

ANTI-CANCER SCHIFF BASES AS PHOTOSTABILIZER FOR POLY(VINYL CHLORIDE)

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ABSTRACT. To prevent or reduce the drawback effect and prolong the life of PVC and preserve its composition and efficiency, compounds are incorporated with PVC. In this work, three highly aromatic anti-cancer Schiff base compounds in symbol (C2, C3 and C5) were applied to photostabilize of PVC against photodegradation, by added it to the polymer in the form of Schiff bases, to increase the stability of polymer when irradiated with ultraviolet (UV) light, ($\lambda_{max} = 365$ nm) at 30 °C, with the intensity of the light wavelength at 1920 lux for a long duration. The PVC was blended with Schiff's base in concentration (0.5 %wt.), with thickness films (40 μ m) were made from the blended materials. Several methods were used, including infrared spectroscopy, surface examination of irradiated films to know the effect of additives on PVC photostabilization and conductivity of films were measured by LCR meter. The results showed that the additives significantly reduced the photodegradation of PVC. C2 compound as additive, stabilize PVC more than other additives, it can absorb harmful radiation, deactivate hydrogen chloride, and scavenge high-energy species such as peroxides. Several mechanisms of photostabilization for C2 compound have been suggested. Therefore it is acting as stabilizers for PVC.

KEY WORDS: PVC, Photostabilizer, UV radiation, AFM, FESEM, LCR-meter

INTRODUCTION

The uses of plastic has increased dramatically due to its numerous applications [1]. Poly(vinyl chloride) PVC is widely used because it has desirable properties including low production cost, can be manufactured in many shapes, acid and alkali resistant and flame retardant. It is used in many areas, including construction, floors, cables, pipes, window frames, children toys and other applications [2-4]. Among the disadvantages of PVC is its weakness to weather factors such as sunlight and high temperature, which leads to a change in the polymeric chain, this change negatively effects on the physical and chemical properties of the polymer, called photodegradation [5]. The photodegradation of the polymer results reactive species such as peroxides, hydrogen chloride, and free radicals that self-catalyze degradation of polymer, it begins breaking the carbon-carbon bonds, results in chain scission and the formation of double bonds (polyene groups) and PVC chains containing aldehyde and ketone groups (carbonyl group C=O) [6]. This leads to a change in the color of polymer from white to yellow, cracking and weight loss, due to the elimination parts of polymeric chain and volatilization of fragments of it [7, 8]. The implying of additives with PVC during manufacture prolong the useful life of polymer [9-11]. PVC additives must be compatible with the polymer, non-volatile, cheap, stable, available, effective, prevent the formation of HCl and compete with PVC to absorb UV rays that cause photodegradation, and convert them into energy away from the surface of PVC, this will keep the color of PVC from changing over time, to prevent the formation of polyene in the polymeric chain [12]. It was found that additives containing nanomaterial (e.g., TiO₂), and metals (e.g., Zn), acted as plasticizers for the polymer and absorb HCl, but some of them are toxic and dangerous to human life and environment, so they should not be used [13-16]. Therefore, more attention has been paid to the design and compatibility of additives with the polymer and the environment. Examples, highly aromatic polyphosphates, Schiff bases and heterocyclic that can act as

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successful PVC photostabilizers [17-20]. In the present work, the photostabilization of PVC was done by using environmentally safe Schiff bases, In addition to be these compounds are anti-cancer. These additives stabilizes PVC by several mechanisms, such as primary stabilizer, UV absorption and radical scavenger [21-23]. In this research, three compounds [C2, C3 and C5] have been synthesized by the method previously described by Dhuha and Wassan [24] and their uses as a photostabilizers for poly(vinyl chloride).

The effectiveness of these compounds as photostabilizer has been proven by several techniques, including: FTIR, UV-Visible spectroscopy, AFM and FESEM. In addition, a new technique was used for the first time, which is by measuring the conductivity of polymeric films by LCR meter, where the measurement proved that when the photodegradation of PVC films increased the conductivity also increased, due to the formation of polyene, hydroxy and carbonyl groups.

EXPERIMENTAL

Poly(vinyl chloride) (BDH) and tetra hydrofuran were from Merck. The compounds that used as photostabilizer were synthesized and characterize by the method previously described by Dhuha and Wassan [24] (Table 1).

Table 1. Symbols, name, and structures of the synthesized compounds.

Symbol compound	Structural formula of compound	Name of compound
C2		3-((3-acetylphenyl)imino)-2-(1,1-dimethyl-1,3-dihydro-2H-benzo[e]indol-2-ylidene)propanal
C3		2-(1,1-dimethyl-1,3-dihydro-2H-benzo[e]indol-2-ylidene)-3-((3-(3-(4-(dimethylamino)phenyl)acryloyl)phenyl)imino)propanal
C5		2-(1,1-dimethyl-1,3-dihydro-2H-benzo[e]indol-2-ylidene)-3-((3-(3-(4-hydroxyphenyl)acryloyl)phenyl)imino)propanal

Method of preparation films

Exactly 3 g of PVC was fully dissolved in 100 mL THF to prepare a solution 3% PVC. 0.0037 g of Schiff base as additive was added to 25 mL of 3% PVC in volumetric flask to prepare a

concentration of 0.5% wt. to make a compatible mixture, and then placed in an ultrasonic mixer for 30 min until completely dissolved, the mixture was poured in glass molds and leave it 48 h to dry at 25 °C to prepare the films. After drying of the films, and the solvent is completely evaporated, the films were remove from the molds and pasted on papers that have a dimensional 3×3 cm [25]. The films of PVC were prepared with thickness (40 μm), calculated by a digital micrometer, type (2610, Germany).

Accelerated testing technique

The PVC films were irradiated for 120 h by a quicker weather-meter (QUV) containing two lamps (18-watt), with a wavelength 365 nm, and the intensity of the light wavelength at 1920 lux. The distance between the PVC films and the light source was 10 cm [26, 27].

Measurement of photodegradation methods

The photodegradation of the PVC films were measured by several techniques including FT-IR spectrophotometer, in the range of 400-4000 cm⁻¹. This technique was used to track the photodegradation of films (pure PVC and PVC with additives) at different irradiation times, by measuring the carbonyl indexes (I_{CO}) of band that increase with irradiation time at 1724 cm⁻¹ and compared it with the reference band at 1427 cm⁻¹. This method called band index method as explained in equation 1:

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

where A_s = absorbance band of sample at 1724 cm⁻¹, A_r = absorbance band of reference at 1427 cm⁻¹, I_s = carbonyl index. The wavenumber of the carbonyl band of PVC is converted to the absorbance (A) by the equation 2

$$A = 2 - \log \%T \quad (2)$$

%T = the transmittance percentage. The real absorbance is calculate through (A top band - base line) [28].

Determination of viscosity average molecular weight (\bar{M}_v)

The (\bar{M}_v) gives information about approximate molecular weight of the polymer, which is calculated through equation 3:

$$[\eta] = K (\bar{M}_v)^\alpha \quad (3)$$

where K and α are constant quantities for PVC at temperature and solvent system. The solvent was THF at 30 °C (K = 0.00015 and α = 0.77). Intrinsic viscosity [η] was determine using the U-tube Ostwald viscometer, which lets reading the times of flowing of PVC solution (t) and the THF solvent (t₀). The viscosities below were calculated by the following equations [29]

$$\text{Relative viscosity } \eta_{rel} = t/t_0 \quad (4)$$

$$\text{Specific viscosity } \eta_{sp} = (t/t_0) - 1 \quad (5)$$

$$\text{Intrinsic viscosity } \eta = [(\sqrt{2}/c)(\eta_{sp} - \eta_{re})]^{1/2} \quad (6)$$

UV-Visible spectroscopic measurements

UV-Visible spectrophotometry technique was used to measure the photodegradation rate constant (kd) of PVC films at different irradiation times, and at maximum absorption peak (λ_{max} = 274 nm).

This wavelength is due to the growth of the carbonyl group, which increases as the polymer degradation increases. The change in the absorbance at ($\lambda_{\text{max}} = 274 \text{ nm}$) indication of photodegradation is occurrence. The kd was calculated through the first order kinetic equation

$$\ln (A_t - A_\infty) = \ln (A_0 - A_\infty) - kd t \quad (7)$$

A_0 signifies the absorption of the PVC film containing additive before irradiation. A_t is the absorption after irradiation time, A_∞ is the absorption at infinite irradiation time, T is the time of irradiation at second. Thus the plot of $\ln (A_t - A_\infty)$ versus irradiation time (t) gives straight line with a slope equal to kd. This indicates that photodecomposition of PVC is first order [30].

The electrical properties

The electric properties of PVC films were tested by LCR-meter [inductance (L), capacitance (C), and resistance (R) of an electronic component] investigated as a function of frequency at (20,000 Hz) at 30 °C by measuring the electrical conductivity (σ_{AC}) of prepared films before and after irradiation. After subjected films to UV light at a maximum wavelength 365 nm, the photodegradation occurred, result the formation of carbonyl, polyene and hydroxy groups, which contain free electron pairs and partial electric charges make increasing in the electrical conductivity. This is evidence of the formed of these groups and the occurrence of photodegradation [31, 32].

RESULTS AND DISCUSSION

The compounds [C2, C3 and C5] were used as additives for photostabilization of PVC films. The PVC films was exposed to UV rays at a maximum wavelength 365 nm, lead to appearance of bands at 1772 cm^{-1} and 1724 cm^{-1} due to the formation of carbonyl groups belonging to compounds (chloroketone and aliphatic ketone), 1622 cm^{-1} and 3448 cm^{-1} related to polyene and hydroxy group, respectively [33].

In the current study, we focused on studying the degradation of the polymer by measuring the carbonyl index only, as it is the most clear and distinct group compared to the polyene and hydroxy.

FTIR spectrophotometer was used to follow the growth of the carbonyl index (I_{CO}), it has been found that the carbonyl group increases with increasing irradiation time. Figure 1 explain the difference in FTIR spectra of pure PVC (control) film before and after irradiation.

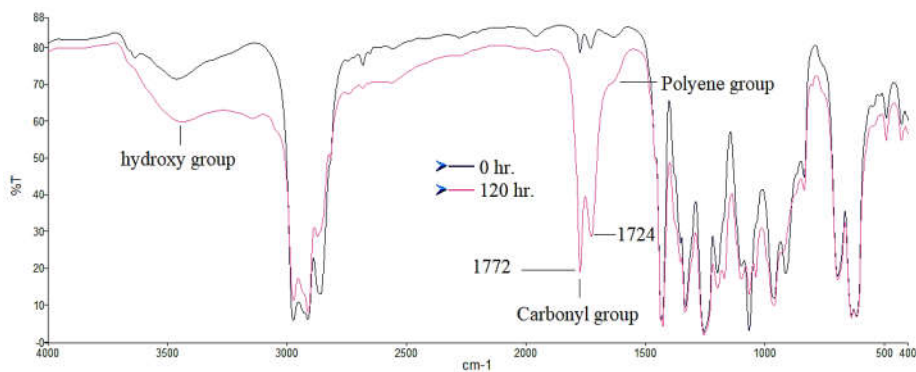


Figure 1. FTIR spectrum of PVC (control) under UV ray degraded for 120 h exposure time.

From calculating the carbonyl index (I_{CO}), it was found that the growth of carbonyl group for PVC control was larger than the same groups in the presence of additives, the PVC film contain C2 additive, had less growth of carbonyl group (carbonyl index) from other compounds. All these additives acted as photostabilizers for PVC polymer.

Effect of additive concentration

The concentration of the additives has an important role in the photostabilization of polymers, The authors of [34] have studied the influence of additive concentration on the photostabilization of PVC, it was found that the photodegradation rate of the polymer decreases with an increasing the concentration of the additives. In other words, the photostabilization increases with increasing the concentration of the additive, and the best concentration of the additives in terms of compatibility, effectiveness and economic cost was 0.5% wt. So, in the current work the photostabilization of poly(vinyl chloride) is studied with additive concentration weight (0.5% wt.) With the films thickness remaining constant at (40 μm). Figure 2 explained the values of carbonyl index (I_{CO}) which calculated with different irradiation time for PVC control and with (C2, C3 and C5) additives.

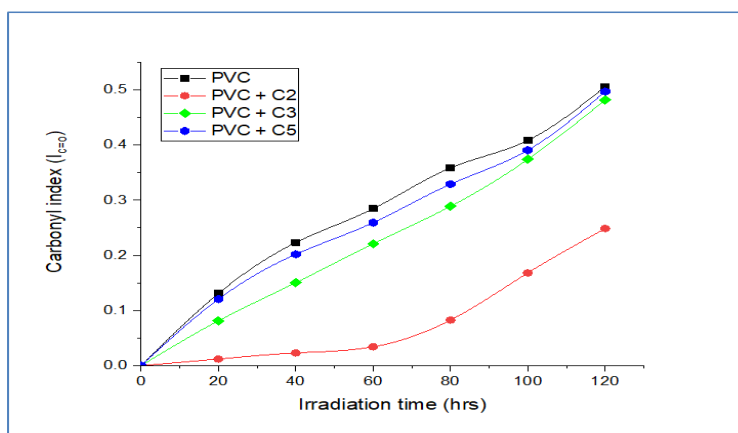


Figure 2. The relationship between carbonyl index (I_{CO}) and irradiation time (h) for PVC control and PVC with additives (40 μm thickness).

From Figure 2, we noticed that the additives have a lower growth of carbonyl index than PVC (control) with irradiation time. This indicates, that these organic compounds as additives have the ability to act as photostabilization of PVC towards UV light at wave length 365 nm which grow in the following trend: C2 > C3 > C5 > PVC. The best additive that did photostabilization for PVC is C2, (less I_{CO}) so the rest of the applications will be limited to this compound and compare it with PVC control. The formation of carbonyl, polyene and hydroxy groups upon photooxidation of PVC polymer by exposure it to UV rays, causes change the color of PVC from white to yellow, these groups make the PVC absorption the light at a longer wavelength, and this is the main reason for the coloration of the polymer when it is exposed to photodegradation [35, 36]. The photodecomposition rate constant (k_d) for PVC is calculated by using the equation 7 from the change in UV spectra of PVC films, It is a reaction of the first order, the graph between $\ln(A_t/A_\infty)$ against irradiation time gives a straight line, the slop value calculated from it represents (k_d) (Table 2).

Table 2. Photodecomposition rate constants (k_d) of PVC control and PVC with C2 compound.

Additives	k_d (s^{-1})
PVC (Control)	4.61×10^{-2}
PVC + C2	1.79×10^{-2}

PVC + C2 additive contain a little values of k_d , this means the PVC film stable towards UV light and does not degraded by it. When the films of PVC control and PVC + C2 compound are irradiated, the viscosity average molecular weight (M_v) decreased with the increase of irradiation time, this indicates chain scission and decreasing in the average molecule weight [29] Figure 3.

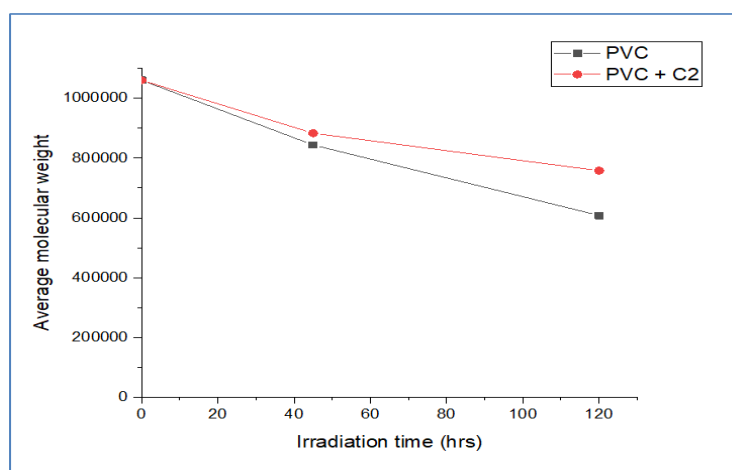


Figure 3. Change in the viscosity average molecular weight (M_v) through irradiation of PVC (control) and PVC + C2 additives.

Figure 3 indicates a reduction in (M_v) this reduction is due to the split of the main chain at numerous sites which are spread over the polymer chain.

The electrical properties of films of PVC control and PVC + C2 additive, before and after irradiated were tested by LCR-meter model of LCR-8105G, manufactured by GW instek, with frequency range (5Hz-5MHz), by measuring the electrical conductivity (σ_{AC}) at (20,000 Hz) as explained in Figure 4.

Figure 4 show that with increasing irradiation time, the conductivity increases, this indicate the photodegradation of PVC polymer occurred, with the formation of carbonyl, polyene and hydroxy groups, which contain free electron pairs and partial electric charges make increasing in the electrical conductivity. The PVC + C2 film is less conductivity than the PVC (control), indicating that the additive C2 (Schiff base compound) Preserves PVC from degradation.

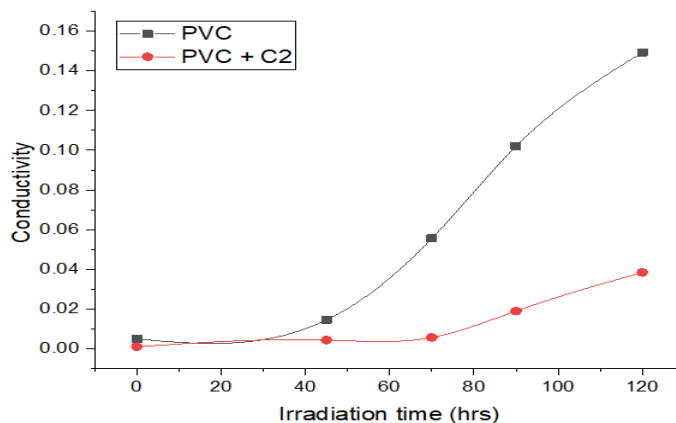


Figure 4. LCR meter of PVC control and PVC + C2 at 20,000 Hz.

Surface morphological study of prepared films by atomic force microscopy (AFM) and field emission scanning electron micrographs (FESEM)

The surface morphology of PVC and organic modified PVC films was estimated using atomic force microscopy (AFM) to determine the roughness and properties of films surface. During irradiation of pure and modified PVC, breaking of bonds was occur, which causing fragmented and rough of PVC surface. Figure 5a-c appears 3D topographic images of PVC and modified PVC surfaces after 300 h irradiation. The results are shown that the interaction between organic compounds (C2 and C3) with PVC films are improved the stability of PVC films. In addition to, it indicated that the surface roughness of the PVC control film was higher than those of the PVC containing C2 and C3. At the end of the irradiation process, the roughness factors (Rq) were 15.86 for PVC control film and 7.1 and 9.22 for the PVC film containing C2 and C3 compounds, respectively [37]. Notably, the use of Schiff base (C2) led to a 2.23-fold reduction in the Rq, which is higher than C3 compound (1.71-fold).

The effect of UV irradiation on the morphology of PVC and organic modified PVC was investigated by field emission scanning electron microscopy. FESEM was utilized to analyze morphology of altered PVC films, the morphology was clearly exported to estimate the impact of UV irradiation on pure and organic modified PVC films as a powerful technique for characterizing the shape and particles size. Figure 6a-d shows the FESEM images of pure and organic modified PVC films, after irradiation via UV light for 300 hrs. The results show roughness of surface, which may be back to the pass-linking or interaction between organic compounds with modified PVC. However, a number of small and large circular holes are estimated (Figure 6b, d) on the films surface, which may be resulted via the high rate of HCl elimination through irradiation [38, 39].

Through previous measurements of FTIR, UV-Visible spectroscopy, viscosity average molecular weight (M_v), LCR-meter, AFM and FESEM, explain that C2 compound have higher photostabilization than other additives, which grow in the following trend: C2 > C3 > C5 > PVC.

Based on the previous results, several mechanisms of photostabilization have been suggested. The main mechanism of photostabilization lies of PVC in the absorption of light (UV-ray) by the stabilizer (Schiff bases) and dispersion of this absorbed energy in the form of harmless heat away from the polymer surface, these mechanisms including: primary stabilizer, UV absorber and radical scavenger.

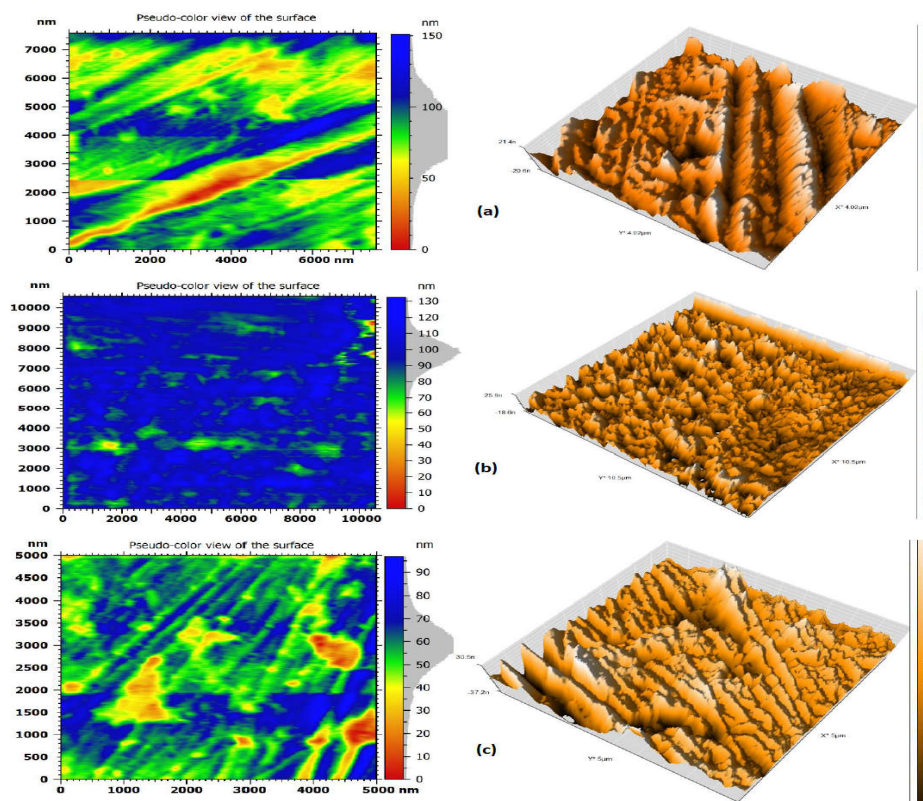


Figure 5. AFM images of the irradiated (a) PVC control, (b) PVC + C2 and (c) PVC + C3.

The first mechanism is primary stabilizer, it is suggested that the chlorine atoms in PVC surface coordinate with the Schiff bases (additives). This coordination and attraction can transform the excited state energy of PVC to a lower level that does not harm the polymeric chain [40], which explains in Scheme 1. The second mechanism is the charge-separated species, it is explain that the excited state allows the absorbed energy to disperse through rotation or increased vibration about the control bond [41] as explained in Scheme 1.

Some groups of additives like amine group, may work as radical scavenger for photostabilization process [41], so, these Schiff bases besides acting as UV absorber they may also act as radical scavenger additives.

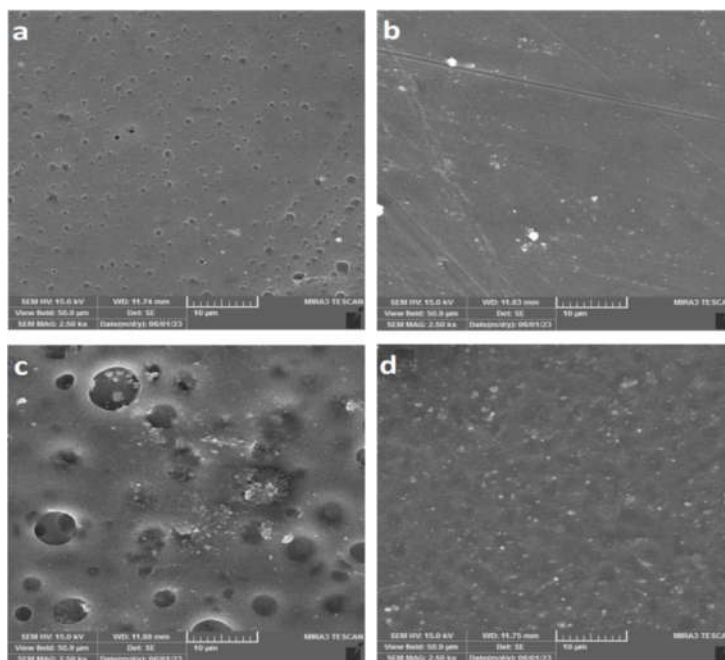
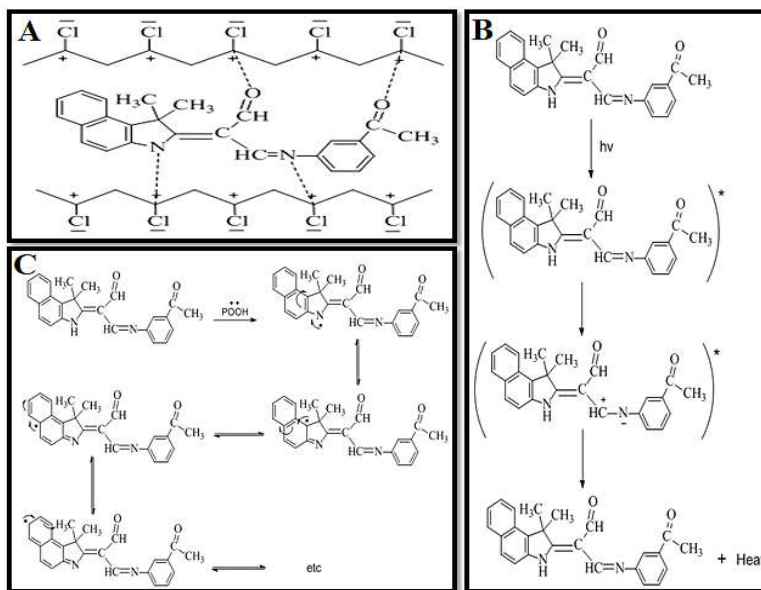


Figure 6. FESEM images of irradiated (a) pure PVC, (b) PVC + C2, (c) PVC + C3, and (d) PVC + C5.



Scheme 1. The mechanism suggested for PVC photostabilization by (C2) compound as A) primary stabilizers, B) UV absorber and C) radical scavenger.

CONCLUSION

Three new highly aromatic anti-cancer Schiff bases compounds were applied to be photostabilizers and antioxidants for PVC, to decrease the PVC degradation when exposure it to sunlight (UV radiation). The photostabilization of (PVC) films containing the additives (0.5 percent by weight) with thickness 40 μm was following the trend $\text{C2} > \text{C3} > \text{C5} > \text{PVC}$. In comparison to PVC control film, the growth of carbonyl index (I_{CO}) for the additive (C2) was less than that of the other compounds. Because of it has the highly compatibility with the PVC polymer, which makes it has the possibility of photostabilization with all the proposed mechanics. In addition it non-volatile, stable, prevent the formation of HCl. These additives forbade PVC films from degradation through several photostabilization mechanisms.

According to the photostability and mechanisms discussed above, all of these additives (highly aromatic Schiff bases) were effective in photostabilization processes. The most effective compound in photostabilization from the rest compounds added is C2. The surface morphological study of the prepared films by FESEM and AFM indicate that PVC stabilizer films exhibited much smoother surface and fewer cracks than the control one after exposure to ultraviolet light.

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