Photochemical and Physical Study of PVC- Amines Polymers

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A R T I C L E   I N F O

A B S T R A C T

The photo-stabilization of polymers derived from poly(vinyl chloride) (PVC) films was investigated. The PVC and modified PVC films were produced by the casting method from tetrahydrofuran (THF) solvent. The photostabilization activities of these compounds were determined by monitoring the carbonyl and hydroxyl indices and weight loss method with irradiation time and morphology study for all the films. The changes in viscosity average molecular weight of PVC with irradiation time were also tracked (using THF as a solvent).

INTRODUCTION

Amines are organic compound and functional group that contain a basic nitrogen atom with a lone pair. Amines are derivatives of ammonia, wherein one or more hydrogen atoms have been replaced by a substituent such as an alkyl or aryl group (Murry and John, 1992). Important amines include amino acides, biogenic amines, aniline and trimethylamine. Poly(vinyl chloride), otherwise known as PVC is a thermoplastic and the third largest production polymer in the world (Allsopp and Vianello, 2012).The low cost and excellent performance of poly(vinyl chloride) (PVC) make it a very attractive and suitable plastic for a wide variety of applications. With respect to the production and consumption of synthetic materials, it stands third in the world after polyethylene and polypropylene. However, PVC suffers from poor thermal and light stability. It undergoes rapid autocatalytic dehydrochlorination upon exposure to heat and light during its molding and use, respectively (Yousif *et al*., 2009, Sabaa *et al*., 2006). As a result, conjugated polyene sequences are formed from the beginning of the reaction, and they give rise to discoloration of the polymer and seriously change its physical properties (Pimentel Real *et al*, 2008). The photodegradation of polymeric chains can often be attributed to photochemical reactions arising from the absorption of UV radiation by polymeric chromophores. A number of carbonyl species including aliphatic type ketones, monomer, alcohols, and esters, as well as a drop in molecular weight resulting fromthe photodegradation, have been identified on the bases of experimental results (Torikai and Shibata, 2002, Geuskens and Lu-Vinh, 1982) but as yet, there is no general agreement on the nature of the products resulting from photodegradation of polymeric chains. Degradation also causes a drastic change in the mechanical properties of the polymer, which is accompanied by a decrease or increase in its average molecular weight as a result of either chain scission or crosslinking of the polymer molecules, respectively (Yousif *et al*., 2011 (A)). Photooxidation of organic materials is a major cause of irreversible deterioration for a large number of substances. It is responsible for the loss of physical properties of plastics (Grassie and Scott, 1985) yellowing, loss of gloss and mechanical properties (cracking), and other problems associated with UV light (Galdi *et al*., 2010, Goldshtein and Margel, 2011, Bojinov and Grabchev, 2005, Pospisil *et al*., 2006). Various defect sites in the polymer chain are thought to be responsible for this instability. Possible defect structures in PVC chains are allylic chlorine, tertiary hydrogen and chlorine atoms, end groups such as double bonds, oxygen-containing

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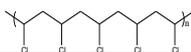E-mail: rahimi@ukm.edu.my

groups, peroxide residues, and head-to-head structures (Crawley and McNeill, 1978). In addition to these abnormalities, the steric order of the monomer units (tacticity) may have some influence on the degradation. The dehydrochlorination most likely proceeds by a chain mechanism involving radical intermediates. However, ultimate user acceptance of the PVC products for outdoor building applications will depend on their ability to resist photodegradation over long periods of sunlight exposure. To ensure weather ability, the PVC resin needs to be compounded and processed properly using suitable additives, leading to a complex material whose behavior and properties are quite different from the PVC resin by itself (Rasheed *et al*., 2009). Recently, scientists have used substituted benzothiazole and benzimidozole ring (Yousif *et al*., 2010) as photostabilizers for rigid PVC. They have also used 1,3,4-oxadiazole and 1,3,4-thiadiazole derivatives as novel photostabilizers for rigid PVC (Yousif *et al*., 2007). All synthetic polymers require stabilization against the adverse effects; it became necessary to find ways to prevent, or at reduce, the damage caused by the environmental parameters such as light, air and heat. That is why the photostability of polymers is one of the most important considerations for application. The photostabilization of polymers involves the retardation or elimination of photochemical process in polymers and plastics that occur during irradiation. The following stabilizing systems have been developed which depend on the action of stabilizer: (a) light screeners, (b) UV absorbers, (c) excited state quenchers, (d) peroxide decomposers and (e) radical scavengers (Yousif *et al*., 2011 (B), Yousif *et al*., 2011 (C), Yousif *et al*., 2013). In this article we report the designing of some Amiens compounds and studied their photostabilizing reagent against degradation.

Experimental:
Materials:
    The following polymers derived from poly(vinyl chloride) were all prepared by the method previously described by (Ahmed, 2014) as shown in table 1.

Table 1: The suggested structures.

Compound	Suggested structure
PVC	
A1	
A2	
A3	
A4	

Experimental techniques:
I) Films preparation:
    A solution of Poly(vinyl chloride) solution or modified Poly(vinyl chloride)(5 g /100 ml) in tetrahydrofuran was used to prepare (30 μm) thickness of polymer films, (measured by a micrometer type 2610 A, Germany). The films were prepared by evaporation technique at room temperature for 24 hours. To remove the possible residual tetrahydrofuran solvent, film samples were further dried at room temperature for three hours under reduced pressure (Shneshil and Redayan, 2010, Yousif *et al*., 2012).

II) Irradiation experiments:
    UV- Light was used for irradiation of PS films, giving wavelength range between (250 to 380 nm) and the maximum wavelength light intensity is at 6.2 X 10^{-9} Ein Dm^{-3} S^{-1}. The polymer film samples were fixed parallel to each other and the lamp of the UV. incident radiation is vertically incident on the samples. The distance between the polymer films and the source was (10 cm). The polymer film samples were vertically fixed parallel to the lamps to make sure that the UV. incident radiation is perpendicular to the samples. The irradiated samples were rotated from time to time to ensure that the intensity of light incident on all samples is the same (Yousif *et al*., 2011 (D)).

III) Photodegradation measuring methods:
A. Measuring the photodegradation rate of polymer films using infrared spectrophotometery:
The degree of photodegradation of polymer film samples was followed by monitoring FTIR spectra in the range 4000-400 cm^{-1} using FTIR 8300 Shimadzu spectrophotometer. The position of carbonyl absorption is specified at 1722 cm^{-1}, and the hydroxyl group at 3500 cm^{-1} (Yousif *et al.*, 2011 (D)). The progress of photodegradation during different irradiation time was followed by observing the changes in carbonyl and hydroxyl peaks. Then carbonyl (I_{CO}) and hydroxyl (I_{OH}) indices were calculated by comparison of the FTIR absorption peak at 1722, 1602 and 3500 cm^{-1} with reference peak at 1328 cm^{-1}, respectively. This method is called band index method which includes.

$$Is = \frac{As}{Ar}$$
(1)

As = Absorbance of peak under study.
Ar = Absorbance of reference peak.
Is = Index of group under study.

Actual absorbance, the difference between the absorbance of top peak and base line (A Top Peak – A Base Line) is calculated using the Base Line method.

B) Measuring the Photodegradation by Weight loss:
The stabilizing efficiency was determined by measuring the % weight loss of photodegraded PVC films in absence and in presence of additives by applying the following equation:

Weight loss % = [($W_1 - W_2$) / W_1] 100
(2)

Where W_1 is the weight of the original sample (before irradiation), and W_2 is the weight of the sample (after irradiation) (Sabaa *et al.*, 2005).

C) Measuring the Photodegradation by Morphology Study:
To examine the surface morphology of the irradiated polymer films, the lab. Microscope was used for this purpose. That shows the top surface of the irradiated films. The surface morphology of films of the non irradiated PVC and PVC in the presence of the additive. Irradiated for 0 h and 250 h was studied (Shi *et al.*, 2006).

D) Determination of Viscosity Average Molecular Weight by Using Viscometer Method:
Viscosity techniques are very popular because they are experimentally simple (Gooch, 2007). By measuring the solution viscosity we should be able to get an idea about molecular weight. The viscosity property was used to determine the molecular weight of polymer, using the Mark- Houwink relation:

$$[\eta] = KM_v^\alpha$$
(3)

$[\eta]$ = intrinsic viscosity.

K, α = are constants dependent upon the polymer-solvent system at a particular temperature.

The intrinsic viscosity of a polymer solution was measured with an Ostwald U-tube viscometer. Solutions were made by dissolving the polymer in a solvent (gm/100 ml) and the flow times of polymer solution and pure solvent are t and t_o respectively. Specific viscosity (η_{sp}) was calculated as follows:

$$\eta_{re} = \frac{t}{t_o}$$
(4)

η_{re} = Relative viscosity .

$\eta_{sp} = \eta_{re} - 1$
(5)

The single – point measurements were converted to intrinsic viscosities by the relation (6).

$$[\eta] = \left(\sqrt{2}/c\right) \left(\eta_{sp} - \ln\eta_{re}\right)^{1/2}$$
(6)

C = Concentration of polymer solution (gm/100ml).

Molecular weights of PS with and without additives were calculated from intrinsic viscosities measured in Chloroform solution.

$$[\eta] = 1.38 \times 10^{-4} M_v^{0.77}$$
(7)

The most common solution viscosity terms are: relative viscosity, specific viscosity, inherent viscosity and intrinsic viscosity (Braun *et al.*, 2005).

RESULTS AND DISCUSSION

The polymers derived from PVC were used as additives for the photostabilization of PVC films. In order to study the photochemical activity of these additives for the photostabilization of PVC films, the carbonyl and hydroxyl indices were monitored with irradiation time using IR spectrophotometry. The irradiation of PVC films with UV light of wavelength, $\lambda = 313$ nm led to a clear change in the FTIR spectrum. Appearance of bands at 1772 cm^{-1} and 1724 cm^{-1}, were attributed to the formation of carbonyl groups related to chloroketone and to aliphatic ketone, respectively. The hydroxyl band appeared at 3500 cm^{-1} was annotated to the OH of the hydroperoxides group as shown in Scheme 1 (Rabek and Ranby, 1975).

Scheme 1 Photooxidation reaction Scheme of PVC:

The absorption of the carbonyl and hydroxyl groups was used to follow the extent of polymer degradation during irradiation. This absorption was calculated as carbonyl index (I_{co}) and hydroxyl index (I_{OH}). It is reasonable to assume that the growth of carbonyl index is a measure to the extent of degradation. However, in Figure (1), the I_{co} of A4, A3, A2 and A1 showed lower growth rate with irradiation time with respect to the PVC control film without additives. Since the growth of carbonyl index with irradiation time is lower than PVC control, as seen in Figure (1), it is suitable to conclude that these additives might be considered as photostabilizers of PVC polymer. Since efficient photostabilizer shows a longer induction period, therefore, the A1 is considered as the most active photostabilizer, followed by A2, A3 and A4 which is the least active.

Fig. 1: The relationship between the carbonyl index and irradiation time for PVC films and modified PVC films (30 μm thickness).

Hydroxyl species were produced during photodegradation of PVC. Therefore, hydroxyl index (I_{OH}) was monitored with irradiation time for PVC and with additives. From Figure (2) the A4, A3, A2 and A1 showed lower growth rate of hydroxyl index with irradiation time compared to PVC blank.
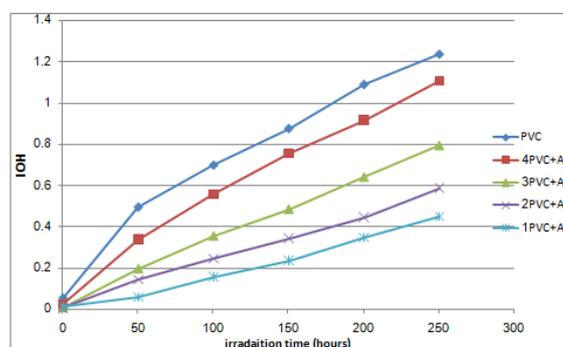

Fig. 2: The relationship between the hydroxyl index and irradiation time for PVC films and modified PVC films (30 μm thickness).

Determination of the stabilizing efficiency by weight loss method:
The stabilizing efficiency was determined by measuring the % weight loss of photodegraded PVC films in absence and in presence of additives by applying the following equation:

Weight loss % = [(W₁ −W₂) / W₁] 100   (8)

Volatile and low molecular weight products (Kuzina *et al*., 1998) formed on photodegradation of PVC led to a weight loss phenomenon. The weight loss of polystyrene films increased gradually with the increasing degradation time (Zan *et al*., 2006, Rabie *et al*., 2013). Figure (3) show the weight loss % as a function of irradiation time. The results indicate the increasing very small with PVC film modified by additives and all of the five additives have stabilizing effect against photodegradation of PVC samples and leading to a considerable decrease in % weight loss compared with blank PVC.
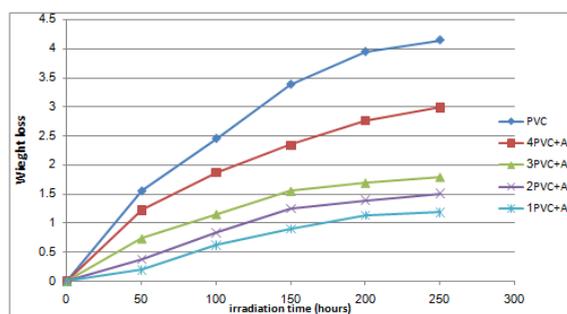

Fig. 3: loss in weight vs. irradiation time for PVC films (40μm) thickness containing 0.5% w\w from the additives.

Surface Morphology for the Films:
The morphological study for the surface of polymers gives a clear Photo about some of the physical properties of the polymer For example, the crystalline case, irregular surface molecules, smoothing the surface and how to build it. And also shows the nature of the surface defects resulting from Photons of light interaction with the polymer molecule (Schultz, 1998). The morphological study also can follow photodecomposition or stabilization of polymers that exposed to the UV. light through that appear on the surface of polymers, and see whether that the decomposition process can occur on chain scission or Decomposition for substitutes groups (Valkoa *et al*., 2001). The morphologic studies also gives a clear indication for the polymers resistance to weathering and how to produce tough polymers as well as to know deformation that occur when polymer exposed to weathering conditions.
The surface morphology of films of the non irradiated PVC blank, PVC and modified PVC in the presence of A2 (irradiated for 0 h and 250 h) was studied with Bio-lab microscope. The PVC (blank) film surface was

smooth and empty of any white spots, whereas the PVC film surface irradiated for 250 h was full of white spots indicating the holes or grooves indicate degradation. In the case of modified polymers the surface was almost smooth, and fewer white spots appeared; this indicated the great stabilizing efficiency of the investigated the stabilizer and how much it protected the polymer surface from deterioration, see Figures (4 and 5).
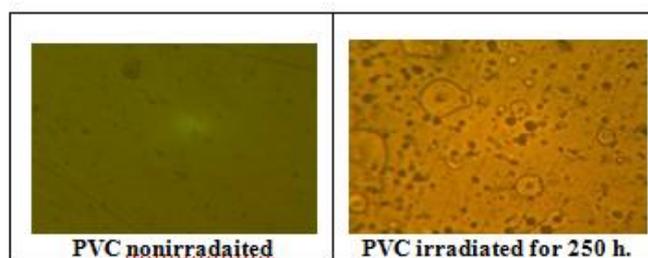

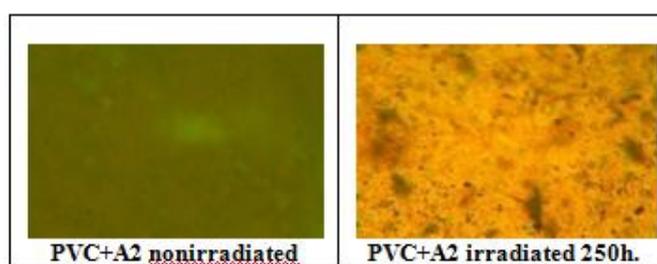**Fig. 4:** Microscopic images of PVC Films.

Fig. 5: Microscopic images of PVC+A2 samples.

Variation of PVC molecular weight during photolysis of modified polymers:
    Analysis of the relative changes in viscosity average molecular weight$_{(\overline{M}_v)}$, has been shown to provide a (Scott, 1973) versatile test for random chain scission. Figure (6) shows the plot of $\overline{M}_v$ versus irradiation time for PVC film with and without additives. $\overline{M}_v$ is measured using equation (3) with THF as a solvent at 25 ^{o}C .
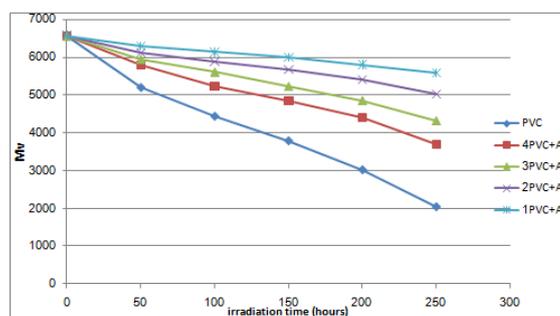

Fig. 5: Changes in the viscosity-average molecular weight $(\overline{M}_v)$ during irradiation of PVC films (control) and
      modified PVC films.

Conclusions:
    In the work described in this paper, the photostabilization of modified polymers of poly(vinyl chloride) films were studied. These modified polymers behave successfully as photostabilizer for PVC films. The additives take the following order in photostabilization activity according to their decrease in carbonyl and hydroxyl indices for PVC films as this trend: A1 > A2 > A3 > A4
    These additives stabilize the PVC films through UV absorption or screening, peroxide decomposer and radical scavenger mechanisms. The A1 was found to be the most efficient in photostabilization process according to the photostability and mechanisms mentioned above. The results obtained support the idea of using modified PVC as commercial stabilizer for PVC.

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