Potential Effect of Ammonium Chloride on the Optical Physical Properties of Polyvinyl Alcohol

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ABSTRACT

The preparation of facile convertible and degradable polymers has received great attention due to their applications in the fields of environmental protection, pharmaceutical industry, and public health. In this work, five samples were prepared by adding the ammonium chloride salt to the polyvinyl alcohol polymer in various ratios including 0.4, 0.8, 1.5, 3, and 6%. The photo-sensitivity study was conducted on the prepared samples utilizing UV light at 356 nm at the following time intervals: 0, 7, 14, 28, and 42 hours. The degradation process was followed up spectroscopically using UV/Vis and FTIR spectrophotometers. This was carried out by calculating many physical and chemical parameters, which are: the absorbance, functional group coefficient, optical partition, optical segmentation rate constant, average molecular weight, average quantum yield of the main chain scission, and degree of partition. The results indicated that the degradation rate constant and the growth factors of the carbonyl and hydroxyl functional groups were directly proportioned to the adding concentration of ammonium chloride salt as well as the time of irritation. It is concluded that the addition of this salt may prevent the polymer from undergoing the polymerization process, reduce the polymeric half-life, and protect the environment from the risk arising from the polymer's stability. Also, this environmentally friendly salt may be considered as a potential additive to improve the applications of polyvinyl alcohol polymer in various fields.

Keywords: Polyvinyl alcohol, Ammonium chloride, Photo-sensitivity, Stability study, Polymer.

INTRODUCTION

Polymers are complex and large molecular weight products that have played requisite functions in many life-concerned fields including those contributed to pharmacy (1). The pharmaceutical implementations of polymers range from their utilization as an additive in the formulation of different dosage forms to their role as a carrier for the selective drug delivery systems (2–6).

The use of different polymers in a huge amount for many industrial purposes resulting in the accumulation of a vast quantity of these polymers as waste products (7). The long half-lives of these waste products as well as their thermal- and photo-stabilities construct an interesting environmental issue. Although the stability of many currently used polymers have been extensively studied under the conditions of the laboratory (8), the informative data concerning the polymeric stability under the environmental conditions are limited (9).

Polyvinyl alcohol (PVAl) is an industrial polymer with variable aqueous solubility that depends on the applied temperature and the polymeric molecular weight (10). Because of its chemical, thermal, and electric stabilities as well as its safety and improved mechanical properties (11), PVAl has been employed in the diverse pharmaceutical intentions (12). The presence of alcoholic hydroxyl groups in the chemical structure of PVA permits the formation of two types of hydrogen bonding. The first one is the intramolecular type that forms within the polymer frame while the other belongs to the intermolecular type and generates between the polymer and the water molecules (13). This property supports the utilization of PVA in many industrial aspects such as the selective absorption and adsorption of gases, metals, and ions (14,15).

As many other polymers, PVAl has attracted a mounting interest and there are continuous attempts to improve its physicochemical properties. Many of these attempts have been directed toward the conjugation of PVAl with other currently-available polymers and its trans-formulation as nanoparticles (16). In the literature, there are many reports documented the utilization of inorganic salts to improve the physicochemical properties of several natural and synthetic polymers (17). In more specific words, the interaction of some inorganic salts with a specific polymer or mixture of polymers has resulted in the improvement of polymeric industrial and practical feasibilities (18).

Ammonium chloride (NH_4Cl) is an interesting inorganic salt which can improve, when mixed with several types of polymers, many polymeric physicochemical properties such as mechanical, electrochemical, and electrical features (19). It is also reported that these improvements are depended on the concentration of the employed salt (20). Also, this salt can be considered as a potent proton donor since it has four protons attached to a positively-charged nitrogen. One of these protons is freely moved alongside on the polymeric surface improving the mechanical and electrochemical properties of the utilized polymer (21–23).

Based on the best of our knowledge, there is no informative data concerning the use of NH_4Cl to improve the optical physical properties of PVAl. Accordingly, this work aims to investigate this issue.

MATERIALS AND METHODS

Preparation of the samples

Five types of PVAl/NH_4Cl samples were prepared via the solvation and casting methods. This was carried out by dissolving PVAl in a minimum amount of ions-free water at 75-80°C, adding the NH_4Cl to achieve different concentrations of the salt (0.4, 0.8, 1.5, 3, and 6 w/w%), and mixing thoroughly to eliminate any air bubbles. The mixture was cast on the glass molds and let the treated plates to dry at the laboratory temperature. The resultant plates

were covered eventually by films of the polymer/salt mixture in the thickness of 80 ± 5 μm (24).

Spectroscopical study

The prepared plates were irradiated by using a UV light lamp operated at the wavelength of 365 nm and intensity (I_O) of 1.5×10^{-8} Ein.dm^{-3}s^{-1}. This treatment was achieved at a laboratory temperature at different time intervals (0, 7, 14, 28, and 42 hr). The prepared plates were placed in front of the UV lamp in a vertical position with continuous movement up and down to ensure that all the plate's surface was exposed uniformly to the light. Then, the mixture was removed from the treated plates by scratching and studied via FTIR (Bruker-Alpha ATR-FTIR spectrophotometer) in the range of 400-4000 cm^{-1}. The studied bands including those attributed to the carbonyl group at 1740 cm^{-1} and the hydroxyl group at 3350 cm^{-1} (25). The intensities of these bands were utilized to quantitatively calculate the influence of the salt on the optical properties of the treated polymer using the following law of the band index (25):

$Is = As/Ar$

Where As represents the absorbance of the band after the treatment, Ar represents the absorbance of the band before the treatment, and Is represents the functional group coefficient.

Based on the Beer-Lambert law, the values of transmittance (T%) were converted to those of the absorbance using the following mathematical formula:

$A = \log100 / T\%$

$A = 2-\log\%$

The optical partition of the prepared samples was followed up spectroscopically via a UV-Vis spectrophotometer to calculate the optical segmentation rate constant by applying the following mathematical relationship:

$\ln (A_\infty - A_t) = \ln (A_\infty - A_o) - k_d\, t$

Where A_∞ and A_t represent the absorbances at infinite and certain times, respectively. A_o and A_∞ represent the absorbances prior to the treatment and at infinitive time, respectively. k_d represents the optical segmentation rate constant while t represents the time which measured in seconds. By plotting the graph of $\ln (A_\infty - A_t)$ versus time (t), the resulted straight line represents the first order kinetics of the accelerated photo-degradation and the slop of this line represented the k_d (26).

Molecular weight measurement study

The average molecular weights of the prepared samples were calculated depending on their intrinsic viscosity by using the Mark-Houwink equation (27):

$[\eta] = K\, (M_V)^a$

where $[\eta]$ is the intrinsic viscosity, M_V is the average molecular weight, and the values of the constants a and K of the polymer dissolved in the water are 0.76 and 2.0×10^{-4}, respectively.

The quantum yield of main chain scission (Φ_{cs}), degree of partition (α), and the average of the quantum yield of main chain scission (S) were calculated from the following relationships (28):

$1/P_t - 1/P_0 = (m\Phi_{cs} \times I_0 \times t) / WN$

$\alpha = 1/P_t - 1/P_0$

$S = \alpha P_0$

Where W: the weight of irradiated sample, m: molecular weight of the untreated polymer, N: Avogadro number, I_0: the intensity of the absorbed light. While P_t, P_0: numerical average degree of polymerization before and after irradiation at time t, respectively.

RESULTS AND DISCUSSION

The non-toxic nature, cheapness, and commercial availability of NH$_4$Cl (29) encouraged the work team to utilize it in an attempt to modify the photo-stability of PVAl.

The results represented the absorbance values of pure PVAl sample and those acquired from the addition of different percentages of NH$_4$Cl calculated at 278 nm by using UV-Vis spectrophotometry are shown in Table 1. These results indicated that the absorbance at the aforementioned wavelength increases as the percentage of salt addition is increased (30). The growth in the absorbance values indicated that the addition of the salt may increase the breakdown of the polymeric framework by destabilizing the hydrogen bonding (31). The presence of salt may be disorganized the inter- and intra-hydrogen bonds found between the water molecules and the polymer and within the polymeric frame, respectively. This disturbance may attribute to the participation of the salt in the formation of the aforementioned two types of hydrogen bonding (32).

Table 1: The absorbance values of pure PVAl sample as well as those containing NH$_4$Cl salt calculated at 278 nm and measured by using UV-Vis spectrophotometer.

Sample (w/w%)	Absorbance (A_t)				
	Time (hr)				
	0	7	14	28	42
PVAl	0.099	0.148	0.223	0.297	0.372
PVAl + 0.4 % NH$_4$Cl	0.110	0.283	0.376	0.495	0.594
PVAl + 0.8% NH$_4$Cl	0.118	0.356	0.445	0.594	0.743
PVAl + 1.5 % NH$_4$Cl	0.123	0.445	0.619	0.789	0.934
PVAl + 3 % NH$_4$Cl	0.126	0.572	0.745	0.965	1.188
PVAl + 6% NH$_4$Cl	0.148	0.707	0.891	1.202	1.429

The results shown in Table 1 are confirmed by those represented in Table 2 and displayed in Figure 1. In Table 2, the value of the optical segmentation rate constant (kd) growths as the w/w% of the adding salt is increased. This is clarified by observing the logarithmic relationship depicted in Figure 1 between the absorbance values of the prepared sample which has the highest % of the adding salt (6%) and the irritation time.

Table 2: The values of k_d for the prepared samples.

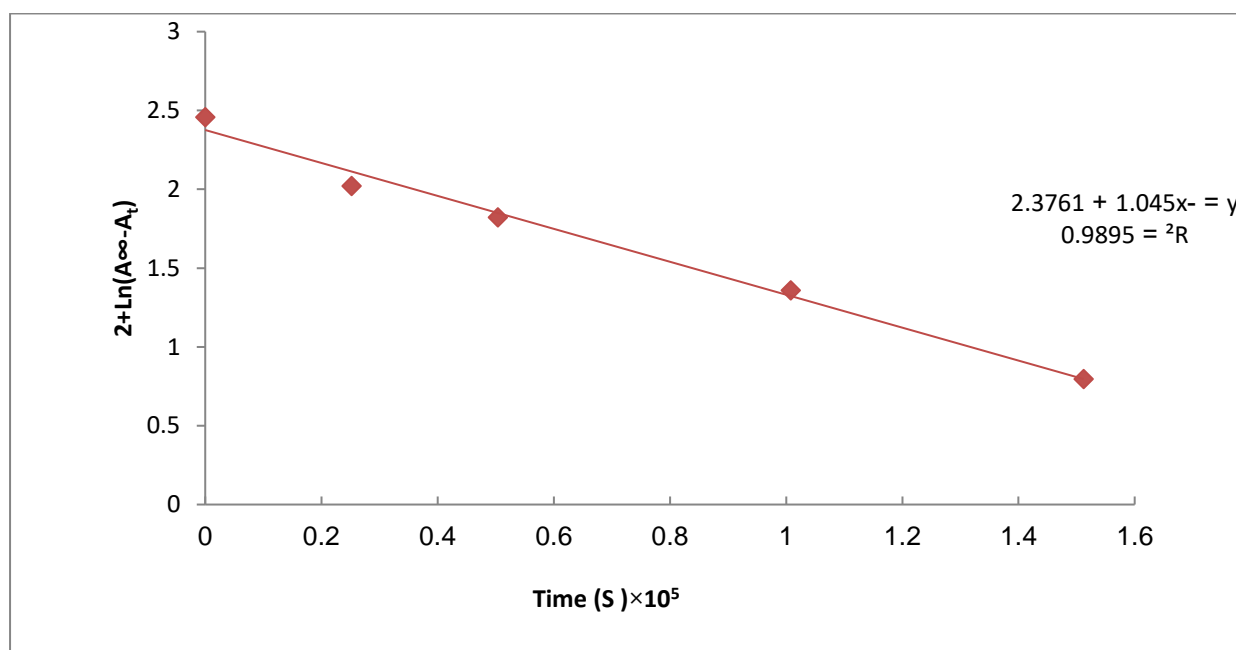| Concentration w/w%	Optical segmentation rate constant $k_d \times 10^{-5}$ (s^{-1})
0.4	0.606
0.8	0.701
1.5	0.826
3	0.937
6	1.045

Figure 1: The logarithmic relationship between the absorbance values of the prepared sample which has the highest % of the adding salt (6%) and the irritation time.

The results shown in Table 3 revealed that the values of the absorption coefficient of the carbonyl and hydroxyl functional groups which are generated in the prepared samples and monitored at 1740 and 3350 nm respectively were increased as the w/w% of the adding salt is increased. This increase may be due to the reaction between the polymer and the adding salt that results in the production of carbon oxide groups mostly belong to the bicarbonate or carbonate group. This leads eventually to the destruction of the polymer chain (33).

During the irritation of the prepared samples with UV light, the carbonyl group is generated and it is responsible for the formation of the polymeric yellow coloration and extension of the sample absorption to longer range of the wavelengths (34). The generated carbonyl groups are then activated to the singlet and triplet excited states as they further exposed to the irritation resulting in the enhancement of the subsequent photo-degradation reactions (30).

Table 3: The absorption coefficient values of the carbonyl (I_{OH}) and hydroxyl (I_{CO}) groups found in the prepared samples calculated at different irradiation times.

Sample (w/w%)	I_{CO}					I_{OH}				
	Time of irradiation (hr)					Time of irradiation (hr)				
	0	7	14	28	42	0	7	14	28	42
PVAl	0.179	0.234	0.325	0.456	0.567	0.375	0.485	0.583	0.754	0.873
PVAl + 0.4 % NH$_4$Cl	0.180	0.332	0.440	0.595	0.727	0.381	0.577	0.715	0.874	0.987

PVAl + 0.8% NH₄Cl	0.181	0.459	0.567	0.732	0.834	0.403	0.647	0.834	1.009	1.113
PVAl + 1.5 % NH₄Cl	0.183	0.567	0.724	0.923	1.008	0.412	0.720	0.958	1.167	1.254
PVAl + 3 % NH₄Cl	0.187	0.641	0.865	1.098	1.206	0.422	0.825	1.104	1.278	1.349
PVAl + 6% NH₄Cl	0.191	0.754	0.973	1.234	1.379	0.435	0.920	1.244	1.379	1.451

Concerning the measurements of the mean molecular weights of the prepared samples based on their intrinsic viscosity, Table 4 and Figure 2 revealed that there is a decline in these weights with the irritation time. This can be contributed to the breakdown of the carbonic backbone of the polymer which is usually started from the weakest bonds moving up toward the strongest ones. Also, the same degree of decline was observed for the values of p, α, and S.

Table 4: The mean molecular weights calculated on the basis of the intrinsic viscosity at different irritation periods for the pure polymer and the prepared sample contained 6% of the salt.

| Time of irradiation (hr)	$Mv x10^3$		$(Mv)^2 x10^9$		$\frac{dM_v}{dt} = \frac{M_{v0} - M_{vt}}{t}$		Degree of polymerization (P)		$\frac{1}{P}x10^{-4}$		Degree of partition α $X10^{-3}$		average chain scission (S)	
	No addition	Addition 6%	No addition	Addition 6%	No addition	Addition 6%	No addition	Addition 6%	No addition	Addition 6%	No addition	Addition 6%	No addition	Addition 6%
0	58.045	58.045	3.369	3.369	∞	∞	1319.204	1319.204	7.580	7.580	0.0	0.0	0.0	0.0
7	48.123	44.630	2.315	1.991	0.393	0.532	1093.704	1014.318	9.143	9.858	0.156	0.227	0.206	0.300
14	42.554	34.198	1.810	1.169	0.307	0.473	967.136	777.227	10.339	12.866	0.275	0.528	0.364	0.697
28	37.610	29.356	1.414	0.861	0.202	0.284	854.772	667.181	11.699	14.988	0.411	0.740	0.543	0.977
42	32.981	25.227	1.087	0.636	0.165	0.217	749.568	573.340	13.341	17.441	0.576	0.986	0.759	1.300
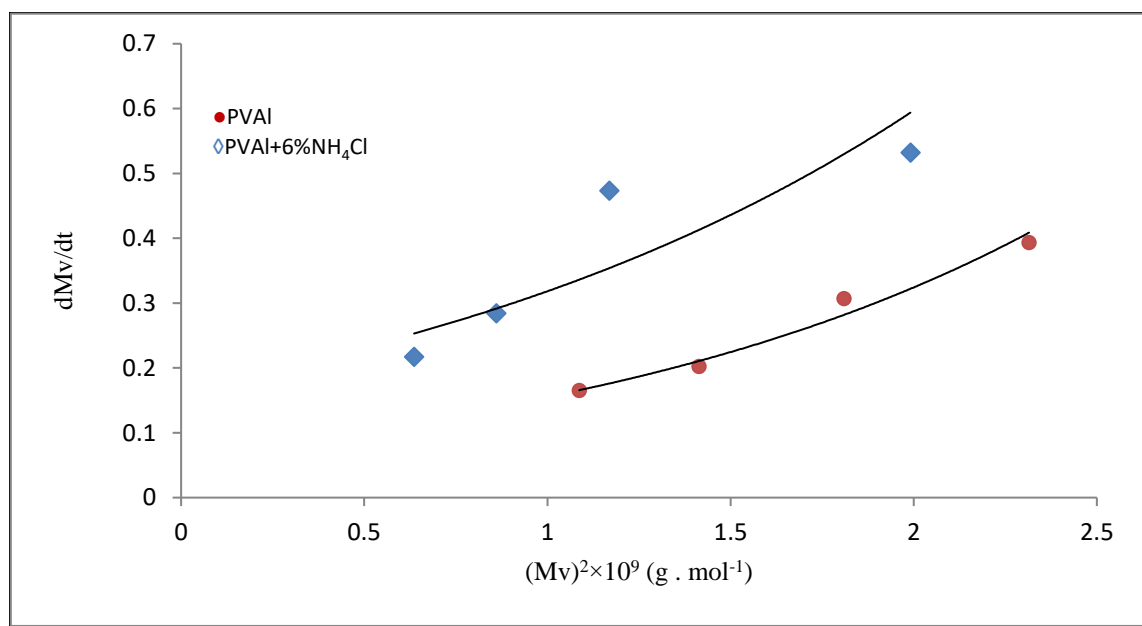
Figure 2: The relationship between the change in the average molecular weights calculated at different time intervals with the square of these weights for the pure polymer and the prepared sample contained 6% of the salt.

The data represented in Tables 4 and 5 and displayed in Figures 3 and 4 indicated that the values of Φ_{cs}, S, and α are increased by increasing the amount of adding salt. This observation conjugated with the data acquired from the

FTIR study exhibited that the addition of the applied salt may enhance the photo-degradation of the employed polymer.

Table 5: The values of Φ_{cs} for the pure polymer and the prepared sample contained 6% of the salt at the irritation time of 24 hr.

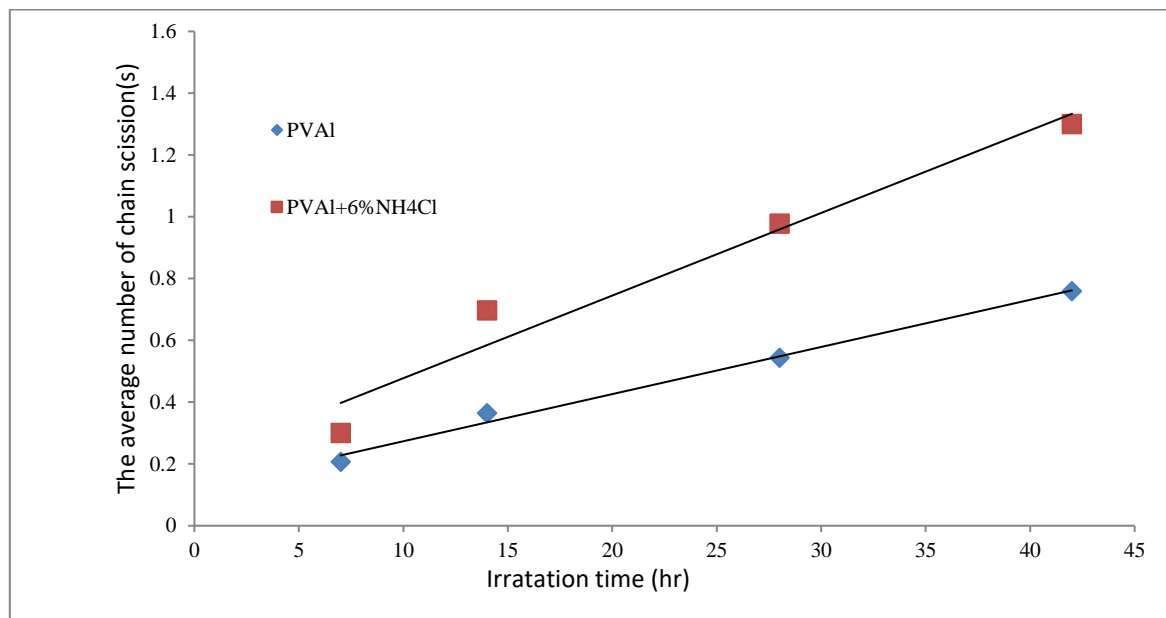| Sample	$\Phi_{cs} \times 10^{-4}$
PVAl	5.567
PVAl + 6% NH$_4$Cl	7.905

Figure 3: The relationship between the values of S for the pure polymer and the prepared sample contained 6% of the salt at different irritation times.
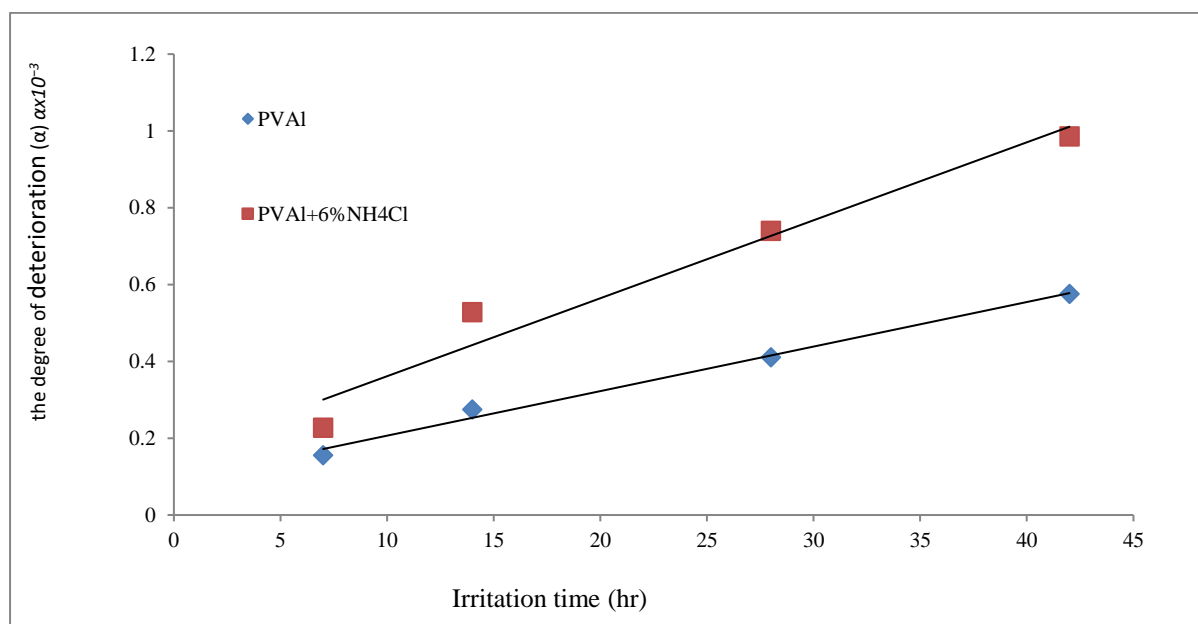

Figure 4: The relationship between the values of α for the pure polymer and the prepared sample contained 6% of the salt at different irritation times.

CONCLUSION

This work involves the preparation of five samples by adding the NH$_4$Cl in various w/w percentages to the PVAl. The parameters results from the photo-stabilization study revealed that as the w/w ratio of the salt to the polymer increased, the photo-stability of the prepared samples is decreased. From this, it is concluded that the addition of this salt may induce the photo-degradation of PVAl to a

significant degree. Also, this salt may regard as a potential additive to eliminate the environmental risk of the applied polymer.

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CONFLICT OF INTEREST

There are no conflicts of interest.

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