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INDUCED PHOTODEGRADATION EFFECT ON THE FUNCTIONALIZED FE(III) COMPLEX ADDITIVE-POLY(VINYL CHLORIDE) THIN FILM

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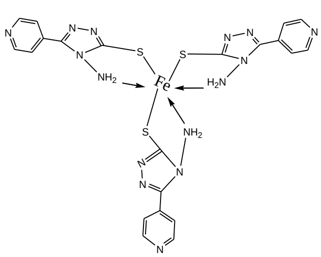
Graphical abstract



Abstract

A complex of Fe(III) with 4-amino-5-(pyridyl)-4H-1,2,4-triazole-3-thiol was prepared and evaluated as a photodegradation for polyvinyl chloride (PVC). Polyvinyl chloride was dissolved in THF solvent (5%, w/w) and functionalized with Fe (III) complex to form PVC films by means of solvent-casting method with a thickness of 40 µm. To study the effectiveness of Fe (III) complex additive, different concentrations (0.01, 0.02, 0.03, 0.04 and 0.05 g) were introduced into the PVC solution. The films' photodegradation was investigated; the photodegradation activity of the compounds was determined by monitoring the carbonyl group, weight loss method and morphological study with irradiation time. The obtained experimental results showed that the additive behaved successfully as a photoinducer for the degradation process for the PVC films and the photooxidation rate increased with the increase of additive concentration.

Keywords: Fe(III) complex, PVC, photochemistry, photooxidation

Abstrak

Kompleks Fe (III) dengan 4-amino-5-(pyridyl)-4H-1,2,4-triazole-3-thiol telah disediakan dan dinilai sebagai penguraian foto untuk polivinil klorida (PVC). Polyvinyl klorida dilarutkan dalam pelarut THF (5%, w/w) dan difungsikan dengan kompleks Fe (III) untuk membentuk filem PVC melalui kaedah *solvent-casting* dengan ketebalan 40 µm. Untuk mengkaji keberkesanan kompleks aditif Fe (III), kepekatan yang berbeza (0.01, 0.02, 0.03, 0.04 dan 0.05 g) ditambah ke dalam larutan PVC. Penguraian foto filem dikaji, aktiviti penguraian foto sebatian ini ditentukan dengan memantau kumpulan karbonil, kaedah penurunan berat dan kajian morfologi dengan masa sinaran. Berdasarkan hasil ujikaji, aditif tersebut berjaya bertindak sebagai agen penguraian bagi filem PVC dan kadar pengoksidaan foto dilihat bertambah dengan peningkatan kepekatan aditif.

Kata kunci: Kompleks Fe(III), PVC, fotokimia. fotooksidasi

1.0 INTRODUCTION

Polyvinyl chloride, or is also known by its abbreviation, PVC, is one of the most versatile polymers and is the third largest produced polymer in the world [1, 2]. 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 [3]. In recent years, the use of polymeric materials has rapidly increased, but it is well established that rapid photodegradation of these materials is possible when they are exposed to natural weathering [4-5].

A wide variety of synthetic and naturally occurring high polymers absorb solar ultraviolet radiation and undergo photolytic, photooxidative, and thermooxidative reactions that result in the degradation of the materials [6]. To ensure the weather ability of the materials, the PVC needs to be compounded and processed properly using suitable additives, which this leads to a complex material whose behavior and properties are quite different from the PVC itself [7].

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 plastic [8] yellowing, loss of gloss and mechanical properties (cracking), and other problems associated with UV light [9-12]. It is well known that all commonly used plastics degrade under the influence of sunlight. Thus, all synthetic polymers require stabilization material to deter the adverse effects. It is necessary to find ways to prevent, or at least reduce the damage caused by the environmental parameters such as light, air and heat. The photostabilization of polymers involves the retardation or elimination of photochemical process in polymers and plastics that occurs during irradiation. The following stabilizing systems have been developed which depend on the actions of stabilizers: (a) light screeners, (b) UV absorbers, (c) excited state quenchers, (d) peroxide decomposers and (e) radical scavengers [13-15]. However, many big industrial manufacturers use a large amount of photostabilization in PVC to increase its shelf-life from weathering. This leads to serious environmental problems as it takes a longer time to be degraded naturally in the landfills. For this reason, this paper intends to report the designing of an additive in PVC films that is used as a photoinducer and to examine the efficacy of PVC degradation process with respect to various additive concentrations.

2.0 EXPERIMENT

2.1 Materials

All the reagents, starting material (additive) and solvents were purchased commercially and used without any further purification.

2.2 Analytical Instruments

The Infrared (FTIR) spectra were recorded by using FTIR.8300 Shimadzu spectrophotometer with the frequency range of 4000-200 cm^{-1}. The ultraviolet-visible (UV-VIS) spectra were recorded by using Shimadzu UV-VIS.160 with an ultra-violet spectrophotometer in the range of 200-1100 nm.

2.3 Synthesis of Fe(III) Complex Additive

A complex of Fe(III) with 4-amino-5-(pyridyl)-4H-1,2,4-triazole-3-thiol additive (Figure 1) was prepared based on the previously described method by Haddad et al. (2013) [16].

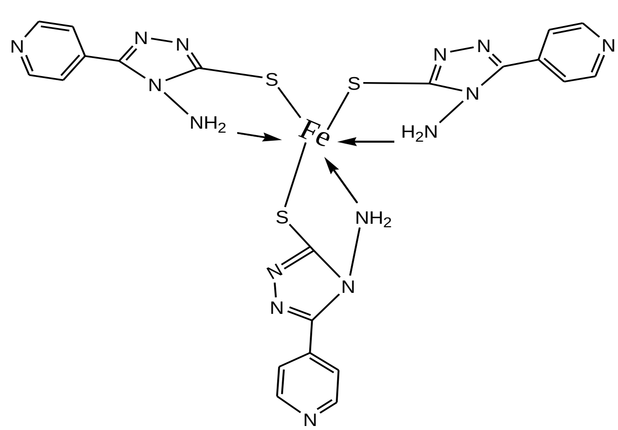


Figure 1 Molecular structure of Fe(III) complex additive

2.4 Film Preparation

The PVC solution (5%, w/w) was dissolved and functionalized with different concentrations of additive (Fe(III) complex) in THF solvent to form PVC films. The films were prepared by using a solvent-casting evaporation technique at room temperature and were left in the fume hood for 24 hours to remove any possible residue of THF solvent. The PVC films' thickness was measured by means of a micrometer of type 2610 A, Germany. The films were then fixed on stands prior to the irradiation exposure [17-19].

2.5 Irradiation Experiment (Accelerated Testing Technique)

The UV- Light was used for the irradiation exposure of the PVC films. The giving wavelength was at the range of 250 to 380 nm and the maximum wavelength light intensity was at 6.2 X 10^{-9} Ein Dm^{-3} S^{-1}. The films were vertically fixed in parallel to the lamps to make sure that the UV incident radiation was perpendicular to the samples. The distance between the films and irradiation source was fixed at 10 cm. The irradiated films were rotated from time to time to ensure that the intensity of light incident on all samples was at the same exposure [20].

2.6 Photodegradation Measuring Methods

2.6.1 Measuring the Photodegradation Rate of Polymer Films Using Infrared Spectrophotometry

The degree of photodegradation polymer films was examined by monitoring FTIR spectra in the range of 4000-400 cm^{-1} using a FTIR 8300 Shimadzu Spectrophotometer. The position of carbonyl absorption was specified at 1720 cm^{-1}. The progress of photodegradation at different irradiation times was observed by means of the changes in carbonyl peak intensity [20]; this is called band index method, which includes:

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

Where, As is the absorbance of peak under study, Ar is the absorbance of reference peak and Is is the index of group under study.

2.6.2 Measuring the Photodegradation by Weight Loss

The stabilizing efficiency was determined by measuring the percentage of the weight loss of the photodegraded PVC films in the absence and presence of different concentrations of additive by applying the following equation:

$$\text{Weight loss \%} = (W_1 - W_2 / W_1)\ 100\% \qquad (2)$$

Where, W_1 is the weight of the original sample (before irradiation), and W_2 is the weight of the sample (after irradiation).

2.7 Measuring the Photodegradation by Morphology Study

To examine the top surface of the irradiated polymer films, the MEIJI TECHNO microscope, (Japan) was used for this purpose. Two types of irradiated polymer films were examined which were the non-irradiated PVC blank and PVC in the presence of additive. The irradiated materials of exposure at 0 h and 250 h were examined and studied [22].

3.0 RESULTS AND DISCUSSION

The complex of Fe(III) with 4-amino-5-(pyridyl)-4H-1,2,4-triazole-3-thiol was used as an additive for the photodegradation of the PVC films. To examine the effectiveness of the additive, different concentrations of complex additive were introduced and exposed to irradiation at a specific time frame. The photochemical activity of the additive was determined by monitoring the carbonyl content with respect to different irradiation times. The irradiation of the PVC films with the UV light wavelength of λ = 365 nm led to a clear change in the FTIR spectrum. The carbonyl groups generated during the photooxidation process extended the polymer film absorption to longer wavelengths [23]. These groups absorb light when they are irradiated with light of the wavelength between 200-700 nm and are activated to singlet and triplet excited states which enhance various successive photooxidation reactions [24]. The appearance of a band at 1720 cm^{-1} was attributed to the formation of the carbonyl groups. The absorption of the carbonyl groups was employed to follow the extent of polymer degradation during irradiation. This absorption was calculated as carbonyl index (I_{CO}).

Additive concentration plays an important role in photodegradation and photostabilization of polymers. Therefore, many investigators [25] have studied the effects of additive concentration in photodegradation and photostabilization of polymers. In the present research, the effect of additive concentration in photodegradation of PVC films at a constant thickness (40 μm) was examined successfully. Figure 2 shows the profile of carbonyl index (I_{CO}) with respect to irradiation time and the use of different concentrations of additive ranging from 0.00 PVC (blank) to 0.05 g (wt).

The results in Figure 2 show that the carbonyl index increased with the increase of Fe(III) complex additive concentration in the films. Therefore, it was expected that at a high complex concentration condition, there was an increased rate of photodegradation mechanism which this indicates an induced degradation of PVC ($p<0.05$). Moreover,

Figure 3 shows the same profile as in Figure 2 as both results corresponded to each other's. Thus, time of exposure and additive concentration were considered as the main factors in a higher photodegradation mechanism in PVC films.

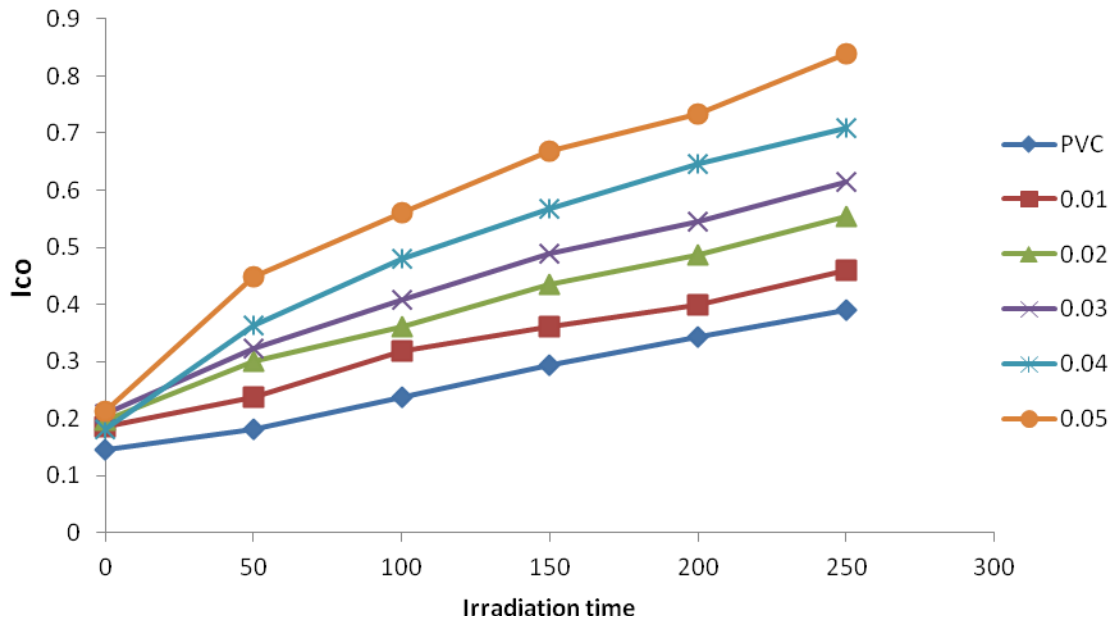


Figure 2 Changes in carbonyl index with respect to irradiation time (hour) for PVC films containing different concentrations of Fe(III) complex

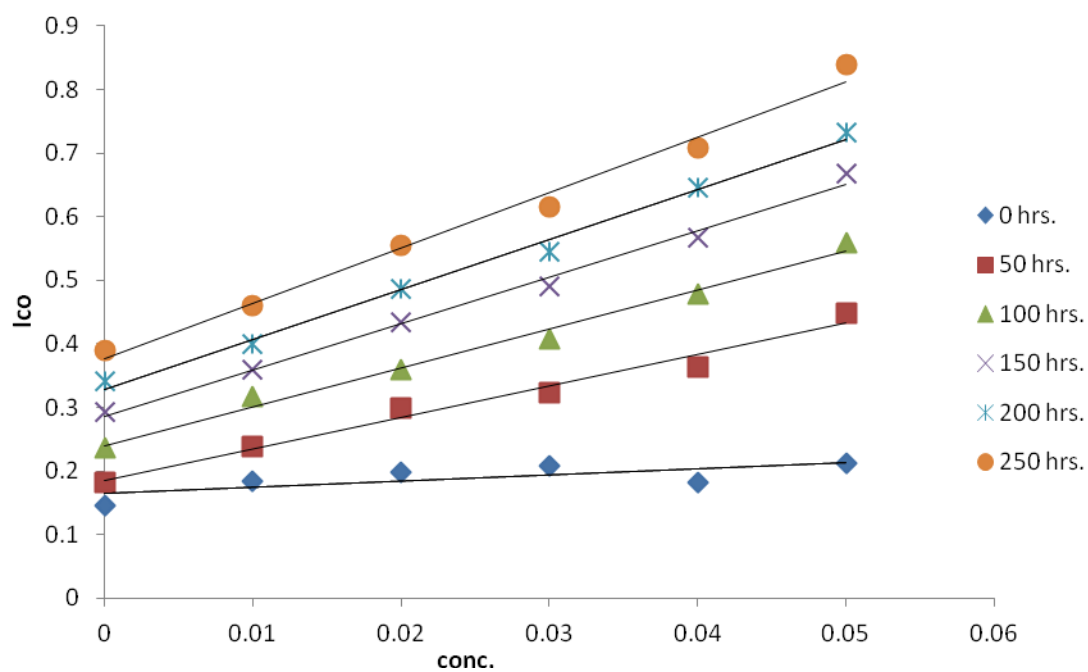


Figure 3 Changes in carbonyl index with respect to Fe(III) complex concentration in PVC films at each irradiation time (hour)

3.1 Determination of the Degradation Efficiency by Weight Loss Method

The degradative efficiency was determined based on Equation 2. The results of weight loss (%, w/w) as a function of irradiation time are presented in Figure 4. The weight loss of the PVC films increased gradually with the increase of degradation time [26-27]. In fact, the weight loss (%, w/w) of all the functionalized PVC films was increased with the increase of additive concentrations ($p<0.05$). The rate of the degradation of the blank PVC film (control) was slower than its respective functionalized PVC films ($p<0.05$). The results indicate that the additive can produce a great degradation effect on PVC and can potentially lead to a considerable increase in weight loss as compared to the control ($p<0.05$).

3.2 Surface Morphology of the Films

The surface morphological characteristics of the functionalized PVC films presented a clear indication of the changes in the physical properties that occurred on the films. The PVC (control - 0 hr) film's surface was smooth and empty of any white spots. In contrast, the functionalized PVC films' surfaces which were irradiated for up to 250 hours were full of scattered white spots to indicate holes or grooves (Figure 5). The spots became intensified as the exposure time increased [21, 28]. This indicates that the photodegradation of the functionalized Fe(III) complex additive-PVC via UV-irradiation had strongly affected the morphological characteristics due to the reduction of its high molecular weight polymer to a smaller monomer.

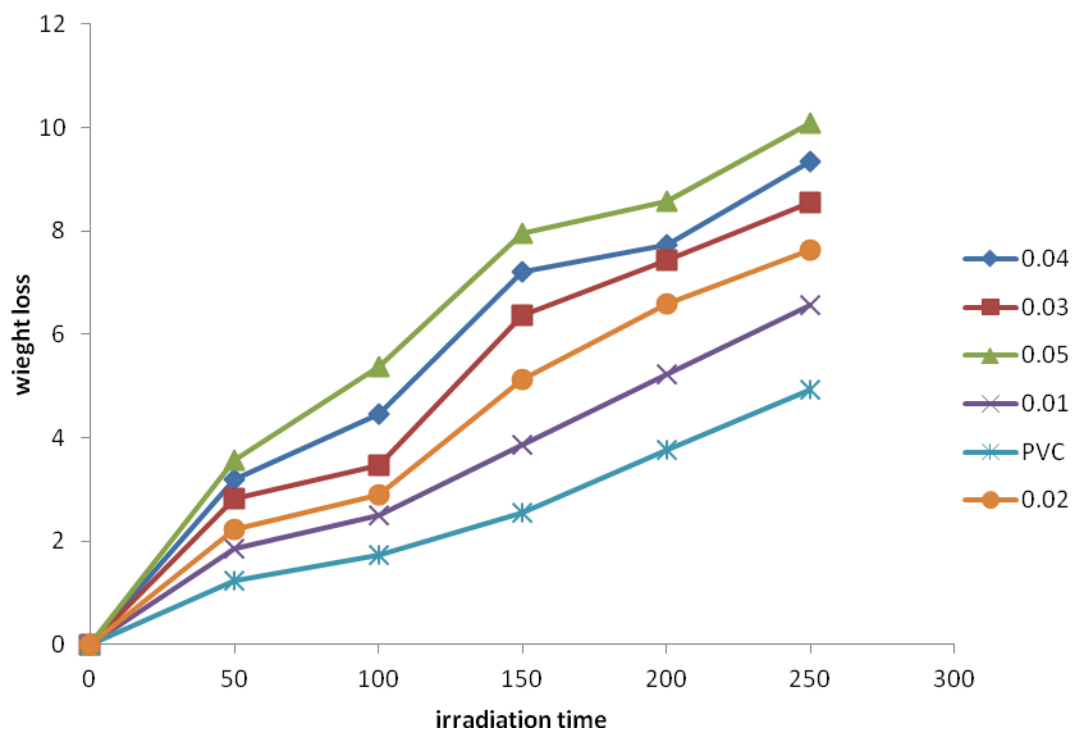


Figure 4 Loss in weight vs. irradiation time (hour) for PVC blank films (control) and modified PVC by different concentrations in a fixed thickness

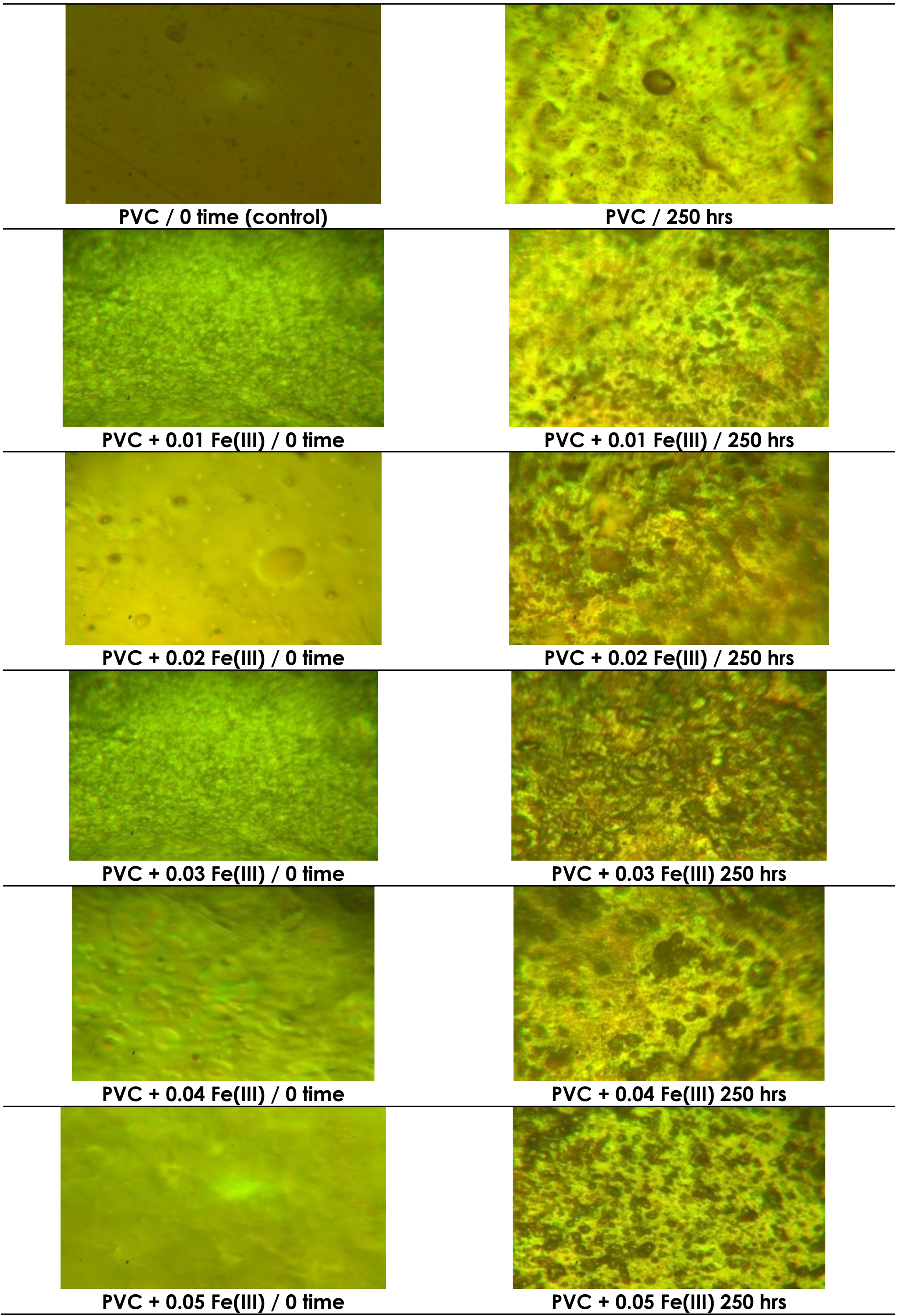


Figure 5 Microscopic images of PVC (control) and PVC + Fe(III) of different concentrations

4.0 CONCLUSION

In this study, the photodegradation of polyvinyl chloride (PVC) films with different concentrations from tris (4-amino-5-(pyridyl)-4H-1,2,4-triazole-3-thiol) Fe(III) complex was investigated. The additives behaved successfully as photoinducers for the degradation process for the PVC films and the photooxidation rate increased with the increase of the additive concentration. The photodegradation effectiveness of the complex additive proved that it has a potential usage to be functional to any weathering resistant polymers as a tunable material. In fact, it can be activated (degradation) once it is exposed to any irradiation sources.

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