

Photostabilization of PVC/PS/PMMA Blend Films by Metal Oxide Nanoparticles under Accelerated UV Aging

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Abstract

Degradation by ultraviolet (UV) radiation is still one of the most important issues affecting the long-term effectiveness and sustainability of polymers used outdoors. In this context, a ternary polymer blend of poly(vinyl chloride) (PVC), polystyrene (PS), and poly(methyl methacrylate) (PMMA) was synthesized by solution casting and loaded with metal oxide nanoparticles (NPs) (e.g., MgO, ZnO, TiO₂, and NiO) at low concentration levels as UV photostabilizers. The incorporation of metal oxide NPs in the polymer system was done under accelerated UV irradiation (up to 300 hours) and the efficiency of the nanoparticles to prevent UV-induced degradation was investigated. The degree of UV photostabilization was evaluated by FTIR spectroscopy, weight loss, and atomic force microscopy (AFM) studies. The FTIR investigations showed a significant concentration of carbonyl groups in the untreated film; this is indicating that the polymer experienced some photo-oxidation during the UV exposure. The films with metal oxide nanoparticles showed comparatively lower carbonyl index than those of the unmodified polymer blend. Besides, the treated samples showed less weight loss compared to the blank samples. In addition, AFM examination revealed that the modified films had a lower surface roughness and cracking, in addition to less morphology degradation following UV irradiation. The higher photostabilization observed is associated with the ability of metal oxides to absorb harmful UV radiation, thus inhibiting radical reactions responsible for the degradation process in the polymer matrix. Metal

oxide nanoparticles can, therefore, be considered an effective method of enhancing UV resistance of polymeric films for use in various applications. The selection of these four nanoparticles was therefore intended to enable a meaningful comparison of their photostabilizing efficiencies rather than to assume equivalent performance. Their incorporation at low concentrations also allows their UV-screening effect to be investigated while minimizing potential adverse effects associated with high nanoparticle loading, such as aggregation and changes in the physical properties of the polymer matrix. The comparison is particularly relevant to the present PVC/PS/PMMA blend, for which the effectiveness of these oxide nanoparticles as UV stabilizers has not been sufficiently established.

1. Introduction

The extensive application of polymeric materials in modern applications has led to a growing need for enhancing their durability towards environmental degradation [1]. Polymers can undergo undesirable physical and chemical changes in long-term exposure when subjected to the combined effects of temperature changes, mechanical forces, chemical interactions, and solar irradiation [2]. These degradation phenomena can lead to the deterioration of mechanical strength, appearance, and overall functionality; they limit the useful life of polymer-based products [3]. Thus, the durability of commercial polymers strongly depends on the stability of the polymer matrix and the addition of efficient stabilizing agents preventing degradation mechanisms [4]. Among various polymeric systems, organic coatings are protective materials designed to resist environmental exposure while maintaining surface integrity of underlying substrates [5]. This large family of coatings includes paints, lacquers, varnishes, enamels, waterborne formulations, organosols, and powder coatings [6]. From a commercial point of view, coating technologies are widely used in trade, industrial, marine, and automotive applications. Automotive finishes are one of the most demanding sectors in terms of durability, weather resistance, and long-term performance [7].

Coating formulations typically contain many ingredients that enhance performance, processing characteristics, and durability. Apart from the conventional components, such as pigments and UV stabilizers [8], coatings may also contain functional additives such as biocides [9], corrosion inhibitors, antistatic agents [10], and flame retardants [11]. Other formulation ingredients like curing catalysts, reaction initiators, and crosslinkers add to the structural and chemical complexity of these systems. The different degradation behavior of each ingredient results in highly variable responses of coatings to environmental exposure [12,13]. This renders the study of coating aging and stabilization particularly difficult, since the understanding of the mechanisms of coating deterioration requires the consideration of the entire formulation and not only of individual components [14].

Degradation of polymeric materials that resulted from the exposure to ultraviolet rays from the sun is one of the main environmental causes [15]. The level of UV radiation on Earth depends on various factors, such as latitude, season, and time of day [16]. The stratospheric ozone layer absorbs a significant portion of high-energy UV-B radiation from extraterrestrial sources under normal atmospheric conditions [17]. However, long-term satellite and ground-based measurements of the atmosphere have shown a continued decrease in ozone concentrations with an estimated global average decrease of about 2.7 ± 1.4 % per decade [18]. Higher levels of UV-B radiation reach the Earth's surface, which improves photo-oxidative degradation reactions and increases the susceptibility of polymeric materials to environmental deterioration due to this reduction in atmospheric protection [19].

The objective of the present work was to study the efficiency of various metal oxide nanoparticles (MgO, ZnO, TiO₂, and NiO) as photostabilizing additives for a poly(vinyl chloride) (PVC)/polystyrene (PS)/poly(methyl methacrylate) (PMMA) polymer blend under ultraviolet irradiation. Films of composite material with low concentration of these nanoparticles were prepared and tested under accelerated UV-ageing. The photostabilization performance of the prepared films was evaluated by Fourier transform infrared spectroscopy (FTIR), weight-loss measurements, and atomic force microscopy (AFM). The study aims at a comparative assessment of the effectiveness of different metal oxide nanoparticles in suppressing the photodegradation caused by UV radiation and boosting the stability of polymer blend films.

2. Materials and Methods

2.1 Materials and Instruments

Commercial-grade PVC, PS, and PMMA were obtained from Sigma-Aldrich Chemical Company (Gillingham, UK). Commercial MgO, ZnO, TiO₂, and NiO nanoparticles were used as received. The nanoparticles were obtained from

Merck, Gillingham, United Kingdom, with purities of 99% and nominal particle sizes of 50, 50, 15, 30 nm, respectively. The chemical modifications of the prepared films were monitored by FTIR spectroscopy in the wavelength range of 4000–400 cm^{-1} using a Jasco FTIR-4200 instrument (Tokyo, Japan). Photodegradation studies were conducted in a QUV accelerated weathering tester (Q-Panel Company, Homestead, FL, USA) at 25 °C under controlled conditions. The irradiation source was operated at a maximum wavelength of 365 nm with an intensity of $6.43 \times 10^{-9} \text{ ein dm}^{-3}\text{s}^{-1}$. Surface topography analyses were performed using a Veeco atomic force microscope (Plainview, NY, USA). The thickness of the composite films was kept around 40 μm and measured with a Digital Vernier Caliper 2610 A micrometer obtained from Vogel GmbH, Kevelaer, Germany. Samples for irradiation experiments were fixed on 0.6 mm aluminium panel supports from Q-Panel Company (Homestead, FL, USA).

2.2 Preparation of Composite Films Doped with Metal Oxide Nanoparticles

Composite films were prepared by the solution casting method. In simple words, 0.3 gm of PS, PMMA, and PVC were separately weighed and mixed in 100 mL of chloroform solution and stirred for 90 min at 25°C to form a homogeneous polymer solution. After that, metal oxides (MgO, NiO, ZnO, and TiO_2) were added in an amount of 0.001 g (0.01 wt% relative to the total polymer mass) was selected. This low concentration was chosen to provide UV-screening activity while minimizing nanoparticle aggregation and preserving the characteristics of the polymer matrix, and stirred for another 30 minutes until a homogeneous dispersion was obtained. The solutions were then deposited on clean glass plates and left for 24 h at 25 °C to obtain composite films of about 40 μm thickness.

2.3 FTIR Spectroscopy of the Composite Films

Changes of the chemical composition of the composite films were monitored by FTIR spectroscopy. The level of photo-oxidative degradation was evaluated by determining the carbonyl index (I_s) calculated according to Equation 1 based on the absorbance of the respective functional groups (A_s) normalized to the absorbance of a reference band (A_r) [20].

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

2.4 Weight Loss of the Composite Films

The resistance of the composite films to photodegradation was assessed by gravimetric analysis. The percentage weight loss was calculated by using the following equation 2 from the difference between the film weight before irradiation (W_1) and the weight measured after UV exposure (W_2) [20].

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

3. Results and Discussion

3.1 Fabrication of Doped Composites with Nano-Metals Oxides

Three polymers (PS, PMMA, and PVC) were mixed and dissolved in chloroform. Metal oxides (0.001 g, corresponding to 0.5% w/w of the polymer) (MgO, NiO, ZnO, and TiO_2) NPs were subsequently added to the solution and stirred for another half an hour to obtain a homogeneous dispersion. The prepared mixture was deposited on clean glass slides to obtain films as schematized in Fig. 1.

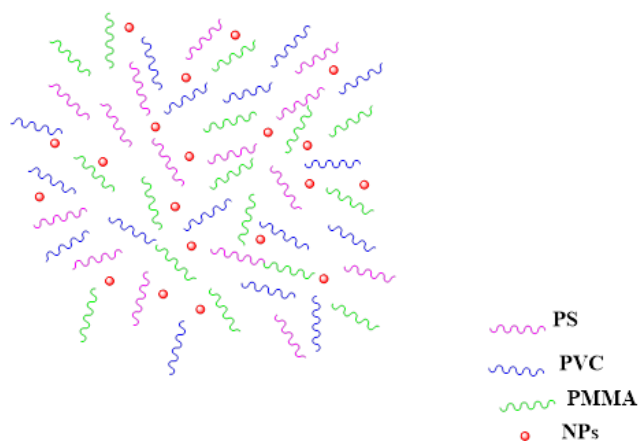


Fig. 1 Composite doped with nano metals oxides

The composite undergoes photo-oxidative decomposition upon prolonged exposure to UV and in the presence of oxygen. This degradation changes many properties of the polymer, e.g., electrical, optical, mechanical, and chemical properties [21]. The intensity of the IR signal attributed to the carbonyl group in the composite is taken as the measure of photodegradation. For this purpose, the FTIR spectra of the composite were measured before and after NPs doping and before and after irradiation treatment. The results show that the C=O absorption peak at 1720 cm^{-1} is significantly increased after irradiation compared to the initial film. The C-C bond at 1328 cm^{-1} was taken as a reference [20]. The carbonyl group index ($I_{\text{C=O}}$) was calculated by Equation 1. Fig. 2 shows the change in $I_{\text{C=O}}$ with irradiation period from 0 to 300 h. Fig. 2 shows the decrease in $I_{\text{C=O}}$ values for the metal oxide nanoparticle composite films under irradiation compared to control films.

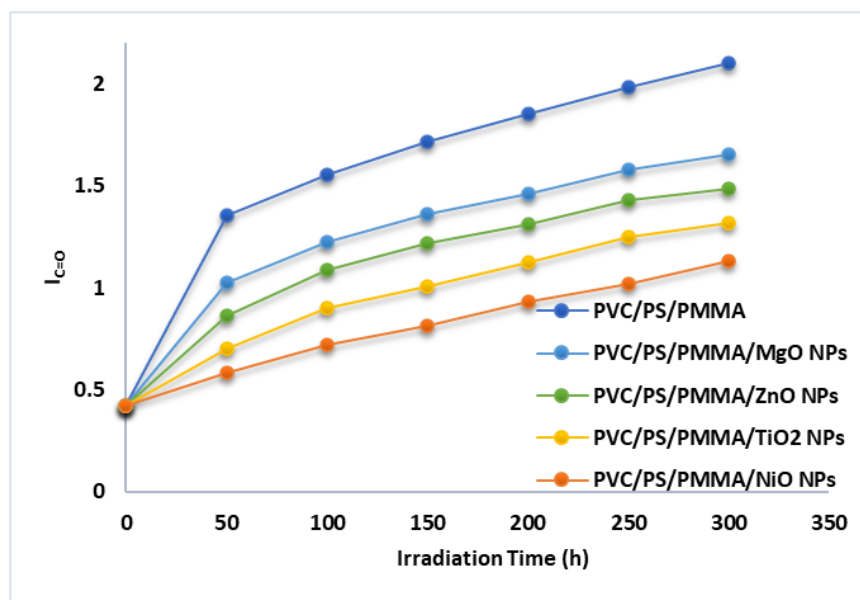


Fig. 2 Impact of irradiation of composite films on the carbonyl index

On exposure to UV light, composites rapidly change from colorless to yellow and gradually become brittle with the formation of fine fragments, reducing their weight [22]. Composite films were thus irradiated up to 300 hours, and their loss in weight was estimated according to Equation 2. Fig. 3 illustrates how the weight of the composite evolved as a function of time during the exposure to irradiation. The largest weight reduction occurred during the first 50 hours, while the weight continued to decrease much more gradually between 50 and 300 hours. The blank films showed significant weight loss compared with those loaded with metal oxide nanoparticles.

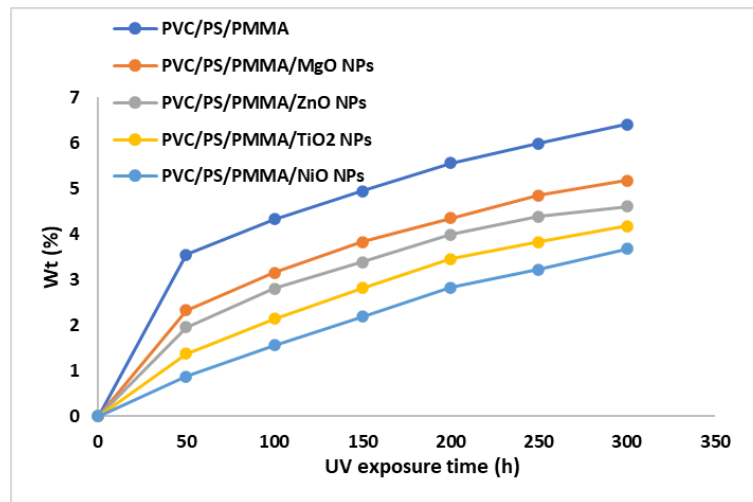
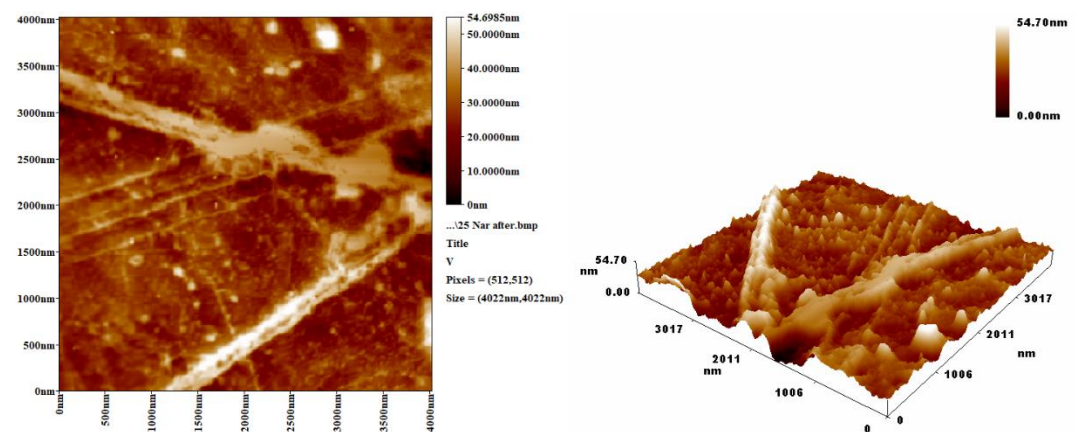
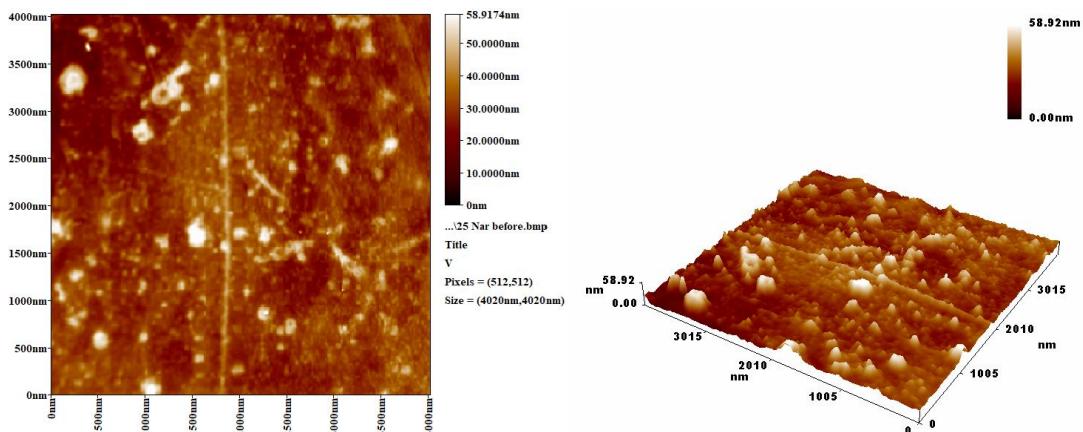


Fig. 3 Weight loss of composite films

AFM is a scanning microscopy technique and is one of the most useful tools to study the morphology of surfaces and particle features of materials [23]. The composite films exhibited initially smooth surfaces in two and three-dimensional AFM images. On the other hand, the composite film showed a rough texture after UV irradiation, which indicated severe photodegradation. However, the surface roughness of the composite films containing metal oxide nanoparticles was lower. The roughness values of PVC/PS/PMMA, PVC/PS/PMMA/MgO NPs, PVC/PS/PMMA/ZnO NPs, PVC/PS/PMMA/TiO₂ NPs and PVC/PS/PMMA/NiO NPs films were measured to be 200.2, 152.1, 148.3, 124.6, and 118.3 nm (Fig. 4).



(a)



(b)

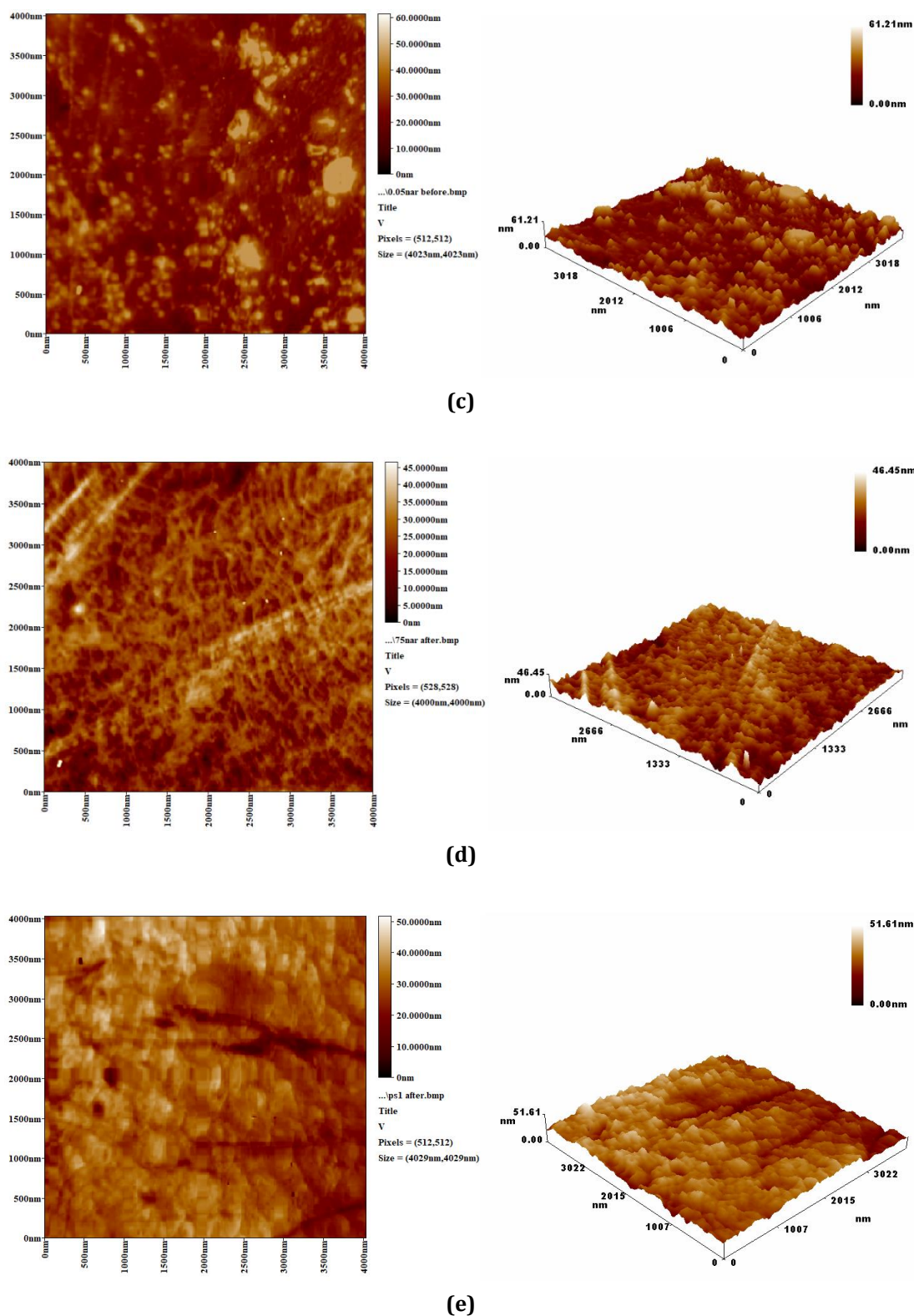


Fig. 4 Two- and three-dimensional AFM surface images of (a) PVC/PS/PMMA blend film; (b) PVC/PS/PMMA/MgO NP composite film; (c) PVC/PS/PMMA/ZnO NP composite film; (d) PVC/PS/PMMA/TiO₂ NP composite film; and (e) PVC/PS/PMMA/NiO NP composite film after UV irradiation

The prepared composite film has a uniform and interpenetrating network structure due to the physical blending of PVC, PS, and PMMA (Fig. 5). All polymer components can be dissolved in a common solvent, such as chloroform, and are thus able to mix at the molecular level in the solution phase [24]. Each polymer brings

different properties in the final film structure. The matrix consists mainly of PVC, which gives mechanical strength and film-forming ability; PS gives rigidity and dimensional stability; and PMMA gives optical transparency and improves the interfacial compatibility between the polymer phases [25]. The polymers are usually randomly but uniformly distributed throughout the film with little macroscopic phase separation. This reveals a good miscibility or partial compatibility between the polymer components in the chosen preparation conditions [26]. Moreover, the incorporated nanoparticles are uniformly distributed in the polymer matrix and they are physically entrapped between the entangled polymeric chains. The interaction between the polymer and the NPs' functional groups can improve interfacial adhesion, thereby the thermal stability, mechanical properties, and optical performance of the composite film are enhanced [27]. The obtained film, in general, is a well-combined nanocomposite system, where the polymer blend is the continuous matrix and the nanoparticles are the reinforcing fillers spread throughout the system [28].

Nanoparticle dispersion is an important factor. Well-dispersed NiO nanoparticles can provide a more uniform barrier to incident radiation and a larger effective polymer-particle interfacial area. This can reduce localized UV exposure and restrict the propagation of degradation reactions through the polymer matrix. The AFM results obtained in the present study support this interpretation because the NiO-modified film exhibited lower surface roughness and fewer cracks after irradiation. A closely related investigation likewise reported substantially lower roughness for NiO-containing PVC films and concluded that the NiO formulation provided the strongest protection against UV-induced morphological deterioration.

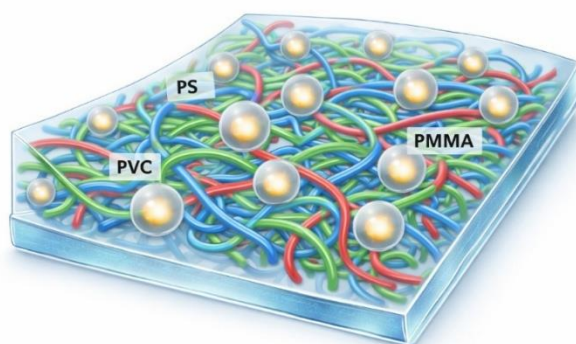


Fig. 5 Composite film incorporated nanoparticles

Therefore, the superior performance of NiO in the present PVC/PS/PMMA system is most appropriately attributed to the combined effects of UV attenuation, interaction with degradation products, possible suppression of radical/peroxide-mediated oxidation, and favorable polymer-nanoparticle interactions/dispersion, rather than to a single stabilization mechanism. These combined effects explain the simultaneous reduction in carbonyl formation, weight loss, surface roughness, and cracking observed after prolonged UV irradiation.

When the PVC/PS/PMMA film is exposed to UV radiation, chromophoric structural defects and impurities in the polymer can absorb UV photons. This initiates photochemical reactions that generate excited states and free radicals.

4. Conclusion

This study provides a systematic comparison of MgO, ZnO, TiO₂, and NiO nanoparticles as potential photostabilizing additives for PVC/PS/PMMA ternary films under identical preparation and accelerated UV-irradiation conditions. The combined FTIR, weight-loss, and AFM results demonstrate that the incorporation of the investigated metal oxide nanoparticles improved the resistance of the PVC/PS/PMMA films to UV-induced degradation compared with the unmodified film. Under the conditions examined, NiO NPs showed the most favorable overall performance based on the combined degradation indicators. The agreement among the chemical, gravimetric, and morphological observations supports its comparatively greater effectiveness in suppressing the effects of accelerated UV exposure. The significance of these findings is that they provide a comparative basis for selecting metal oxide nanoparticles for improving the UV stability of multicomponent polymer blends. However, the conclusions are limited to the accelerated UV resistance evaluated in the present study, and the proposed stabilization mechanisms should be considered as interpretations rather than directly confirmed mechanisms. Future investigations should further examine the structure-property relationships of these nanocomposites using complementary techniques to evaluate polymer phase behavior and nanoparticle distribution, together with direct mechanistic measurements. Additional studies of mechanical, thermal, optical,

adhesion, barrier, and natural-weathering performance would also be valuable for determining the broader performance and potential application range of the developed films.

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Conflict of Interest

Authors declare that there is no conflict of interests regarding the publication of the paper.

Author Contribution

The authors confirm their contributions to the paper as follows: **study conception and design:** Amani Husain, Emad Yousif; **data collection:** Dina Ahmed, Thura Alyasiri, Shams Ismael; **analysis and interpretation of results:** Mohammed Kadhom, Muna Bufaroosha, Ahmed Ahmed; **draft manuscript preparation:** Amani Husain, Dina Ahmed, Emad Yousif. All authors reviewed the results, contributed to the revision of the manuscript, and approved the final version.

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