Al-Nahrain Journal of Science
ANJS, Vol.25 (1), March, 2022, pp. 9-13

The Influence of the UV Light on the PVC Sheets Adopted with Some Aromatic Amines

Salah M. Abdullah[1,*], Aseel F. Alwan[1] and Atheer M. Majeed[2]

[1]Polymer Research Unit, College of Science, Al-Mustansiriyah University, Baghdad-Iraq
[2]College of Arts, Al-Mustansiriyah University, Baghdad-Iraq

Article's Information

Received:
02.01.2022
Accepted:
21.03.2022
Published:
28.03.2022

Keywords:
PVC
UV stabilizer
Adopted polymer
Aromatic amines
Surface morphology

Abstract

Adopted PVC with aromatic amines, (dimethyl amino benzyldehyde (No.1), aminophenol (No.2), benzidine (No.3) and 4,4-diaminodiphenylsulphone (No.4) were investigated using UV light source at 340 nm. the changing in FTIR spectroscopy for carbonyl and polyene groups was monitored, $I_{(C=C)}$ and $I_{(c=o)}$ was calculated during different period of irradiation time, in addition, the molecular weight of PVC and PVC adopted sheets was obtained using viscosity method. the results show the aromatic amines behave as a good photostabilizer in order: No.1 ≈ No.2≈ No.3 > No.4. The morphology of the sheets surface achieved by AFM analysis which assigned that the roughness factor (Rq) of the blank, No.2 and No.4 sheets was (Rq=73.0), (Rq=240), (Rq=213) before irradiation and (Rq=180), (Rq=281), (Rq=285) after radiation respectively.

DOI: 10.22401/ANJS.25.1.02

*Corresponding author: salah_md@uomustansiriyah.edu.iq

1. Introduction

PVC is one of the most worldwide used thermoplastic materials in industrial applications, related to its durability and low costs [1]. It was first produced in USA and Germany in the early 1930's and the production was largely extended through the world war ɪɪ due to the valuable properties. However, the photo and thermal stability of PVC are weak restricted its use in the construction field [2]. PVC undergoes gradual degradation when exposed to UV-light in the presence or absence of oxygen [3]. The degradation cause changes in the properties of PVC which effect on the structure and chemical composition. The degradation occurs by elimination of hydrogen chloride (HCl), which leads to forming long polyene chains that cause a change in its mechanical properties and formation of a surface micro-cracking [4]. To protect the PVC from degradation, the properties of the polymer must improve by adding various additives act in different mechanisms. These additives could be inorganic, organic [5], heteroaromatic [6] or aromatic [7]. As the global industry step towards green chemistry, hence the additives should be non-toxic in order not to contribute in maximizing the environmental pollution. Furthermore, the additives should also be cheap available and easy to produce [8]. The mechanisms in which the additives stabilize PVC Could be HCl scavengers [9], peroxide decomposers [10], light absorption, and radical scavengers [11]. PVC photostabilization continued to be an enthusiastic field for scientific research because the existence of stabilizers can dramatically reduce the rate of oxidation. This paper studied the use of some PVC-aromatic amines as a PVC photo-stabilizer.

2. Experimental Work

2.1 Materials and methods:

PVC, THF was obtained from Scharlau, and Romil respectively 4 (Dimethylamino)-benzaldehyde, 4-aminophenol, 4,4-diaminodiphenyl sulfone and Benzidine were obtained from BDH. FTIR spectra were recorded on 4200 (JASCO) with frequency range of (400-4000) cm^{-1}. Atomic force microscopy (AFM) supplied by Veeco (plainview, NY, USA) power sonic410 supplied by Daihan lab tech Co. Ltd (Korea) and Q.U.V the Q-PANEL company Weathering Accelerated tester.

2.2 Purification of PVC [12]:

In this study, the PVC was reprecipitated from THF solution by alcohol many times and finally dried at room temperature for 24 h under vacuum.

2.3 Preparation of PVC sheets:

The PVC sheet adopted with different amines (4% wt/wt) were prepared by dissolving PVC with amines dimethyl amino benzyldehyde (No.1), aminophenol (No.2), benzidine (No.3) and 4,4-diaminodiphenylsulphone (No.4) separately in 30 ml THF with hard stirring at 60 °C. The volume was adjusted to 50 ml using volumetric flasks, and then samples poured into the fumigation glass to form films with thickness (50 μm) for irradiation. Films were collected and characterized by FTIR spectroscopy.

2.4 U.V irradiation:

The prepared sheets were irradiated by UV source at 340 nm in periods (83,133,163,213,256,303) hours using accelerated weathering tester. The viscosity and the FTIR spectrum examined after each period.

2.5 Determination of PVC Photodegradation Using FTIR Spectrophotometry:

The photodegradation of PVC films was studied Using FTIR Spectrophotometry in the range of 400-4000 $cm^{-1.}$ The appearance of (C=C; 1602 cm^{-1}) and (C=O; 1722 cm^{-1}) groups present an evidence on a formation of fragments containing carbonyl and polyene groups [13]. The absorption of these peaks was used to follow the extent of polymer degradation during different irradiation time. Then carbonyl index (Ico) and polyene index (I_{PO}) were calculated by comparison the FTIR absorption peaks with a CH_2 group peak (reference peak) at 1328 cm^{-1} This method known as band index method [14]:

$$I_s = A_S / A_r \qquad (1)$$

where:

I_s = Index of group under study.

A_s represent the Absorbance of peak under study.

A_r represents the absorbance of the reference peak.

2.6 Determination of average molecular weight (Mv) using viscometer method:

The average molecular weight of the polymer calculated using the Mark- Houwink relation [15].

$$[\eta] = KMv^{\alpha} \qquad (2)$$

Where $[\eta]$ = the intrinsic viscosity; K, α are constants for every polymer with a particular solvent and temperature. Solutions with different concentrations (gm/100 ml) were prepared by dissolving the polymer sheets in THF, both the polymer solutions and the solvent (THF) transferred separately to Ostwald capillary viscometer which is placed in 25 ^{o}C controlled temperature water bath.The flowing time of the solvent (t^{o})and the polymeric solutions (t) was determined respectively by a stopwatch, the types of viscosity (relative η_{re}, specific η_{sp} and intrinsic $[\eta]$ were calculated according to the relations below:

$$\eta_{re} = t / t^{o} \qquad (3)$$

$$\eta_{sp} = \eta_{re-1} \qquad (4)$$

The single step equation used to calculate intrinsic viscosity before and after degradation

$$[\eta] = (\sqrt{2}/c)(\eta_{sp} - \ln \eta_{re})^{1/2} \qquad (5)$$

C = concentration of polymeric solution (g /100 ml). Molecular weights of PVC with and without additives were calculated from intrinsic viscosities measured using the Mark -Houwink equation (2):

$$[\eta] = KMv^{\alpha}$$

Where $K = 1.38\times10^{-4}$, $\alpha = 0.77$ for PVC, THF solvent at 25˚C.

2.7 Morphology studying the of PVC sheets:

The morphology of PVC sheets surface was inspected using atomic force microscopy (AFM), supplied by Veeco (Plainview, NY, USA).

3. Result and Discussion

Estimation of PVC photodegradation by FTIR spectrophotometry: When PVC expose to UV irradiation in the existence of an oxygen it undergoes photooxidative degradation by free radical mechanism [13], which lead to a fragmentation in the polymeric chain forming small fragments containing carbonyl (C=O) and polyene (C=C) groups [16]. The absorption of the carbonyl and polyene groups was monitored, using FTIR spectroscopy to follow the degradation of polymer during UV irradiation. To achieve that, the baseline method was used to determine the peak index depending on the reference peak 1330 cm^{-1}. The behavior of aromatic amines (No.1, No.2, No.3, and No.4) as additives to PVC films was study by following the changing of carbonyl and polyene peaks after UV irradiation in period time. The carbonyl peak band appears in 1722 cm^{-1} and polyene peak band in 1602 cm^{-1}. The results showed the amines No1. No2, No3. and No.4 have lower growth rate with irradiation time comparing with the PVC film without additives. This lead to conclude that, these aromatic amines might be considered as photostabilizers of PVC polymer. The additive amines are efficient PVC photostabilizer according to the order: No.1 = No.2 = No.3 > No.4. Irradiation time from (83) h up to (**303**) h was plotted against values for $I_{(C=O)}$ and $I_{(C=C)}$ for the PVC sheets Figure 1 and Figure 2 respectively, the two indices $I_{(C=O)}$ and $I_{(C=C)}$ show remarkable changes for the pure PVC sheet(with no additives) in comparison with PVC sheets adopted with amines (No.1, No.2, No.3, No.4). The less change in $I_{(C=O)}$ and $I_{(C=C)}$ was showed in No.1, No.2, No.3 because of they are more stabilized by resonance when they converted to free radicals by UV irradiation.

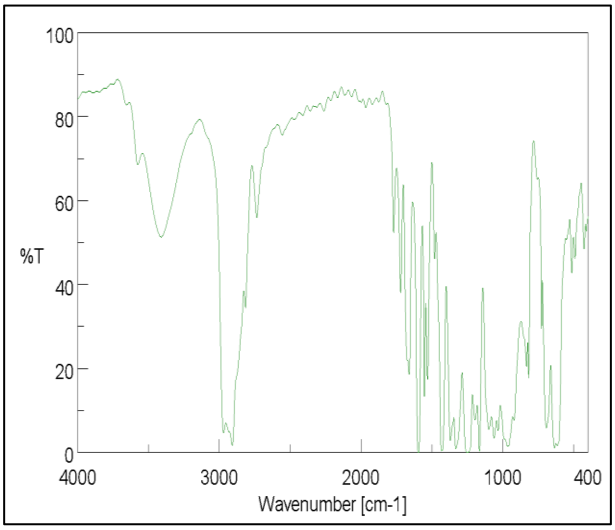

Figure 1. FTIR spectra of PVC adopted with 4,4-diaminodiphenylsulphone before irradiation.

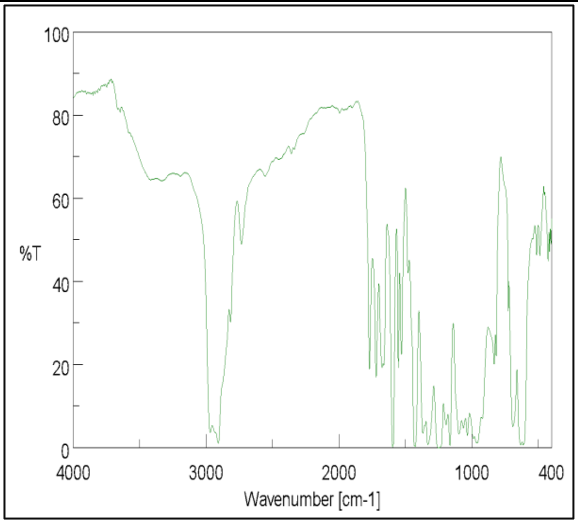

Figure 2. FTIR spectra of PVC adopted with 4,4-diaminodiphenylsulphone after irradiation for 303 h.

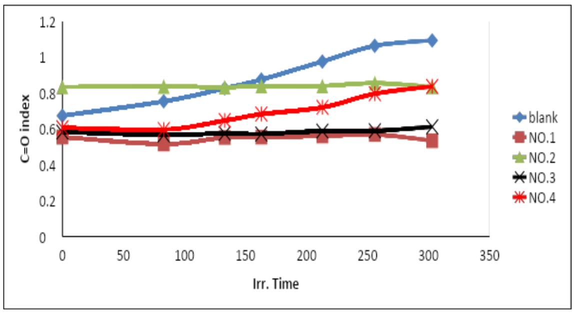

Figure 3. Effect of irradiation time on $I_{C=O}$ index for PVC sheets.

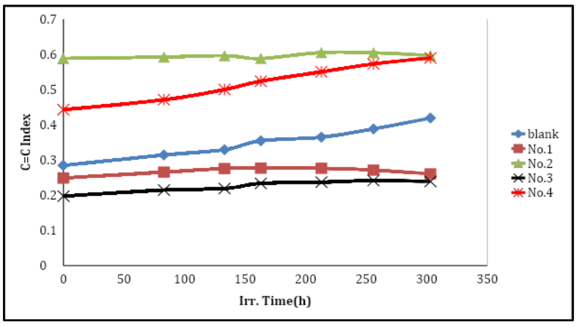

Figure 4. Effect of irradiation time on $I_{C=C}$ index for PVC sheets.

Molecular weight of polymer is the viscosity method. The irradiated PVC sheets for different periods were measured their viscosity using an Ostwald U-tube viscometer after dissolving in THF [12]. The viscosity molecular weight for PVC sheets was calculated at each period of irradiation using Mark-Hewink equation (2) the result shows in Figure 5. At zero time, the blank PVC shows higher molecular weight than the adopted sheets due to the presence of additives reveal increasing of chain number. Each molecule of additives behaves as independent chain. The molecular weight of the adopted PVC No.1, 2, 3 shows lower changing in molecular weight than No.4. In general, the additives aromatic amines are stabilizing photo degradation of PVC.

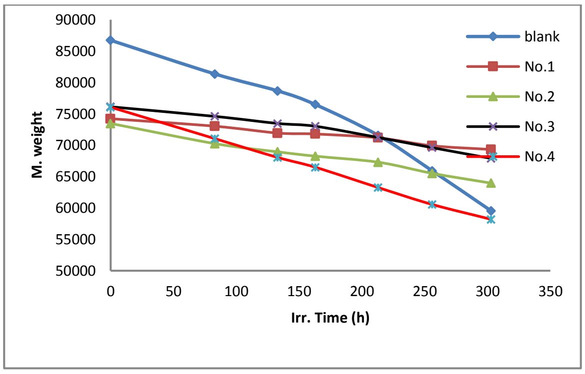

Figure 5. Changes in the viscosity average molecular weight (Mv) during irradiation of PVC sheets (blank) and modified PVC.

No.2, No.4 and blank sheets Generally, the adopted PVC sheets have a higher roughness factor (*Rq*) than blank sheets either before or after irradiation. Clearly, the AFM images assigned an increasing in (*Rq*) after irradiation [18,19]. The roughness factor for blank, No.2 and No.4, sheets before irradiation was 73.0, 240 and 213, while the (*Rq*) after irradiation 180, 281, 285, respectively.

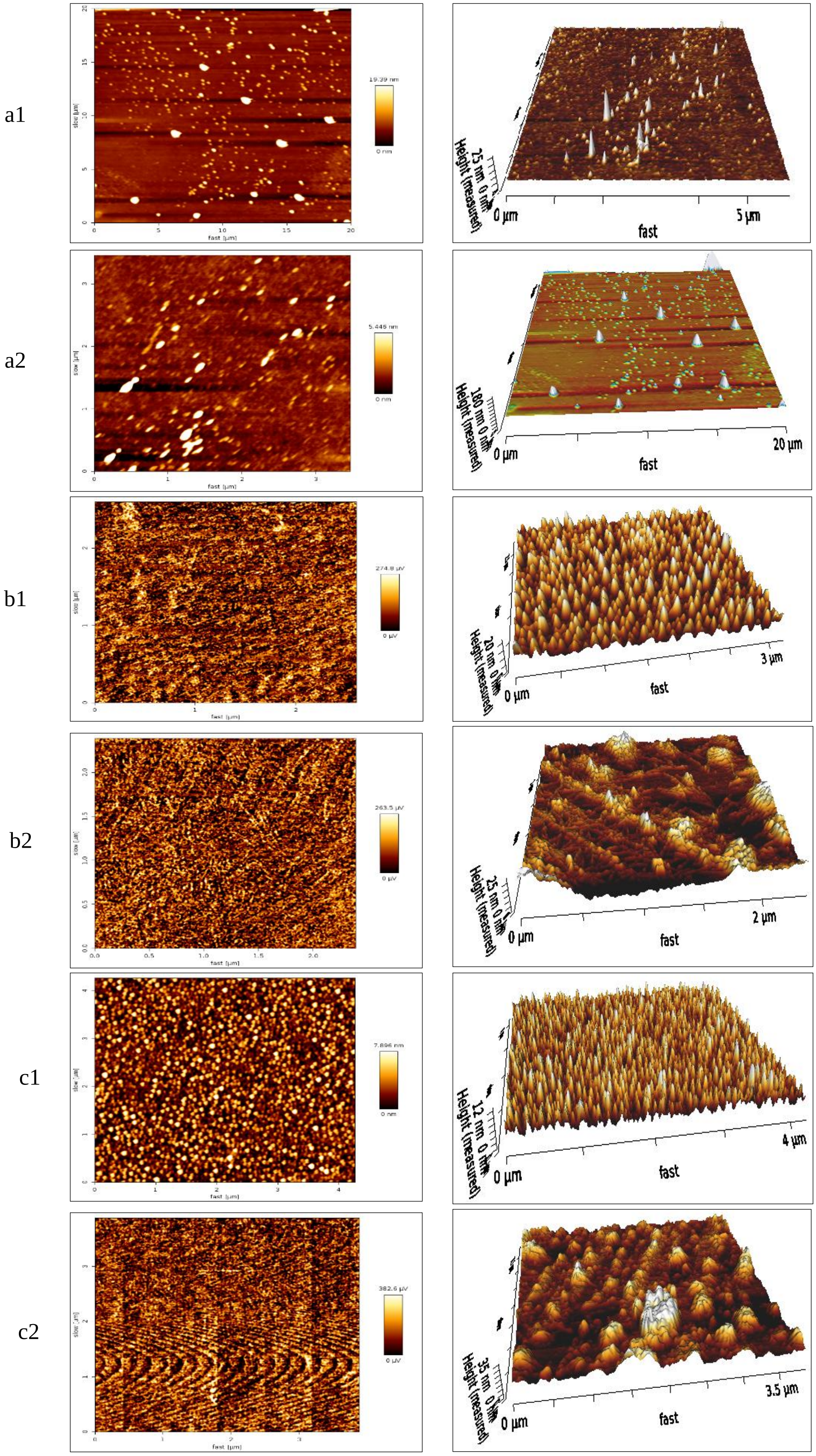

Figure 6. The AFM images (two and three dimensions) for (a) blank, (b) No.2 and (c) No.4 (1) before and (2) after 303 h. of irradiation.

4. Conclusion

The result pointed that the aromatic amines are efficient for photo stabilize of PVC sheets against UV light at 340 nm, we concluded that by calculating the indices (for carbonyl and polyene) and monitoring of the molecular weight of the adopted PVC sheets. The order of the used aromatic amines as photostabilizers is: No. 1 ≈ No. 2≈ No. 3> No.4. The morphology of the sheets surface adopting with aromatic amines revealed that the rough factor *(Rq)* for the blank more less than the adopted PVC and for all *(Rq)* increased with irradiation.

Conflicts of Interest

The authors declare that there is no conflict of interest.

References

[1] Ameer A.; Abdallh B. and Ahmed A. E. Y.; "Synthesis and characterization of polyvinyl chloride chemically modified by amines", Open J. Polym. Chem., 3: 11-15. 2013.

[2] Nicholson J. W.; "The chemistry of polymers", 2012.

[3] Kumar A. and Gupta R. M. D.; "Fundamentals of Polymer Engineering", Fundam. Polym. Eng.: 50-52, 2003.

[4] Jakubowicz I. and Yarahmadi N. G. T.; "Effects of accelerated and natural ageing on plasticized polyvinyl chloride (PVC)",. Polym Degrad. Stab., 66: 415-421, 1999.

[5] Mohamed N.A.; Yassin A.A.; Khalil K.D. and Sabaa M. W.; "Organic thermal stabilizers for rigid poly (vinylchloride) I. Barbituric and thiobarbituric acids", Polym. Degrad. Stab.: 70, 5-10, 2000.

[6] Mohammed A.; El-Hiti G. A.; Yousif E. and Ahmed D. S.; "Protection of poly (vinyl chloride) films against photodegradation using various valsartan tin complexes", Polym.; 12, 2020.

[7] Folarin, O.M. and Sadiku, E. R.; "Thermal stabilizers for poly(vinyl chloride): A review", Int. J. Phys. Sci., 6: 4323-4330, 2011.

[8] Chai R.D. and Zhang J.; "Synergistic effect of hindered amine light stabilizers/ultraviolet absorbers on the polyvinyl chloride/powder nitrile rubber blends during photodegradation", Polym. Eng. Sci., 53: 1760-1769. 2013.

[9] Karayıldırım T.; Yanık J.; Yüksel M.; Saˇglam M. and Haussmann M.; "Degradation of PVC containing mixtures in the presence of HCl fixators", J. Polym. Environ.; 13: 365-379, 2005.

[10] Adil H.; Yousif E.; Salimon E. J.; "New stabilizers For PVC based on benzothiazole complexes", Lambert Acad. Publ. Ger., 2011.

[11] Naser S.; Nawres L.; El-Hiti G. A.; Raad M. and Ahmed D. S.; "Poly (vinyl chloride) photostabilization in the presence of schiff bases containing a thiadiazole moiety", Molecules, 23, 2018.

[12] Yousif E.; Yusop, R. M. and Ahmed D. S.; "Photostability of PVC films by using safety synthetic biolubricant as additives",. Malaysian J. Chem., 21: 36-42, 2019.

[13] Gardette J. L.; Gaumet S. and Lemaire J.; "Photooxidation of poly (vinyl chloride). A reexamination of the mechanism", Macromol., 22: 2576-2581, 1989.

[14] Rabek J. and Ranby B.; "Photodegradation, photo-oxidation and Photostabilization of Polymers", John Wiley, New York, 1975.

[15] Mark J.; "Physical properties of polymers", in Handbook, Springer: New York, 2007.

[16] Bacaloglu R. and Fisch M.; "Degradation and stabilization of poly (vinyl chloride). V. Reaction mechanism ofpoly (vinyl chloride) degradation", Polym. Degrad. Stab., 47: 33-57, 1995.

[17] Allcock H.; Lampe F. and Mark J. E.; "Contemporary polymer chemistry", 3rd ed.; Pearson Prentice-Hall Up. Saddle River, NJ, USA, 2003.

[18] Valko L.; Klein E.; Kovaˇrík P.; Bleha T. and Šimon P.; "Kinetic study of thermal dehydrochlorination of poly(vinylchloride) in the presence of oxygen: III. Statistical thermodynamic interpretation of the oxygen catalytic activity", Eur. Polym. J., 37: 1123-1133, 2001.

[19] Awaja F.; Zhang S.; Tripathi M.; Nikiforov A. and Pugno N.; "Cracks, microcracks and fracture in polymer structures: Formation, detection, autonomic repair", Prog. Mater. Sci., 83: 536-573, 2016.