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The Enhancement of Photodegradation Stability of Poly(Vinyl Chloride) Film by Surface Modification with Organic Functional Groups Doped with Different Type of Nano-Metal Oxides

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Abstract

Poly(vinyl chloride) (PVC) films were synthesized by incorporating organic groups, specifically amino groups derived from ethylene di-amine (en). The casting process was employed, with tetrahydrofuran (THF) utilized as the solvent. The incorporation of 4 metal oxide nanoparticles (NPs), namely MgO, ZnO, NiO and TiO_2, was carried out to enhance the stability of the films during light exposure. The effect of UV radiation dose was significant. Subsequent exposure of the PVC films to ultraviolet light enabled the evaluation of resulting damage through various analytical and morphological techniques. The utilization of infrared spectroscopy and weight loss study suggested that the films incorporating additives exhibited less harm and little alterations on the surface, as compared to the unaltered film. Among the modified films, the PVC-en/TiO_2 NPs film exhibited the highest resistance against the photodegradation process, as evidenced by the data derived from FTIR spectra, weight loss measurements, and surface morphology analyses. Titanium dioxide nanoparticles have been good PVC photostabilizer because of its capacity to block ultraviolet (UV) radiation. The atomic force microscopy (AFM) photographs of the PVC-en/TiO_2 NPs film after irradiation revealed a smooth surface, exhibiting a roughness factor (Rq) of 34.3, in contrast to the PVC (blank) which had a roughness factor of 282.2. SEM images for irradiated PVC films reveal the existence of cracks, cavities, protrusions, blemishes and formless, uneven surfaces. Microscopic images revealed that the surface of untreated PVC films exhibited significantly more pronounced damage and anomalies following irradiation compared to modified PVC films incorporating nano-metal oxides.

Keywords: Polyvinyl chloride, Surface modification, Nucleophilic substitution, Microscopic images, Atomic force microscopy.

Introduction

In recent times, polymers have become increasingly significant as biomaterials, owing to their exceptional versatility and favorable physico-chemical properties. Notably, polyvinyl chloride (PVC) holds a prominent position within this category of materials due to its exceptional balance of properties, which encompasses excellent durability against physical and chemical forces, lack of reactivity to biological fluids and a diverse range of available manufacturing methods. As a result, PVC finds extensive usage in various biomedical applications [1], accounting for over 5 % of its total application. PVC finds a diverse range of applications in the medical domain, including the production of various medical articles. Various medical devices encompass a wide range of items, including but not limited to blood bags, breathing tubes, blood transfusion tubes, indwelling catheters and various prostheses such as cardiovascular implants, orthopaedic replacements, intraocular implants, as well as intravascular and urine catheters. It is noteworthy, however, that devices which are partially inserted into internal cavities or traverse tissues by penetrating the skin are especially prone to the risk of infection [1].

Consequently, there exists a significant impetus to enhance the resistance of polymer surfaces against bacteria, prompting exploration into methodologies such as chemically altering the surface of polymer to achieve this objective. Surface modification can be accomplished through various techniques. Procedures that directly modify chemicals by oxidation, hydrolysis, chemical grafting, plasma therapy and corona discharge, among others. Particularly effective in accurately changing surfaces' chemical composition and physical characteristics have been wet-chemical treatments that use typical organic reactions [2]. In the last few years, there has been an enormous rise in the industrial production of plastics as a result of greater consumer interest. The production of PVC has experienced a substantial growth, increasing from 3 million tons in 1965 to an impressive 40 million tons in 2018. Projections suggest a continued upward trajectory, with an anticipated production volume of 60 million tons by 2025. PVC is therefore considered as one of the most widely produced plastics for commercial use. The high chlorine content imparts toughness and hardness to PVC. Consequently, it finds utility in an extensive range of sectors, including but not limited to packing, furniture, electrical wire insulation, construction materials and toys. The employment of conventional membranes for the separation of biomacromolecules (e.g., proteins, polysaccharides), microbial cells containing tiny molecules, and organic dyes is restricted. PVC, although being a widely used synthetic polymer, is distinguished from alkyl halide equivalents with low molecular weights by its relatively low vulnerability to simple nucleophilic substitution processes. Instead, under many condensation reaction conditions, it tends to favour dehydrochlorination, leading to the generation of dark-colored products via consecutive double-bond formation [3]. Nucleophilic substitution reactions involving thiols and thioethers have shown promising results [4]. Notably, effective alterations have also been achieved through the utilization of dithiocarbamates [5], NaN_3 [6] and $Na_2S_2O_3$, leading to the formation of the corresponding Bunte Salt [7].

Recently, there has been a notable emphasis on the adoption of environmentally friendly solvents, non-toxic chemicals, and renewable materials in the field of green chemistry and chemical processes. Nanocomposites (NCs) represent a unique class of organic-inorganic hybrid materials that have attracted significant attention at the start of the 21st century [8]. Clustering or dispersion of the incorporated additives occurs often when nanoparticles are integrated with polymer chains. Microparticles' dimensions, structural morphology, chemical components, energy of the surface, crystal shape and area all have a significant impact, alongside the interplay between the polymer and the nano-filler, significantly impacting the physical and chemical traits of polymer NCs [9]. The exploration of surface modifications for PVC has been undertaken to mitigate the release of the inclusion of additives in the surrounding media [10] serves to enable polymer recycling [11] and improves mechanical and interfacial qualities within the context of applications that require interaction with the biological solutions [12] and prevent bio-fouling, a critical concern in the realm of medical-grade PVC [13].

A wide range of chemical and physical techniques have been studied for altering PVC surfaces. These methods include oxygen and argon plasma exposure [14], polymer grafting of brush layers [15], UV radiation [16] and substitution of nucleophilic molecules by wet-chemical treatment [17]. Thiols with a strong smell successfully substitute chlorine atoms on the PVC backbone. This has been demonstrated to work well in solution, aqueous suspensions, and when the PVC is melted [18]. This study showcases the most recent research that illustrates the effective integration of ethylenediamine and nano-metal oxides to create pendants of functionalized PVC, resulting in improved photostability.

Materials and methods

Materials and instrumentations

From Petkim Petrokimya in Istanbul, Turkey, commercial-grade PVC was procured. The PVC had an average molecular weight of around 233,000 g/mol and a degree of polymerization of approximately 800 monomers. Ethylenediamine, 98 - 99 % pure metal oxide nanoparticles (NPs) and analytical-grade solvents were obtained from Merck, Gillingham, United Kingdom. The sizes of the metal oxide nanoparticles (NPs) as follows were determined: 15 nm for titanium dioxide (TiO_2), 50 nm for zinc oxide (ZnO), 30 nm for nickel oxide (NiO) and 50 nm for magnesium oxide (MgO). Infrared spectral analysis was performed using an FTIR Shimadzu 8400 spectrophotometer manufactured by Shimadzu Corporation in Tokyo, Japan. PVC films were subjected to UV irradiation with a wavelength of 365 nm and a light intensity of 6.2×10^{-9} Einstein $dm^{-3}\times s^{-1}$ at a temperature of 25 °C. The irradiation was carried out within an accelerated weather tester (Q-Panel Company, Homestead, FL, USA) equipped with 2 40-watt fluorescent lamps positioned on the sides. The prepared PVC films were arranged parallel to the lamps, maintaining a distance of 10 cm from the light sources. To achieve uniform exposure, the polymeric materials were periodically rotated throughout the irradiation process. The surface morphology of the PVC films was assessed using optical microscopy, scanning electron microscopy (SEM) and AFM. Optical images were obtained using a Meiji Techno microscope from Tokyo, Japan. SEM images were acquired with a SIGMA 500 VP microscope from Carl Zeiss Microscopy, White Plains, NY, USA. AFM measurements were performed employing a Veeco instrument from Plainview, NY, USA.

PVC incorporating ethylenediamine preparation

A solution of 5 g of PVC in 15 mL of THF solvent was prepared at 25 °C under continuous agitation for 10 min. The resulting polymer was subsequently isolated, dried, and immersed in a solution of 29.5 g of ethylenediamine ($H_2N(CH_2)_2NH_2$) in 15 mL of THF. After refluxing the mixture for 1 h while stirring continuously, the solvent was extracted. Following this, the aminated polymer was dried naturally at 25 °C for 24 h.

Preparation of PVC containing ethylenediamine and nano-metal oxides

A sonication was performed for 1 h on a solution containing 0.4 g of PVC-ethylenediamine and 0.1 g of metal oxide nanoparticles (NPs), specifically titanium dioxide (TiO_2), zinc oxide (ZnO), magnesium oxide (MgO) and nickel oxide (NiO), which were dissolved in 4 mL of THF. The resultant solution was subsequently deposited onto glass plates, yielding films of around 40 µm in thickness. These films were allowed to dry at 25 °C for 24 h and subsequently subjected to a vacuum for 3 h to remove any residual solvents.

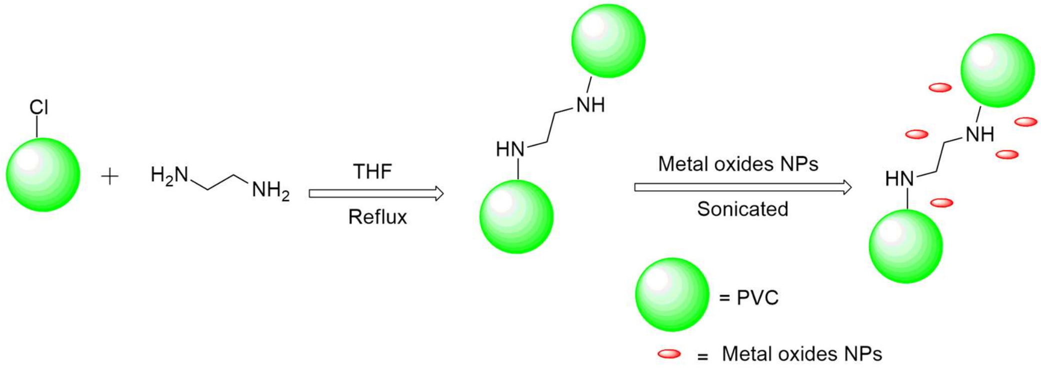
Irradiation of PVC films

PVC films were subjected to UV irradiation utilizing a QUV tester equipped with an accelerated weather meter (Q-Panel Company; Homestead, FL, USA). The apparatus comprised a chamber made of stainless steel, which was adorned on opposing sides with 2 40-watt UV fluorescent lamps (UV-B 365). The PVC films were exposed to UV radiation at a precise light intensity of 6.2×10^{-9} Einstein dm^{-3} s^{-1} and a regulated temperature of 25 °C. The irradiation process continued for 300 h, with samples analysed at regular intervals of 50 h.

Results and discussion

PVC surface fabrication

Chemical changes can occur in solution by nucleophilic substitution reactions involving the chlorine atoms of PVC. For this objective, ethylenediamine has proven to be an exceptionally efficient reagent, enabling substantial levels of modification while preventing the manifestation of undesired side reactions. Research has also established that these reactions can be restricted to the film surface when the reaction takes place at the interface between a PVC film and a modifier solution in a solvent/non-solvent polymer blend. A concentration gradient of modifier groups can be formed within the film when the nucleophilic substitution reaction advances at a pace greater than the diffusion of the modifier and the modification process is interrupted prior to the modifier having completely permeated the whole film. The specific characteristics of this gradient depend on factors such as reaction time, temperature and solvent composition [19]. **Scheme 1** depicts the process for incorporating pendant modifications into PVC. The process commences with the aminolysis of PVC in THF, which enables ethylenediamine to become attached to the backbone of the polymer. Following this, nano-metal oxides are added via sonication in the 2nd stage.



Scheme 1 PVC modification reaction.

Effect of UV radiation dose

The impact of the radiation dose on the alteration was examined. This phenomenon could potentially be attributed to the increased generation of radicals, which may engage in the reaction as the dose and monomer concentration are elevated.

FTIR spectra

The capability of nano-metal oxides to lessen the rate of photo-degradation in PVC films was examined utilizing an FTIR spectrophotometer. The emergence of undesirable compounds containing small, destructive polymeric fragments featuring carbonyl (C = O; carboxyl and ketone) groups was detected. Moreover, the presence of polyene groups was noted [20]. **Figure 1** depicts an illustration based on peak intensity. FTIR analysis revealed a distinct difference in the functional group composition of irradiated PVC films compared to unaltered ones. Specifically, the peaks corresponding to C = O (1722 cm^{-1}) and C = C (1602 cm^{-1}) were significantly more pronounced in the irradiated blank PVC film, indicating the formation of new functional groups as a result of radiation exposure.

In contrast, modified PVC doped with nanoparticles (NPs), particularly TiO_2, exhibited a noticeable decrease in the intensity of these peaks. This suggests that the presence of NPs, particularly TiO_2, may have mitigated the formation of new functional groups during irradiation, possibly due to their interaction with the PVC matrix or their inherent UV-shielding properties.

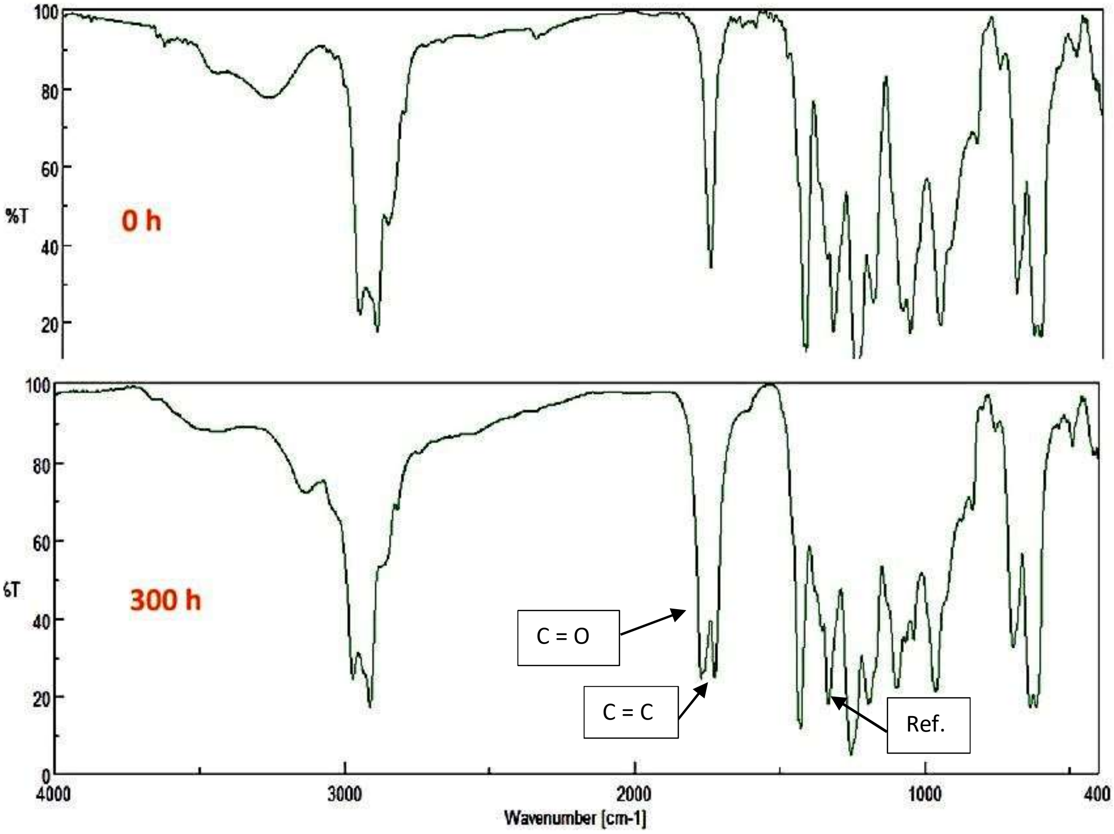


Figure 1 Fourier-transform infrared (FTIR) spectra representing 2 distinct states of a PVC film: Before (a) and after exposure to radiation for 300 h (b).

The initial spectrum, representing the unexposed film, likely displays characteristic peaks corresponding to the functional groups within the pristine PVC polymer. The subsequent spectrum, depicting the irradiated film, might exhibit changes in the intensity or presence of these peaks, signifying potential modifications to the polymer's chemical structure as a result of radiation exposure.

The evaluation of both unaltered and adjusted PVC films was conducted by examining the measured carbonyl index ($I_{C=O}$) and polyene index ($I_{C=C}$) (**Figures 2** and **3**). As per Eq. (1), Is denotes the functional group index, while As and Ar represent the absorbance of the reference peak and functional group, respectively [21].

$$\mathrm{Is} = \mathrm{As}/\mathrm{Ar} \qquad (1)$$

Evidently, the presence of NPs stabilized the PVC following 300 h of irradiation. The escalation in the growth rate of carbonyl and polyene groups was observed with prolonged irradiation time and diminished with the addition of NPs.

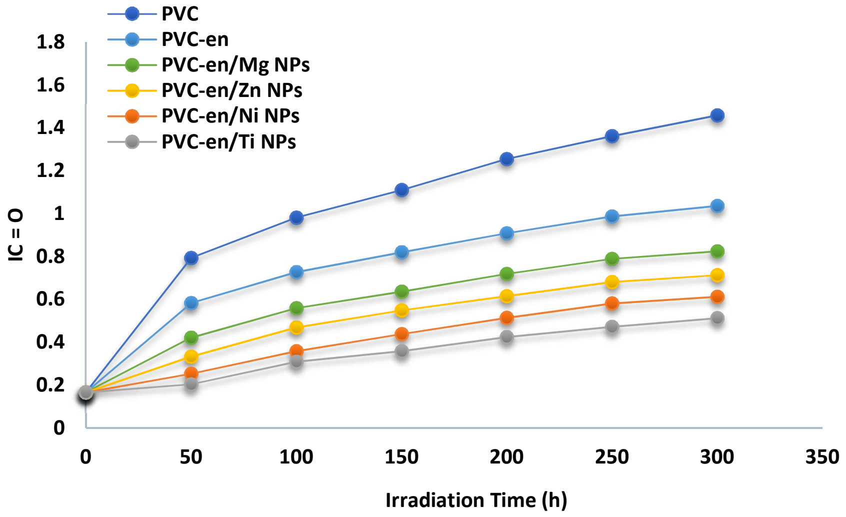


Figure 2 $I_{\mathrm{C=O}}$ for PVC films during the irradiation process.

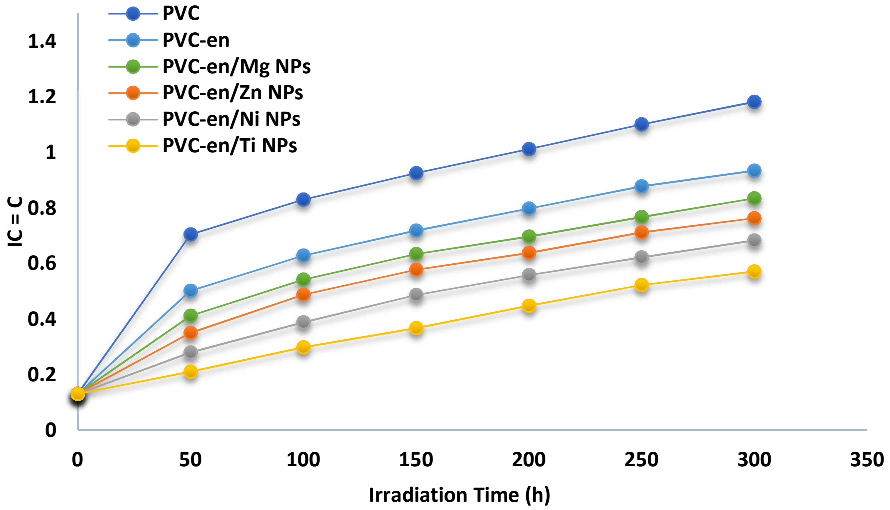


Figure 3 $I_{\mathrm{C=C}}$ for PVC films during the irradiation process.

Weight loss method

Irradiation of PVC results in a decrease in mass, which can be attributed to the development of more minute particles. By employing Eq. (2), one can ascertain the proportion of weight reduction in PVC over a specific period (t) of irradiation [22]. The weight reduction was calculated by comparing the pre-irradiation (W_0) and post-irradiation (W_t) weights of the PVC films [22].

$$\text{Weight loss (\%)} = [W_0 - W_t]/W_0 \times 100 \tag{2}$$

The photodegradation process in PVC leads to the liberation of volatile compounds, which subsequently causes a drop in weight [23]. The weight loss percentages of the PVC films as a result of irradiation were calculated using Eq. (2) and are illustrated graphically in **Figure 4**. Typically, weight loss intensifies with the advancement of radiation duration. The PVC film demonstrated the highest weight loss, whereas the incorporation of nano-metal oxides in the modified PVC films as photostabilizers notably curbed the weight loss. Notably, the modified PVC films containing nano-metal oxides exhibited the most significant stabilizing effect.

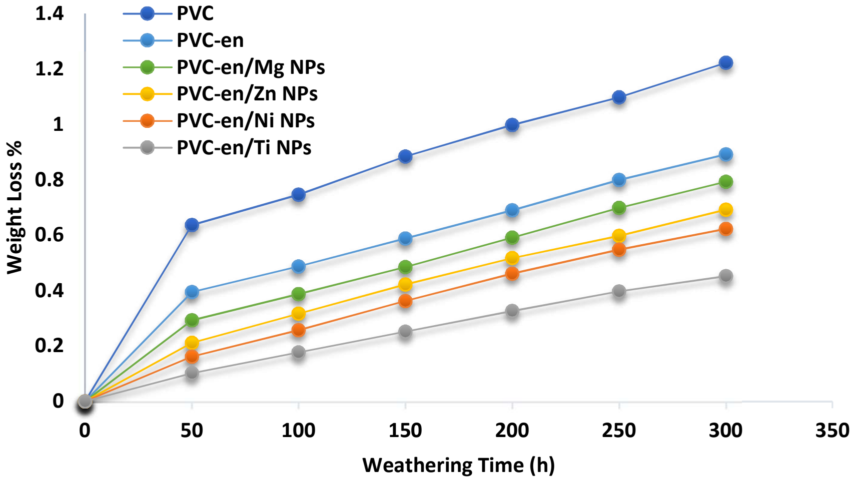


Figure 4 Percentage of weight loss for PVC films during the irradiation procedure.

Morphological studies of PVC films

An exploration of the surface morphology of polymers can yield crucial insights into the degradation incurred from weathering and alterations in the dimensions and configuration of particles.

Optical microscope

Microscopic analysis employing various techniques can reveal with high accuracy the surface alterations induced by irradiation on the PVC film. As such, the non-irradiated film surface is expected to exhibit uniformity, consistency and smoothness, as depicted in **Figure 5**.

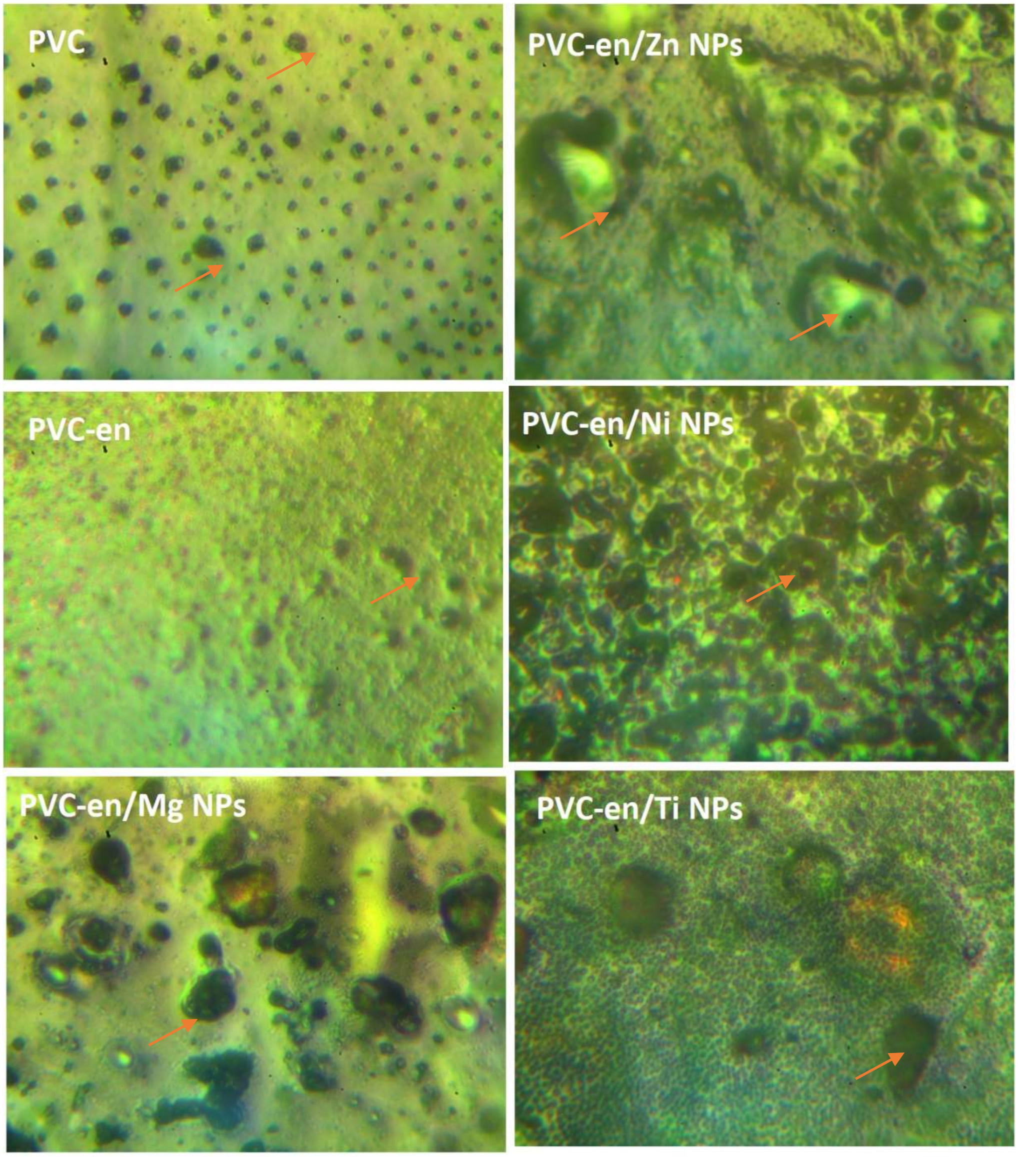


Figure 5 Microscopic images for PVC films before irradiation.

An examination of the optical microscopy images (**Figure 6**) revealed that the surface of untreated PVC films exhibited significantly more pronounced damage and anomalies following irradiation compared to modified PVC films incorporating nano-metal oxides. Hence, the integration of nano-metal oxides in the modified PVC films protected photodegradation upon UV exposure.

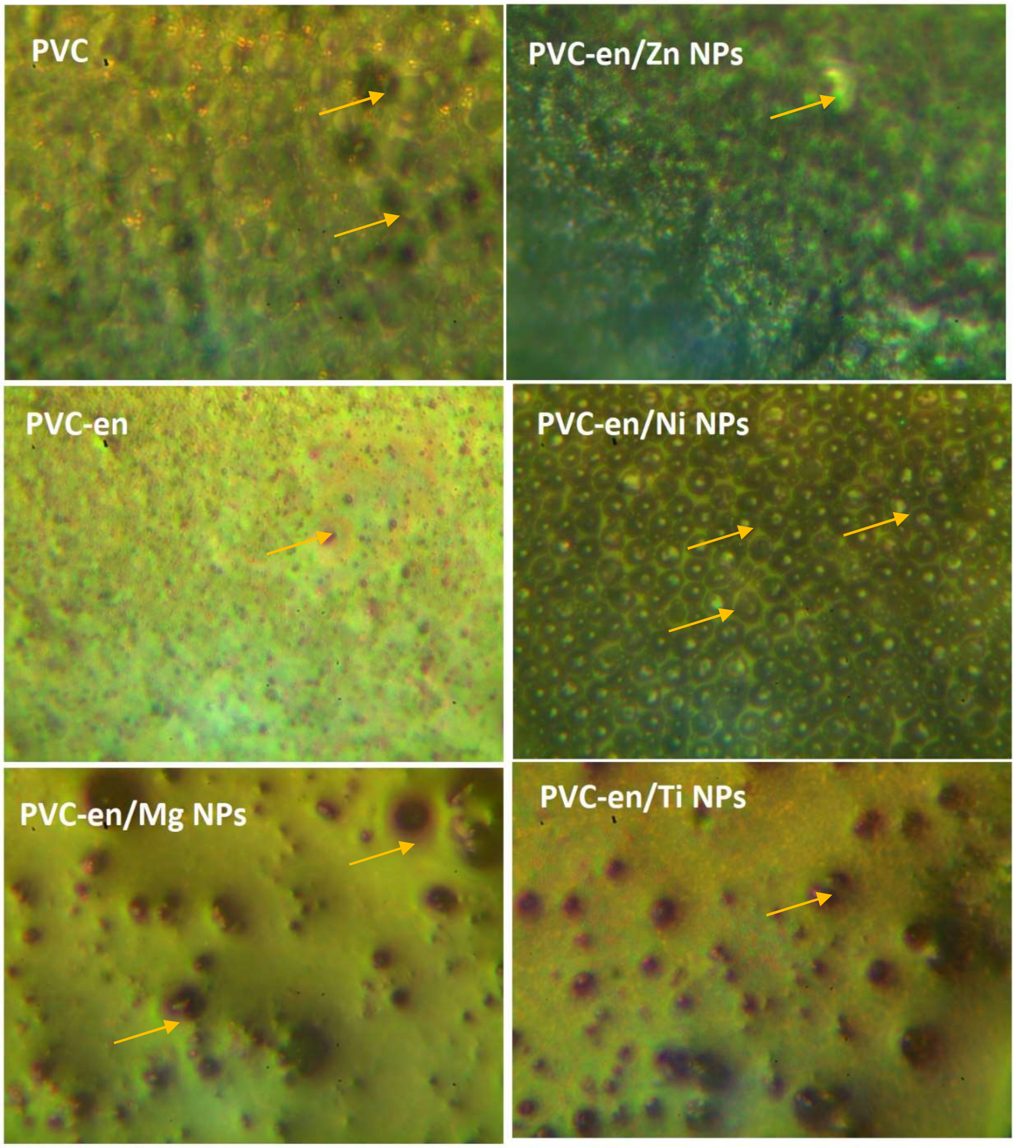


Figure 6 Microscopic images for PVC films after irradiation.

Scanning electron microscopy (SEM)

The utilization of SEM provides valuable information on particle size, surface variation, distortion and homogeneity [24]. The irradiated PVC films reveal the existence of cracks, cavities, protrusions, blemishes and formless, uneven surfaces. These alterations primarily arise from dehydrochlorination, chain fragmentation and cross-linking. Nevertheless, the presence of UV absorbers restrained surface impairment in polymers relative to the untreated polymers (**Figure 7**).

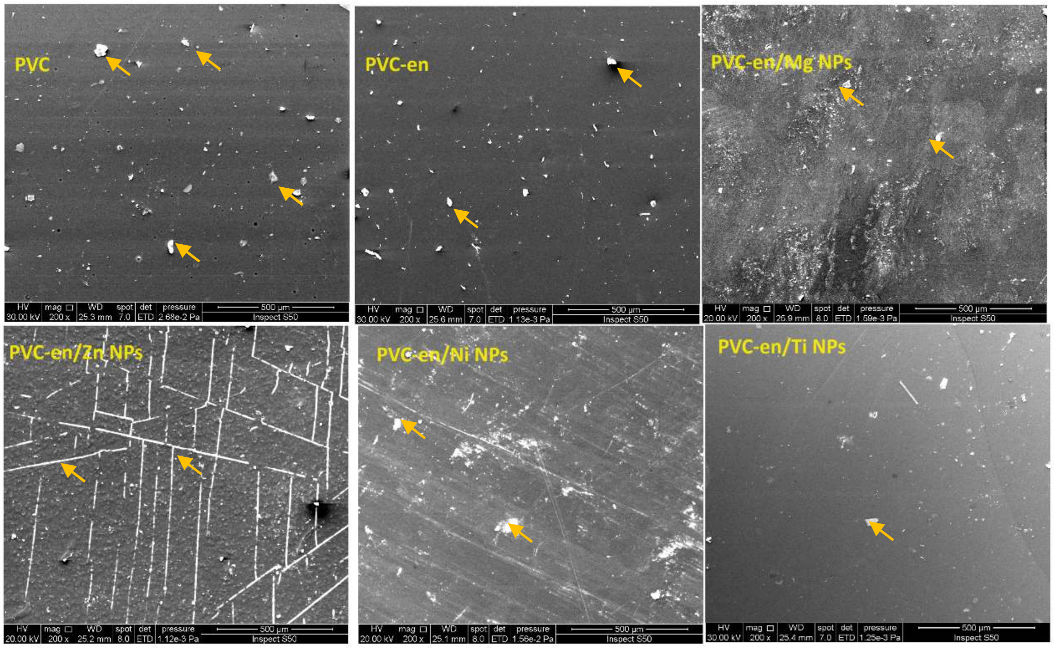


Figure 7 SEM images of irradiated PVC films.

Atomic force microscopy (AFM)

In order to evaluate the extent of photodegradation, AFM was employed to examine the surface morphology of the polymer blends [25]. As illustrated in **Figure 8**, the AFM picture of the PVC film prior to irradiation revealed a smooth and uniform surface.

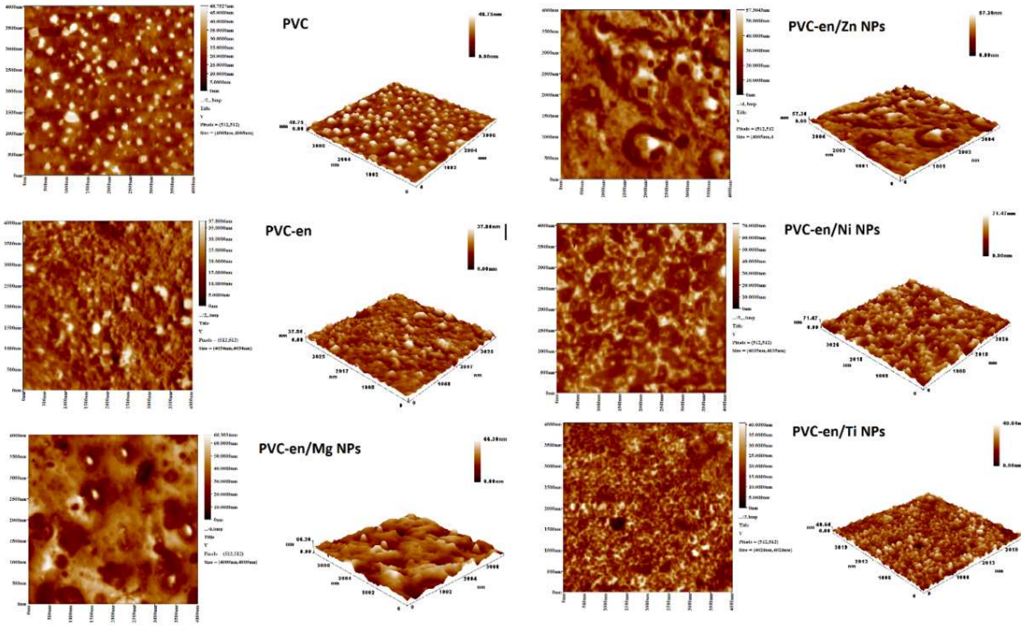


Figure 8 AFM images for PVC films before irradiation.

Irradiated, unmodified PVC film had irregular surface features that were revealed by the AFM image (**Figure 9**). In the adjusted films, the occurrences of dark spots were significantly less than those identified in the pristine PVC film. These findings validate that the adjusted PVC films combined with nano-metal oxides effectively functioned as photostabilizers.

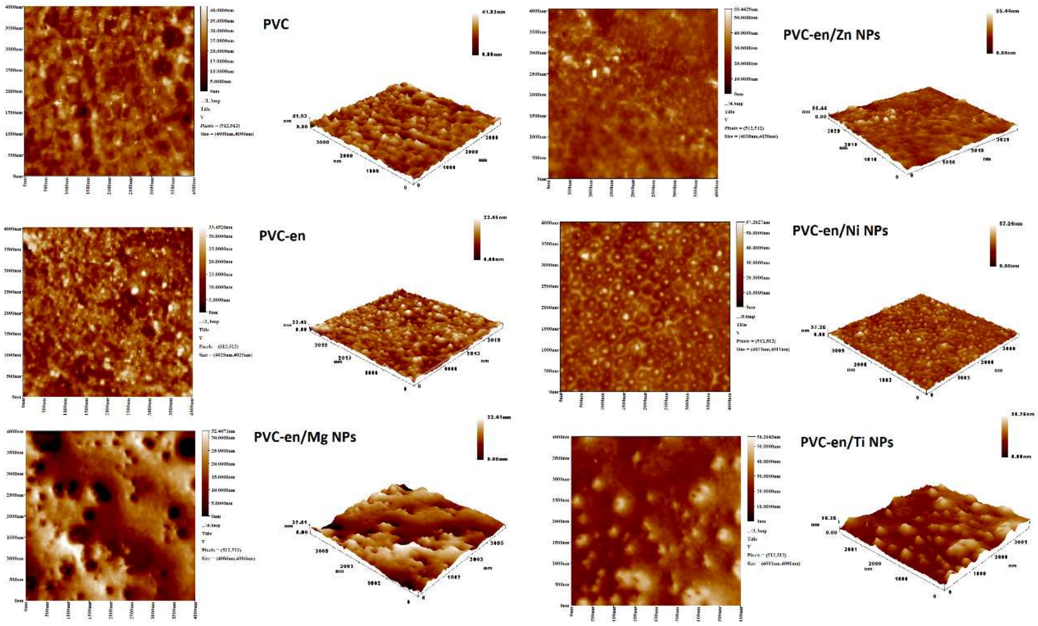


Figure 9 AFM pictures of (PVC) films following radiation exposure.

The roughness factor (Rq) serves as an indicator of the surface smoothness of materials. The incorporation of nano-metal oxides into the PVC resulted in a decrease in the Rq value of the PVC. The calculated Rq values for the irradiated PVC mixtures were 282.2, 79.5, 52.6, 41.8 and 34.3 for the unmodified PVC film and the modified PVC films including nano-metal oxides MgO, ZnO, NiO and TiO_2, respectively.

Conclusions

PVC film surfaces can be selectively modified via nucleophilic reactions under appropriate conditions. FTIR spectroscopy serves as a powerful tool for monitoring and confirming the success of such surface modifications. The effectiveness of the films was assessed using various techniques including FTIR spectroscopy, the weight loss approach, as well as optical microscope, AFM and SEM analyses. After irradiation, the modified PVC films containing TiO_2 exhibited a substantial reduction in weight loss compared to both the unmodified PVC and other fabricated films. Analysis of the modified PVC films with TiO_2 revealed a significant improvement in surface morphology compared to the unmodified films. Microscope, AFM and SEM images all demonstrated reduced surface roughness and a decrease in the number of cracks present on the surface of the TiO_2-modified PVC films.

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