

UV-Absorbing Gallic Acid Derivatives as Functional Reinforcing Fillers in Poly(Vinyl Chloride) Films

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Abstract

The poly(vinyl chloride) PVC was photostabilized by gallic acid derivatives (0.5% by weight). The photodecomposition rate constant was reduced significantly in the existence of gallic acid derivatives along with PVC (blank). R1 compound was found to be the most effective stabilizer in photostabilization of PVC. The photodecomposition rate constant for PVC films containing R1 was found to be 1×10^{-4} compared to $8 \times 10^{-4} \text{ sec}^{-1}$ for PVC films in the absence of any additives. Different mechanisms of photostability for PVC films that involve gallic acid derivatives have been proposed.



Article History

Received: 19 October 2017

Accepted: 5 January 2018

Keywords:

Photodecomposition rate constant;
Gallic acid;
Photostability;
PVC films; Additives.

Introduction

Plastics have played an indispensable role in our life and production as the most significant material of the 21st century. Plastics are closely utilized in different parts of civil life, manufacturing, and aerospace technology because of their excellent material features, including cheap, strength and lightweight¹. There are 10,000 companies in the United State alone that are interested in manufacturing, processing and fabricating polymeric materials^{2,3}.

Polymers are classified into natural and artificial types. Polystyrene, Polyester and poly(vinyl chloride) are examples of synthetic polymers^{4,5}. Poly(vinyl chloride) is the most extensively employed thermoplastic materials worldwide, with more than 31 million tons produced per annum⁶⁻⁹. PVC the second most widely consumed plastic, is a 21st century material^{10,11}, mostly utilized in several industrial applications such as toys, tubes, food packaging, medical devices, building applications, electronics and furnishings¹²⁻

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¹⁴. Photodegradation occur as a result of chemical reaction, or photochemical degradation, which could be started by the UV solar radiation energy¹⁵. However, long term exposure of PVC to sunlight and/or high temperature lead to its photo degradation¹⁶. Neat PVC is usually mixed with other additives to get a plastic with desired properties depending on the intended industrial use¹⁷.

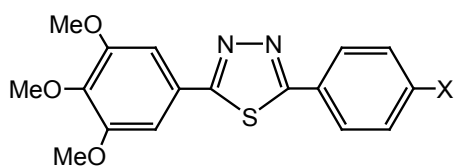
Photostabilization of PVC can be established through the use of various additives. The addition just a little content by weight of additives progress polymer properties, occasionally, it due to a unique combination of properties^{18,19}. The most common additives are Schiff base complexes²⁰, heterocycles²¹, plasticizers²², metal complexes and inorganic salts²³, aromatics^{24,32}. In the present study, we investigated the (k_d) photodecomposition rate constant of PVC polymeric films including gallic acid derivatives on irradiation with UV light.

Experimental

Materials

From Sigma-Aldrich (Gillingham, UK) all reagents and solvents were purchased and have been utilized without further purification. K value and polymerization degree of PVC = 67, 800 respectively, it was purchased from Petkim Petrokimya (Istanbul, Turkey).

Preparation of materials



R₁, X = OCH₃ R₂, X = CH₃ R₃, X = Cl R₄, X = H

Fig. 1: Structures of gallic acid derivatives.

Gallic acid derivatives Fig. (1); R₁, R₂, R₃ and R₄ were synthesized based on a literature procedure²⁵.

Films Preparation

Commercial PVC was re-precipitated in tetrahydrofuran (5 g/100 mL) with ethanol and dried for 24 h at 20°C under reduced pressure. The gallic acid derivatives (0.5% by weight) were mixed with PVC at 20°C based on literature procedure²⁵ then aluminum plate stands (Q-Panel Company,

Homestead, FL, USA) were utilizing to fix PVC films²⁶. 40 μm Thickness of PVC films was measured by a Digital Caliper Vernier (Kevelaer, Germany).

Accelerated Testing Technique

Irradiation (290-360 nm; $\lambda = 313$ nm) of PVC films was carried out using a standard procedure with an accelerated weather-meter QUV tester (Philips, Saarbrücken, Germany) for 250 h²⁷.

Photodecomposition Rate (k_d) of PVC Films using UV Spectrophotometer²⁸

A Shimadzu UV-Vis 160A-Ultraviolet Spectro photometer (Shimadzu Cooperation, Kyoto, Japan) was utilized to measure changes in the UV-visible spectra of PVC films during irradiation ($\lambda_{max} = 313$ nm). k_d of PVC films were calculated using Equation (1).

$$\ln(a-x) = \ln a - k_d t \quad \dots(1)$$

Where, $a = A_0 - A_\infty$, $x = A_0 - A_t$, a = PVC concentration at $t = 0$ and x = change in concentration of PVC at time t during irradiation as seen in Equation (2), A_0 = the absorption intensity of the PVC at t_0 , A_∞ = the absorption intensity at t_∞ and A_t = the absorption intensity after irradiation time t .

$$a - x = A_0 - A_\infty - A_0 + A_t = A_t - A_\infty \quad \dots(2)$$

Equation (3) was got by substituting $a-x$ in Equation (1) by its value in Equation (2).

$$\ln(A_t - A_\infty) = \ln(A_0 - A_\infty) - k_d t \quad \dots(3)$$

The plot of $\ln(A_t - A_\infty)$ against time of irradiation (t) gives straight line in which the slope = k_d . The PVC photodecomposition follows a first order kinetics.

Table 1: Photodegradation rate constant (k_d) values for PVC films on UV irradiation (250 h)

PVC film	K_d (sec ⁻¹)
PVC (blank)	8×10^{-4}
PVC + R ₄	5×10^{-4}
PVC + R ₃	4×10^{-4}
PVC + R ₂	2×10^{-4}
PVC + R ₁	1×10^{-4}

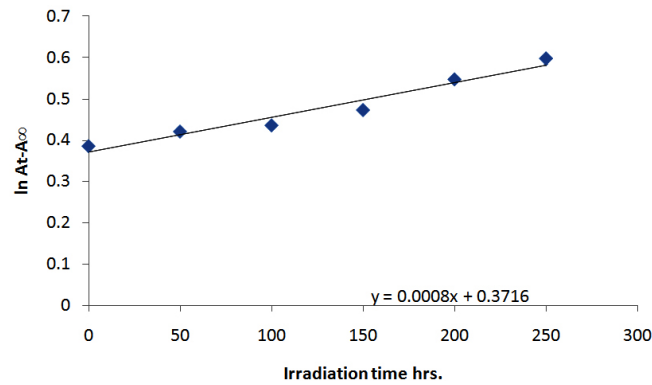


Fig. 2: Changes in $\ln(A_t - A_{\infty})$ for PVC (blank) film with irradiation time.

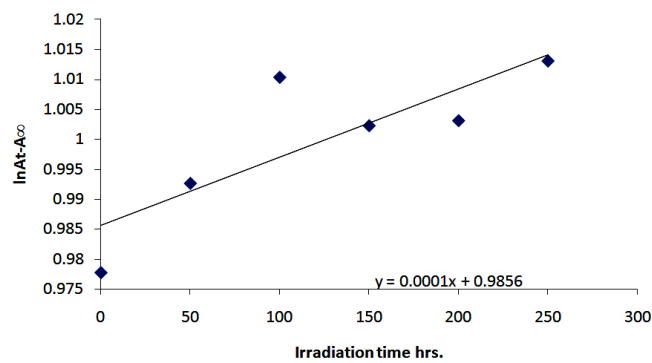


Fig. 3: Changes in $\ln(A_t - A_{\infty})$ for PVC film containing R_1 with irradiation time.

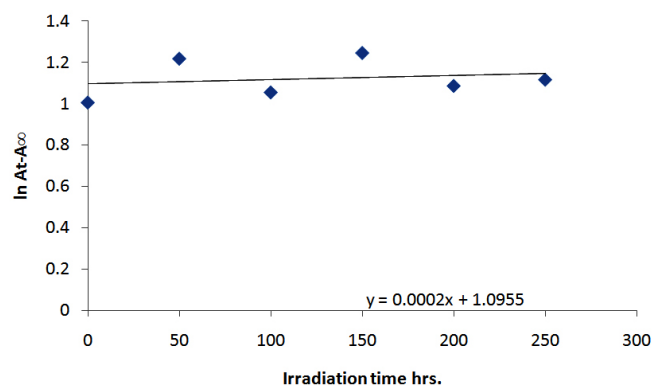


Fig. 4: Changes in $\ln(A_t - A_{\infty})$ for PVC film containing R_2 with irradiation time.

Results and Discussion

The effect of gallic acid derivatives (R_1, R_2, R_3, R_4) on the PVC films photodecomposition was investigated. The PVC films (40 μm thickness) containing gallic acid derivatives (0.5% by weight) were irradiated with a UV light ($\lambda_{\text{max}} = 313 \text{ nm}$) for 250 h. The UV

irradiation due to a clear change in PVC films and decomposition took place. $\ln(A_t - A_{\infty})$ plot against time of irradiation (t) gave a straight line. The graphs showed first order kinetics in which the slope equaled k_d constant for PVC films. Fig.2 demonstrates the change in $\ln(A_t - A_{\infty})$ against time of irradiation (t) of

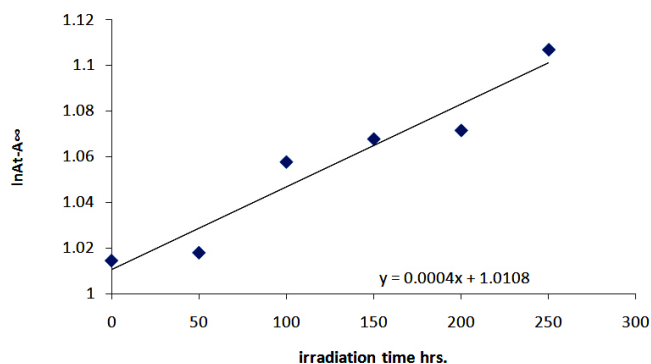


Fig. 5: Changes in $\ln(A_t - A_\infty)$ for PVC film containing R_3 with irradiation time.

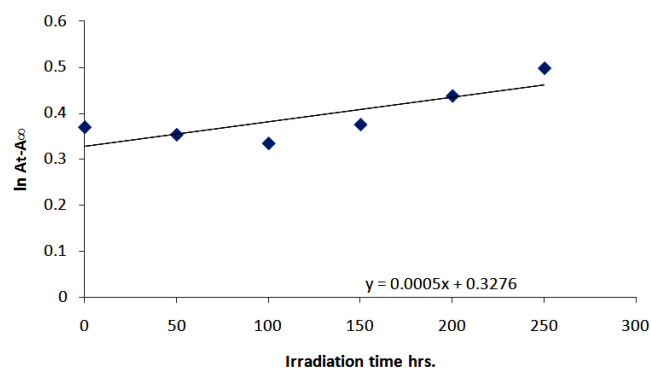


Fig. 6: Changes in $\ln(A_t - A_\infty)$ for PVC film containing R_4 with irradiation time.

PVC films in the absence any additives. Figures 3-6 show the changes in the $\ln(A_t - A_\infty)$ against time of irradiation of PVC films including gallic acid derivatives (0.5% by weight) as stabilizers for PVC films on irradiation with light.

The first order photodecomposition rate constant (k_d) for PVC films containing gallic acid derivatives (0.5 wt %) along with that for PVC (blank) is shown in Table (1). Table (1) and Figures (2-6) show that the rate constant (k_d) values are sensitive to the presence of gallic acid derivatives and its substitution. The PVC photodecomposition rate constant was high ($8 \times 10^{-4} \text{ sec}^{-1}$) in the absence of any additives. Such rate constant has been reduced significantly ($1-5 \times 10^{-4} \text{ sec}^{-1}$) when gallic acid derivatives were used as additives. The photostabilization of PVC in the presence of gallic acid derivatives follow this order $R_1 < R_2 < R_3 < R_4$. The R_1 was the most efficient than the other derivatives in photostabilization of PVC films. Clearly, these derivatives have acted

as photostabilizers for the photostabilization of PVC films. The photodecomposition rate constant was highest for PVC (blank) and lowest in the presence of R_1 derivative. Such photostabilizers could play as HCl scavengers, primary stabilizers, peroxide decomposers, radical scavengers and UV absorbers²⁹.

Propose Mechanisms of PVC Photostabilization

The efficiency of additives as PVC photostabilizers was measured as a function of the changes in the photodecomposition rate constant value. The values were smaller in PVC films containing gallic acid derivatives along with PVC itself. Different mechanisms of photostabilization process of PVC films containing gallic acid derivatives can be proposed schemes 1 and 2.

Two different atoms and different electro-negativity (nitrogen and sulfur) in the 1,3,4-thiadiazole ring. The thiadiazole ring polarity demonstrates the attraction

between the PVC chains and stabilizer as shown in scheme 1. This mechanism can be due to that the crosslinking could occur by UV irradiation, which may be correct for all compounds³⁰.

The heteroaromatic and aromatic rings can play as UV absorbers³¹. These systems have electron rich within stabilizer backbone structures can absorb the UV radiation energy directly and dissipates it to harmless heat energy, scheme 2.

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