



Synthesis, characterization and *in-vitro* antimicrobial evaluation of thermally and photostable Schiff base-modified PVC/nanocomposites



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Abstract

Two Schiff base derivatives, 4-[(2, 5-dimethoxy phenylimino)-methyl] phenol, **SB1** and 4-[(2-hydroxy benzylidene)-amino] phenol **SB2**, have been prepared and used as modifiers for polyvinyl chloride (PVC). Chemical modification of PVC was performed using these Schiff base in presence of AgNO₃ to obtain two modified PVC nanocomposite, PVC-SB1/AgNPs and PVC-SB2/AgNPs, and their chemical structures were confirmed by FTIR, ¹H-NMR, ¹³C NMR and Mass spectroscopy. Scanning and transmission electron microscopy were performed for the modified polymer nanocomposites. The SEM and TEM micrographs of PVC-SB/AgNPs showed homogeneous surface polymeric matrix with uniform distribution of AgNPs, and their diameters are in the nanoscale. Moreover, thermal and photostabilities as well as mechanical properties of the modified polymer nanocomposites were also investigated. Moreover, mechanical properties of PVC-SB/AgNPs were also investigated. Antimicrobial activity of the modified PVC was evaluated against two Gram +ve bacteria (*Bacillus subtilis* and *Staphylococcus aureus*) and two Gram -ve bacteria (*Escherichia coli* and *Pseudomonas aeruginosa*) as well as *Candida albicans* as fungus.

Keywords: Modified PVC, Schiff base, photostability, antimicrobial activity

1. Introduction

Biomedical industries gave a great attention to some medical polymers that are directly connected to patient's health in case of some diseases treatment [1]. As these polymers are usually implanted inside human bodies in purpose of providing a suitable environment for bacterial adhesion [2]. Currently, biopolymeric food industry shows a rapid development in technology consideration material types that are used for prolonged food preservation [3]. For example, polymers with anti-infective properties that can be obtained by mixing with some

antimicrobial agents are of importance to food packing industries [4]. Incorporation of such antimicrobials to these materials such as paper, fibers and plastics leads to an increase in the shelf life as well as the foodstuff stability during storage [5]. Silver and some silver salts such as silver nitrate (AgNO₃) are well known examples of antimicrobial agents, with high antimicrobial potential, due to their efficiency against various types of bacteria, fungi and yeasts. Silver also has been known for its potency to destroy microorganisms by changing their metabolic process [6]. Polyolefin as polyethylene (PE) and polypropylene (PP) are the two commonly used plastics in manufacturing of food packaging materials, as they possess good mechanical

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properties, e.g. flexibility, strength and lightness. They are also characterized by moisture and chemical resistance; in addition, they are easily processed and are suitably recycled and reused [7]. Besides PE and PP, PVC is considered to be a unique thermoplastic material in the medical field as it used in manufacturing of indwelling catheters that are used in hospitals as well as its use in food packaging applications [8]. This is attributed to its special properties such as versatility and ductility. Simultaneously it is characterized by being relatively light in weight, easily processed, compatible in cost and non-toxic in resin [9]. These characteristics have led to the PVC exponential use in manufacturing of wide range products with various applications; for example, food and beverages industries, medical devices and hospital products, automobiles, civil construction, textiles. Antibacterial PVC products are considered as water hoses and for flooring purposes. The main disadvantage of PVC is its poor thermal and light stability, since it undergoes a rapid autocatalytic dehydrochlorination when subjected to heat [10-11] or exposed to light [12-13] during its molding and usage, respectively. In order to reduce this disadvantage some additives are applied to retard both thermal and photodegradation of PVC polymer, namely thermal and photostabilizers. Basic salts [14], soaps [15] and some organic stabilizers [16] are used as thermal stabilizers. Toxicity, environmental pollution and high cost of these additives have imposed a limitation on their use. So, attention is directed towards economical substitutes and eco-friendly materials [17]. Salicylates, some derivatives of hydroxybenzophenones, and benzotriazoles are used commercially as UV absorbers or photostabilizers. Also, some organic compounds such as phenyl urea, some glycoside derivatives and other organic compounds were synthesized to be used as photostabilizers for PVC [18–21]. Antibacterial properties of PVC can be developed by various techniques. For example, surface modification of PVC by zirconium phosphate loaded with silver as antibacterial agent is considered to be an efficient technique to obtain antibacterial PVC [22]. Also, impregnation of PVC polymer in antibiotics as well as its azidation is in another example for the same purpose [23]. In case of addition of either triclosan (2,4,4-p-trichloro-2P-hydroxy di-phenylether) or bronopol (2-bromo-2-nitropropane-1,3-diol) to PVC, a significant antimicrobial activity is exhibit against a

broad-spectrum of microorganisms. Similarly, poly (vinyl chloride)-based films treatment with zinc oxide nanoparticles has confirmed food pathogen inactivation upon investigation. This is attributed to the inhibition effect that is exhibited by ZnO nanoparticles coated film on the growth of *Escherichia coli* and *Staphylococcus aureus* bacterial strains [24]. Further studies have also elucidated that the use of PVC thin film loaded with silver nanoparticles have led to the formation of polymeric based material that can be used for active packaging with high antimicrobial activity [25-26]. Some chemical modifications for PVC via introducing biologically active organic compounds with or without loading metal nanoparticles have been carried out to examine the antimicrobial activity of the modified polymers [27-30]. The present work aims to synthesize and characterize Schiff base modified PVC/AgNPs for antimicrobial evaluation to be used in either medical or food packaging applications.

2. Experimental

2.1. Materials

Suspension PVC, with K value of 70, was supplied by Al-Aemria Company for Petrochemicals, Alexandria, Egypt. Hydroxyl amine hydrochloride and silver nitrates were of laboratory grade chemicals. Phenyl salicylate was obtained from El-Nasr Company for Medicinal Chemical, Egypt. All other fine chemicals were of analytical grade. Solvents were purified and distilled before use.

2.2. Instrumentation

Infrared spectra were recorded as potassium bromide pellets on a Perkin-Elmer 1650 spectrophotometer, National Research Centre, Cairo, Egypt. ¹H-NMR spectrum was determined on a Jeol-Ex-500 NMR spectrometer and chemical shifts were expressed as part per million; (δ values, ppm) against TMS as internal reference, National Research Centre, Cairo, Egypt.

2.2.1. Scanning electron microscope

The dry sample was spread on a conducting adhesive tape, pasted on a metallic stub. The morphology of the tested samples was investigated and imaged with scanning electron microscope (SEM) (QUANTA FEG 250 ESEM). This was accompanied by energy dispersive X-ray spectroscopy (EDAX AMETEK Inc.; Mahwah, NJ, USA) at an acceleration voltage of

15 kV. The films were fixed on the surface of a sticky tape.

2.2.2. Transmission electron microscope

Micrographs of the colloidal nanogel particles were taken using a JEOL JEM-2100 (JEOL, Japan). The TEM sample was prepared and placed on a Copper grid by mixing one dilute drop of prepared aqueous particles dispersed in 5 ml acetone; to become slightly turbid solution and allowing it to dry well. The images of representative areas were captured at suitable magnifications that clarify the morphology and the size of the nanoparticles.

2.2.3. Thermal gravimetric analysis

Thermogravimetric analysis was carried out on TGA-50H thermogravimetric analyzer, Shimadzu, Japan. Samples were heated up to 500 °C in a Platinum pan with a heating rate of 10°C /min, in N₂ atmosphere of flow rate 25 mL/min.

2.2.4. Mechanical properties

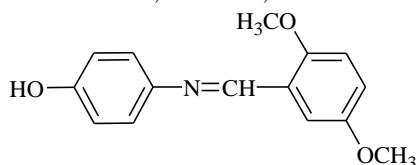
Tensile strength, modulus at 100 % and 200% elongation and elongation at break were measured at room temperature on a tensile testing machine (Zwick/Roell Z010) according to ASTM: D412-06.

2.3. Preparation of Schiff base derivatives

Schiff base derivatives were prepared as described before [31].

2.3.1. Synthesis of 4-[(2, 5-dimethoxy phenylimino)-methyl] phenol SB1

Equimolar ratios of 4-amino phenol and 2,5-dimethoxybenzaldehyde were reacted in methanol as a solvent with addition of few drops of glacial acetic acid under reflux for 12 hr. After cooling, the precipitate was filtered and recrystallized from ethanol as pale yellow powder; m.p 168°C; yield(89); IR (KBr, cm⁻¹): 3423(OH); 3088(C-H, aromatic); 2836 (C-H, aliphatic); 1618 , 1422(C=C aromatic); 1605(C=N). ¹H-NMR(300 MHz, DMSO-d₆, TMS, δ, ppm), 10.15(s, 1H, -OH); 7.88(s, 1H, -N=CH-); 7.40(d, 2H, aromatic, J=9Hz); 7.26(d, 2H, aromatic, J=9Hz); 6.71-6.98(m, 3H, aromatic); 3.89(s, 3H, -OCH₃); 3.69 (s, 3H, -OCH₃). Chemical formula; C₁₅H₁₅NO₃: Calcd. C 70.02%; H 5.88%; N 5.44%, found C 71.52%; H 5.41%; N 5.92%.

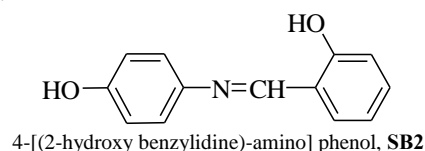


4-[(2, 5-dimethoxy phenylimino)-methyl] phenol, SB1

2.3.2. Synthesis of 4-[(2-hydroxy benzylidene)-amino] phenol SB2

Equimolar ratios of 4-amino phenol and 2-hydroxybenzaldehyde (salicylaldehyde) were reacted in methanol as a solvent with addition of few drops of glacial acetic acid under reflux for 12 hr. After cooling, the precipitate was filtered and recrystallized from ethanol as pale yellow powder; m.p 187°C; yield (84%); IR (KBr, cm⁻¹): 3431(OH); 3109(C-H, aromatic); 2981 (C-H, aliphatic); 1631, 1420 (C=C aromatic) 1610(C=N); ¹HNMR (300MHz, DMSO-d₆,TMS, δ, ppm) 9.52(s, 1H,-OH, D₂O exchangeable); 8.20(s,1H,-OH, D₂O exchangeable); 7.98(s,1H, -CH=N-);7.70(d, 2H, aromatic, J=9Hz.); 7.14-7.59(m, 3H, aromatic); 6.89(d, 2H, aromatic, J=9Hz.).

Chemical formula: C₁₃H₁₁NO₂ Calcd. C 73.23%; H 5.20%; N 6.57%, found C 72.05%; H 4.36%; N 6.12%.



4-[(2-hydroxy benzylidene)-amino] phenol, SB2

2.4. Synthesis of Schiff-bases modified PVC/AgNPs

1 mol of each prepared Schiff base derivative was added to 4 mol of dissolved PVC in freshly distilled THF, in a round bottom flask. The reaction mixture was refluxed for 2h, and then silver nitrate (3% by weight ratio of PVC) and an equimolar ratio of hydroxyl amine hydrochloride, as a reducing agent, were added [32]. The refluxing was continued at 60°C under stirring for another 6 h. After cooling, the reaction mixture was poured on cold methanol; the new modified polymeric solid material was collected, filtered, washed with warm water, dried under vacuum and the two Schiff-bases modified PVC/AgNPs (PVC-SB1/AgNPs and PVC-SB2/AgNPs) were then obtained

2.5. Preparation of PVC samples for thermal degradation

200 mg of Schiff-base modified PVC/AgNPs samples were well mixed 3% Ca-Zn stearate as thermal stabilizer and added to the least amount of freshly distilled THF, left overnight and stirred well to attain maximum homogeneity. The viscous solution was poured into a Petri-dish of 12 cm diameter. The solvent was evaporated by ventilation for 24 h in a desiccator to obtain a film of 0.25 mm thickness. The

PVC film was washed with, warm water to get rid of any residuals, diethyl ether to remove the rest of the THF and dried under vacuum at 30°C overnight, to get PVC pieces with dimensions of 1cm x 1cm x 0.25mm. Thermal stabilization of the modified PVC samples was investigated with the method reported by Braun and Thallmaier [33]. The samples were thermally treated under N₂ atmosphere and the evolved HCl was determined conductometrically.

2.6. Determination of photostability of Schiff bases modified PVC/AgNPs

2.6.1. Preparation of Schiff bases modified PVC/AgNPs films for UV Irradiation

The Schiff-base modified PVC/AgNPs films were prepared by casting from THF. 1gm of the previously prepared modified PVC-Schiff-base/AgNPs was dissolved in 30 mL freshly distilled THF. The polymer solution was stirred and left overnight to attain maximum homogeneity. The solution was then poured into a Petri-dish of 18.5 cm diameter. The solvent was evaporated by ventilation for 24 h in a desiccator to obtain a film of 30 μm thickness. The PVC film was washed with, warm water to get rid of unreacted AgNO₃ residues, diethyl ether to remove the rest of the THF, and dried under vacuum at 30°C overnight.

For mechanical properties measurements, 20% by weight of di(2-ethylhexyl)phthalate (DEHP) as a plasticizer was added to the polymeric solution.

2.6.2. Photodegradation

PVC and Schiff-base modified PVC/AgNPs samples were subjected to a high-pressure mercury lamp (HPK-125 W) with a λ max at 365 nm. The distance between the light source and the samples under investigation was 25 cm and the surrounding ambient temperature was ~35°C. The investigated samples were exposed to UV radiation for various time intervals, 2, 4, 6, 8, and 10 h.

2.6.3. Methods of evaluating the stabilizing efficiency

Weight loss measurements were carried out according to the following equation.

$$\text{Weight loss \%} = (W_1 - W_2)/W_1 \times 100$$

Where W₁ is the weight of the original sample (before irradiation) and W₂ is the weight of the irradiation sample.

The formed gel content of the photodegraded PVC samples was determined by dissolving constant weights (0.5 g) of each sample, after different irradiation times in 20mL THF and left overnight. The insoluble fractions were separated by centrifuge, washed with solvent and then dried to constant weight in an air oven.

The percentage of gel content was evaluated using the following relation:

$$\% \text{ Gel content} = W_2/W_1 \times 100$$

Where W₁ is the weight of the original sample and W₂ is the weight of the insoluble (gel) fraction.

Moreover, the soluble fractions were precipitated in cold methanol, filtered and dried in an air oven to constant weight. The % of soluble fractions were determined in order to confirm the amount of gel previously determined.

$$\% \text{ Soluble fraction} = W_2/W_1 \times 100$$

Where W₁ is the weight of original sample and W₂ is the weight of soluble fraction after precipitation in methanol (after complete evaporation of solvent and complete dryness).

2.6.4. Extent of discoloration

The photostability of PVC and Schiff-base modified PVC/AgNPs samples was determined by following their color changes that occurred upon UV-irradiation. The UV absorption spectra of samples under investigation were measured using the Shimadzu UV-2401 Double-Beam UV-VIS spectrophotometer apparatus.

2.7. Determination of photostability of PVC Schiff bases blends

2.7.1. Preparation of PVC Schiff bases blends films for UV Irradiation

The PVC films in the absence and in the presence of 2% by weight of either the reference stabilizer; phenyl salicylate (salol), or the two Schiff bases under investigation were prepared by dissolving the polymer and the stabilizer in freshly distilled tetrahydrofuran (THF). The polymer-stabilizer solution was stirred to attain maximum homogeneity. The solution was then poured into a Petri-dish of known diameter. The film was formed after complete solvent evaporation, washed with diethyl ether, and then dried to get rid of any residual THF. The film thickness was ~ 0.25 mm. Photodegradation process

and methods of evaluation of the stabilizing efficiency of the investigated Schiff-bases by determining both weight loss and extent of discoloration of the photodegraded samples of PVC-Schiff bases blends were carried out as described before.

2.8. Antimicrobial assay

The antibacterial activities of the synthesized compounds were tested against *Escherichia coli* NRRL B-210 and *Pseudomonas* NRRLB-23 (Gram -ve bacteria), *Bacillus subtilis* NRRL B-543 and *Staphylococcus aureus* NRRL B-313 (Gram +ve bacteria) using nutrient agar medium. The antifungal activity of these compounds was also tested against *Candida albicans* NRRL Y-477 using Sabouraud dextrose agar medium.

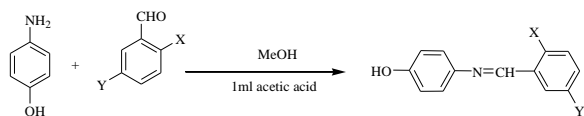
2.8.1. Agar Diffusion Medium

The synthesized compounds were screened in vitro for their antimicrobial activity against, by agar diffusion method [34]. 0.5 mL suspension of each of the aforementioned microorganisms was added to sterile nutrient agar media in case of bacteria and Sabouraud dextrose agar medium in case of fungi at 45°C and the mixture was transferred to sterile Petri dishes and allowed to solidify. Holes of 9 mm diameter were made using a cork borer. Amounts of 0.1 mL of the synthesized compounds dissolved in 1 mL DMSO were poured inside the holes. A hole filled with DMSO only was also used as control. The plates were left for 1 hour at 4°C temperature as a period for complete diffusion of synthesized compounds samples before microorganism's growth. The plates were then incubated at 30°C for 24 hours and observed for antimicrobial activity. The diameters of the inhibition zone were measured and compared to that of the standard and the values were tabulated. Ciprofloxacin (10 mg/mL) and Nystatin (10 mg/mL) were used as standard for antibacterial and antifungal activity respectively.

3. Results and Discussion

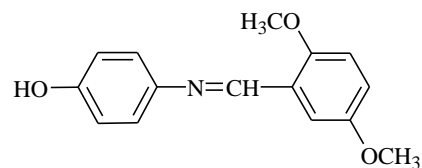
3.1. Synthesis of Schiff base derivatives

Schiff base derivatives were prepared as described in the experimental part and represented in Scheme 1.

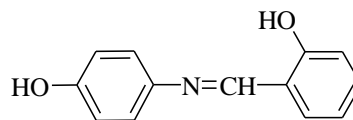


SB1: X= OCH₃, Y=OCH₃; SB2: X= OH, Y= H

Scheme 1: Synthesis of Schiff base derivatives



4-[(2,5-dimethoxy phenyl imino)-methyl] phenol, SB1

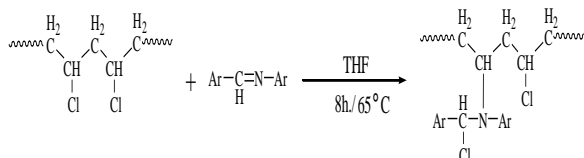


4-[(2-hydroxy benzyldiene)-amino] phenol, SB2

The chemical structures of the two Schiff bases SB1 and SB2 were confirmed by various spectroscopic analyses. FTIR of SB1 derivative showed the IR peak at 3423 cm⁻¹ which is related to the OH group of p-aminophenol while the two peaks that appeared at 3088 and 2836 cm⁻¹ are corresponding to the aromatic and aliphatic C-H. the aromatic C=C are represented by the two bands at 1618 and 1422 cm⁻¹. The imine group which is the most characteristic peak in the Schiff base derivative, C=N, appeared at 1605 cm⁻¹. ¹HNMR of SB1 showed all proton signals that confirmed its structure. The three protons of the two methoxy groups appeared as singlet at 3.69 and 3.89 ppm. The aromatic protons of the aldehydic moiety have appeared as multiplets at 6.71-6.98 ppm, whereas the two doublets of doublets of the aniline aromatic ring was at 7.26, 7.30 ppm and 7.40, 7.45 ppm respectively. The proton signals of the imine and the OH groups have appeared as singlets at 7.98 and 10.15 ppm respectively. For SB2, the IR peak that appeared at 3431 cm⁻¹ is due to the -OH groups in the Schiff base molecule. There are two IR peaks at 3109 and 2981 cm⁻¹ are correlated to both aromatic and aliphatic C-H whereas that appeared at 1631 and 1420 are of the aromatic C=C. The imine group (C=N) of the Schiff base is characterized by the appearance of IR band at 1610 cm⁻¹. The ¹HNMR of SB2 has also confirmed the formation of the Schiff base derivative. There are two doublets of doublet for the aromatic protons of the aniline ring have appeared at 6.89, 6.95 and 7.70, 7.75 respectively, while the aldehydic aromatic protons have appeared as multiplets at 7.14-7.59. The singlet proton of the imine group CH=N has appeared at 7.98 ppm and the singlet proton of the OH group appeared at 8.20 ppm.

3.2. Synthesis of Schiff bases modified PVC/AgNPs

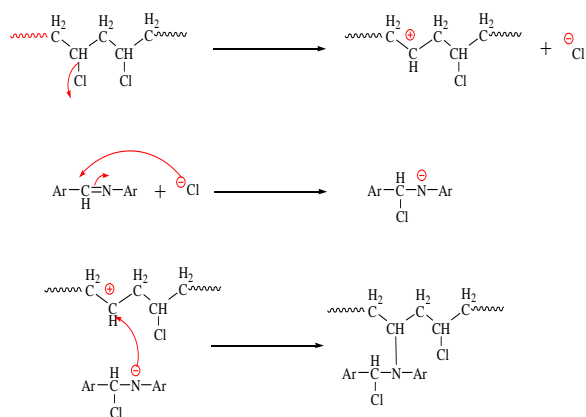
Chemical modification of PVC with either of the two Schiff base derivatives, SB1 and SB2 was performed according to the procedures that was previously described in the experimental section and represented in **Scheme 2**. AgNPs are formed into the modified PVC samples by introducing 3% by weight of AgNO₃ and equimolar ratio of hydroxylamine hydrochloride as a reducing agent to obtain two modified samples of PVC silver nanocomposites. The two formed PVC-SB samples were characterized using both FTIR and ¹HNMR spectrophotometric analysis. Thermal and photo stabilities as well as mechanical properties of the modified PVC were studied. Further studies were carried out via scanning and transmission electron microscopes to examine both the morphological changes and the incorporation of silver into the polymeric structure. Finally, antimicrobial investigation of the two formed modified PVC samples was performed. Further investigations for the effect of the prepared Schiff base derivatives on thermal and photo stabilities as well as antimicrobial activity of PVC were also performed by its blending with 2% of each Schiff base derivative.



Scheme 2: Schiff base modified PVC

Figure 1 represents the IR spectrum of modified PVC with the Schiff base, SB2 which clearly discloses that the polymeric PVC backbone modification is retained. The modified PVC spectrum reveals the main characteristic bands at 3403 cm⁻¹ that is related to the –OH group of the Schiff-base moiety, in addition to those peaks at 3055 and 2923 cm⁻¹ due to aromatic and aliphatic –CH stretch, respectively. It is clearly noticed that the IR characteristic peak at 1580 cm⁻¹ of the imine group, –CH=N, of the SB2 Schiff base derivative has disappeared and a new peak at 1617 cm⁻¹ is observed. This new IR band is considered to be due to the formation of –CH–N that illustrate the mechanism by which the Schiff base reacts with PVC. It is postulated that an addition reaction of the constituents of PVC chains on the double bond of the Schiff base. There are also two characteristic bands at

1453 and 629 cm⁻¹ which are correlated to bend and stretch vibration aliphatic –CH₂ and –CCl of PVC, respectively. Besides, the finger print region has three IR bands appearing at 1366, 1254 and 970 cm⁻¹ which are assigned to both stretch and bend vibrations of the –CH of PVC. In addition to the IR spectral data of the SB-modified PVC, results of elemental analysis indicated the presence of nitrogen in 8% and this led to propose an ionic mechanism for modification of PVC via introducing the Schiff-base under investigation. This mechanism can be outlined by the following equations that represented in **Scheme 3**. According to the suggested mechanism, the tertiary chlorine anion that detached from the polymeric PVC chain attacks the carbon atom of CH=N of Schiff base molecule to leave a negative charge on the nitrogen atom which in turn can easily block the carbocation created on the PVC chain. The nucleophilic attack of the weak base chloride anion on the unsaturated double bond of Schiff base molecule has been proved previously in literatures [35].



Scheme 3: Mechanism of nucleophilic reaction of Schiff base on PVC

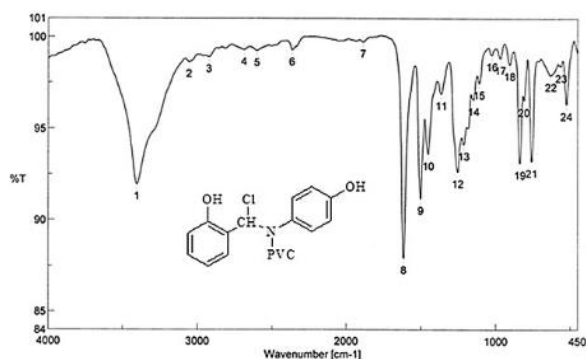


Figure 1: IR spectrum of Schiff base PVC nanocomposite, PVC-SB2/AgNPs.

The chemical structure of PVC-SB2 derivative is also confirmed by $^1\text{H-NMR}$ spectroscopy and is represented in **Figure 2**. The PVC protons ($-\text{CH}$, and $-\text{CH}_2$) have appeared as multiplet signals at δ 1.23-2.37 and 3.87- 4.02 ppm, whereas the signal at 4.44 ppm is attributed to $-\text{ClCH-N-}$. The multiplet signals detected at δ 7.11-7.36 and 7.67-7.89 ppm refer to the aromatic protons of the two phenyl rings, while the two singlet protons at δ 9.87 and 10.25 ppm are correlated to the two $-\text{OH}$ groups of Schiff-base moiety.

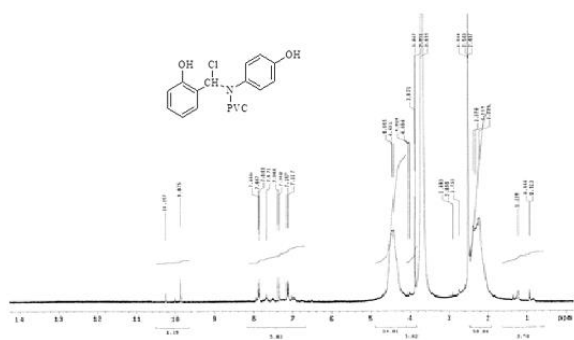


Figure 2: $^1\text{H-NMR}$ spectrum of Schiff base PVC nanocomposite, PVC-SB2/AgNPs.

3.3. Scanning and transmission electron microscopy (SEM and TEM)

Figure 3 (A, B, and C) represents the images of the surface SEM, TEM, and EDX, micrograph of PVC-SB1 loaded with AgNPs. As shown in **Figure 3** (A), the silver metal nanoparticles have appeared in the SEM images as light spherical spots through the dark surface of PVC. The surface of the Schiff base modified PVC demonstrates an appropriate homogenous polymeric matrix with a uniform distribution of AgNPs into the polymeric substrate. AgNPs also exhibited in spherical forms with minimum extent of aggregation across the tested samples. This confirms the good dispersion of silver nanoparticles through the polymeric matrix. Further morphological investigation, TEM is performed to assist and describe the quantitative determination the structural properties of AgNPs inside the polymeric matrix. **Figure 3** (B) shows the TEM micrograph in which the AgNPs are formed in spherical and regular shape with slightly different sizes. Silver nanoparticles appeared in dark colors that are surrounded by light layers of PVC. **Figure 3** (B) also demonstrates the deposition of AgNPs onto the modified PVC sample with the Schiff base derivative, SB. The particle sizes of the deposited nanoparticles are in the range of 2.83–9.37nm. The good deposition

of AgNPs may be attributed to its attachment on the nitrogen atoms of Schiff-base molecules [36]. **Figure 3**(C) shows the data of EDX analysis of PVC-SB1/AgNPs that is produced from 3% reduced AgNO_3 . The characteristic peaks of Ag appeared around 3keV with 5.09% as an elemental composition or atomic percentage. The characteristic peaks of the C, and Cl of PVC appears at 0.25 and 2.7keV; as the main components of PVC.

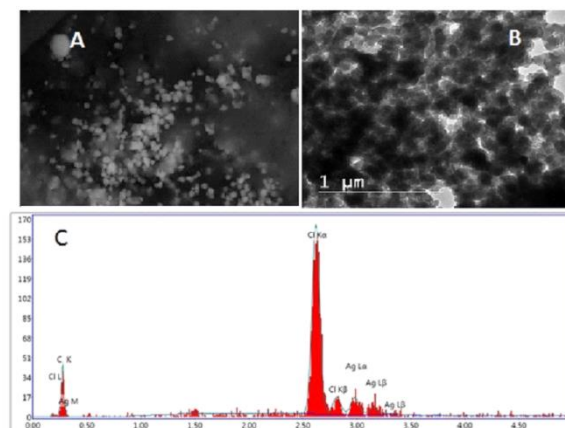


Figure 3: (A) SEM of PVC-SB1/AgNPs, (B) TEM of PVC-SB1/AgNPs, and (C) EDX of PVC-SB1/AgNPs

Moreover, the SEM image for the surface of PVC-SB2/AgNPs which is represented in **Figure 4** (A) shows a relatively good homogeneity for the polymeric matrix. Silver nanoparticles are uniformly distributed into the polymeric substrates with minimum agglomeration. The type of interaction between the Schiff base nitrogen atom lone pair of electrons and the developed partial positive charge on the surface of Ag have led to immobilization and thus causing stabilization of Ag nanoparticles after being reduced. TEM micrograph of the same sample is elucidated in **Figure 4** (B). For the PVC-SB2/AgNPs, it is noticed that small spherical nanoparticles of Ag are present in the polymeric substrate with a slight intense in their colors. Diameters of the deposited nanoparticles are in the range of 1.74 and 2.80nm. **Figure 4**(C) displays the corresponding EDX spectrum of the PVC-SB2/AgNPs. It illustrates the presence of Ag embedded in the polymeric matrix. The characteristic peak of silver nanoparticle confirms the presence of the elemental silver and it appeared at 3keV. The characteristic maximum peak for the chlorine as a main constituent of PVC appeared at 2.7keV.

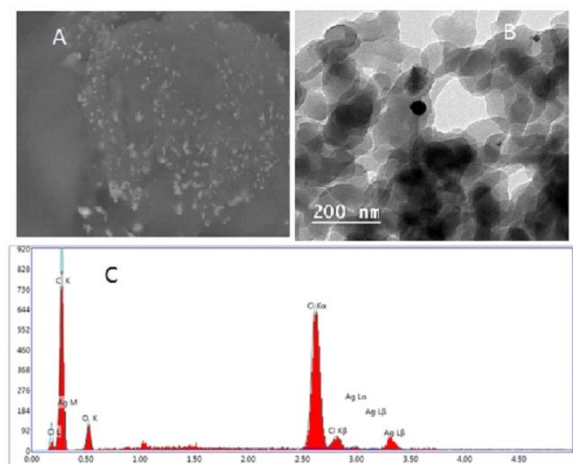


Figure 4: (A) SEM of PVC-SB2/AgNPs, (B) TEM of PVC-SB2/AgNPs, and (C) EDX of PVC-SB2/AgNPs

3.4. Thermal Analysis

Thermal gravimetric analysis (TGA) of the investigated samples, blank PVC and the modified PVC with the two prepared Schiff bases is represented in **Figure 5**.

TGA thermograms demonstrate the process of thermal degradation of blank PVC and its modified Schiff-bases nanocomposites with onset and different decomposition temperatures. The blank PVC starts to decompose at nearly 225 °C by the effect of elimination of hydrogen chloride that is followed by conjugated polyene formation and thermal cracking of the polymeric matrix [37]. On the other hand, thermal degradation both of PVC-SB1/AgNPs and PVC-SB2/AgNPs onsets at higher temperatures, 260 and 240 °C respectively. For blank PVC, gradual degradation occurred up to 275 °C with weight loss of 38% that is followed by higher rate of decomposition causing weight loss of 62% at 350 °C. The second degradation stage at temperature range of 350 to 425 °C occurred with loss of molecular mass equal to 62% and 68%, respectively, whereas at nearly 500 °C loss of weight reached about 90%. This increase in degradation rate may be due to further elimination of hydrogen chloride molecules from PVC backbone chains and this rate remains constant till 600 °C. Regarding the two Schiff base modified PVC nanocomposites, the PVC-SB1/AgNPs, exhibited higher thermal stability in the than PVC-SB2/AgNPs. It is clearly obvious that a very low degree of thermal decomposition of this sample till 300 °C followed by gradual degradation to reach loss of mass of 42% at about 375 °C. At higher

temperature, 500 °C, the % weight reached 68% and seems to be constant till 600 °C. For PVC-SB2/AgNPs, thermal stability is lower than that of both blank PVC and PVC-SB1/AgNPs, since 50% of the molecular mass of this sample was lost at 350 °C which is followed by lower degree of degradation to get 62% weight loss at 450 °C. At 600 °C, the weight loss of PVC-SB2/AgNPs reached about 90. The higher thermal stability of the PVC-SB/AgNPs than that of the blank one may be correlated to the presence of the silver nanoparticles that are embedded in the polymeric matrix in a better manner, where the increased stability of PVC-SB1/AgNPs when compared to PVC-SB2/AgNPs can be attributed to the effect of the greater volume of the dimethoxy groups as compared to that of the two hydroxyl groups in the SB2/AgNPs.

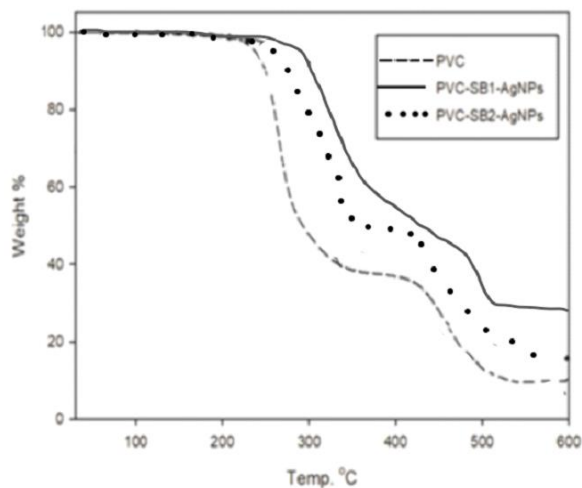


Figure 5: TGA curves of PVC, PVC-SB1/AgNPs, and PVC-SB2/AgNPs

3.5. Evaluation of thermal stability of Schiff base modified PVC/AgNPs

The thermal stability of Schiff base modified PVC/AgNPs in absence and in presence of 3% Ca-Zn stearate as reference heat stabilizer was carried out at 180 °C under nitrogen atmosphere conductometrically. The results of thermal stability are represented in terms of the induction period (T_s), and given in **Table 1**, in comparison with that of blank PVC. The results revealed that the two Schiff base modified PVC/AgNPs have high thermal stability values (T_s), in particular PVC-SB1/AgNPs when compared to the blank PVC sample and that stabilized with 3% Ca-Zn stearate. Moreover, the results revealed also that the modified PVC/AgNPs showed higher T_s values when

blended with 3% Ca-Zn stearate. The higher thermal stability of modified PVC/AgNPs samples, in comparison with the blank one, may be attributed to the decrease in the content of labile chlorine atoms which are substituted with the Schiff base moiety that leading to a decrease of liberation of HCl. Also, the

alkaline nature of the Schiff base moiety may neutralize the amount of liberated HCl which in turn which lower its degradation effect on more PVC chains.

Table 1: Thermal stability values of Schiff base modified PVC/AgNPs in absence and in presence of 3%Ca-Zn stearate, in N₂, at 180 °C

Type of stabilizer	Ts/min
Blank PVC	4
PVC/3%Ca-Zn stearate	9
PVC/SB1/AgNPs	13
PVC/SB2/AgNPs	8
PVC/SB1/AgNPs/3% Ca-Zn stearate	19
PVC/SB2/AgNPs3% Ca-Zn stearate	15

3.5.1 .Extent of discoloration of Schiff base modified PVC/AgNPs as a criterion for thermal stability

Table 2 shows the extent of discoloration occurred for the investigated samples on thermal degradation, which is considered as an experimental proof for their high thermal stability. The results revealed that the rate of color changes of Schiff base modified PVC/AgNPs are of lower extent at different intervals of time relative to the blank PVC and PVC in

presence of 3%Ca-Zn stearate. The lower extent of discoloration of the modified PVC samples can be attributed to the lower content of labile chlorine atoms present on PVC chains that are substituted by the Schiff base moieties. This substitution may lead to a decrease in the formation of conjugated double bonds that are responsible for the changes in colors. It is obvious also that the degree of discoloration of PVC/SB1/AgNPs is lower than that of PVC/SB2/AgNPs.

Table 2: Extent of discoloration of thermally degraded Schiff base modified PVC/AgNPs in absence and in presence of 3%Ca-Zn stearate, in N₂, at 180 °C

Type of stabilizer	Color at 0 min	Color at 20 min	Color at 40 min	Color at 60 min
Blank PVC	White	Light brown	Dark brown	Black
PVC/3%Ca-Zn stearate	White	Dark yellow	Light brown	Dark brown
PVC/SB1/AgNPs	Pale yellow	Pale yellow	Dark yellow	Dark yellow
PVC/SB2/AgNPs	Pale yellow	Dark yellow	Light brown	Brown
PVC/SB1/AgNPs/3% Ca-Zn stearate	Pale yellow	Pale yellow	yellow	Dark yellow
PVC/SB2/AgNPs3% Ca-Zn stearate	Pale yellow	yellow	Dark yellow	Light brown

3.6. Photostability of Schiff base modified PVC/AgNPs against UV irradiation

3.6.1. Weight loss, gel content and soluble fractions of irradiated Schiff base modified PVC/AgNPs

The poor photostability of PVC may lead to physical and mechanical changes to the polymeric matrix on exposure to UV radiation. This exposure is usually accompanied by evolution of HCl gas via dehydrochlorination process with a consequent

occurrence of weight loss and formation of conjugated double bonds (polyene formation), that increased with the increase in the irradiation time. So, photostability of modified PVC nanocomposite samples can be easily determined by following the changes occurred in weight loss, content of the formed gel, as well as the soluble fractions of the irradiated samples as a function of irradiation time. Extent of discoloration of the investigated samples

can also be determined by following their changes in colors which occurred upon UV- irradiation. All these investigations were carried out for PVC sample in presence of 2% by weight of phenyl salicylate as reference UV absorber for comparison.

Regarding the weight loss percentage of the different irradiated PVC samples, it can be considered as a good measure for the extent of degradation and consequently the stability of these examined samples.

Figure 6 clearly reveals that the degree of weight loss increases with the increase of irradiation time. It is noticed also that there is a decrease in the extent of weight loss for samples of Schiff base modified PVC/silver nanoparticles as compared to that of the blank PVC and the samples stabilized with the reference UV absorber. The results show that modification of PVC with the SB1 Schiff base has led to higher photo stability than that modified by SB2 derivative. The photostability of PVC-SB1/AgNPs is so pronounced, as it gives the lowest percentage weight loss upon UV irradiation. The observed weight loss percentages after irradiation of 2h are 1.1 and 1.7 for PVC-SB1/AgNPs and PVC-SB2/AgNPs, respectively. After the same irradiation time, these percentages have reached 3.4 and 2.1 for both blank PVC sample and that have been stabilized with the reference UV absorber. On increasing the irradiation time and after 10h irradiation, the extent of weight loss increases, so this percentage for PVC-SB1/AgNPs and PVC-SB2/AgNPs have reached 3.4 and 4.2, in comparison with both samples blank PVC and that stabilized PVC with the reference UV absorber, these values became 7.5 and 6.3 respectively.

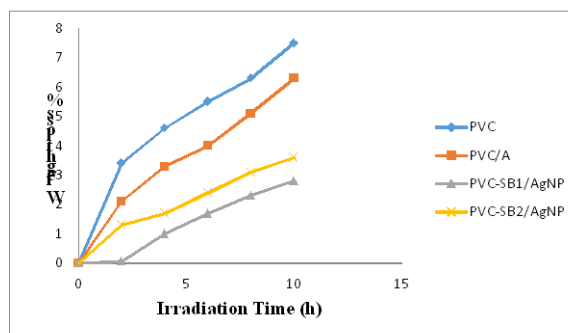


Figure 6: Effect of irradiation time on % weight loss of PVC-SB1/AgNPs, PVC-SB2/AgNPs, compared to blank PVC, and PVC/A as reference UV absorber

Further investigations on photodegraded samples of PVC-SB/AgNPs, blank PVC and PVC stabilized with the reference UV absorber have proven the formation of gels and so, the content of formed gel as a result of UV irradiation of the polymer samples can be taken as a measure for the rate of degradation and therefore an extent measure for photostable polymer. **Table 3** shows that the results of % gelation of all investigated PVC samples increase in values with the increase of the irradiation time. The results also have shown that the % gel content of photo degraded modified PVC either with the SB1 or SB2 Schiff bases nanocomposites are lower than these values of the blank and that stabilized with reference UV absorber. Furthermore, the formed gel content of PVC-SB1/AgNPs is lower than that of PVC-SB2/AgNPs either in earlier or later stages of irradiation.

Moreover, the results of **Table 3** show the percentage of soluble fraction for photo-degraded samples of PVC-SB/AgNPs, blank PVC, as well as for photo-degraded PVC in presence of reference UV absorber as a function of irradiation time. These results agree well with the data of the % gelation and are considered to be an additional proof that the modified PVC with Schiff bases is characterized with high photostability.

Table 3: Measurements of soluble fraction (%) and gel content (%) for photodegraded Schiff base modified PVC/AgNPs in comparison with PVC stabilized with phenyl salicylate (A) as reference UV absorber

Sample code	Gel content %	Soluble fraction %
PVC (2h)	12.87	86.10
PVC (4h)	16.42	82.78

PVC (6h)	18.33	80.57
PVC (8h)	21.57	77.48
PVC (10h)	23.20	75.12
PVC/A(2h)	9.37	88.73
PVC/A (4h)	12.59	86.21
PVC/A(6h)	13.12	84.52
PVC/A (8h)	16.26	81.94
PVC/A (10h)	18.73	80.25
PVC/SB1 (2h)	2.19	96.14
PVC/SB1(4h)	4.38	95.62
PVC/SB1(6h)	6.53	93.13
PVC/SB1(8h)	7.49	92.22
PVC/SB1(10h)	9.26	90.05
PVC/SB2 (2h)	4.55	94.75
PVC/SB2 (4h)	7.82	92.38
PVC/SB2 (6h)	9.28	88.42
PVC/SB2 (8h)	11.56	87.39
PVC/SB2 (10h)	13.63	85.24

3.6.2. Extent of discoloration of photodegraded Schiff base modified PVC/AgNPs

The extent of discoloration for the investigated Schiff base modified PVC/AgNPs samples against UV irradiation for various time intervals (2, 4, 6, 8 and 10h) is taken as an additional proof for photostability of these samples. Data of both blank PVC and that stabilized with phenyl salicylate as a reference UV absorber are also given for comparison. **Figure 7** illustrates the discoloration changes with the irradiation time. This was performed by measuring the absorbance of samples under investigation at 450 nm with a concentration of 200 mg/10 mL THF. It is clearly observed that the degree of discoloration of modified PVC with Schiff bases, in particularly PVC modified with SB1 Schiff base exhibited lower rates of color changes other than PVC-SB2 discoloration. The results also clarified that the extent of discoloration of modified PVC with Schiff bases is

lower than that of both blank PVC and the stabilized sample with the reference UV absorber.

The decrease in rate of discoloration of the modified PVC samples as compared to that of the blank PVC may be due to the decrease of chlorine content in the polymeric PVC chains after introducing the Schiff

bases derivatives into the backbone chains of PVC. This may lead to a relative diminishing in the rate of dehydrochlorination (liberation of HCl) with lower probabilities of conjugated double bonds formation [38]. The lower extent of discoloration which indicates the good photostability of PVC-SB1/AgNPs than that of PVC-SB2/AgNPs may be due to the presence of the two electron donating methoxy groups in SB1 molecule. These groups increase the electron density within the phenyl ring allowing delocalization to better stabilized molecules, and this may consume part of the incident UV light leading to more protection of the polymeric matrix against photodegradation.

Moreover, the photostability of the modified PVC with SB1 than that modified with SB2 can be also attributed to the ease of hydrogen atom of the hydroxyl group of SB2 to be released on UV irradiation to react with the detached chlorine from PVC chains, which in turn enhances the rate of dehydrochlorination and hence, the polyene formation that is accompanied with a darkness in color takes place. Photostability of Schiff base modified PVC nanoparticles may also be due to the presence of the reduced silver particles in the polymeric matrix. It is well known that the absorption

spectrum of AgNPs produced by reduction methods is characterized by UV absorption band with a λ maximum at 420 nm. This region which lies between 300 and 450 nm is considered to be the most harmful UV radiation range for PVC [39-40]. Therefore, the introduction of AgNPs to the polymeric matrix can improve its photostability.

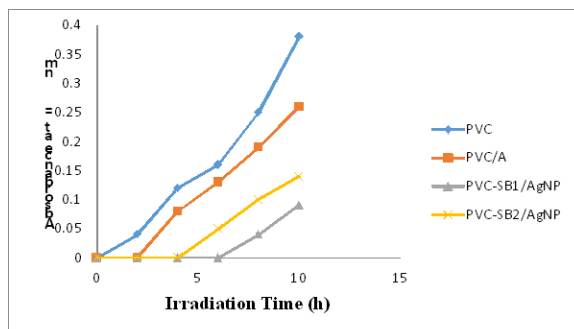


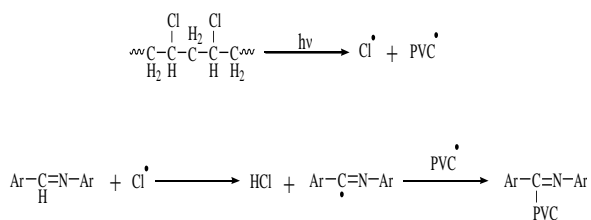
Figure 7: Effect of irradiation time on extent of discoloration of PVC-SB1/AgNPs, PVC-SB2/AgNPs, compared to blank PVC, and PVC/A as reference UV absorber

3.7. Photostability of PVC Schiff bases blends against UV irradiation

3.7.1. Weight loss of photodegraded PVC Schiff bases blends

The effect of the prepared Schiff bases as photostabilizers for PVC was studied to compare their efficiency as an additive with that as a main constituent in the backbone PVC chains. Photostability of PVC samples in absence and in presence of 2% by weight of each of the two prepared Schiff bases SB1 and SB2 were determined by following the changes occurred in both percentage weight loss and also their extent of discoloration as a function of irradiation time. Weight loss and extent of discoloration of samples of blank PVC and that in presence of 2% by weight of phenyl salicylate as reference UV absorber were also studied for comparison. **Figure 8** showed that the weight loss percentages of PVC-SB1 and PVC-SB2 blends increase by the increase of irradiation time and are of lower rates than that of either the blank PVC or the stabilized sample with the reference UV absorber. It is also found that the rates of weight loss of these sample blends are slightly lower than that of PVC-SB/silver nanocomposites at the same UV irradiation time exposure. It is clearly shown that SB1 has higher

photostabilizing efficiency on photodegraded PVC than SB2. The relatively higher stabilizing efficiency of the PVC-Schiff bases blends than that of the Schiff bases modified PVC/nanocomposites may be due to the expected mode of action of the Schiff base molecules as photostabilizer additive. The most probable mechanism of Schiff base as photostabilizer is the free radical one. The chemical structure of the investigated Schiff base photostabilizer is considered to be electron rich due to the presence of two aromatic phenyl rings that are conjugated with the double bond of the imine group. This may enhance its ability to absorb UV radiation energy with dissipating the harmless heat energy that is leading to protection of the PVC matrix against photodegradation [41]. The hydrogen atom of the CH=N group of the Schiff base can be also easily abstracted by the detached chlorine atom of PVC chain to leave an electron site on the imine carbon atom which can easily block the PVC radical chain. **Scheme 4** represents the photostabilization mechanism of PVC by the effect of Schiff base derivatives.



Scheme 4: Photostabilization mechanism of PVC in presence of Schiff base derivative

3.7.2. Extent of discoloration of photodegraded PVC Schiff bases blends

Determination of the color changes occurred for the investigated PVC-Schiff bases blends against UV irradiation for different time intervals can also be taken as an additional proof for photostability of these samples. Extent of discoloration of both blank PVC and that stabilized with phenyl salicylate as reference UV absorber are also given for comparison. **Figure 9** illustrates the degree of discoloration of the investigated samples with the irradiation time which was performed by measuring their absorbance under the same previous conditions described before. It is clearly noticed that the rate of discoloration of all samples are increased with the increase of the irradiation time and PVC-Schiff bases blends exhibited lower rates of color changes than that of

blank PVC and PVC stabilized with phenyl salicylate. It is obvious also that the PVC-SB1 shows lower degree of discoloration than PVC-SB2. It is considered that the lowering in rates of discoloration of PVC-Schiff bases blends can be discussed according to **Scheme 4**. The decrease in the liberation of more HCl molecules from the polymeric chains by the effect of the Schiff base as photostabilizer can minimize the formation conjugated double bonds and consequently formation of polyenes which causes the discoloration phenomenon for the PVC matrix.

3.8. Mechanical properties

The mechanical properties of PVC are of interest according to its application field. Di(2-ethylhexyl)phthalate (DEHP) is a widely used as a plasticizer to render poly(vinyl chloride) (PVC) soft and malleable. Plasticized PVC is used in hospital

equipment, food wrapping, and numerous other commercial and industrial products [42]. So, mechanical properties of both blank PVC and the two Schiff-base modified PVC/AgNPs were performed using 20% by weight of DEHP and the data are represented in **Table 4**. These results clearly show the values of tensile stress, elongation at break, as well as the modulus at 50, 100 and 200 % elongation. It is obvious from the data of **Table 4** that tensile strength, elongation at break are of higher values for the two modified PVC samples on comparison with those of the blank one. Furthermore, the modulus of all samples increases as the % elongation increased from 50% to 200%, and this indicates the improvement of the mechanical properties of the investigated samples.

Table 4: Mechanical properties of PVC/SB1/AgNPs, PVC/SB2/AgNPs, compared to blank PVC

Sample codes	TS	Elongation at break	T ₍₅₀₎	T ₍₁₀₀₎	T ₍₂₀₀₎	Thickness	A
	MPa	%	MPa	MPa	MPa	mm	mm ²
Blank PVC	20.16	227.04	13.12	15.63	19.60	0.14	0.56
PVC/SB1/AgNPs	22.06	263.09	12.32	15.35	19.62	0.13	0.52
PVC/SB2/AgNPs	21.74	271.87	11.21	14.36	18.79	0.14	0.56

3.9. Antimicrobial activity

Antimicrobial activity of the two prepared Schiff-bases (SB1 and SB2), Poly(vinyl chloride), and two Schiff bases modified PVC silver nanocomposites have been examined against two Gram +ve bacteria (*Bacillus subtiles* and *Staphylococcus aureus*) and (*Escherichia coli* and *Pseudomonas aeruginosa*), as Gram -ve bacterial type. The antifungal activity of the abovementioned compounds has also been investigated against *Candida albicans*. Ciprofloxacin and Nystatin are used as antibacterial and antifungal reference drugs for comparison.

Results of antimicrobial activity of these investigated compounds are given in **Table 5**. The results clearly exhibited good antibacterial efficiencies of the two prepared Schiff-bases, SB1 and SB2, against Gram

+ve and Gram -ve bacterial strains, that compared to ciprofloxacin as standard antibacterial drug. It is noticed that the antibacterial activity of SB1 is higher than that of SB2. The values of antibacterial activity of SB1, which is represented in mm inhibition zone, against the two Gram +ve bacteria (*B. subtiles* and

St. aureus) are 12 and 13mm, respectively, with inhibition efficiency of 63 and 65% of the reference drug. The same Schiff-base derivative exhibited higher inhibitory effect against the two Gram -ve bacterial type (*E. coli* and *P. aeruginosa*) that reached 70 and 72% when compared to standard antibacterial drug.

The data have also shown comparable antibacterial efficiency of SB2 towards the two Gram +ve bacterial strains (*B. subtiles* and *St. aureus*) and recorded 53 and 55% respectively. Meanwhile a higher antibacterial activity values against the two Gram -ve bacteria when compared to those of the reference antibacterial agent has been recorded. It showed inhibitory effect of 61 and 60% with respect to the reference antibacterial agent. So, the two examined compounds showed higher antibacterial activity against the Gram -ve bacterial type than against the Gram +ve bacterial one. Antifungal activity of the two investigated Schiff base derivatives, SB1 and SB2, has efficiency of 74 and 61% against the *C. albicans* when compared to the reference antifungal agent. Regarding the investigated modified PVC samples,

PVC/SB1/AgNPs and PVC/SB2/AgNPs, it is obvious that they are characterized by enhanced antibacterial activity, with higher efficiency for PVC/SB1/AgNPs, when compared to the blank nonmodified PVC. The results show also that PVC/SB1/AgNPs has higher antibacterial potency against Gram +ve and Gram -ve bacterial types and they affected the Gram -ve bacterial strains in higher extent than the Gram +ve one. Antibacterial activity of PVC/SB1/AgNPs exceeds that of the reference drug except in case of *P. aeruginosa* the efficiency reached 96%. The two modified PVC nanocomposites showed good antifungal activity against the *C. albicans* that reached 78 and 70% for PVC/SB1/AgNPs and PVC/SB2/AgNPs, respectively.

The aforementioned obtained results can be illustrated on the basis of both the chemical structure and physicochemical properties of the substituents for each compound separately. Starting with the prepared Schiff base derivatives, it is reported that they have been shown to be interesting moieties for the design of promising antimicrobial agents. The main efficient functional group in these molecules; is the imine-CH=N-group that might interfere in the action of cell mitosis and hence stop further growth of bacteria. Furthermore, aromatic-based Schiff bases have shown more potentiality in biological applications as a result of the free electron delocalization with the ring structure [43-44]. So, it could be said that the antimicrobial activity of both SB1 and PVC/SB1/AgNPs is higher than that of

SB2 and PVC/SB2/AgNPs may be due to the stability of SB1 which is more than that for SB2 and after mixing (PVC with SB1) and (PVC+SB2) the antimicrobial activity of PVC/SB1/AgNPs was significantly better than PVC/SB2/AgNPs.

The observed higher antibacterial activity of the prepared Schiff bases against the Gram -ve bacterial strains more than the Gram +ve ones can be rationalized on the basis of the nature and the structure of the cell wall membranes of both types, since the Gram +ve bacteria is characterized by thick wall than the other type [45].

On using the prepared Schiff base derivatives in PVC modification in presence of 3% by weight of AgNO₃ to obtain the modified PVC nanoparticle, a significant enhancement of the antimicrobial activities of PVC was observed as compared to blank PVC sample activity. It is well known established that silver metal is characterized by antibacterial activity, but the mode of its potency to inhibit or delay the bacterial growth was just recently discussed. This antibacterial activity of silver may be due to its ability to entering the microbial cell, causing damage through its binding with the thiol groups (-SH) of the enzymes of microorganisms which can deactivate them [46]. Further inhibitory effect of silver as antibacterial agent increases as its particle size is reduced, since the contact surface area of silver particles with bacteria increased by 10⁹ times with the decrease of the particle size from 10 μm to 10 nm [47].

Table 5: In vitro antimicrobial activity by agar diffusion method of tested compounds

Samples codes	Gram +ve bacteria		Gram -ve bacteria		Fungi
	<i>B. subtilis</i>	<i>St. aureus</i>	<i>E. coli</i>	<i>P. aeruginosa</i>	<i>C. albicans</i>
Ciprofloxacin	19	20	23	25	-ve
Nystatin	-ve	-ve	-ve	-ve	23
PVC	16	15	15	13	14
SB1	12	13	18	16	17
PVC-SB1/AgNPs	23	22	27	24	18

SB2	10	10	14	14	14
PVC-SB2/AgNPs	19	17	24	25	16

4. Conclusion

Two Schiff base derivatives, namely, 4-[(2, 5-dimethoxy phenylimino)-methyl] phenol, SB1 and 4-[(2-hydroxy benzylidine)-amino] phenol SB2, have been prepared and used in chemical modification of PVC in presence of 3% by weight AgNO₃ to obtain two Schiff base modified PVC samples, PVC-SB1/AgNPs and PVC-SB2/AgNPs. FTIR, ¹H-NMR, ¹³C NMR and Mass spectroscopic analyses elucidated and confirmed the chemical structures of both Schiff bases and the modified PVC nanocomposites. The SEM micrographs of the modified PVC-SB/AgNPs have showed surface homogeneity and uniform distribution of Ag nanoparticles with good adhesion on polymeric surface. EDX spectrum shows that the silver contents in the two modified PVC samples are 5.09 and 0.28%, respectively. The TEM images of the two modified PVC samples, PVC-SB1/AgNPs and PVC-SB2/AgNPs showed that Ag nanoparticles are of diameters of 2.83–9.37nm and 1.74–2.80nm respectively. The two modified PVC nanocomposites have exhibited good thermal stability via thermogravimetric analysis and their extent of discoloration is lower than both the blank PVC sample and that stabilized by reference heat stabilizer. Photostability has also been evaluated by measuring weight loss, gel content, soluble fractions, in addition to the degree of discoloration of the UV irradiated samples and compared to blank PVC and that in presence of the reference UV absorber. Mechanical properties are investigated for the plasticized samples of modified PVC-SB/AgNPs and the results show their good mechanical properties with respect to the blank one. Antibacterial activity of the investigated samples is evaluated against two Gram +ve bacteria (*Bacillus subtilis* and *Staphylococcus aureus*) and two Gram -ve bacteria (*Escherichia coli* and *Pseudomonas aeruginosa*). The two samples of Schiff-base modified PVC have exhibited high antibacterial efficiency against both types of bacteria, Gram -ve and Gram +ve, when compared to that of the blank PVC. Antifungal activity of these compounds has also been tested

against *Candida albicans* and the results show also high antifungal activity.

Competing Interests

The authors declare that there is no conflict of interests regarding the publication of this paper

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References

- [1] Jones, D.S.; Djokic, J.; Gorman, S.P., The resistance of polyvinyl pyrrolidone-Iodine-poly (ε-caprolactone) blends to adherence of *Escherichia coli* biomaterials. *Biomaterials*, **26**, 2013–2020 (2005).
- [2] Bower, C.K.; Parker, J.E.; Higgins, A.Z.; Oest, M.E.; Wilson, J.T.; Valentine, B.A.; Bothwell, M.K.; McGuire, J., Protein antimicrobial barriers to bacterial adhesion: In vitro and in vivo evaluation of nisin-treated implantable materials. *Colloid Surf B Biointerf.*, **25**, 81–90 (2002).
- [3] Vermeiren, L.; Devlieghere, F.; Van Been, M.; De Kruijf, D.; Debevere, J., Development in the Active Packaging of Foods. *J of Food Technol. in Africa.*, **5**, 6-13 (2000).
- [4] Lakshmi, S.; Pradeep, S.S.; Kumar, J.A., Bacterial adhesion onto azidated poly (vinyl chloride) surfaces. *J. Biomed. Mater. Res.*; **61**, 26–32 (2002).
- [5] Cooksey, K., Effectiveness of antimicrobial food packaging materials. *Food Additives Contaminants.*, **22**, 980–987 (2005).
- [6] Lubick, N., Nanosilver toxicity: Ions, nanoparticles-or both? *Environm. Sci. Technol.*, **42**, 8617-8617 (2008).
- [7] Colin-Chávez, C.; Soto-Valdez, H.; Peralta, E., Diffusion of carotenoids from mono and bilayer polyethylene active packaging into soybean oil. *Food Packaging and Shelf Life.*, **1**, 170–178 (2014).
- [8] Federic, C.; Ferri, M.; Morelli, A.; Dipaol, L.; Latini, G., Perspectives on alternatives to

- phthalate plasticized poly(vinyl chloride) in medical devices applications. *Progress in Polymer Science*, **38**, 1067-1088 (2013).
- [9] Cushen, M.; Kerry, J.; Morris, M.; Cruz-Romero, M.; Cummins, E., Migration and exposure assessment of silver from PVC nanocomposite. *Food Chemistry*, **139**, 389-397 (2013).
- [10] Starnes, W.; H., Structural and mechanistic aspects of the thermal degradation of poly(vinyl chloride).
- [11] D. Braun, D.; Rabie, S.; T., Photostabilizing Effect of Some Thermal Stabilizers for Poly(vinyl chloride) in the Presence of Filler. *Jof Vinyl and Additive Technol.*, **15**, 224-228 (2009). *Prog. Polym. Sci.*, **27** 2133-2170 (2002).
- [12] Rabie, S.; T.; Nada, A.; A., *J of Vinyl and Additive Technol.*, **14**, 79-83 (2008).
- [13] Shi, W.; Zhang, J.; Shi, Xu-M.; Jiang, Guo-D., Influence of UV Absorber on Photodegradation Processes of Poly(vinyl chloride) with Different Average Degrees of Polymerization. *Polym. Eng. and Sci.*, **47**, 1480-1490 (2007).
- [14] Xiang, X.; Shuangjun, C.; Zhang, J.; Cha, R., Photodegradation of plasticized poly(vinyl chloride) stabilized by different types of thermal stabilizers *Prog. Polym. Sci.*, **51**, 624-631 (2011).
- [15] Folarin, O.; M.; Sadiku, E.; R., Thermal stabilizers for poly(vinyl chloride): A review., *Int. J of the Phys. Sci.*, **6**, 4323-4330 (2011).
- [16] Safronov, A.; Somov, T.; Suvorov, A.; Fisch, M.; H.; Stewen, U.; Bacaloglu, R.; Dooley, T., Mechanism of organotin stabilization of poly(vinyl chloride). 6. Compatibility of organotin stabilizers with PVC. *J of Vinyl and Additive Technol.*, **9**, 127-137 (2003).
- [17] Kobayashi, N.; Honmyo, T.; Kakamoto, T.; Yamamoto, A., Mg-Al-based hydrotalcite-type particles, chlorine-containing resin composition and process for producing the particles. *U.S. Patent.*, **6,939,909** (2005).
- [18] Sabaa, M.W.; Mohamed, R.R., Phenyl urea derivatives as organic stabilizers for rigid poly (vinyl chloride) against photo-degradation. *J Appl Polym Sci.*, **103**, 2217-2226 (2007).
- [19] Braun, D.; Richter, E.; Rabie, S.T.; Nada, A.A.; Abd-El-Ghaffar, M.A.; Yassin, A.A., Glucoside derivatives as novel photostabilizers for rigid PVC. *Die Ang Makromol Chem.*, **271**, 93-100 (1999).
- [20] Rabie, S.T.; Khalil, A.M., Antimicrobial agents as photostabilizers for rigid poly (vinyl chloride). *Polym Adv Technol.*, **23**, 1394-1402 (2013).
- [21] Rabie, S.T.; Khalil, A.M.; Nada, A.A., Diamide derivatives as photostabilizers for plasticized poly(vinyl chloride). *J of Vinyl and Additive Technol.*, **14**, 191-196 (2008).
- [22] Chen, X.; Li, C.; Zhang, L.; Xu, S.; Zhou, Q.; Zhu, Y.; Qu, X., Main factors in preparation of antibacterial particles/PVC composite. *China Particuology.*, **2**, 225-226 (2004).
- [23] Lakshmi, S.; Kumar, S.; Athipettah, J., Bacterial adhesion onto azidated poly(vinyl chloride) surfaces. *J of Biomed. Mat. Res.* **61**, 26-32 (2002).
- [24] Xihong, L.; Yage, X.; Yunhong, J.; Yulong, D.; Weili, L., Antimicrobial activities of ZnO powder-coated PVC film to inactivate food pathogens. *Int J Food Sci Technol.*, **44**, 2161-2168 (2009).
- [25] Afzal, A.B.; Akhtar, M.J., Effect of inorganic silver nanoparticles on structural and electrical properties of polyaniline/PVC blends. *J of Inorganic Organometallic Polymers and materials.*, **20**, 783-792 (2010).
- [26] Saadatabadia, N.M.; Nateghib, M.R.; Zarandia, M.B., Determination of the dispersive optical constants of the poly (vinyl chloride) transparent nanocompositelayers containing nanosilver intercalated graphene. *Polymer Science Series A.*, **57**, 480-488 (2015).
- [27] Rabie, S.T.; El-Saidi, M.M.T.; Mohamed, N.R., Synthesis of biologically active and photostable rigid poly (vinyl chloride). *J Biomed Mater Res Part A.*, **100A**, 3503-3510 (2012).
- [28] El-Sayed, A.A.; Khalil, A.M.; El-Shahat, M.; Khareldin, N.Y.; Rabie, S.T., Antimicrobial activity of PVC-pyrazolone-silver nanocomposites. *J of Macromol Sci., Part A: Pure and Applied Chemistry.*, **53**, 346-353 (2016).
- [29] Gaballah, S.T.; Khalil, A.M.; Rabie, S.T., Thiazole derivatives-functionalized polyvinyl chloride nanocomposites with photostability and antimicrobial properties. *J of Vinyl and Additive Technol.*, **25**(S1), E137-E146 (2018).

- [30] Abdel-Monem, R.; Gaballah, S.T.; El-Nazer, H.; Rabie, S.T., *Egypt. J. of Chem.*, DOI: 10.21608/EJCHEM.2019.14908.1904 (in press).
- [31] Fasina, T. M.1, Ejiah, F. N. Dueke-Eze, C.U. and Idika N; Synthesis and Antimicrobial Activity of Schiff Bases Derived from Substituted Salicylaldehyde with 2-aminophenol and 2-aminothiophenol. *Journal of Sci. Res. Dev.*, 14, 95 – 98 (2013).
- [32] Leopold, N.; Lendl, B., A New Method for Fast Preparation of Highly Surface Enhanced Raman Scattering (SERS) Active Silver Colloids at Room Temperature by Reduction of Silver Nitrate with Hydroxylamine Hydrochloride. *J of Physical Chemistry B.*, **107**, 5723–5727 (2003).
- [33] Braun, D.; Thallmaier, M. Measurement of the evolution of hydrogen chloride from poly vinyl chloride at elevated temperatures. *Kunststoffe.*, **56**, 80-83 (1966).
- [34] Cruickshank, R.; Duguid, J.P.; Marmion, B.P.; Swain, R.H.A., *Medicinal Microbiology, twelfth ed., Churchill Livingstone, London.*, 2, 196–202 (1975).
- [35] Sabaa, M.W.; Mohamed, R.R.; Yassin, A.A., Organic thermal stabilizers for rigid poly(vinyl chloride) VIII. Phenylurea and phenylthiourea derivatives. *Polym Degrad Stabil.*, **81**, 37-45 (2003).
- [36] Jimenez, J.; Chakraborty, I.; Rojas-Andrade, M.; Mascharak, P.K., Silver complexes of ligands derived from adamantylamines: Water-soluble silver-donating compounds with antibacterial properties. *J Inorg Biochem.*, **168**, 13–17 (2017).
- [37] Liu, H.; Wang, J.; Wen, S.; Dong, L.; Xiong, C.; Yao, J., Morphological, thermal, and mechanical properties of poly(vinyl chloride)/acrylonitrile butadiene rubber blend using $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ as cross-linking agent. *Polym Eng Sci.*, **54**, 1864–1870 (2014).
- [38] Sabaa, M.W.; Oraby, E.H.; Abdel Naby, A. S.; Mohamed, R.R., Anthraquinone derivatives as organic stabilizers for rigid poly (vinyl chloride) against photo-degradation. *Eur Polym J.*, **41**, 2530–2543 (2005).
- [39] Key, J.; Leary, J.F., Nanoparticles for multimodal in vivo imaging in nanomedicine. *Int. J Nanomedicine.*, 9, 711–726 (2014).
- [40] Sosa, I.O.; Noguez, C.; Barrera, R.G., Optical Properties of Metal Nanoparticles with Arbitrary Shapes. *J Phys. Chem. B.*, 107, 6269–6275 (2003).
- [41] Yousif, E.; Bakir, E.; Salimon, J.; Salih, N., Evaluation of Schiff bases of 2,5-dimercapto-1,3,4-thiadiazole as photostabilizer for poly(methyl methacrylate) *J. Saudi Chem. Soc.*, **16**, 279–285 (2016).
- [42] Erythropel, H.C.; Maric, M.; Nicell, J.A.; Leask, R.L.; Yargeau, V., Leaching of the plasticizer di(2-ethylhexyl)phthalate (DEHP) from plastic containers and the question of human exposure. *Appl Microbiol Biotechnol.*, **98**, 9967–9981 (2014).
- [43] Qin, W.; Long, S.; Panunzio, M.; Biondi, S., Schiff Bases: A Short Survey on an Evergreen Chemistry Tool. *Molecules.*, **18**, 12264–12289 (2013).
- [44] Xia, L.; Xia, Y.F.; Huang L.R.; Xiao, X.; Lou, H.Y.; Liu, T.J.; Pan, W.D.; Luo, H., Benzaldehyde Schiff bases regulation to the metabolism, hemolysis, and virulence genes expression in vitro and their structure–microbicidal activity relationship. *Eur J Med Chem.*, **97**, 83–93 (2015).
- [45] Javier, E.; Julia, O.; Leonora, M.; Alejandro, U.; Marcela W., Structure-Activity and Lipophilicity Relationships of Selected Antibacterial Natural Flavones and Flavanones of Chilean Flora. *Molecules.*, **22**, E608 (2017).
- [46] Gavanji, S.; Larki, B.; Mehrasa, M., A review of destructive effect of nano silver on human health, environment and animals. *Int. J Sci Res Environ Sci.*, **1**, 231–239 (2013).
- [47] Sukdeb, P.; Yu K.T.; Joon, M.S., Does the Antibacterial Activity of Silver Nanoparticles Depend on the Shape of the Nanoparticle: A Study of the Gram-Negative Bacterium *Escherichia coli*. *Appl Environ Microbiol.*, 73, 1712–1720 (2007).