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Effects of ZnO and SiO_2 nanoparticle additions on the structural, water absorption and mechanical properties of Polyvinyl Alcohol (PVA) films

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Abstract. Nanocomposite films were prepared with polyvinyl alcohol (PVA) as a base matrix and ZnO, SiO_2 nanoparticles as a filler material. SiO_2 and ZnO nanoparticles were synthesized using sol-gel and co-precipitation methods, respectively. PVA-ZnO, PVA-SiO_2, and PVA-ZnO-SiO_2 hybrid nanocomposite films were prepared by a solution film casting method. The presence of ZnO and SiO_2 nanoparticles within the films has been confirmed by structural and morphological analysis of the films. Water solubility, water absorption and tensile strength were evaluated for all the films produced. The addition of both types of nanoparticles in the PVA matrix led to a reduction in water absorption in addition to the water solubility capability of the material when compared to the pure PVA film. The addition of nanoparticles resulted in an increase in the tensile strength of the composite films compared to the pure PVA films by 14%, 23%, and 66% for the PVA-ZnO, PVA-SiO_2, and PVA-ZnO-SiO_2 films respectively. This work provides a simple route to tune the properties of PVA embedded with metal oxide nanoparticles for food packaging and medical applications.

1. Introduction

In recent years, polymer-nanoparticle-based composite materials have attracted the interest of several researchers, due to their collegial and hybrid properties. Such composites show properties determined by the interaction between the filler and the matrix [1]. Synthesis of composite materials mixed with nanoparticles is an effective way to improve the characteristics of polymers and increase the number of potential applications [1-3]. The incorporation of inorganic nanoparticles as fillers and organic polymers allows the formation of nanocomposites with improved mechanical, thermal, electrical, and optical properties [4-14]. These nanocomposites are widely employed in the processing, textile, aerospace, automotive, biotechnology, pharmaceutical materials, electronics, electrical, mechanical and food industries. They are reported to be the materials of the 21st century due to the appearance of having a unique design and combinations of properties not found in conventional composites.

Polyvinyl alcohol (PVA) is a synthetic-artificial polymer obtained from polyvinyl acetate with a melting point of 180 to 190°C and a density of approximately 1300 kg/m^3 [15, 16]. The molecular weight of the PVA is between 20,000-400,000 g/mol, which depends on the degree of hydrolysis with a pH in the range of 5.0 to 6.5 (5% PVA solution) [17, 18]. It can be classified as a special synthetic polymer with biodegradable characteristics that do not show any negative impact on the environment [19-22]. PVA is a non-toxic, biocompatible, water-soluble, chemically stable, polymer that can also be formed into fibers [15, 19, 22, 23]. It has also an adhesive quality, good mechanical properties that strengthen textile yarn and paper, as well as improving resistance to oil and grease and shows excellent suitability for making thin films with metal oxide nanostructures [7, 22]. In recent years, the use of biodegradable materials such as PVA has increased in food industries, especially for food packaging applications that must protect food from deterioration due to the action of the external environment that contains microorganisms, humidity, gases, dust, odors as well as mechanical forces [5, 6, 24]. This will ultimately preserve the food product without any health concerns for the consumer. Due to all these properties, PVA is widely used in the food, pharmaceutical, medical, materials, textile and electronics-electrical industries [25-27].

In this era of nanotechnology, metal oxide nanoparticles are particularly important because they are chemically stable and able to resist oxidation. Metal oxide nanoparticles have lower densities than their metal counterparts, reducing the problem of irregular particles settling [28]. Hence, these materials are becoming vitally important for their applications in the synthesis of nanofluids and nanocomposites. Among metal oxide nanoparticles, the ZnO nanoparticle is a multifunctional material due to its unique physical and chemical properties. It has various applications in cosmetics, medicine and pharmacology (drug delivery), and the rubber, textile and electronics industries, in addition, it can also exhibit photocatalytic properties. [29]. ZnO is also registered as a potentially safe compound by the US Food and Drug Administration (FDA) and used by food industries as a supplement to the element zinc which has antimicrobial properties, which is an essential micronutrient for growth and development in humans and animals [6, 30-32]. Also, the silica-based nanocomposite demonstrates its potential to extend the shelf life of food products since it can act as a barrier against moisture, oxygen or other gases [33, 34]. SiO_2 in the chitosan film is used to preserve the quality of fresh food for extended periods since it delays the ageing of nanocomposite films [35, 36]. Thus, the combination of ZnO and SiO_2 nanoparticles can improve the strength, moisture, and oxygen barrier properties of these films [37]. Hence it will be beneficial to use a combination of ZnO and SiO_2 nanoparticles as a filler in nanocomposite films with a PVA matrix.

PVA-ZnO and PVA-SiO_2 nanocomposites are promising areas of research in recent years. The tensile strength of the PVA thin films prepared by the solution casting method has been reported to increase with the addition of ZnO and is also dependent on the film thickness [38]. These films were also established for their antibacterial properties which can benefit their use in food packaging applications [38, 39]. Aslam et al. found that 1% by weight of ZnO in the PVA matrix has shown a tensile strength of almost 45 MPa. These films can also be used in various applications such as UV protection and optoelectronic devices [40]. The effect of PVA-SiO_2 composite polymer coatings on wood substrates results in improved mechanical robustness of the substrate with super repellency to water [41]. It is also found that for a silica content of 20% by weight, the tensile strength increased by a factor of 1.9 compared to pure PVA. These films can be used in medical materials as a biomaterial, as this improved mechanical strength is also waterproofing properties [41]. Jia et al. prepared PVA-SiO_2 for very low silica contents in the PVA matrix and found a great enhancement in the mechanical properties of these films [42].

In this work, we have prepared PVA film using a solution casting method with ZnO, SiO_2, and ZnO+SiO_2 nanoparticles as a filler material. The effect of nanoparticle addition on the structural, water absorption, water solubility, and tensile strength of the films formed was investigated.

2. Experimental

2.1 Synthesis process

a. Synthesis of SiO_2 Nanoparticles

SiO_2 nanoparticles were synthesized using the sol-gel method with Tetraethoxysilane (TEOS) solution (1M) as a precursor [43]. The TEOS solution was dissolved in a mixture of 10 ml ethanol and 35 ml deionized (DI) water and stirred for 10 minutes. 1M HCl was added drop-wise into the above mixture and stirred magnetically for 50 minutes at 60°C until a white transparent homogeneous solution was formed. The solution was then maintained at room temperature for hours allowing a gel to form. The gel obtained was then dried in an oven for 6 hours at 110°C to obtain SiO_2 nanoparticles in the form of a white powder.

b. Synthesis of ZnO Nanoparticles

ZnO nanoparticles were synthesized using a co-precipitation method. Zinc acetate [$Zn(C_2H_3O_2)_2.2H_2O$, 0.1M] and sodium hydroxide [NaOH, 0.2M] solutions were prepared in DI water before being mixed and stirred continuously for 2 hours at 60°C. The liquid obtained was then centrifuged and washed with DI water and acetone several times to remove organic impurities. Finally, it was dried in an oven at 75°C for 6 hours to obtain ZnO nanoparticles [44].

c. Preparation of the nanocomposite film

The nanocomposite films were prepared to employ a solution casting technique [45]. PVA was dissolved in DI water and the solution was then heated and stirred at 80°C for 2 hours. The solid content of the PVA solution was maintained at 5% by weight. To form a PVA film a sufficient amount of solution was spread over a polycarbonate Petri dish and kept at room temperature for 48 hours. For the preparation of nanocomposite films, ZnO and SiO_2 nanoparticles (1 % by weight) were mixed with PVA solution and ultra-sonicated at 80°C for 1 hour. The solution was then spread over polycarbonate Petri dishes and kept at room temperature for 48 hours to obtain PVA nanocomposite films. Fig.1 shows the photograph of PVA and PVA based nanocomposite films.

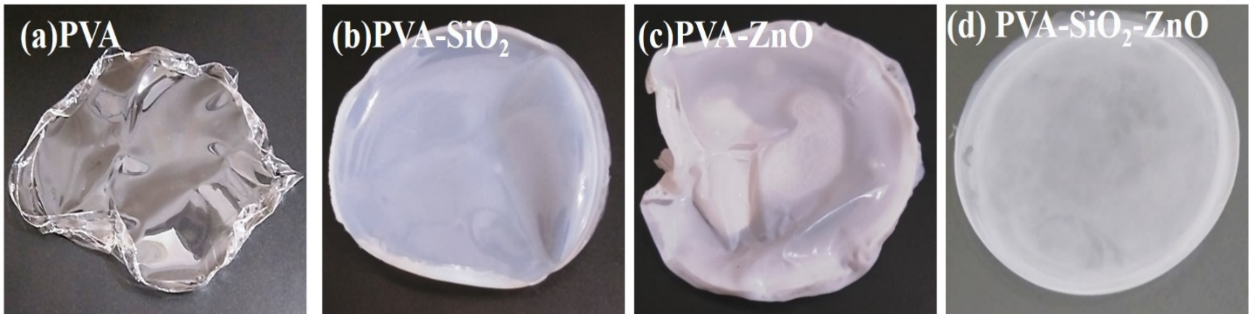

Figure 1. Photographs of the (a) polyvinyl alcohol (PVA) (b) PVA-SiO_2 (c) PVA-ZnO (d) PVA-SiO_2-ZnO composite films.

2.2 Characterization

The structural analysis of the as-synthesized nanoparticles and thin films was obtained by X-ray diffraction (Bruker AXS advanced, Cu-Kα-1.54Å). The surface morphology of the thin films was studied by using atomic force microscopy (AFM, NT-MDT Solver NEXT) in semi-contact mode. The FTIR spectra of the thin films were obtained by using Bruker ALPHA-E single reflection ATR (attenuated total reflection) spectrophotometer. For the water absorption and solubility test square pieces (10 mm × 10 mm) were cut from each film type of the prepared nanocomposite film. The initial weight (W_0) of each piece of film was then measured and immersed in DI water for 24 hours. After completion of immersion time, the weights of each film were measured (W_1). The degree of swelling or water absorption of each piece of sample film was calculated using equation 1 below.

$$\text{Water Absorption } (W_a) = (W_1 - W_0) / W_0 \tag{1}$$

After this, swelled pieces of sample film were dried at 60°C for 24 hours. The weight of the samples was measured (W_2) after drying and the water solubility of each piece of sample film was calculated as:

$$\text{Water Solubility } (W_s) = (W_0 - W_2) / W_0 \tag{2}$$

Strips of each film type 75 mm × 15 mm were prepared for tensile strength testing which was performed over a gauge length of 55 mm. The thickness of each type of prepared film was 0.125 mm, therefore the cross-sectional area (A_0) was 15 mm × 0.125 mm. The tensile strength (σ_{TS}) was calculated using equation 3, where the F_{max} is the maximum load.

$$\sigma_{max} = F_{max} / A_0 \tag{3}$$

3. Results and discussion

3.1 Structural analysis

Fig.2 (a) shows the XRD pattern of the ZnO and SiO_2 nanoparticles. A broad peak centred around 2θ=22.6° confirms the formation of amorphous SiO_2 nanoparticles [43]. The diffraction pattern of the ZnO nanoparticles is well-matched with the JCPDS card no.36-1451, which confirms the hexagonal wurtzite structure of pure ZnO. The average crystallite size of the ZnO nanoparticles was calculated as 18 nm by using the Debye-Scherrer formula [46].

The XRD patterns of PVA and nanocomposite films are shown in Fig.2(b). The three XRD peaks appear at 19.6°, 23.1°, and 41.2° related with the (100), (200), and (202) planes of the orthorhombic lattice which is the characteristics of the semicrystalline nature of the PVA [47]. The (101) and (200) peaks are merged, which also indicates that the crystalline phase is insufficient to make separate diffraction peaks [47]. The interplanar separation d, for the PVA film, is calculated as 4.403Å which is close to the previously reported result for the pure PVA film [48]. In nanocomposite films, the peaks of the PVA are still present in addition to the peaks of the metal oxide nanoparticles. This indicates that the crystalline phase of the PVA is not affected due to the embedding of nanoparticles into the polymer matrix. The peaks of the ZnO phase are observed in the XRD pattern, but the SiO_2 peak is merged with the PVA peak. PVA-SiO_2-ZnO nanocomposite films showed peaks for PVA and ZnO, but the presence of SiO_2 masked the peak intensities of ZnO nanoparticles.

Fig.3(a). shows the XRD data of the (101) plane of the PVA, which appears in the pure PVA and PVA based nanocomposite films. The area of the XRD peak increases and it becomes broad due to the addition of nanoparticles into the polymer matrix. It indicates that the crystallinity of the PVA reduces due to the addition of ZnO and SiO_2 nanoparticles.

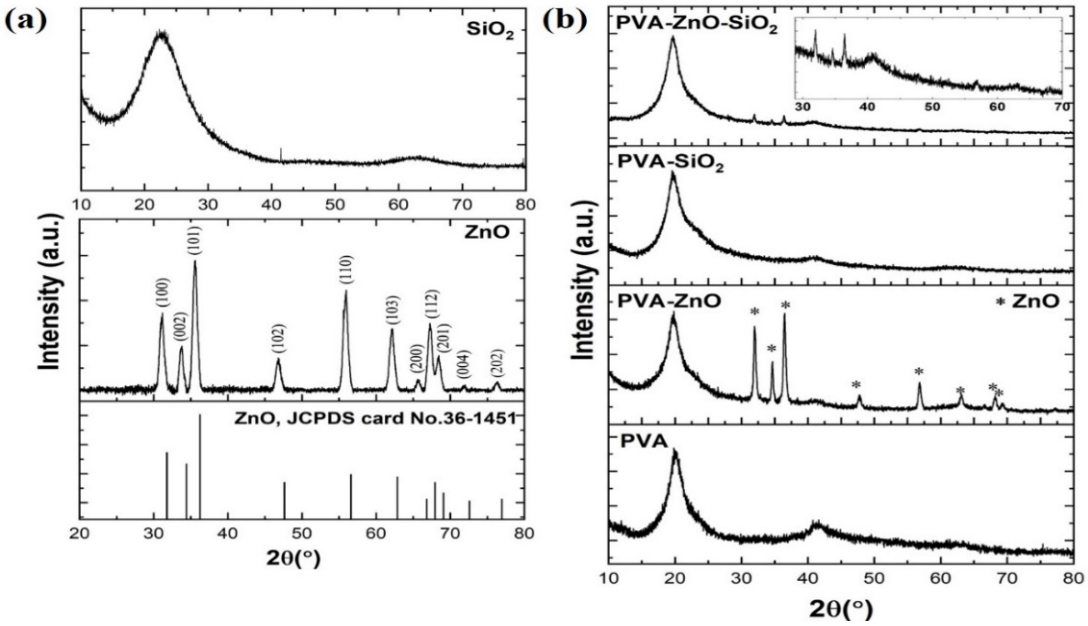

Figure 2. X-ray diffraction (XRD) patterns of (a) crystalline ZnO and amorphous SiO_2 nanoparticles, (b) Polyvinyl alcohol (PVA) and PVA-based nanocomposite films containing ZnO and SiO_2 nanoparticles.

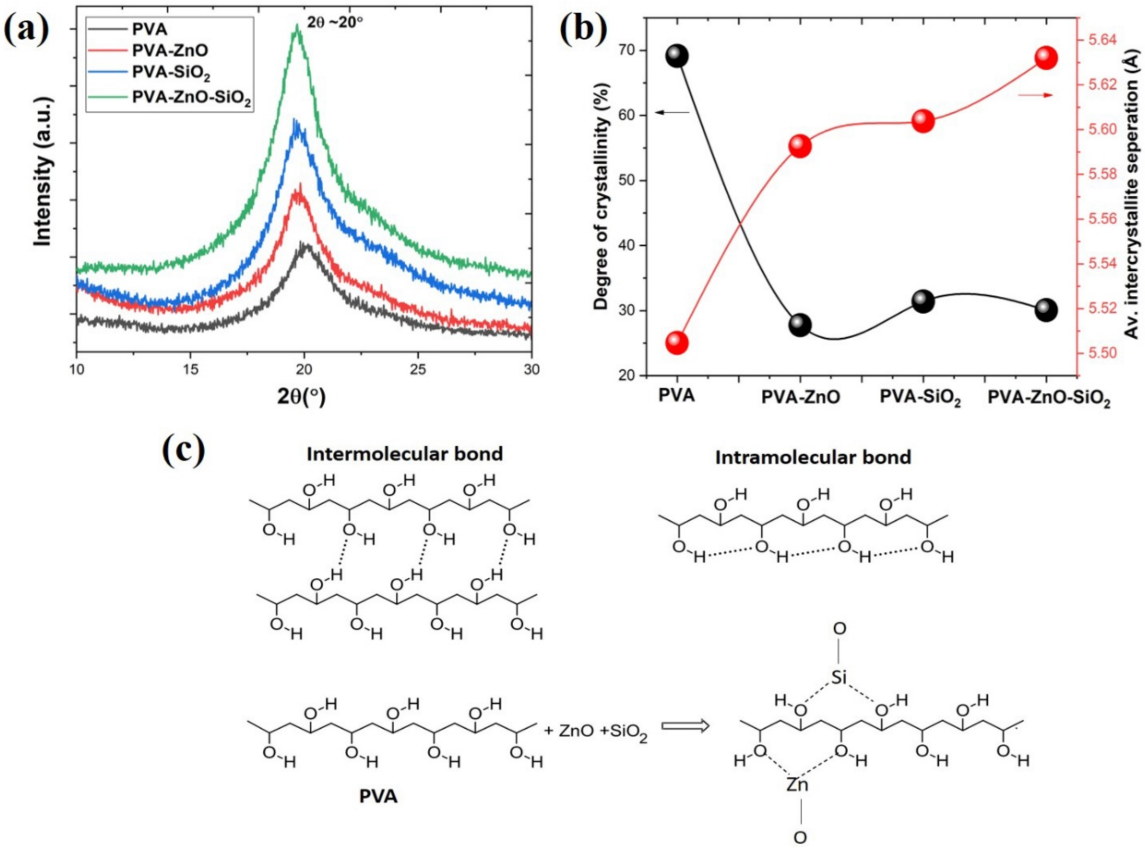

Figure 3. (a) Enlarged view of the X-ray diffraction (XRD) pattern between 2θ values of 10° and 30°, (b) Degree of crystallinity and average intercrystallite separation (R), and (c) Schematic representation of the PVA and its interaction with ZnO and SiO_2.

The average intercrystallite separation (R) can be calculated for the reflection peak around 2θ=20°, which corresponds to the position of maximum haloes by using mathematical relation given as [49]:

$$R = \frac{5\lambda}{8\sin\theta} \tag{4}$$

where, λ and θ is the X-ray wavelength (1.54Å) and Bragg's angle, respectively. The value of R increases due to the incorporation of ZnO and SiO_2 nanoparticles in the polymer matrix [Fig.3(b)]. The degree of crystallinity is an important parameter used to explain various properties of the PVA film [49]. The degree of the crystallinity (C) of a polymer sample is defined as the ratio of the area under the crystalline peak to the total area of the peak. The degree of crystallinity is calculated as 69.1%, 27.76%, 31.4%, and 29.95% for the pure PVA, PVA-ZnO, PVA-SiO_2, and PVA-ZnO-SiO_2 films, respectively. Thus, the incorporation of ZnO and SiO_2 nanoparticles in the

PVA matrix results in a change in the structural properties of PVA. Fig.3(c) shows a schematic representation of the structure of the PVA polymer and its interaction with nanoparticles. There are two types of hydrogen bonds present in the PVA: intermolecular and intramolecular. The semicrystalline nature of the PVA is attributed to the intermolecular bonding between two PVA chains through hydrogen bonding. When nanoparticles are embedded with the polymer, the hydroxyl group is attached to the nanoparticles and reduces the extent of hydroxyl intermolecular bonding between the polymer chains.

Fig.4 shows the FT-IR spectra of pure PVA, PVA-SiO_2, PVA-ZnO, and PVA-SiO_2-ZnO films. The broadband observed nearly at 3250 cm^{-1} in all the films is due to the (O-H) group from the intermolecular and intramolecular hydrogen bonds. The band nearly at 2915 cm^{-1} shows (C-H) from alkyl groups, while peaks nearby to 2920 and 2850 cm^{-1} show (C-H_2) asymmetric and symmetric stretching respectively which can be seen in PVA-SiO_2, PVA-ZnO, and PVA-SiO_2-ZnO films [38]. The peaks around 1705 cm^{-1}, 1422 cm^{-1}, 1415 cm^{-1}, and 1080 cm^{-1} are related to the C=O, C-H_2, C-C stretching, and C-O-C stretching bond of the PVA acetyl group respectively [38]. The peak at about 558 cm^{-1} shows the presence of ZnO nanoparticles in the PVA. Peak close to 1028 cm^{-1} were observed in the PVA-SiO_2 film and relate to the antisymmetric stretching vibration of (Si-O-Si), which corresponds to the presence of SiO_2 [38]. Also, a strong peak at 1083 cm^{-1} shows the overlapping of asymmetric stretching of (Si-O-Si) and (Si-O-C) [36]. The (O-H) bond peak of PVA around 3250 cm^{-1} was considerably reduced for the PVA-SiO_2 film when SiO_2 was added in the PVA, indicating intermolecular interactions between (O-H) group of PVA and SiO_2 [38].

Fig.5 (a-d) shows the AFM image (2µm x 2µm) of the PVA and nanocomposite films. It shows the structural arrangement of the PVA molecular chain, which depends mostly on the film preparation method. The PVA film shows a smooth, uniform and homogenous surface morphology. The RMS roughness for the PVA film is calculated as 0.92nm. It can be observed that the roughness of the composite films increases due to the incorporation of nanoparticles in the PVA base matrix (Fig.6). The AFM images of the composite films clearly show the presence of nanoparticles in the PVA matrix. The increase in the roughness of the composite film when compared to the PVA indicates a high rate of agglomeration of nanoparticles in localized areas attributed to strong interactions between the nanofillers and the base matrix. Additionally, it may be due to the processing conditions [48].

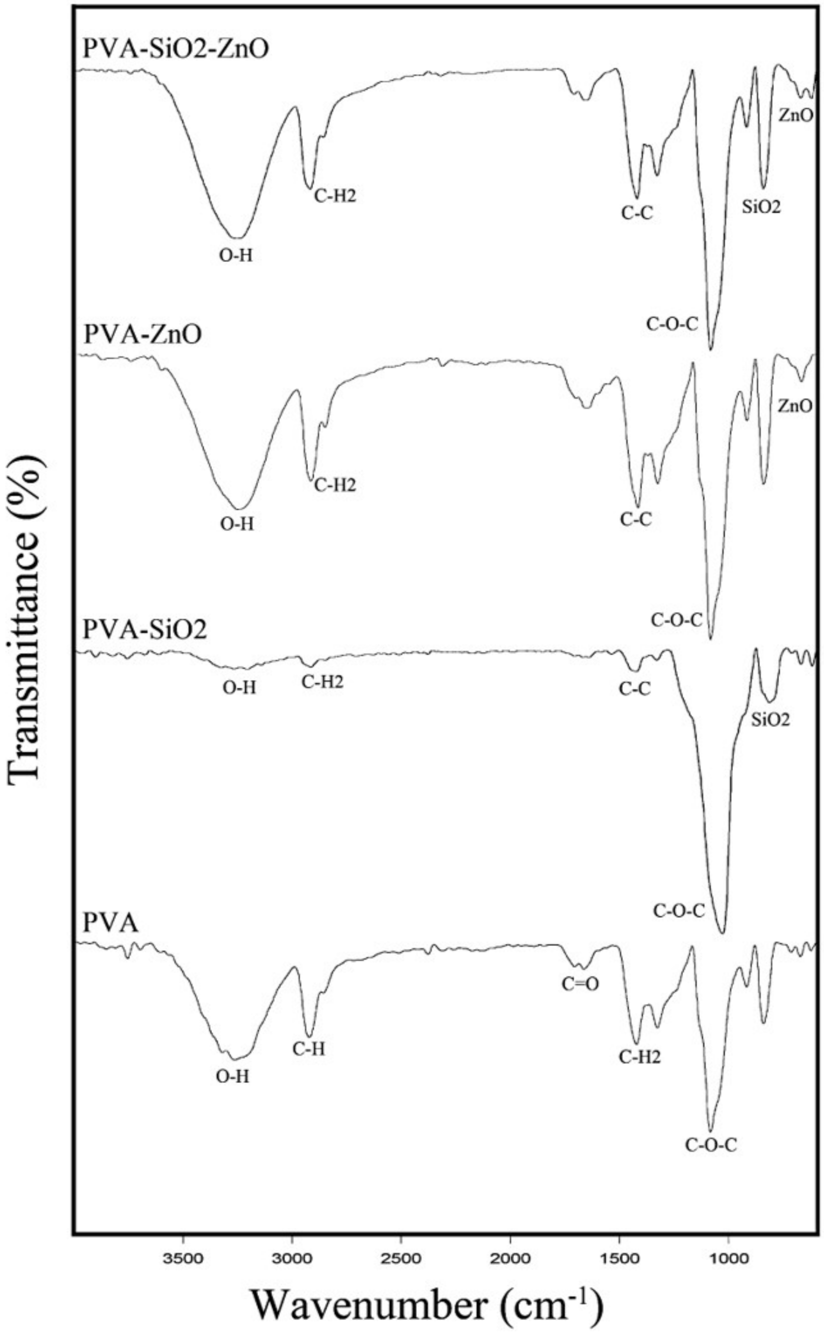

Figure 4. FTIR spectra of polyvinyl alcohol (PVA) and PVA-based nanocomposite films containing SiO_2, ZnO and SiO_2 & ZnO nanoparticles.

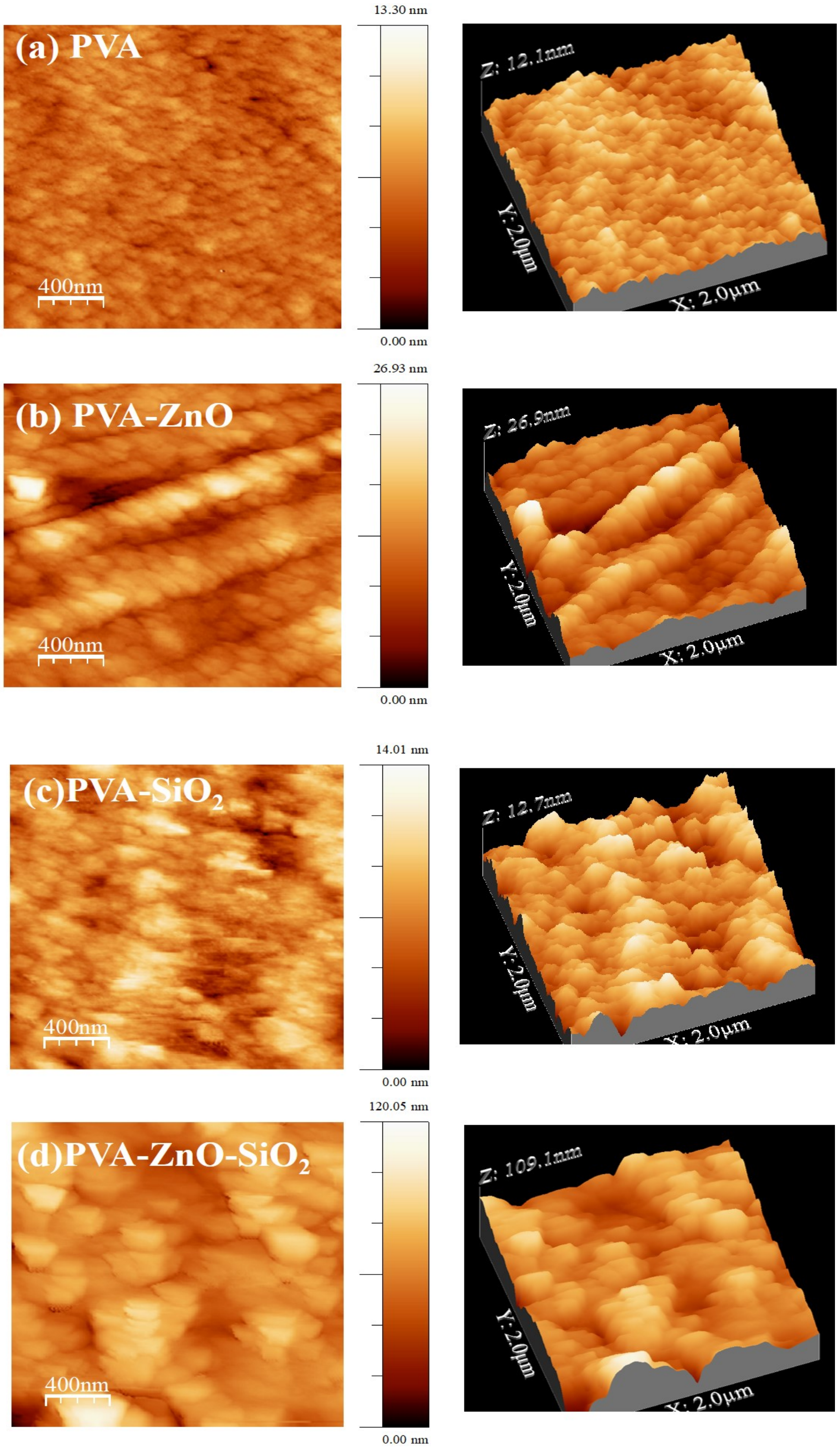

Figure 5. Atomic force microscopy (AFM) images (2µm x 2µm) of the (a) Polyvinyl alcohol (PVA) (b) PVA-ZnO, (c) PVA-SiO_2, and (d) PVA-ZnO-SiO_2 films.

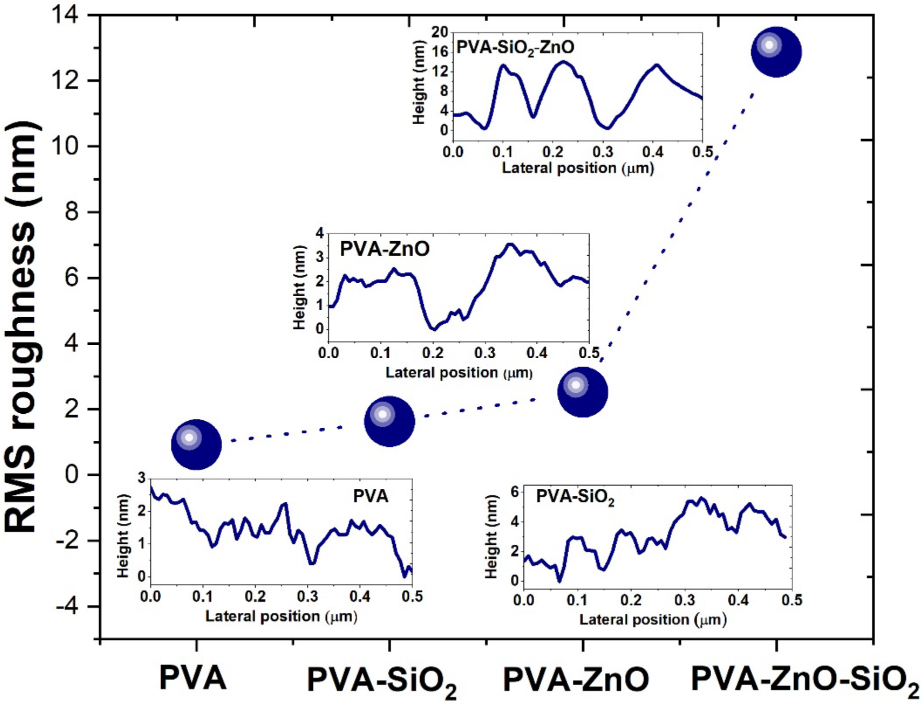

Figure 6. Root mean square (RMS) roughness of the Polyvinyl alcohol (PVA) and PVA-based composite films containing SiO_2, ZnO and SiO_2 & ZnO nanoparticles with the line scan along the x-axis.

3.2 Water absorption and water solubility test

Water or moisture absorption and water solubility of polymeric films are important for a variety of industries ranging from microelectronics, adhesives, coatings, and food industries. For these tests (10 mm × 10 mm) pieces of the sample, were cut from each type of nanocomposite film prepared.

Fig.7 shows the water absorption and water solubility of the PVA and PVA-based composite films which are summarized in Table-1. It is observed that the water absorption, as well as water solubility of pure PVA film, was found to be highest. Over the time stipulated the pure PVA film absorbed the maximum amount of water compared to composite films and caused swelling and a change in the shape of the film. Similarly, nearly 80% of pure PVA film was dissolved in water, because the PVA is a water-soluble polymer. Generally, when material films have high a water absorption ability (W_a), they dissolve (W_s) more readily. This is attributed to the absorption of water molecules, promoted by hydrogen bonding, onto hydroxyl groups. Hence, it can be seen from Table 1 that, W_a and W_s of all types of nanocomposite films have shown a very similar overall trend. The PVA-ZnO film had the second-highest values of water absorption as well as water solubility, while the PVA-ZnO-SiO_2 film showed moderate values of water absorption as well as water solubility. PVA-SiO_2 shows the lowest values for water absorption as well as water solubility compared to other films.

The decrease in water absorption capacity was due to the increase in interfacial adhesion between the PVA matrix and nanoparticle fillers. The presence of SiO_2 and ZnO nanoparticles provided a barrier to the passage of water [41]. An increase in water absorption of the PVA-ZnO film compared to the PVA-SiO_2 film indicates a more hydrophilic nature of ZnO compared to SiO_2 nanoparticles. The decrease in moisture or water absorption of the composite films with nanoparticles is mainly due to hydrogen bonding between nanoparticles and PVA [50]. Nanoparticles strongly interacted with the PVA matrix, forming a more compact film that reduced the moisture or water absorption of the material, as strong interaction leads to a lower number of hydroxyl groups within the nanocomposite films. Better distribution of nanoparticle fillers in the polymer matrix gives greater water barrier properties, while agglomeration of nanoparticles at a higher amount of incorporation of fillers may result in increased water absorption.

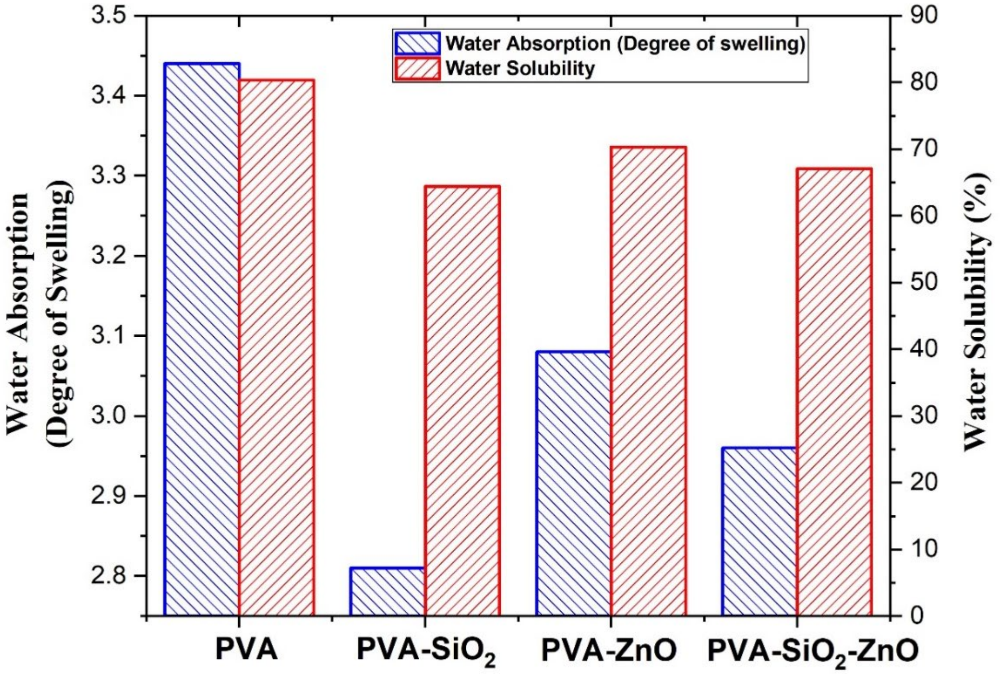

Figure 7. Water Absorption and Water Solubility data of the Polyvinyl alcohol (PVA) and PVA-based composite films containing SiO_2, ZnO and SiO_2 - ZnO nanoparticles.

3.3 Tensile strength measurement

The tensile test was carried out to measure the maximum load that each type of prepared nanocomposite film can withstand. Factors affecting the tensile properties include (i) the presence of additives, impurities, or fillers, (ii) environmental conditions such as temperature, humidity, and (iii) physical properties including geometric size and shape, orientation, morphology, crystallinity and surface condition. The importance of specific tensile properties of a nanocomposite film is directly related to a product requirement or design specification.

The mechanical properties of nanocomposites are influenced by factors including dispersion, particle surface area, and the intermolecular interactions of different functional groups present in the matrix and filler of the composites [49]. Generally, the incorporation of nanoparticles improves the tensile strength of the materials. Initially, the tensile strength of pure PVA was measured which showed a breaking load of nearly 71.2 N with a breaking load of 37.97 MPa. For the PVA-ZnO film, a breaking load and tensile strength of 80.9 N and 43.14 MPa was obtained, respectively. The increase in tensile strength of the PVA-ZnO film was 14 % compared to the pure PVA film. The PVA-SiO_2 film showed a breaking load of nearly 87.4 N and tensile strength of nearly 46.61 MPa. The increase in tensile strength of the PVA-SiO_2 film was approximately 23 % as compared to pure PVA film. Among all the films, PVA-ZnO-SiO_2 showed the highest tensile strength nearly 63.14 MPa and this film required the greatest load of all the films to break it completely, which was nearly 118.4 N. The increase in tensile strength for PVA-ZnO-SiO_2 was approximately 66 % in comparison with the pure PVA film. Hence, the incorporation of both types of nanoparticles in the matrix caused the highest increment in tensile strength. The variation of mechanical properties of different nanocomposite films is shown in Fig.8. This is due to the molecular level dispersion of nanosized ZnO and SiO_2 in the PVA polymer matrix, and their strong interfacial adhesion attributed to the hydrogen bonding Fig.3(c) [38]. Hence a strong interaction between the base matrix and nanoparticle filler enhances the tensile strength of the films.

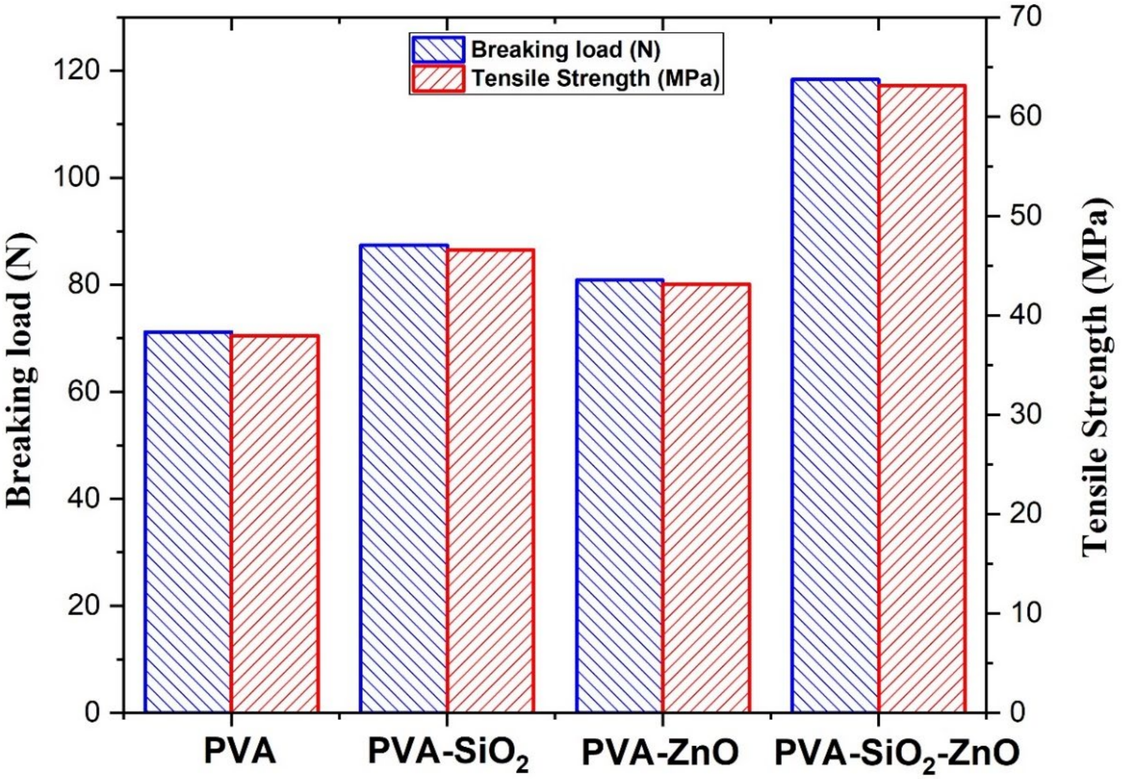

Figure 8. Breaking load and tensile strength of the polyvinyl alcohol (PVA) and PVA-based composite films containing SiO_2, ZnO and SiO_2 - ZnO nanoparticles.

Table 1. Results obtained from the structural, water absorption/solubility, and mechanical properties of the PVA and PVA based nanocomposite films.

Sample	**Structural properties**				**Water absorption/Solubility**		**Mechanical properties**	
	2θ (°)	**R (Å)**	**C (%)**	**RMS (nm)**	**Water Absorption (W_a) (%)**	**Water solubility (W_s) (%)**	**Breaking Load (N)**	**Tensile strength (MPa)**
PVA	20.14	5.504	69.12	0.921	3.44	80.33	71.2	37.97
PVA-ZnO	19.82	5.592	27.76	1.629	2.81	64.4	87.4	46.61
PVA-SiO_2	19.78	5.603	31.42	2.522	3.08	70.31	80.9	43.14
PVA-ZnO-SiO_2	19.68	5.632	29.95	12.87	2.96	67.04	118.4	63.14

4. Conclusions

In summary, we have synthesized the PVA and PVA-based nanocomposite film by using the solution film casting technique. For the nanocomposite film, filler nanoparticles of ZnO and SiO_2 were synthesized by chemical co-precipitation and sol-gel methods, respectively. The structural analysis confirms the formation of ZnO and SiO_2 without any impurity phase with an average crystallite size of 18 nm for ZnO. XRD patterns of all nanocomposite films show many additional peaks compared to pure PVA film, which is associated with ZnO and SiO_2 fillers in the nanocomposites. The morphology analysis shows that the PVA film was smoother compared to the remaining film and the incorporation of nanoparticles in the PVA base matrix tends to increase the roughness of the film. FT-IR analysis showed that intermolecular hydrogen bonds were formed between filler ZnO, SiO_2 nanoparticles and PVA matrix and no other impurities were present in the material. The addition of both types of nanoparticles in the PVA matrix tends to reduce water absorption as well as the water solubility capability of the material compared to pure PVA film. The maximum reduction was observed for PVA-ZnO-SiO_2 nanocomposite films. A remarkable increment in the tensile strength was found for all types of nanocomposite films. The tensile strength was enhanced by 14%, 23%, and 66% for the PVA-ZnO, PVA-SiO_2, and PVA-ZnO-SiO_2 film as compared to the pure PVA film. These films can be used in mechanical and material applications due to their mechanical robustness. The biodegradability, non-toxicity, and antimicrobial properties of these materials have been established already, hence there are no harms in using these films in medical, pharmaceutical and food industry applications.

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