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Improving UV Light Protection: Enhancing the Physical Properties of Poly(Vinyl Chloride) through Metal Oxide Nanoparticle Filling

M. Kadhom[1], A. Mohammed[1], H. Hashim[2], R. Yusop[3], H. Mujbil[4], L. Al Jebur[4], E. Yousif[*5]

1. Department of Environmental Science, College of Energy and Environmental Sciences, Al-Karkh University of Science, P.O. Box: 10081, Baghdad, Iraq
2. Department of Physics, College of Science, Al-Nahrain University, P.O. Box: 64021, Baghdad, Iraq
3. School of Chemical Science and Food Technology, Faculty of Science and Technology, University Kebangsaan Malaysia, P.O. Box: 43600 Bangi, Selangor, Malaysia
4. Department of Chemistry, College of Science, Tikrit University, P.O. Box: 34001, Tikrit, Iraq.
5. Department of Chemistry, College of Science, Al-Nahrain University, P.O. Box: 64021, Baghdad, Iraq.

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ABSTRACT

Poly(vinyl chloride) (PVC) finds wide-ranging applications, including protective clothing, pipes, gloves, and tubing. Recent studies have prioritized the enhancement of PVC's performance to meet specific criteria. This study delves into the impact of incorporating metal oxide nanoparticles into PVC films to bolster their UV light protection and chemical stability. Five modified PVC films, each laden with distinct metal oxide nanoparticles, were prepared and juxtaposed against the unaltered PVC film. These films endured 300 hours of UV light exposure and underwent assessment through gel content analysis, scanning electron microscopy (SEM), and UV-Vis spectroscopy. The outcomes divulged that the modified PVC films, especially those embedding Cr_2O_3 nanoparticles, exhibited diminished UV light absorbance and minimal gel content after an overnight immersion in tetrahydrofuran solvent. This attests to an elevated UV protection level and heightened chemical stability when compared to the plain PVC film. Our findings underscore the potential of metal oxide nanoparticle modification in amplifying the attributes of PVC films for demanding applications. Prog. Color Colorants Coat. 17 (2024), 113-119© Institute for Color Science and Technology.

1. Introduction

Poly(vinyl chloride) (PVC) serves as a widely employed polymer in the manufacturing of diverse products, ranging from siding, windows, pipes, and wires to protective clothing. Additionally, it finds extensive usage in medical realms, such as gloves, oxygen tents, tubing for blood transfusions, and bags. PVC boasts a plethora of advantages, encompassing favorable chemical and mechanical properties, crack resistance, non-flammability, ease of shaping, and cost-effectiveness [1, 2]. These remarkable attributes render PVC suitable for outdoor applications, where direct exposure to environmental factors, especially ultraviolet (UV) light, is prevalent. Nonetheless, UV light exposure can trigger color alteration and a reduction in mechanical performance, owing to the generation of double bonds and oxygenated compounds, thereby inducing photo- or oxidative degradation of PVC [3-5].

*Corresponding author: * emad.yousif@nahrainuniv.edu.iq
emad_yousif@hotmail.com
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The identification and quantification of double bonds or carbonyl groups within PVC can be achieved through techniques like UV spectroscopy, ^{1}H-NMR, and ^{13}C-NMR spectroscopy. Dehydrochlorination in PVC gives rise to the creation of allylic structures, thereby introducing double bonds, accompanied by the release of hydrochloric acid. Furthermore, the terminal double bonds present in PVC are susceptible to direct oxidation in the presence of abundant oxygen, resulting in the formation of ketone or aldehyde groups [6]. As a countermeasure, the utilization of PVC incorporated with appropriate stabilization additives is advised to avert degradation. These additives need to exhibit specific attributes, including colorlessness and high efficiency, where even minute quantities can exert a substantial enhancement effect [7].

Recent investigations have centered around the utilization of organotin (IV) complexes as photostabilizers for PVC. Experimental findings underscore their efficacy in safeguarding polymeric films from UV light [8-10]. An array of additional additives has been explored as potential PVC photo-stabilizers, encompassing Schiff bases [11-14], polyphosphates [15-17], and organic-metal complexes [18-20]. The influence of nanoparticles on polymer composition has been scrutinized through optical property spectroscopy and morphology tests. Metal oxide nanoparticles have been harnessed as sacrificial materials to absorb light [21-23]. To bolster the endurance of PVC under arduous weather conditions, polymer modifications have been implemented. In a recent approach, the incorporation of metal oxide nanoparticles (NPs) and captopril was employed to heighten the effectiveness of PVC films [24].

Within this project, an examination was conducted on modified PVC films containing four distinct metal oxide nanoparticles (NPs) [25]. Multiple characterization techniques, encompassing UV-Vis spectroscopy, gel content analysis, and morphology investigation, were employed to assess the films. The outcomes unveiled an enhancement in the attributes of the polymeric films upon the integration of NPs into their structure. Among the diverse metal oxide-infused films, the Cr_2O_3-filled variant demonstrated the most favorable performance.

2. Experimental

2.1. Materials and apparatuses

In this study, PVC films were prepared as detailed in our previous work [25], involving the incorporation of metal oxide nanoparticles (NPs) such as CuO (58.43 nm), Cr_2O_3 (18.51 nm), TiO_2 (48.82 nm), and Co_2O_3 (15.14 nm) [25]. The synthesized films underwent comprehensive characterization to evaluate their properties. The ultraviolet-visible (UV-Vis) absorption spectra of both the unmodified (blank) and modified PVC sheets were acquired using a Shimadzu UV-1601 spectrophotometer subsequent to irradiation. This enabled the assessment of variations in absorption traits due to the presence of metal oxide NPs and exposure to UV light. For the investigation of the modified PVC sheet morphology following UV irradiation, SEM analysis was conducted using a SIGMA 500 VP microscope produced by ZEISS Microscopy (Jena, Germany). This SEM analysis furnished insights into the surface and structural attributes of the modified PVC films.

2.2. Gel content percentages of modified PVC films

To ascertain the gel content percentage of each film across various exposure durations, 0.2 g of each film was dissolved in 8 mL of tetrahydrofuran (THF) at room temperature (RT), and the mixture was allowed to stand overnight to ensure complete dissolution. Following this, the insoluble components, which signify the gel content, were subjected to filtration, subsequent rinsing, and drying within an oven. The gel content percentage was subsequently calculated using the ensuing equation (Eq. 1).

$$\text{Gel content (\%)} = (W_2/ W_1)\times 100 \qquad (1)$$

where W_1 and W_2 present the weight of the original specimen and gel content released in the solution, respectively [26].

2.3. Absorbance of modified PVC films

To monitor the alterations in the modified PVC sheets during irradiation, absorption spectra were captured at a specific wavelength of 313 nm. Employing the first-order kinetic law, the photo-decomposition rate constant (K_d) for the modified PVC films following irradiation can be ascertained using the subsequent equation (Eq. 2) [27].

$$\ln(a - x) = \ln(a) - K_d\times t \qquad (2)$$

where $a = (A_0 - A_\infty)$, and $x = (A_0 - A_t)$

Within this equation, a signifies the initial concentration of stabilizer before irradiation, x represents the change in stabilizer concentration after a specific exposure time (t), A_0 denotes the absorption intensity of the PVC films at the outset of irradiation (t_0), A_∞ stands for the absorption intensity at the conclusion of irradiation (t_∞), and At indicates the absorption intensity at a given irradiation time (t). Through substituting these values into equations 2 and 3 can be derived.

$$ln(A_t - A_\infty) = \ln(A_0 - A_\infty) - K_d t \qquad (3)$$

Plotting the natural logarithm of (A_t - A_∞) against the irradiation time (t) will result in a linear relationship, with the slope of the line corresponding to the K_d value.

3. Results and Discussions

3.1. Gel content measurements

Upon subjecting the modified PVC films to irradiation, the polymeric chains within the PVC undergo cross-linking, resulting in the formation of insoluble fractions when the irradiated films are dissolved in THF over the course of the night. This phenomenon can be attributed to the process of photo-degradation, which transpires when the material is exposed to UV light at 313 nm. At this specific wavelength, the bonds absorb energy and subsequently disintegrate [26-28].

The gel content percentage, as determined by equation 1, was plotted against the irradiation time, as illustrated in Figure 1. Analysis of the gel content outcomes demonstrates that modified PVC films containing NPs exhibit diminished gel content percentages in comparison to the pristine PVC film following 300 hours of irradiation. Notably, the gel content decreased from 73 to 33 % upon the integration of Cr_2O_3 nanoparticles into the unadulterated PVC film. This points to the modification of PVC films augmenting the interlinking of polymer chains, culminating in a reduction of soluble material and a strengthening of the insoluble gel portion. The observed reduction in gel content percentage underscores the efficacy of PVC film modification in fostering intermolecular connections, thereby amplifying the overall structural robustness of the films.

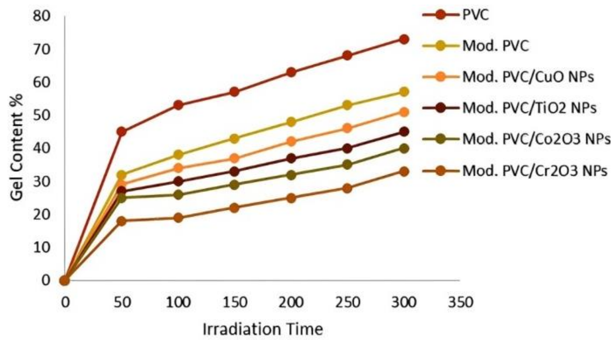

Figure 1: Variation of the gel content of the pure and NPs-filled PVC films.

3.2. UV light absorbance measurements

The exposure of PVC films to UV radiation induces the formation of unsaturated groups and oxidized structures, including carbonyl and polyene groups, which possess the capacity to absorb UV light beyond a wavelength of 220 nm. These chemical transformations contribute to the yellowing phenomenon observed in PVC films [29, 30]. Notably, the incorporation of nanoparticles (NPs) into modified PVC films has demonstrated a resistance to color alteration. To gauge the extent of degradation, the absorbance levels of the films were determined using a UV-Vis spectrophotometer, specifically at a wavelength of 313 nm. Figure 2 visually presents the absorbance values post 300 hours of irradiation. As the films undergo degradation, the absorbance values escalate due to the formation of chromophoric compounds.

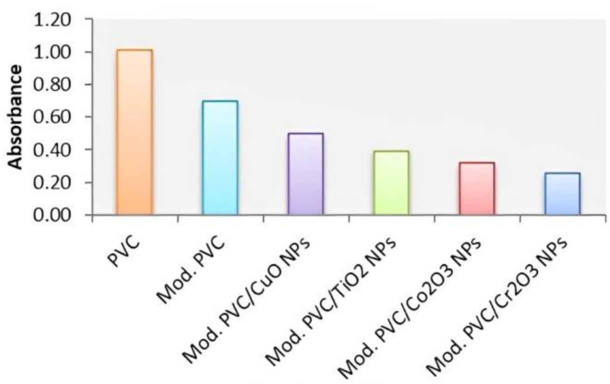

Figure 2: The absorbance of PVC films at 313 nm for 300 h of irradiation.

Further exploration of the photodecomposition of the films involved the computation of the photodecomposition rate constant (k_d). This was achieved by plotting the natural logarithm of (A_t - A_∞) against the irradiation time (t), employing equation 2. The resulting graph demonstrated a linear correlation, indicative of first-order kinetics. The gradient of the line corresponds to the k_d constant. Figures 3 to 8 offer a depiction of the variations in ln(A_t - A_∞) over irradiation time (t) for both additive-infused and unaltered PVC films. Table 1 provides the k_d values for each film. The findings showcase that the modified PVC films manifest lower rate constant values in comparison to the pristine PVC sheet. This indicates that the modification of PVC films with additives yields a reduction in the rate of photodecomposition, suggesting heightened resistance to degradation.

3.3. Surface morphology of PVC films

The analysis of the PVC film topography was conducted using scanning electron microscopy (SEM). Figure 9 presents morphological images of the unmodified PVC sheets before and after a 300-hour irradiation period. Prior to irradiation, the surface of the plain PVC exhibited greater uniformity, smoothness, and freedom from cracks in comparison to the same film post-irradiation [31]. However, after exposure to irradiation, the PVC surface showcased increased roughness and the presence of cracks. These alterations in surface morphology can be attributed to the release of hydrogen chloride resulting from the rupture of bonds within the polymeric chains [32].

Table 1: The values of the rate constant (k_d) of the PVC films.

Film	k_d (h^{-1}) $\times 10^{-4}$
PVC	66.05
Mod. PVC	18.97
Mod. PVC/CuO_2	9.640
Mod. PVC/TiO_2	5.250
Mod. PVC/Co_2O_3	3.240
Mod. PVC/Cr_2O_3	2.900

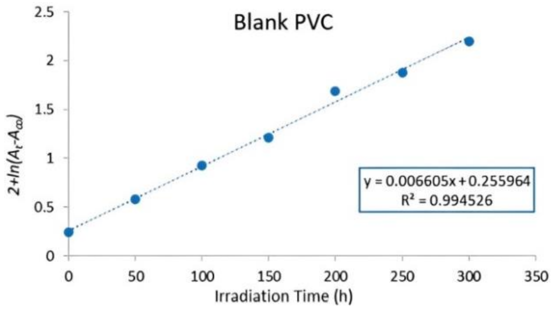

Figure 3: Changes in *ln(A_t−A_∞)* for blank PVC film with irradiation time.

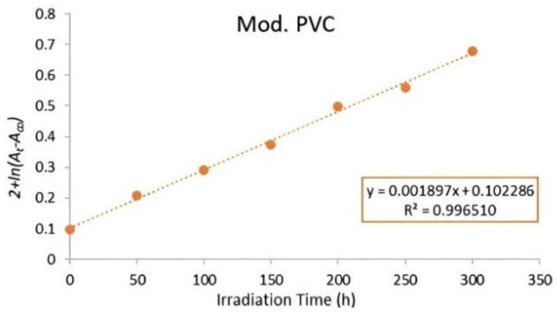

Figure 4: Changes in *ln(A_t−A_∞)* for modified PVC film with irradiation time.

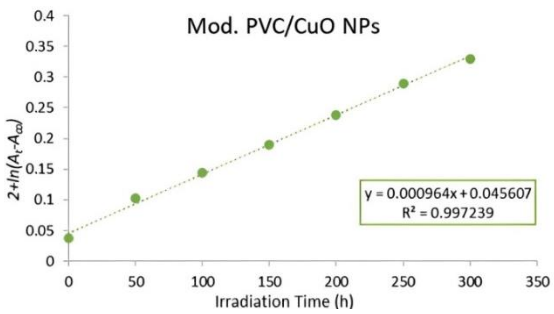

Figure 5: Changes in *ln(A_t−A_∞)* for Mod. PVC film in presence of CuO NPs with irradiation time.

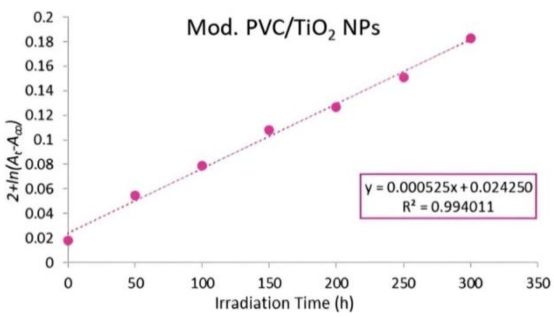

Figure 6: Changes in *ln(A_t−A_∞)* for Mod. PVC film in presence of TiO_2 NPs with irradiation time.

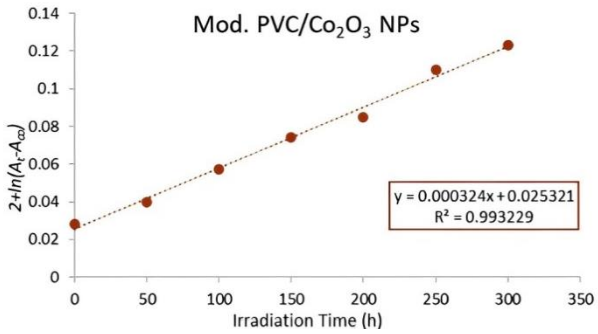

Figure 7: Changes in $ln(A_t{-}A_\infty)$ for Mod. PVC film in presence of Co_2O_3 NPs with irradiation time.

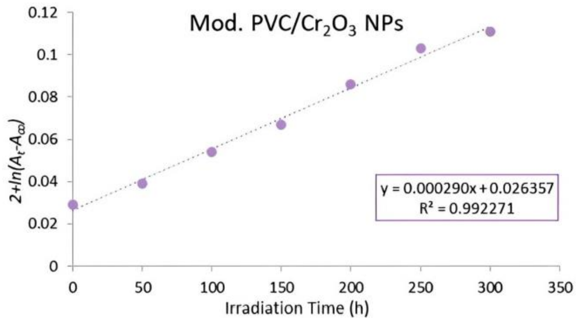

Figure 8: Changes in $ln(A_t{-}A_\infty)$ for Mod. PVC film in presence of Cr_2O_3 NPs with irradiation time.

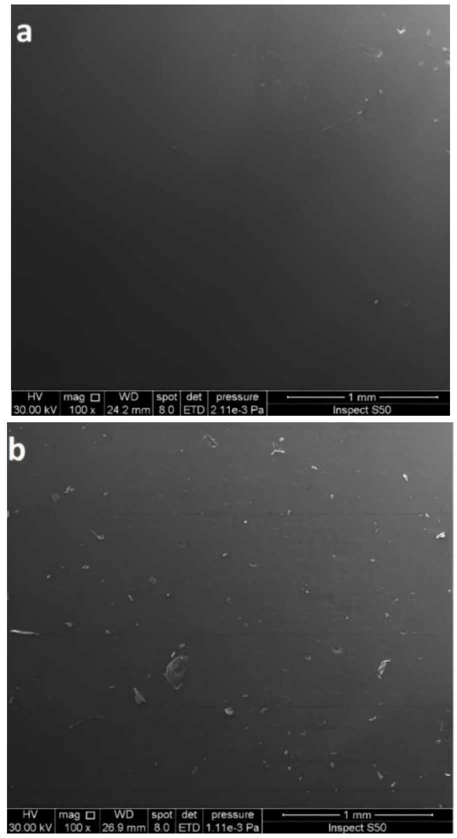

Figure 9: SEM images of the plain PVC film (a) before and (b) after 300 h to UV irradiation.

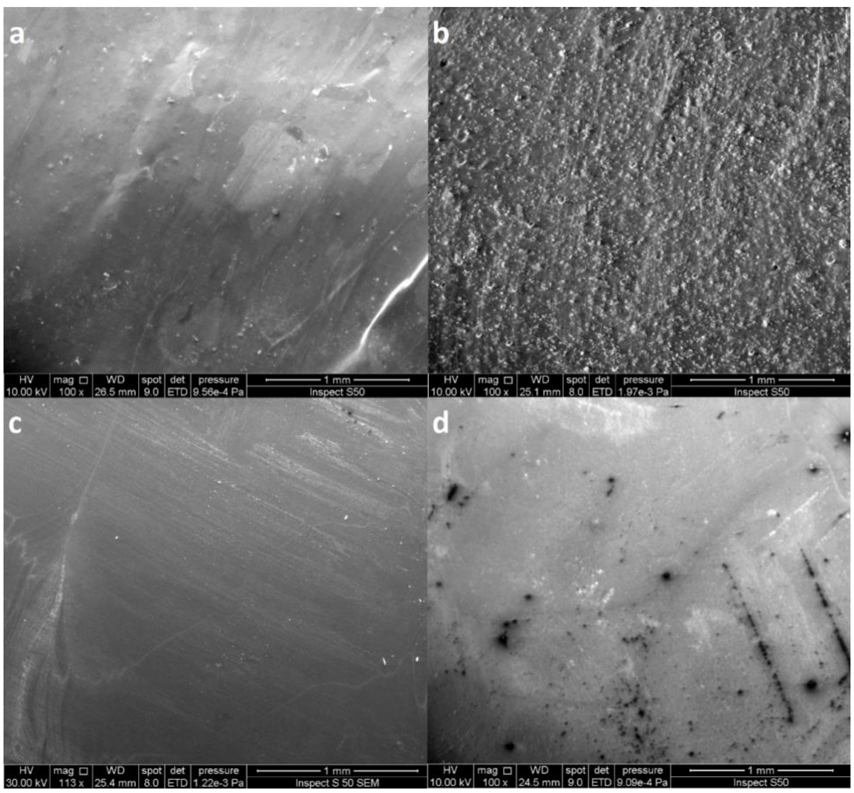

Figure 10: SEM images of filled PVC films with (a) CuO_2, (b) TiO_2, (c) Co_2O_3, and (d) Cr_2O_3 after 300 h UV irradiation.

Moving on to Figure 10, SEM images of PVC films modified with nanoparticles (NPs) are displayed after irradiation. These images imply that the modified PVC films effectively hindered the process of photodegradation. The incorporation of NPs into the modified films contributed to the retention of surface morphology and a reduction in crack formation. This observation indicates an improved resistance to photo-degradation achieved through the presence of NPs in the modified films.

4. Conclusions

In this study, PVC films, encompassing both formulations with and without the introduction of metal oxide nanoparticles (PVC, PVC/CuO_2, PVC/TiO_2, PVC/Co_2O_3, and PVC/Cr_2O_3), underwent thorough examination, effectively showcasing the potency of nanoparticle incorporation in enhancing resistance against UV light. The films were subjected to irradiation at a wavelength of 313 nm for a duration of 300 hours under ambient temperature conditions. The comprehensive assessment involving gel content, absorbance measurements, and SEM analysis yielded outcomes that unmistakably pointed to the PVC/Cr_2O_3 film as the most efficacious in curbing photo-degradation.

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