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A Detailed Examination of UV Radiation Effects on the Structural and Morphological Properties of Polyvinyl Butyral Films Containing Different Nanoparticles

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ABSTRACT

Herein, polyvinyl butyral (PVB) films were synthesized using casting method and added to the PVB solution to make composites of PVB-nanoparticles were made via mixing 0.001 wt/wt % each time of each of the following metal nanoparticles (CuO, Cr_2O_3, NiO, TiO_2 and Co_3O_4(NPs)) with PVB solution at room temperature. The PVB-NP composites as films were irradiated with UV light for prolonged period which demonstrated spectral, and weight-loss changes. Those changes were much more significant than that of the blank PVB films undergo under identical conditions. Incorporating surface morphology examination of the composites were conducted using scanning electron microscopy (SEM), energy x-ray dispersive (EDX) spectroscopy and atomic force microscope. Overall, findings revealed that PVB-(CuO, Cr_2O_3, NiO, TiO_2 and Co_3O_4) NP composites showed a higher weight loss in compared to the PVB blank suggestive of higher photodegradation of the PVB-NP composites compared to the neat PVB film. A proposed photodegradation mechanism will be discussed. Prog. Color Colorants Coat. 14 (2021), 209-219© Institute for Color Science and Technology.

1. Introduction

Polyvinyl butyral (PVB) has been largely used in optical devices, photovoltaics, and military equipment due to its exceptional characteristics, such as radiation resistance and adhesiveness [1-5]. Furthermore, PVB has been implemented as dosimeter in nuclear industry [6]. Unfortunately, polymers are vulnerable to degradation due to the exposure to the light has become on of the major concerns in the polymer science, technology and industry [7]. Because of the light-induced damage of polymers in some high-tech industries, such as aviation, nuclear, and aerospace there have been a serious research effort to alleviate this problem. Such a light-induced damage occurs due to the interaction between incident light and matter which initiate secondary reactions in polymers. More precisely, rupturing the polymer structure because of the electronic excitation and ionization of polymers which affects bonds between atoms in polymers [8-10]. Long-term exposure of polymers to UV radiation is the main cause of discoloration, deterioration of mechanical properties, weight loss, and the reduction in average molecular weight. PVC is chemically stable and has good mechanical and physical properties. However, at high temperatures (>100°C), PVC undergoes a dehydrochlorination process to produce

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small fragments, along with the evolution of hydrogen chloride. This process leads polymer chains crosslinking, causing the material to become discolored and brittle. Therefore, polymers, such as PVC, produced for outdoor applications must be resistant to photodegradation and photooxidation to elongate their lifetime [18].

In this article, a synthesized PVB was subjected to UV light were investigated. At first, PVB was synthesized and casted into a glass substrate as film. PVB-NP composites were prepared as films and all were irradiated with UV light for 300h. The degradation of PVB neat film as well as composites was monitored by weight loss method, FTIR, EDX spectroscopy. Surface morphologies of films were also explored via using SEM technique.

2. Experimental

2.1. Materials

Polyvinyl alcohol (PVA) of molecular mass (MM) of (72,000 g.mol^{-1}) and hydrolysis of (98%). Butyraldehyde (MM=72.11 g.mol^{-1}) were sourced from AppliChem (Germany). The nanoparticles already provided from Sigma Aldrich company, the size of the nanomaterial that utilized in research dissertation with inspecting their sizes and diameters by AFM device of nanoparticles (CuO, Cr_2O_3, NiO, TiO_2 and Co_3O_4) are 56.43, 18.51, 30.69, 48.82 and 15.14 nm, respectively.

2.3. Synthesis and preparation of polyvinyl butyral (PVB) films

PVB polymer was synthesized according to an established protocol [11]. A solution of PVB in methanol was stirred at (25 °C) for (30 min); various nanoparticles (CuO, Cr_2O_3, NiO, TiO_2 and Co_3O_4 (0.001) wt/wt%) were added to the PVB solution, and the mixtures placed in an ultrasonic bath for 30 min. The mixtures were casted onto glass substrate, and the film were left for (24 h) at (25 °C) under a vacuum to dry [12].

2.4. UV light exposure

Q.U.V Accelerated Weathering Tester was used for irradiation PVC films with UV light (λ_{max} = 313 nm and light intensity = 6.43×10^{-9} ein.dm^{-3}.s^{-1}) at room temperature (26200 FIRST ST., CLEVELAND, OH44145 USA) Q-panel Company. The PVB films were rotated with consistently to ensure uniform supplying of light intensity on all the samples sides [13].

2.5. Characterization of systems

The FTIR spectra were collected on a FTIR 8300 Shimadzu spectrophotometer (Shimadzu, Tokyo, Japan). An accelerated weather-meter QUV tester obtained from Q-Panel Company (Homestead, FL, USA) was used to irradiate the PVB with a UV light (λ_{max} = 313 nm) at 25 °C. The surface morphology of PVB films was inspected using Field Emission Scanning Electron Microscopy (FESEM, TESCAN MIRA3, Kohoutovice, Czech Republic) at an accelerating of PVB surface spotted utilizing voltage up to 10 kV), while PVB films depth (ca. 50 µm) deliberated utilizing Digital Vernier Caliper 2610 A micrometer apparatus. Energy-dispersive X-ray spectroscopy (EDX) measurements were performed using the Bruker XFlash® 6|10 detector (Tokyo, Japan).

3. Result and Discussion

The synthesized PVB with the structure depicted in (Figure 1) was confirmed by various spectral and analytical data and were consistent with those reported [11].

The weight reduction of PVB films treated samples (50µm thickness), at different nanoparticles (0.001 %wt) against irradiation (300 h), extracted and referred to that acquired for unmodified PHB film. Figure 2 represents those changes in PVB weight loss percentage. Evidently, the PVB films with different nanoparticles show higher weight loss compared to blank PVB. Therefore, Co_3O_4 nanoparticles, shows the most photocatalytic effectiveness with PVB photodegradation.

Various nanoparticle (Co_3O_4, CuO, NiO, TiO_2 and Cr_2O_3) were used as photocatalysts in the process of PVB film photodegradation. The PVB samples (50 µm thickness) were irritated (λ_{max} = 313 nm) for (300 h) and

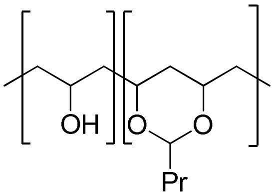

Figure 1: Polyvinyl butyral (PVB).

the changes in their FTIR spectra were monitored. The photodegradation of PVB samples (50 µm thickness) were investigated by recording the changes in carbonyl (1740 cm^{-1}) index vs. irradiation time. The relationships between carbonyl (I_{CO}) index vs. irradiation time for PVB films (50 µm thickness) photodegradation in the presence of different nanoparticals (0.001% wt/wt%) of (Co_3O_4, CuO, NiO, TiO_2 and Cr_2O_3) nanoparticles as photocatalysts are represented in (Figure 3). The results clearly indicate that PVB films, in the presence of Co_3O_4 nanoparticles, have a higher growth rate with increasing irradiation time compared to films in the absence of (PVB Blank). (Figure 3) shows that I_{CO} was the highest when photocatalysts nanoparticles was Co_3O_4 and lowest when the photocatalysts nanoparticles was Cr_2O_3. Therefore, Co_3O_4 nanoparticles, can be considered as a photocatalyst for PVB (50 µm thickness) photodegradation.

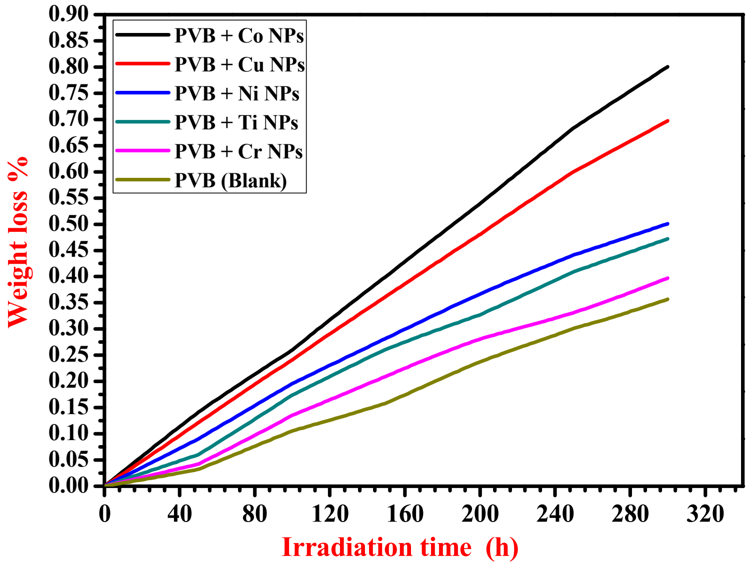

Figure 2: Weight loss of PVB films containing different nanoparticles (0.001 wt/wt%).

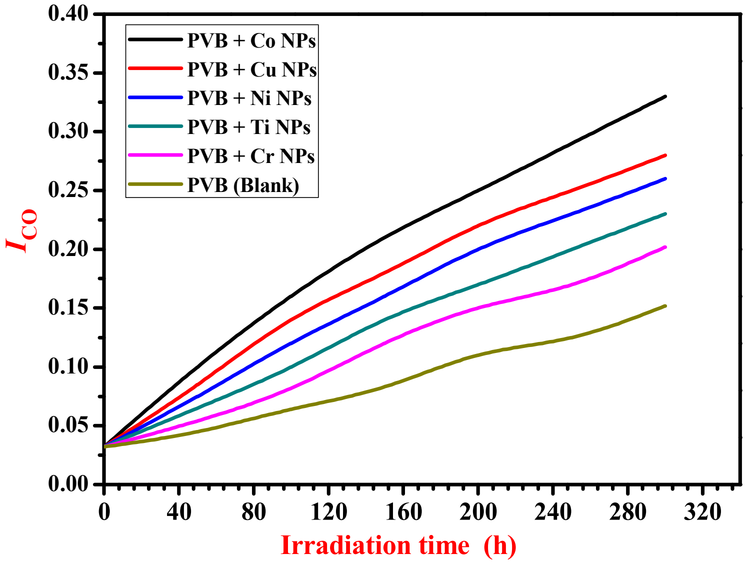

Figure 3: I_{CO} for PVB (blank) and PVB-NPs composites.

Figure 4 represents microscopic images for PVB films containing different nanoparticles (Co_3O_4, CuO, NiO, TiO_2 and Cr_2O_3) before and after irradiation. Discoloration and degradation was observed on the surface of PVB-NP composite surface upon the irradiation as clearly seen in Figures 4 and 5 which are indicative of photodegradation. PVB (blank) and those composite samples (Co_3O_4, CuO, NiO, TiO_2 and Cr_2O_3) before irradiation demonstrated a round cross-section using optical microscopy with a relatively smooth surface. Additionally, the formation of fine pigment particles with uniform distribution was observed. After irradiation, PVB treated revealed characteristic surface cracks. Despite surface affected by holes, sporadic and surfaces rakish states, which are particularly visible at the edges, are steady with the mechanical breakage of larger chains, which may be strengthened by oxidative weathering. Compared to before irradiation, the PVC films images show the presence of grooves, white spots and cracks on the surface following irradiation. Also, the surface was rough and underwent a color change. Such surface irregularity is a result of photodegradation of PVC due to dehydrochlorination.

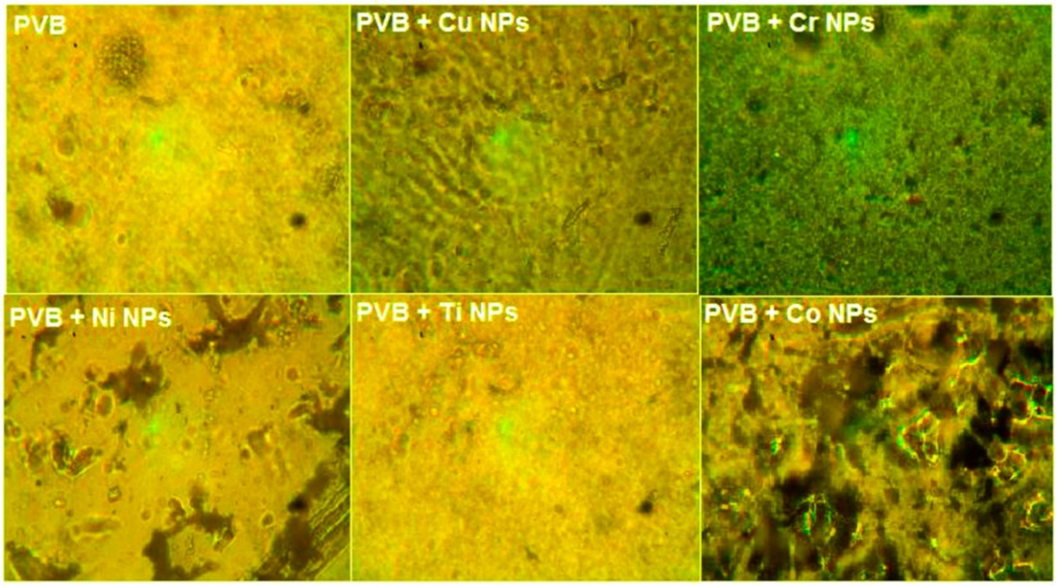

Figure 4: Microscopic Images (400× magnification) for PVB films containing different nanoparticles before irradiation.

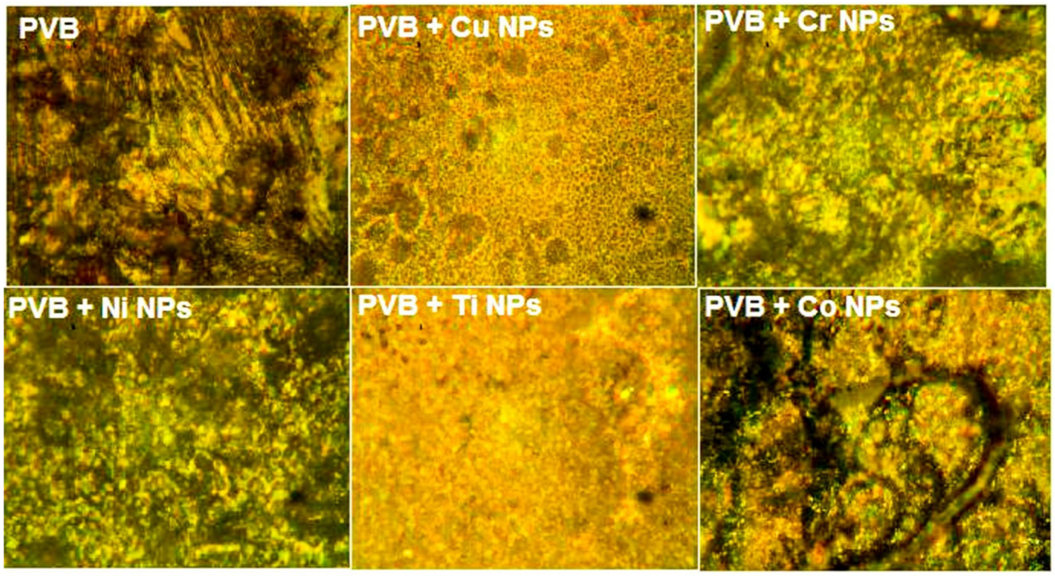

Figure 5: Microscopic Images (400× magnification) for PVB films containing different nanoparticles after irradiation.

The surface morphology of the PVB-NP composites has been analyzed using FESEM characterization from (10 to 300.00 Kx) magnifications. The presented FESEMs morphology for PVB (blank) as well as PVB-NP composites exhibited an entirely rough surface structure in the latter. Figure 6 shows the damages on the PVB-NPs composites' surfaces upon the irradiation with UV-light.

EDX spectroscopy was implemented as a robust technique to obtain the elemental mapping of PVB-NP composites. The EDX spectra of the PVB (blank) film showed strong absorption bands, corresponding to the carbon and oxygen atom of PVB, from the weather (Figure 7). which are homogeneously distributed within the surface of the polymeric blends. The surface atomic percentage of the elements within the PVB films was very similar [13, 19, 20].

The EDX spectra of the PVB-NP composites showed strong absorption bands, corresponding to the Cr, Ti, Ni, Cu and Co NPs, as shown in Figures 8-12 respectively suggestive of the presence of these elements within composite samples.

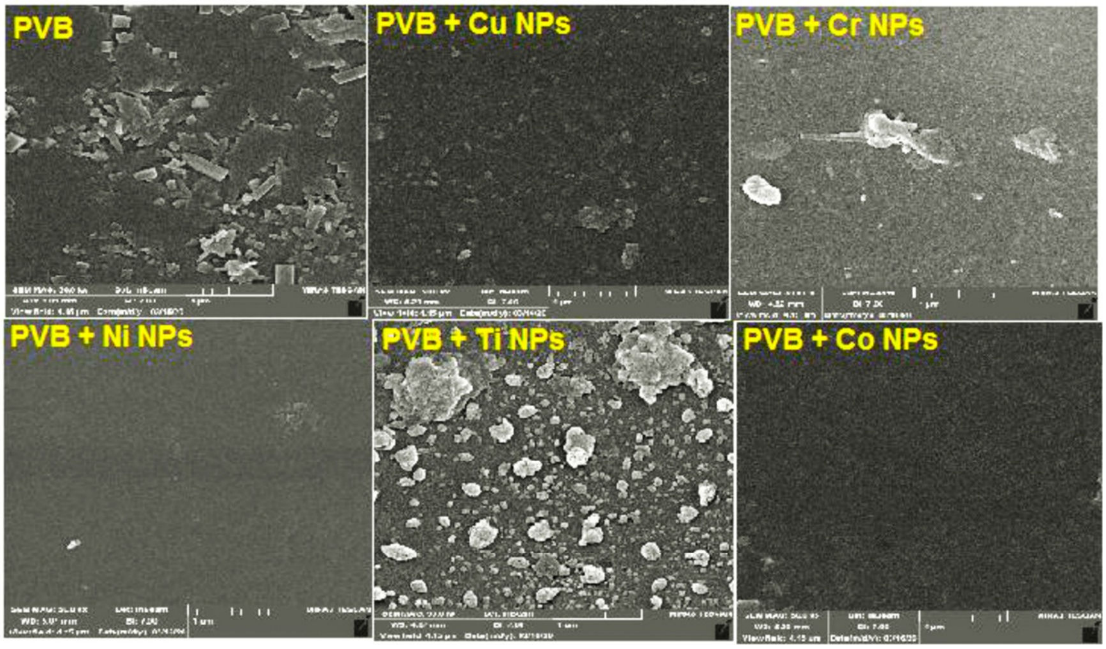

Figure 6: FESEM micrographs for PVB (blank), PVB-Cu, PVB-Cr, PVB-Ni, PVB-Ti, and PVB-Co composites, respectively after irradiation.

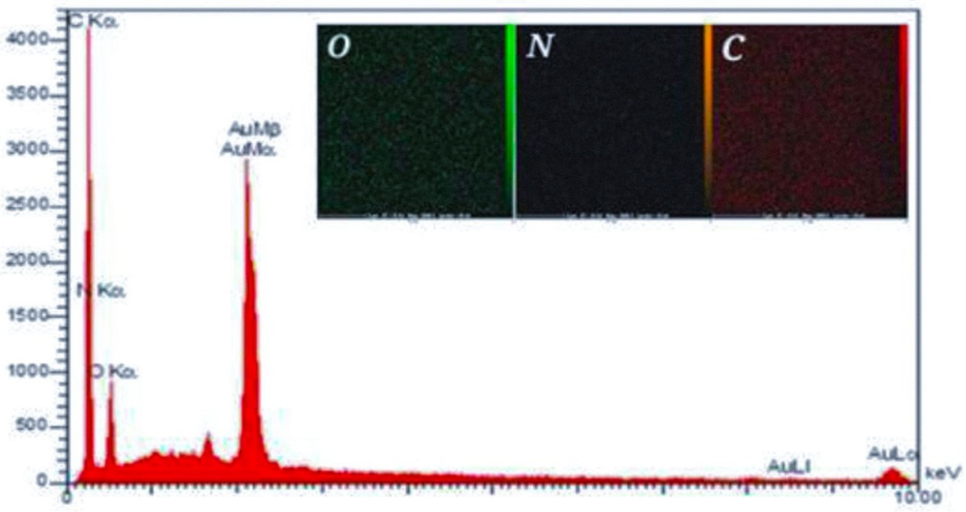

Figure 7: EDX spectra of PVB (blank) film after irradiation.

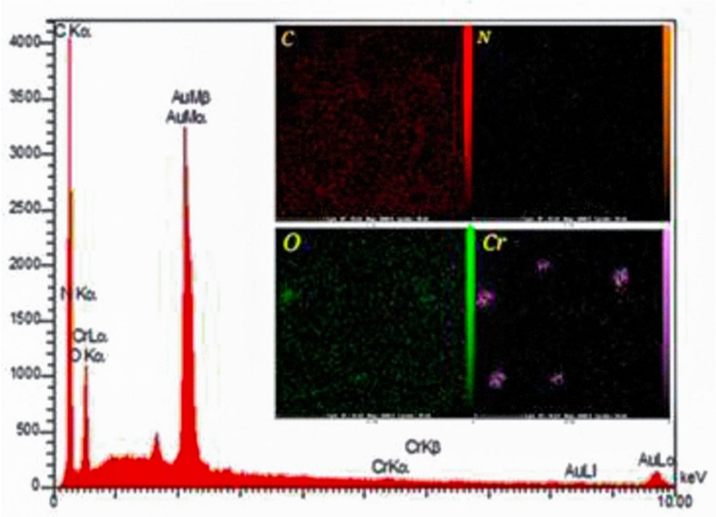

Figure 8: EDX spectra of PVB film containing Cr NPs after irradiation.

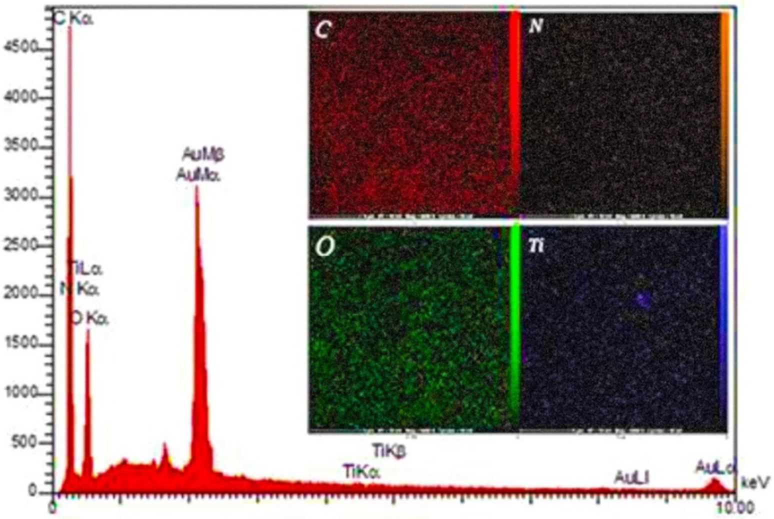

Figure 9: EDX spectra of PVB film containing Ti NPs after irradiation.

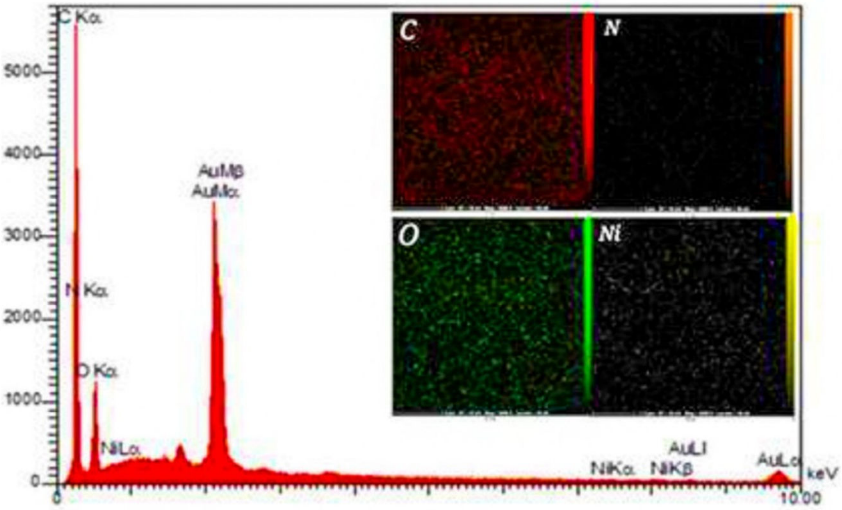

Figure 10: EDX spectra of PVB film containing Ni NPs after irradiation.

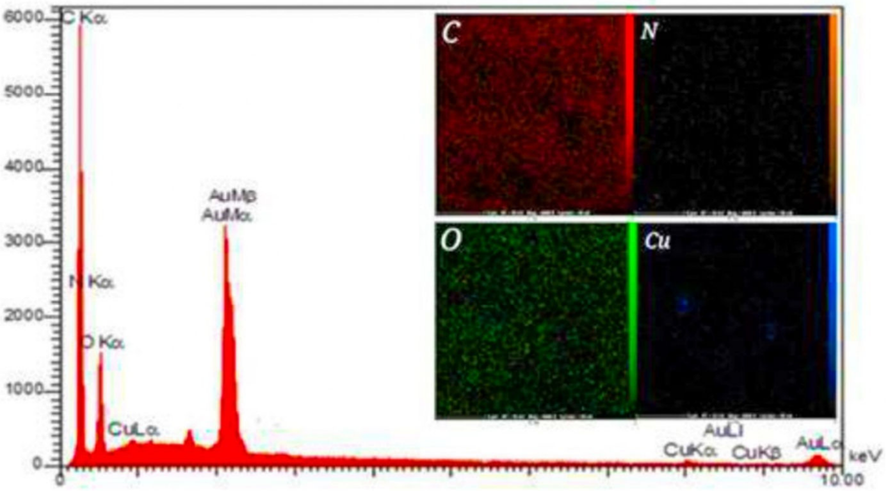

Figure 11: EDX spectra of PVB film containing Cu NPs after irradiation.

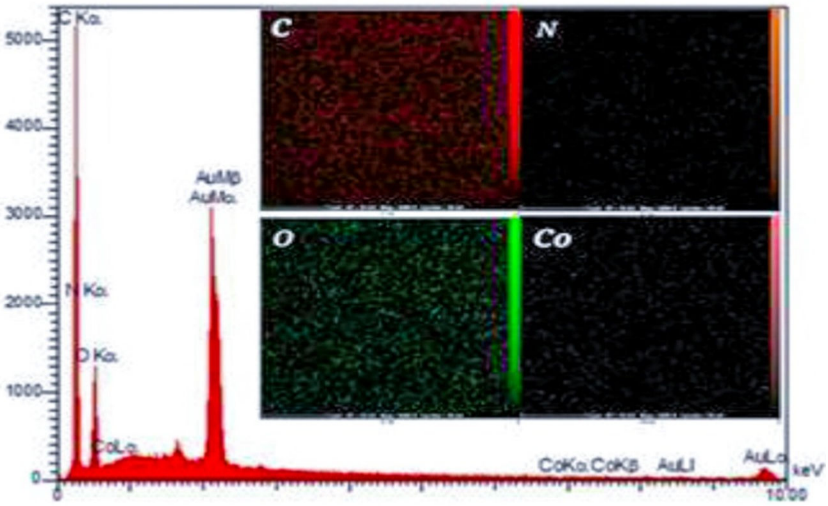

Figure 12: EDX spectra of PVB film containing Co NPs after irradiation.

Atomic force microscopy for the nanomaterials particles (NiO, Cr_2O_3, Co_3O_4, TiO_2 and CuO) was carried out in the chemistry lab to show the particles size and peaks height for them for the prepared samples prior, then these figures from 13 to 17 illustrates the pictures for the size of the nanomaterial that utilized in research dissertation with inspecting their sizes and diameters by AFM device. Then the Figure 13 illustrate the particle size of nickel oxide nanomaterial (NiO) is (30.69 nm) when inspected by AFM device.

Figure 14 illustrate the average particle size of chromium oxide nanomaterial (Cr_2O_3) is 18.51 nm when inspected by AFM device. Figure 15 illustrate the average particle size of cobalt oxide nanomaterial (Co_3O_4) is 15.14 nm when inspected by AFM device. Figure 16 illustrate the average particle size of titanium oxide nanomaterial (TiO_2) is 48.82 nm when inspected by AFM device. Figure 17 illustrate the average particle size of copper oxide nanomaterial (CuO) is 58.43 nm when inspected by AFM device.

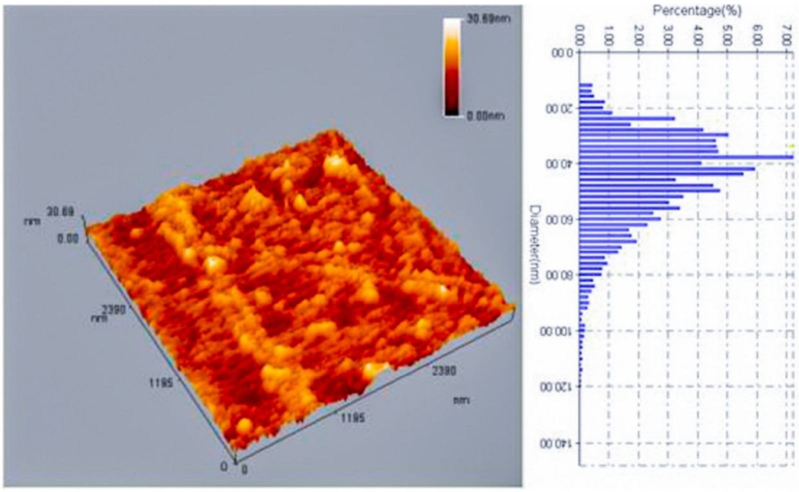

Figure 13: illustrates the size of NiO Nanomaterial by AFM device.

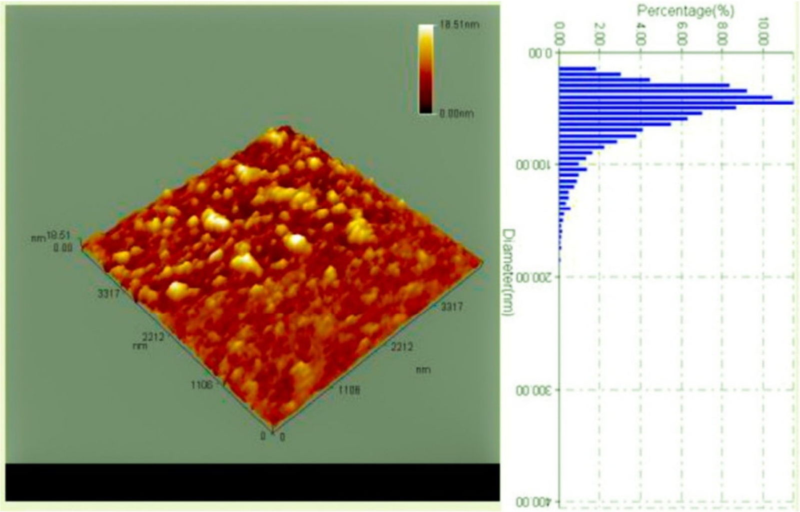

Figure 14: illustrates the size of Cr_2O_3 Nanomaterial by AFM device.

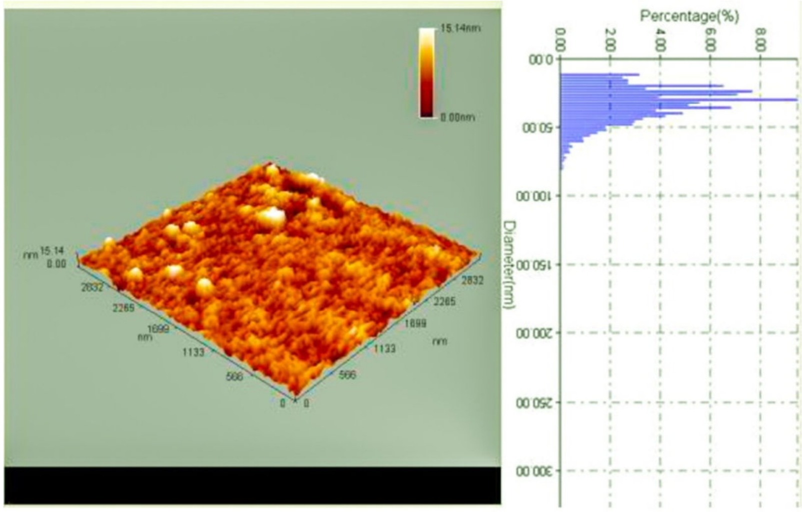

Figure 15: illustrates the size of Co_3O_4 nanomaterial by AFM device.

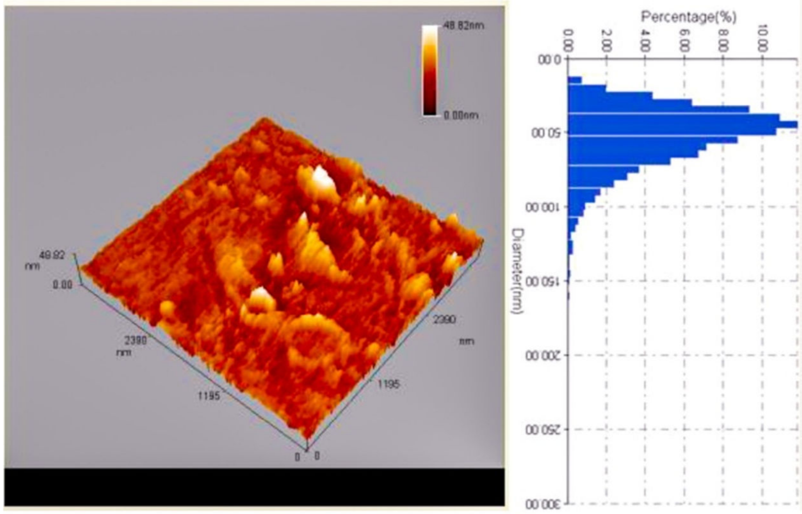

Figure 16: illustrates the size of TiO_2 nanomaterial by AFM device.

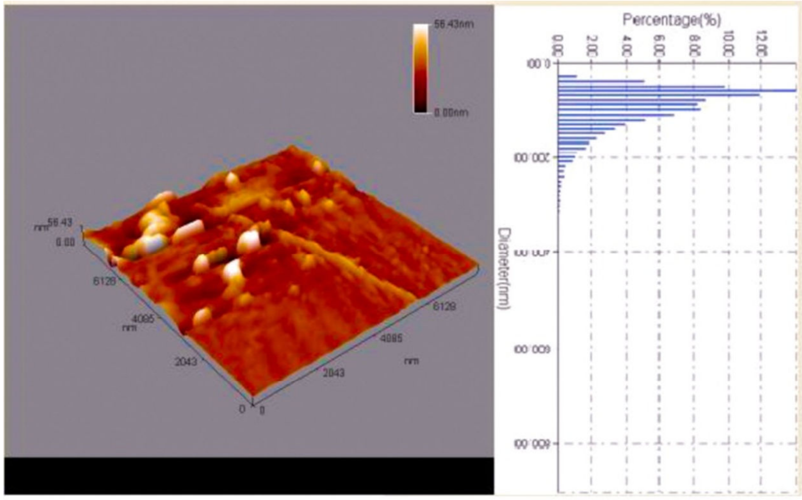

Figure 17: illustrate the size of CuO nanomaterial by AFM device.

After confirming the structure of the PVB and its composites, these should be a rationalization for the photodegradation process of them upon the exposure to the UV-light. This necessitates proposing a mechanism for the degradation to reveal the chemicals formed or degraded through the exposure to the light. In this regard, literature showed that reactive oxygen species (ROS) are formed as superoxide anion radical ($\cdot O^{2-}$), highly reactive hydroxyl radical (•OH), non-radical hydrogen peroxide (H_2O_2), singlet oxygen ($^1O_2$), and ozone (O_3) [14, 15, 21].

A mechanistic pathway for the photodegradation was proposed and illustrated in (Scheme 1). Upon irradiation with the UV-light, the PVB polymer molecules were excited to generate two charge carriers, namely electron and hole (e^-, and h^+). These charge carriers then react with the ROS formed. Hydroxyl and superoxide radicals which target the PVB polymeric chains and initiate the photodegradation process. This will generate some reactive intermediates which lead to further degradation products. Additionally, hydrogen peroxide (H_2O_2) is generated during the interaction with light via disproportionation reactions. This has been also reported in the literature and well quantified [15-17].

$$H_2O + XO_2 \rightarrow H\dot{O} + H\bar{O} + XO_2$$
$$PVB^{\cdot+} + H\bar{O} \rightarrow PVB + H\dot{O}$$
$$PVB^{\cdot+} + 2H\dot{O} \rightarrow H_2O + oxidation\ product$$
$${}^{\cdot}O_2^{-} + H^+ \rightarrow HO_2^{\cdot}$$
$$HO_2^{\cdot} + H^+ + XO_{2(e-CB)} \rightarrow H_2O_2 + XO_2$$
$$PVB^{\cdot+} + O_2^{\cdot-} \rightarrow Intermediates \rightarrow Degradation\ products$$
$$PVB^{\cdot+} + H\dot{O}_2\ or\ H\dot{O} \rightarrow Degradation\ products$$

Scheme 1: The proposed photodegradation mechanism of the PVB polymer.

4. Conclusions

In conclusion, PVB polymer was synthesized and a composite with five different NPs were made and tested for photodegradation. Wight loss measurements showed a significant increase of the PVB weight loss upon the introduction of NPs. Chemical changes on the molecular structure of the PVB polymer was observed via the monitoring of the carbonyl group absorption band via the FTIR measurement. These measurements confirmed the photodegradation of the PVB-NP composites after the exposure to the UV-light. The proposed mechanism for the photodegradation of the PVB polymer indicted that excited PVB molecules generate charge carriers which further trigger reactions with reactive organic species within the solid films and lead to the formation of degradation products. PVB-Co NP composite showed the highest photodegradation compared to other NP composites as well as the neat PVB.

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