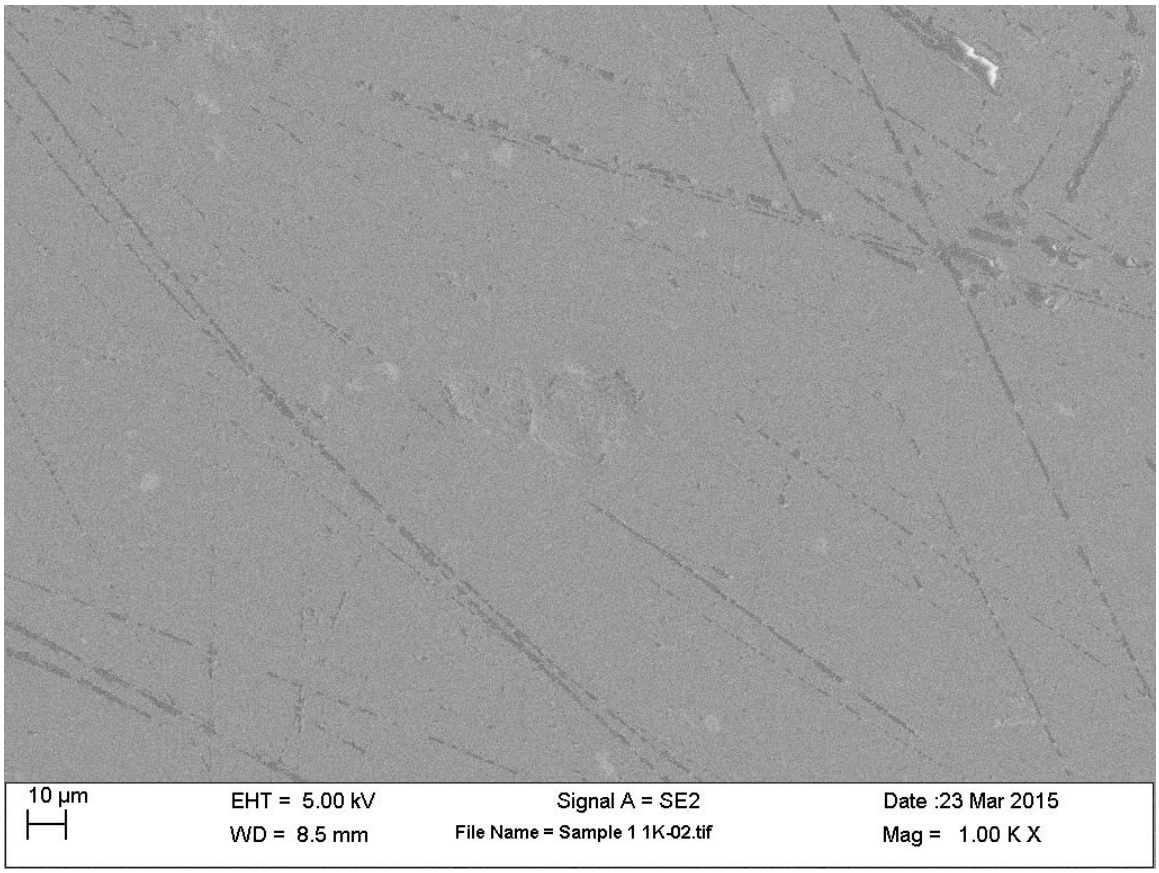
Date :23 Mar 2015
Mag = 1.00 K X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Date :23 Mar 2015
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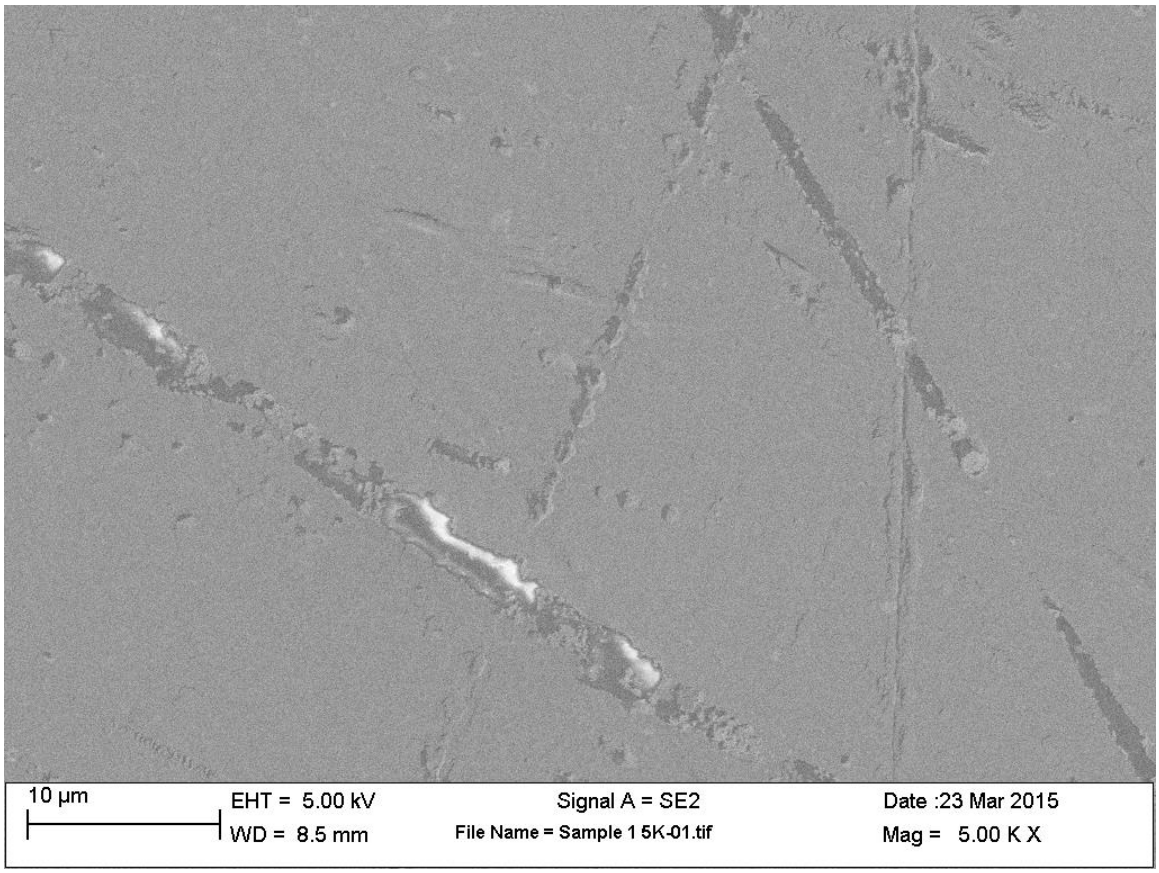
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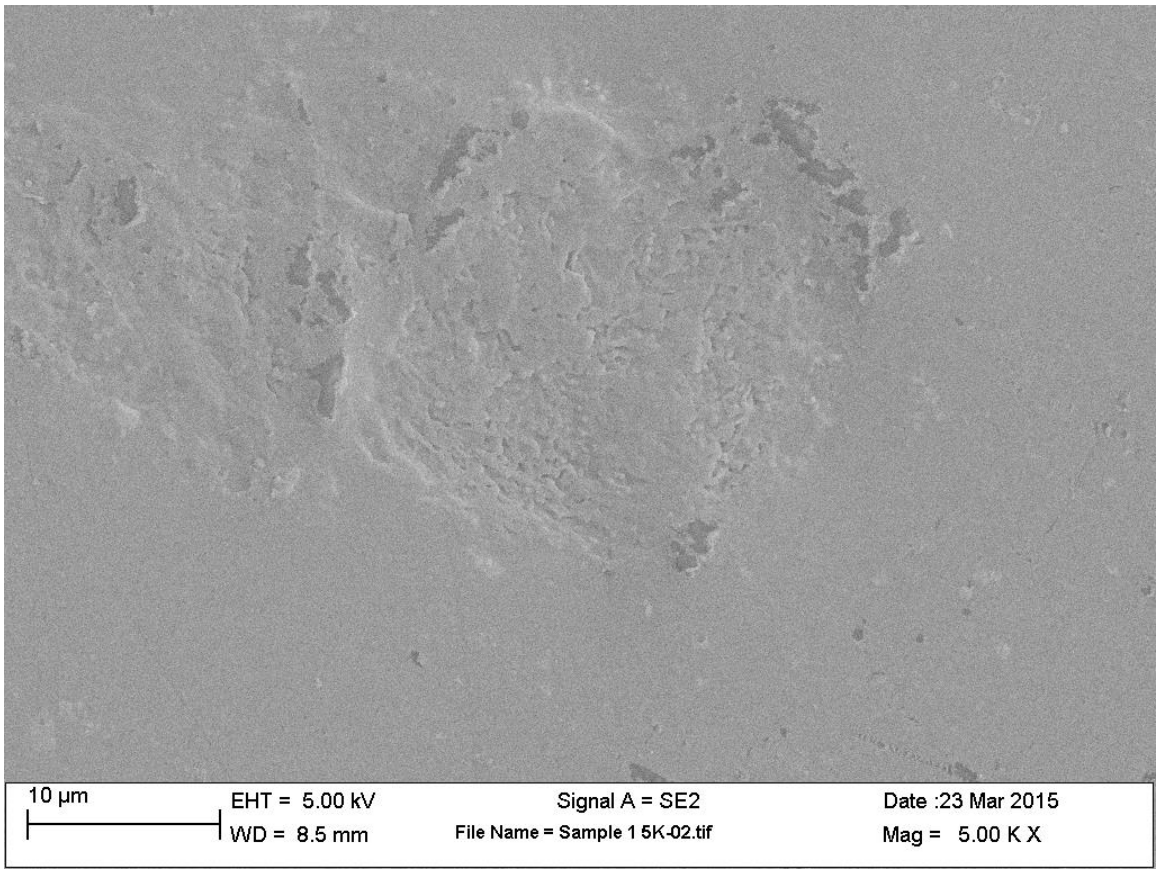
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WD = 8.5 mm
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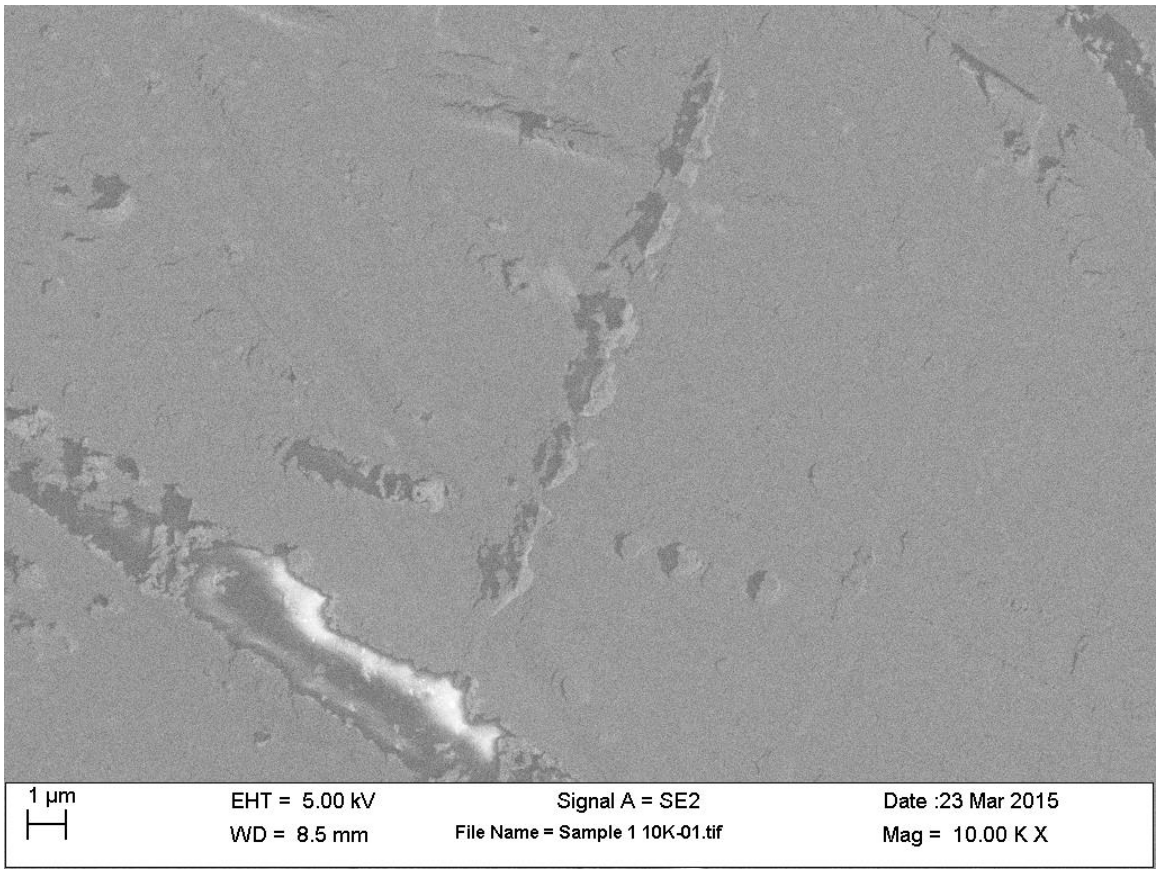
Mag = 5.00 K X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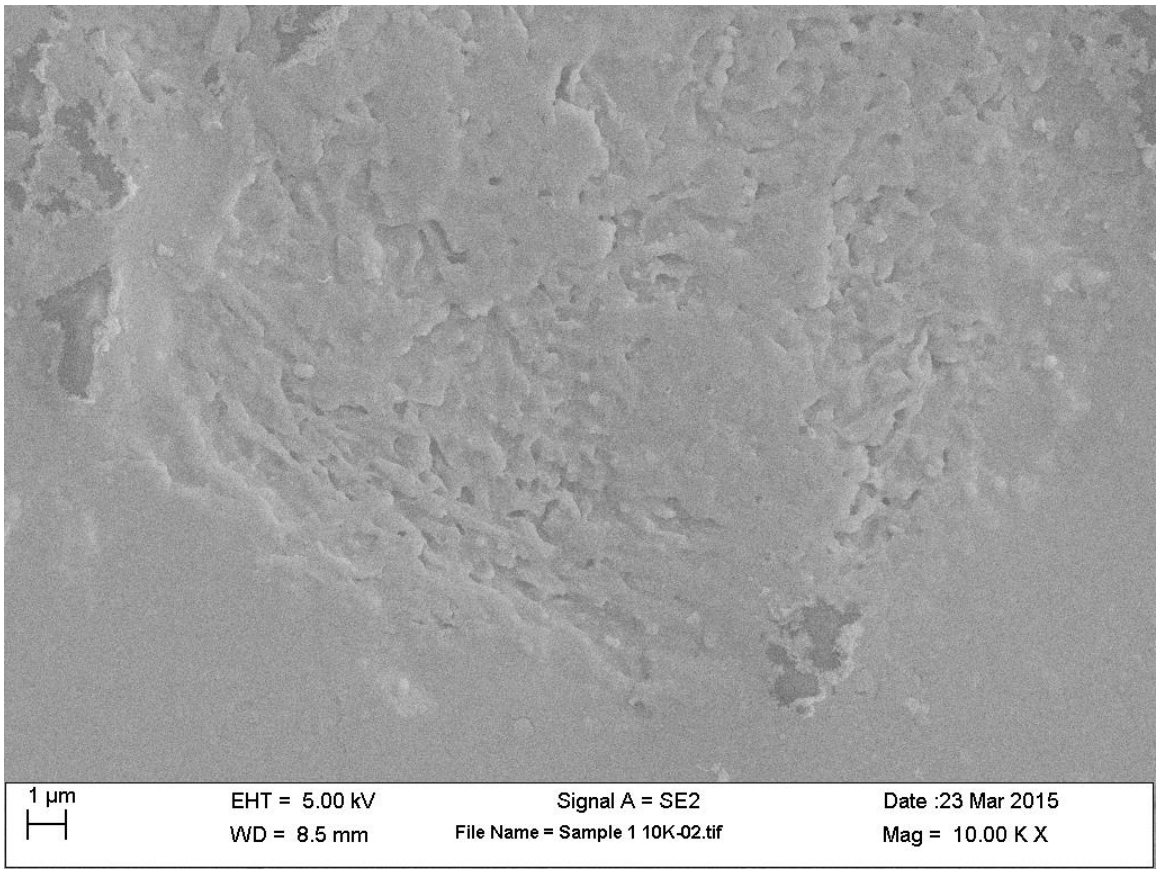
File Name = Sample 1 10K-01.tif
Date :23 Mar 2015
Mag = 10.00 K X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WD = 8.5 mm
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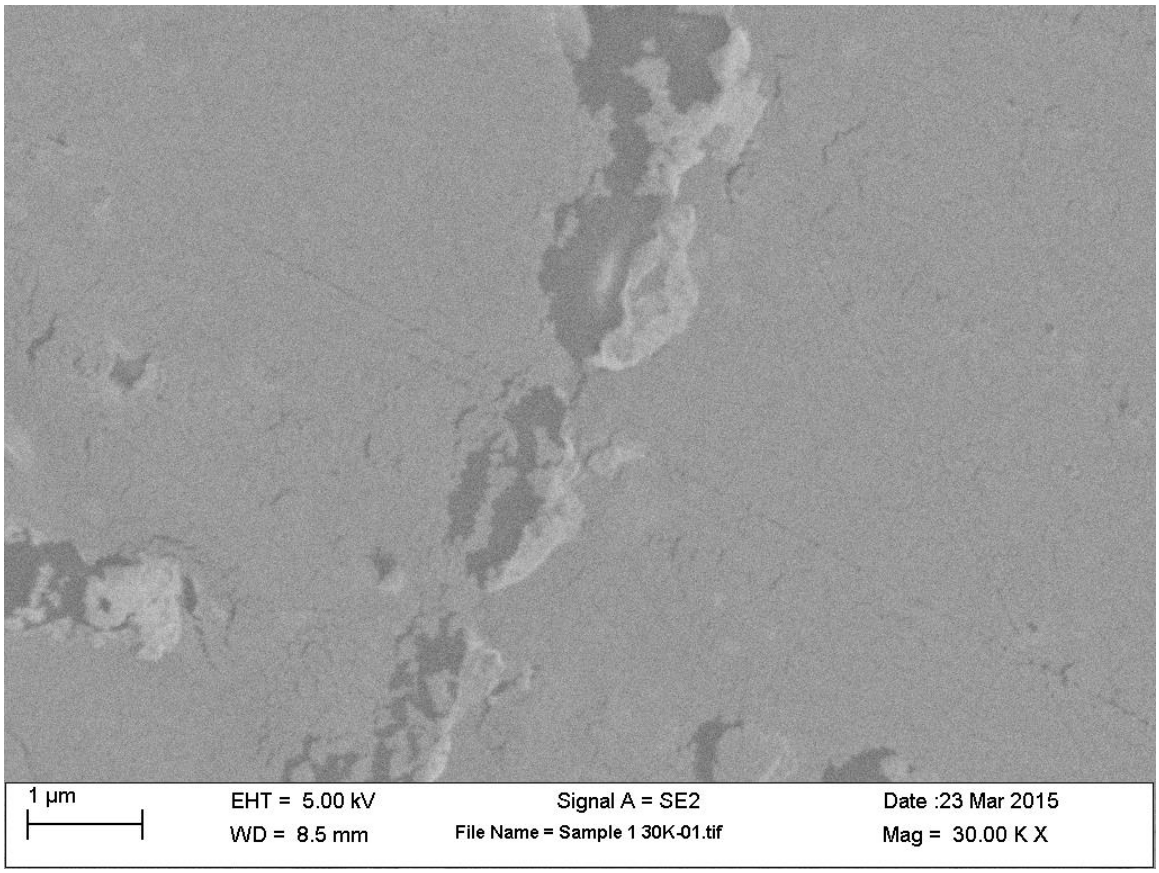
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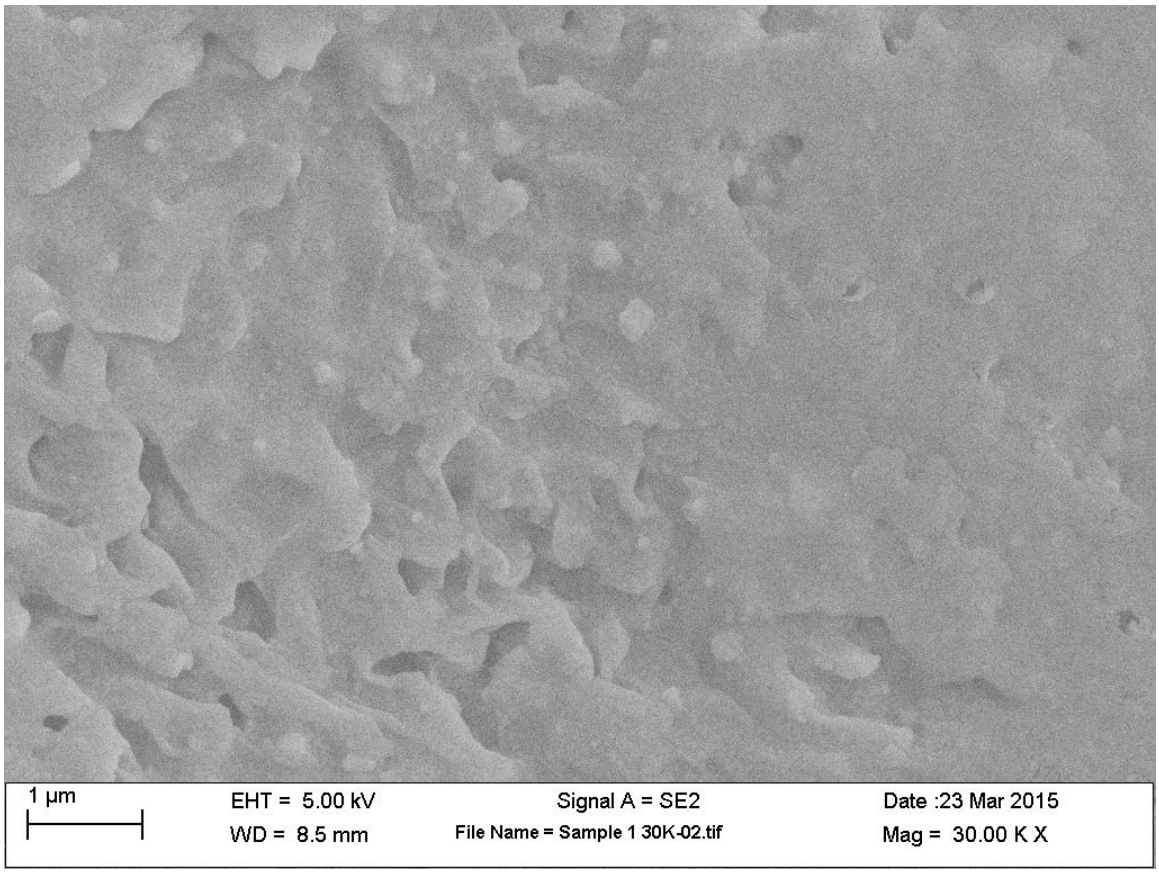
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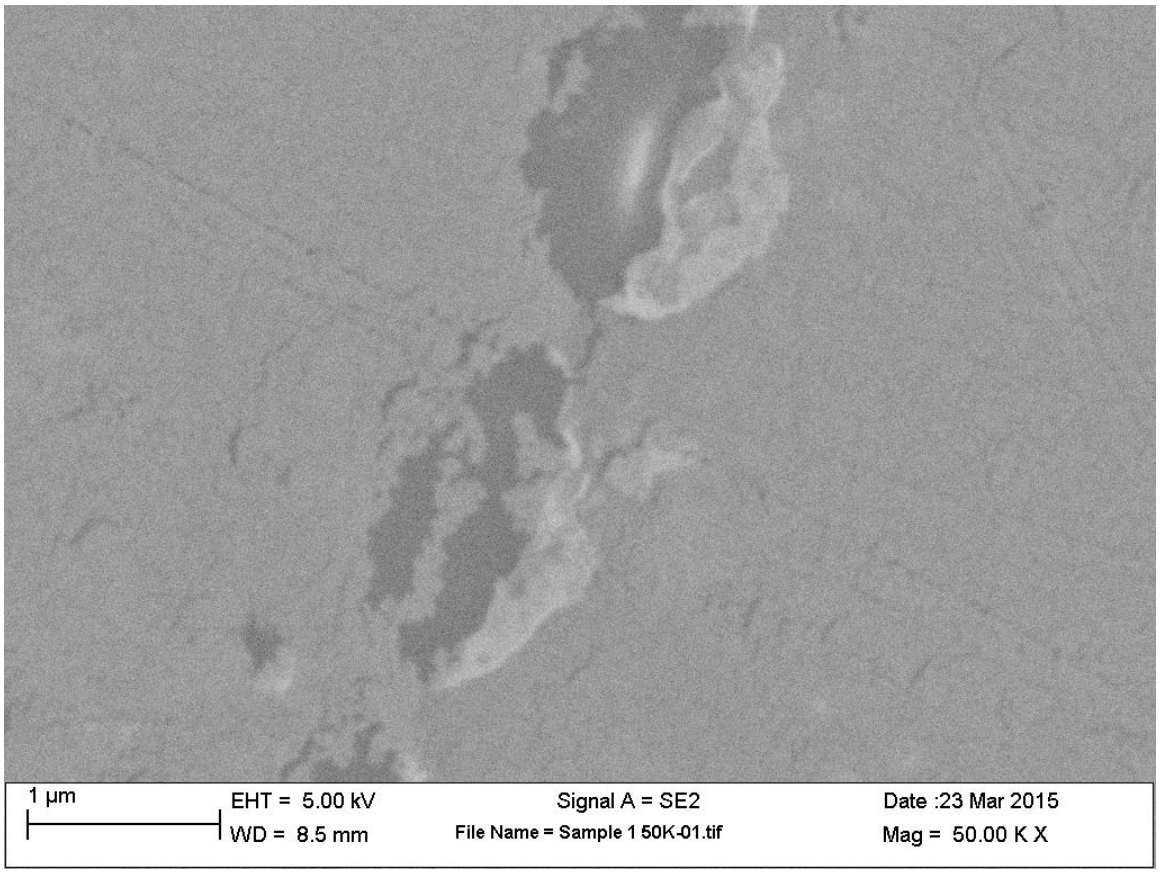
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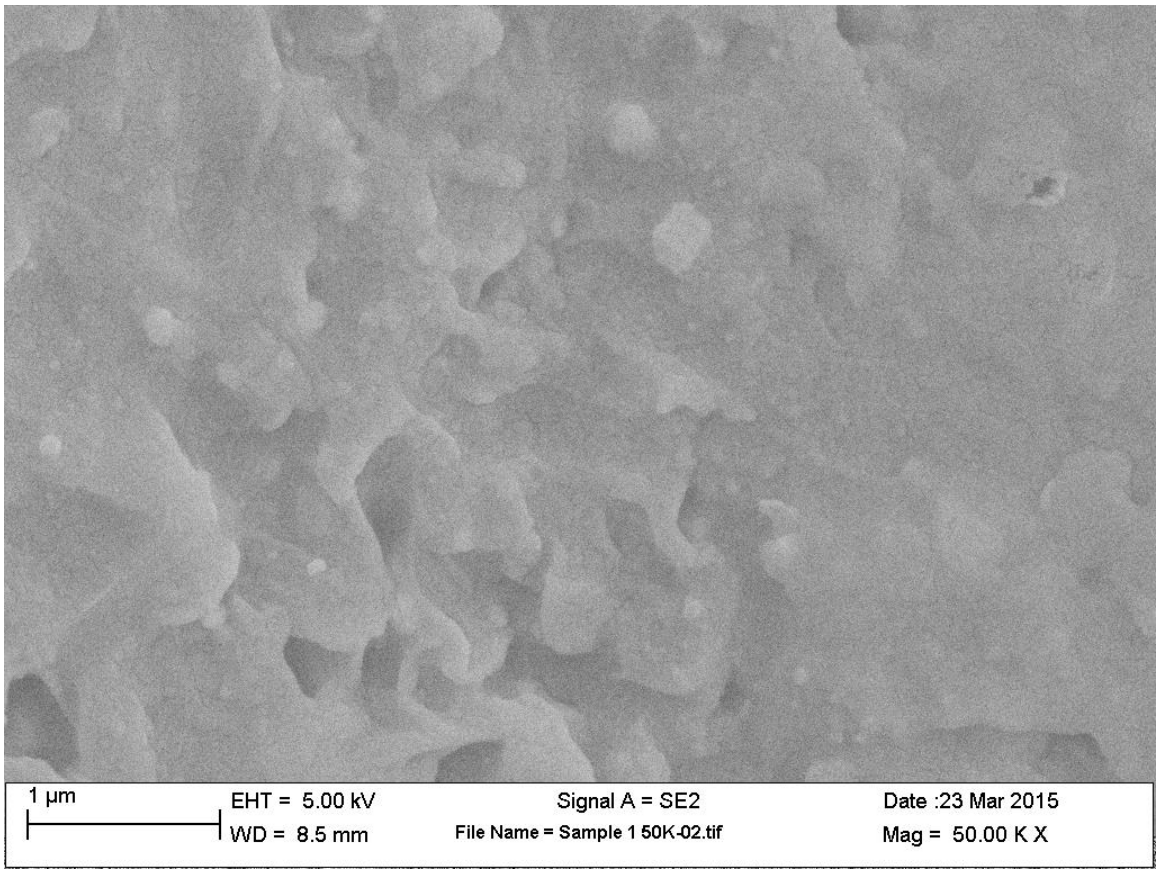
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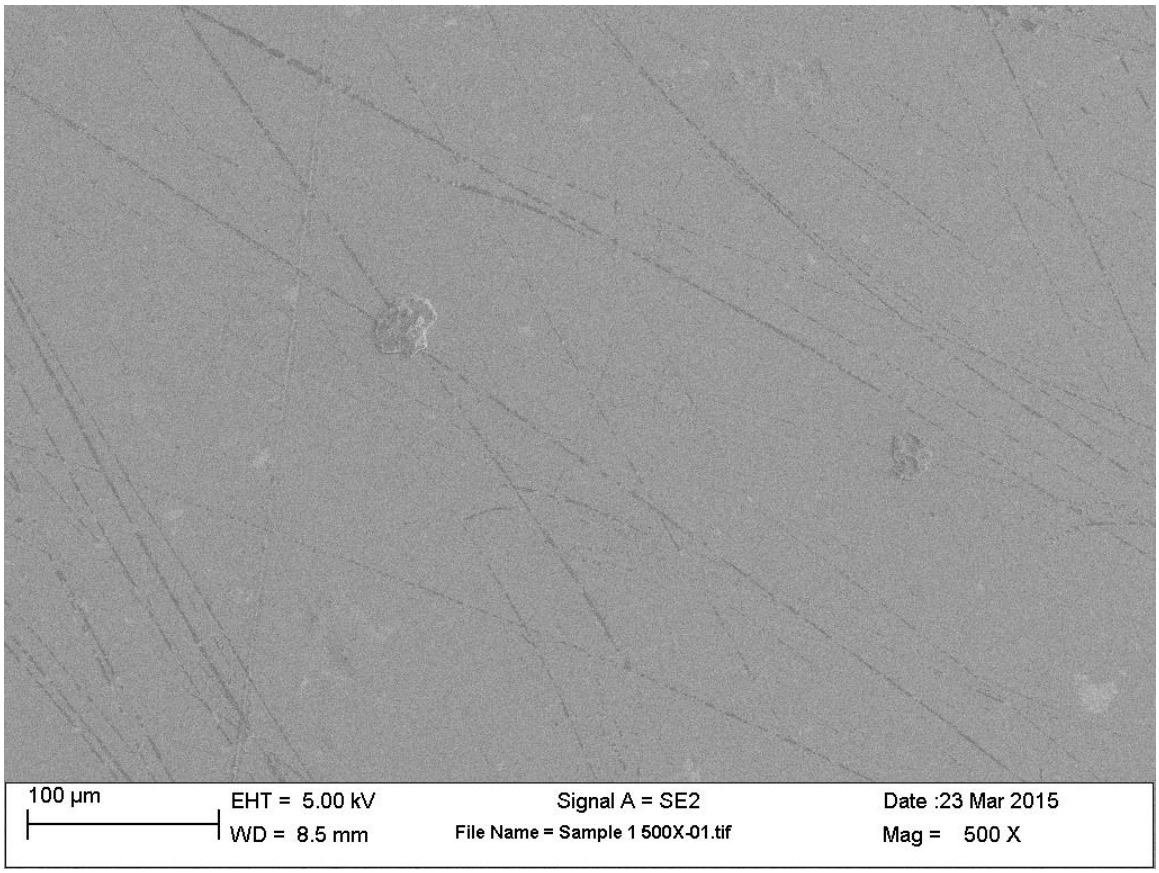
Date :23 Mar 2015
Mag = 50.00 K X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Date :23 Mar 2015
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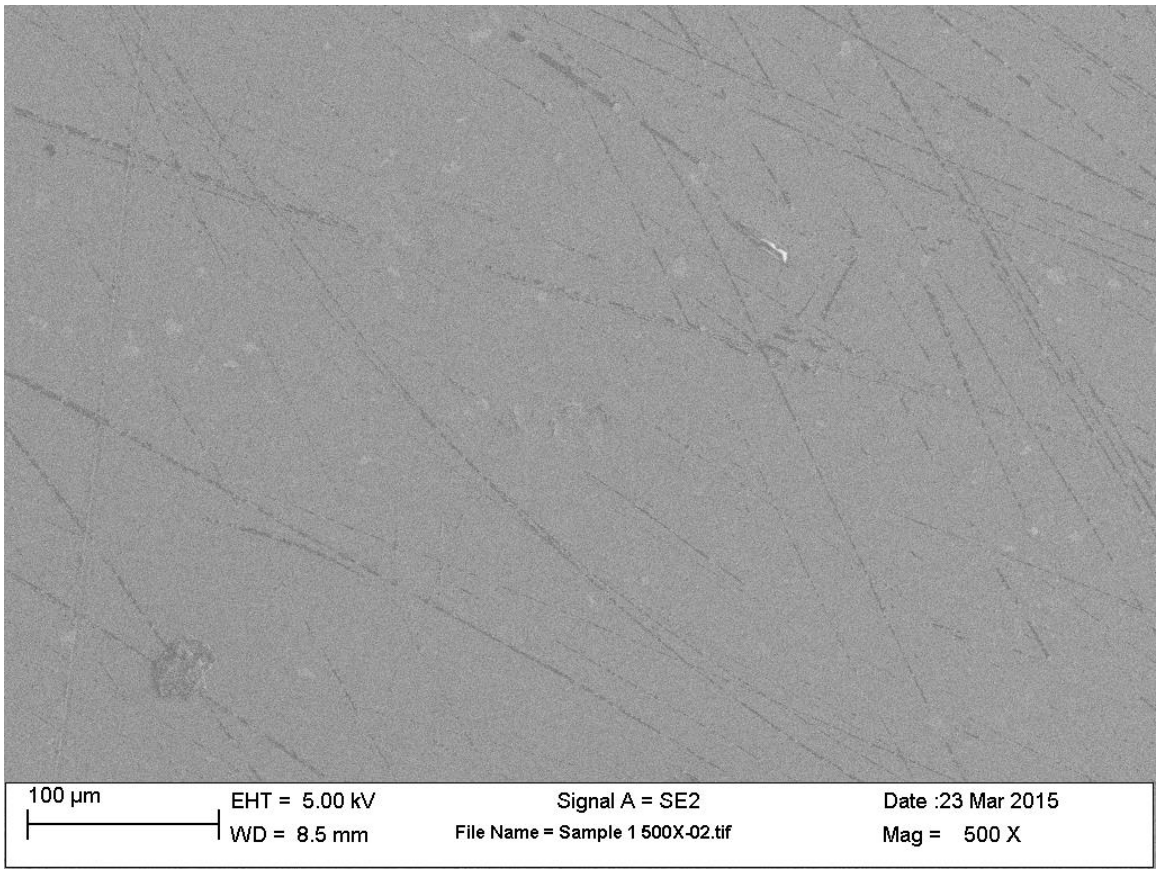
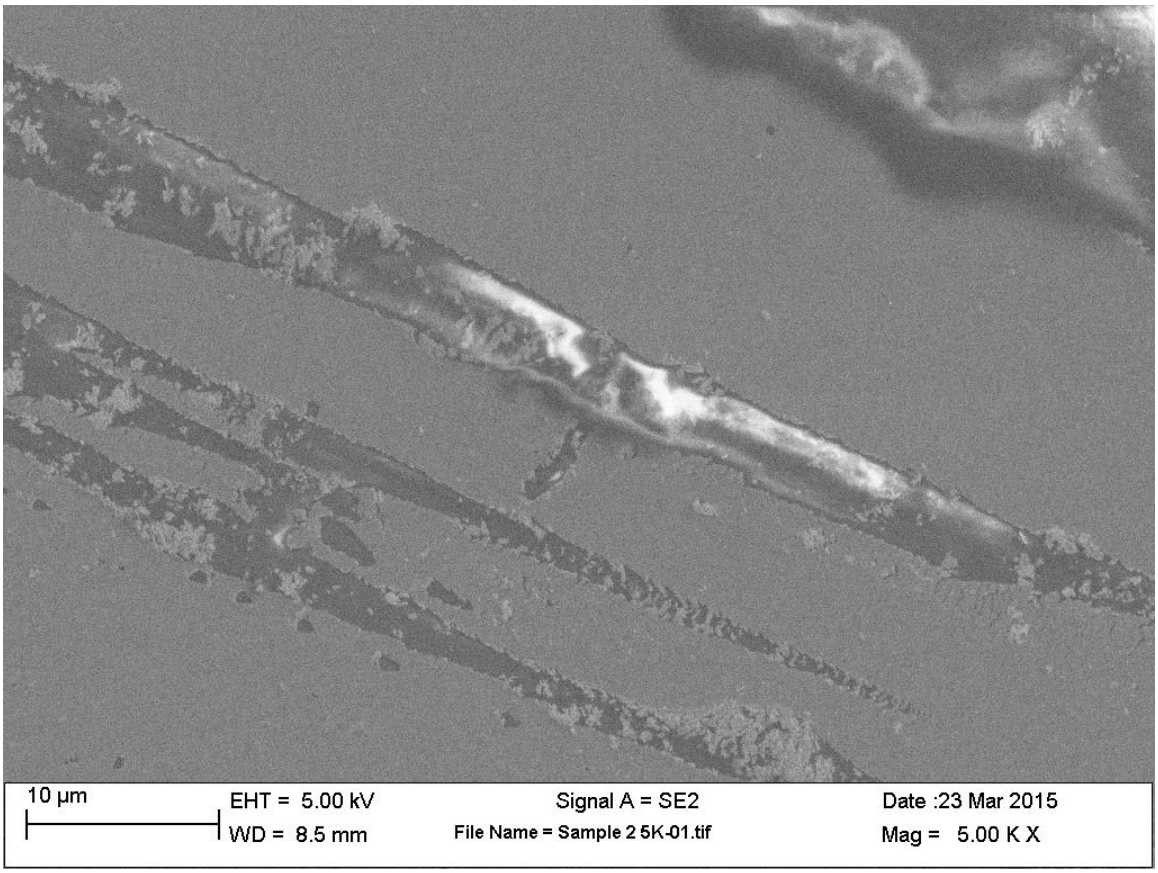


Figure 14 SEM surface image of 1:4 PhTMS:MeOH hybrid glass coating material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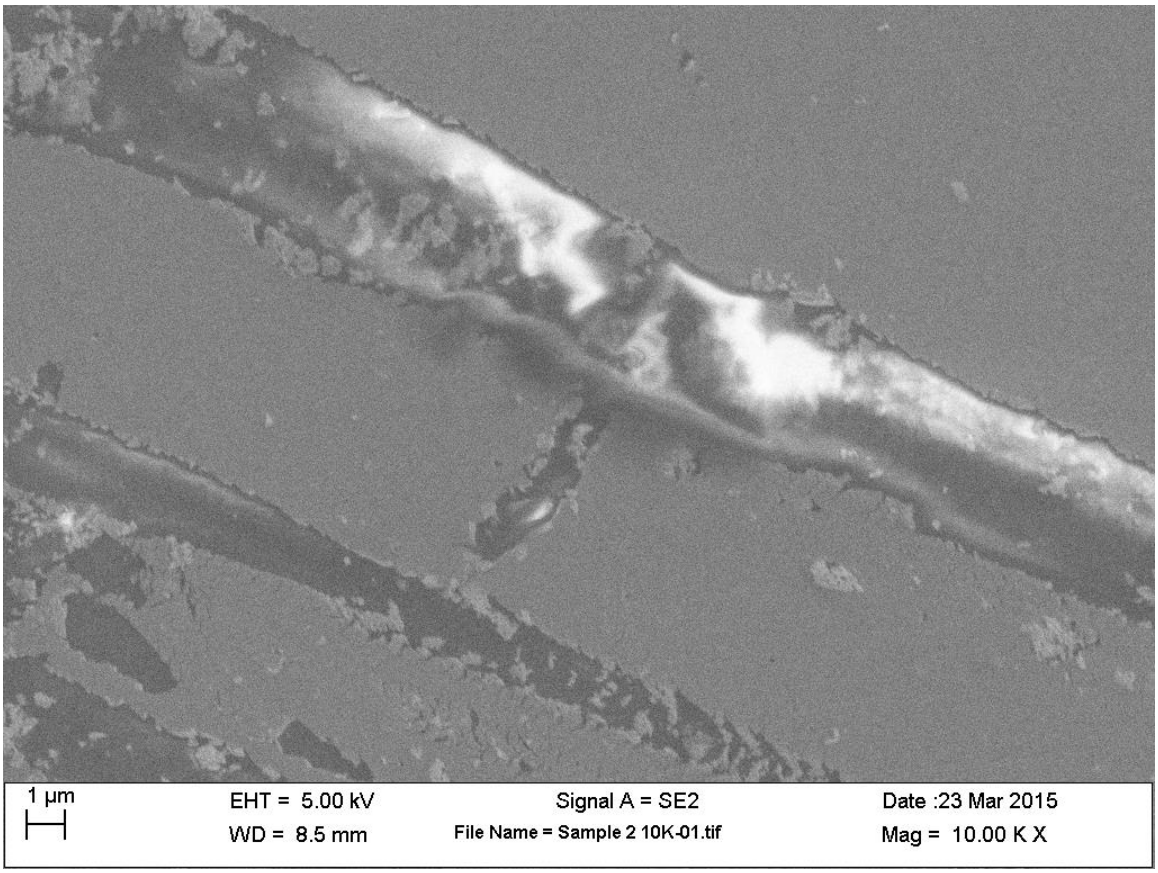
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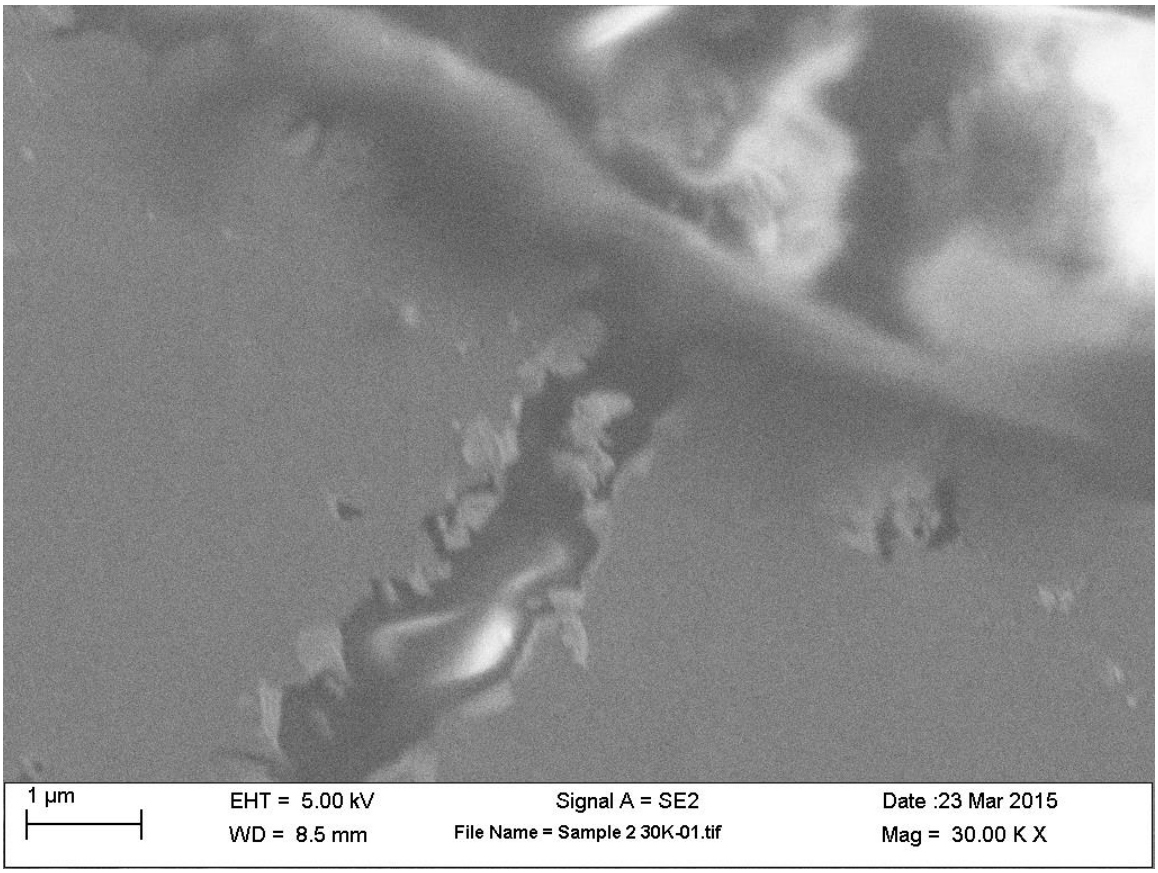
Date :23 Mar 2015
Mag = 10.00 K X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File Name = Sample 2 30K-01.tif
Date :23 Mar 2015
Mag = 30.00 K X

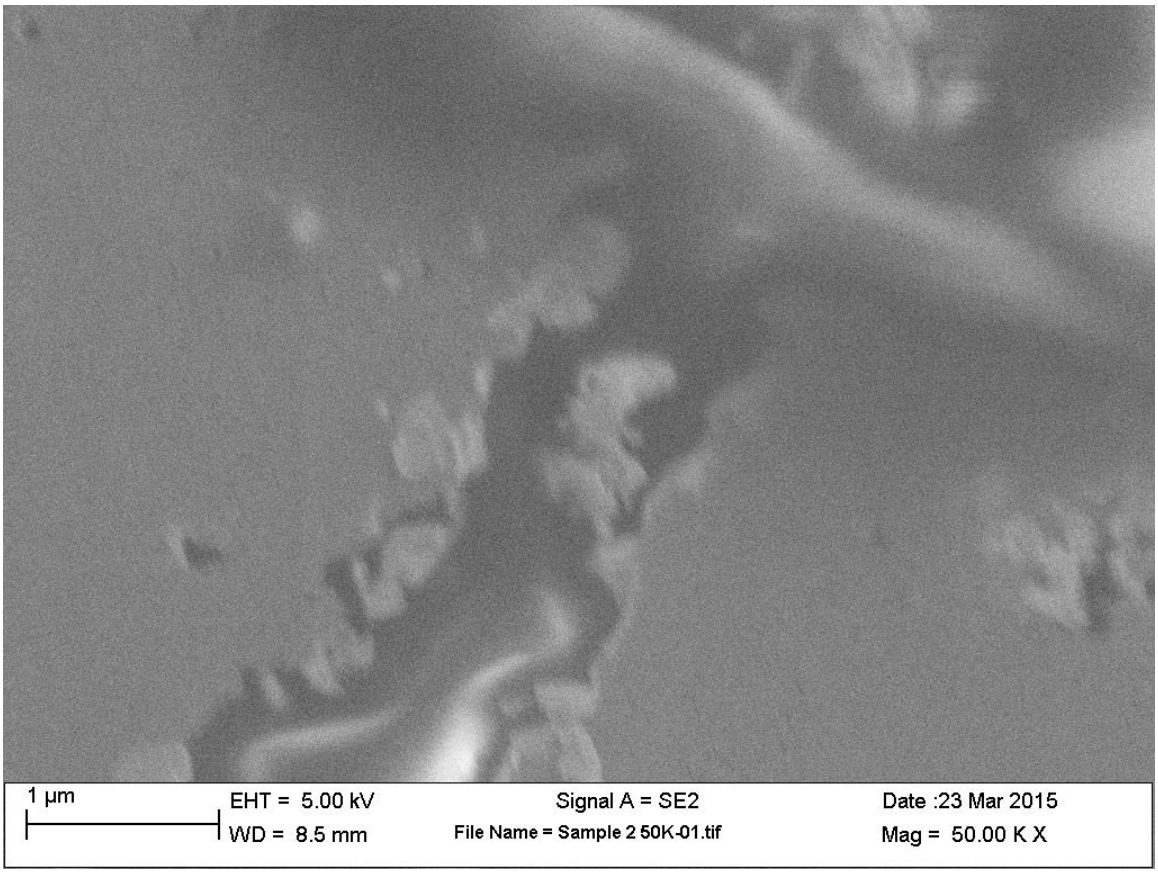
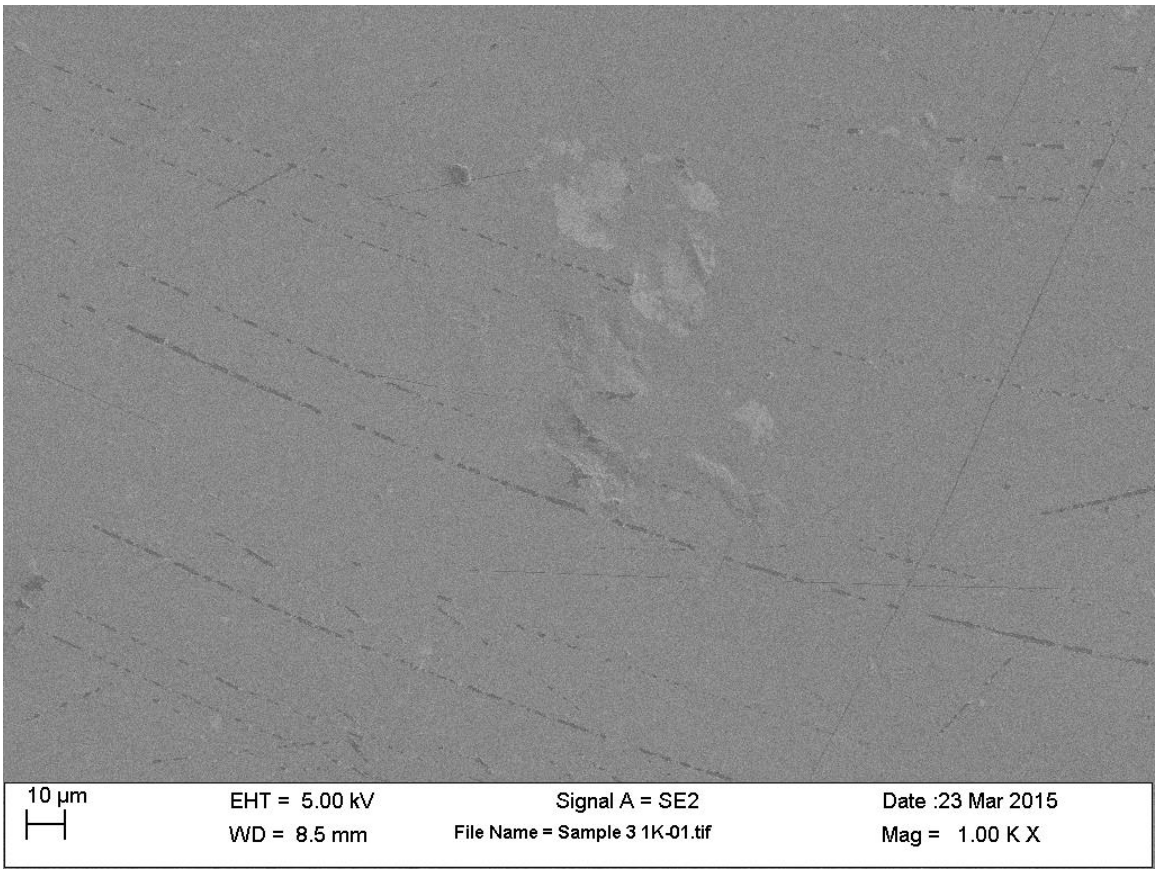


Figure 15 SEM surface image of 1:8 PhTMS:MeOH hybrid glass coating material


10 µm
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WD = 8.5 mm
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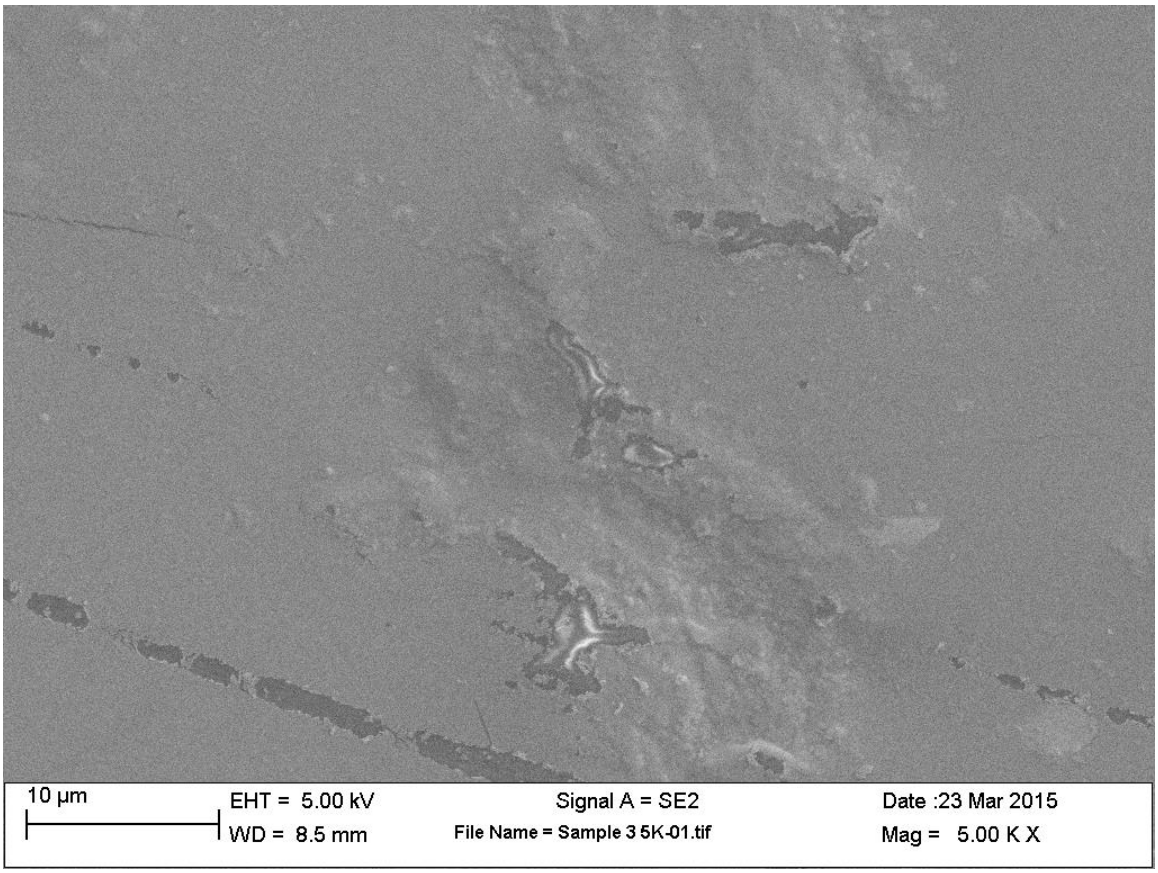
Date :23 Mar 2015
Mag = 1.00 K X


10 µm
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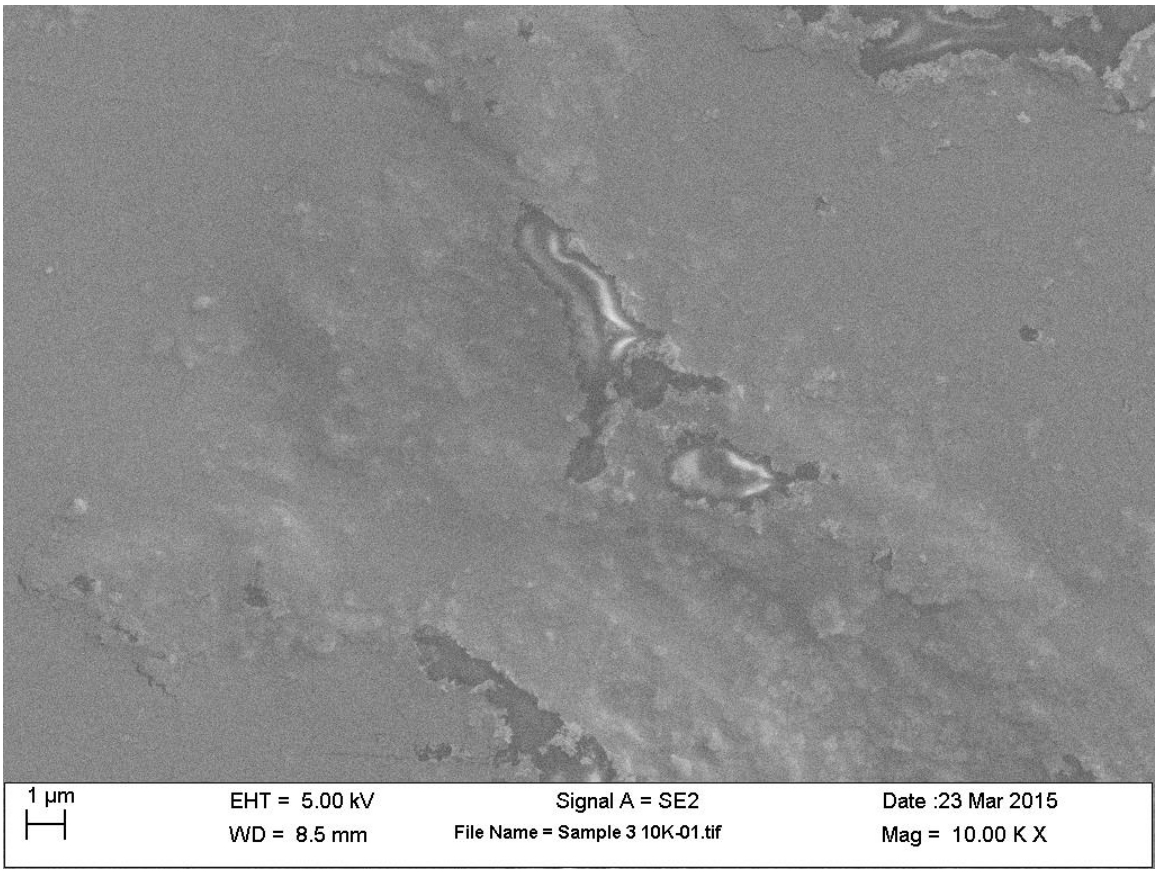
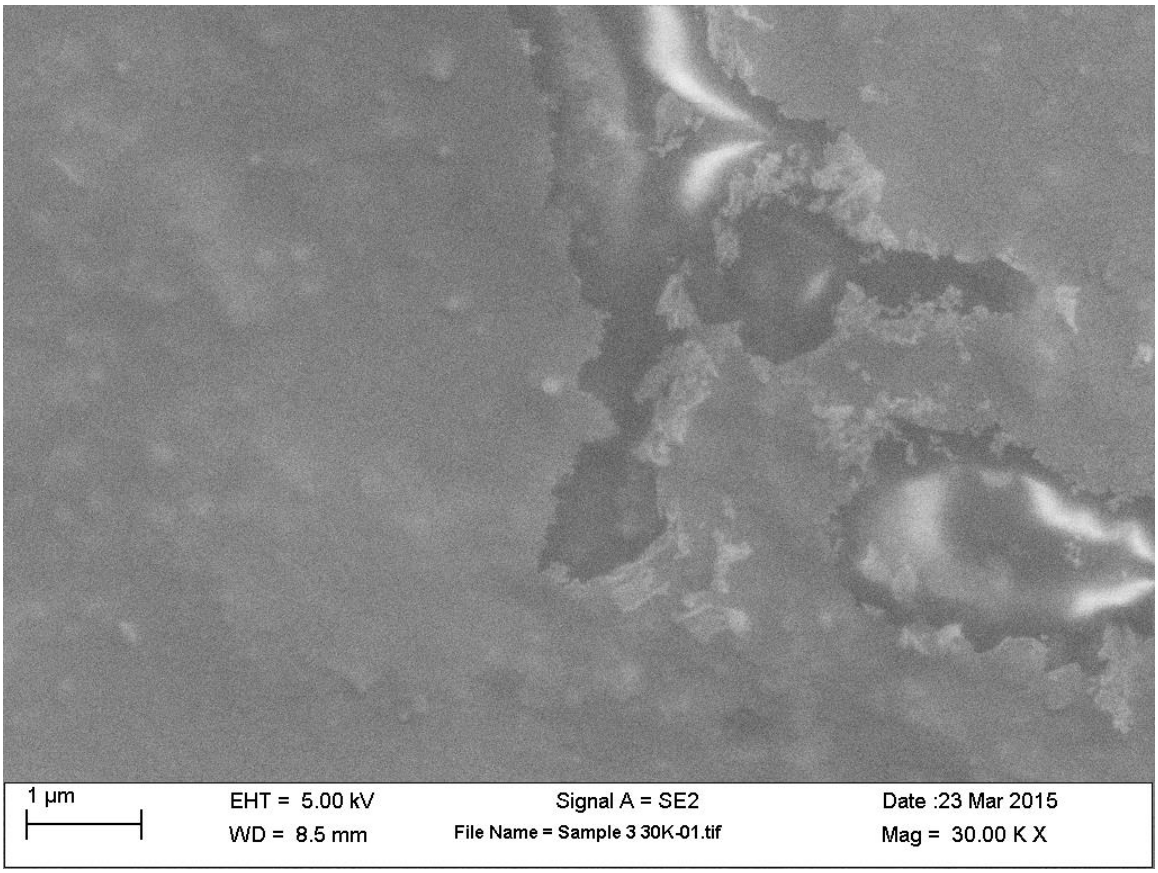
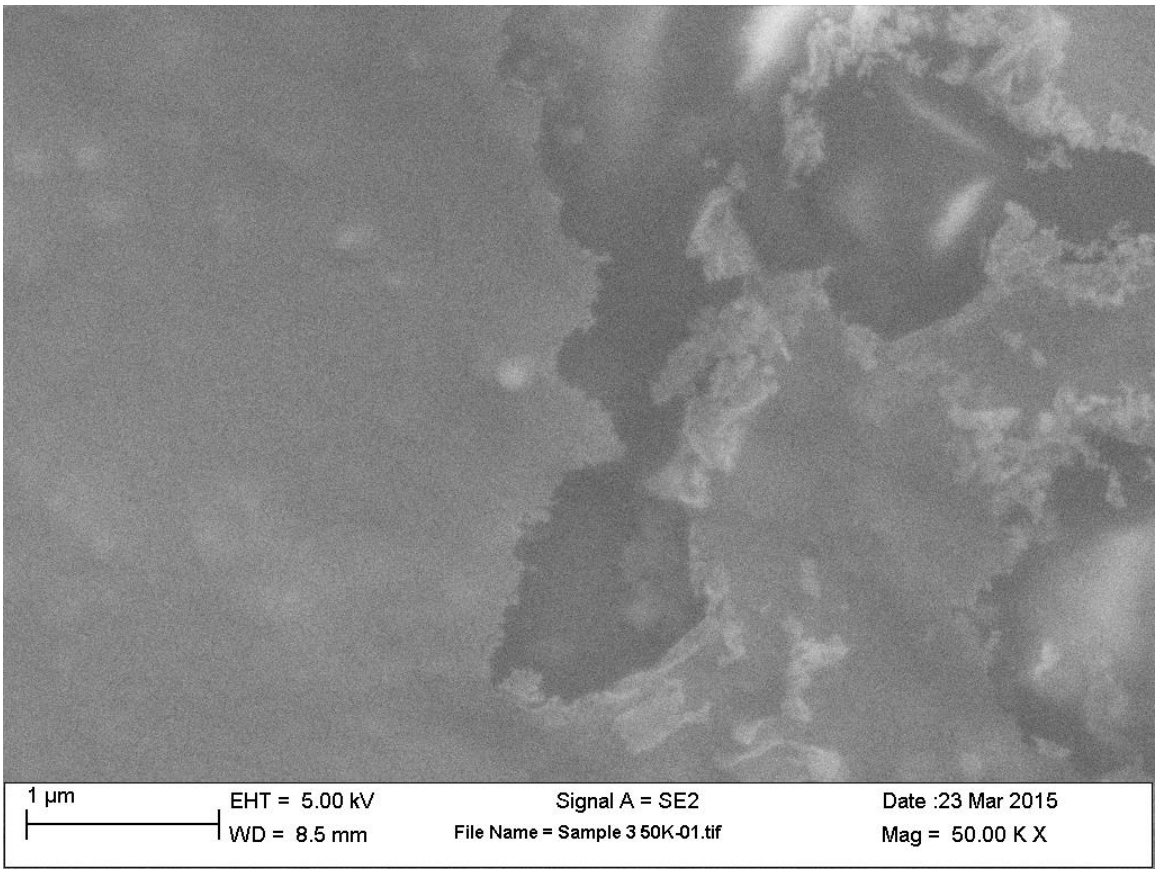
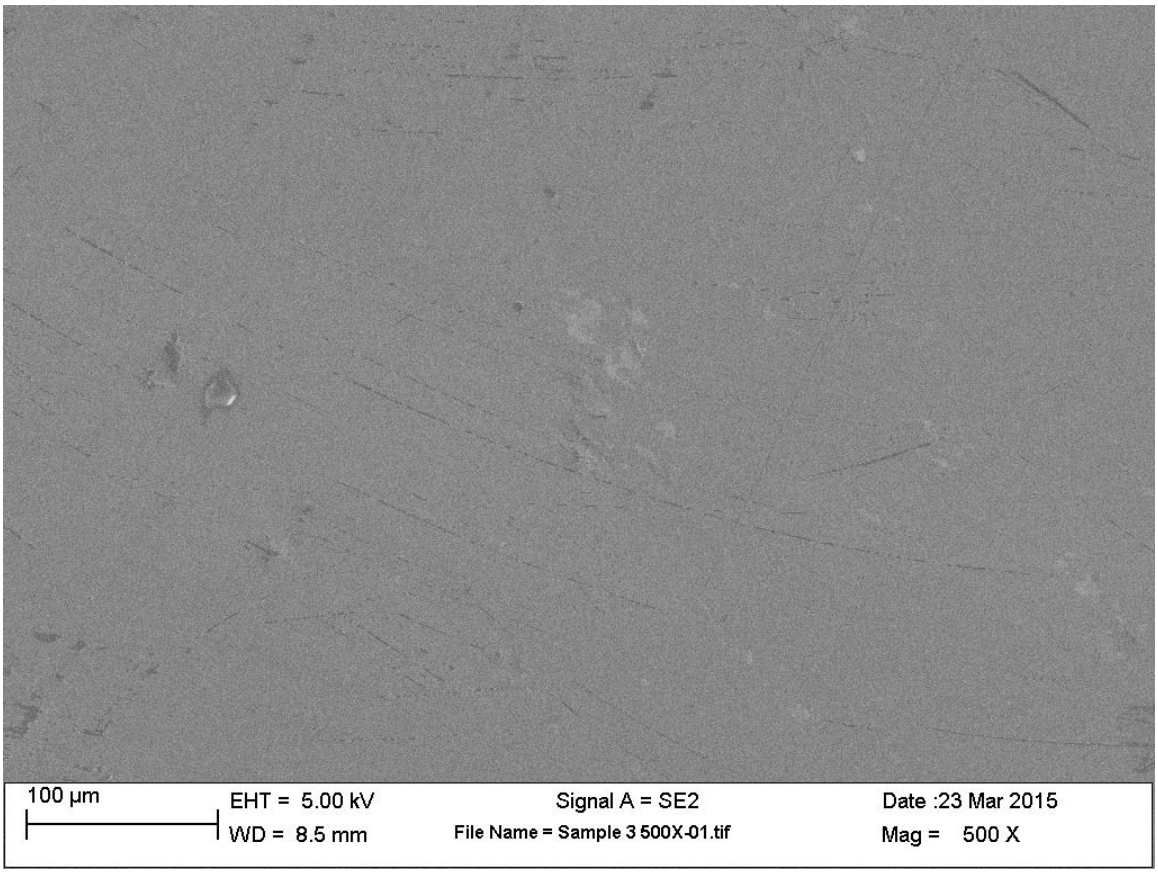
Date :23 Mar 2015
Mag = 5.00 K X


1 µm
EHT = 5.00 kV
WD = 8.5 mm
Signal A = SE2
File Name = Sample 3 10K-01.tif
Date :23 Mar 2015
Mag = 10.00 K X


1 µm
EHT = 5.00 kV
WD = 8.5 mm
Signal A = SE2
File Name = Sample 3 30K-01.tif
Date :23 Mar 2015
Mag = 30.00 K X


1 µm
EHT = 5.00 kV
WD = 8.5 mm
Signal A = SE2
File Name = Sample 3 50K-01.tif
Date :23 Mar 2015
Mag = 50.00 K X


100 µm
EHT = 5.00 kV
WD = 8.5 mm
Signal A = SE2
File Name = Sample 3 500X-01.tif
Date :23 Mar 2015
Mag = 500 X

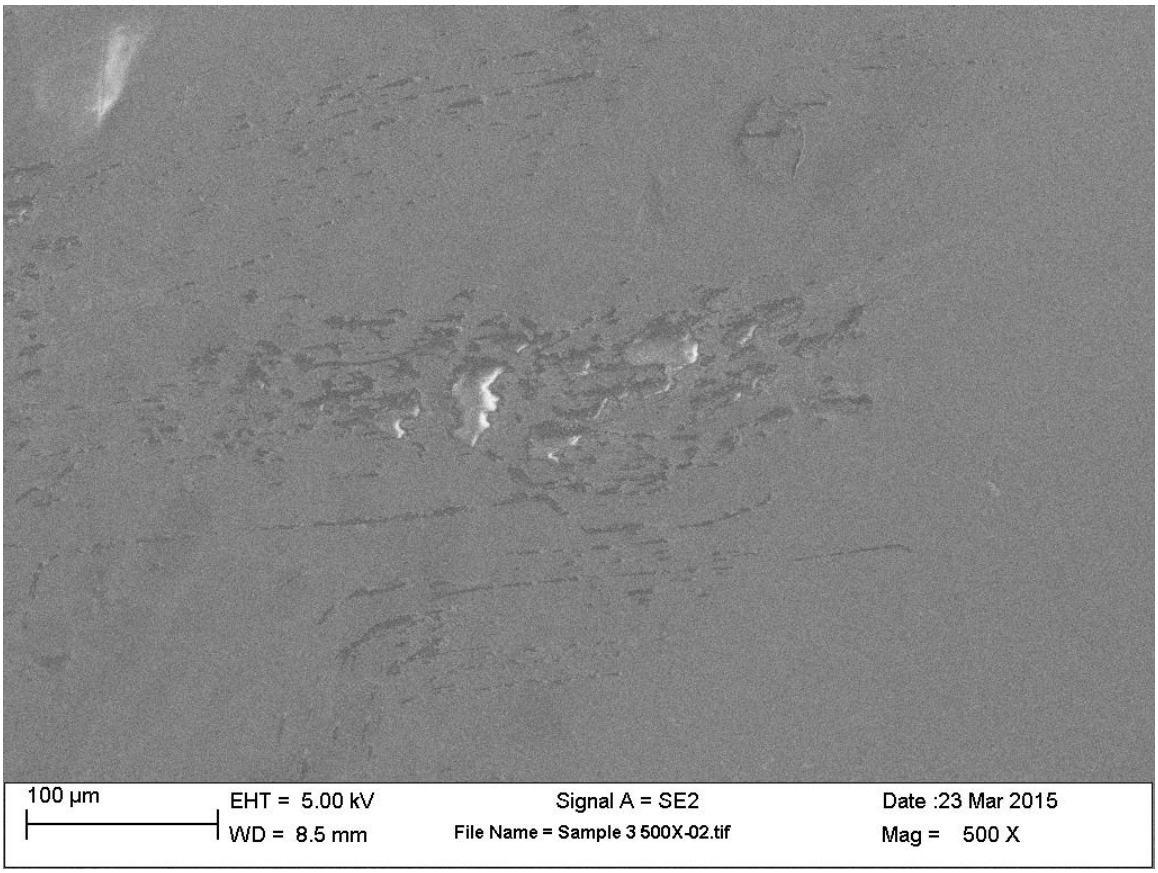


Figure 16 SEM surface image of 1:16 PhTMS:MeOH hybrid glass coating material

All SEM images showed smooth, nonporous surfaces. This uniformity is needed for corrosion resistance to protect the surface of the titanium alloy or any other metal substrate.

The surfaces of the samples were analyzed using EDS. In table 9 the percentage of the elements on the surface of the hybrid glass coating materials are shown. The synthesis had 1:4 PhTMS:MeOH with scanning area 10 μm^2.

Table 9 list the elements percentage on the surface of hybrid glass coating materials

Chemical composition			**Heat Treatment for 1 day at 150º, followed by 6 days at 110ºC**					
mole			**Element percentage under scanning area 10 µm^2**					
PhTMS	**DPhDMS**	**MeOH**	**Weight %**			**Atomic %**		
			C %	**O %**	**Si %**	**C %**	**O %**	**Si %**
1	0.25	4	69.22 ± 1.13	27.48 ± 1.07	3.30 ± 0.59	75.85	22.61	1.54
			Totals 100.00			Totals 100.00		

Figure 17 presents quantitative elemental analysis using EDS technique for sample PhTMS:MeOH 1:4.

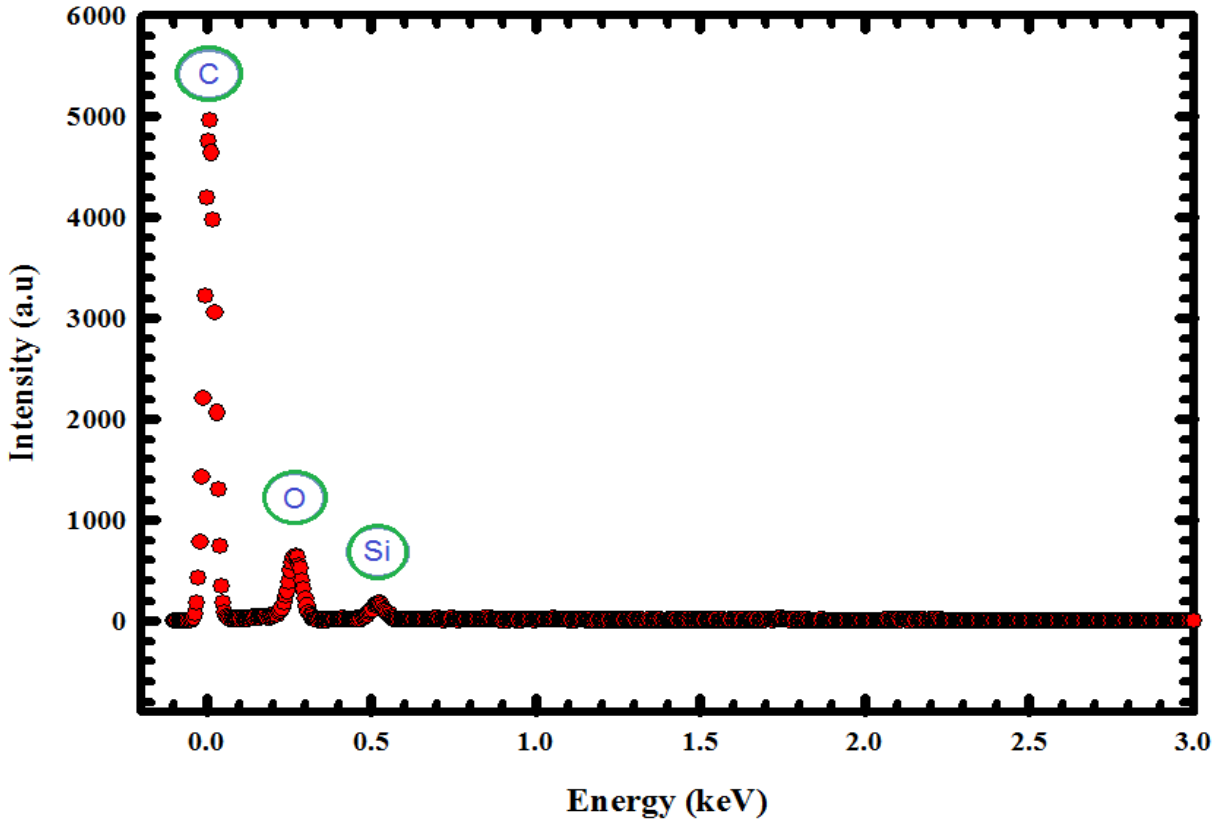


Figure 17 An EDS spectrum for sample PhTMS:MeOH 1:4

From mapping technique, atomic percentage of the carbon was higher than other elements because carbon molecules were located more on the surface of the hybrid glass. The silica was the lowest atomic percentage because silica molecules were located in the bottom of the hybrid glass.

5.4 Summary of Results and Discussion

The best combination of solvent and temperature was 8 moles of methanol for 1 mole of PhTMS for all heat treatments used. This ratio resulted in the highest hardness among all of the syntheses. In addition, this ratio resulted in a surface with the lowest roughness.

To explain these observations, it is known that methanol acts as a solvent in the early stages of hydrolysis. During hydrolysis, the precursor reacts with water. At the same time more solvent means that the precursors in the solution are diluted during the hydrolysis or are farther apart. The ratio of water to precursor was not changed. The product of hydrolysis is methanol which further increases the dilution.

While the solvent can facilitate the hydrolysis, it can also delay condensation reactions between the precursor molecules until hydrolysis is further advanced. In a sol-gel process, hydrolysis and condensation polymerization are usually simultaneous, especially when an acid is used to catalyze the reactions, as it is in this study. The products of condensation are both water and methanol. Because of the continuous change of the amounts of water and methanol, it is difficult to know exactly what is controlling the reactions.

For this reason, it was necessary to make a systematic study by varying the amount of methanol. Based on the observations of the resulting gels, based on microscopy, roughness and hardness, it was possible to select the molar ratio of 8 moles of methanol and conclude that this ratio was a good combination of solvent and dilution. This ratio allowed the activation of the precursors during hydrolysis and sufficient condensation polymerization between hydrolyzed precursors, so that the heat treated hybrid glass had higher hardness and smoothness than hybrid glasses prepared with either less methanol or more methanol. In other words, the molar ratio of 8 was better than 4 or 16.

CHAPTER 6

6.0 Conclusion

The melting gel had reversible process at 110°C. When the melting gel reaches the consolidation temperature of 150°C the reactivity of the melting gel will increase, the gel cannot be re-soften (irreversible process) and the 3D networks of the silica chains will be formed. The melting gels were derived from silica and poured continuously for coating on the titanium alloy substrate. The surface of hybrid glass is smooth with sub-nano roughness and non-porous material. PhTMS-DPhDMS provides excellent coating protection against corrosion. Three synthesis of the melting gel were investigated. There are several advantages of the melting gel providing barrier mechanism for corrosion protection, surface hydrophobic, coatings nonporous and limiting diffusion through the layer. Doubling the methanol made the gel more fluid for pouring but harder when consolidated. These samples cracked. Increasing methanol to 4x introduced surface stickiness. Crack-free coatings were formed using a treatment of 1 day at 150°C, followed by 6 days at 110°C and 4 hour furnace cooling to room temperature. Doubling the time from 1 day to 2 days at 150°C increased the hardness somewhat. Hardness was independent of load (1mN vs 3mN). The best synthesis of the melting gel was investigated and depended on the quantity of the molar ratio of the solvents.

CHAPTER 7

7.0 Suggestions for Future Work

The following are suggestions for future work to improve the thermal and mechanical properties of melting gel and hybrid glass:

- It would be interesting to add Graphene during the sol gel process to improve thermal properties and hardness of melting gel and hybrid glass.
- A suggestion for coating process melting gel dried under inert gas.
- Study the effects of carbon nanotube on the melting gel and the hybrid glass behaviors.
- Study the hybrid glass and applied as protective optical or anti-reflective optical coatings.
- Examination on the synthesis of the hybrid glass by using galvanic cell to determine the corrosion rate.
- Study the water effects on the melting gel by changing the molar ratio of water.

CHAPTER 8

8.0 References

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