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# Chemical Modification of Poly(Vinyl Chloride) Using Some Aminopyrimidine Derivatives for Photo, Thermal, Mechanical, and Antibacterial Evaluation

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CHEMICAL modification of poly(vinyl chloride), PVC, was performed via its substitution reaction with 6-amino-2-thioxo-tetrahydropyrimidin-4-one (**1**) and three of its derivatives (**1A-C**). The chemical structures of the modified PVC samples have been confirmed via FTIR and $^1$HNMR spectroscopic analyses. Photostability of the modified PVC were investigated by following the rates of dehydrochlorination of the 6-aminopyrimidine derivatives modified PVC samples conductometrically in comparison with both blank PVC and that stabilized with 2-hydroxy-4-(octyloxy)-phenyl-benzophenone as reference UV absorber. Moreover, thermal stability as well as physicomechanical properties of all investigated PVC samples have also been determined. Modified PVC samples exhibited enhanced photo and thermal stability as well as mechanical properties when compared to the blank unmodified sample. Antimicrobial properties of the tested PVC samples were explored against Gram +ve bacteria (*Staphylococcus aureus*), Gram -ve bacteria *(Escherichia coli*) as well as *A. flavus* and *C. albicans* as fungi. However, incorporation of 6-aminopyrimidine derivatives to the PVC backbone chains enhanced their inhibitory effect against the examined microorganisms.

**Keywords**: PVC, 6-aminopyrimidines, photostability, antimicrobial activity

## Introduction

Medical polymers are of important issue in the treatment of some diseases that have a direct consequence on patient's health [1,2]. These medical polymers are implanted inside humans and they can become places for bacteria to breed [3]. Polymeric materials such as polyethylene and poly (vinyl chloride) are used on a large scale in hospital care and this has led to an increase in the rate of biomaterial-related infections (BRI) [4]. So, development of the anti-infective medical polymers to be used in the biomedical industry became important. The anti-infective properties of medical polymers can be obtained by mixing with some antibacterial or antimicrobial agents. Poly(vinyl chloride), PVC, is considered to be one of the common medical polymers [5]. Besides, PVC and polyethylene are the most common used polymeric materials that used for food packaging applications. Hence, in order to solve the problems of undesirable microorganisms on food surfaces, it is beneficial to treat the surface of the plastic film by coating with antimicrobial agents or incorporate the antimicrobial agents into the polymeric matrix [6].

PVC like other polymers are widely used in fabrication of indwelling catheters for hospital cares. It is also used in other industrial applications of antibacterial products such as water hoses and flooring. Developing the antibacterial properties of PVC can be attained through surface modification technique using zirconium phosphate that loaded with silver as antibacterial agent [7]. The surface modification of polymers using azides showed

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significant reduced bacterial adherence to bacterial strains [8]. Some organic compounds as bis-alkylthiocyanates have high efficient in killing some types of bacterial strains. Thus, plasticized PVC has reacted with sodium thiocyanate and nucleophilic substitution of chlorine by thiocyanate on the PVC surface was carried out. Blank and thiocyanated PVC surfaces were subjected to two bacterial strains that are commonly implicated in device-associated infections, as Staphylococcus aureus and Staphylococcus epidermidis. The results exhibited a significant reduced retention of Staphylococcus epidermidis on the thiocyanated PVC surface [9]. In some publications, the possibility of modifying PVC by nucleophilic substitution was investigated.

PVC was also modified by chemical substitution reaction with 2-aminothiazole and its ester separately in absence and in presence of silver and/or copper nanoparticles. The functionalized PVC exhibited significant antimicrobial activity against the some types of Gram –ve and Gram +ve bacteria [10]. Some maleamate derivatives were also prepared and used for chemical modifications for PVC to obtain antibacterial PVC [11]. PVC has unfortunately low thermal and photostabilities throughout the manufacturing and applications processes. The stabilities were boosted either by some chemical modifications of the chains via substituting the detached labile chlorine atoms with more stabilizing moieties [12–14] or by adding some additives. Some prepared photostabilizers were added to PVC to enhance the photostability of the polymer upon UV exposure during its use, in particular, for outdoor applications [15]. It was found that the antimicrobial properties of PVC has been enhanced by the addition of some amide derivatives of ethylene glycol tetraacetic acid (EGTA) that act as photostabilizers for PVC [16]. Rabie and coworkers have demonstrated that PVC-pyrimidine adduct, prepared by chemical substitution reaction of the PVC chlorine atom with N,N-Dimethyl-N0-(6-oxo-2-thioxo-1H-pyrimidine-4-yl) formamidine and the results exhibited significant antimicrobial activities compared to blank nonmodified PVC [17]. This work aims to prepare a chemically modified form of PVC by its substitution reaction with some 6-amino-2-thioxo-tetrahydropyrimidin-4-one derivatives to enhance photo and thermal stability, mechanical properties as well as the antibacterial activity of the modified PVC to be used in either medical devices or packaging applications.

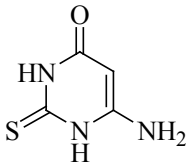
## Experimental

*Materials*

Suspension PVC, with K value of 70, was supplied by Al-Amria Company for Petrochemicals, Alexandria. 6-amino-2-thioxo-tetrahydropyrimidin-4-one (**1**) was supplied from sigma aldrich. All other fine chemicals were of analytical grade and all solvents were purified and distilled before use.

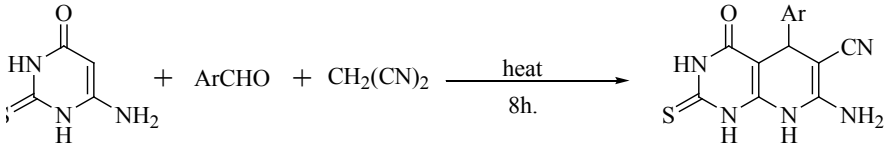
*Preparation of 6-aminopyrimidine derivatives*

6-aminopyrimidine derivatives (**1A-C**) were synthesized according to the following procedures [18]. To a solution of compound **1** (0.01 mol) in dimethyl formamide, DMF, (0.01 mol) of different aromatic aldehydes (**A-C**), and malononitrile were added. The reaction mixture was heated under reflux for 8 h. After completion of the reaction, the reaction mixture was cooled to room temperature then poured on ice water in presence of drops of HCl. The solid product was collected by filtration and purified by recrystallization from ethanol to obtain 6-aminopyrimidine derivatives (**1A-C**), scheme 1 illustrate the preparation of these derivatives.



6-amino-2-thioxo-tetrahydropyrimidin-4-one (**1**)

The three aromatic aldehydes used are: **A**: Benzaldehyd, **B**: 2,5-Dimethoxybenzaldehyd **C**: p-Nitrobenzaldehyde,



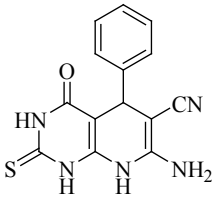

1A, Ar = -$C_6H_5$
1B, Ar = 2,5-$CH_3C_6H$
1C, Ar = 4-$NO_2C_6H_4$

**Scheme 1**

*Analytical data of 6-aminopyrimidine derivatives*

*7-amino-4-oxo -5-phenyl- 2-thioxo-1,2,3,4,5,8-hexahydro-pyrido[2,3-d]pyrimidine-6-carbonitrile (1A):*

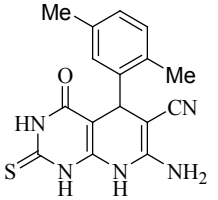
Yellow crystals, mp, 309 °C (EtOH), yield, 79%. IR (KBr, ν, $cm^{-1}$): 3410 ($NH_2$), 3120 (-NH), 3098 (C-H, Aromatic), 2910 (C-H, Aliphatic), 2215 (-CN), 1675 (C=O). $^1$H NMR (400 MHz, DMSO) δ 8.53(s, 1H, NH, $D_2O$ exchangeable); 7.81 (s, 1H, NH, $D_2O$ exchangeable); 7.65 (s, 1H, NH, $D_2O$ exchangeable); 7.14-7.24 (m, 5H, aromatic); 3.52 (s, 1H, -CH); 2.98 (s, 2H, -$NH_2$, $D_2O$ exchangeable).



**1A**

*7-amino-5-(2,5-dimethyl-phenyl)-4-oxo-2-thioxo-1,2,3,4,5,8-hexahydro-pyrido[2,3-d]pyrimidine-6-carbonitrile (1B)*

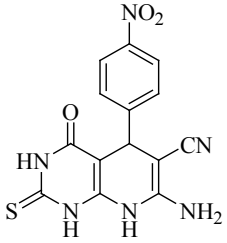
Yellow crystals, mp, 325 °C (EtOH), yield, 76%. IR (KBr, ν, $cm^{-1}$): 3420 ($NH_2$), 3151 (-NH), 3102 (C-H, Aromatic), 2935 (C-H, Aliphatic), 2211 (-CN), 1695 (C=O), 1331(C=S). $^1$H NMR (400 MHz, DMSO) δ 8.39 (s, 1H, NH, $D_2O$ exchangeable); 7.96 (s, 1H, NH, $D_2O$ exchangeable); 7.57 (s, 1H, NH, $D_2O$ exchangeable); 7.00- 6.71(m, 3H, aromatic); 3.71(s, 1H, -CH); 2.90 (s, 2H, -$NH_2$, $D_2O$ exchangeable); 1.90 (s, 3H, -$CH_3$); 1.77 (s, 3H, -$CH_3$).



**1B**

*7-amino-5-(4-nitrophenyl)-4-oxo-2-thioxo-1,2,3,4,5,8-hexahydro-pyrido[2,3-d]pyrimidine-6-carbonitrile (1C)*

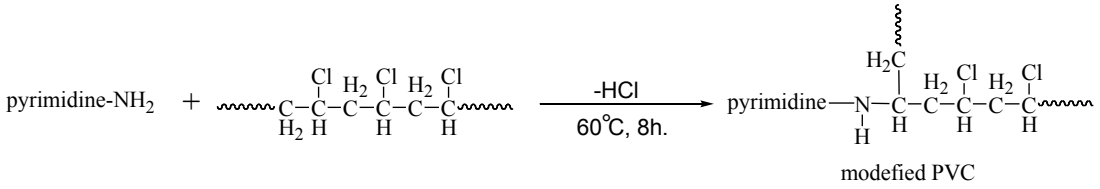
Pale brown crystals, mp, 276 °C (EtOH), yield, 81%. IR (KBr, ν, $cm^{-1}$): 3415 ($NH_2$), 3351 (-NH), 3112 (C-H, Aromatic), 2915 (C-H, Aliphatic), 2212 (-CN), 1685 (C=O) 1555 ($NO_2$). $^1$H NMR (400 MHz, DMSO) δ 11.53(s, 1H, NH, $D_2O$ exchangeable); 7.96 (s, 1H, NH, $D_2O$ exchangeable); 7.79 (s, 1H, NH, $D_2O$ exchangeable); 7.51, 7.49 (dd, *J = 7.50*, 2H, aromatic); 7.34, 7.32 (dd, *J = 7.33*, 2H, aromatic); 3.35 (s, 1H, -CH); 2.90 (s, 2H, -$NH_2$, $D_2O$ exchangeable).



**1C**

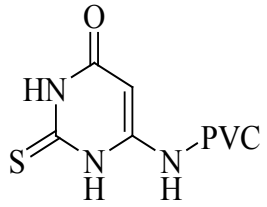
*Synthesis of 6-aminopyrimidine derivatives modified PVC*

Synthesis of modified substituted PVC was performed by taking 0.05 mol of each prepared 6-aminopyrimidine derivative with 0.10 mol of PVC in freshly distilled tetrahydrofuran (THF) and refluxed at 60°C using water bath for 8 h. A pale yellow precipitate of modified PVC was precipitated and filtered. The product was purified by dissolving in THF and reprecipitated in cold methanol. The modified 6-aminopyrimidine derivatives modified PVC samples were, **PVC-1, PVC-1A**, **PVC-1B** and **PVC-1C**, and scheme 2 represents the preparation of the 6-aminopyrimidines modified PVC.




**Scheme 2**

*Analytical data of 6-aminopyrimidine derivatives modified PVC*

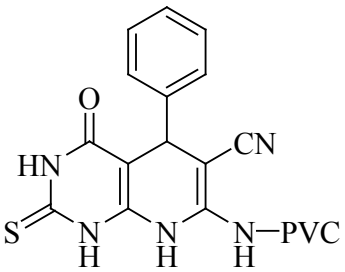


***6-amino-2-thioxo-tetrahydropyrimidin-4-one (PVC-1).***

Pale yellow powder, yield, 75%, IR (KBr, ν, $cm^{-1}$): 3396 (-NH); 2970 (C-H aliphatic); 1772 (C=O); 1671&1426 (C=C aromatic); 1331(C=S). $^1$H NMR (400 MHz, Chloroform) δ 12.91 (s, 1H, NH); 11.39 (s, 1H, NH); 6.91 (s, 1H, -CH); 4.63 (s, 1H,CH-NH); 4.41(s, 1H,NH -CH); 2.46-1.98 (m, PVC protons).

*- 7-amino-4-oxo -5-phenyl- 2-thioxo-1,2,3,4,5,8-hexahydro-pyrido[2,3-d]pyrimidine-6-carbonitrile-PVC (PVC-1A):*

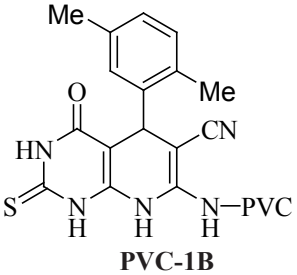
Yellow powder, yield, 72%, IR (KBr, ν, $cm^{-1}$): 3304(NH); 3226(C-H aromatic); 2971(C-H aliphatic); 2213(CN); 1697(C=O); 1626&1434(C=C aromatic); 1331(C=S). $^1$H NMR (400 MHz, DMSO) δ 12.75(s, 1H, NH, $D_2O$ exchangeable); 12.09 (s, 1H, NH, $D_2O$ exchangeable); 7.26(s, 1H, NH, $D_2O$ exchangeable); 7.41-7.26 (m, 5H, aromatic); 4.43 (s, 1H,-NH-CH); 4.31(s, 1H, -CH-NH-, , $D_2O$ exchangeable); 3.31 (s, 1H, -CH); 2.50-2.19 (m, PVC protons).




**PVC-1A**

*-7-amino-5-(2,5-dimethyl-phenyl)-4-oxo-2-thioxo-1,2,3,4,5,8-hexahydro-pyrido[2,3-d] pyrimidine-6-carbonitrile (PVC-1B)*

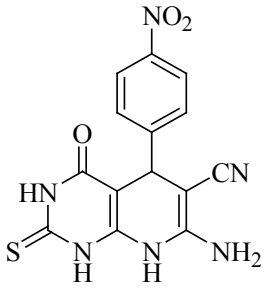
Yellow powder, yield, 82%. IR (KBr, ν, cm-1): 3306 (NH); 3216 (C-H aromatic); 2967 (C-H aliphatic); 2215 (CN); 1692 (C=O); 1624&1425 (C=C aromatic); 1331(C=S). 1H NMR (400 MHz, DMSO): δ 12.78 (s, 1H, NH, D2O exchangeable); 12.22 (s, 1H, NH, D2O exchangeable); 7.74 (s, 1H, NH, D2O exchangeable); 7.02- 6.73 (m, 3H, aromatic); 4.50 (s, 1H,-NH-CH); 4.34 (s, 1H, -CH-NH-, D2O exchangeable); 3.71(s, 1H, -CH); 3.63 (s, 3H, -CH3); 3.33 (s, 3H, -CH3); 2.51- 1.25 (m, PVC protons).




**PVC-1B**

*-7-amino-5-(4-nitrophenyl)-4-oxo-2-thioxo-1,2,3,4,5,8-hexahydro-pyrido[2,3-d]pyrimidine-6-carbonitrile (PVC-1C)*

Yellow powder, yield, 77%, IR (KBr, ν, cm-1): 3296 (NH); 3219 (C-H aromatic); 2967 (C-H aliphatic); 2216 (CN); 1694 (C=O); 1624&1434 (C=C aromatic); 1331 (C=S). 1H NMR (400 MHz, DMSO): δ 12.82(s, 1H, NH, D2O exchangeable); 12.18 (s, 1H, NH, D2O exchangeable); 7.81 (s, 1H, NH, D2O exchangeable); 7.51, 7.49 (dd, J = 7.50, 2H, aromatic); 7.34, 7.32 (dd, J = 7.33, 2H, aromatic); 4.52 (s, 1H,-NH-CH); 4.35 (s, 1H, -CH-NH-, D2O exchangeable); 3.33(s, 1H, -CH); 2.46- 2.24 (m, PVC protons).




PVC-**1C**

*Preparation of PVC samples for UVirradiation*

600 mg of modified PVC in 100 mL of freshly distilled THF were stirred in absence and in the presence of the prepared 6-aminopyrimidine derivative in addition to a PVC sample containing 2% by weight of 2-hydroxy-4-(octyloxy)-phenyl-benzophenone as reference UV absorber (RUVA). The solution was then poured into a Petri dish of 18.5 cm in 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 then washed with diethyl ether to remove the THF residue and was 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.

*Photodegradation*

A high-pressure mercury lamp (Philips HPK 125 W) was used as a light source. The photocell applied consists of a reaction chamber in which the PVC film is placed and exposed to the light source at a distance of 30 cm. The carrier gas ($N_2$ 99% purity) passes through this reaction chamber which is covered with a metal ring. The second chamber is connected to a water bath to keep the reaction temperature at 25°C.

*Quantitative determination of HCl*

The evolved HCl was measured through the most sensitive method by continuous recording of the electrical conductivity. This method was described by Braun et al [19]. The amount of HCl evolved during UV irradiation of the PVC film is determined by applying the equation derived by Braun and Thallmaier [20]

$$X = 1/R \cdot 1/q \cdot M_{HCl} \cdot V/\Lambda\alpha$$

Where X is the amount of HCl evolved (in g), 1/R is the measured conductivity ($\Omega^{-1}$), $M_{HCl}$ is the molar mass of HCl (g $mol^{-1}$), 1/q is the cell constant ($cm^{-1}$), V is the cell volume ($cm^3$) Λαis the equivalent conductivity of HCl at 25°Cat infinite dilution (379 $cm^2mol^{-1}\Omega^{-1}$).α

*Preparation of PVC samples for thermal degradation*

200 mg of 6-aminopyrimidine modified PVC 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 [20]. The samples were thermally treated under N2 atmosphere and the evolved HCl was determined conductometrically.

*Preparation of PVC Films for Physicomechanical Measurements*

For physicomechanical measurements, modified PVC films were prepared as described before in presence of 20% by weight Di(2-ethylhexyl)phthalate (DEHP) as plasticizer. Three specimens were used for each test. The sample dimensions were about 40mm×6 mm×0.12 mm. Mechanical properties of the modified polymer films were measured on a Shimadzu Autograph in air at room temperature.

*Instrumentation*

All melting points are uncorrected and measured using Electro-Thermal IA 9100 apparatus (Shimadzu, Japan). Infrared spectra were recorded as potassium bromide pellets on a Perkin-Elmer 1650 spectrophotometer, National Research Centre, Cairo, Egypt. 1H-NMR spectra were recorded 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.

*Thermogravimetric analysis*

Thermogravimetric analysis (TGA) measurements were made with a Shimadzu TG-50 H thermal analyzer system. Samples were heated from 0 to 500°C in a platinum pan at a heating rateof 10°C $min^{-1}$ in a nitrogen atmosphere (30 mL $min^{-1}$).

*Antibacterial assay*

The synthesized compounds were screened in vitro for their antimicrobial activity against *Escherichia coli* (Gram -ve bacteria), *Staphylococcus aureus* (Gram +ve bacteria), *Aspergillus flavus* and *Candida albicans* as fungi by agar diffusion method [21]. 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 0.1mL of the synthesized compounds dissolved in 1mL 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. Tetracycline (10 mg/mL) and Amphotericin B (10 mg/mL) were used as standard for antibacterial and antifungal activity respectively.

## Results and Discussion

*Synthesis of 6-aminopyrimidine modified PVC*

Chemical modification of PVC using some 6-aminopyrimidine derivatives and confirmation of their chemical structures using FTIR, and $^1$HNMR spectroscopy have been performed.

For PVC-1, the IR spectral data showed the presence of two characteristic peaks at 3396 and 2970 $cm^{-1}$ for –NH and aliphatic –CH respectively, whereas the IR peaks that appeared at 1772, 1671&1426, and 1331 $cm^{-1}$ are related to –C=O, –C=C (aromatic) and –C=S.

$^1$HNMR of this sample showed the presence of the two –NH of the pyrimidine ring as singlet protons at δ: 12.91 and 11.39 ppm respectively, while the singlet proton that appeared at δ: 6.91 ppm is of the –CH pyrimidine ring. There are also two singlet protons that due to –CH of PVC chain and the free side chain –NH and they appeared at δ: 4.63 and 4.41 ppm respectively. The multiplet protons that appeared at δ: 2.46-1.98 ppm are due to aliphatic –CH and $–CH_2$ of PVC chains.

IR and $^1$HNMR spectral data of **PVC-1A** illustrates its chemical structure. The IR peaks that appeared at 3304, 3226, and 2971 $cm^{-1}$ are due to the –NH, –CH (aromatic), and –CH (aliphatic) respectively. The IR peaks of –CN and –C=O have appeared at 2213 and 1697 $cm^{-1}$ while the aromatic –C=C and –C=S have IR bands at 1626&1434 and 1331 $cm^{-1}$ respectively. $^1$HNMR of **PVC-1A** clarifies the presence of proton signals at δ: at 12.75, 12.09, and 7.26 ppm are due to the three –NH of both pyrimidine and pyridine rings respectively. The presence of the phenyl ring is confirmed by the multiplet five protons that appeared at δ: 7.41-7.26 ppm. The two singlet protons that appeared at δ: 4.43 and 4.31 ppm are related to the –CH of PVC chain attached to free –NH and the other is for this side chain –NH that attached to PVC whereas the pyridine ring –CH proton appeared at 3.31 ppm. Multiplet protons of PVC chains have appeared at 2.50-2.19 ppm.

Regarding the modified PVC sample **PVC-1B**, there are three characteristic IR peaks at 3306, 3216 and 2967 $cm^{-1}$ which are related to –NH, –C-H (aromatic) and –C-H (aliphatic) respectively. The IR bands of –CN and –C=O groups have appeared at 2215 and 1692 $cm^{-1}$ whereas the aromatic –C=C at 1624&1425 and –C=S at 1331. $^1$H NMR of the same sample showed the three singlet protons that appeared at δ: 12.78, 12.22 and 7.74 ppm and related to the pyrimidine and pyridine rings respectively. The three singlet hydrogen protons of the phenyl ring have appeared as multiplet at δ: 7.02-6.73 ppm, whereas the other two singlets that appeared at 4.50 and 4.34 ppm are due to the –CH of PVC bonded to –NH and the free –NH. The pyridine –CH singlet proton appeared at δ: 3.71 ppm. The two methyl substituents are confirmed by the presence of one singlet three protons at δ: 3.63 and the second at δ: 3.33 ppm. PVC chains multiplet protons have appeared at δ: 2.51-1.25 ppm.

The chemical structure of the third modified PVC sample, **PVC-1C** is confirmed by both IR and $^1$HNMR spectral data. The characteristic IR peaks that appeared at 3296, 3219 and 2967 $cm^{-1}$ are related to –NH, –C-H (aromatic) and –C-H (aliphatic) respectively. The IR bands of –CN and –C=O groups have appeared at 2216 and 1694 $cm^{-1}$ whereas the aromatic –C=C at 1624&1434 and –C=S at 1331. $^1$H NMR of **PVC-1C** sample showed three singlet protons appeared at δ: 12.82, 12.18 and 7.81ppm and they are related to the pyrimidine and pyridine rings respectively. There are two doublet of doublet proton groups of the phenyl ring, the first one at δ: 7.51, 7.49 ppm with J equal to 7.50 where the second at δ: 7.34, 7.32 and J value of 7.33. Two singlets have appeared at 4.52 and 4.35 ppm and they are due to the –CH of PVC bonded to –NH and the –NH itself. The pyridine –CH singlet proton appeared at δ: 3.33 ppm. PVC chains multiplet protons have appeared at δ: 2.46-2.24 ppm.

So, both IR and $^1$HNMR spectroscopic data of the 6-aminopyrimidine derivatives modified PVC confirmed the incorporation of the 6-aminopyrimidine moiety in the backbone chain of PVC.

*Rate of dehydrochlorination of photodegraded 6-aminopyrimidines modified PVC*

The rate of dehydrochlorination of photodegraded 6-aminopyrimidine derivatives modified PVC samples at 25°C under $N_2$ was measured conductometrically as described in the experimental part. The results of blank PVC as well as for sample and that stabilized with 2% by weight of 2-hydroxy-4-(octyloxy)-phenyl-benzophenone as reference UV absorber (RUVA) were also given for comparison. The results of photostability of the investigated PVC samples are shown in Figure 1. The results clearly show that the rate of dehydrochlorinatin increases as a function of the irradiation time. The higher photostabilizing efficiency was observed for 6-aminopyrimidines modified PVC samples when compared to blank PVC and that stabilized with 2% by weight of RUVA. This could be illustrated mainly on the basis of the observed well-defined longer induction periods, *Ts* values, during which no detectable amounts of hydrogen chloride were liberated. The lower rates of dehydrochlorination during either the first or the later stages of the photodegradation process also indicates the photostabilitiy of the modified PVC samples. The recorded $T_S$ values of the modified PVC samples in comparison with blank PVC and that stabilized with 2% by weight of RUVA are given

in Table 1. These Results clearly reveal the higher induction periods of all modified PVC samples using the 6-aminopyrimidine (**1**) and its prepared derivatives **1A**, **1B**, and **1C**. It is observed that the $T_S$ value of **PVC-1** is almost 3 and 1.4 times higher than values obtained for the blank PVC sample and RUVA stabilized one respectively. Higher $T_S$ values are observed for **PVC-1A**, **PVC-1B**, and **PVC-1C** samples and reached 6, 7, and 10.7, respectively times the blank PVC sample. The obtained results indicated that the **PVC-1C** sample is characterized by the highest photostability among the other investigated derivatives.

*Rate of dehydrochlorination of thermally degraded 6-aminopyrimidine modified PVC*

The thermal stability of blank PVC, PVC/3% by weight of Ca-Zn stearate as reference heat stabilizer and the four 6-aminopyrimidines modified PVC samples was carried out at 180°C under nitrogen atmosphere, and the rate of dehydrochlorination was determined conductometrically. The results of rate of dehydrochlorination of thermally degraded modified PVC samples are represented in Figure 2, and Table 2 showed the *Ts* values. It is obvious that the rate of dehdrochlorination increases with increase of the degradation time. The investigated modified PVC samples show higher thermal stability when compared with the blank PVC sample and that in presence of 3% Ca-Zn stearate. A higher thermal stability is clearly observed for the modified sample PVC-**1C**, and this is illustrated by the observed lower rates of dehydrochlorination than that of other modified samples. The *Ts* values are also taken as another proof for the thermal stability of the modified PVC samples. The *Ts* values recorded for blank PVC and that stabilized with reference heat

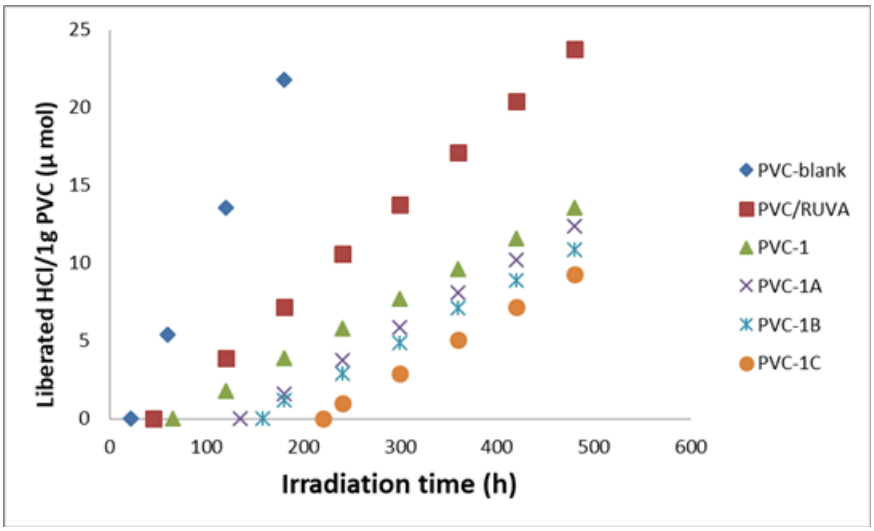



**Fig. 1: Rate of dehydrochlorination of 6-aminopyrimidine derivative modified PVC photodegraded at 25°C under $N_2$ in comparison with blank PVC and PVC/2% by weight of 2-hydroxy-4-(octyloxy)- phenyl-benzophenone as reference UV absorber (RUVA)**

**TABLE 1: Values of induction periods (Ts) of photodegraded 6-aminopyrimidines modified PVC samples**

| Material | Ts/min |
|---|---|
| Blank PVC | 22 |
| PVC/RUVA | 45 |
| **PVC-1** | 65 |
| **PVC-1A** | 134 |
| **PVC-1B** | 158 |
| **PVC-1C** | 236 |

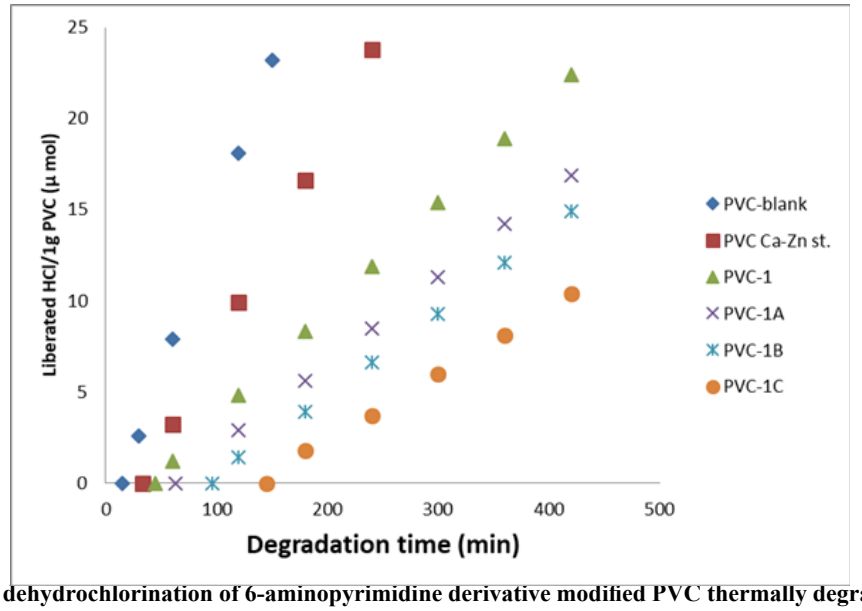



**Fig. 2: Rate of dehydrochlorination of 6-aminopyrimidine derivative modified PVC thermally degraded at 180°C under N2 in comparison with blank PVC and PVC/2% by weight of 3% by weight Ca-Zn stearate as reference heat stabilizer**

stabilizer were 15 and 33 minutes respectively, whereas these values reached of 45, 63, 96, and 144 minutes for the modified samples **PVC-1**, **PVC-1A**, **PVC-1B** and **PVC-1C** respectively.

So, it is obvious that the modified PVC sample **PVC-1C** exhibited the highest stability against either photo or thermal degradation. This may be due to the substituent effect of the nitro group in the phenyl ring with its withdrawing properties. This effect may increase the electron density on the system which in turn increase the structural stabilization of the whole compound and the covalently bonded PVC chain with the 6-aminopyrimidine derivative moiety.

*Thermogravimetric analysis*

Thermogravimetric data for blank PVC, PVC stabilized with Ca-Zn stearate as heat stabilizers and 6-aminopyrimidine derivatives modified PVC samples are shown in Table 3. It is observed that the introduction of the 6-aminopyrimidine derivatives as substituents in the main backbone chains of PVC improved the thermal stability of modified polymer samples. The recorded initial decomposition temperature (IDT) of **PVC-1**, **PVC-1A**, **PVC-1B** and **PVC-1C** are; 226°C, 239°C, 254°C and 278°C respectively, where the IDT of the blank PVC and that stabilized with Ca-Zn stearate was found to be 180°C and 214°C respectively. Results of Table 3 clearly reveals the higher thermal stability of modified PVC samples when compared to both the blank sample and that stabilized with Ca-Zn stearate heat stabilizer. At 300 °C the blank PVC lost 39% of its mass, while PVC stabilized with Ca-Zn stearate lost 21% of its mass. On the other hand, at the same temperature the four modified PVC samples, **PVC-1**, **PVC-1A**, **PVC-1B** and **PVC-1C** lost 13, 9, 5, 0% of their masses respectively. This thermal behavior is also shown for elevated degradation temperatures. From the aforementioned results, it was clear that the incorporation of the 6-aminopyrimidine derivatives as substituents in the PVC chains enhance the thermal stability of obtained modified polymer.

*Physicomechanical properties of 6-aminopyrimidie derivatives modified PVC*

For this investigation, blank PVC, PVC blended with 2% of RUVA, and the 6-aminopyrimidines modified PVC samples are casted from THF in presence of 20% by weight of Di(2-ethylhexyl) phthalate (DEHP) as plasticizer.

Table 4 shows the physicomechanical properties of all investigated PVC samples after UV irradiation for 4 and 8 hours.The values of both stress and strain at yield of blank PVC after UV irradiation of 4h were 28.5 and 95.4 MPa, respectively. These values were highly decreased after 10h of UV irradiation and reached 7.8 and 25.2 respectively. This behavior could be attributed to the acting stress that leads to chain scission of PVC chains by the effect of UV irradiation for prolonged exposure time. It is noticed also that

**TABLE 2: Values of induction periods (Ts) of thermally degraded 6-aminopyrimidines modified PVC samples**

| Material | Ts/min |
|---|---|
| Blank PVC | 15 |
| PVC/RUVA | 33 |
| **PVC-1** | 45 |
| **PVC-1A** | 63 |
| **PVC-1B** | 96 |
| **PVC-1C** | 144 |

**TABLE 3: Thermogravimetric analysis of blank PVC and 6-aminopyrimidine derivatives modified PVC**

| T(°C) | PVC blank | PVC-Ca-Zn st. | PVC-1 | PVC-1A | PVC-1B | PVC-1C |
|---|---|---|---|---|---|---|
| **IDT(°C)** | **180 °C** | **214** | **226** | **239** | **254** | **278** |
| **T(°C)** | **Mass loss % of PVC** | **Mass loss % of PVC-Ca-Zn st.** | **Mass loss % of PVC-1** | **Mass loss % of PVC-1A** | **Mass loss % of PVC-1B** | **Mass loss % of PVC-1C** |
| 200 | 7 | 0 | 0 | 0 | 0 | 0 |
| 250 | 14 | 10 | 7 | 4 | 0 | 0 |
| 300 | 39 | 21 | 13 | 9 | 5 | 0 |
| 350 | 51 | 32 | 18 | 12 | 8 | 7 |
| 400 | 63 | 40 | 29 | 22 | 16 | 13 |
| 450 | 71 | 53 | 36 | 29 | 22 | 18 |
| 500 | 79 | 61 | 49 | 37 | 31 | 24 |

**TABLE 4: Physicomechanical properties of blank PVC and 6-aminopyrimidines derivatives modified PVC after UV-irradiation**

| Sample | Stress at yield | Strain at yield | Stress at rupture | Strain at rupture |
|---|---|---|---|---|
| | **σ B ($MP_a$)** | **ΣB%** | **σ R ($MP_a$)** | **ΣR%** |
| | **σ B** | | **σ R** | |
| Blank PVC | | | | |
| 4h | 28.5 | 95.4 | 15.8 | 108.1 |
| 10h | 7.5 | 25.2 | 2.1 | 37.6 |
| PVC-1 | | | | |
| 4h | 31.7 | 109.8 | 23.9 | 117.8 |
| 10h | 8.7 | 51.6 | 16.1 | 93.5 |
| PVC-1A | | | | |
| 4h | 42.4 | 116.3 | 30.7 | 125.2 |
| 10h | 26.8 | 102.9 | 20.9 | 111.6 |
| PVC1B | | | | |
| 4h | 57.3 | 121.2 | 41.3 | 132.5 |
| 10h | 41.4 | 109.6 | 31.1 | 121.7 |
| PVC-1C | | | | |
| 4h | 65.6 | 130.2 | 47.9 | 138.9 |
| 10h | 52.1 | 114.1 | 38.6 | 127.2 |

there is an enhancement for the physicomechanical properties of PVC sample stabilized with the RUVA in the form of improvement of both the tensile strength and the flexibility of this sample. For modified PVC samples with the prepared three 6-aminopyrimidine derivatives, a significant improvement in both the tensile strength and the elongation of the investigated samples are clearly observed and the **PVC-1C** sample showed the best behavior. This may be attributed to the presence of the 6-aminopyrimidine derivatives as a substituent in the main backbone PVC chains. These results could be explained on the basis of the effect of the 6-aminopyrimidine moiety which substitutes the detached labile chlorine atom that lead to a decrease in the rate of dehydrochlorination to get retained good mechanical properties. Furthermore, the large volumes of the substituents may act as displacers between PVC chains and this prevent the dehydrochlorination process, to some extent, as well as a decrease rates of crosslinking which in turn may maintain the mechanical properties of the polymeric matrix. The observed improved results of physicomechanical properties of modified PVC samples are matched well with all above obtained investigations.

*Antimicrobial activity for 6-aminopyrimidie derivatives modified PVC*

According to Table 5, blank PVC has no high antibacterial or antifungal activity; while 6-aminopyrimidine modified PVC samples exhibited significant antimicrobial activity with respect to the used reference antimicrobial agents. The two kinds of bacterial strains used in this study are, *E. coli* (G -ve) and *S. aureus* (G +ve), whereas *Aspergillus flavus* and *Candida albicans* are the fungi. The antibacterial activity of the modified polymers **PVC-1**, **PVC-1A**, **PVC-1B**, **PVC-1C**, reaches 37, 48, 63 and 92.6% against the bacterial strain *S. aureus* as Gram +ve type when compared to the reference antibacterial agent. Regarding the *E. coli* Gram –ve bacteria the inhibitory effect reaches 34.4, 43.8, 50 and 84.3% for the same investigated samples. The higher antibacterial activity of the modified sample, **PVC-1C** can be illustrated on the basis of the presence of the nitro-phenyl substituent in the 6-aminopyrimidine moiety. The high electron withdrawing power of this substituent may increase the positive charge on investigated compound and this can facilitate the electrostatic interaction between the positively charged compound and the negatively charged cell membrane of bacteria [22-23].

The antifungal activity of the modified polymers was performed against two kinds of Fungi, *A. flavus* and *C. albicans*. It was found that all modified polymers exhibited high antifungal activities against the two tested fungi when compared to the blank PVC sample.

## Conclusion

Chemical modification of PVC has been carried out by its substitution reaction with 6-amino-2-thioxo-tetrahydropyrimidin-4-one (**1**) and three of its derivatives (**1A-C**). The chemical structures of the modified PVC samples was confirmed using FTIR and $^{1}$HNMR spectroscopic analyses. Photostability of the modified PVC were investigated by following the rates of dehydrochlorination of the 6-aminopyrimidine derivatives modified PVC samples conductometrically in comparison with both blank PVC and that stabilized with

**TABLE 5. In vitro antimicrobial activity by agar diffusion method of 6-aminopyrimidines derivatives modified PVC**

| Sample | Inhibiation zone diameter (mm/mg sample) | | | |
|---|---|---|---|---|
| | S. aureus | E. coli | Aspergillus flavus | Candida albicans |
| | Gram +ve | Gram -ve | | |
| **Tetracycline** | 27 | 32 | - | - |
| **Amphotericin B** | - | - | 20 | 18 |
| Blank PVC | 11 | 10 | 2 | 3 |
| PVC-1 | 10 | 11 | 8 | 9 |
| PVC-1A | 13 | 14 | 11 | 12 |
| PVC-1B | 17 | 16 | 13 | 12 |
| PVC-1C | 25 | 27 | 16 | 15 |

2-hydroxy-4-(octyloxy)-phenyl-benzophenone as reference UV absorber. The results exhibited the higher photostability of the modified samples by the observed longer *Ts* values and lower rates of dehydrochlorination of the investigated samples. Thermal stability as well as physicomechanical properties of all modified PVC samples have also been studied. All modified PVC samples exhibited enhanced photo and thermal stability as well as mechanical properties when compared to the blank PVC sample. Antimicrobial properties of the 6-aminopyrimidines modified PVC samples were explored against Gram +ve bacteria (*Staphylococcus aureus*), Gram -ve bacteria *(Escherichia coli*) as well as *A. flavus* and *C. albicans* as fungi. However, incorporation of 6-aminopyrimidine derivatives to the PVC backbone chains enhanced their inhibitory effect against the microorganisms under test when compared to the blank PVC.

*Competing Interests*

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

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