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Effect of Cr2O3 Nanoparticles on the Spectroscopic Properties of PVA/PEO Nanocomposites

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Annotation

Nanocomposites have applications in various fields. Hence, the possibility of developing its optical properties. In this work, flexible films were prepared by casting method using polymer matrix of “Poly Ethylene Oxide (PEO) “and “Poly Vinyl Alcohol (PVA)” and with various concentrations of Chromium oxide (Cr2O3) nanoparticles(NPs) as the filler. The spectral properties of the synthesized films were Checked by "Fourier transform infrared (FTIR)", X-ray diffractometry analysis (XRD), and "UV/Vis" for morphological ,structural, and optical features. XRD analysis shows that the PVA/PEO/Cr2O3 nanocomposite films are semicrystalline, and that the degree of crystallization increases, in addition to the appearance of new peaks after loading nanoparticles of Cr2O3. FTIR spectroscopy confirmed the presence of complex compounds in the polymer mixture after the introduction of $Cr2O_3$ nanoparticles. Also, deviation in the locations of the existing bands , development of new peaks, in addition to the changes that occurred in the intensity of the infrared absorption bands, indicate that there is an interaction and compatibility that has occurred between the PVA/PEO mixture and the Cr_2O_3 nanoparticles. depending on UV/Vis spectra, band gap affected by the increase of $Cr2O_3$ nanoparticles in the mixture. This can be imputed to the charge transfer between $Cr2O_3$ nanoparticles and the PVA/PEO matrix; hence, the absorption intensity of the films doped with $Cr2O_3$ nanoparticles increased compared to the pure mixture, while the magnitudes of energy gap decreased for all direct and indirect transitions with the increase in the concentration of $Cr2O_3$ nanoparticles.

Keywords: Nanocomposite, Cr_2O_3 NPs, Metal oxide nanoparticles, PVA, PEO.

1. Introduction

Composites are substances made up of two or more components. The purpose of composite materials is to create a new material that combines the strengths of both constituents while often mitigating the weaknesses of the original materials. Composite materials are classified based on the type of reinforcements used to strengthen them. These reinforcements are embedded within a matrix that binds them together. The continuous component that is present in greater quantity in composites is referred to as the matrix. The prevailing view is that the properties of the matrix improve when another component is incorporated to form composites. Such composites may possess a metallic, ceramic, or polymeric matrix. Particulate reinforcements can have approximately equal dimensions in all directions, and the shape of the reinforced particles may be either regular or irregular geometrical shapes [1]. In nanocomposites, one of the constituents has dimensions on the nanoscale (<100 nm), or the composite structure exhibits nanoscale phase separation of the individual components [2].

Due to the exceptional properties of nanomaterials, they are widely used for various applications by mixing them with bulk polymeric materials to enhance their features. Nanocomposites are chemical compounds supported by nanoparticles. Based on the components of the composite matrix, nanocomposites can be categorized into metal, polymer, and ceramic matrix composites. In polymer matrix composites, emphasis should be placed on the dispersion of nano-reinforcers within the bulk polymer matrix. A homogeneous distribution of nanofillers results in enhanced properties; conversely, the agglomeration of particles caused by van der Waals forces between nanomaterials leads to inferior properties [2-7].

There are numerous metal nanoparticles and metal oxides with unique properties that serve as catalysts, adsorbents, bactericides, reducing agents, and sensors [8-11]. These materials provide rapid kinetics and enhance absorption due to their "high surface area" to "volume ratio." However, their tendency to aggregate, loss of characteristic interactions in "complex systems," and weak mechanical strength often pose significant obstacles to repetitive applications. It is important to note that "biopolymers" and functional polymers represent a different category from "organic materials," characterized by chemical stability, durability, and the ability to be chemically modified depending on the intended application needs [12-13]. Studies have shown that metal oxide nanoparticles hybridized with polymeric materials to form nanocomposites exhibit unique applications and properties that are not found in either polymeric host materials or inorganic nanoparticles alone.

It is worth noting here that in nanocomposites the metal oxide is always present in the form of nanoparticles, while the morphology of polymeric materials varies widely, from granular form, films, spherical beads, fibers, etc.. In nanocomposite, the polymer molecules and reinforced nanoparticles retain their intrinsic properties but can be easily modified in several ways to complement the general properties of the nanocomposite. From the above, We note that the type and features of the nanocomposites are subject on several factors, the most important of which are the type of harbor material (polymer) and its morphology, in addition to the concentration and type of functional groups.”, and the methods of fixation on the final advantages of the produce [14].

Physical properties of the "host" matter like shape, surface area, size, micropore shape, etc. have a great influence on determining the size and nature of the metal oxide nanoparticles dispersed among the particles of the host material [15]

Hybrid polymer mixture can enable easier casting and preprocessing with nanofillers to prepare novel nanocomposite films according to their structural, morphological,electrical and optical properties[16]

Thermoplastic polymer (PVA) has good solubility in water and is used in a variety of industrial applications as well as medical and optoelectronic applications. [17,18]

PVA has the property of easily combining with other substances to produced mixtures or compounds[19]. (PEO) is a semi-crystalline, at laborotary temperature, PEO is fully soluble in water .At higher temperatures (>98°C) the solubility diminishes.[11] PEO polymers are used in the medical and cosmetic industries, as thickeners, lubricants, film-forming agents, agglomerants, and binders in implementations inclusive adhesives, incrustation, inks, water treatment, ceramics, papermaking, agricultural chemicals, and electronics[20-22]. One of the most important features of polyethylene oxide (PEO) is its efficiency in forming complexes with nanomaterials.. In addition to its good mechanical and electrical properties. Thanks to its good electrical and mechanical properties, and its chemical structure which is determined by the presence of “ether and –OH” end groups, which makes it possible to form hydrogen bonds, which was confirmed by the process of mixing PEO with other polymers. [23].

In recent decades, nanomaterials have gained great importance due to their physical properties and numerous applications in various fields. A large number of researchers interested in studying nanocomposites have studied the diffusion of nanoparticles in polymers.. By adding some nanoparticles to the polymer or polymer mixture, its unique properties will be enhanced, especially with regard to the composition, size and quantity of nanoparticles, in addition to the degree of homogeneity between them. [24,25]. Cr2O3 nanoparticles have received more attention in the latest years because of their unique properties.Many researchers have been interested in studying the diffusion of Cr2O3 nanoparticles in polymer matrix[26,27]

From former research, unique advantages of metal - nanoparticles, and nanocomposites full of with them, are Interesting because of its use in extensive ranging applications. There are not many studies that study the interaction of chromium oxide nanoparticles with PEO/PVA polymer blends and their effect on the "physical properties of PEO/PVA" blends. In this work, we focus on the synthesis of a new polymer nanomaterial resulting from mixing Cr2O3/PVA/PEO at low weight ratios. We study the change in structural, optical and electrical conductivity properties and compare them with previous results.

2. Experimental

2.1 Materials

As a polymer matrix, “polyvinyl alcohol with a molecular weight of about 115,000 g/mol and 99% purity”, “polyethylene oxide with a repeating unit (CH2CH2O)$_n$ with a molecular weight of about 3,000,000 g/mol and a density range of 1.15 to 1.22 g/cm^3”, and “chromium oxide nanoparticles with an average particle size of 20 to 30 nm” were used

2.2 Preparation of PVA/PEO/Cr2O3 NPs blend films

PVA/PEO was mixed at a weight ratio of 80:20 percent to form the film he components were melted in 35 ml of doubl-distilled water and the mixture was stirred continuously for 2 h at 60 °C to obtain a uniform viscous liquid.. According to the proportions shown in Table {1}, nano chromium oxide powder was added to the polymer mixture based on formula (1) to fulfilment the doping process. To obtain a homogeneous mixture of polymer solution and chromium oxide nanoparticles, the mixture was stirred for 1 h. Then, pure PVA/PEO mixtures and PVA/PEO mixtures mixed with differing concentrations of Cr2O3 nanoparticles were prepared using casting technique. After cast the prepared mixtures into Petri dishes, they were After pouring the prepared mixtures into Petri dishes, they were left at laboratory temperature until they dried for eight days,and after the films dried, they were separated from the Petri dishes and keep for analysis..

$$W_t \% = \frac{w_{cr}}{w_{blend}+w_{cr}} \times 100 \ldots\ldots\ldots\ldots\ldots\ldots\ldots.(1)$$

Table 1. PVA/PEO/Cr2O3NPs weight percentages

PVAw%	PEOw%	Cr$_2$O$_3$w%
0.8	0.2	0
0.8	0.160	0.04
0.8	0.148	0.052

3. Measurement techniques

Using “CuKa radiation (where k=0.9, the tube operated at 40 kV), X-ray diffraction (XRD)” inspection were conducted on “a Bruker AXS D2 PHASER diffractometer”. Bragg's angle (2Ɵ) was measured between 30° and 50°. To study the optical features of the prepared samples, their absorption spectra were measured using a “Shimadzu UV-IR 210A dual-beam spectrometer”in the wavelength range of (200 – 800) nm.From the absorption data, the absorption coefficients at different wavelengths were obtained using formula (2) [28], and then the energy band gaps for each sample were calculated

$$\alpha = (2.303A)/t \qquad (2)$$

where α :absorption coefficient, **A:absorbance, t:** thickness of the film

To measure the" thickness "of the "films", which were "in the range" of 0.97 to 1 micrometer, a digital micrometer was used.

"Fourier transform infrared spectroscopy (FTIR) "is an analytical method used to examine samples and look at the chemical properties and functional groups using infrared light, which gives details about the individual molecular structure of a substance and chemical bonds.The “SHIMADZU FT-IR-8400 spectrophotometer” was used to record infrared (IR) spectra in the 3500–500 cm–1 range.

4. “Results and discussion”

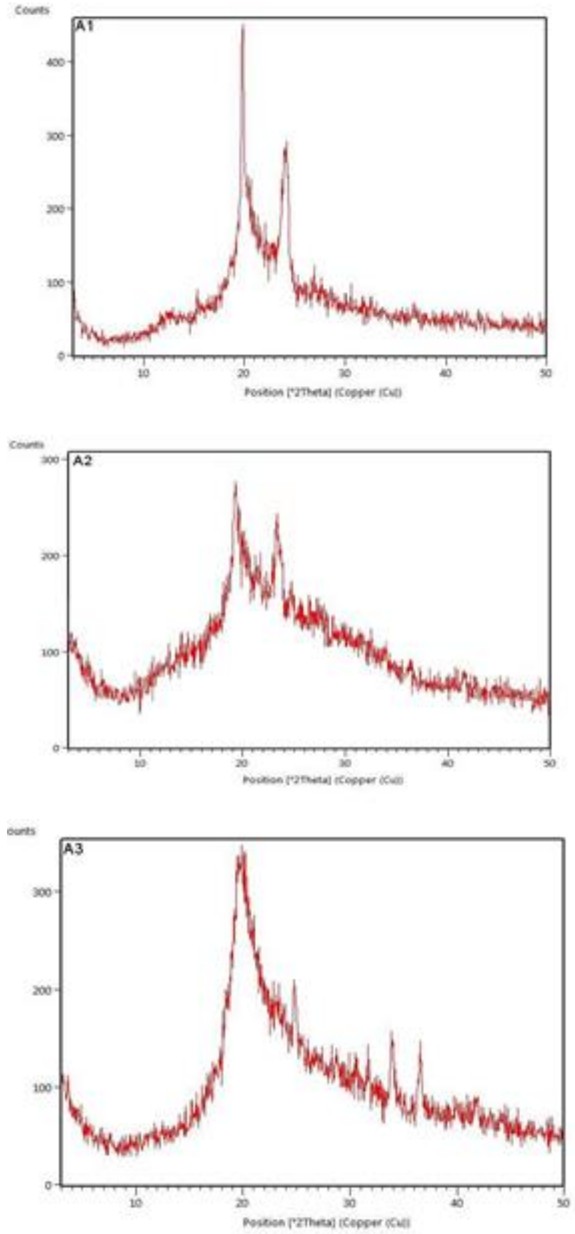
4.1 X-ray diffractometry analysis

“Figure 1 shows” the XRDs of pure PVA/PEO polymer blends and PVA/PEO polymer mixtures that were blended with various concentrations of Cr_2O_3 (0.0, 0.04, and 0.052 wt%). Two peaks at $2\theta = 19.88°$ and 24.03° were observed in the XRD spectra of the pure polymer blend PVA/PEO which exhibited a semi-crystalline nature as shown in Fig. 1(A1). After adding the Cr_2O_3 nano powder, the positions of the two peaks slightly changed. In addition, some peaks associated with chromium oxide appeared as shown in Fig. 1(A2,A3), which can be attributed to the increased crystallinity of the nanoparticle-loaded samples. It is evident that the broadening of the diffraction peaks of the polymer matrix is associated with the increase in the proportion of nanoparticles in the polymer blend; this can be explained by the variation in the degree of deacetylation of PVA and PEO [29].Crystalline size was calculated by Scherrer formula(3)

$$D = k\lambda / \beta cos(\theta) \qquad (3)$$

"Where (λ) and Ɵ represent the mean wavelength of the X-ray (λ~0.154 nm) ,and the angle between the incident and the scattering beams, respectively, and Crystal size (D nm), crystals factor (k = ~0.9), and (β) is (FWHM)" [30,31].

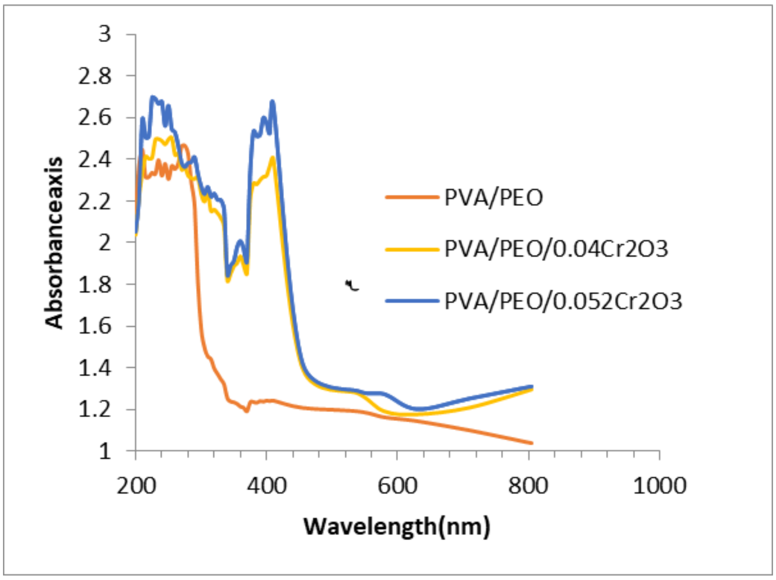
The results showed that the The results confirmed the good dispersion of Cr_2O_3NPs in polymer matrices caused a notable change in the polymer crystal size, Which may be a result of the interaction of the polymer mixture and Cr_2O_3 nanoparticles during the formation of the composite nano films.



Figuar 1. XRD scan of pure PVA /PEO blend with different wt.% of Cr2O3

4.2 UV–visible analysis (UV–Vis)

Figure 2 shows the “UV–vis absorption spectra” of PVA/PEO composites with diverse concentrations of chromium oxide nanopowder at laboratory temperature for films in the "range of 200–900 nm". As is clear in the figure, the UV-visible absorption progress with the increase of chromium oxide nanoparticles inside the PVA/PEO polymer matrices. In the spectra of the prepared nanocomposites, two absorption edges at wavelengths of 245 nm and 410 nm were found, which may be related to the construction of charge transfer complexes. The absorption spectrum of the prepared nanocomposites has low values in the near-infrared and visible regions, While the absorption increases in the short wavelength region where the interaction of the incoming photons with the mixture occurs.. It is evident that the addition of chromium oxide nanoparticles to the polymer mixture led to the development of absorption bands. This may be considering that the fact that the chromium oxide nanoparticles were homogeneously diffused the polymer blends [32].

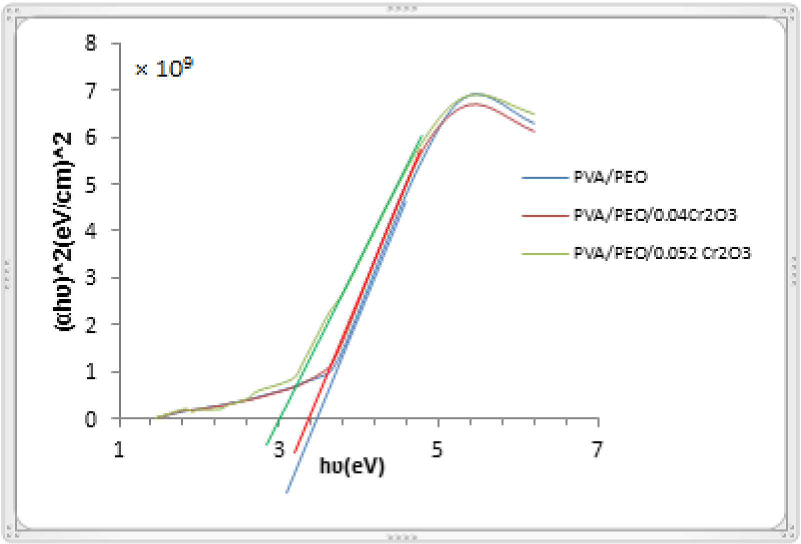


Figuar. 2 Absorbance spectra of a PVA /PEO/Cr2O3 composites

From the absorption spectrum, the "direct and indirect optical energy gap" of PVA/PEO/Cr2O3 films can be calculated using" Tauc's relation" [33]

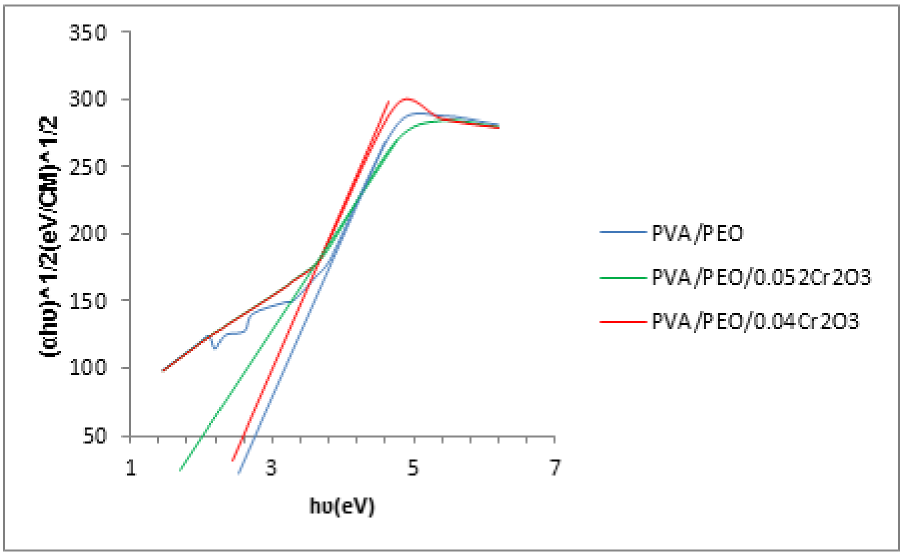
$$.(\alpha h\nu) = C(h\nu - Eg)\ n$$

where n is associated with the type of transition, Eg is the "averaged band gap" for the matter, C is a constant, and α is the "absorbtion coefficient" for prepared samples. Tacu's plot of the (αhν)2 and (αhν)1/2 as a photon energy function (hʋ̈) are presented in Figs. 3 and 4. The band gap value is given by the linear part of the curves that crosses the photon energy axis. From the curves, it can be observed that with the increase of the proportion of nano chromium oxide in the PVA/PEO blend, the values of direct and indirect band gaps decrease, this may be due to increased shifting of the "valence and conduction bands". Also, increasing the concentration of carriers in the conduction and valence bands has a great effect in enhancing the carrier-carrier interaction and thus reducing the band gap [34]. The optical energy gap may also be reduced due to defects in the polymer matrices. As a result of these defects, local cases appear in the optical band gap. Figure 4 represents the photon energy (hν) of PVA/PEO/Cr2O3 nanocomposites versus $(\alpha h\nu)^2$. It was found that the value of the optical energy gap of pure PVA/PEO composites is 3.5 eV at 0 wt% Cr2O3. The figure shows the variation of the band gap energy and its relationship with the weight percentage of Cr2O3 nanoparticles observed according to the direct proportional relationship. It was found that the energy gap decreased by a maximum of 3 eV for 0.052 wt% Cr2O3 in the nanocomposites.



“Figuar. 3 shows of (αhv)2 as a function of photon energy (hv). of blend polymer/Cr2O3Nps at different weight percentages”

“Figure 4 indicates the relationship of (αhv)1/2 and photon energy (hv) for PVA/PEO/Cr_2O_3 nanocomposites. It is clear that the optical energy band gap gets smaller with increasing Cr2O3 loading in the polymer blend. Evidence of this is that at 0 wt% Cr_2O_0, the band gap was 2.85 eV for pure PVA/PEO. While at 0.052 wt% Cr_2O_0, the band gap became smaller to 2 eV, which may be due to the localized states formed inside the band gap.

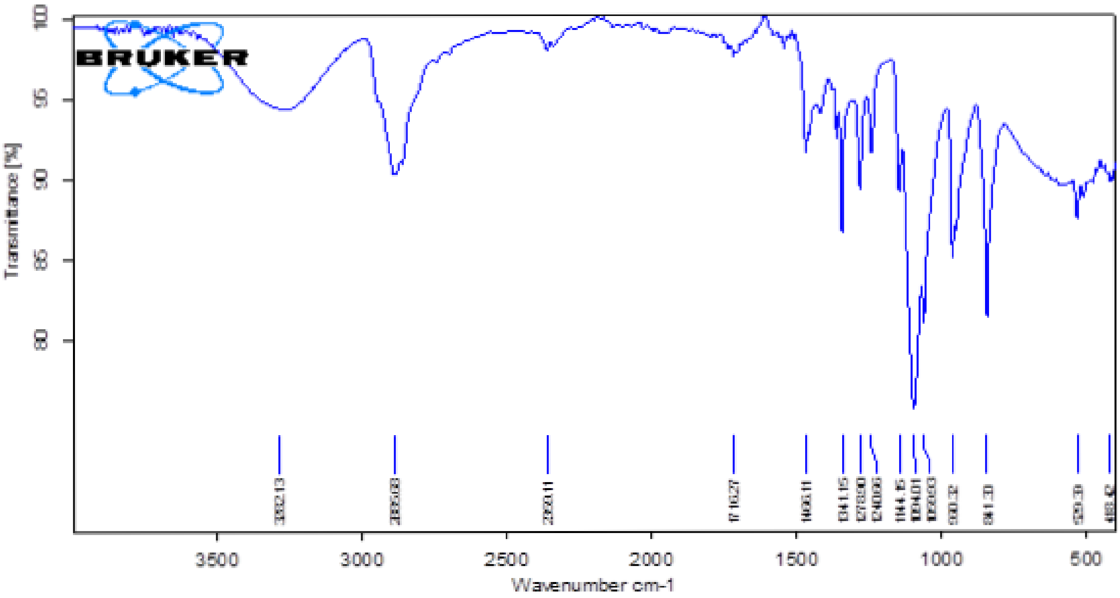


“Figuar. 4 shows of (αhv)1/2 as a function of photon energy (hv). of blend polymer/Cr2O3Nps at different weight percentages

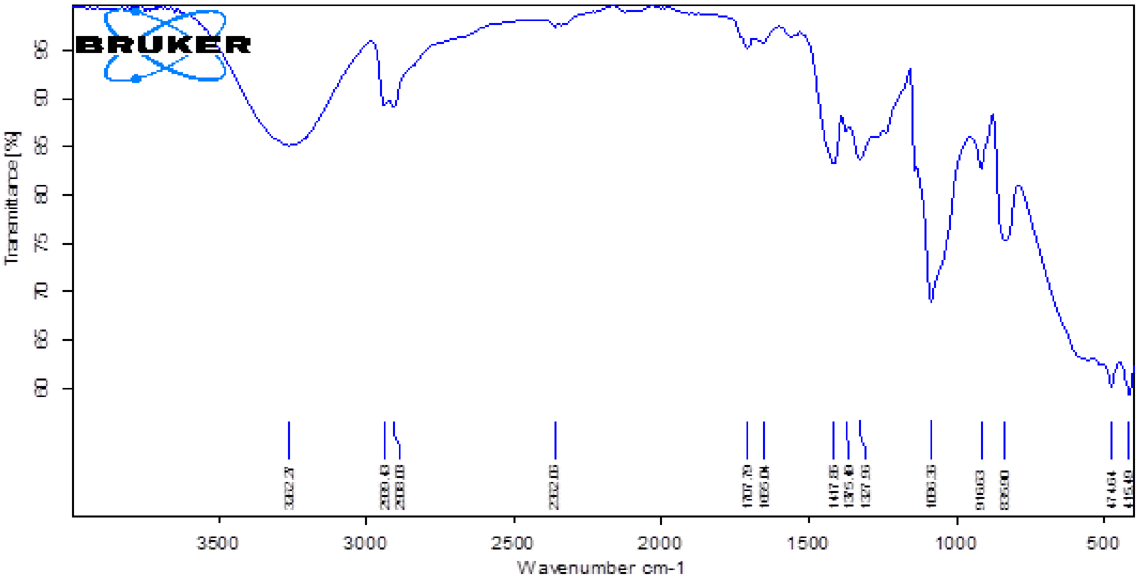
4.3 FT-IR analysis

“FT-IR spectroscopy” is Used to identify and describe the interaction between motifs in prepared models.Figure 5: “FTIR absorption spectra of pure PVA/PEO” polymer before loading $Cr2O_3$ nanoparticles in the range of 3500-500 cm^{-1}. A wide O-H “stretching band” is observed at 3282 cm^{-1}. whil relatively “narrow band” at 2885 cm^{-1} corresponds to SP^3 C-H stretching, resulting in additional band at 2359 cm^{-1}, the carbonyl (C=O) stretching is observed at 1716 cm^{-1}, C-O stretching is the reason for the bands at 1341 cm^{-1}, 1278 cm^{-1}, 1240 cm^{-1} and 1143 cm^{-1}. In addition, the stretching vibrations of C-C can be identified at 1466 cm^{-1}, and the C-O "stretching band" causes a sharp and intense band at 1094 cm^{-1} and 1059 cm^{-1}. While the "double olefinic bonds with single vinyl" (C=CH2) and "trans-unsaturated vinyl" (CH=CH) cause medium intensity bands at 960 cm^{-1} and 841 cm^{-1}, respectively. These peaks indicate that the combined materials are physically interacting, giving the blend new physical properties [35]. The infrared absorption spectra of PVA/PEO blends at different Cr2O3 concentrations are shown in Fig. 6 and Fig. 7. It is clear that most of the peaks in Fig. 5 have slightly shifted their positions in Fig. 6. The molecular bond variation due to the hybridization state between the nanoparticles and the polymer blend.The hydrogen bond strength of the O-H functional group increases, which also causes the peak at position 3282 cm-1 to broaden.

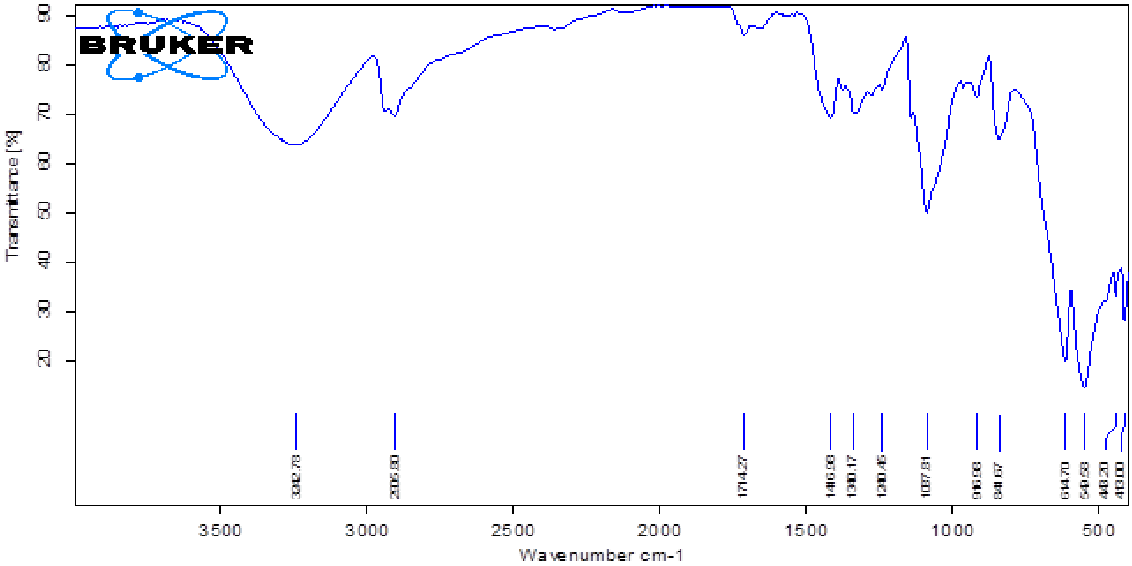
Figure 7 shows that all the FTIR absorption bands decreased with the increase of chromium oxide concentration; on the other hand, the intensity of the bands at 529 cm-1 and 418 cm-1 increased obviously, which can be attributed to the bonding between chromium oxide nanoparticles and the functional group in the blended polymers.



Figuar 5. Absorption Spectrum of Pure Blend PVA/PEO by FT-IR



Figuar 6. FTIR spectrum of PVA/PEO)/0.04 Cr2O3 W%NPs.



Figuar 7. FTIR spectrum of PVA/ PEO)/0.052 W%Cr2O3NPs

5. Conclusion

In summary, in this work, XRD, UV-Vis and FT-IR techniques were used to study and analyze pure PVA/PEO blends along with blends containing different amounts of Cr2O3. It was observed that the optical behavior of the polymer blend changed to some extent when the loading ratio of CrO nanoparticles increased. The enhancement of the absorption peaks from 2.32 to 2.69 at 230 nm and the decrease of the optical band gap (Eg) values from 3.5 to 3 eV may be related to the crystalline "defect" in the polymer matrix. These "defects" led to the presence of centralized cases in the optical band gap. According to XRD, there is a noticeable effect on the crystalline behavior of the reactants. Moreover, FTIR analysis also indicates the existence of hydrogen bonds and intense interaction between the matrix components.

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