

Effect of Vanadium Pentoxide on the Mechanical, Thermal, and Electrical Properties of Poly(vinyl alcohol)/Vanadium Pentoxide Nanocomposites

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ABSTRACT: In this study, we examined the effect of vanadium pentoxide (V_2O_5) on the mechanical, thermal, and morphological properties of poly(vinyl alcohol) (PVA)/ V_2O_5 nanocomposites. The PVA/ V_2O_5 nanocomposites were prepared by solution mixing, followed by film casting. The results show that the Young's moduli of the resulting nanocomposites films were higher than the pure PVA modulus with increasing V_2O_5 content, and it reached a maximum point at about 0.4 wt % V_2O_5 content at 8.55 GPa. The tensile strength and stress at break increased with increasing V_2O_5 content. The addition of V_2O_5 did not affect the melting temperature. The crystallization temperatures of PVA were significantly changed with increasing V_2O_5 content. The 5% weight loss degradation temperature of the nanocomposites was measured by thermogravimetric analysis. The degradation temperatures of the V_2O_5 nanocomposites increased with increasing filler content and were higher than the degradation

temperature of pure PVA; this showed a lower thermal stability compared to those of the nanocomposites. The results show that the thermal stability increased with the incorporation of V_2O_5 nanoparticles. The dielectric constant of PVA had a tendency to improve when the dispersion of particles was effective. The morphology of the surfaces the nanocomposites was examined by scanning electron microscopy. We observed that the dispersion of the V_2O_5 nanoparticles was relatively good; only few aggregations existed after the addition of the V_2O_5 nanoparticles at greater than 0.4 wt %. In perspective, the addition of 0.4 wt % V_2O_5 nanoparticles into PVA maximized the mechanical, thermal, and electrical properties. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 121: 2870–2876, 2011

Key words: mechanical properties; nanocomposites; thermal properties

INTRODUCTION

The use of inorganic fillers is a common practice in the plastics industry to improve some properties of the thermoplastics, such as the heat distortion temperature, mechanical properties, thermal stability, and flame retardance.^{1–8} The effects of fillers on the mechanical, thermal, and other properties depend strongly on the filler's nature, shape, particle size, aggregate size, surface characteristics, and degree of dispersion in the polymer.^{1,9–11} Poly(vinyl alcohol) (PVA) is the largest synthetic water-soluble polymer produced in the world. It is prepared by the hydro-

lysis of poly(vinyl acetate). The degree of solubility, the biodegradability, and other physical properties can be controlled by the variation of the molecular weight and the degree of hydrolysis (saponification) of the polymer. Indeed, the chemical characteristics of these polymers, for example, the reactivity of the numerous hydroxyl groups depends strongly on the residual acetyl group content and the degree of hydrolysis.¹² PVA was chosen for this study as it exhibits a high tensile strength, good flexibility, and high thermal and chemical stability and is widely used in applications for sizing processes of the textile industry and paper coatings.¹³

Chae and Kim¹⁴ prepared polystyrene (PS)/zinc oxide (ZnO) nanocomposites by solution mixing and investigated the effects of ZnO nanoparticles on the physical properties of PS. They found that the thermal stability of PS was enhanced with increasing ZnO content. Peng and Kong¹⁵ studied the thermal degradation mechanism of PVA/silica (SiO_2) nanocomposites. The PVA/ SiO_2 nanocomposites, similar

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to the pure PVA, thermally degraded in a two-step degradation in the temperature ranges 300–450 and 450–550°C, respectively. However, the introduction of SiO₂ nanoparticles led to a remarkable change in the degradation mechanism.

Mahmoud et al.¹³ investigated the effect of nanoscale vanadium pentoxide (V₂O₅) on the conductivity and mechanical properties of PVA. The V₂O₅ nanoparticles were well dispersed and uniform in shape and the diameter of the particles was confined to within 8 nm. The addition of small amounts (0.2–1 wt %) of nanoparticulate V₂O₅ to PVA increased the electrical conductivity and the modulus of elasticity. Tang et al.¹⁶ prepared several starch/PVA/nano-SiO₂ biodegradable blend films by a solution casting method. The physical and biodegradable properties of these films were also studied. From the results, the nano-SiO₂ content about 2.5 wt% (SPS5) was found to have the best tensile strength at about 15.0 MPa, and its elongation at break was 120%. With increasing nano-SiO₂ content, the water resistance of the films also improved. Additionally, SPS5 had the best optical transparency of all of the films. Moreover, the results indicate that an intermolecular hydrogen bond and a chemical bond (C—O—Si) were formed in the nano-SiO₂ and starch/PVA. Therefore, the miscibility and compatibility between starch and PVA increased, and the physical properties of the additional nano-SiO₂ improved.

In this study, we examined the influence of the effect of nanoscale V₂O₅ on the mechanical, thermal, and electrical properties of the PVA/V₂O₅ nanocomposites. The PVA/V₂O₅ nanocomposites with various concentrations of V₂O₅ were prepared by a solution casting method. The different aspects of results were examined further from Mahmoud et al.,¹³ and the results of the thermal properties were used to explain the phenomenon in the mechanical properties.

EXPERIMENTAL

Materials

PVA, with a molecular weight range of 77,000–82,000, was obtained from Ajax Finechem, Australia. The melting temperature (T_m) of PVA was around 214°C. V₂O₅, in the form of an orange powder with an average particle size of 42 nm, was purchased from Fluka, USA. The water used was deionized water.

Sample preparation

The nanocomposites of PVA/V₂O₅ were prepared with a solvent casting method at various compositions. Deionized water was used as a solvent. Amounts of V₂O₅ nanoparticles and PVA were dis-

solved in deionized water at various desired compositions by a hot-plate stirrer at 90°C for 3 h with vigorous stirring to give a viscous transparent polymer nanocomposite solution. The V₂O₅ contents were 0, 0.2, 0.4, 0.6, 0.8, and 1.0 wt % on the basis of PVA. The solutions were cast on a glass plate and left for 1 h to dry in a dry atmosphere at room temperature. The samples were transferred to an electric oven held at 110°C for 3 h to completely remove any residual water. The range of sample thicknesses was 0.07–0.12 mm.

Sample characterization

Tensile tests were conducted according to ASTM D 882-2 (ISO 527-3) with a universal tensile testing machine (LR 50K, Lloyd Instruments, UK). The tensile tests were performed at a crosshead speed of 5 mm/min. Each value obtained represented the average of five samples.

Thermogravimetric analysis thermograms were obtained with a Diamond thermogravimetric/differential thermal analyzer, PerkinElmer, USA. The sample weights were 2–5 mg. The temperature range was 50–800°C at a heating rate of 10°C/min with a nitrogen purge flow rate of 50 mL/min.

Differential scanning calorimetry (DSC; model DSC, Pyris I, PerkinElmer) was performed to investigate the crystallization and melting behaviors of the nanocomposites. The heating (and cooling) rate used was 10°C/min in a nitrogen atmosphere for both the heating and cooling scans. The crystallinity for unfilled PVA and the PVA matrix of the PVA/V₂O₅ nanocomposites were calculated according to the DSC data from the heating scan. The T_m , crystallization temperature (T_c), and glass-transition temperature (T_g) values of PVA for the different nanocomposites were measured.

The dielectric properties of the PVA/V₂O₅ nanocomposites were obtained via the capacitance method, and they were measured at room temperature and 1 V with an Agilent E 4980A Precision LCR meter, USA. The specimen size was 1.5 × 1.5 (cm).

Scanning electron microscopy (SEM) was used to study the morphology of the surface of the PVA/V₂O₅ nanocomposites and to evaluate the dispersion quality of the V₂O₅ nanoparticles. All specimens were coated with gold before the SEM study.

RESULTS AND DISCUSSION

Effect of V₂O₅ on the mechanical properties

The tensile strength and percentage increase in the tensile strength for the PVA/V₂O₅ nanocomposites as a function of composition are shown in Figures 1 and 2. The data were compared with results from

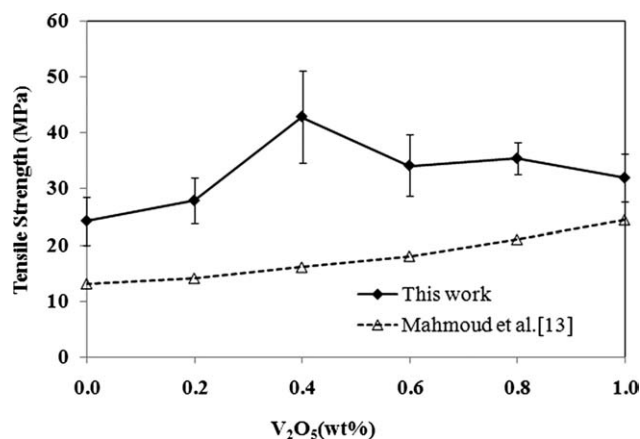


Figure 1 Tensile strength of the pure PVA and PVA/ V_2O_5 nanocomposites at various contents of V_2O_5 .

Mahmoud et al.,¹³ who used a lower molecular weight PVA (17,000 Da) and lower nanoparticle size (8 nm). The values of the percentage increase in tensile strength increased with increasing V_2O_5 content; hence, V_2O_5 enhanced the percentage increase in the tensile strength of PVA specimens prepared by solution mixing. The data from Mahmoud et al.¹³ showed the same tendency as our data. However, the Mahmoud et al.¹³ nanocomposite did not show a maximum, but our results showed a maximum at 0.4 wt % V_2O_5 . This might have been due to the different nanoparticle sizes and the different characteristics of the molecules after they were mixed with nanoparticles.

The dependence of the Young's modulus on the V_2O_5 content of the nanocomposites films is shown in Figure 3. The Young's modulus of the PVA film was 2.72 GPa. When the V_2O_5 was added to the PVA matrix, the Young's modulus of the resulting

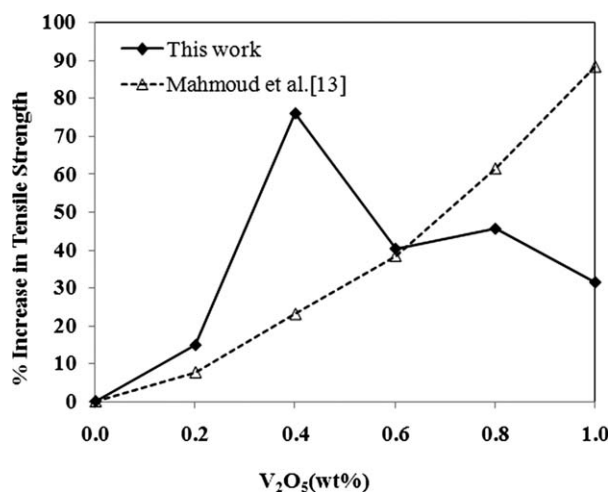


Figure 2 Percentage increase in the tensile strength of the pure PVA and PVA/ V_2O_5 nanocomposites at various contents of V_2O_5 .

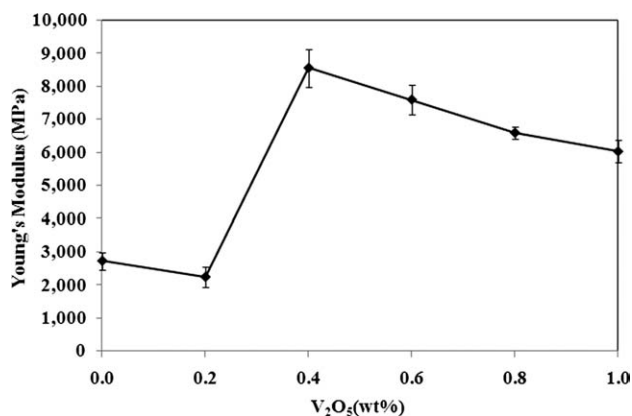


Figure 3 Young's modulus of the pure PVA and PVA/ V_2O_5 nanocomposites at various contents of V_2O_5 .

nanocomposites film increased over the pure component modulus with increasing V_2O_5 content. The Young's modulus reached a maximum point at about 0.4 wt % V_2O_5 content and reached 8.55 GPa. When the V_2O_5 content exceeded 0.4 wt %, the Young's modulus of the nanocomposites film decreased with increasing V_2O_5 content, but it was still much higher than that of the pure PVA film. The remarkable increase in the Young's modulus of the nanocomposites films indicated the presence of intermolecular interactions between V_2O_5 and PVA in the nanocomposites films.¹⁶ Unfortunately, Mahmoud did not give the absolute value of his Young's modulus. However, the trend of the Young's modulus could be compared. In the Mahmoud et al.¹³ study, the Young's modulus steadily increased when the amount of V_2O_5 increased without any maxima in the range 0–1 wt % V_2O_5 . The differences in the trends might have occurred because of the differences in the size of the nanoparticles and the different characteristic of molecules after they were mixed with nanoparticles.

The dependence of the stress at break and percentage increase in the stress at break on the V_2O_5 content of the nanocomposites films is shown in Figures 4 and 5. The percentage increase in the stress at break of the nanocomposites film increased along with increasing V_2O_5 content. However, a significant enhancement in the stress at break was achieved when 0.4 wt % V_2O_5 was introduced. A similar trend between the stress at break and the tensile strength was found. Moreover, in Mahmoud et al.'s¹³ study, the stress at break showed an increase in value when the percentage of nanoparticles increased, the same as our results. However, for the tensile strength, the data of Mahmoud et al.¹³ did not show maxima at a certain level of nanoparticles like our results, and the causes might have been the same.

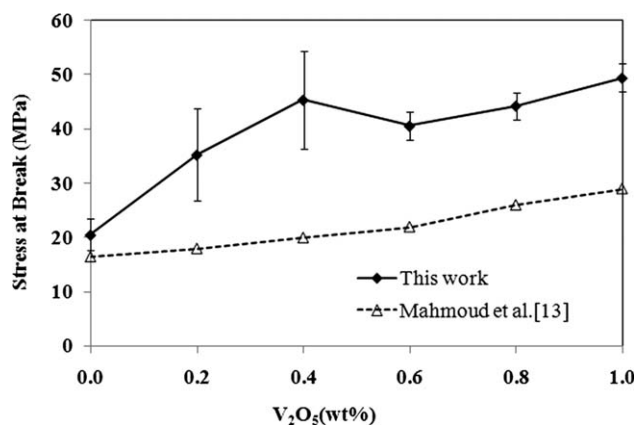


Figure 4 Stress at break of the pure PVA and PVA/V₂O₅ nanocomposites at various contents of V₂O₅.

Effect of V₂O₅ on the thermal properties

The T_m values of the pure PVA and PVA/V₂O₅ nanocomposites at various filler contents is presented in Table I. The results show that the T_m 's were not significantly changed when V₂O₅ was incorporated into the polymer matrix; this implied that the quality and type of the crystal of PVA were not affected by the nanoparticles. The DSC curve of T_m for the PVA/V₂O₅ nanocomposites is shown in Figure 6.

T_c is the temperature at which the PVA in the nanocomposites started to crystallize during the cooling ramp in DSC after complete melting at a higher temperature. In Table I, the T_c values at a cooling rate of 10°C/min of the pure PVA and PVA/V₂O₅ nanocomposites are compared. The addition of V₂O₅ had a significant effect in decreasing the T_c values of the PVA/V₂O₅ nanocomposites about 11–21°C from the pure PVA. In other words, the T_c 's of PVA were significantly changed with

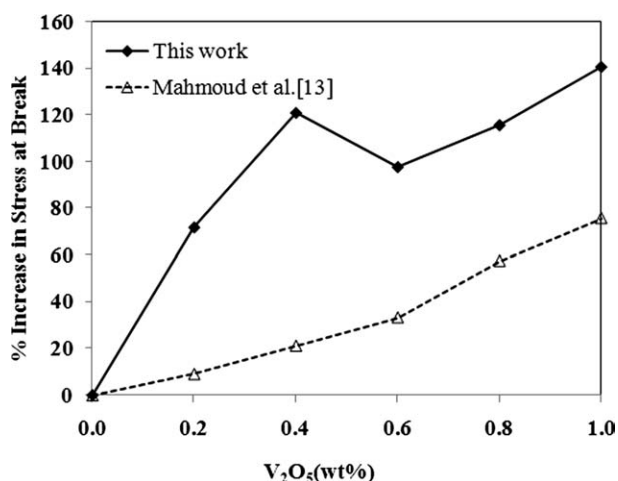


Figure 5 Percentage increase in the stress at break of the pure PVA and PVA/V₂O₅ nanocomposites at various contents of V₂O₅.

TABLE I
Values of T_m and T_c of the PVA/V₂O₅ Nanocomposites at Various V₂O₅ Contents

Sample	T_m (°C)	T_c (°C)	T_g (°C)	Crystallinity (%)	X_c (%)
Pure PVA	214.1	176.7	83.6	46.6	46.6
0.2 wt % V ₂ O ₅ /PVA	213.6	165.7	84.7	31.0	38.7
0.4 wt % V ₂ O ₅ /PVA	213.8	167.6	89.9	26.3	43.8
0.6 wt % V ₂ O ₅ /PVA	212.8	158.1	82.9	22.9	57.3
0.8 wt % V ₂ O ₅ /PVA	211.8	145.7	84.0	16.8	83.8
1.0 wt % V ₂ O ₅ /PVA	211.4	156.2	83.5	15.5	—

increasing V₂O₅ content. This implied that the nanoparticles affected the movement of the PVA molecules and made them harder to crystalline, so T_c moved to the lower values. This might have been due to the V₂O₅ nanoparticles inserted into the PVA chains; therefore, the nanoparticles might have impeded the molten PVA chain movement and made PVA more difficult to crystallize. The impeding process tended to increase when the amount of nanoparticles increased; thus, the crystalline temperatures were lower than that of the pure PVA. The DSC curve of T_c for the PVA/V₂O₅ nanocomposites is presented in Figure 7.

The degree of crystallinity (X_c) was determined from the enthalpy evolved during crystallization with the following equation:¹⁷

$$X_c(\%) = \frac{\Delta H_c}{(1 - \phi)\Delta H_m} \times 100 \quad (1)$$

where ΔH_c is the apparent enthalpy of crystallization, the extrapolated value of the enthalpy corresponding to the melting of a 100% crystalline sample (ΔH_m) is 138.6 J/g, and ϕ is the weight fraction of the V₂O₅ nanoparticles in the nanocomposites. The X_c values of the pure PVA and PVA/V₂O₅ nanocomposites at various filler contents are shown

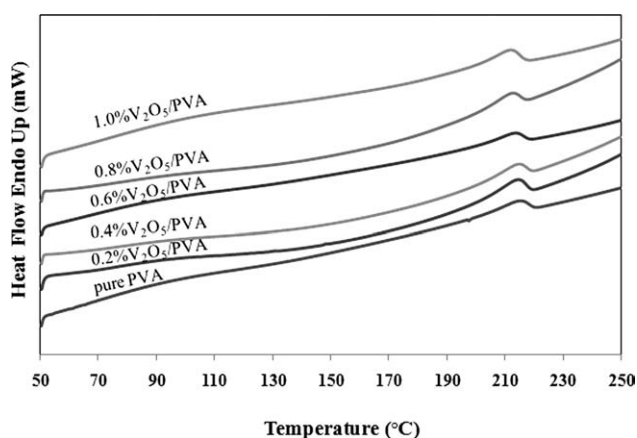


Figure 6 DSC curves of T_m for the pure PVA and PVA/V₂O₅ nanocomposites at various contents of V₂O₅.

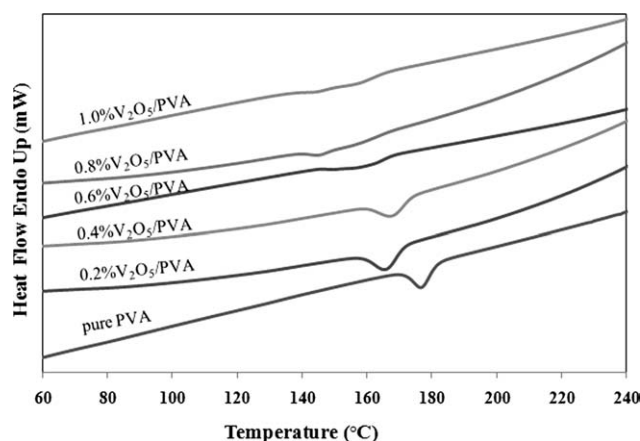


Figure 7 DSC curves of T_c for the pure PVA and PVA/ V_2O_5 nanocomposites at various contents of V_2O_5 .

in Table I. X_c of the PVA nanocomposites decreased with increasing V_2O_5 content.

The percentage crystallinity values of the pure PVA and PVA/ V_2O_5 nanocomposites at various filler contents are shown in Table I. The addition of V_2O_5 significantly decreased the percentage crystallinity of the PVA/ V_2O_5 nanocomposites about 7–34% from the pure PVA. In other words, the percentage crystallinity of PVA significantly changed with increasing V_2O_5 content. Because V_2O_5 was a poor conductor for heat, it greatly affected the heat transfer during crystallization and, therefore, retarded the crystallization. Furthermore, when V_2O_5 was homogeneously distributed within the PVA matrix, it acted as a barrier; this may have restricted the PVA molecular chains' thermal motion to form crystals and, consequently, delayed the overall crystallization process.¹⁷

The T_g values of the pure PVA and PVA/ V_2O_5 nanocomposites at various filler contents is presented in Table I. T_g of the pure PVA film was 83.59°C. The T_g 's of the PVA/ V_2O_5 nanocomposites increased higher than pure PVA T_g when the V_2O_5 content increased. T_g reached a maximum point at about 0.4 wt % V_2O_5 content; then, the T_g values decreased slightly along with increasing V_2O_5 content. The higher T_g showed the stiffness of the amorphous part of the PVA. This implied that at 0.4 wt % V_2O_5 , the amorphous part of the nanocomposite had the highest stiffness of the molecules. The stiffness of the molecules resulted in higher mechanical properties at this composition. That is why the Young's modulus, tensile strength, and stress at break showed maxima at 0.4 wt % V_2O_5 . However, the stiffness in the molecules or the high T_g did not persist at higher levels of V_2O_5 . This might have been because of the tendency toward agglomeration of the nanoparticles at higher levels of V_2O_5 , so the effects from the nanoparticles were reduced, and the stiffness decreased.

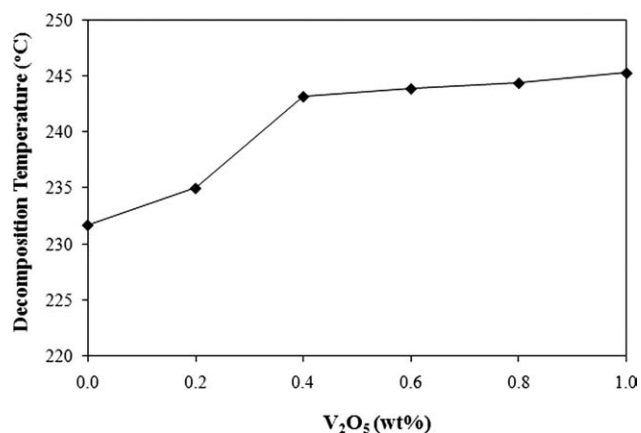


Figure 8 Decomposition temperatures of the pure PVA and PVA/ V_2O_5 nanocomposites at various contents of V_2O_5 .

The effect of V_2O_5 on the degradation temperature of all of the nanocomposites is shown in Figure 8. The degradation temperature was measured by thermogravimetric analysis and was noted at 5% weight loss. The degradation temperature of the V_2O_5 nanocomposites increased with increasing filler content and was higher than the degradation temperature of pure PVA; this showed that pure PVA had a lower thermal stability than the nanocomposites. The increase in the decomposition temperatures might have resulted from the amount of V_2O_5 cooperated that finally affected the thermal stability of the nanocomposites,¹⁸ and V_2O_5 was an inorganic material that exhibited heat resistance, and so the presence of V_2O_5 retarded the thermal degradation or delayed the thermal degradation of the nanocomposites.¹⁹

Effect of V_2O_5 on the electric properties

The dependency of the dielectric constant of the PVA/ V_2O_5 nanocomposites on the filler content is shown in Figure 9. The results found that the dielectric constant increased with increasing V_2O_5 content,

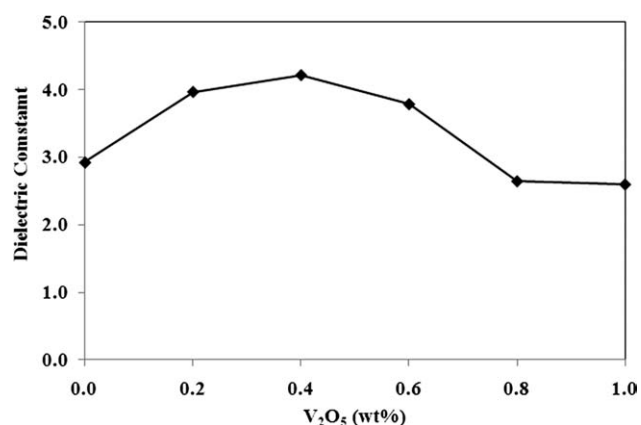


Figure 9 Dielectric constant of the pure PVA and PVA/ V_2O_5 nanocomposites at various contents of V_2O_5 .

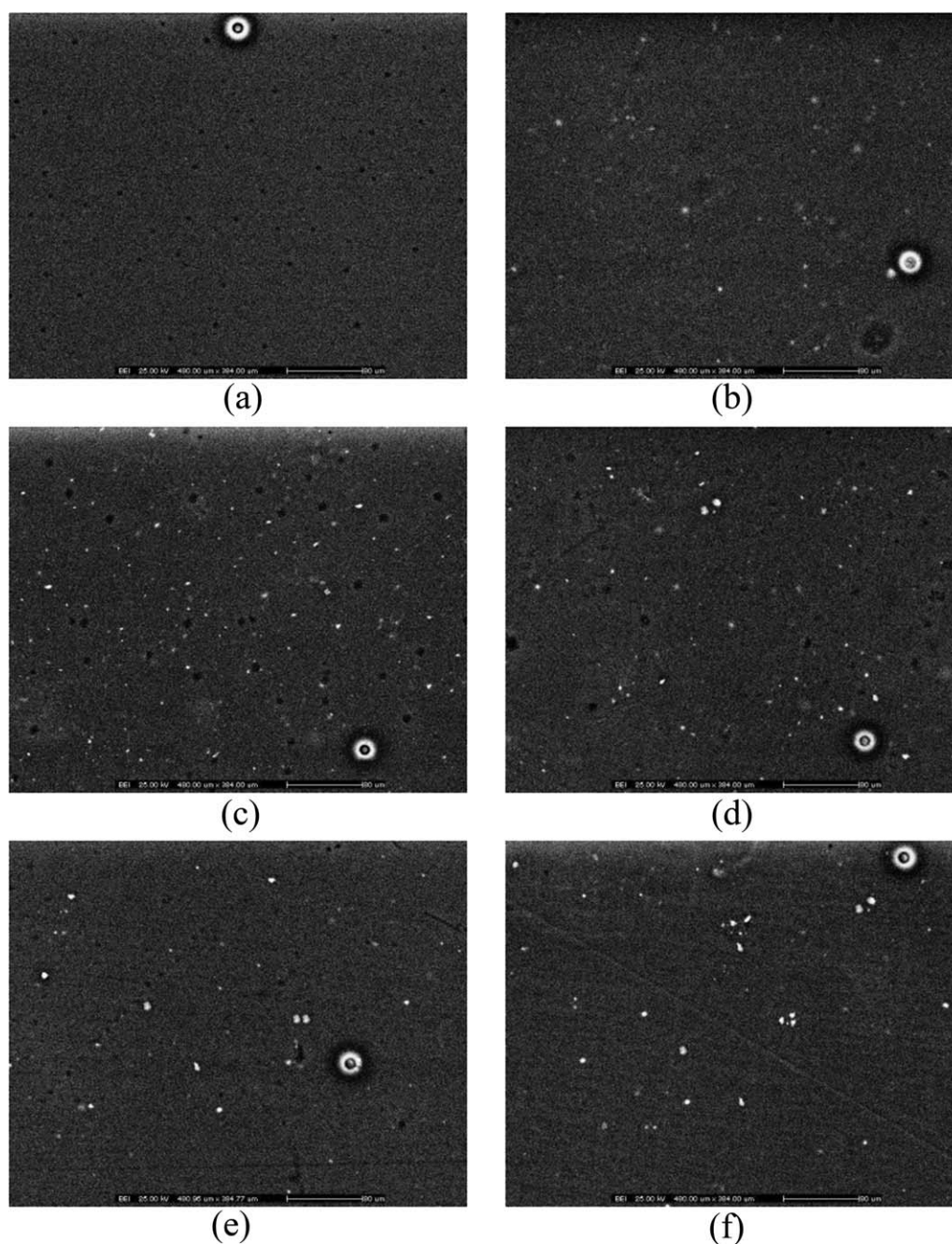


Figure 10 SEM micrographs of the (a) pure PVA, (b) PVA after the addition of 0.2 wt % V₂O₅, (c) PVA after the addition of 0.4 wt % of V₂O₅, (d) PVA after the addition of 0.6 wt % V₂O₅, (e) PVA after the addition of 0.8 wt % V₂O₅, and (f) PVA after the addition of 1.0 wt % V₂O₅.

and the concentration of 0.4 wt % V₂O₅ showed the maximum value; this was followed by sharp increases in the dielectric constants. This showed that the dielectric constants of the nanocomposites increased up to a V₂O₅ content of 0.4 wt % for the PVA/V₂O₅ nanocomposites and then decreased due to the dispersion of V₂O₅ nanoparticles at higher concentrations, like T_g . The Mahmoud et al.¹³ data showed an increase in the conductivity abruptly at 0.4–0.5 wt % nanoparticle contents and leveled off at higher nanoparticle percentages; this showed a percolation ratio of

V₂O₅ nanoparticles of around 0.4–0.5 wt %. This might implied a maximum in the dielectric constant at 0.4 wt % V₂O₅. However, the tendency toward agglomeration at higher concentrations of V₂O₅ might have been the cause of the decrease in the dielectric constant.

Effect of V₂O₅ on the morphology

The morphology of the surfaces of the nanocomposites was examined by SEM. Figure 10(a) shows the

micrographs of the surface of the pure PVA, whereas Figures 10(b–f) shows the micrographs of the surfaces of the PVA nanocomposites filled with 0.2, 0.4, 0.6, 0.8, and 1.0 wt % V_2O_5 , respectively. The dispersion of the V_2O_5 nanoparticles was relatively good; only few aggregations existed after the addition of the V_2O_5 nanoparticles at contents greater than 0.4 wt %, as shown in Figures 10(d–f). There was good adhesion inside the PVA/ V_2O_5 nanocomposites. These observations supported the results of the mechanical properties, where the PVA/ V_2O_5 nanocomposites at 0.4 wt % displayed the best mechanical properties. Moreover, the aggregation of V_2O_5 nanoparticles in the polymer matrix increased little with increasing V_2O_5 content, and the dispersion of V_2O_5 particles could have influenced the mechanical properties of the PVA nanocomposites.

CONCLUSIONS

In this study, we prepared PVA/ V_2O_5 nanocomposites by solution mixing. The properties of the nanocomposite films improved through the addition of V_2O_5 . The results of the experiment show that the mechanical properties of the film were enhanced by the addition of V_2O_5 . The PVA/ V_2O_5 nanocomposites showed an increase in the tensile strength, Young's modulus, and stress at break with increasing filler content. The dielectric properties increased with increasing V_2O_5 content. T_m 's of the PVA nanocomposites did not change after the addition of the V_2O_5 nanoparticles. The T_c and percentage crystallinity values of PVA decreased significantly with increasing V_2O_5 content. The degradation temperature of the PVA/ V_2O_5 nanocomposites increased

with increasing filler content. The SEM results showed that the dispersion of the V_2O_5 nanoparticles was relatively good; only few aggregations existed after the addition of V_2O_5 nanoparticles at contents greater than 0.4 wt %.

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