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Spectroscopic Studies of PVA/PEO Hydrogel Filled With Cesium Chloride.

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ABSTRACT

The molecular structures of Poly(vinyl alcohol) (PVA)/ poly(ethylene oxide) (PEO) hydrogel filled with different amount of cesium chloride were prepared and studied via FTIR, UV-Vis. and X-ray spectroscopy. Morphological properties were studied using scanning electron microscopy (SEM). X-ray diffraction shows two sharp characteristic bands at $2\theta = 18$ and 23° related to the presence of PEO and additional bands at $2\theta = 31, 37, 43$ and 58 attributed to 110, 111, 200 and 210 planes of cesium chloride. A shift in stretching vibrations of OH groups in the FTIR spectra with addition of cesium salt was interpreted in terms of reaction between salt ions with OH groups of water and other hydroxyl-containing molecules. Change in peak position and/or intensity attributed to the interaction between polymeric matrix and cesium salt. Direct and indirect optical energy gap from UV-Vis. data were calculated and interpreted. SEM microscopy shows a rough surface comprise small aggregates with homogenous distribution compared to pure blend attributed to increase of lamellar twisting period and to an increase in the crystalline regions within the polymeric matrix.

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

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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]. Polymers with improved characteristics are produced by blending two or more polymers in order to combine their properties for certain applications.

Polyvinyl alcohol (PVA) has different internal structures, which may be considered as amorphous or semicrystalline. Semi-crystalline PVA characterized by the formation of both crystalline and amorphous regions. Moreover, PVA is also nontoxic, potential material having high dielectric strength and good charge storage capacity.

Poly(ethylene oxide) (PEO) based amphiphilic block copolymers exhibit interesting self- assembling properties both in solution as well as in bulk [3]. The hydrophobic sequences in these polymers are generally based on styrene [4] dienes [5] or hydrogenated aliphatic polyolefin blocks [6]. PEO is a simple chain polymer with enteric linkages, while PVA is a polymer with a carbon chain backbone with hydroxyl (OH) groups attached to methane carbons. These OH groups are sources of hydrogen bonding (H-bonding) and hence of assistance in formation of polymer blend [7]. Recent investigations of our research group revealed that metal halide fillers modify significantly the structure and physical properties of other polymers [13, 14].

Fillers are used with polymer blend for several reasons: cost reduction, improved processing, density control, optical effect, thermal conductivity, and electrical, etc. [8]. Alkali earth metal has influence on the structural, optical, morphological and thermal properties of polymer blend. The present work is devoted to shed more light on the role of Cs ions (3-d state) in modification and development of the structural and optical properties of PEO/PVA blend doped with different concentrations of cesium chloride.

Quintana et al. have described the near total miscibility of PEO with PVA, Although, they did have some reservations about just how complete this miscibility was [12]. In addition, they suggest also that only the primary OH in polyvinyl alcohol interacts with the oxygen of PEO.

MATERIALS AND EXPERIMENTAL WORK

Materials

Both polyethylene oxide supplied from ACROS, New Jersey, USA with $M_w \approx 40,000$ gm/mol and polyvinyl alcohol from Merck, Germany) with $M_w \approx 72,000$ gm/mol were used as a basic polymeric materials. Cesium chloride (CsCl) were purchased from Sigma-Aldrich Co., All chemicals were used as received.

Equimass 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 50 °C until a homogenous viscous liquid was obtained. The inorganic filler (CsCl) was dissolved in double distilled water at the same condition. The resulting solution of CsCl was added to the polymer blend with different mass fraction x , where ($x=0.5, 1.0, 2.0, 4.0, 10$ and 20 wt%). The resulting solution was then cast to Petri dishes at 50 °C for about 3 days. After drying, the films were peeled from Petri dishes. Films of thickness ranging from 0.15 to 0.20 mm were obtained and kept in vacuum desiccators until use.

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 CuK_α radiation (where, $\lambda = 1.540$ Å, the tube operated at 30 kV, the Bragg's angle (2θ) in the range of (5° - 50°)). UV-Vis absorption spectra were measured in the wavelength region of (190-1100) nm using spectrophotometer (JASCO 630, Japan) to study the change in optical properties accompanied with structural changes introduced as a result of filler addition. The morphology of the films was characterized using scanning electron microscope using (Quanta FEG 250), operating at 200V-30 kV accelerating voltage magnification 14× up to 1000×. 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 spectra were used to establish the interaction between PEO and PVA doped with CsCl as filler, which causes some changes in the vibrational modes and bands position. Figure 1 depicts the IR spectra of pure PEO and pure PVA.

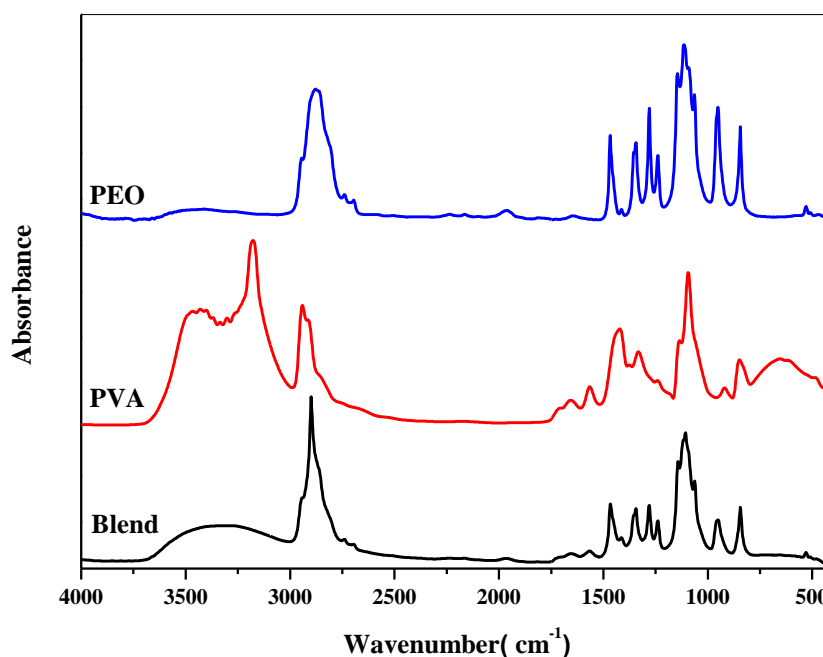


Figure 1: FT-IR spectra of pure blend, pure PEO and pure PVA

The main characteristic bands of PEO can be observed. A sharp band at 2887 cm^{-1} is attributed to CH_2 stretching of methylene group. The bands at about 1464 cm^{-1} and 1344 cm^{-1} represent CH_2 scissoring and CH_2 asymmetric bending, respectively. The relatively small band at around 1242 cm^{-1} is assigned to CH_2 symmetric twisting, C-O-C stretching mode has sharp band at 1114 cm^{-1} out-of-plane rings C-H bending mode at 950 cm^{-1} . A sharp band at 840 cm^{-1} is attributed to C-O stretching.

While the characteristic absorption bands of pure PVA, at about 3349 and 1427 cm^{-1} are assigned to OH stretching and bending vibration of hydroxyl group. The band corresponding to methylene group (CH_2) asymmetric stretching vibration occurs at about 2940 cm^{-1} . The vibrational band at about 1736 cm^{-1} corresponds to C=O stretching of PVA. The band at about 840 cm^{-1} is assigned to stretching mode of CH_2 . The band at about 1093 cm^{-1} corresponds to C-O stretching of acetyl group present on the PVA backbone. The absorption band at 954 cm^{-1} is assigned to CH_2 stretching [18-20].

Figure 2 shows FT-IR absorption spectra of pure blend and samples that filled with 0.5, 1.0, 2.0, 4.0, 10, and 20 wt. % of CsCl. From the figure, the relative intensities of some characteristic vibrational bands for those CsCl blends are decreased. This indicates that the amorphous regions of the prepared samples are augmented with increasing the filler. The shifts of CH_2 stretching vibration from 2900 cm^{-1} to 2892 cm^{-1} , CH_2 asymmetric bending from 1344 cm^{-1} to 1336 cm^{-1} and out-of-plane rings C-H bending mode from 961 cm^{-1} to 953 cm^{-1} were observed. These indicate the chemical interactions of CsCl with the polymer blend.

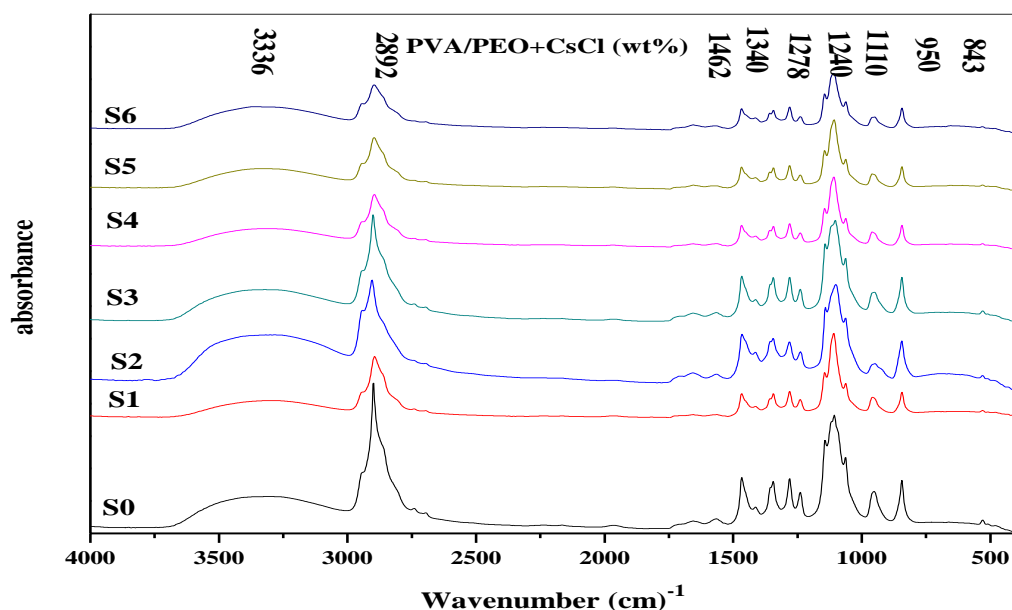


Figure 2: FT-IR spectra of blend and the blend with different concentrations of CsCl.

X-ray diffraction analysis (XRD)

Figure 3 shows the X-ray diffraction scans of pure PVA/PEO blend and the blend filled with different concentrations of CsCl as filler. The observed spectra exhibit an amorphous feature and shows broad bands at about $2\theta = 19^\circ$ and $2\theta = 23^\circ$. The peak intensity was found to decrease with increasing CsCl concentration due to the interaction between the polymer blend and CsCl. This implies a decrease in the degree of crystallinity and causes an increase in the amorphous regions this indicated that an intermolecular hydrogen bonding interaction occurred between the blend and CsCl; this reveals the semicrystalline nature of the blend that contains crystalline and amorphous structure [21]. This behavior demonstrates that complexation between the filler and polymer blend took place in the amorphous regions. Also the change of the peaks position in the filled samples this indicates the complexation between the polymers blend and CsCl, and that the filler significantly influence of the degree of crystallinity.

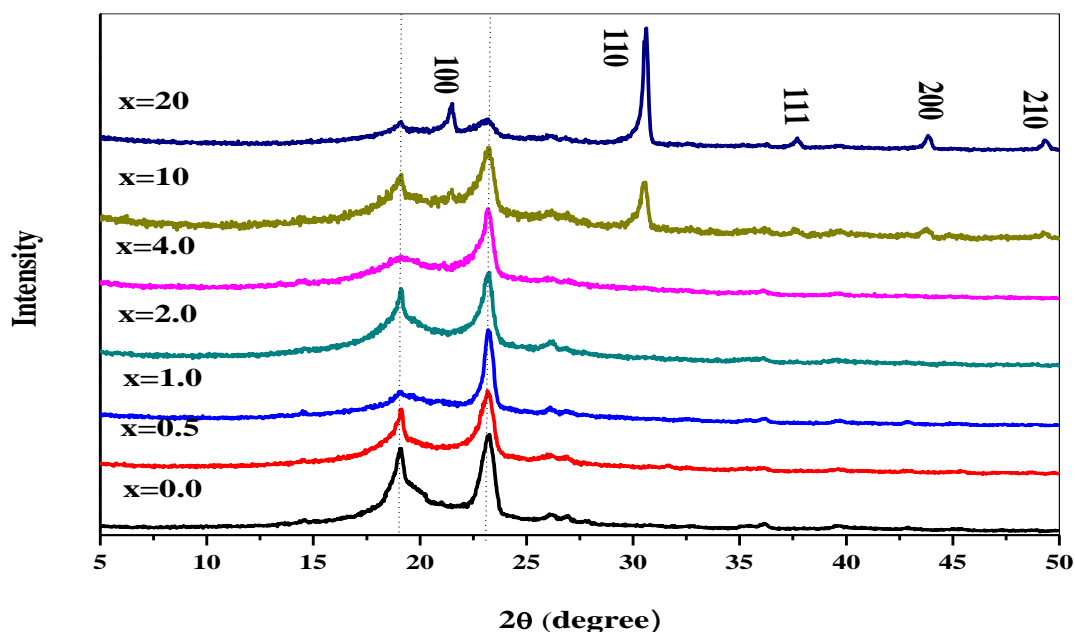


Figure 3: X-ray diffraction scans of PVA/PEO blend with different mass fractions of CsCl%.

UV/vis. Optical studies

Figure 4 reveals the UV/vis. absorption spectra of prepared blend before and after doping with different mass fractions of CsCl in the wavelength range 190-1100 nm at room temperature. Obtained spectra are characterized by the main absorption edge around 200 nm for all curves that shifted towards longer wavelengths with increasing CsCl content. These shifts indicate the complexation between the filler and the polymer blend and maybe also attributed to change in crystallinity due to filler addition [23, 24]. The absorption bands are due to electronic transition from the ground states to excited states. During such transition in a molecule, electrons are promoted from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) [25]. The changes in transmitted radiation can decide the types of possible electron transitions.

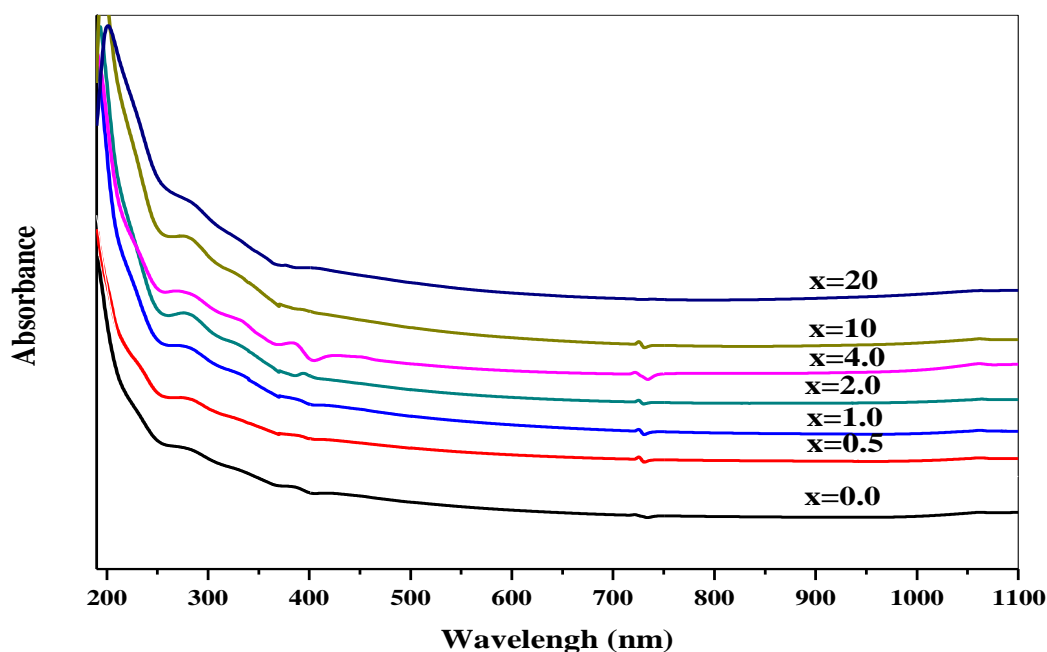


Figure 4: UV/Vis. spectra of pure PVA/PEO blend and the blend filled with different concentrations of CsCl wt%.

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. The analysis of Thutpalli and Tomlin[26] is based on the following relations:

$$(n\alpha hu)^2 = C_1(hu - E_{gd}) \quad (1)$$

$$(n\alpha hu)^{1/2} = C_2(hu - E_{gi}) \quad (2)$$

Where, hu 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 [27]:

$$\alpha(\nu) = 2.303 \times A/d \quad (3)$$

A is the absorbance and d is thickness of the sample under investigation. Davis and Shalliday [28] 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 5, shows a plot of $(\alpha h\nu)^{1/2}$ and $(\alpha h\nu)^2$ respectively, as a function of photon energy ($h\nu$), and can be used to calculate its optical energy gap. The nature and width of the band gaps can be evaluated from both Figure 5 and Figure 6 and absorption edge values were obtained by extrapolating the linear portions. The values of indirect band gap and direct band gap are listed in table 1 and selected samples showed in both (Figure 5.a) and (Figure 6.a), while a plot of variation in optical energy gaps were showed in both figures 5.b, 6.b. It is clear from table 1 and the figures that the indirect and direct band gap values showed a decrease with increasing CsCl 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 defects produce the localized states in the optical band gap. These overlaps are responsible for decreasing energy band gap when content CsCl is increased in the polymer matrix [29]. These results are supported by the data obtained from XRD studies.

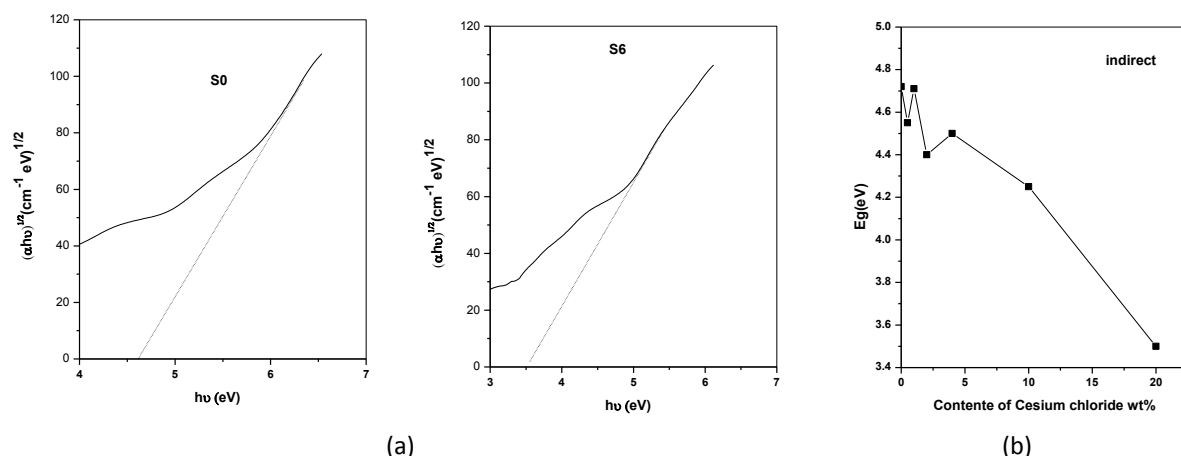


Figure 5: Relation between $(\alpha h\nu)^{1/2}$ versus photon energy ($h\nu$) for selected samples, (b) Relation between optical energy gap (E_g) with cesium chloride concentrations wt%

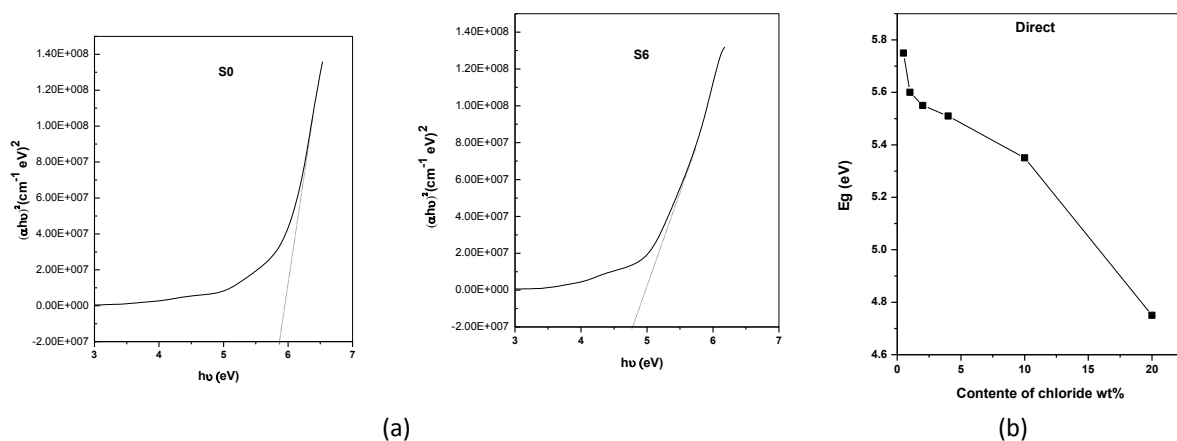


Figure 6: Relation between $(\alpha h\nu)^2$ versus photon energy ($h\nu$) for selected samples, (b) Relation between optical energy gap (E_g) with cesium chloride concentrations wt%

Table 1: Relation between content filler and Optical Energy gap for direct and indirect with content filler in PVA/PEO blend films.

CsCl Content (wt%)	Optical Energy gap (eV)	
	Direct	indirect
0.0	5.75	4.72
5.0	5.70	4.55
1.0	5.60	4.71
2.0	5.55	4.40
4.0	5.51	4.50
10	5.35	4.25
20	4.75	3.50

Scanning electron microscopy

The SEM is used to investigate fully the effect of CsCl content and to examine the dispersion of CsCl particles in the polymeric matrix. Figure 7 shows the SEM micrograph of the surface of pure blend and filled films with different concentrations of CsCl at magnification 500 times, and shows pure polymer Morphology which is transparent and is shown to be in a uniform morphology revealing a rather smooth surface. By increasing the concentration of CsCl appear a large granules and granule groups randomly distribution on the surface. The grown ones were of different sizes and irregular shapes, uniformly distributed in the amorphous matrix, and the number of the granules increases with increasing concentration of CsCl, this indicates that these granules may be are of CsCl, and indicating the occurrence of a homogeneous growth mechanism. An interesting pattern is observed for the case of w=30wt% which contains an aggregation of filler and a highly condensed number of very small granules at the surface, because access to the state of saturation as in figure 8 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.

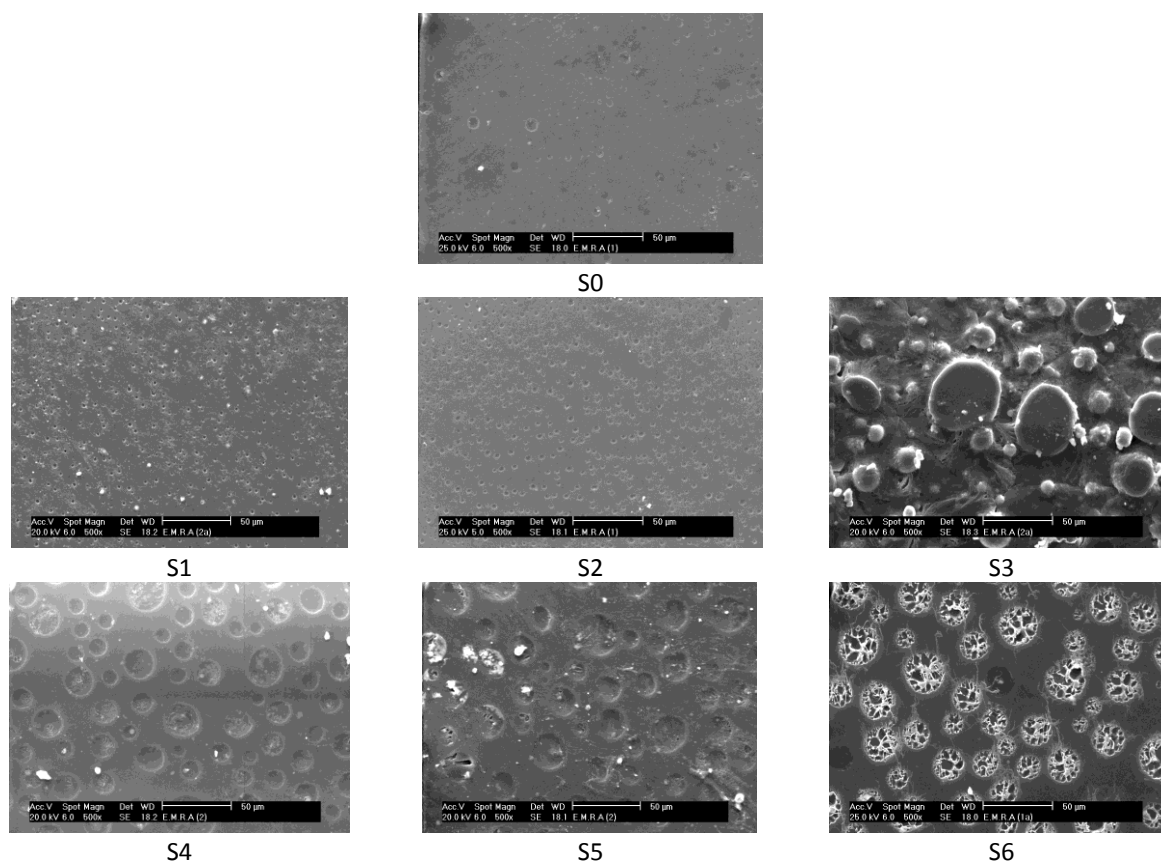


Figure 7: SEM micrograph of the surface of: pure blend, 0.5, 1.0, 2.0, 4.0,10 and 20wt%of different concentrations of CsCl at magnification 500 times.

CONCLUSION

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 CsCl. X-ray diffraction shows sharp characteristic bands at $2\theta = 31, 37, 43$ and 58 attributed to $110, 111, 200$ and 210 planes of cesium chloride. The values energies gap(direct and indirect) were decreased with increasing Cs-ions content due to charge transfer complexes arose between the polymer blend and Cs-ions. 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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