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ORIGINAL PAPER

Monitoring physicochemical properties of transparent PVC films containing captopril and metal oxide nanoparticles to assess UV blocking

Taiseer A. Saleh[1] · **Emaad T. B. Al-Tikrity**[1] · **Dina S. Ahmed**[2] · **Gamal A. El-Hiti**[3] ·
Benson M. Kariuki[4] · **Anaheed A. Yaseen**[1] · **Ahmed Ahmed**[5] · **Emad Yousif**[6]

Abstract

Various polyvinyl chloride thin films containing captopril and several metal (cobalt, copper, and nickel) oxide nanoparticles were produced. Low concentrations of both captopril (0.5% by weight) and metal oxides (0.01% by weight) were used to produce transparent films. The role played by both captopril and metal oxide nanoparticles as ultraviolet blockers for pho-todegradation of polyvinyl chloride was investigated. The addition of both metal oxides and captopril to polyvinyl chloride films enhances the stability of polymeric materials more than captopril alone. Observation of weight loss, changes in infrared spectra and surface morphology of blends on irradiation showed that a combination of captopril and nickel oxide nanopar-ticles efficiently blocks ultraviolet light and provides a high level of protection to polyvinyl chloride.

Keywords Polyvinyl chloride · Metal oxide nanoparticles · Ultraviolet irradiation · Weight loss · Roughness factor · Surface morphology

Introduction

Plastics are versatile materials that are widely accessible and utilized in many applications. They are cheap to produce, strong, durable, can be molded in different shapes, and can be colored to be used for different purposes [1, 2]. Plastic is an excellent replacement for construction materials such as wood which is expensive, metals that are heavy and easily corroded, and ceramics and glass which are easily break-able and costly. Polyvinyl chloride (PVC) is an adaptable thermoplastic with a wide range of uses. PVC has many advantageous properties, including resistance to weathering, electrical insulation, flame retardance, durability, thermal and acoustic isolation, low maintenance cost, and excel-lent aesthetic qualities [3]. It is used in the production of construction materials, electronics, medical products, automobile components, plastic cards, sports materials, office equipment, clothing, and packaging [4]. Due to its excel-lent properties, there is high demand for PVC and it is pro-duced on an industrial scale to meet a global requirement that increases year on year. The majority of PVC is used in the manufacture of tubes, cables, threads, and connections.

Although PVC has many advantages with different applications, its high chlorine content is a problem since it leads to environmentally hazardous waste. In addition, undesirable physical and chemical changes take place in the PVC on exposure to high temperature and ultraviolet (UV) light with oxygen present in a humid environment leading to weathering [5, 6]. The low thermal and photochemical stability of PVC promotes dehydrochlorination. The release of hydrochloric acid (HCl) forms polyenes and residues containing other functional groups (e.g., hydroxy and carbonyl) [7, 8].

✉\ Gamal A. El-Hiti
\ gelhiti@ksu.edu.sa

[1]\ Department of Chemistry, College of Science, Tikrit University, Tikrit 34001, Iraq
[2]\ Department of Medical Instrumentation Engineering, Al-Mansour University College, Baghdad 64021, Iraq
[3]\ Department of Optometry, College of Applied Medical Sciences, King Saud University, Riyadh 11433, Saudi Arabia
[4]\ School of Chemistry, Cardiff University, Main Building, Park Place, Cardiff CF10 3AT, UK
[5]\ Polymer Research Unit, College of Science, Al-Mustansiriyah University, Baghdad 10052, Iraq
[6]\ Department of Chemistry, College of Science, Al-Nahrain University, Baghdad 64021, Iraq

The released HCl, other chlorinated organics, and toxic volatiles result in the corrosion of treatment systems during pyrolysis of PVC [9–11]. The dehydrochlorination process starts at thermally labile defect sites in polymeric materi-als. High levels of both HCl and polyene residues initiate the formation of polyenyl cation radicals bringing about an autocatalytic degradation process [12, 13]. The dehydrochlorination process causes discoloration of the PVC as well as deterioration of mechanical and physical properties. Oxidative reactions take place, in the presence of oxygen, leading to the cleavage of the chains and formation of small frag-ments which degrades the properties of the material [14–16].

UV radiation represents a very small proportion of sunlight but is the major cause of photodegradation of PVC and other polymeric materials. Photodegradation is irreversible and leads to permanent changes in the properties and performance of the polymeric materials [17]. Improving the resistance of PVC to sunlight and reducing its photodegradation, therefore, is vital for extending the useful lifetime of the polymeric material. Stabilizers are commonly mixed with polymers to offer adequate protection from light, par-ticularly UV irradiation [18 , 19]. The most commonly used PVC additives are phenolic and nonphenolic UV absorbers, phenolic antioxidants, plasticizers, metal chelates, pigments, and hindered amines [15, 20–22]. However, the health and safety risks associated with many conventional UV stabilizers need to be taken into consideration and hence the need to design and use new PVC stabilizers [23].

Various organometallics including captopril tin com-plexes have been synthesized in our investigation and their potential use as photostabilizers for polymeric materials investigated [24–33]. In the current work, captopril (Fig. 1) has been tested as a PVC photostabilizer. A number of metal oxide nanoparticles (NPs) were also used along with cap-topril to investigate their effect on the photodegradation of PVC. The proposed additives do not require a synthetic step since they are a mix of captopril and NPs.

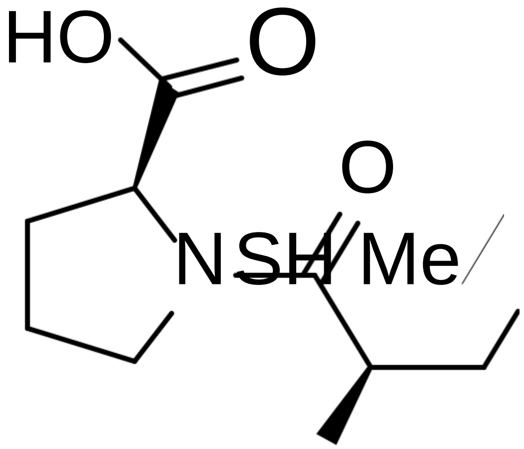

Fig. 1 Structure of captopril (ligand; L)

Experimental

General

Captopril (98%), metal oxides nanoparticles (98–00%), and solvents were obtained from Merck (Gillingham, UK). The diameters of Co_3O_4, CuO, and NiO NPs were found to be 15, 56, and 31 nm, respectively [34]. PVC, with a polymerization degree of about 800 and average molecular weight of about 233,000 and was sourced from Petkim Petrokimya (Istanbul, Turkey). FTIR data were recorded on a FTIR 8400 Shimadzu spectrophotometer (Shimadzu, Tokyo, Japan). Irradiation of the PVC films was at 25 °C using an accelerated weather-meter QUV tester (Q-Panel Company; Homestead, FL, USA). A Meiji Techno microscope (Tokyo, Japan) was used to record the optical images of the sample surfaces. An accelerating voltage of 15 kV at 25 °C was used to obtain the scanning electron microscopy (SEM) images on a SIGMA 500 VP microscope (ZEISS Microscopy, Jena, Germany). The atomic force microscopy (AFM) images were acquired on a Veeco instrument (Plainview, NY, USA).

Fabrication of films

PVC films were fabricated using the solvent-casting method. A mixture of PVC (5 g), captopril (25 mg), and metal oxide nanoparticles (Co, Cu, and Ni oxides; 0.5 mg) in tetrahydrofuran (THF; 100 mL) was stirred for 1 h. The mixture was then sonicated for 30 min to remove any air bubbles and poured into a glass tray and the solvent allowed to evaporate at 25 °C for a day. The films were peeled off from the tray and kept at 25 °C in a vacuum oven for 6 h.

PVC exposure to UV light

The PVC films were exposed to UV light with an intensity of 6.0×10^{-9} ein.dm^{-3}.S^{-1} at a λ_{max} of 313 nm for 50–300. The films were occasionally turned to ensure that the samples were exposed evenly to UV light.

Results and discussion

FTIR spectroscopy monitoring of photodegradation

Several thin films (ca. 40 μm) of pure PVC and those containing captopril (0.5% Wt%), and captopril and metal oxide

NPs (Co_3O_4, CuO, and NiO; 0.01 wt%) were used. The low concentration of the captopril was based on our previous work [24–33]. In addition, the low concentration (0.01 wt%) of metal oxide NPs did not cause a change in the color of the PVC. The films were irradiated with UV light and FTIR spectroscopy was used to monitor the effect of the additives on the photostability of PVC. Photooxidation leads to the formation of ketone, polyene, and alcohol-containing small fragments when PVC is irradiated in the presence of oxygen [35, 36]. Therefore, the increase in the intensity of peaks corresponding to C = C (alkenes; 1605 cm-$^{-1}$) and C = O (ketones; 1725 cm-$^{-1}$) was monitored for PVC films irradiated for different periods. The changes in the intensities of the peaks were compared with that of a standard or a reference peak -(CH_2; 1330 cm^{-1}) [37]. Figure 2 shows the increase in the intensity of the peaks corresponding to the C = C and C = O groups in the FTIR spectrum of pure PVC on irradiation.

Equation (1) was used to calculate the functional group index (I_s) for both C = O and C = C. The absorbances for C = O and C = C (A_s) and for -CH_2 (A_r) were used to calculate I_s. $I_{C=O}$ and $I_{C=C}$ were calculated for different irradiation times in the 50 to 300 h range and the results are shown in Figs. 3 and 4, respectively.

$$I_S = A_S/A_r \tag{1}$$

It is clear that both $I_{C=O}$ and $I_{C=C}$ are much higher for the unblended PVC films. All the additives used led to lower $I_{C=O}$ and $I_{C=C}$ values demonstrating their abilities to decrease the photodegradation of PVC. The use of captopril without metal oxide NPs also lead to some improvement in

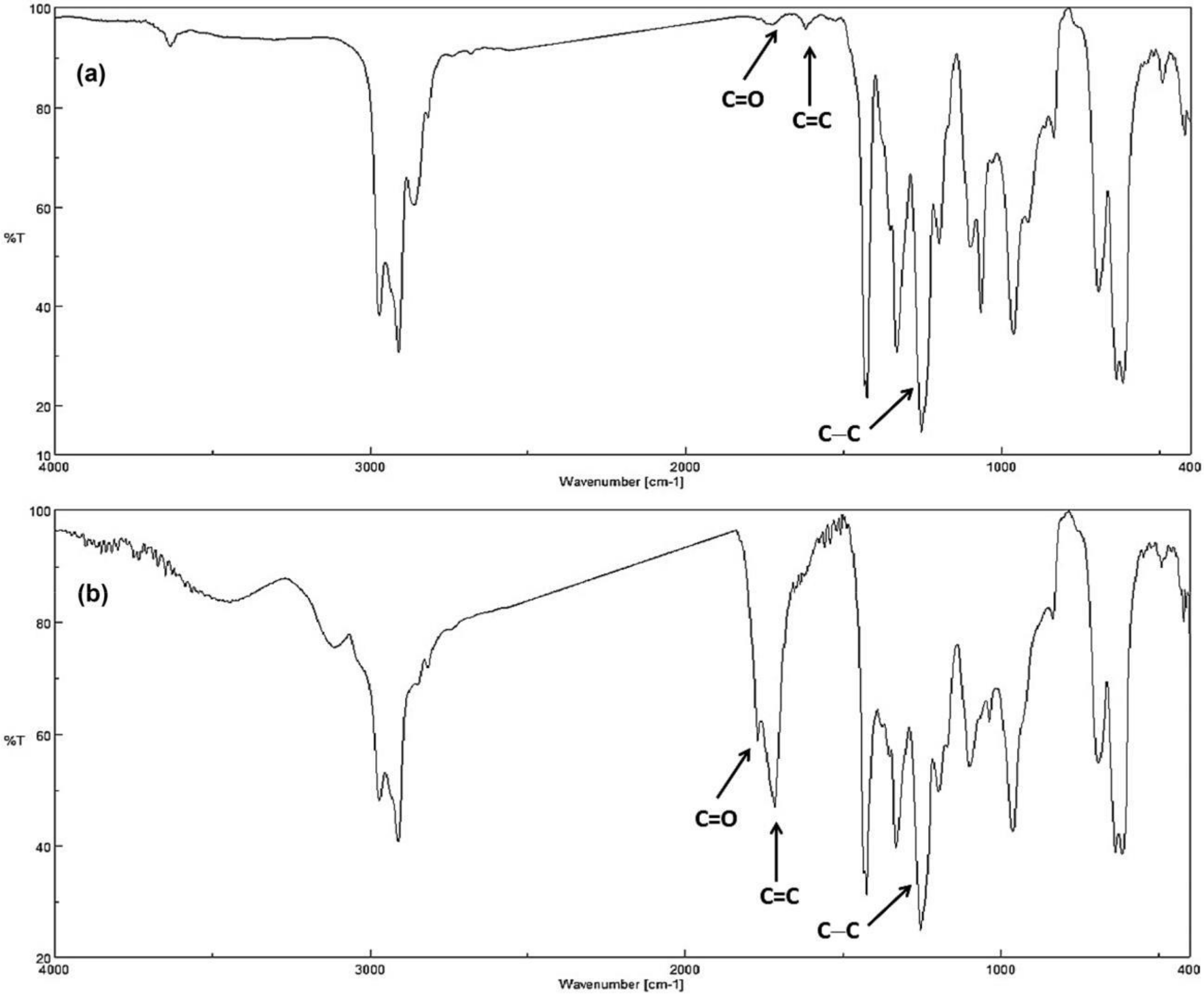

Fig. 2 FTIR spectra of pure PVC film **a**: before irradiation and **b**: after 300 h of UV irradiation

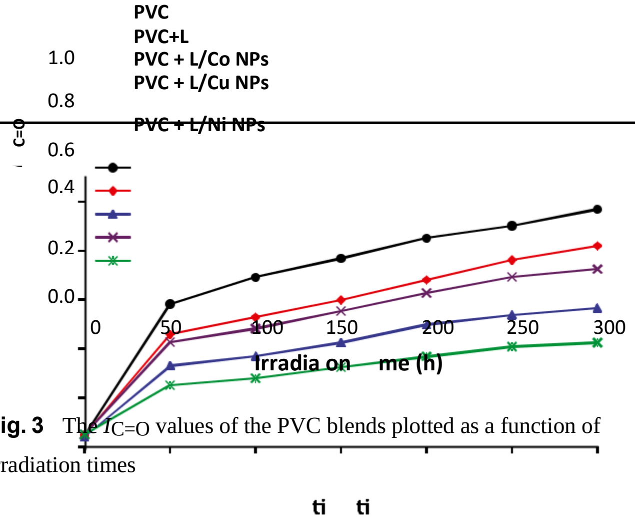

Fig. 3 The $I_{C=O}$ values of the PVC blends plotted as a function of irradiation times

the photostability of PVC but the use of a combination of captopril and metal oxide NPs was more efficient. The PVC films containing captopril and nickel oxide NPs showed the lowest $I_{C=O}$ and $I_{C=C}$ followed by the ones including cobalt and copper oxides. For example, the $I_{C=O}$ at the end of the irradiation process was 0.97, 0.82, 0.57, 0.72, and 0.43 for the films containing PVC, PVC/L, PVC/L/Co oxide, PVC/L/Cu oxide, and PVC/L/Ni oxide, respectively. Similarly, after 300 h of irradiation, the $I_{C=C}$ was 0.83, 0.68, 0.53, 0.60, and 0.42 for the blends containing PVC, PVC/L, PVC/L/Co oxide, PVC/L/Cu oxide, and PVC/L/Ni oxide, respectively.

Weight loss on UV irradiation

Oxidative degradation of PVC is associated with weight loss because of the elimination of hydrogen chloride (HCl) through a process of dehydrochlorination. This process leads to bond cleavage and cross-linking with the formation of polymeric fragments of small molecular weight [8]. As the degree of dehydrochlorination is proportional to the duration of irradiation, the weight loss is expected to increase with irradiation time. For pure PVC and blends irradiated for different durations, the weight loss (%) was calculated from the weight of films taken before (W_0) and after (W_1) irradiation using Eq. (2) [7]. The weight losses (%) at different irradiation times are shown in Fig. 5.

$$\text{Weight loss}(\%) = \frac{W_0 - W_1}{W_0} \times 100 \tag{2}$$

Generally, the weight loss increased with irradiation time. All the additives led to a reduction in weight loss in comparison with the pure PVC film. The reduction in PVC photodegradation is greatest for the blends containing metal oxide NPs. The weight loss was highest for the pure PVC film and lowest for the blend containing nickel oxide NPs. For example, the weight loss (%) after 300 h of irradiation was 0.43, 0.34, 0.25, 0.29, and 0.13% for PVC, PVC/L, PVC/L/Co oxide, PVC/L/Cu oxide, and PVC/L/Ni oxide films, respectively.

Morphology study on UV irradiation

After UV irradiation, inspection of the surface of the film using an optical microscope provides valuable information about irregularities, cracks, dark spots, and chain-scission [38]. The damage in the surface of the irradiated PVC film is mainly due to dehydrochlorination [39]. The surface of the non-irradiated pure PVC is usually homogenous, smooth and does not contain spots or cracks whereas the irradiated surface shows cracks, spots, and irregularities [40]. The microscopy images (400 × magnification) of pure PVC film as well as the irradiated (300 h) PVC blended with either captopril or captopril along with appropriate metal oxide NPs are shown in Fig. 6. The surface of the pure PVC film was more seriously damaged on irradiation, as shown by the appearance of cracks, holes, dark spots and irregularities, compared with the film containing additives.

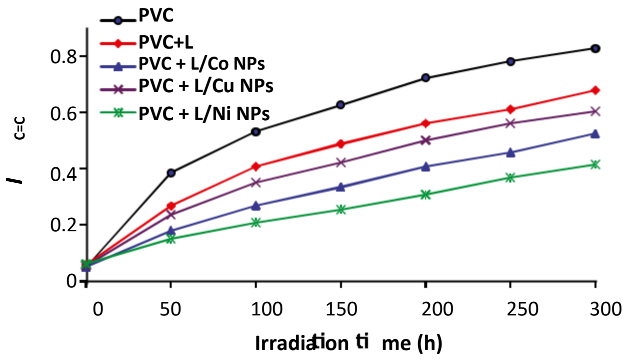

Fig. 4 The $I_{C=C}$ values of the PVC blends plotted as a function of irradiation times

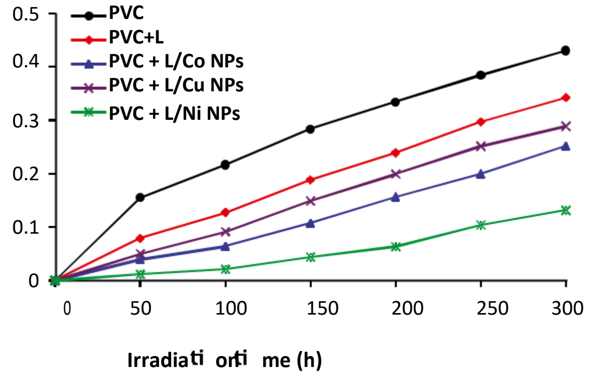

Fig. 5 The weight losses (%) of pure PVC and blends as a function of irradiation times

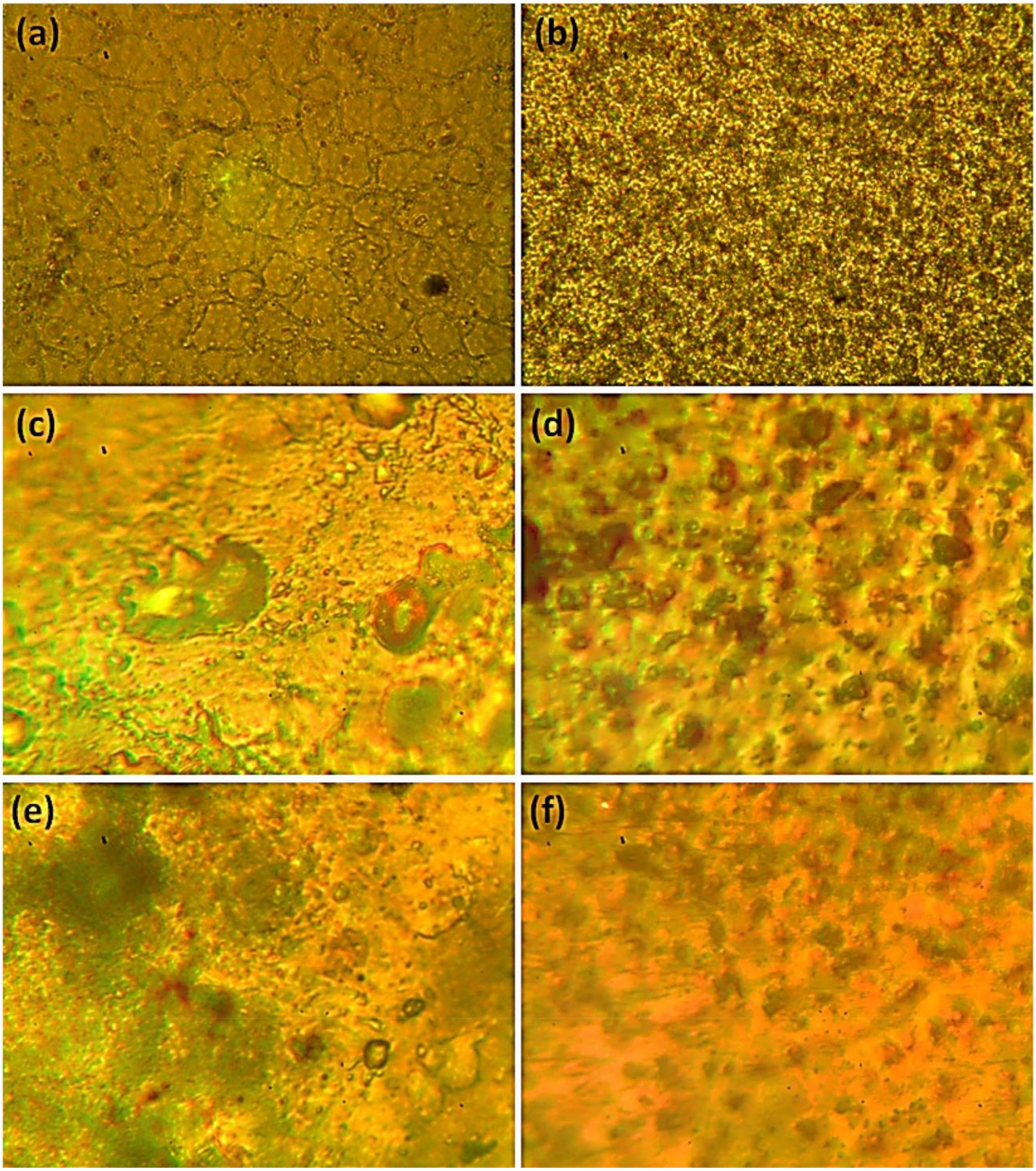

Fig. 6 Microscopy images of **a**: non-irradiated pure PVC film, **b**: UV irradiated (300 h) pure PVC film, **c**: irradiated PVC film containing captopril, **d**: irradiated PVC film containing captopril and Co oxide NPs, **e**: irradiated PVC film containing captopril and Cu oxide NPs, and **f**: irradiated PVC film containing captopril and Ni oxide NPs

The damage was also investigated using the SEM. The SEM technique provides clear images that show the presence of white spots and grooves and contain information about homogeneity of the surface, and particles size and shape [41]. The SEM images (Fig. 7) of the irradiated PVC con-taining additives showed irregularities in the surface, lumps,

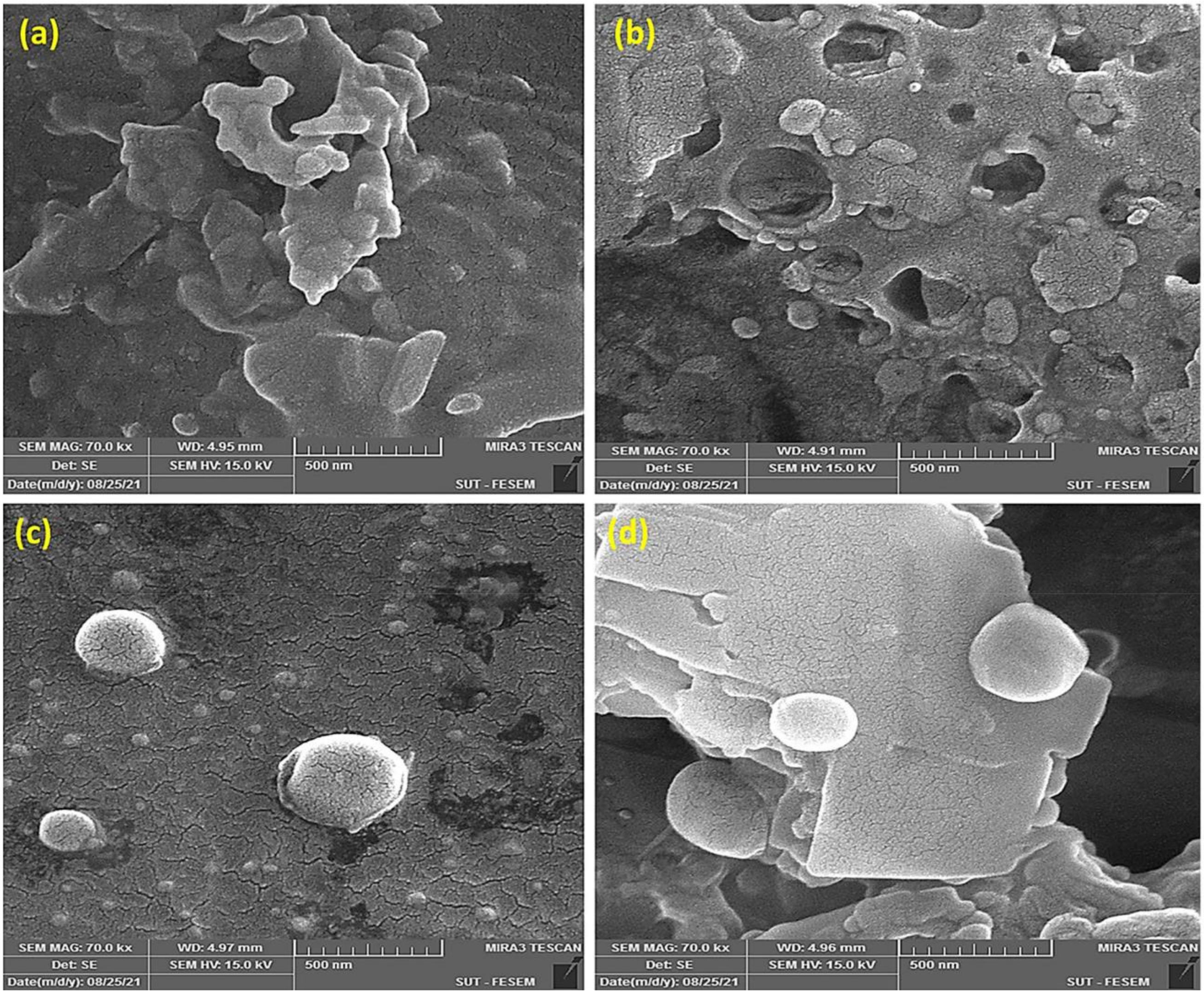

Fig. 7 SEM images (70 k × magnification) of PVC blends containing **a**: captopril, **b**: captopril/Co oxide NPs **c**: captopril/Cu oxide NPs, and **d**: captopril/Ni oxide NPs blends after UV irradiation

white spots, and grooves resulting from photodegradation. The size (30–282 nm) and the shape of particles varied with the type of additive used. The SEM images revealed the presence of irregular quasi-spherical nanoparticles. Additionally, it was observed that the metal oxides formed aggregates of several nanoparticles. The SEM images of the irradiated PVC films containing captopril and Ni oxide NPs at a lower magnification power are shown in Fig. 8.

Another invaluable technique in the investigation of polymer surfaces is AFM [42]. Figure 9 shows the two and three-dimensional AFM images for PVC films after irradiation. The degree of the roughness and number of dark spots on the surface of the film was found to depend on the type of additive used. It has been reported that irradiated pure PVC film exhibits a high degree of roughness, irregularities, and dark spots compared with films containing additives [43]. The roughness factor (*Rq*) for the pure PVC film after irradiation was 238.0 which is very high when compared with values for blends containing additives. The *Rq* for the irradiated PVC blends containing, captopril, captopril/Co NPS, captopril/ Cu NPs, and captopril/Ni NPs were 46.2, 26.2, 31.5, and 23. 2, respectively. The use of captopril and Ni oxide NPs led to a reduction in the roughness factor by 10.3- fold. The reduction in the *Rq* for PVC films containing other additives is summarized in Table 1.

The additives used in this study provided more protection for the PVC than the organotin complexes containing captopril [27]. For example, the additive containing captopril and Ni oxide NPs improved the *Rq* by 10.3-fold compared with sevenfold for the diphenyl tin-captopril complex [27]. In addition, the diphenyl tin-captopril complex requires synthetic and purification steps. Clearly, the

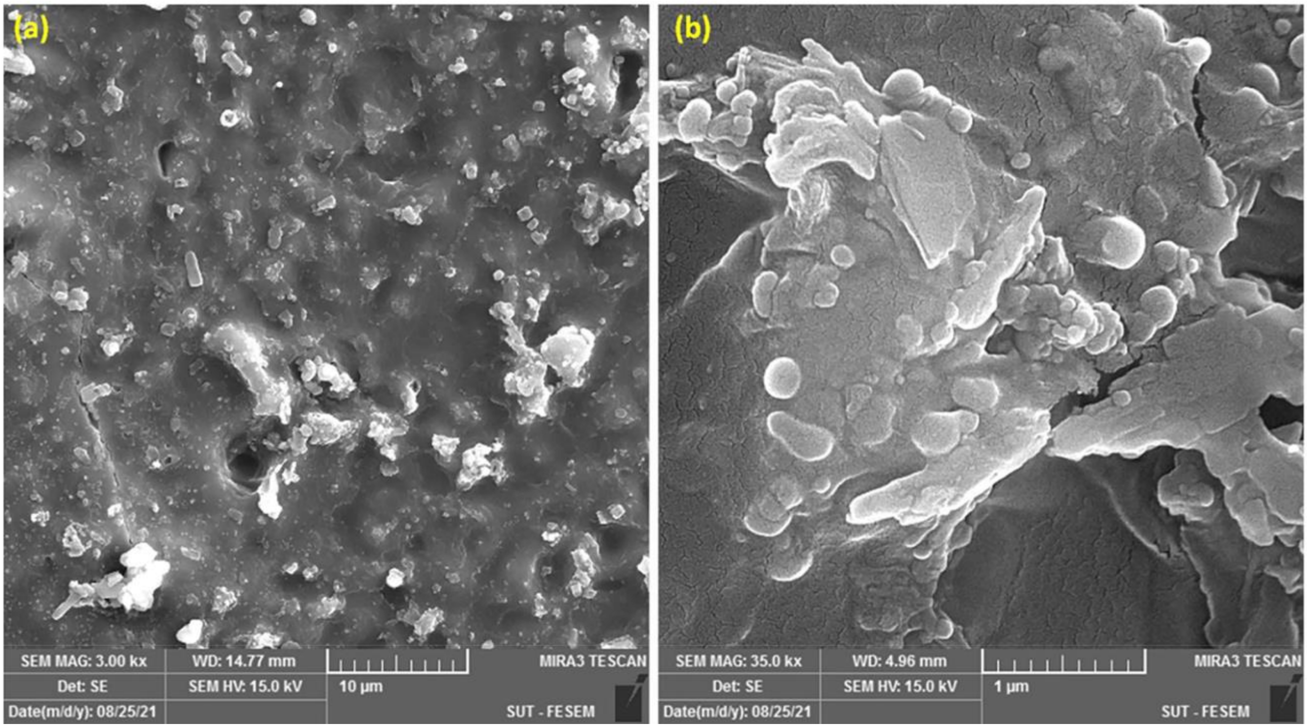

Fig. 8 SEM images of UV irradiated PVC film containing captopril and Ni oxide NPs at **a**: 3 k× magnification and **b**: 35 k × magnification

use of a combination of captopril and metal oxide NPs has advantages over their organotin counterparts. The additive containing Ni oxide NPs showed better performance in stabilizing PVC compared with many tin complexes [24–29]. Conversely, the tin complexes containing trimethoprim [30], ciprofloxacin [31], benzenesulfonamide [32], and 4-methoxybenzoic acid [33] were more efficient in stabilizing PVC than the blends containing metal oxide NPs. However, it

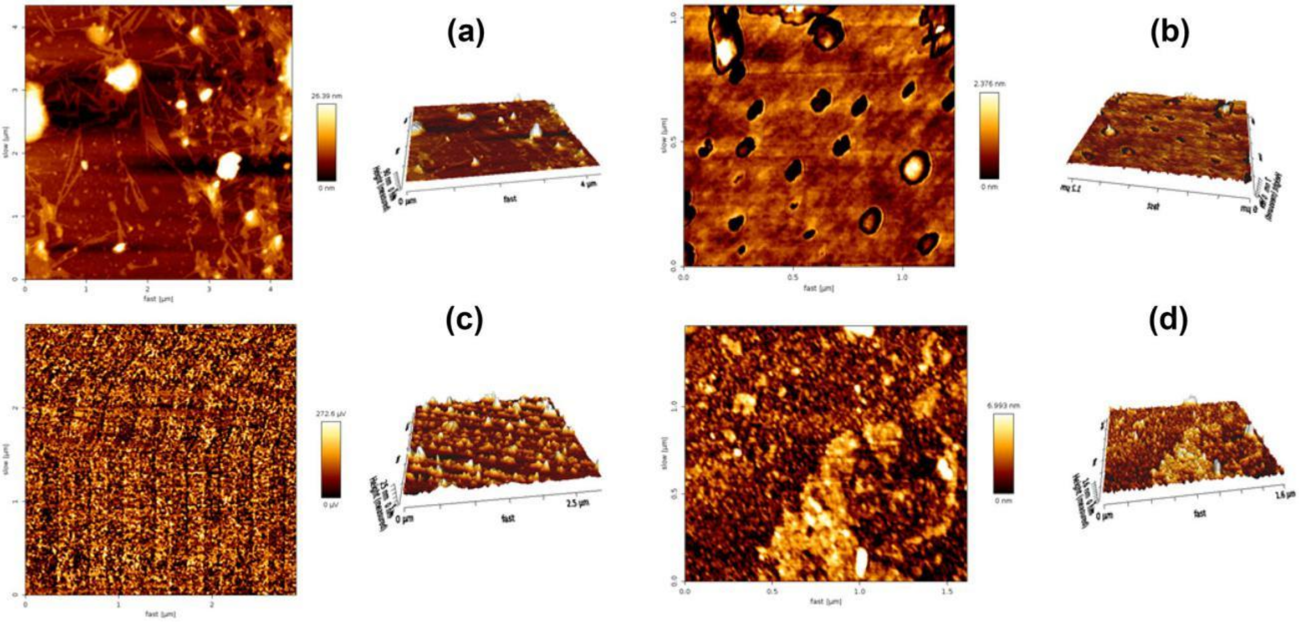

Fig. 9 AFM images of PVC blends containing **a**: captopril, **b**: captopril/Co oxide NPs **c**: captopril/Cu oxide NPs, and **d**: captopril/Ni oxide NPs blends after irradiation

Table 1 The effect of various additives containing metals on the reduction of *Rq* (by fold) for PVC

Additive	*Rq* reduction (Fold)	Reference
Captopril and metal oxide NPs	5.2–10.3	[current work]
Sn-naproxen complexes	3.5–5.2	[24]
Sn-carvedilol complexes	1.7–6.4	[25]
Triphenyl Sn-furosemide complex	6.6	[26]
Triphenyl Sn-captopril complex	7.0	[27]
Sn-valsartan complexes	4.0–7.4	[28]
Sn-telmisartan complexes	2.2–9.4	[29]
Sn-trimethoprim complexes	5.8–11.3	[30]
Dimethyl Sn-ciprofloxacin complex	16.6	[31]
Sn-4-(benzylideneamino)benzenesulfonamide complexes	7.8–18.4	[32]
Sn-4-methoxybenzoic acid complexes	11.8–21.2	[33]

should be noted that the metal oxide NPs have been used in very low concentration (0.01%) compared with the tin complexes (0.5%).

Both captopril and metal oxide NPs led to the stabilization of PVC blends on irradiation with UV light. The metals act as acidic sites and can scavenge the HCl released during PVC photodegradation with formation of metal chlorides [13]. The metals could also act as hydrogen peroxide and hydroperoxides decomposers and therefore reduce the photooxidation rate of PVC [44]. In addition, the metals and heteroatoms (O and S) within captopril can coordinate with the electronegative centers of the polarized C–Cl bonds in the PVC chains [45]. Moreover, captopril is aromatic and is capable of stabilizing the PVC chains through the direct absorption of the energy of UV irradiation [46, 47]. It is not clear why Ni oxide NPs were more efficient compared with the other additives in stabilizing PVC films and it is difficult to speculate without further experimental work. The use of NPs can improve the physical and mechanical properties of PVC. Recently, attention has been paid to the use of NPS in several industrial applications including the production of polymers [48].

Conclusions

Thin films of polyvinyl chloride containing captopril and metal oxide nanoparticles were made to test the effect of these additives on the photostability of polyvinyl chloride. The additives were used in very low concentration to pro-duce homogenous, non-colored, and transparent polymeric films. The use of a combination of metal oxide nanoparticles and captopril was found to be more efficient in reducing the damages caused by irradiation compared with the use of cap-topril alone or in the case where no additive was used. The undesirable changes in the weight, infrared spectra, and the surface of the irradiated films were much less in the presence of captopril and nickel oxide nanoparticles. The additives used are better PVC photostabilizers than the tin complexes of captopril with the additional advantage that no synthetic and purification steps were required.

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Declarations

Conflict of interest The authors have no conflict of interest to declare.

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