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Formulating nanocomposite materials based on polymers to get high performance and extra properties

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Abstract. Nowadays, production nanocomposites based on polymer by blending nanoparticles as a filler with a polymer-matrix had attracted the major concentration of researchers, these materials used now for several modern application and in multiple fields (semiconductors, sensors, photovoltaic cells, optics, electronic-device,…). So it should be concentrated on comprehensive the relation between the polymer-matrix and the nano-particle to achieve more advance in this field. In this paper, the effect of adding SiO_2 to PVP/PEO matrix by concentrations (0.1, 1.2,2.5,5.5,6.1 $wt\%$) are investigated. The optical and thermal properties are evaluated. The properties of the studied films presented the new additions and specifications produced by this process. Briefly, results had shown enhancing in the absorbance, melting-temperature is increased. Additionally, the crystallinity degree of the nanocomposites is examined.

Keywords: Polymer, nanofiller, composite, optical, absorbance

Introduction:

Composite-materials is a term which represents mixed two different materials at least to get particular and unique features, which give more flexibility in the process of designing [1]. This concept aims to select compounds in some way to get the desired features of strength, toughness, special stiffness, weight and conductivity…,There are two basic components of composite-materials, Matrix which is the basic component and the other components is the filler, or reinforcement. The composite-materials should achieve a compound of multi-components have difference in their physical characteristics as well as the capability to separate them mechanically[2]. Recently, polymers-engineering rapidly advanced to implement flexible, lightweight and cost-effective electronic-device, [3] studied the range absorbance of ultraviolet-visible (UV-Vis), spectra of reflectance and other optical properties of the polymer-nanocomposite films consisting of poly (vinyl- pyrrolidone) PVP and this is the basic part which called matrix, the fillers which represent the non-continuous part (oxide) such as alumina(Al_2O_3), Silica(SiO_2), [4] is reported preparation of hybrid polymer PVA/PVP and Titanium-oxide TiO_2 to investigate the mechanical and optical characteristics for this compound. [5] studied the effect of adding SnS filler to polymer-composite (PVP/PVA) to experience the conductivity of this compound material. Ti was found that the electrical conductivity of this compound had increased and the both properties mechanical and electrical are improved. .[6] explained that the forming of PVA/PEO loaded with carbon-black improved the electrical properties of polymer nanocomposites. [7] presented a review about studying the band-gap by two different methods to evaluate accurately the band-gap and select the way of transition of electron.[8] studied preparing PVA/PVP/SnO_2, Fourier transform based on infrared is done to explain the interacts of nanoparticle(SnO_2) with PVA/PVP. This nanocomposite forming thin films which get additional features such as conductivity enhancement as well as transparent optically.

In this study, the Impact of adding SiO_2 to the PVP/PEO matrix is concentrated to investigate the various extra achieved properties. The major interest is concentrated to nanocomposites preparing for various application such as sensors, nano-dielectric substrates, energy storage, electronic device…, The Implementation of nanocomposites based on polymer depending basically on their physical features, this achieved by specifying the preparation conditions[9].

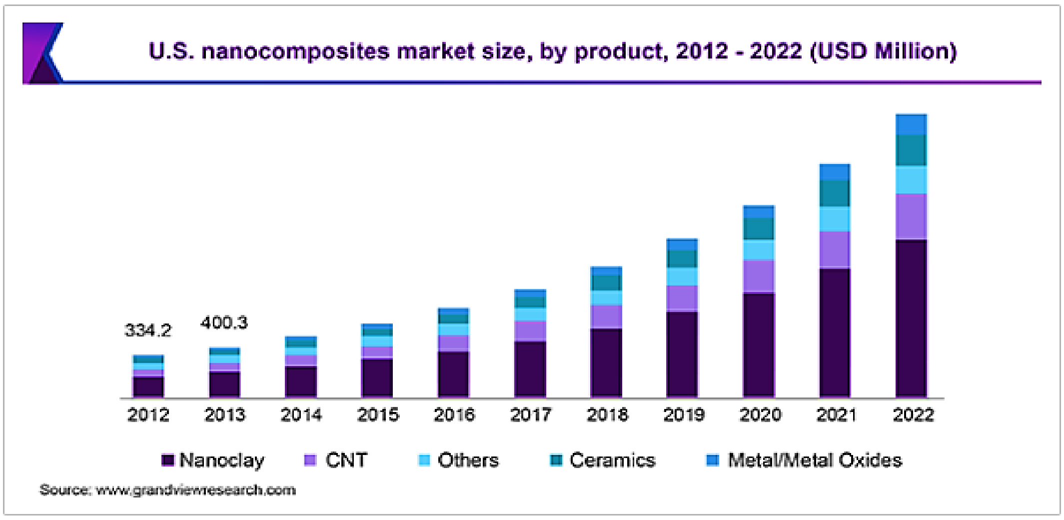

fig (1): Market size of nanocomposites between 2012-2022

Nanocomposite-materials:

1-Components:

A. Polymer-matrix:

Polymer-matrix is a special order of multiple polymers, biopolymers, thermosets, thermoplastics, ..had been used in polymer-matric production. The basic parameters of this matrix include : the kind of required polymer, the surface-nature, the chemistry nature of the polymer, its structure . Polymer-matrix has important properties such as adhesion and satisfying toughness [10]. It is introduced as a continuous and basic part of composite-materials. There are many scientific searches about combined a polymer-matrix with other materials have electric, dielectric, optical conductivity properties which improve its features.

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Investigating the dynamic characteristics has a basic role in fabricating, designing, and producing the polymer nano-composites.

B. Nano-Fillers (Reinforcement): This is the changeable part of composite-materials, adding this component to the polymer-matrix results in improving the physical properties of structure of final materials[11].

The main feature of adding filler is that the mechanical properties optimization. Nanoparticles are extremely fine in their size and composition, the size of this particles range between(1-100 nm) [12]. Combining process of nanoparticles as filler to poly-matrix resulting in other conception is called nanocomposite, this offers particular structure as well as new physical, chemical characteristics. Nano-fillers could be categorized according to their physicochemical structure and properties and their special form, Depending on the interaction between the adding nanofillers and the host- polymer matrix, the electrical, optical, mechanical and other features could be controllable. Dispersing the nanoparticles in the matrix result in forming zone by the surface-area of the filler which is called (interaction-Zone).

2-Formation:

As previously mentioned, the produced material from adding process of the nanoparticles into the polymer-matrix is called nanocomposite. The resulting nanocomposite will have its own structure with additional feature, combining the features of each component, the new specifications depending on the content. The nanoparticles could change the behavior of polymer as well as the morphology due to their considerable interaction-area. The interaction process with the polymer is characterized by complexity because there are several complex mechanisms of interaction such as electrostatically interaction, diffusion, also there are surface-tension, process of absorption, chemically bonding, mechanically interlock and wetting the surface.

The definition of materials used in this work:

Poly-vinyl-pyrrolidone PVP: one of the polymers family, it characterized by biocompatible, echo-friendly, biodegradable, belongs to the functional (-OH, C=O) hydroxyl and carbonyl groups respectively.

Poly-ethylene oxide PEO: It is an important material and had played a basic role in enhancement the electrolytes of polymer to implement specific applications.

Silicon dioxide or silica SiO_2: it has a linear formation, produced through a combination process of silicon monoxide and oxygen.

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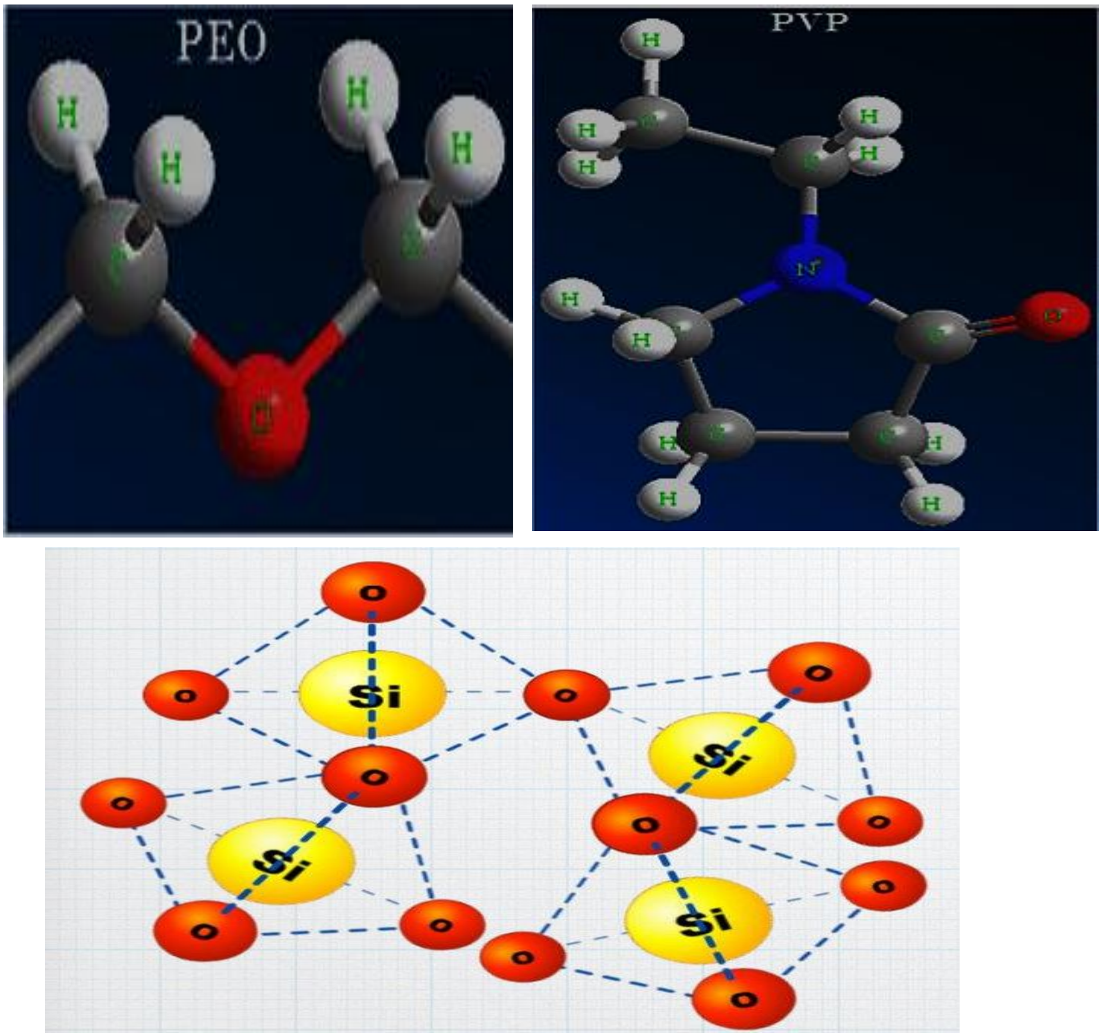
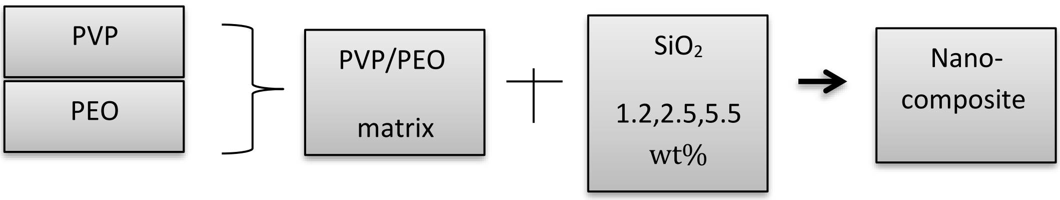


Fig(2): The chemical structure of PVP &PEO, SiO_2

Study the main properties which result from mixing PVP/PEO with SiO_2:

Experiments:



Technium Sustainability
Technium Sustainability
Vol. 3, pp.41-53 (2023)
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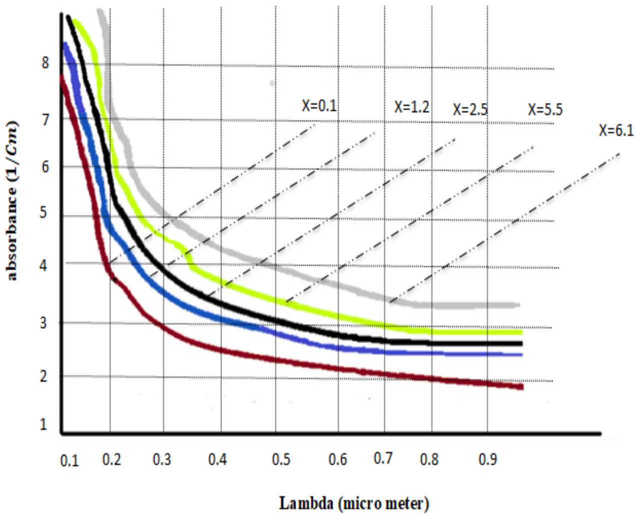
www.techniumscience.com

1-The absorbance of the compound studied:

The absorbance-spectra of the studied nanocomposite. It could be noticed that the absorbance values had been changed when the concentrations of the silica had been increased.

Wt%	wavelength-photons μm	Absorbance
0.1	0.75	0.91
1.2		
2.5		1.99
5.5		1.1
6.1		1.17
0.1	0.52	1.09
1.2		
2.5		1.23
5.5		1.3
6.1		1.34
0.1	0.25	1.5
1.2		
2.5		1.8
5.5		1.9
6.1		1.95

Table 1: The values of absorbance for different values of concentrations



Fig(3) : The graphs of absorbance for different values of concentrations

this value is raised whit the decreasing of $\lambda > 400$ nm , the highest value is getting at $\lambda \approx 250$nm. The absorbance of PVP is weak within the visible domain. However PEO has lower transparency, so the blend of (PVP/PEO) give a notable absorbance .This results related to absorbance due to electrons transmission from the bond C=O in PVP to oxygen atom in PEO.

2- **energy band-gaps E_g (direct & indirect):**

This is a significant parameter to decide whether this composite material is convenient to particular application or not, briefly, it helps to achieve agreement between the optical properties and the required application.

$(\alpha hv)^m = B(hv - E_g)$ where, hv is energy of photon at the frequency of (v), h: Plank constant, B: proportionality constant, m: take the values(1 & 1/2) to determine the type of E_g direct or indirect. The results related to E_g are presented in table(2).

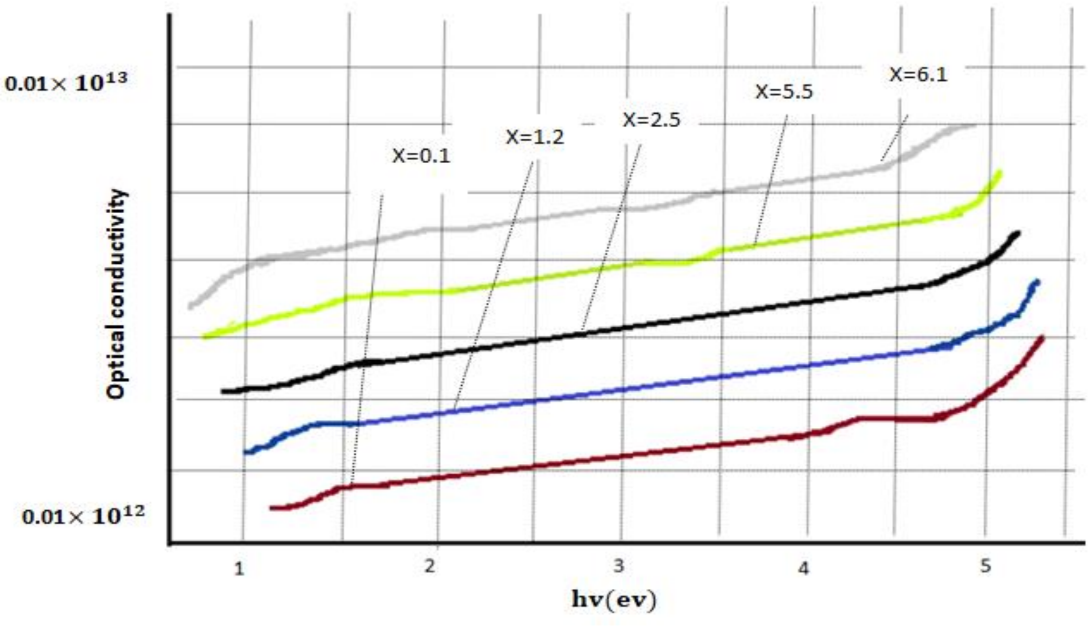
Nano-filler $(x)wt\%$	$E_{gd}(eV)$	$E_{gi}(eV)$	$E_u(eV)$
0.1	4.6	4.21	1.13
1.2	4.77	4.22	1.28
2.5	4.65	4.02	1.31
5.5	4.48	3.88	1.6
6.1	4.51	3.91	1.68

Table(2): Values of E_{gd}, E_{gi}, E_u,for (PVA/PEO)/x $wt\%$ SiO_2

3-Urbach-energy E_u:

It explains the optical properties and represented by this equation:

$\alpha = \alpha_0 \exp\left(\frac{hv}{E\infty}\right)$, α_0 is the minimum value of absorbance-coefficient, and by using this relation we could obtain the Urbach-energy



Fig(4):The variation of $ln\alpha$ with hv(eV)

4-Refractive-index n and extinction-coefficient K:

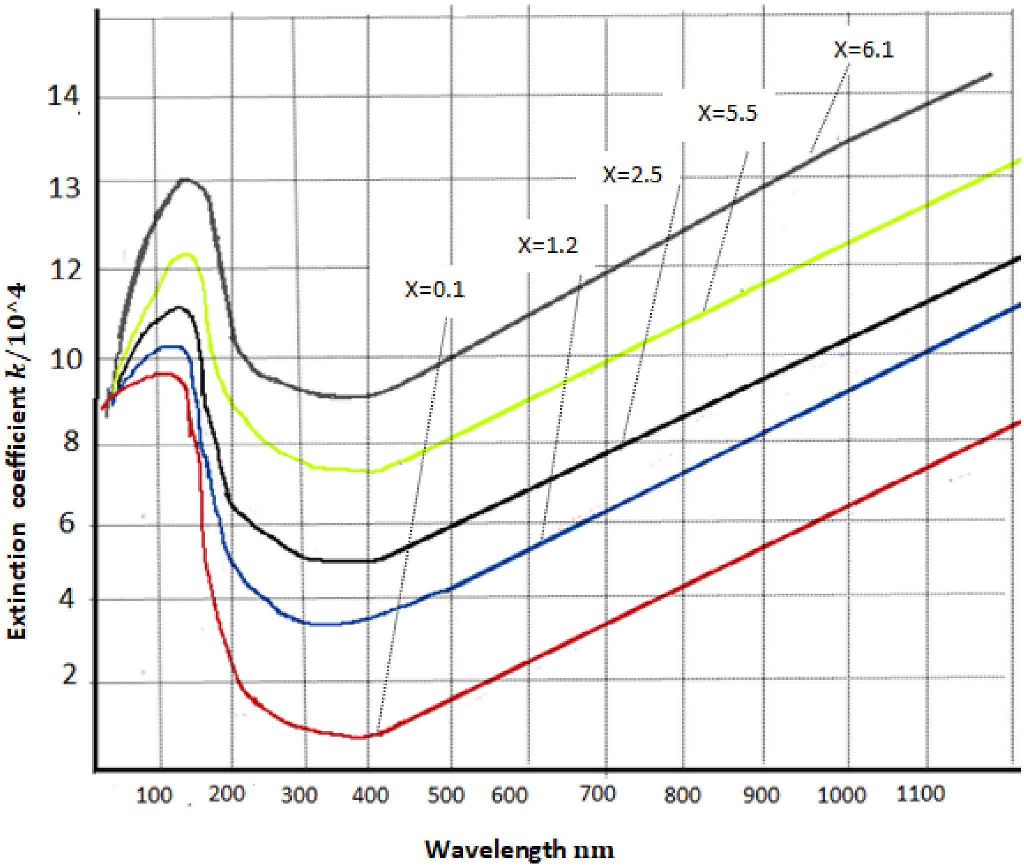
Linear-refractive index n: the suitability of nano-composites polymers in optic filed and the optoelectronic apparatuses is ruled by this index, when the inorganic nano-composite polymer is added into the matrix, the packing-density is obviously increased, which tends to increase the refraction-points per unit volume, as well as this improve the index n. The values of n could extracted from the relation :

$$(n^2-1)/(n^2+2) = 1 - \left(\frac{E_g}{20}\right)^{\frac{1}{2}}$$

extinction-coefficient K: This coefficient is specified repeatedly to comprehend the attenuation of the photons propagations through a specific material has fixed thickness. Therefore, the values of this coefficient related to SiO_2, including those nanocomposites are specified by this equation :

$$K = \frac{\alpha\lambda}{4\pi}$$

it could be seen that the SiO_2 addition to the PVP/PEO results in increasing the values of n. fig(5) presented the relation between K and hv



Fig(5): The relation between extinction-coefficient K and hv(eV)

Technium Sustainability
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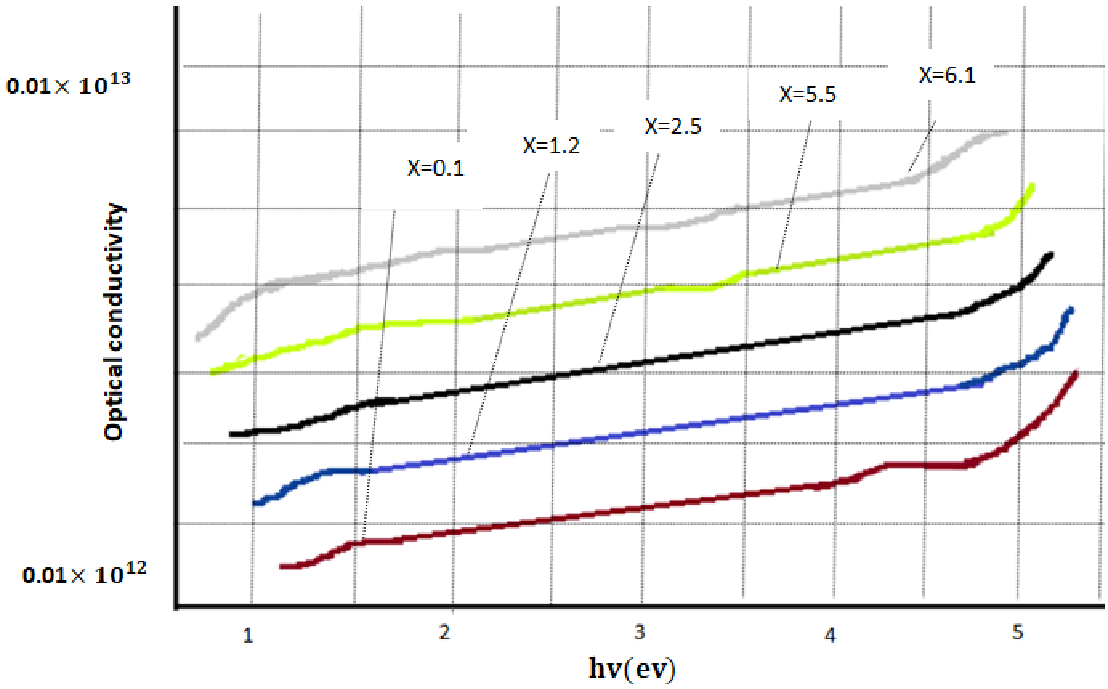
www.techniumscience.com

5-Optical-conductivityσ_{opt}:

It is determined as following:

$$\sigma_{opt} = \frac{n\alpha c}{4\pi} \; ; n = \frac{1 + R^{0.5}}{1 - R^{0.5}}$$

Where R is the reflectance. Fig (6) explained the relation between σ_{opt}& $h\nu$, it could be seen how the σ_{opt} is changed from 0.1^{13} *to* 0.1^{14} when the energy of photon is high ($h\nu = 5\ ev$), In these materials, the σ_{opt}increasing depend on Abundance of charge-carriers that are free. The relations between values of σ_{opt} are specified for the $(PVP/PEO/SiO_2)/x$ wt% films and $h\nu$ values is presented by fig(9).



Fig(6):The relation between Optical-conductivity and hv(eV)

6-**Diffieriential scanning calorimetry DSC to detect the thermal properties of the studied compound:**

DSC is a technique that used to measure the variety of heat-amount.

Fig(7) presented the thermograms of the studied compound. The temperature rang (40-105℃) this is done for a heat-cycle for the studied sample. From curves shown in fig(7), it could be notices the peaks of endothermic according to the crystalline-melting stage of PEO quantity of (PVP/PEO)matrix,

Technium Sustainability
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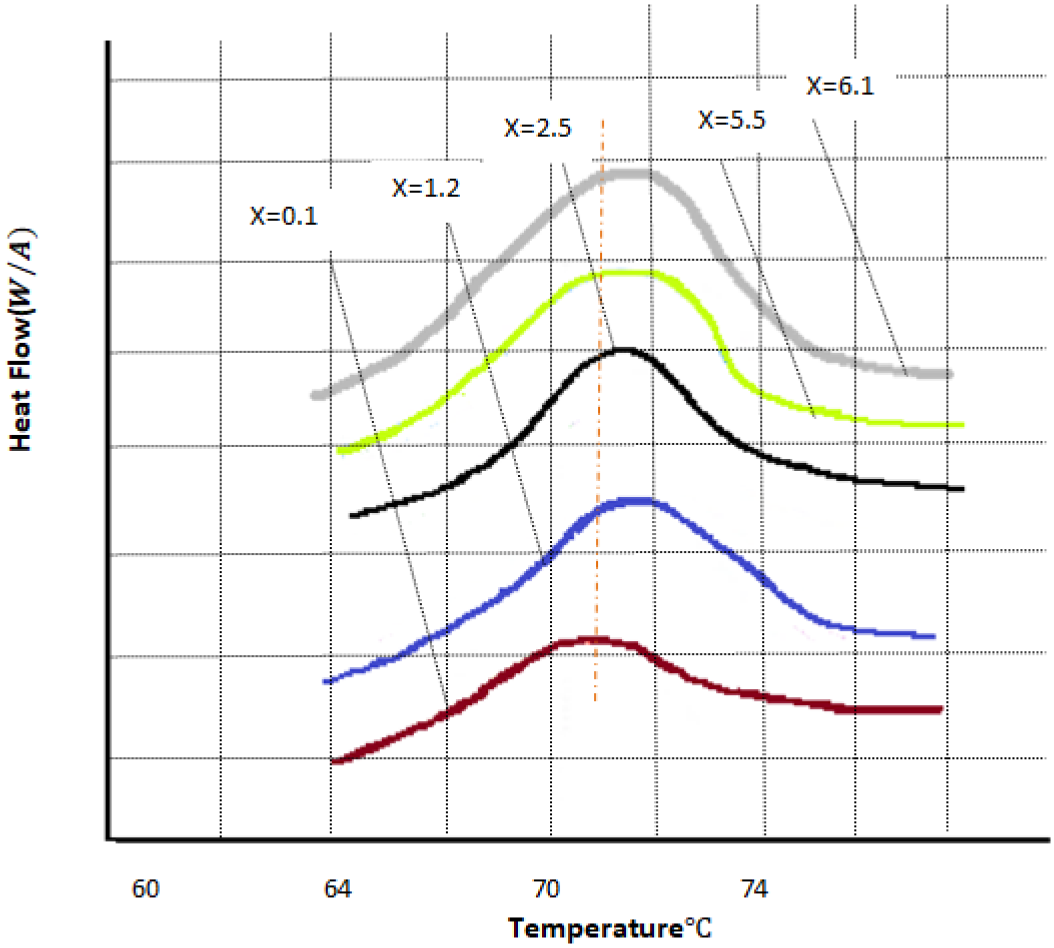

Fig(7) : Thermograph of (PVP/PEO)/x wt% SiO_2)

The parameters T_{on}, T_{end}, T_p represent the (onset, end ,peak) temperature respectively. ΔH_m represent the melting- enthalpy. The temperature of PEO crystallites-melting is represented by T_p. The increasing of T_p values on the adding nano-fillers is due to the larger sizes of (PEO) crystallite, this increasing in the size values is referred to add SiO2 to the composite-material. $T_p$values of polymer-composites higher than the polymer-matrix. This is explained by the stability of thermal performance of the (PVP/PEO) matrix. The values of $\Delta H_m, T_{ON}, T_{end}, T_p$, at multiple values of $x(wt\%)$ are arranged in table 3

Nano-filler $(\boldsymbol{x})\boldsymbol{wt\%}$	$\boldsymbol{T_{on}}$°C	$\boldsymbol{T_p}$°C	$\boldsymbol{T_{end}}$°C	$\boldsymbol{\Delta H_m}$
0.1	67	68.5	69.4	81.22
1.2	67.5	68.8	70.5	81.55
2.5	67.8	68.7	70	82.3
5.5	67	68.5	70.2	81.22
6.1	66.7	69	71	80.20

Table (3): The values of $\Delta H_m, T_{ON}, T_{end}, T_p$, at (1.2,2.5,5.5,6.1) of $x(wt\%)$

Technium Sustainability
Technium Sustainability
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www.techniumscience.com

7.XRD – Spectra : the angular domain within $10° \leq 2\theta \leq 40°$. from the figure it could be seen that the PEO presented peaks from the XRD-patterns of the compound studied we could observe the semi-crystalline structure of the compound material, and the existence of SiO_2 improve the crystalline-mature of the matrix. From the graphs it could be seen the effect of concentrations $(x = 0.1, 1.2, 2.5, 5.5, 6.1)wt\%$

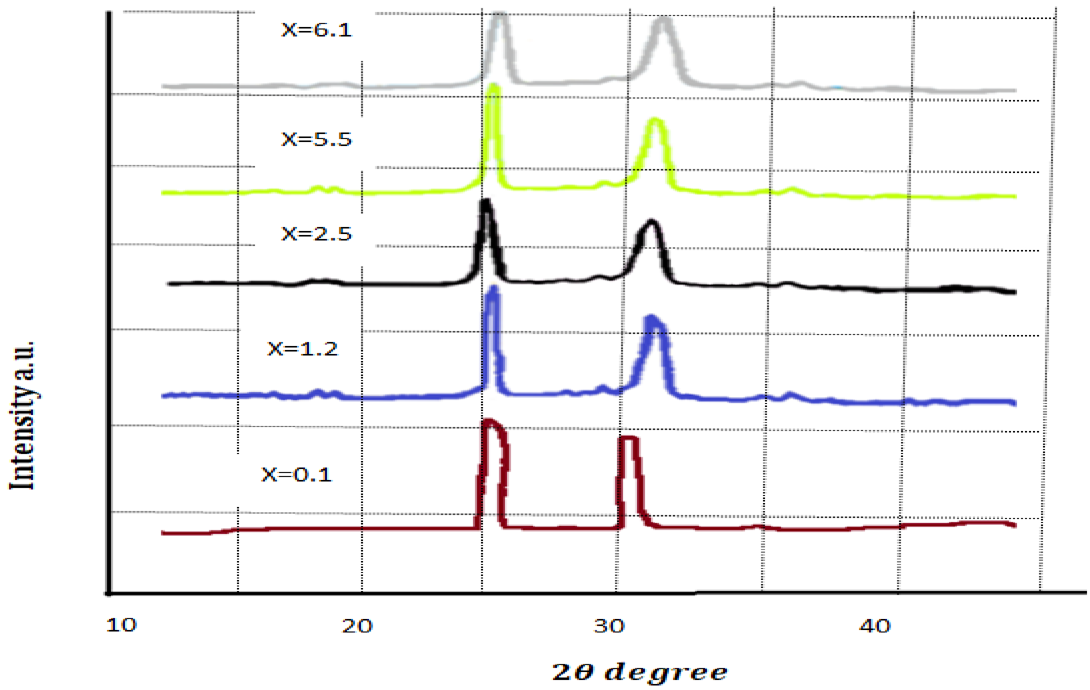

Fig (8): The XRD-patterns of SiO_2 nano-filler and (PEO– PVP)– x wt% SiO_2 nano-composite containing $x = 0.1, 1.2, 2.5, 5.5,$ and 6.1.

Table (8): 2θ angle values for $(PEO–PVP)– x\ wt\%\ SiO2$

$X\ wt\%$	0.1	1.2	2.5	5.5	6.1
2θ	25.1	25.3	25	25.2	26

8.FTIR-Spectra:

From fig (9), it could be observed that on 1.2 wt% of SiO_2 dispersion in the matrix, intensities of the whole bands of mixture decrease as well as the position of these bands is considerably varied. Also, extra bands had appeared with larger number , however these stay without change with the concentration increase over to 6.1 wt%. this emphasizes the powerful interactions which occurred among the components of the blend. Characteristic bands intensity are(2980 and 400 1/cm) of SiO_2 are repressed**.** The multi-bands which appearance in the spectra of the studied compound around the powerful bands emphasizes on the increase of vibrational-modes number of the nano-filler which occurs due to the interaction between the nanoparticles.

Technium Sustainability

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www.techniumscience.com

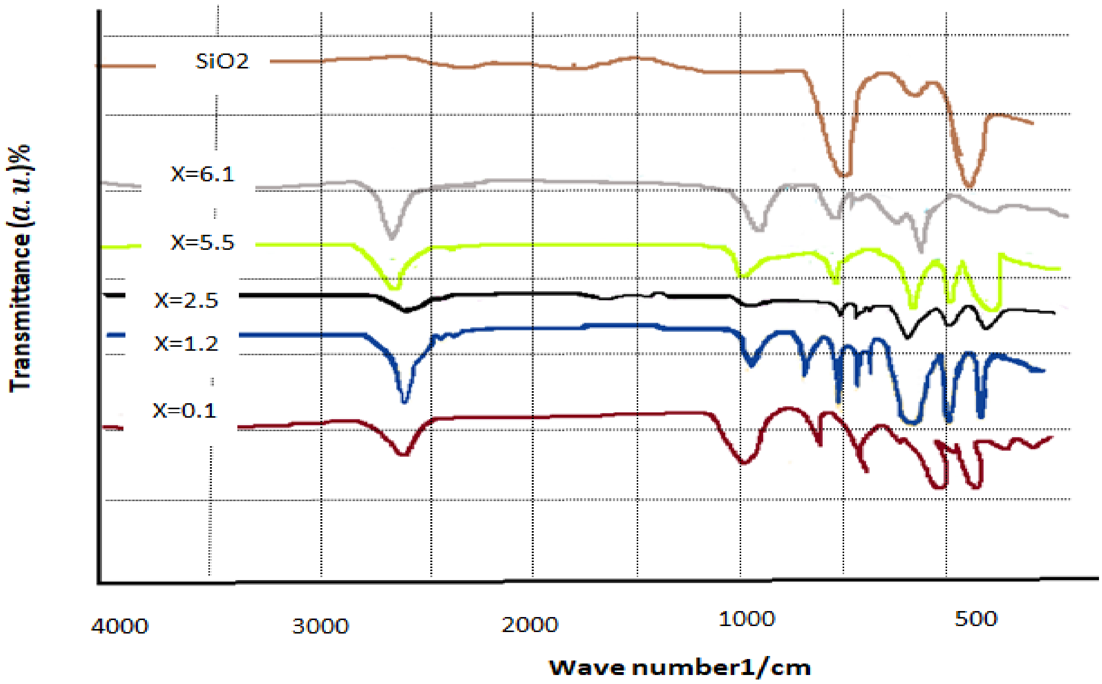

Fig (9): FTIR-spectra of $(PEO-PVP)$–x wt% /SiO_2 for (a) $x = 0.1,1.2,2.5,5.5,6.1$ and SiO_2 nano-filler

Conclusion:

The effect of adding SiO_2 to PVP/PEO on the polymer-composite proprieties (optical, mechanical, thermal) are investigated. The results shows that the refractive-index, energy-gap, optical-conductivity of the PVP/PEO filled with SiO_2 are controllable, this is achieved for a specific range. The thermal examination observed that the increasing of temperature values of PVP/PEO/SiO_2 is an evidence to thermal stability enhancement, From this experimental study, It could be observed that adding SiO_2 to the matrix PVP/PEO improve its most important characteristics, this enable to meet the required quality for various application. Generally, nano-composite material had improved its affectivity in the various modern application.

Appendix:

Preparation of material:

PVP ($M_w = 60 \times 10^4 \frac{g}{mole}$), $PEO\left(M_v = 60 \times \frac{10^4 g}{mole}\right)$, and the nanoparticles size (SiO_2 nanoparticle sizes $5nm \leq t_p \leq 15nm$)

Deionizing-water had used to solve the selected powder

$PVE/$(PVP,0.5 g (PVP)& 0.5g (PEO) for $\frac{50}{50}$ wt %) initially, then 0.1,1.2,2.5,5.5,6.1 $wt\%$ had considered of SiO_2 nano-powder had taken. Firstly, specific amount of polymer had been dissolved, then, the nanoparticles had been dispersed within deionized- water. After that, the components had been mixed. Through the ultrasonication as well as magnetic tape stirring, the suspension of the blended nano-particles within polymeric aqueous solution had been implemented. Finally, molding the prepared mixed solutions PVP/PEO/SiO_2 had been formed.

Measurements:

X-ray diffraction (XRD), patterns of nanofiller (SiO_2) in our study, and the matrix (PVP/PEO) − x wt% nano-filler had recorded with $0.05°S^{-1}$ scan-rate, by reflection-mode.

ultraviolet–visible (UV− Vis), for absorption-spectra of the nanocomposite materials with (0.1,1.2,2.5,5.5,6.1)wt% had been obtained within range(0.25,0.75 μm).

References:

[1] Amir, S.M.M.,Sultan, M.T.H., Jawaid, M., Ariffin, A.H., Mohd, S., Salleh, K.A.M.; Ishak, M.R.; Shah, A.U.M. Nondestructive testing method for Kevlar and natural fiber and their hybrid composites. In Durability and Life Prediction in Biocomposites, Fibre-Reinforced Composites and Hybrid Composites; Elsevier: Amsterdam, The Netherlands, 2019; pp. 367–388

[2] Sapuan, S.M. Composite Materials. In Composite Materials; Sapuan, S.M., Ed.; Elsevier: Boston, MA, USA, 2017; pp. 57–93.

[3] Dhatarwal, P., Poly(vinyl pyrrolidone) matrix and SiO2, Al2O3, SnO2, ZnO, and TiO2 nanofillers comprise biodegradable nanocomposites of controllable optical properties for optoelectronic applications, Optik, International Journal for Light and Electron optics,(2021)

[4] Rajesh, K., Crasta, V., Kumar, N., Shetty, G., Redkha, P., Structural, optical, mechanical and dielectric properties of titanium dioxide doped PVA/PVP nanocomposite, Journal of Polymer Research, 2019.

[5] Badawi, A., Alharthi, S., Alotaibi, A., Althobaiti, M., Investigation of the mechanical and electrical properties of SnS filled PVP/PVA polymeric composite blends, Journal of Polymer Research, 2021.

[6] Abbasi, H., Antunes, M., Velasco, J., Recent advances in carbon-based polymer nanocomposites for electromagnetic interference shielding, Progress in Materials Science, 2019.

[7] Aziz, S., Brza, M., Nofal, M., Abdulwahid, R., Hussen, S., Hussein, A., Karim, W., A Comprehensive Review on Optical Properties of Polymer Electrolytes and Composites, Materials, 2020.

[8] Guruswamy, B., Ravindrachary, V., Shruthi, C., Hegde, S., Sagar, R., Praveen, S., Optical, Electrical and Thermal Properties of SnO2 Nanoparticles doped Poly Vinyl Alcohol-Poly Vinyl Pyrrolidone Blend Polymer Electrolyte, Advances in Chemical Science,2018.

[9] Ali, A., Salim, S., Kamoun, E., Novel glass materials-based (PVA/PVP/Al2O3/SiO2) hybrid composite hydrogel membranes for industrial applications: synthesis, characterization, and physical properties, J Mater Sci: Mater Electron, 2022.

[10] Rahman, M.R., Hamdan, S. bin Study on physical, mechanical, morphological and thermal properties of styrene- co -glycidyl methacrylate/fumed silica/clay nanocomposites. In

Technium Sustainability
Vol. 3, pp.41-53 (2023)
ISSN: 2810-2991
www.techniumscience.com

Silica and Clay Dispersed Polymer Nanocomposites; Elsevier: New Delhi, India, 2018; pp. 71–85.

[11] Arumugaprabu, V.; Ko, T.J.; Uthayakumar, M.; Joel Johnson, R.D. Failure analysis in hybrid composites prepared using industrial wastes. In Failure Analysis in Biocomposites, Fibre-Reinforced Composites and Hybrid Composites; Elsevier: Amsterdam, The Netherlands, 2019; pp. 229–244.

[12] Khan, I.; Saeed, K.; Khan, I. Nanoparticles: Properties, applications and toxicities. Arab. J. Chem. 2019, 12, 908–931.

[13] Alibe, I., Matori, K., Sidek, H., Yaakob, Y., Rashid, U., Alibe, A., Zaid, M., Nasir, S., Nasir, M., Effects of polyvinylpyrrolidone on structural and optical properties of willemite semiconductor nanoparticles by polymer thermal treatment method, Journal of Thermal Analysis and Calorimetry,2019.

[14]Mishra, A.K. Conducting Polymers: Concepts and Applications. J. At. Mol. Condens. Nano Phys. 2018, 5, 159–193.

[15] Romero-Fierro, D., Bustamante-Torres,M., Bravo-Plascencia, M., Magaña, H., Bucio, E., Polymer-Magnetic Semiconductor Nanocomposites for Industrial Electronic Applications, Polymers, 2022.

[16] Topolniak, I., Chapel, A., Gaume, J., Bussiere, P., Chadeyron, G., Gardette, J., Therias, S., Applications of polymer nanocomposites as encapsulants for solar cells and LEDs: Impact of photodegradation on barrier and optical properties, Polymer Degradation and Stability, 2017.