Analysis of hybrid nano composite pva-pdms thin films for hydrophobic applications

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ABSTRACT

In the present study, electrical and physical properties of Polydimethylsiloxane (PDMS) and polyvinyl alcohol (PVA) polymer were combined with zinc oxide (ZnO) and silicon dioxide (SiO_2) nanoparticles to form the zinc silicate ($ZnSiO_3$) hybrid nanocomposites thin films using sol-gel process. The samples were prepared with a ratio of 50:48:02 and named as P_0, P_1, P_2, P_3 and P_4.The electrical properties such as ac conductivity (σ_{ac}) dielectric constant (ε_r) and dissipation factor (tan δ) of developed PDMS/PVA/$ZnSiO_3$ nanocomposites thin films were studied using high frequency LCR meter with a frequency range from 100Hz to 1MHz. From the physical properties, the surface hydrophobicity of the thin films was studied using contact angle meter measurement and it was inferred that the films are hydrophobic in nature with increase in the nanofiller content. The Scanning Electron Microscopy (SEM) was used to examine the surface morphology of the developed films. The X-ray diffraction (XRD) was used to investigate the structure and crystalline size of the nanoparticles within the nanocomposite films. These nanocomposites thin films are used in hydrophobic materials like waterproof covers and waterproof glass surfaces.

Keywords *– Sol-gel, hybrid nanocomposites, hydrophobicity, electrical properties, crystalline size*

INTRODUCTION

Polymers are amorphous or polycrystalline substances with a high capacity for charge storage. Due to its good clarity and exceptional durability, PVA (polyvinyl alcohol) is found to be most promising polymeric compounds with several ideas for its use in electronics, packaging, textiles, and food goods. It is utilised in the manufacture of polarising sheets and is useful in a variety of biomedical applications due to its ease of manufacture, great chemical resistance, and outstanding mechanical capabilities.

The Polydimethylsiloxane (PDMS), initially released way back twenty years ago. This polymer is utilized for quick prototyping of microfluidic devices using a replica mounding technique. However, PDMS's widespread use is not limited to its ease of processing, but also its chemical and physical qualities. This polymer has been proposed for numerous optical sensing applications due to its intriguing characteristics, strong permeability and low selectivity. The zinc oxide (ZnO) nanoparticles are being studied because they are a wide-band-gap semiconductor with a high exciting energy and great thermal and chemical stability. These characteristics make ZnO an excellent candidate in photoelectronic devices, sensors, photocatalysis, and other electrical applications. Because of their low toxicity, stability, and ability to be functionalized with a wide range of chemicals and polymers, silicon dioxide (SiO_2) nanoparticles offer a lot of fascinating properties in the scientific field. [1].

The goal of this project is to synthesis zinc oxide and silicon dioxide nanoparticles to obtain zinc silicate ($ZnSiO_3$) nanoparticles by the method of solution-combustion technique. The synthesized nanoparticles are

Then thoroughly mixed into PVA and PDMS polymers to obtain hybrid nanocomposites thin films. The process of mixing nanoparticles to polymers is carried out by sol-gel method. There are plenty of research articles available where the researchers fabricated the nanocomposites using a single polymer with a nanoparticle, [2] single polymer and hybrid nanoparticles [3] and single polymer with micro and nanoparticles [4]. But in the present research work the nanocomposites thin films are developed by selecting hybrid polymers viz., PVA and PDMS and hybrid nanoparticles of ZnO and SiO_2. The literature available for the selected hybrid polymers and nanoparticles are very scanty. Hence it was found that the selected materials of polymers and nanoparticles as fillers were novel. They are synthesized and developed as nanocomposite thin films which can be used in applications such as waterproof covers and waterproof glass surface. Scanning Electron Microscopy (SEM) and X-Ray Diffraction were used to characterize the produced nanocomposites for morphological studies (XRD).Then the electrical and physical properties were studied which provides the database for the developed novel hybrid nanocomposite films.

EXPERIMENTAL DETAILS

The primary support for preparing the thin films are PVA and PDMS which are low cost polymer materials along with ZnO and SiO_2 nanoparticles used as nanofillers to fabricate the thin film nanocomposites by sol-gel process.

Materials

Polyvinyl alcohol (PVA) of very high purity (99.9%), the polymer Polydimethylsiloxane (PDMS) with a viscosity of 3500 centistokes (cSt) was obtained from padmashri scientific company. The Trimethoxymethylsilane is a curing agent or crosslink with molecular weight of 136.22 g/mol was obtained from padmashri scientific. Tetrahydrofuran (THF) is a solvent with molecular weight of 72.11 g/mol was obtained from padmashri scientific. Zinc oxide (ZnO) of high purity (99%) with molecular mass of 81.38 g/mol was purchased from padmashri scientific. Silicon oxide (SiO_2) of purity (99.96%) with molecular mass of 60.08 g/mol was purchased from padmashri scientific.

Preparation of $ZnSiO_3$ nanoparticles

$ZnSiO_3$ nanoparticles were synthesized by solution combustion method using zinc oxide (ZnO) and silicon dioxide (SiO_2). In this work, zinc oxide (40% of the weight of ZnO) and silicon dioxide (40% of the weight of SiO_2) dissolved in distilled water and mixing under vigorous stirring for 30 min. Adding 10% of Trimethoxymethylsilane is a curing agent and 10% of Tetrahydrofuran as a solvent again mixing the solution under stirring for 20 min. The mixture is heated at 90˚C to evaporate the solvent to get a viscous gel. Then the obtained viscous gel is allowed for cool to room temperature and then a $ZnSiO_3$ nanoparticle is obtained. Figure 1 shows that the flowchart for the processing of $ZnSiO_3$ nanoparticles.

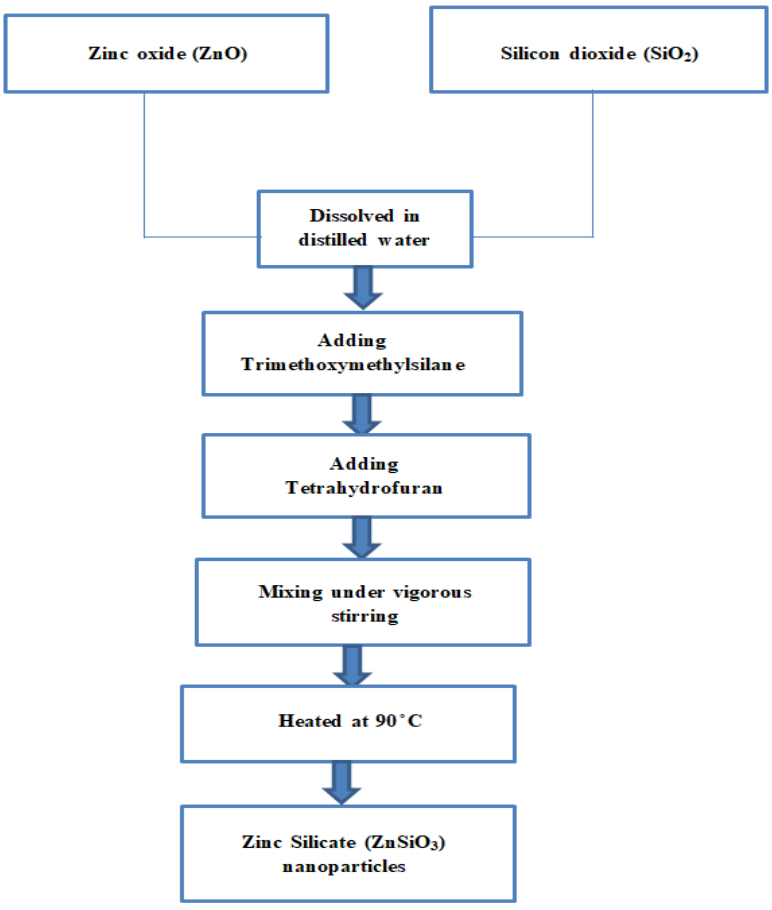

Figure 1: **Flowchart for the processing of $ZnSiO_3$ nanoparticles**

Preparation of hybrid nanocomposites thin films

Figure 2 shows the synthesis methods procedure for PVA/PDMS/$ZnSiO_3$ hybrid nanocomposites thin films. Using the solution heating approach, pure PVA/PDMS polymers and $ZnSiO_3$ nanocomposites films with various loadings of 0 to 2wt% $ZnSiO_3$ nanoparticles were synthesised. For 3 hours at 60 °C, 50% PVA and 48% PDMS polymer powder were dissolved in distilled water in a hot air oven. For the next 2 hours, a magnetic stirrer was employed to constantly spin the PVA/PDMS solution at room temperature. Simultaneously, 0.5wt% $ZnSiO_3$ nanoparticles were sonicated for 3 hours at room temperature in distilled water before being combined with the PVA/PDMS solution. This complex solution was stirred with a magnetic stirrer overnight before being poured into a Teflon petri dish and dried for 4 hours in a hot air oven at 60°C. The PVA/PDMS/$ZnSiO_3$ nanocomposites films that formed were peeled from the petri dish and stored in vacuum desiccators for further investigation. [7] A similar procedure was used for nanoparticles containing 1 to 2 wt% $ZnSiO_3$.

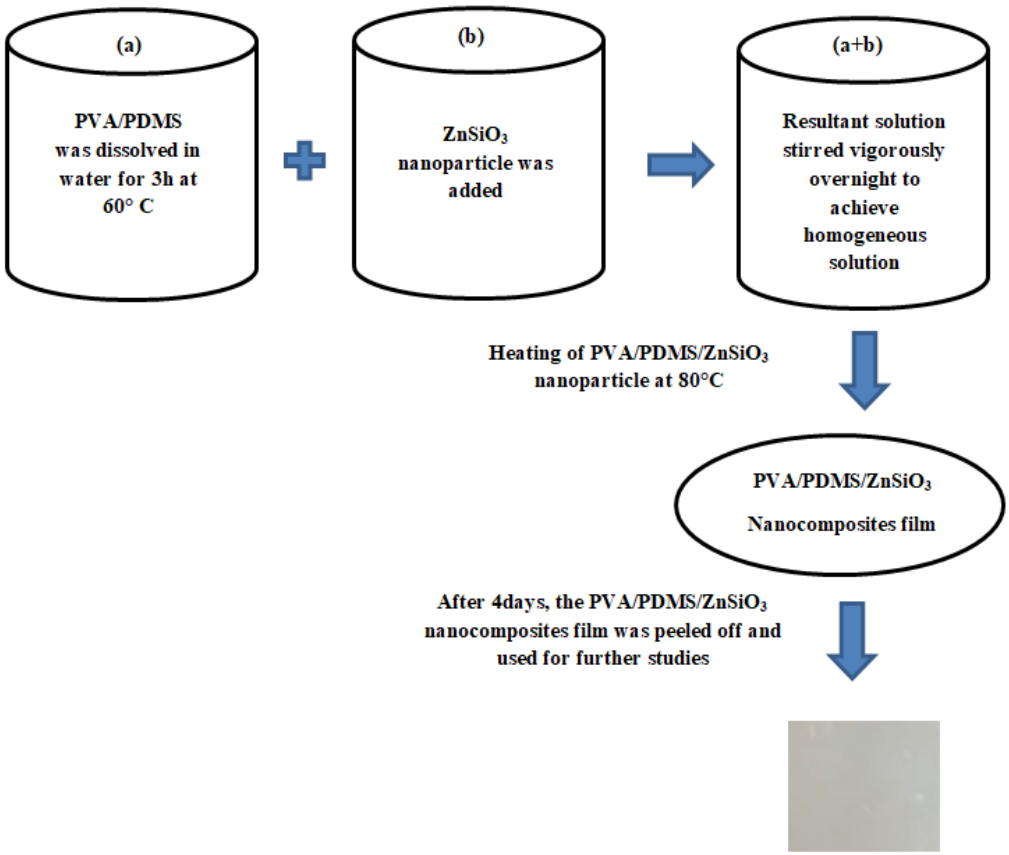

Figure 2: **Synthesis protocol of PVA/PDMS/$ZnSiO_3$ nanocomposites films**

RESULTS AND DISCUSSIONS

The experimental observation such as morphology, electrical properties and contact angle measurement results are discussed in the following section.

Surface Morphological Analysis

Figure 3 shows images from a scanning electron microscope (SEM) equipment used to investigate the produced thin film formations. The high-resolution SEM microscopy of the PVA/PDMS/$ZnSiO_3$ nanocomposites thin film is rather good because it is free of cracks, compact, homogenous, and evenly covered, revealing its compact microcrystal structure with a spherical shape and almost homogeneous size distribution. [8]This discovery is consistent with the appearance of the films, which were continuous throughout the surface of the substrate. The thin films that were formed are dense, smooth, and homogeneous, with no visible pores, and the Nano fillers are spherical in shape.

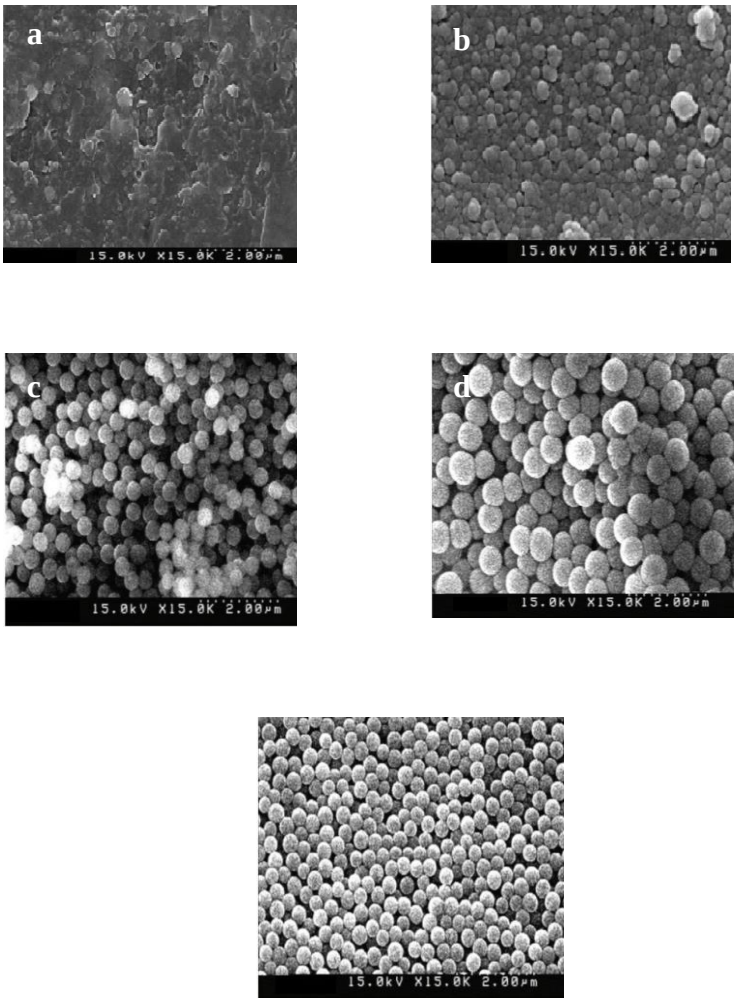

Figure 3: SEM images of the $ZnSiO_3$ nanocomposites: (a) pure PVA&PDMS (b) 0.5 (c) 1.0 (d) 1.5 (e) 2.0 wt % $ZnSiO_3$

X-ray Diffraction Analysis

The XRD technique is commonly used to identify and characterize polymer electrolyte films. The XRD patterns of pure PVA/PDMS polymer blend electrolyte and $ZnSiO_3$ nanocomposites thin films are shown in Figure 4. PVA has a characteristic peak at 2θ in its XRD pattern, indicating that it is semi-crystalline. When $ZnSiO_3$ nanoparticles are introduced to the polymer, the strength of this peak gradually increases, indicating that the degree of crystallinity of the PVA/PDMS mix polymer complex increases, causing disruption of the crystalline structure [9].

The intensity of XRD pattern significantly increases as the addition of $ZnSiO_3$ nanoparticles. For higher concentration of $ZnSiO_3$ nanoparticles the sharp peak were observed, As a result of the polymer blend's flexible backbone, there is increased ionic diffusivity with high ionic conductivity. The absence of a peak indicates that the $ZnSiO_3$ nanoparticles are totally dissolved in the polymer blend mixture.

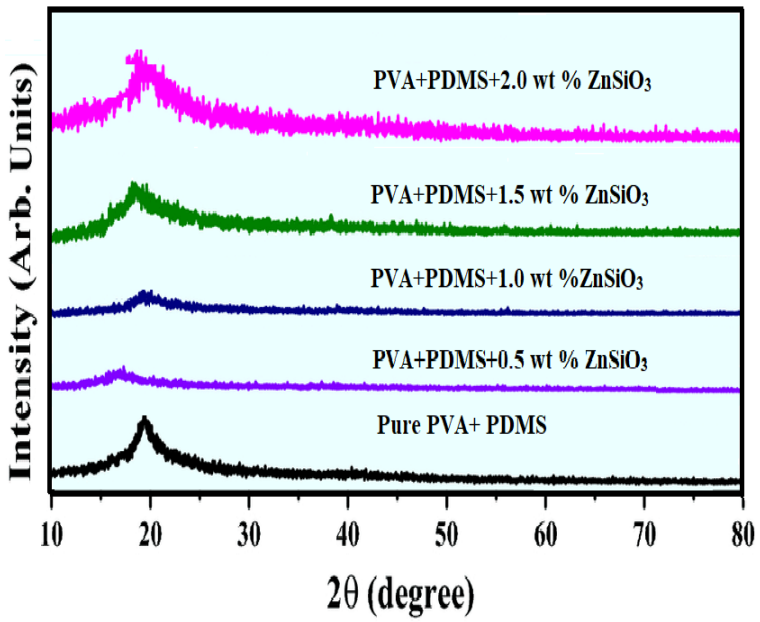

Figure 4: **XRD image of PVA/PDMS/$ZnSiO_3$ thin films**

Electrical properties

AC Conductivity Studies

The electrical properties such as resistance, capacitance and dissipation factor using High Frequency LCR meter were measured. Firstly, the resistance and capacitance reading of that thin film were noted. Secondly the dissipation factors reading of that thin film were noted. Similar measurements are carried out for different nanocomposites samples.

The resistivity (ρ) and ac conductivity (σ_{ac}) was calculated for PDMS/PVA/$ZnSiO_3$ thin films from the following formula

Resistivity (ρ) = $\frac{RA}{L}$

Conductivity (σ) = $\frac{1}{\rho}$

Where R is the resistance, A is the area of the films; L is the length of the films. Figure shows frequency dependent AC conductivity of PDMS/PVA/$ZnSiO_3$ nanocomposites thin film. AC conductivity behavior for thin film has been studied. It is seen that the value of AC conductivity increases with increases in frequency. The increase of AC conductivity in the frequency range from 100Hz to 1MHz.

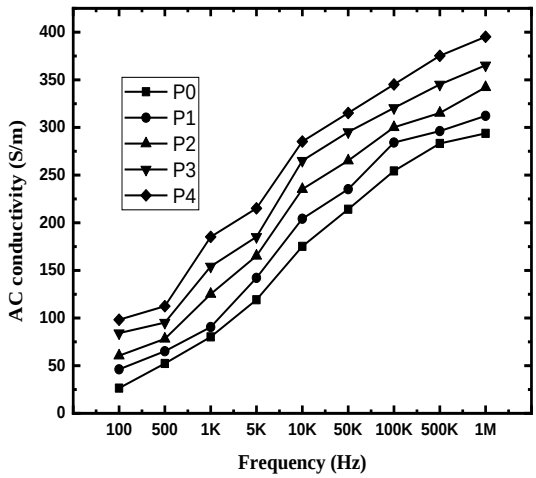

Figure 5: Variation of AC conductivity with frequency

Figure 5 shows the variation of AC electrical conductivity of PVA/PDMS and its composites containing varying concentrations of $ZnSiO_3$ nanoparticles. From the figure it is observed that the conductivity increases with increases in frequency as well as $ZnSiO_3$ concentration. This increase is attributed to the formation of excess charge carriers developed in the polymer matrix. The higher conductivity of PVA/PDMS and $ZnSiO_3$ is due to the uniform dispersion and the spatial arrangement of thin films within the polymer matrix. The AC conductivity of PVA/PDMS and $ZnSiO_3$ nanocomposites is observed to increase with increase in frequency range from 100Hz to 1MHz and $ZnSiO_3$ nanoparticle range from 0.5 to 2wt%. Thus it can be concluded that by dispersion of $ZnSiO_3$ in polymer matrix brings out an improvement in the charge transport property and electrical conduction.

Dielectric Constant Studies

Figure 6 displays the dielectric constant as a function of frequency. Using the formula, the dielectric constant was obtained.

$$\text{Dielectric constant} = \frac{Cd}{\varepsilon_{\circ} A}$$

Where 'C' is the capacitance, 'd' is the thickness of the films, '$\varepsilon_{\circ}$' is the permittivity of free space, and 'A' is the area of the films. The variation of dielectric constant parameters with frequency and composition have been different $ZnSiO_3$ concentration as function of

frequency range from 100Hz to 1MHz. It is observed for pure PVA/PDMS and for all weight fractions of $ZnSiO_3$ nanocomposites. The dielectric constant decreases with increase in frequency. At low frequency (here <100Hz) the dipoles have sufficient time to align themselves with the electric field resulting in a higher value of dielectric constant. Contrary to it in the high frequency (here 1MHz) region, due to rapid periodical reversal of the electric field the dipoles are unable to orient themselves along the electric field so that there is no excess ion diffusion in the electric field direction leading to observed decreases in the value of dielectric constant. [13]

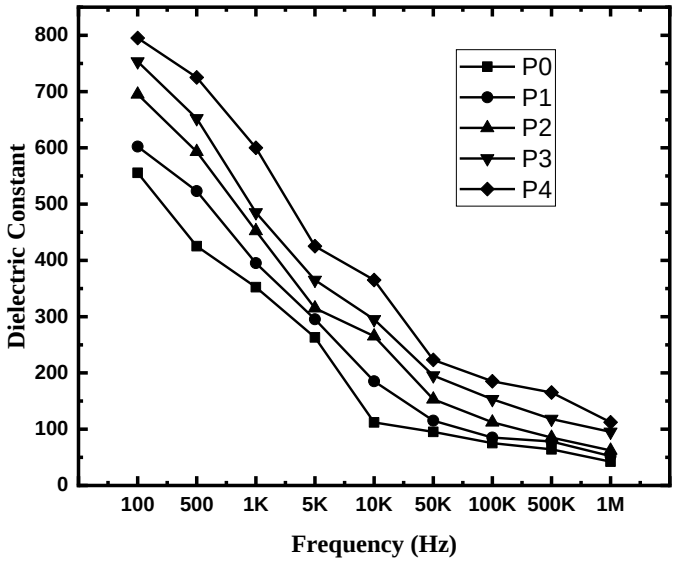

Figure 6: Variation of dielectric constant with frequency

Dissipation factor studies

Figure 7 shows the variation of the dissipation factor of PVA/PDMS/$ZnSiO_3$ nanocomposites as a function of frequency range from 100Hz to 1MHz. The dissipation factor decreases with increasing frequency. As the value of dissipation factor at low frequencies is due to motion of free charges it is higher as compared to that at higher frequencies where due to ion hopping the conduction losses and ion polarization losses come into existence. [14] The vibration of ions may be yet another source of loss in this range of frequencies. On increasing the concentration of filler nanoparticles there is an enhancement in the amount of charge carriers so the dissipation factor value also increases.

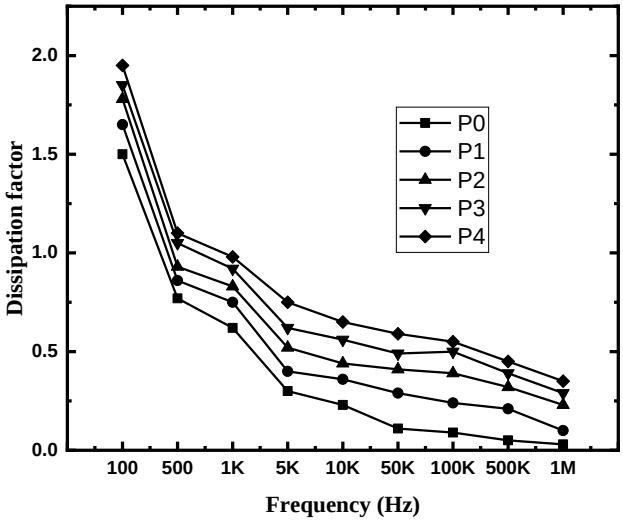

Figure 7: Variation of dissipation factor with frequency

Physical Properties

Contact Angle Measurement

The contact angle quantifies the ability of a liquid to wet the surface of a solid. The surface tension of the fluid and the composition of the surface affect the shape that a drop takes on the surface. It is based on the observation of the surface's intermolecular interactions with a small drop of water as it comes into contact with it [15]. It is usually used to determine a surface's wettability.

- Contact angle measurements are used to determine whether a surface is hydrophilic or hydrophobic.
- Angle between 0° and 90° = wettable, hydrophilic surface
- Angle between 90° and 180° = nonwettable, hydrophobic surface
- Near-180° angle = ultra-hydrophobic surface, fully liquid- repelling, lotus effect.

Figure 8 shows that the different composition of nano composites thin film samples contact angle measurements. The figure 8a shows the 50% of PVA and 50% of PDMS without adding nanoparticles its shows hydrophilic in nature. Similarly the figure 8b, 8c, 8d, and 8e shows the 98% of PVA/PDMS and 0.5 to 2wt% $ZnSiO_3$ nanoparticles added. By adding these nanoparticles the thin films lose hydrophilic property and gain hydrophobic property. The overall summary of these results is by adding $ZnSiO_3$ nanoparticles the thin films are hydrophobic in nature. When the surface energy of a material is low, the molecules in water droplets are more attracted to each other rather than the surface, resulting in a high contact angle and greater hydrophobic qualities in nature.

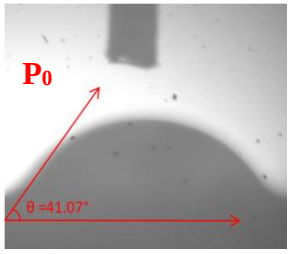

Figure 8a (P_0)

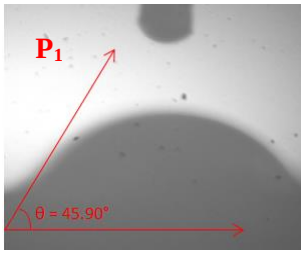

Figure 8b (P_1)

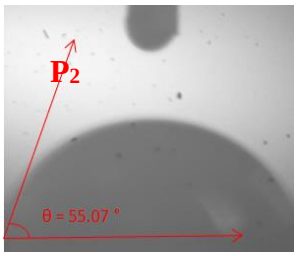

Figure 8c (P_2)

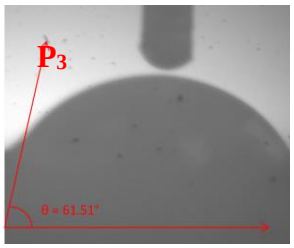

Figure 8d (P_3)

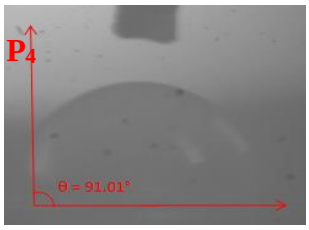

Figure 8e (P_4)

Figure 8: Image of contact angle measurement

CONCLUSIONS

The solution combustion approach was used in this study to create zinc silicate ($ZnSiO_3$) nanoparticles. The sol-gel technique was used in this study to create hybrid nanocomposites thin films. The structure and morphology of a PVA/PDMS/$ZnSiO_3$ thin film were investigated using XRD and SEM. In addition, an electrical property investigation was performed. The dielectric constant and dielectric loss of the film were determined using various frequencies. The behaviour of AC conductivity in thin films has been studied. When the frequency range is increased from 100Hz to 1MHz, the value of ac conductivity increases by 400 S/m. When the frequency range is increased from 100Hz to 1MHz, the dielectric constant decreases by 800. Similarly, as the frequency range extends from 100 Hz to 1MHz, the dissipation factor decreases by 2.0. In addition, contact angle measurements were taken to confirm the thin films 92°C of surface hydrophobicity. These nanocomposites thin films are used in hydrophobic materials like waterproof covers and waterproof glass surfaces.

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