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Application of Metal Oxides Nanoparticles to Enhance Ultraviolet Light Resistance of Polyvinyl Chloride Films

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Abstract

Polyvinyl chloride (PVC) films were chemically modified by including organic groups, amino group of ethylenediamine (en), and furtherly treated with aromatic aldehyde. The modification process included synthesizing the films by casting utilizing tetrahydrofuran (THF) as the solvent. The films were enriched with five metal oxide nanoparticles (NPs), specifically: TiO_2, Co_2O_3**,** Cr_2O_3, NiO and CuO, in order to enhance their resistance to photodegradation. The films were subjected to UV light. The resulting damage was assessed both analytically and morphologically. The methods used for examination of the chemical structure comprised FT-IR, ^{1}H-NMR, and ^{13}C-NMR spectroscopies. SEM and AFM were utilized to test the morphology of polymeric films. The efficiency of the modified PVC films to resist UV light was assessed by measuring the roughness factor (Rq) of the irradiated PVC films. The incorporation of NPs into the modified PVC resulted in films with high resistance to UV light, as confirmed by FT-IR spectroscopy and weight loss measurement. The film made from modified PVC/Schiff base CuO NPs showed superior resistance to photo-degradation, as evidenced by the findings obtained from FT-IR spectra, surface morphological analysis, and weight loss.

Keywords: *PVC modification; photodegradition; metal oxides; polymeric films; nano particles; weight loss; carbonyl index*

1. Introduction

From the inception of plastic manufacturing, ultraviolet (UV) rays have consistently caused significant damage to the outdoor use of polymers (Song et al., 2017; Mahdi et al., 2022; de Oliveira et al., 2018; Prasita et al., 2021). Plastic undergoes photo-oxidation when exposed to harsh circumstances such as high temperature, prolonged sunlight exposure, moisture, and oxygen **(**Fotopoulou, & Karapanagioti, 2019; Andrady et al., 2022). This process is characterized by the appearance of fractures, discoloration, and a deterioration in its mechanical and physical qualities (Biber et al., 2019; Cai et al. 2018). There has been a tremendous increase in the demand for commercially manufactured plastic over the past decades. (Al-Mashhadani et al., 2022; Borrelle et al., 2020). The output of PVC has significantly increased from 3 to 40 million tons over the period from 1965 to 2018 (Petrović, & Hamer, 2018; Khan et al., 2022; Chen et al., 2022). The output of polyvinyl chloride (PVC) has had a significant growth from 3 million tons in 1965 to an impressive 40 million tons in 2018 (Miliute-Plepiene et al. 2021). Therefore, PVC is recognized as one of the polymers that is produced on a large scale for commercial purposes (Yu et al., 2016). PVC's hardness and toughness are attributed to its elevated chlorine concentration (Li et al., 2023). Consequently, it is used in many applications, including construction materials, healthcare equipment, apparel, furniture toys, electrical wire insulation, and packaging (Abdulla, 2023). The mechanism of plastic degradation in the environment can follow two pathways: firstly, Physical degradation pathway comprises the change in the overall structure of the plastic materials such as embrittlement, cracking and flaking. Second, Chemical degradation pathway which involves alteration at molecular structure, such as breaking bond or oxidation to produce shorter polymer chains (Ashfaq et al., 2020). It is necessary to take into account the possible environmental risks linked to the soluble chemical byproducts that result from the breakdown of plastics (Watt, 2021). Researchers have made significant efforts to enhance the optical stability of PVC especially for outdoor use (Al-Mashhadani et al., 2021). The strategy involves the addition of appropriate additives to avoid photolysis (Yaseen et al., 2021). The photolysis of the compound occurs owing to the de-chlorination process and the formation of C=C bonds in its polymer chain, resulting in the production of fragments and polyene residues (Abed et al., 2023). Impurities or distortions within the polymer backbone might trigger the formation of radicals which can cause the C-H bonds to break down (Vohlídal, 2021). Furthermore, the replication process generates peroxy-reactive radicals in the presence of oxygen. In addition, hydroperoxides may form, potentially resulting in the oxidation of the polymer (Bracco et al., 2018). Lately, there has been significant interest in the photochemical stability of these polymers, with the aim of discovering an efficient approach to avoid photochemical disintegration (Huang et al., 2015, Yokesahachart, & Pajareon, 2020). One effective strategy for improving the physical, mechanical and thermal characteristics of polymers is the introduction of additives, which has shown significant results (Raad, & Abdallh, 2022). In this context, additives may serve as plasticizers, stabilizers, softeners, UV absorbents, blowing agents, lubricants, fillers, flame retardants, colorants and crosslinking agents. UV stabilizers are capable of reducing the rate of photo-oxidation. The selection of additives is influenced by several aspects, including the intended stability, color, compatibility with volatility, and cost. Moreover, they need to possess the capacity to absorb or deflect ultraviolet (UV) radiation and convert it into heat or harmless rays at a moderate rate. The ultimate objective is to create PVC polymers that include plasticizers to produce a resilient polymer suitable for outdoor applications (Quitadamo et al., 2019). Common additives for plastics include a variety of substances, such as colorants, plasticizers, flame retardants, and stabilizers. Additive production must be cost effective and simple. They should be very efficient even at low concentrations without changing the physical properties of the plastics such as color. In addition, additives should not have any adverse effect on the environment (Kim et al., 2013). They should also have chemical stability, low volatility, and the ability to blend homogenously within the polymer’s matrix. Additives can be utilized effectively as powders flakes, spheres, and beads. The introduction of such materials aims to mitigate the photooxidation and photocomposition of the polymer by serving as light absorbers, energy quenchers, radical decomposers and antioxidants (Jhuo et al., 2016). PVC optical characteristics were improved by the introduction of the Cr_2O_3 nanoparticles to polymer films (Chayanisa et al. 2021). The changed polymers exhibited a reduced energy gap, leading to enhanced conductivity. Consequently, the modified polymers showed increased photostability. Furthermore, polyvinyl chloride (PVC) was altered using Tin (IV) complexes to prolong the rate of photodecomposition and enhance surface characteristics (Mohammed et al., 2022). The use of metallic additions resulted in significant enhancement, with distinct components exhibiting varying levels of performance (Ahmed et al., 2021). To test the photostability of PVC film under environmental conditions, it was subjected to radiation for 300 hours (Kadhom et al. 2023). In the last example, PVC films were treated with Schiff base containing nickel to achieve a homopolymer. The resulting polymer exhibits a resistance to degradation caused by the incident light over the whole film. Factors affecting the surface of the homopolymer have caused an increase in porosity. This is a result of the change in the volume of molecules, which enhances the material performance of them when exposed to incoming light. The study used ethylenediamine, 5-Nitrosalicylaldehyde and five distinct metal oxide nanoparticles (TiO_2, Co_2O_3, Cr_2O_3, NiO, and CuO) for experimentation. Alter the PVC films and improve their performance under the influence of 365 nm UV light. The ability of the new modified PVC film to resist UV light was examined using a variety of spectroscopic methods.

2. Objectives

The primary objective of this study is to develop PVC films with enhanced resilience and photostability for improved outdoor performance. This involves incorporating various additives, such as metal oxide nanoparticles, to strengthen the physical, mechanical, and thermal properties of PVC.

3. Experimental

3.1 Materials and Equipment

5-Nitrosalicylaldehyde (98%), ethylenediamine (98%), metal oxide nanoparticles CuO (58.43 nm), Cr_2O_3 (18.51 nm), TiO_2 (48.82 nm), Co_2O_3 (15.14 nm), and NiO (10 nm), together with THF solvent, were purchased from a supplier in Gillingham, UK. Polyvinyl chloride with a degree of polymerization (DOP) of 3000 was acquired from Petkim Petrokimya in Istanbul, Turkey. The FT-IR spectra of the modified PVC films were analyzed using a Shimadzu Spectrophotometer Model no. 8400 (Japan) with a frequency range of 400–4000 cm^{-1}. The QUV tester, equipped with UV-B 365 lamps, was acquired from Philips in Saarbücken, Germany. The ^1H-NMR and ^{13}C-NMR spectra of PVC films were acquired using a Bruker DRX300NMR spectrophotometer (Bruker, Zürich, Switzerland). PVC film surface, which had been exposed to radiation and changed, was examined using scanning electron microscopy (SEM). The samples were also examined using a SIGMA 500 VP microscope (ZEI Microscopy, Jena, Germany). The morphology of the films was analyzed via Veeco atomic force microscopy (AFM). Additionally, a MEIJI TECHNO microscope was used to further examine surface morphology. In order to avoid deformation, the materials for the AFM test were placed in a nitrogen environment. The 3D pictures were obtained using a tapping mode, with a scanning rate of 0.8 Hz.

3.2 Preparation of Modified PVC

The preparation of PVC films modified with ethylenediamine involved dissolving PVC (5 g) and ethylenediamine (30 mg) in THF (50 mL) as a solvent, followed by the addition of 5-Nitrosalicylaldehyde (30 mg). Following this, acetic acid (1 mL) was added (Figure 1), and the solvent (THF) volume was increased to 100 mL. Finally, the reaction mixture was stirred for another 3 hours. The reaction mixture was stirred for another 3 hours. The modified PVC was dried for 24 hours at room temperature after the solvent was removed.

3.3 Preparation of PVC/Schiff base Film Doped with Different Metal Oxides Nanoparticles

A mixture of 5 g of PVC, 30 mg of PVC/Schiff base, and 0.35 mg of metal oxide (TiO_2, Co_2O_3**,** Cr_2O_3, NiO and CuO) nanoparticle were firstly dissolved in 100 mL THF, sonicated for 1 hour at room temperature, and then stirred for 3 hours under refluxed conditions.

3.4 UV light illumination

A set of samples, including pristine, modified and doped PVC samples, was prepared in the form of films. The film thickness was around 40 µm. All the specimens were subjected to UV light under accelerated conditions using QUV tester (Q-Panel Company; Homestead, FL, USA). The UV light is centered at 365 nm with an intensity of 6.2×10^{-9} Einstein dm^{-3} s^{-1} and at room temperature.

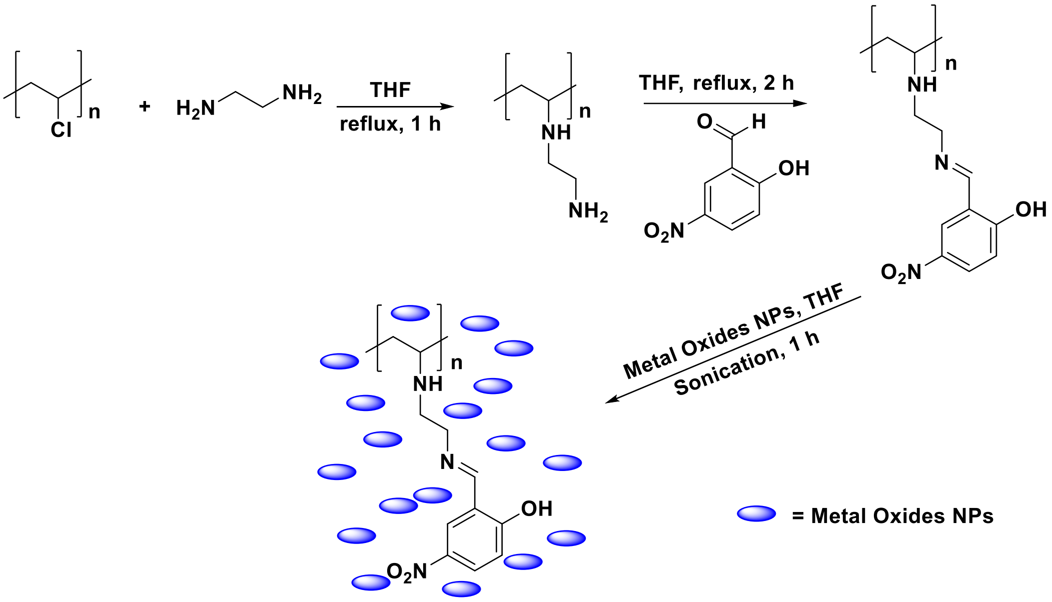


Figure 1 The synthesis rout of modified and doped PVC films.

4. Results and Discussion

4.1 Characterization.

FT-IR spectroscopy was used to characterize the modified PVC film. The modification of PVC with ethylenediamine was confirmed by the appearance of new broad peaks at 3100 cm^{-1} belonging to the symmetric and asymmetric NH_2 stretching vibration, as illustrated in Figure 2. It does not appear as two sharp peaks, which is evidence that ethylenediamine is linked to the polymer backbone. It is more likely that the stretching band for secondary amine group N-H is overlapped by this broad peak. The stretching of aliphatic C-H bonds was shown by the strong, distinct peaks at around 2925 cm^{-1}. Additionally, the stretching of the C-Cl bond, seen by the peak at roughly 752 cm^{-1}, indicates that the substitution reaction has occurred to the part of labile chlorine atoms. The next step includes the reaction of PVC-ethylenediamine with 5-Nitrosalicylaldehyde. FT-IR of the product confirms the successful reaction between the primary amine group attached to PVC backbone and the corresponding aldehyde. The NH_2 band disappears, and a new sharp peak appears at 1643 cm^{-1} attributed to formation of a new imine (C=N) bond. In addition to distinctive peaks for the new polymer appear at 3058 cm^{-1} assigned for aromatic C-H, 2958, 2872 cm^{-1} assigned to aliphatic C-H, as well as N-H secondary amine peak at 3269 cm^{-1}. Finally, a broad, strong peak between 3300-3550 cm^{-1} belongs to OH groups of attached aldehyde unit, as shown in Figure 3.

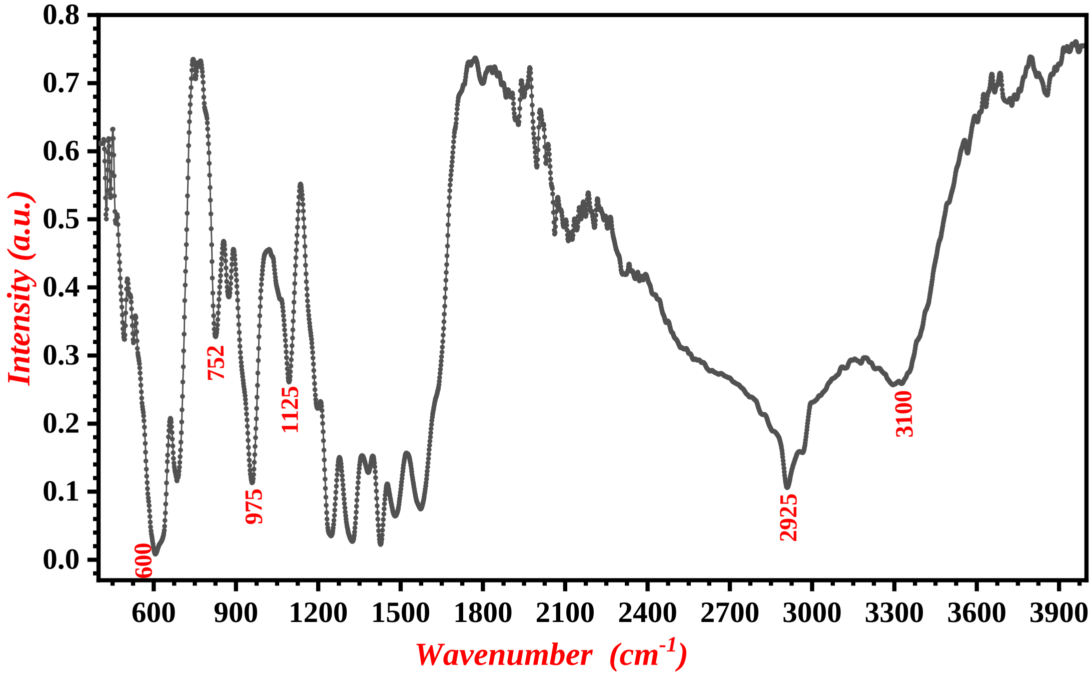


Figure 2 FT-IR spectrum of PVC linked to ethylenediamine.

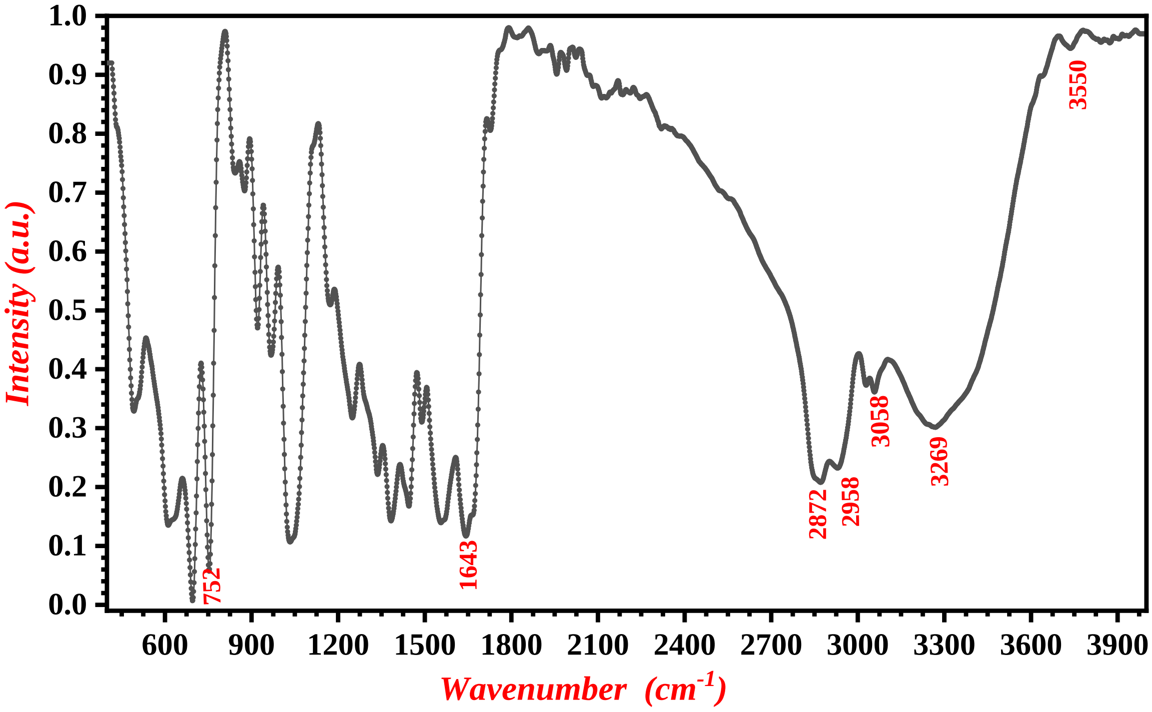
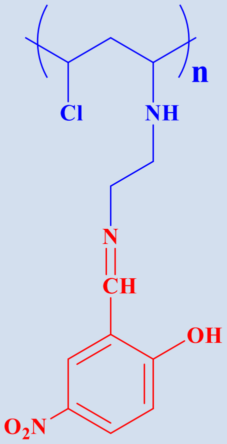


Figure 3 FT-IR spectrum of modified PVC/Schiff base.

Table 1 ^{1}H-NMR and ^{13}C-NMR of synthesized modified PVC.

Modified PVC	**^{1}H-NMR (DMSO-d$_6$, δ, ppm)**
 **Modified PVC**	8.95 (s, 1H, N=CH), 8.90-7.80 (m, 3H, Ar), 6.59 (s, 1H, OH), 4.05-2.55 (m, 6H, next to high electronegative atoms, 1H, NH), 1.83 (m, 2H, CH_2).
	^{13}C-NMR, (DMSO-d$_6$, δ, ppm)
	174.81, 174.23, 170.29, 161.95, 133.63, 128.20, 127.74, 124.85, 120.80, 118.93, 66.97, 60.21, 37.76, 36.94, 36.64, 35.37, 30.33, 25.06, 22.70, 22.49.

The new polymeric structure was also confirmed via NMR spectroscopy. The shifts for the Schiff base containing polymers were analyzed by ^{1}H-NMR and ^{13}C-NMR spectra. All the spectra were compared to those of pristine and modified PVC samples. This polymer has a poor solubility in common solvents even after heating. Only deuterated DMSO can dissolve it in a ratio of 20 mg to 2 mL of deuterated DMSO under heating at 50 °C for an overnight period until it fully dissolves.

A pristine sample of PVC was dissolved in deuterated DMSO. ^{1}H-NMR spectroscopy has shown a broad multiplet chemical shift at 4.43 ppm assigned to the proton attached to C-Cl. On the other hand, the CH_2 protons appear as a multiplet chemical shift at 2.33 ppm. The terminal methyl groups on the PVC chains appeared as two small signals at 2.09 and 1.23 ppm. The ^{1}H-NMR of PVC coupled with ethylenediamine revealed an additional peak at 2.85 ppm attributed to $2CH_2$ linked to amine groups. The chemical shifts of the primary and secondary amine overlapped with those of H_2O chemical shifts at 3.05-3.9 ppm (Table 1) (Hasan et al., 2022).

The next step involves the synthesis of a polymer modified with 5-Nitrosalicylaldehyde to form a final product via a Schiff base reaction. This Schiff base was characterized by ^{1}H-NMR and ^{13}C-NMR as shown in Figures 3 and 4. A new chemical shift peak appears at 8.95 ppm attributed to the formation of imine group (N=CH), as well as the absence of a peak corresponding to the amine group. In addition, a new peak appears in the aromatic region correlated to protons of the phenyl group. It is important to mention that the broad singlet peak at 6.59 ppm belongs to OH group. This group is a donating group and causes shielding for the proton at ortho position, corresponding to its position which leads to decreasing the chemical shift of this proton. On the other hand, ^{1}H-NMR of the ortho position protons linked to the NO_2 group showed a chemical shift at 8.90 ppm higher than those chemical shifts in the aromatic region. This is due to the effect of the hydroxyl group as it is a strong donating group, which increases the protons shielding making them appear at lower chemical shifts. The electrons around the aromatic protons resonate at higher chemical shifts due to the effect of the nitro group, which is a strong electron withdrawing group by resonance, creating a de-shielding effect to those electrons. In all cases, the protons at the ortho position are highly influenced by the full charge resonance status on the ortho position. In the ^{13}C-NMR spectrum, there are two peaks at 174.81, and 174.23, belonging to the carbon atom of Schiff base group C=N, as shown in Figure 5. This is because it is a polymer, and it is possible to see more than one peak in the same region returning to the same functional group. The units attached to the polymer chain could have slightly different environments, which leads to slightly different chemical shifts. The ^{13}C-NMR spectrum shows all needed peaks in the aromatic and aliphatic regions to demonstrate the chemical structure for modified PVC.

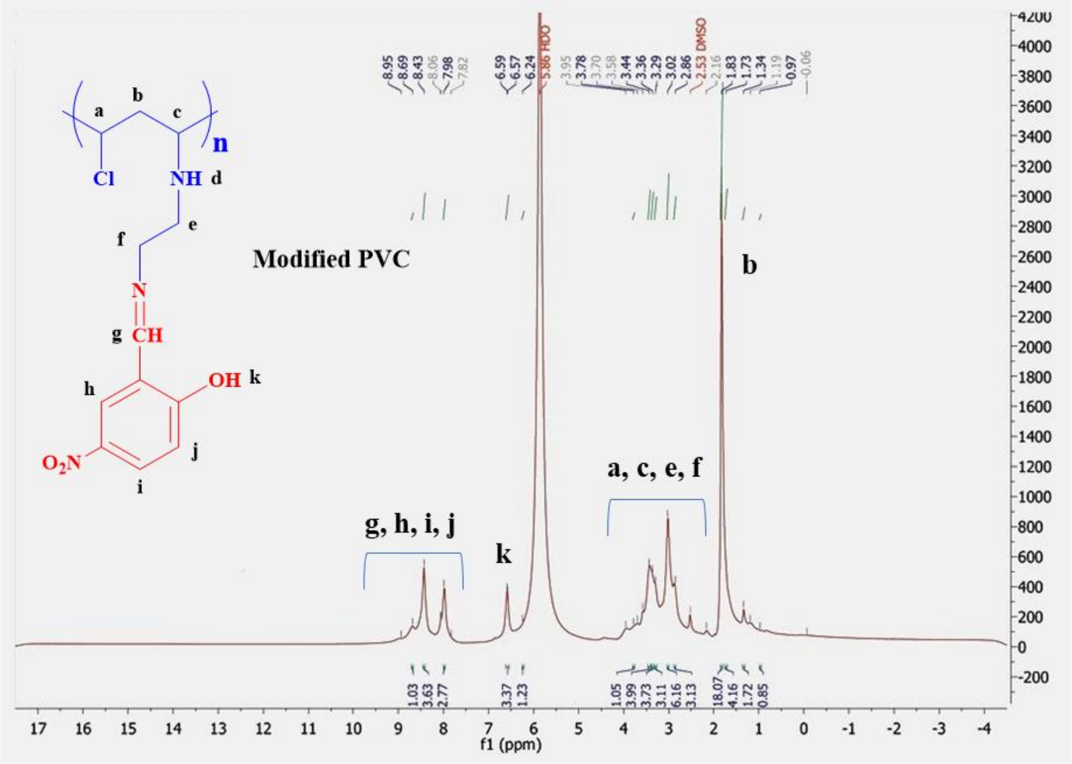


Figure 4 ^{1}H-NMR spectrum of modified PVC.

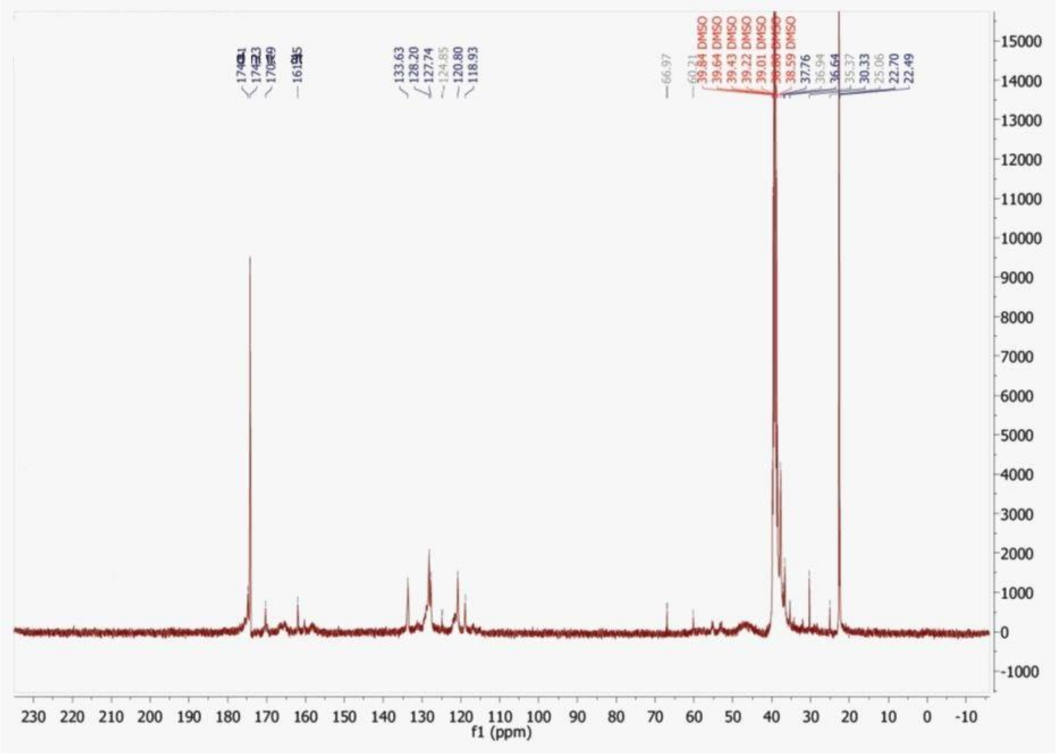


Figure 5 ^{13}C-NMR spectrum of modified PVC.

4.2 Photodegradation Rate Observation by FT-IR Spectrophotometer

FT-IR spectroscopy was used to evaluate the capability of the modified PVC and nanoparticle composite to resist photodegradation. The pristine, modified, and composite films were exposed to oxidative photodegradation for 300 hours at a wavelength of 365 nm. As a result, a small amount of undesired polymeric fragments containing carbonyl (C=O; carboxyl and ketone) and hydroxyl groups are formed. In addition, polyene (C=C; carbon–carbon double bond residues) groups also appear (Arraq et al., 2023). Figure 6 shows (a) the blank before irradiation and (b) the blank after irradiation, depending on the peak intensity.

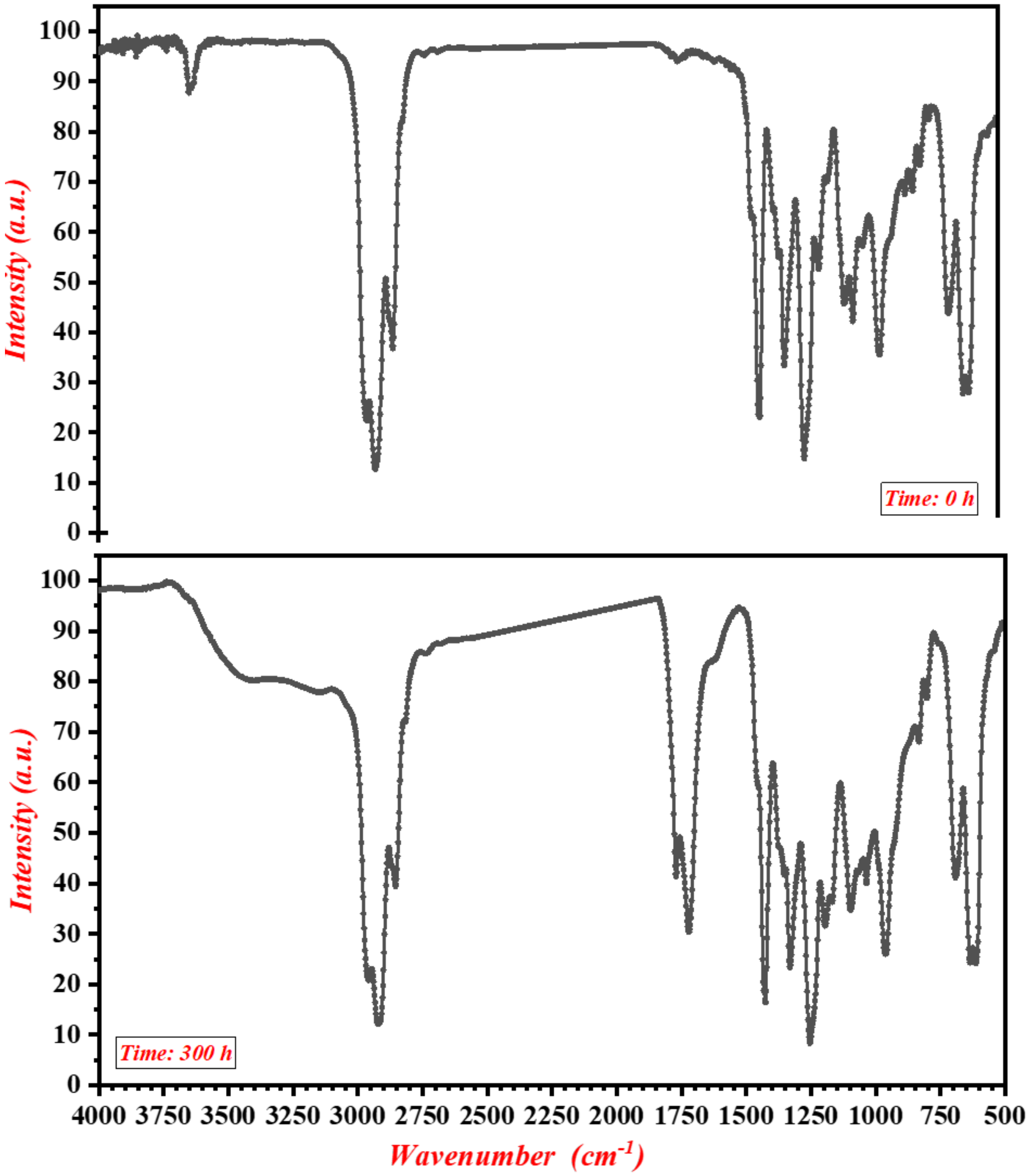


Figure 6 FT-IR spectra of PVC (blank) film (a) before irradiation, (b) after 300 h irradiation.

The irradiated blank PVC films have shown a remarkable increase in the peaks of O-H (3500 cm^{-1}), C=O (1722 cm^{-1}), and C=C (1602 cm^{-1}) in comparison to those of the unirradiated films. In contrast, modified PVC-NPs composite films (in particular PVC/Schiff base CuO NPs) have shown a more resistance to irradiation, in which the peaks intensities of the main functional groups are significantly reduced. The ability of the polymers to resist UV light of the blank and composite polymeric films was calculated by measuring the carbonyl index (IC=O), polyene index (IC=C) and hydroxyl index (IOH) (Arraq et al., 2023). The intensities of these main absorption peaks were assessed in comparison to the internal reference peak at 1328 cm^{-1} of the CH group.

According to Equation (1), the I_s is the functional group index, while A_s and A_r are the absorbance of functional group and reference peak, respectively:

$$I_s = \frac{A_s}{A_r} \qquad (1)$$

The peak intensities of the targeted functional groups are plotted against time in 50 h intervals as illustrated in Figures 7-9.

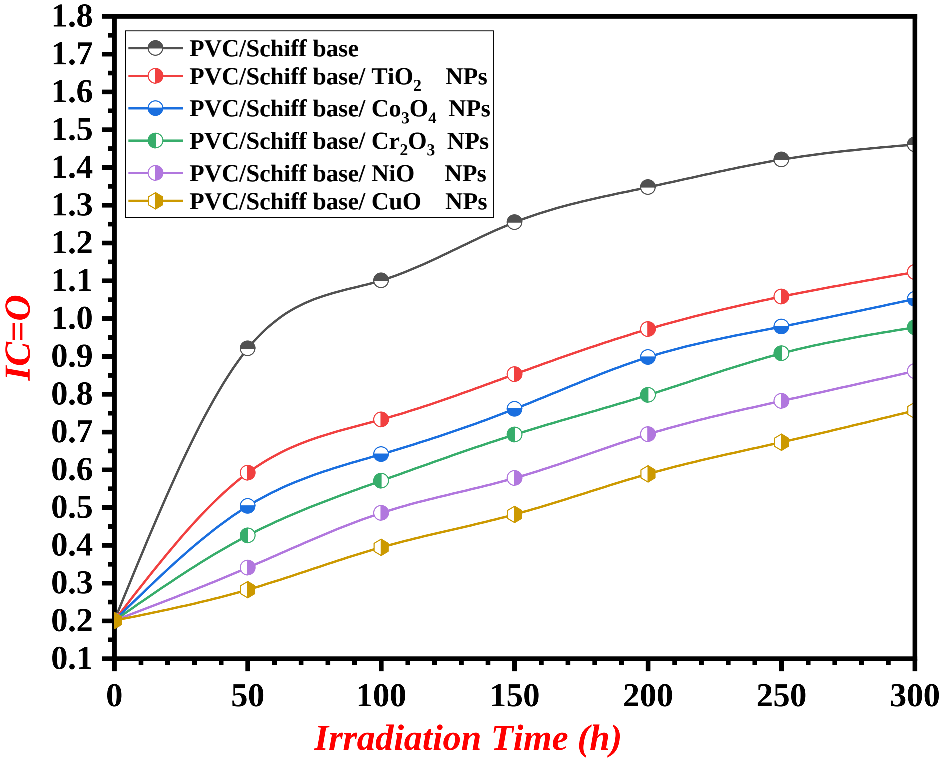


Figure 7 Changes in the IC=O index for PVC films versus irradiation time.

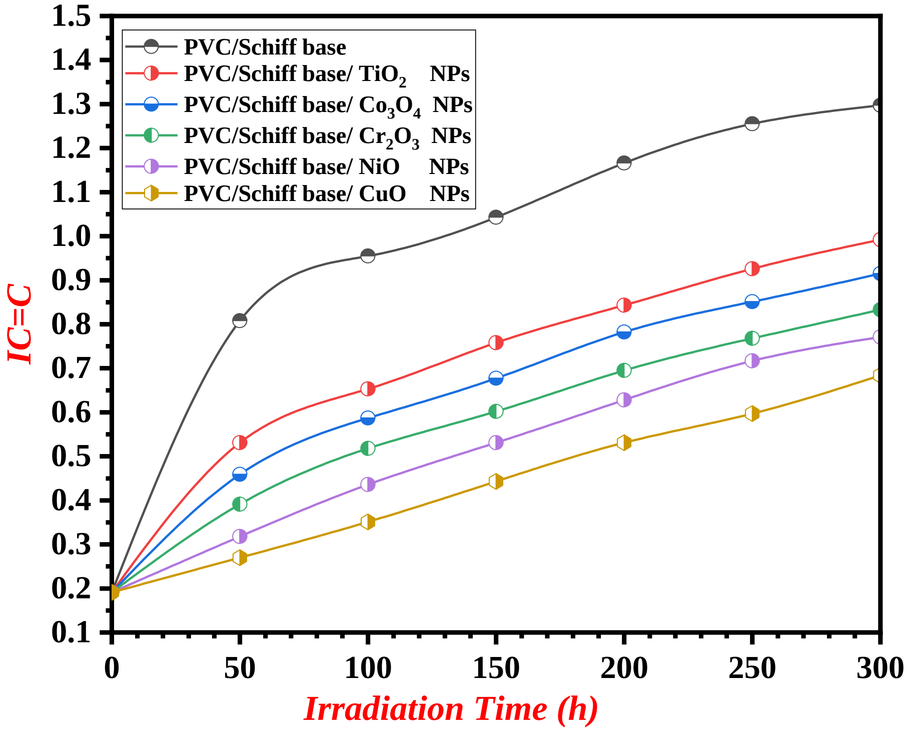


Figure 8 Changes in the IC=C index for PVC films versus irradiation time.

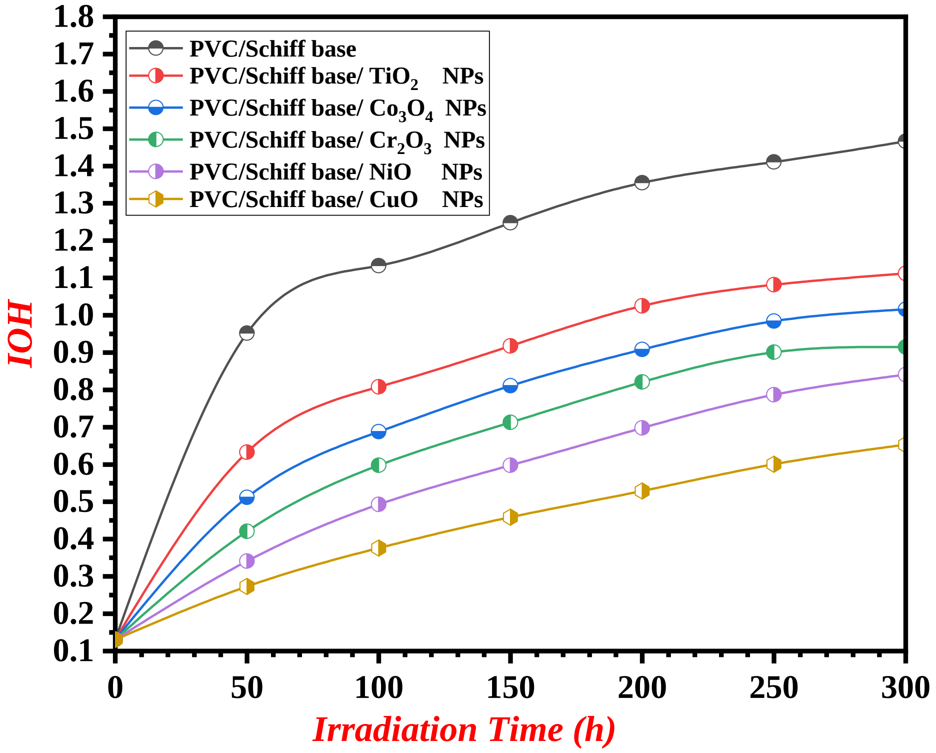


Figure 9 Changes in the IOH index for PVC films versus irradiation time.

The results have shown that the polymer composites have reduced the effect of the UV light unlike the pristine PVC specimens which were severely damaged.

4.3 Photodegradation Rate Assessment by Weight Loss

Polymers usually lose some fragments under the UV irradiation as a result of the degradation process. The weight loss was assessed using Equation (2). The weight change was recorded at different time periods for the pristine and composite samples.

$$\text{Weight loss\%} = \frac{W_0 - W}{W_0} \times 100 \qquad (2)$$

Where W_0 and W are the weight of films before and after irradiation, respectively (Arraq et al., 2023). PVC undergoes photo-oxidation, which results in dehydrochlorination (the removal of HCl) and the release of volatile organic compound residues, which induce weight loss [49]. The influence of UV light on polymeric films was illustrated in figure 10. The results revealed that the modified PVC film composite containing CuO NPs has the lowest weight loss percentage in comparison to other samples. The weight loss after 300 h irradiation of the modified PVC/Schiff base CuO NPs film was compared with the blank PVC film.

4.4 Surface Analysis

4.4.1 Optical Microscope

The changes in the surface morphology of the modified PVC composite films were recorded using the optical microscope with a magnification of 400x. A smooth surface was obtained for the samples before exposure to UV light. The illuminated films with UV light for 300h exhibited dark spots, color changes, and surface roughness, especially for the blank film. These changes are attributed to the photodegradation process where small fragments and HCl molecules are eliminated from the surface of the samples under UV irradiation. The alteration is correlated to bond cleavage and HCl removal at the surface as a result of photodegradation process. Thus, the new polymer composite reduces the effect of photodegradation and subsequently reduces the elimination of HCl and other fragments (Hasan et al., 2022). Figure 11 illustrates the polymeric sample films both before and after exposure to UV.

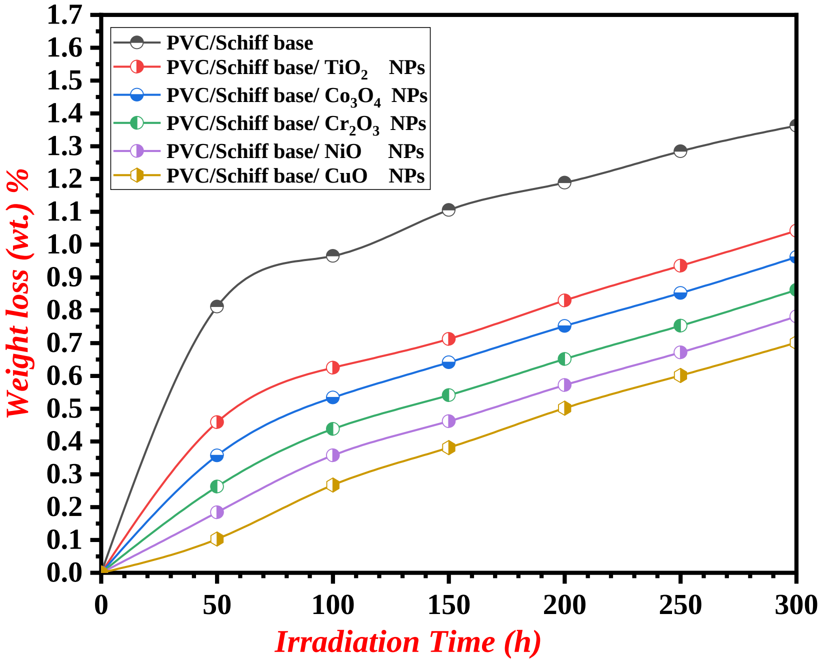


Figure 10 PVC films weight loss at different exposure times.

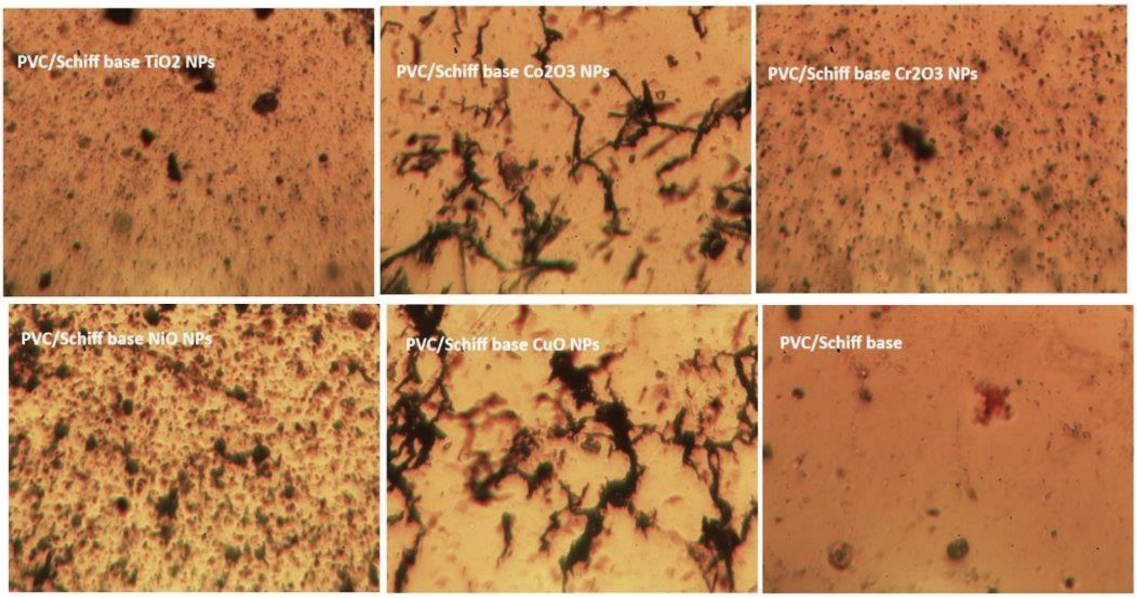


Figure 11 Microscope images (400× magnification) of modified PVC composite films.

4.4.2 Atomic Force Microscope (AFM)

The surface roughness measurements were further supported using an atomic force microscope (AFM) (Ahmed et al., 2021). Surface roughness and bond breakage are the results of relatively long radiation exposure times for films. The AFM pictures of the surface of polymeric films before and after 300 hours of irradiation are displayed in Figure 12. Surface roughness and bond breakage are the results of relatively long radiation exposure times for films. While the blank PVC film suffered severe damage, the surface of the modified polymer composite has shown a smoother surface after being exposed to UV light. As illustrated in Table 2, the *Rq* values of polymer composite films indicated that the polymer composite containing CuO has less surface roughness compared to other samples.

Table 2 the average roughness of polymer composites after irradiation

Sample	***Rq* (Average Roughness) (nm)**
PVC/Schiff base	125.1
PVC/Schiff base TiO_2 NPs	90.6
PVC/Schiff base Co_2O_3 NPs	84.3
PVC/Schiff base Cr_2O_3 NPs	80.7
PVC/Schiff base NiO NPs	64.3
Modified PVC/CuO NPs	50.8

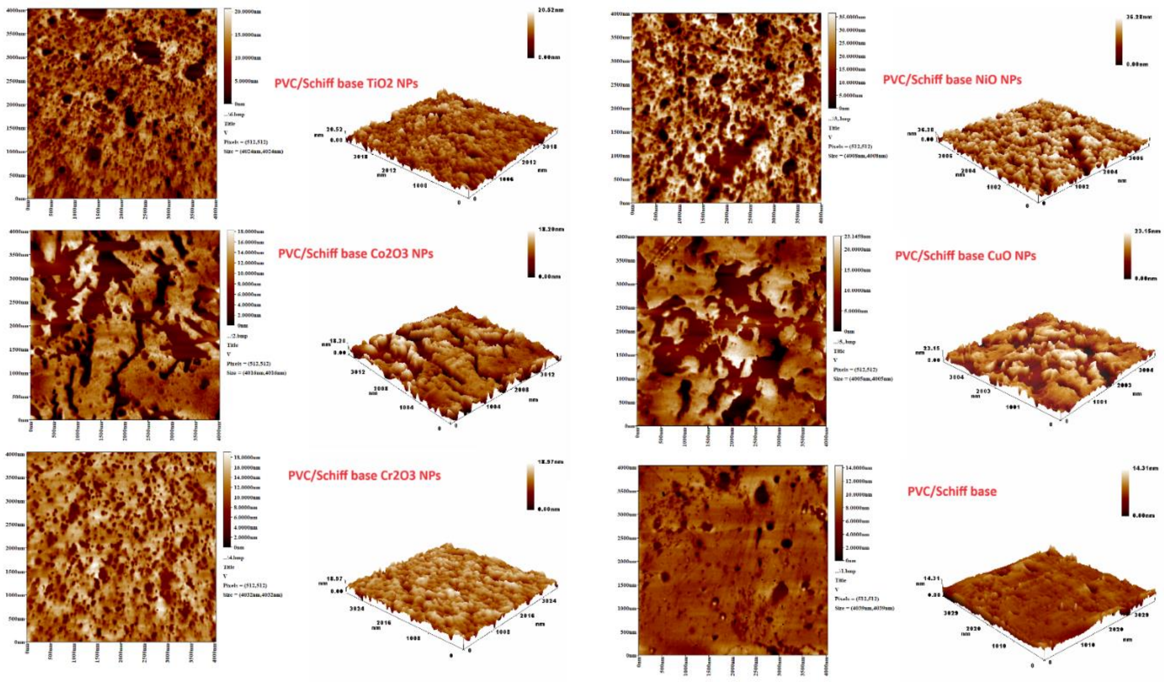


Figure 12 AFM images of PVC films.

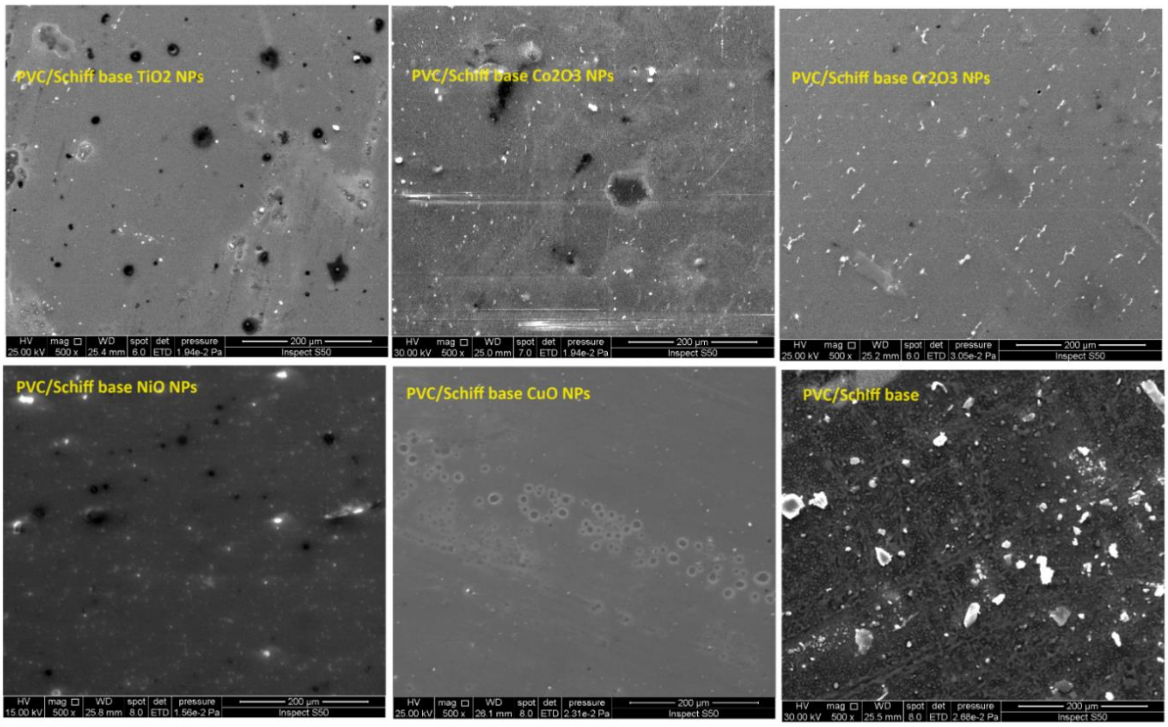


Figure 13 SEM images of modified PVC films.

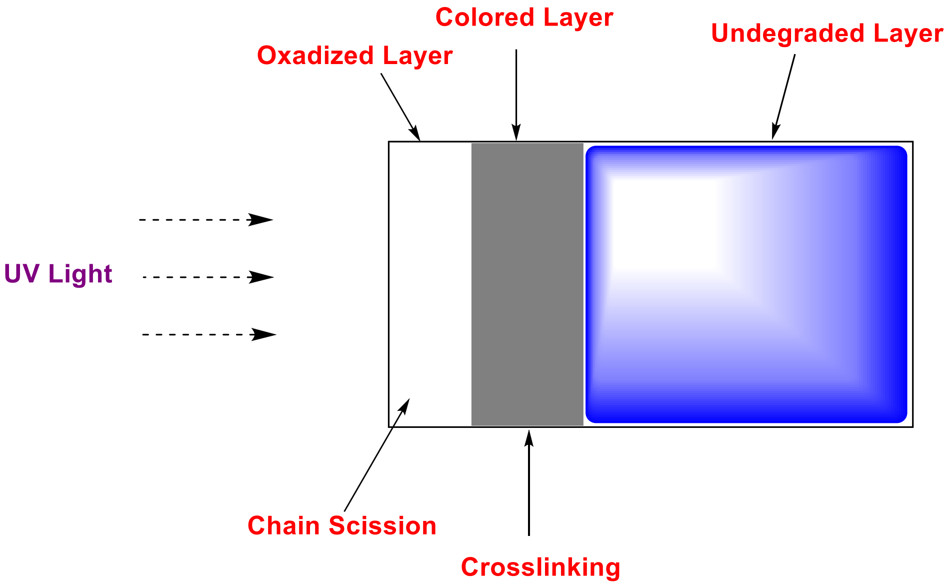


Figure 14 Segmentation of degradation layer.

4.4.3 Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) was utilized to obtain sharp, high-resolution images of the surfaces of polymeric films (Abed et al., 2023). The PVC surface film SEM images following irradiation are displayed in Figure 13. According to earlier studies, non-irradiated polymers often have a more uniform surface than radiated samples. SEM images were taken at 200 times magnification after the modified PVC films were exposed to radiation. New morphological surfaces were introduced by the particles, which could appear as pores in the modified PVC films.

4.5 UV exposure effect

There are three zones, roughly represented by the various colors in Figure 14, that run the length of a PVC object exposed to sunlight:

1. Outer Layer: This layer is roughly 50 microns in thickness and is primarily composed of oxidation products and chain scission. Oxygen diffusion regulates oxidation in this area, and chain scission is a consequence of oxidation reactions, followed by chalking.

2. Lower Underskin Zone: This zone, ranging from 50 to 300 microns in size, is dominated by conjugated polyenes. Polyene development and crosslinking brought on by C• radicals predominate in this area.

3. Core Zone: This zone remains intact beyond 300 microns. Photochemical reactions do not occur in this area because, after a certain period, photons are filtered by polyenes (Wirawan et al., 2011).

5. Discussions

The PVC films were exposed to 365 nm wavelength radiation for up to 300 hours at ambient temperature. The films' effectiveness was assessed using weight loss, AFM, SEM, FT-IR, and a microscope. After being exposed to radiation, the FT-IR spectra of PVC sheets showed absorption bands for the hydroxyl group (O-H) at 3500 cm^{-1}, the carbonyl group (C=O) at approximately 1720 cm^{-1}, and the polyene group at 1604 cm^{-1}. The growth rate of the hydroxyl, carbonyl, and polyene groups rises with longer exposure times. Compared to pristine PVC and other modified samples, the modified PVC composite containing CuO film shows a significantly lower weight loss after irradiation. The superior performance of the CuO-modified PVC films can be attributed to the effective interaction between the CuO nanoparticles and the polymer matrix, which likely provides a more robust barrier against UV-induced degradation. In addition, the PVC containing CuO film displayed decreased roughness and cracking, according to the microscope, SEM, and AFM images.

5. Conclusions

In conclusion, the study successfully demonstrated that the chemical modification of polyvinyl chloride (PVC) films with amino groups and aromatic aldehyde, followed by the incorporation of metal oxide nanoparticles (NPs), significantly enhances their resistance to photodegradation. Among the various metal oxides tested, the PVC films enriched with CuO nanoparticles exhibited the most remarkable improvement in UV resistance. These findings suggest that the incorporation of CuO nanoparticles into PVC films holds significant potential for applications requiring enhanced durability and longevity under UV exposure, paving the way for further research and development in the field of polymeric materials.

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