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Selenium based Nanocomposites: synthesis and. medical applications

This study
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بسمِ اللهِ الرحمن الرحيمِ

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DEDICATION

I dedicate my graduation to the one who harvested thorns from

My path, to pave the path of knowledge for me, my dear father ,

To the one who nursed me with love, tenderness and healing

Balm, my beloved mother, to the tender hearts and Innocent

Souls of my brothers

Thanks and appreciation

Praise be to God, Lord of the worlds, and prayers and peace be upon the most honorable of the prophets

And the Messengers, our master Muhammad and his good and pure family, and after ..

I thank God Almighty for His bounty for allowing me to accomplish this work By His grace, praise be to God first and foremost .

Then I thank those kind people who helped me during this period, and in their introduction (Dr. Qahtan Adnan Muhammad .)

who spared no effort in helping me, as he played the main role In completing my research through his wise supervision and guidance. him all Thanks, appreciation, love and respect, and may God grant him a shining beacon in His scientific career in the service of science. May Allah reward them well . ..

I also extend my sincere thanks to all my dear teachers who worked diligently during the university years and spared nothing on our behalf . And to those who are not mentioned, I offer them my heartfelt thanks and gratitude .

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Abstract

In this research, an attempt is made to prepare an organic-inorganic hybrid material that aims to improve some of the physical properties of polymeric mixtures composed of poly ethelyne oxide (PMMA) and polystyrene (PS) by adding Selenium Se nanoparticles to the single polymers as well as by adding them to the mixture whereby 5 % of nanoparticles were added to the polymer. The effect of the addition was studied by SEM and UV-visible spectrophotometer. The results of the XRD proved that the hybrid superposition is due to the presence of diffraction peaks belonging to the polymer as well as belonging to the Se NPs. The optical properties were studied by means of the absorption spectrum of the nano-hybrid, and the direct energy gap was calculated, and it was approximately equal to 3.71 eV. The morphological characteristics, as shown by the microscope images, were in the form of nano porous .

1.1 Introduction

A material with dimensions on the nanoscale is referred to as a nanomaterial (1-100 nm). This material is extremely valuable for its commercial uses due to its exceptional set of characteristics. Nanoparticles are characterized by their small particle size, narrow size distribution, low aggregation, and excellent dispersion. These are the four important features. Nanomaterial has a wide range of potential applications, including but not limited to those in the fields of solar cell, memory devices, photodetectors, diodes, medicine and so more applications [1].

Some of the micro material's physical features, such as the growth in surface area relative to volume, alter when the micro material is converted to nanoparticles (NPs), and the particle size enters the realm of quantum

effects. A high ratio of surface area to volume is one of the main characteristics of NPs. This means that the atoms on the surface of a nanoparticle make up a significant portion of the total number of atoms in the nanoparticle. Therefore, this ratio, in conjunction with the size and generally regular morphologies, results in the creation of novel attributes in comparison to bulk particles. In addition, when particles are tiny enough, they exhibit behavior consistent with quantum mechanics[2,3].

New kinds of polymeric materials can be classified as inorganic/polymeric hybrid structures. These materials have inorganic particles enclosed within the polymer matrix. The qualities of both of these components are combined in these materials. This indicates that a polymer component that possesses outstanding optical properties, flexibility, and toughness could improve the brittleness of inorganic particles, and furthermore, inorganic particles could raise the strength and modulus of polymer[4].

Composite systems, in which one or more phases are in the nanoscale state, have drawn increased attention in recent years. The boundary position of the nanoparticles between the atomic-molecular and macroscopic state of matter determines the appearance of unusual physicochemical and biological effects at this level of dimension, which can be used to

implement new effective approaches to immunology, visualizing diagnostics, and drug therapy [5]. The use of polymers as a matrix for the encapsulation of nanoparticles provides the nanocomposite with additional properties which can enhance or weaken the biological effect of these nanoparticles. At present, the synthesis of metal-containing nanocomposites using highmolecular compounds (polypyrrole, polyvinylpyrrolidone, polyvinyl alcohol, carboxymethylcellulose, arabinogalactan, etc.) is of particular interest. The methodological approach to the directed development of hybrid organic–inorganic nanocomposites, which are nanoparticles of silver, selenium, tellurium, and other elements encapsulated in macromolecules of natural and synthetic matrices, has been developed and is being improved intensively[6-8]

. 1.2 Hybrids materials

Attention to hybrid compounds grew based on the assumption that by combining diverse construction blocks into one material, one could combine and sometimes improve particular properties (advantages). In Hybrid materials, the link of a minimum two components of definitely diverse in chemical natures through simple blending or via connecting the

parts together via specific bonds, such as covalent, ionic, coordination, or bonds of hydrogen. Each hybrid constituent owns its chemicals uniqueness and can exist independently of the hybrid material. The hybrid materials properties might be affected from the dispersion of the second part in the matrix and the interface between the the two parts. The following stage in the direction of the properties alteration of nanomaterials is the combination of dissimilar nanoparticles together. Such nano-structures show adjusted properties compared to the single component, such as retaining of the original properties of both materials but with accomplishing of some novel amalgamation in one common nanoparticle system or a strong change of the properties of one material due to the presence of a second material. Hybrid nano-structured material is a special class of composites systems collected of inorganic and organic constituents dispersed on theM nanoscale. the manufactured of hybrid materials from both organic and inorganic portions by specific method will represent advantages for both. Consequently, it combines structural diversity, manageability, tuning, and characteristic flexibility of organic portion with thermals stability and 9 rigidity of the inorganic part. Additionally, the inorganic portion, depending on its structure, may increase uncommon and interesting optical, magnetic and electronic properties [9-12].

1.3. Polymer/Nanopowder Composites Synthesis

Nanopowders primarily involve metals, semiconductors, metal oxides. This subsection primarily reviews how to form nanocomposites with metal oxides and polymers. Generally, three ways have been applied to disperse nanopowders in polymers. The first is direct mixing or blending of the polymer and the nanopowder either as discrete phases (known as melt mixing) or in solution (solution mixing). The second is sol-gel process which starts with molecular precursor at ambient temperature and then forms metal or metal oxide framework by hydrolysis and condensation. The third is in situ grafting polymerization of macromolecular chains on [13].

1.3.1 Direct Mixing

Melt mixing is the fastest method for introducing new nanocomposites to market since it can take full advantage of well-built polymer processing equipments including extruders or injectors. For example, nanoscale silica or CaCO3 filled Nylon composites have successfully been produced by using high velocity oxy-fuel (HVOF) combustion spray process [14]

1.3.2. The sol-gel

The sol-gel processing of the nanopowders inside the polymer dissolved in non-aqueous or aqueous solution is the ideal procedure for the formation of interpenetrating networks between inorganic and organic moieties at the milder temperature in improving good compatibility and building strong interfacial interaction between two phases. This process has been used successfully to prepare nanocomposites with silica, alumina, calcium oxide, titania in a range of polymer matrices [15].

1.3.3. Graft Polymerization

Another method for avoiding phase-separate is graft polymerization, where nanopowders are dispersed in the monomer or monomer solution, and the resulting mixture is polymerized by standard polymerization methods. This process provides flexibility in our ability to engineer the powder surface being placed in composites. Besides tailoring specific properties in composites via relatively strong interaction, the layer of polymer bonded to the nanopowders can control aggregation of the nanopowders [16].

1.4. Nanoporous polymers

Nanoporous polymers with a well-defined open pore structure and tunable mass transport characteristics are of major importance in drug delivery devices and porous membrane materials for liquid separations. Today, these materials are mainly prepared by phase inversion of polymer solutions. The demixing process, which stops at the vitrification point of the polymer rich phase, can be initiated either by a temperature quench or by diffusive solvent-nonsolvent exchange (immersion precipitation) of binary, ternary, or multicomponent mixtures. A serious drawback of these techniques is the presence of solvents during the preparation procedure. In addition to not being environmentally benign, the solvent contaminates the porous material and often needs to be removed in excessive posttreatment processes. Partially, these contaminants are removed by intense washing procedures. However, for medical and pharmaceutical applications, totally solvent-free membrane materials are required [17-20].

1.5. The aim of the present study

The present study aims to: Synthesize and study of the structural , morphological and optical properties of prepared (PS-PMMA-Se) nanocomposites.

2 Experimental Section

2.1. Synthesis of PS/PEO/Se Composites

The PS/PMMA/Se Composites materials were produced by inserting SeNPs as additive material into the PS/PMMA polymer blend. This led to the formation of the composites. After dissolving 0.05 g of PS and 0.05 g of PMMA together in 10 mL of chloroform, 1 percent polymeric blend were produced, and 5 percent of Se NPs were added into the solution. After

stirring with a magnet for three hours, the fillers were evenly distributed throughout the matrix solution and a homogenized suspension was produced as a result.

2.2 Characterization techniques

There is a variety of diagnostic methods that can be used to test some important properties of materials such as crystalline structures, surface morphologies, chemical compositions, optical properties. “X-ray diffractions (XRD), fields emissions scanning electrons microscopy (FESEM), transmissions electrons microscopy (TEM), Fourier transformation infrared spectroscopy (FTIR), UV-Visible spectroscopy (UV-Vis) .

2.2.1 X-ray diffractions

X-ray diffraction was a commonly used procedure to structure categorization of the samples. This procedure is also beneficial to define the average particle size. By using Bragg's law

2dsin□ □ n□…….2.1 Where d signify the interplane spacing. The limited crystallites size has an obvious

influence on the diffraction of line width of x ray. With decline in particle size, major extending of diffraction positions was detected. The average grain size (G) of the crystalline material can be estimated from the value of full Width Half Maximum (FWHM) and Scherer Formula [21]:

G = k □/□cos□B……2.2

Where, k is the Scherer constant with a value among (0.8 – 1.0), □ is the diffracted radiations wavelength, □B is the Brag angle and □ is (FWHM). In this study D2 phaser Bruker company – Germany was used. The beam of X-ray had been produced by target from copper (Cu) with CuKα wave length of 1.544 nm. 30 KV to the voltage and current 10 mA. These measurements were made at the Tehran University.

2.2.2. Transmissions Electrons Microscopy (TEM)

(TEM) is procedure can be used to imaging the nanoscale materials, by means of electrons beam that was focused on top of a sample producing an enlarged version to seem on a luminous monitor or a photographic film, or to be sensed via a CCD camera.

In this study, the transmission Electron Microscopy model a JEOL JEM.

2010 electron microscopy . This device is conducted at the Tehran University.

2.2.3. Field Emissions Scanning Electrons Microscopy (FESEM) This technique can be used to study and explore the morphology of materials surface. Attraction between the beam accelerated by electromagnetic fields and path with the atoms of the sample is the principle of FESEM works that depends on.

In this study, the Field Emissions Scanning Electrons Microscopy FESEM model MlRA3 from TE SCAN Company. This device is conducted at Tehran University.

2.2.4. Energy Dispersive X-ray Spectroscopy

For a semi-quantitable analyzation of components, EDX has become one of the essential methods that determines as both a mass or weight fraction percentage of sample components. Some of the EDX detectors are

SEM radiation, SEM field and microscope radiation transmission. It delivers data from the incident beam of electrons on the fixated point by a raster scanning of sample superficial. Furthermore, a map of the products to be tested can be supplied. Analysis atomic composition of the sample occurs while the electron-beam energy is enough to remove the electron

from the internal orbit of the atoms when the interaction of electrons with the material. The vacuum resulting from the expulsion of the electron from the internal orbit was occupied by means of an electron from the outside orbit of the same atom

In this study, the Field Emissions Scanning Electrons Microscopy FESEM model MlRA3 from TE SCAN Company. This device is conducted at Tehran University.

2.2.5. The FTIR Measurement

It was considered one of the important techniques for distinguishing the bonding between atoms and molecules of organic matter and determining the presence of effective groups and it also represents the fingerprint , Where it is used to determine the purity of a compound or to detect impurities.

The spectrophotometer ALPHA II from Bruker was used in this study which available at the university of Kufa collage of science

2.2.6. Ultra Violet-Visible Spectroscopy UV-VIS

With the aim of measure the optical absorption, the absorption coefficients and energy gaps of the prepared materials, the optical measurements have involved absorbance spectra that have been measured in the range of wavelengths (290-900) nm .

In this study, the UV-Visible kind 1800 Shemadzu Spectroscope has been used which is available at the university of Kufa -College of Science.

Results and discussion

The nature of the crystalline phase for PS/PMMA/Se nanocomposite that prepared by physical mixing were determined by using X-ray diffraction. The XRD patterns obtained show the main peaks characteristic of crystalline Se (COD-9008579) at 2θ values of 22.6°, 29.7°, 41.4°corresponding to the crystal planes (100), (101), (110) respectively.

The peaks below 20 degree are belong to PS and PMMA polymers and confirms the amorphous nature of polymers.

Figure 2 shows SEM images of a film containing 5% Se in PS/PEO matrix (all compositions are based on weight). We observed closed-cell pores (meaning the pores are not connected) at the nanometer length scale. The pores we obtained are nearly spherical in shape. The elongation of some pores in the direction parallel to the film surfaces was due to the deformation during SEM sample preparation. The effective pore size is the average of the longest and shortest diameters of the elongated pores can be measure from the SEM pictures.

EDX analysis was utilized in order to determine the elemental build of the composite. Figure 3 presents EDX spectra of PS/PMMA/Se, and the inset table presents an analysis of the elemens ratio of the sample.

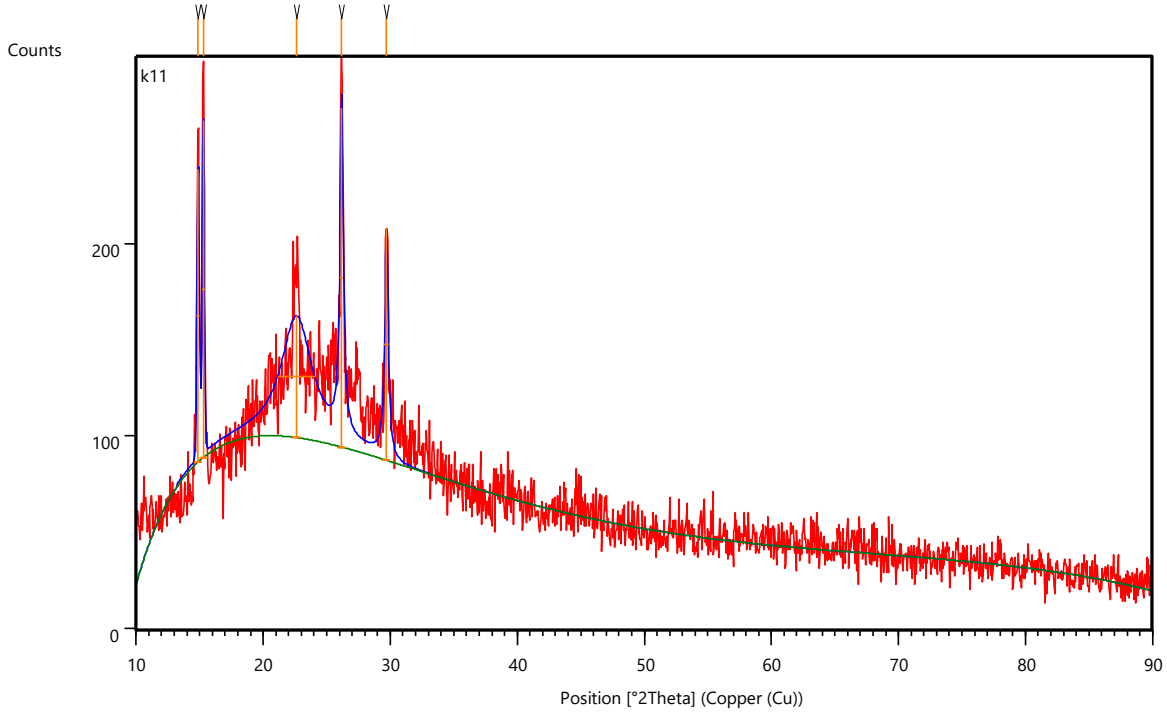
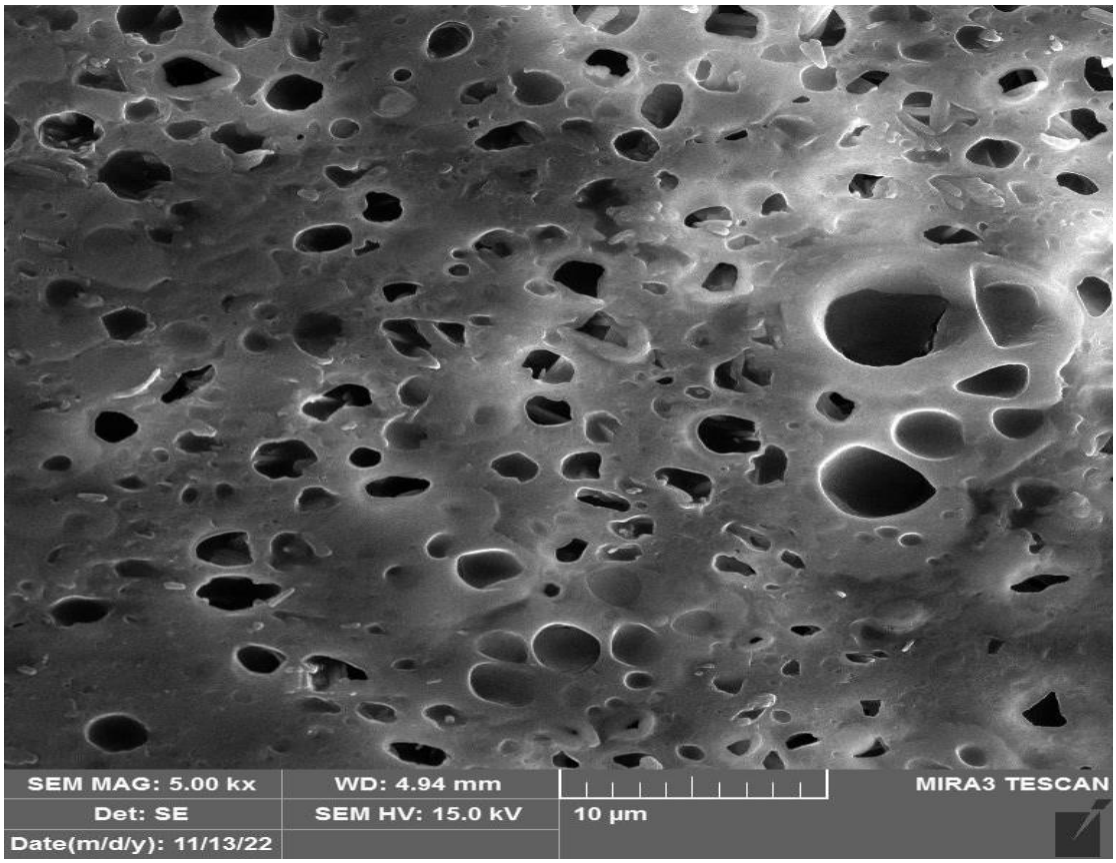


Figure 1. XRD patterns of nanocomposite

Table 1. peak position and inter atomic spacing of prepared sample

Pos. [°2Th.]	Height [cts]	FWHM Left [°2Th.]	d-spacing [Å]	Rel. Int. [%]	Tip Width	Matched by
14.888(7)	152(12)	0.24(1)	5.94561	86.17	0.2849	

15.288(6)	175(13)	0.21(1)	5.79091	99.32	0.2487
22.63(6)	63(5)	2.9(2)	3.92639	35.92	3.5070
26.183(8)	176(12)	0.32(3)	3.40083	100.00	0.3841
29.71(1)	121(9)	0.33(3)	3.00417	68.36	0.3952


SEM MAG: 5.00 kx
WD: 4.94 mm
MIRA3 TESCAN
Det: SE
SEM HV: 15.0 kV
10 µm
Date(m/d/y): 11/13/22

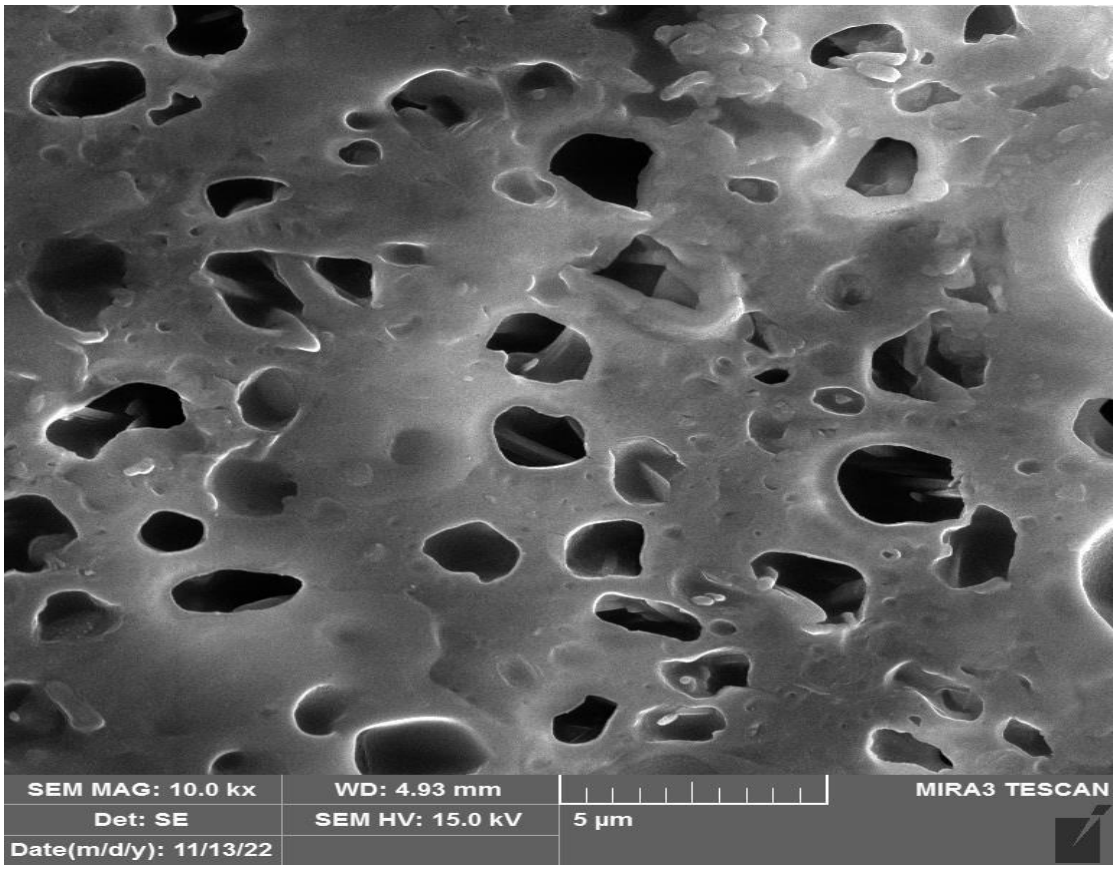
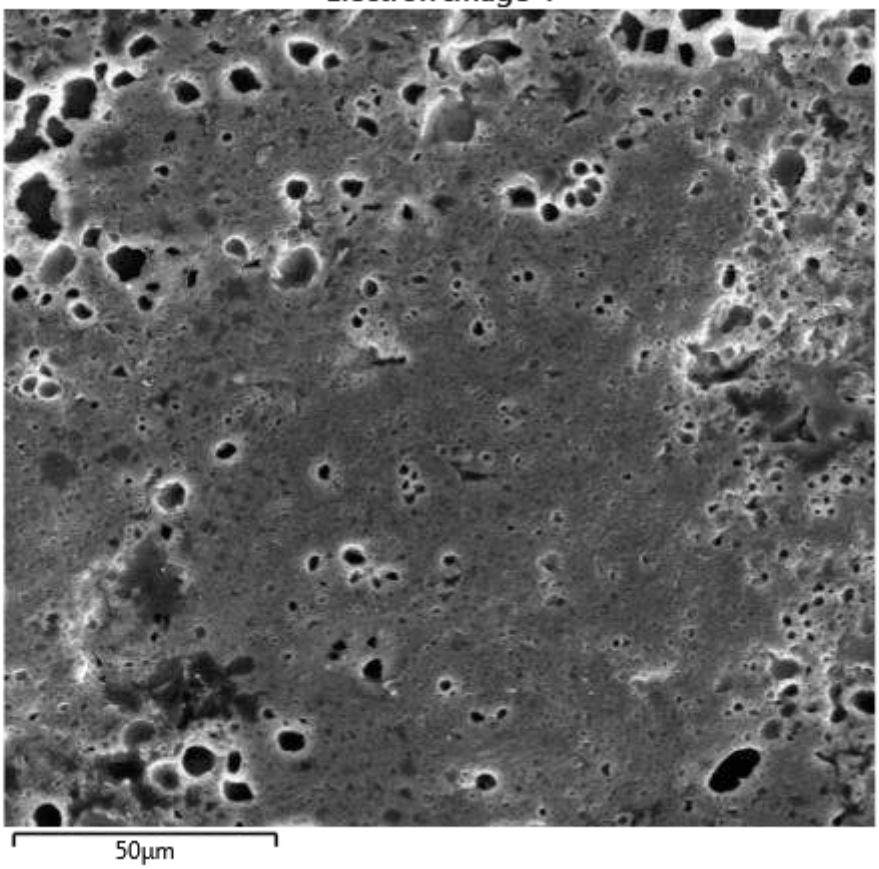


Figure 2. FESEM of nanocomposite

Electron Image 4



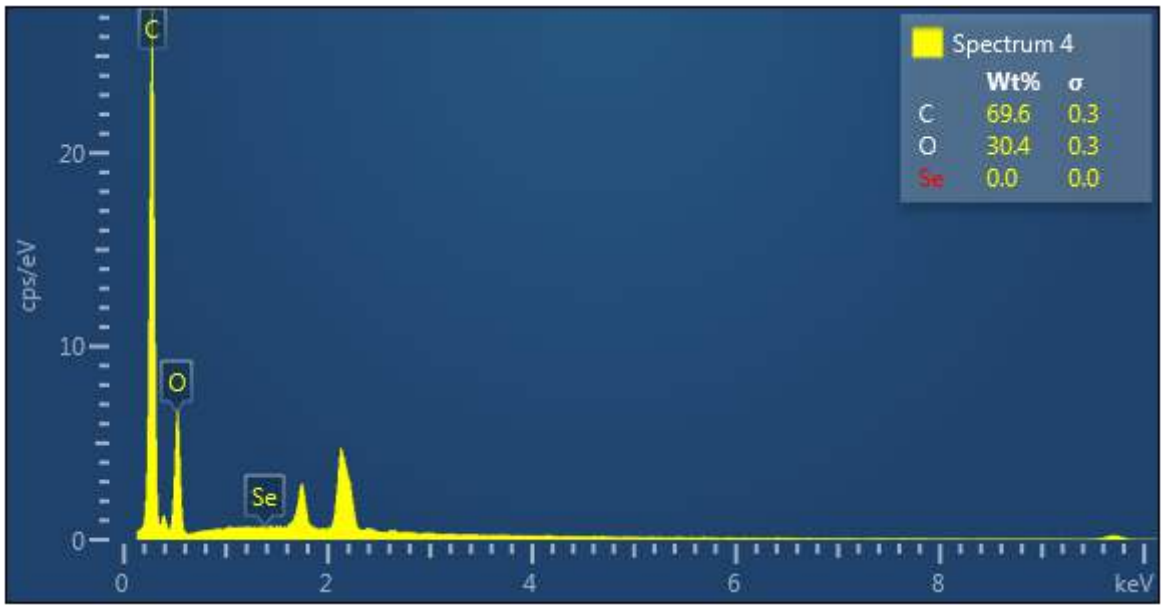


Figure 3. EDX of nanocomposite

UV-Vis spectroscopy is used to study the absorption spectrum of PS/PMMA/Se nanocomposite. Figure 4 shows the UV–Vis absorption spectrum of PS/PMMA/Se nanocomposite. the figure display the peak position at 250 nm belong to the PS/PMMA blend. An absorption shoulder appeared at 350 t0 450 nm. This result demonstrates the creation of Se based nanocomposite.

UV-Vis spectroscopy is used to study the transmission spectrum of PS/PMMA/Se nanocomposite. Figure 5 shows the UV–Vis transmission

spectrum of PS/PMMA/Se nanocomposite. the figure display the composite film is transparent.

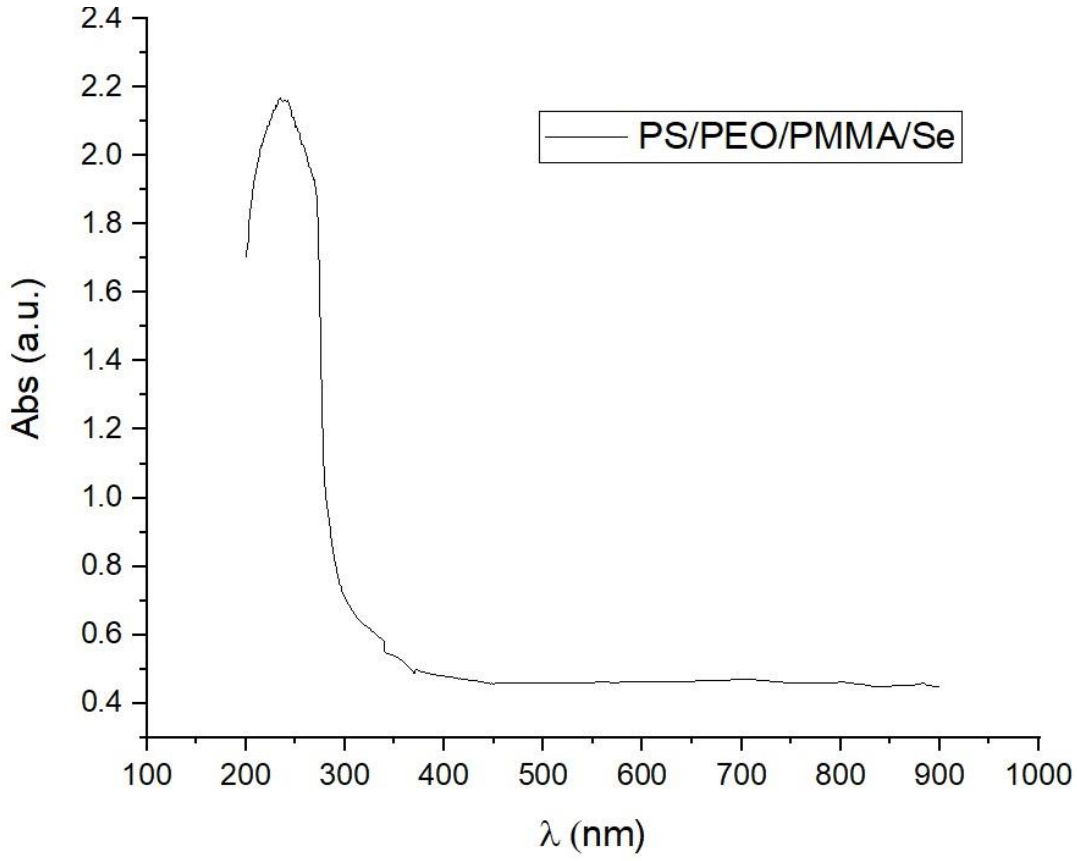


Figure 4. absorbance spectrum of nanocomposite

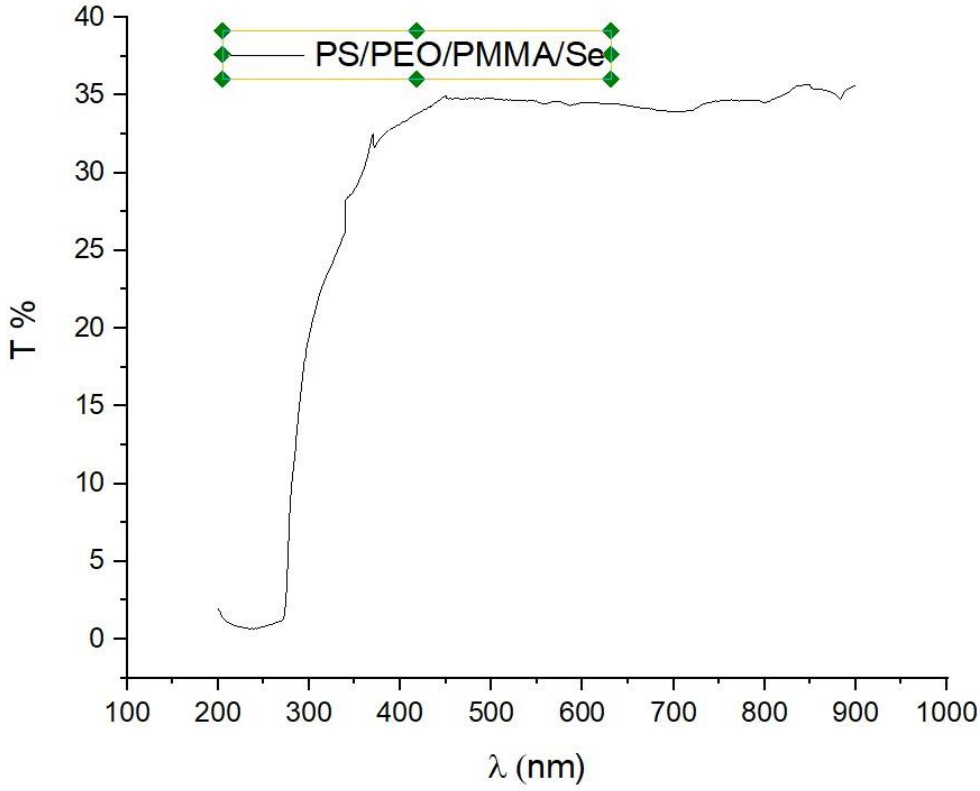


Figure 5. transmission spectrum of nanocomposite

Conclusions

The present study describes a method to create nanoporous films by using polymer blends mixed with Se nanoparticles . Nanometersize pores were created due to the fast phase separation during the drop casting process. Scanning electron microscopy was used to observe the pore structures. The pores obtained were found to be closed cells. Image analysis was used to measure the sizes of the pores.

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