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Preparation of AgCl-PEO/PVA Composite via Combination of a Polymer Microgel Template and a Reverse Micelle Technique.

AM Abdelghany^{1*}, MS Meikhail², and HY Salah².

¹Spectroscopy Dept., Physics Division, National Research Center, Cairo, 12311, Egypt

²Physics Dept., Faculty of Science, Mansoura Univ., Mansoura, 35516, Egypt.

ABSTRACT

A new route was created for the preparation of AgCl-PEO/PVA nano composite with patterned surface structures. The route is a combination of a polymer microgel template method and a reverse micelle technique. Scanning electron microscopy shows that the size of the AgCl nano particles existing on the surfaces of the composite microspheres and the clearness of the surface patterns of the composite can be altered by simply adjusting the amount of precipitated AgCl and the rate of the reaction. X-ray diffraction shows two sharp characteristic bands at $2\theta = 18$ and 23° related to the presence of PEO and additional bands at $2\theta = 27, 32, 39$ and 46 attributed to 111, 200 and 111 and 200 planes of silver chloride. It is observed that upon increasing filler content, FTIR spectrum shows obvious changes in intensity and position of some bands. These results manifested the conclusion about the specific interaction in polymer matrices and hence the occurrence of complexation. UV-Vis. data indicate the presence of a well defined $\pi-\pi^*$ transition associated with the formation of conjugated electronic structure and the decrease in the optical energy gap was correlated to increase of the degree of disorder and overlap in the localized states.

Keywords: PEO/PVA blend; XRD; FTIR; UV-Vis. Spectroscopy; SEM; AgCl.

*Corresponding author

INTRODUCTION

Polymer blends play an important role because of their relatively simple preparation methods and diverse resulting properties [1]. Interest in studying polymer blends has considerably increased due to their significant industrial applications [2]. Blends with improved characteristics are produced by blending two or more polymers in order to combine their properties for certain purposes.

Poly(vinyl alcohol) (PVA) is a polymer that has been studied intensively due to its several interesting physical properties, which are useful in technical applications including biochemical and medical. The important feature of semicrystalline PVA is that the presence of crystalline and amorphous regions and its physical properties, which are resulting from the crystal–amorphous interfacial effects. These two regions are well separated by portions of an intermediate degree of ordering, which enhances the macromolecule, producing several crystalline and amorphous phases [3]. Moreover, it contains a carbon backbone with hydroxyl groups attached to methane carbons. These hydroxyl groups can be a source of hydrogen bonding, hence the assistance in the formation of polymer blends. [4]. PVA has been found to have a wide range of applications in the industrial sector and it has been attractive in different areas of science and technology [5, 6].

Poly(ethylene oxide) (PEO) based amphiphilic block copolymers exhibit interesting self- assembling properties both in solution as well as in bulk [7]. The hydrophobic sequences in these polymers are generally based on styrene [8] dienes [9] or hydrogenated aliphatic polyolefin blocks [10].

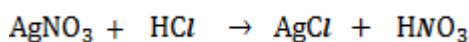
Filler additives were added to polymer or polymer blend to improve and modify its properties. Transition metals have influence on the structural, optical, morphological and thermal properties of polymer blend. Most of the early works on metal/polymer composites are patented, and little systematic investigation has been carried out in this field, especially on the particulate composite systems.

In the present work, PEO/PVA blend doped with different concentrations of AgCl have been prepared by casting method. The structural, optical, thermal and morphological characteristics of the prepared composites were studied with various techniques to verify the influence of Ag-ions on their physical properties.

MATERIALS AND METHODS

Materials

Both polyethylene oxide supplied from ACROS, New Jersey, USA with MW≈40000 and polyvinyl alcohol from Merck, Germany) with MW≈72.000 were used as a basic polymeric materials. Silver chloride was prepared from interaction between HCL and AgNO₃ according to the following equation



Preparation Method

Silver chloride nanoparticles were synthesized through direct reaction of Silver nitrate (AgNO₃) and hydrochloric acid (HCl) in aqueous media. Equi-mass fractions of both PEO and PVA were dissolved in double distilled water separately and then the polymer blend solution was stirred continuously about 6 h at 70 °C until a homogenous viscous liquid was formed. Nano composite of AgCl- PEO/PVA were synthesized by adding prepared silver chloride to the resulting blend. The polymeric matrix containing PVA act as dispersing agent and silver ions interact with PEO/PVA which restrict the bulk growth of AgCl and keep it in nanosized domain.

Resulting solution of AgCl particles was added to the polymer blend solution with pre-calculated fraction ($x = 0.5, 1, 2, 4, 8$ and 12 wt%) see table (1). The resulting solution was then cast to Petri dishes at 60 °C for about 72 h. After drying, the films were peeled from Petri dishes and films of thickness ranging from 0.10 to 0.16 mm were obtained and kept in vacuum desiccators until use.

Table 1: Sample constituents and composition

Sample	PVA	PEO	AgcCl
	Wt%		
S0	50.00	50.00	0.00
S1	49.75	49.75	0.50
S2	49.50	49.50	1.00
S3	49.00	49.00	2.00
S4	48.00	48.00	4.00
S5	46.00	46.00	8.00
S6	44.00	44.00	12.0

Measurement Techniques

FT-IR absorption spectra were carried out for different films using the single beam Fourier transform-infrared spectrometer (Nicolet iS10, USA) at room temperature in the spectral range of 4000-400 cm^{-1} . X-ray diffraction scans were obtained using PANalytical XPert PRO XRD system using $\text{CuK}\alpha$ radiation (where, $\lambda = 1.540 \text{ \AA}$, the tube operated at 30 kV, the Bragg's angle (2θ) in the range of (10° - 50°)). UV/Vis. absorption spectra were measured in the wavelength region of (190-1100) nm using spectrophotometer (JASCO 430 Spectrometer, Japan) to retrace the structural changes resulting from filler varying concentrations. The morphology of the films was characterized by scanning electron microscope using (Quanta FEG 250), operating at 200V-30 kV accelerating voltage magnification 14x up to 1000x. Surfaces of the samples were coated with a thin layer of gold (3.5 nm) by the vacuum evaporation technique to minimize sample charging effects due to the electron beam.

RESULTS AND DISCUSSION

Fourier Transform -Infrared Analysis

In the present work, IR absorption spectra were used to demonstrate the interaction between PEO/PVA polymeric matrices with silver chloride (AgCl) as a dopant material, which causes some minor changes in the vibrational modes and/or in the intensity in specified bands. Figure 1 shows the FTIR absorption spectra of pure blend and samples that filled with 0.5, 1, 2, 4, 8, and 12 wt% of AgCl. The figure reveals some changes in the intensities of some characteristic vibrational bands accompanied with increased AgCl content. This indicates that the amorphous regions of the prepared samples are augmented with increasing the filler. The shifts of CH_2 stretching vibration from 2907 cm^{-1} to 2892 cm^{-1} , out-of-plane rings C-H bending mode from 945 cm^{-1} to 953 cm^{-1} were observed. These indicate the chemical interactions of AgCl with polymeric matrices [11-13].

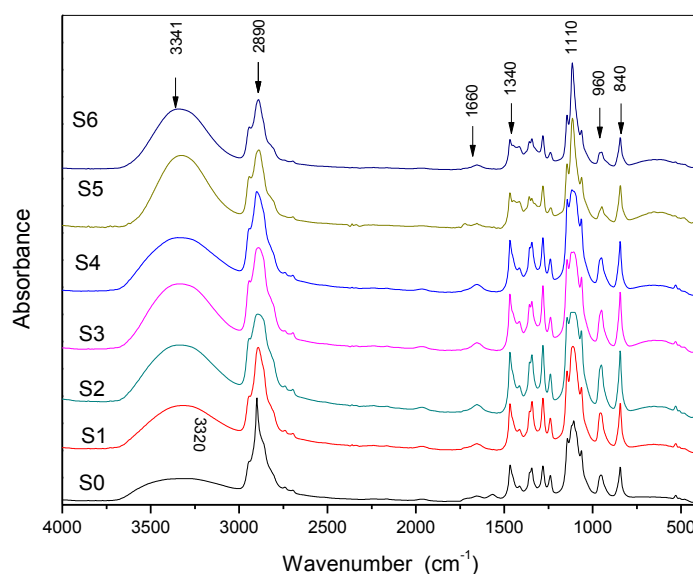


Figure 1: FT-IR absorption spectra of PVP/PEO polymeric blend and samples that contain concentrations of AgCl.

X-ray diffraction analysis (XRD)

Figure 2 shows the X-ray diffraction scans of pure PVA/PEO blend and samples that filled with different concentrations of AgCl. The observed spectra exhibit an amorphous feature and shows two distinct sharp characteristic bands at $2\theta = 18$ and 23° related to the presence of PEO. Intensity of additional bands at $2\theta = 32.17, 39$ and 46 increases with increased silver chloride [14] content and can be correlated with 111, 200 and 220 planes of silver chloride. The tendency of apparently diminution of crystallinity with the increase of AgCl content in blend sample implies a decrease of the number of hydrogen bonds that are formed between PEO and PVA if present. Also, this might be a result of dilution effect of Ag when mixed with polymer, which suppress recrystallization of broken blend polymer chains and inhibit crystal growth. The two peaks at $2\theta = 18^\circ$ and 23° [15], have been found to be increased in broadness and decreased in intensity for wt=12%. This results reveal the increase in amorphous nature the films. From all previously mentioned results, the interaction between the filler and polymer blend results in decreasing crystallinity with rich amorphous phase. This amorphous nature confirms the complexation between the filler and the polymer blend.

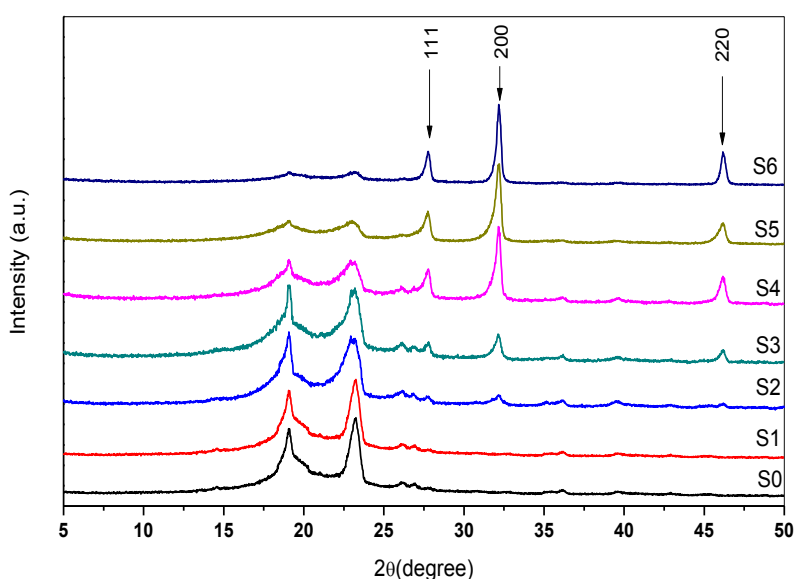


Figure 2: X-ray diffraction scans of PVP/PEO blend and blend filled with different concentrations of AgCl.

Ultraviolet-visible Spectroscopy (UV/vis.)

Figure 3 shows the UV/vis. absorption spectra in the range of (190 – 1100) nm of pure PEO/PVA polymer blend and samples that filled with various concentration of AgCl content exhibit very small absorbance in the ultra-violet range (200-380 nm) while in visible region show very high absorbance. Consequently it may be used as optically transparent UV absorbing film materials that are easily manufactured by processes that do not utilize volatile organic compounds, and whose polymer components are not environmentally hazardous.

The spectrum of pure blend sample exhibited three absorption bands, an intense band at 192 nm ascribed to the presence of some residual acetate groups of PVA and/or chromophoric groups of PEO, were assigned to the existence of carbonyl groups associated with ethylene unsaturation [16] and a hump or shoulder at 215 nm and very small band at 375 nm may be due to $\pi \rightarrow \pi^*$ (K-band) and $n \rightarrow \pi^*$ (R- band) electronic transitions respectively [17]. In addition, there are no absorption bands on the visible region for all samples since the films are transparent.

The absorption intensity of the AgCl band at 215 nm and 375 nm become faint at concentrations higher than 4 wt%. However, only the peak position of the band at 210 nm shifted toward higher wavelengths by about 10 nm with increasing AgCl concentrations. These shifts in the bands indicate the formation of inter/intra molecular hydrogen bonding mainly between Ag ions with the adjacent OH groups that are in consistence with IR results.

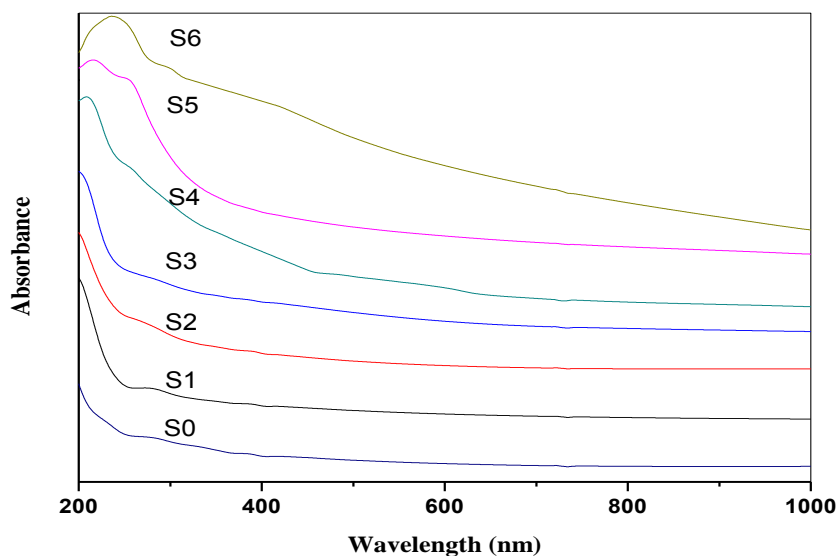
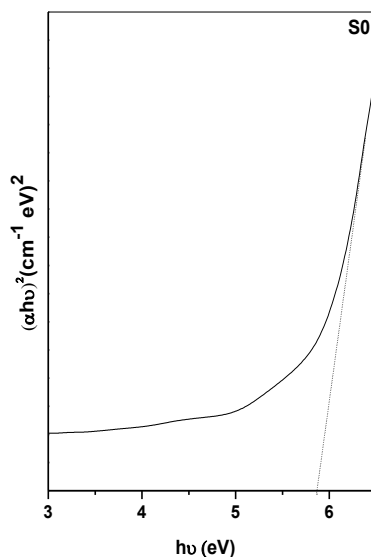


Figure 3: UV/vis. spectra of PEO/PVA blend and samples that filled with different concentrations of AgCl.

Determination of optical energy gap (E_g)

The study of optical absorption gives information about the band structure of organic compound. In the absorption process an electron is excited from a lower to higher energy state by absorbing a photon of known energy. The changes in the transmitted radiation can decide the types of possible electron transitions. Fundamental absorption refers to band-to-band or exciting transition. The fundamental absorption shows a sudden rise in absorption, known as absorption edge, which can be used to determine the optical band gap ($E_g = hc/\lambda$). Absorption is expressed in terms of a coefficient α , which is defined as the relative rate of decrease in light intensity.



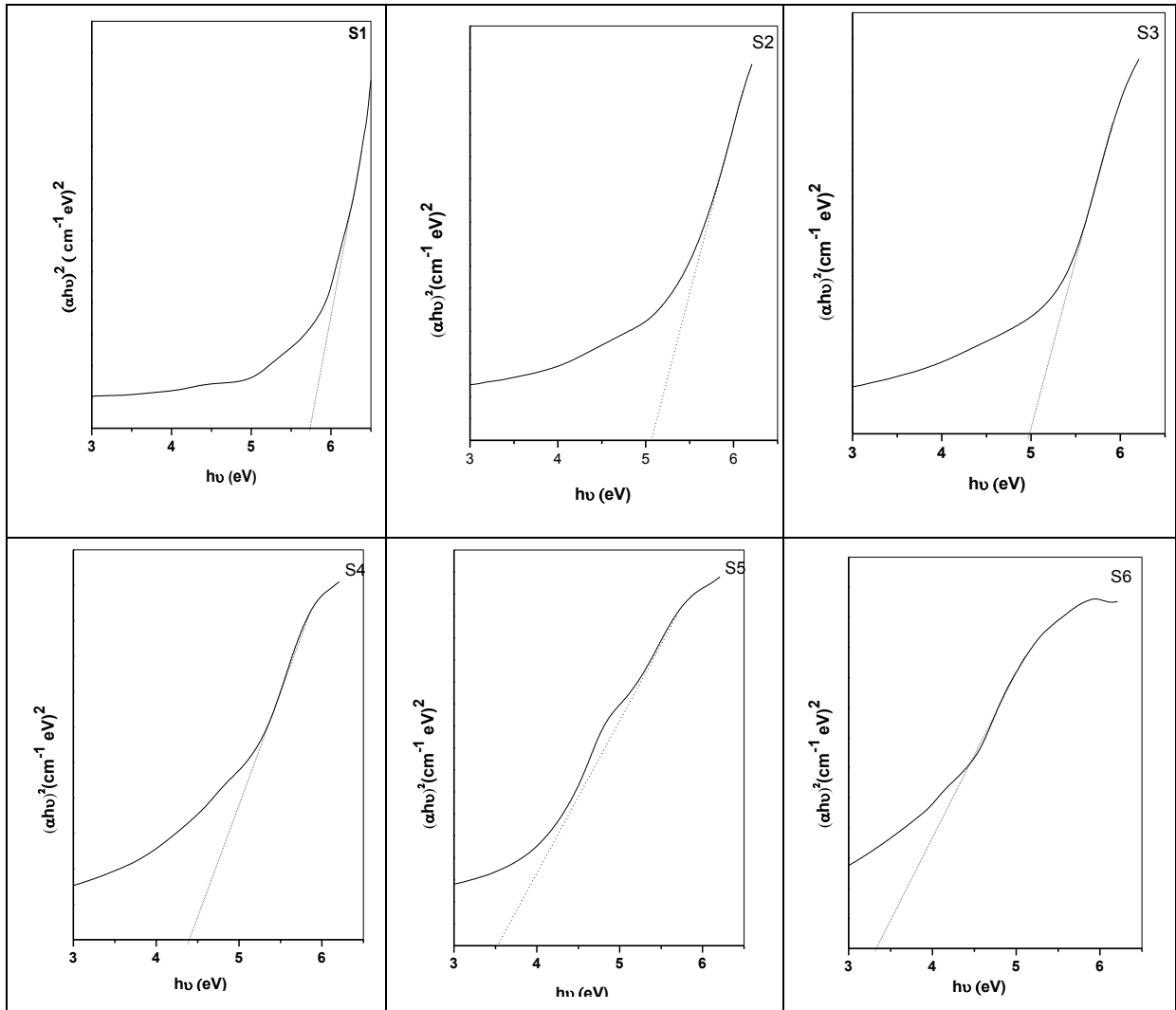


Figure 4: Relation between $(\alpha h\nu)^2$ versus photon energy ($h\nu$)

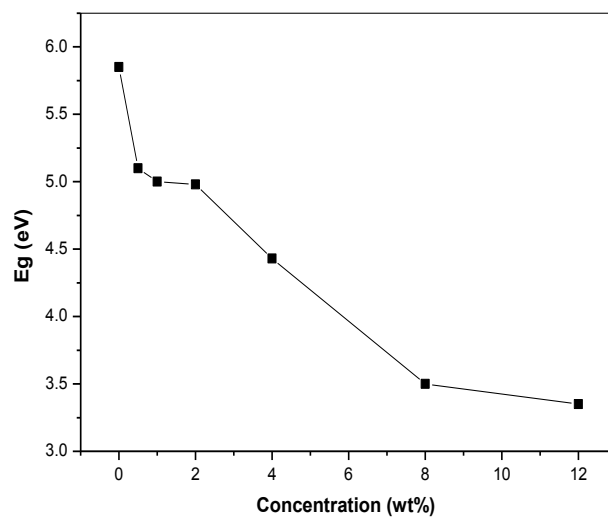


Figure 5: Relation between optical energy gap (E_g) and filler concentrations wt%
 Table 2: Values of Optical Energy gap and AgCl concentration Wt%.

Sample	Concentration wt%	E _{g,d} (eV)
S0	0	5.80
S1	0.5	5.10
S2	1	5.00
S3	2	4.98
S4	4	4.43
S5	8	3.50
S6	12	3.35

The analysis of Thutupalli and Tomlin [18] is based on the following relations:

$$(n\alpha h\nu)^2 = C_1(h\nu - E_{gd}) \tag{1}$$

$$(n\alpha h\nu)^{1/2} = C_2(h\nu - E_{gi}) \tag{2}$$

where, $h\nu$ is the photon energy, E_{gd} , the direct band gap, E_{gi} , the indirect band gap, n , integer, C_1 , C_2 , constants and α is the absorption coefficient. The absorption coefficient (α) can be determined as a function of frequency using the formula [19]:

$$\alpha(\nu) = 2.303 \frac{A}{d} \tag{3}$$

where, A is the absorbance and d is thickness of the sample under investigation. Davis and Shalliday [20] reported that near the fundamental band edge, both direct and indirect transitions occur and can be observed by plotting $(\alpha h\nu)^2$ and $(\alpha h\nu)^{1/2}$, respectively, as a function of energy ($h\nu$), where h is Planck's constant. Figure 4 shows the plots of $(\alpha h\nu)^2$ as a function of photon energy ($h\nu$), and can be used to calculate the optical energy gap (table 2). Figure 5 shows a decrease in the values of direct optical band gap energies with increasing AgCl content. This decrease may be attributed to the formation of defects in the polymeric matrix and an increase in the degree of disorder in the films. These types of defects produce localized states in the optical band gap. These overlaps are responsible for decreasing energy band gap with increasing AgCl content in the polymeric matrix. These results are supported by the data obtained from XRD studies.

Scanning electron microscopy

The SEM is used to investigate fully the effect of AgCl content and to examine the dispersion of AgCl particles in the polymeric matrix, Figure 6 shows the SEM micrograph of the surface of pure blend and samples that contains variable amount of silver chloride at magnification $\times 500$. Pure polymeric films are transparent with uniform morphology revealing a smooth surface while a small granules and granule groups randomly distribution on the surface was observed with increasing AgCl content. Further increase in AgCl concentration leads to grow up of such granules with different sizes and irregular shapes, distributed in the amorphous matrix; this indicates that these granules are related to the presence of AgCl, and indicating the occurrence of a homogeneous growth mechanism. An interesting pattern is observed for the case of $x = 12$ wt% which contains an aggregation of filler and highly condensed number of very small granules at the surface, because of the state of saturation as in figure 6 and this confirmed the complexation between the filler and the polymer blend and attributed to the partial compatibility between the polymer blend and the filler. These results confirm measurements of XRD and UV/Vis. Measurements.

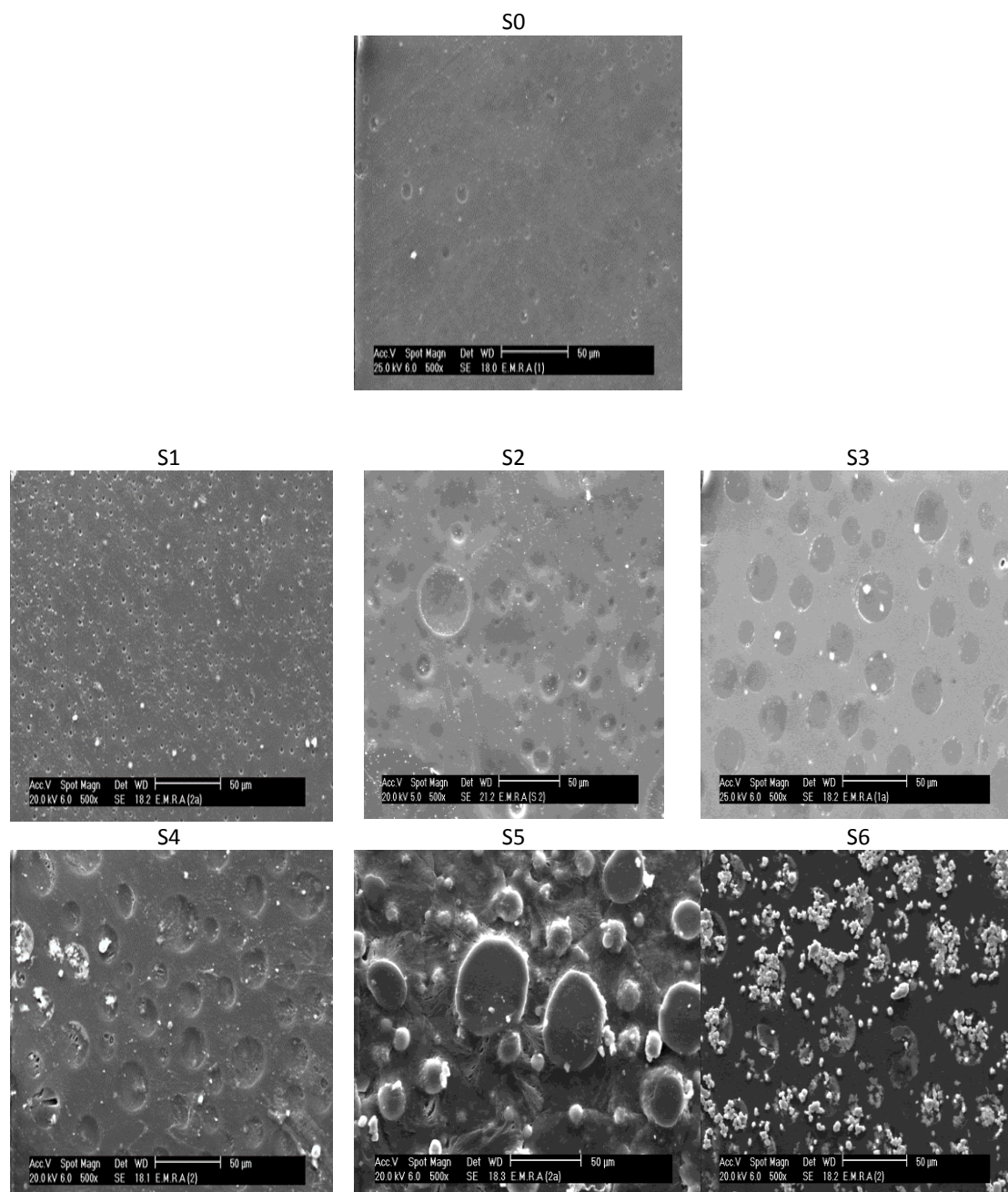


Figure 6: SEM micrograph of pure blend and samples that contains different concentrations of AgCl.

CONCLUSIONS

Polymer electrolytes based on PVA/PEO blend with AgCl as the filler at different concentrations were prepared using a solvent casting technique. FT-IR data revealed that the intensities of some vibrational bands for the prepared films are decreased indicates that the amorphous regions are augmented with increasing AgCl. XRD showed that there are some new peaks appeared at wt12% for AgCl indicating the un complete dissolution of the filler in amorphous regions in this concentration and we cannot add an concentration to the polymer. The formation of intermolecular interactions and complexation between the PVA/PEO and the filler (AgCl) was confirmed by XRD, FT-IR, UV-Vis. Optical absorption edge and optical band gaps (direct transition) showed a decreasing trend with increased concentration of the AgCl. These data suggest that the present electrolyte system is a worthy candidate for electrochemical device applications. SEM shows a transparent, soft and a uniform pure PVA/PEO and it a smooth surface, while after adding the filler to the polymer by increasing the concentration a large granules and granule groups randomly distribution on the surface.

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