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ORIGINAL ARTICLE

Evaluation of Schiff bases of 2,5-dimercapto-1,3,4-thiadiazole as photostabilizer for poly(methyl methacrylate)

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Schiff base

Abstract The photostabilization of poly(methyl methacrylate) (PMMA) films by Schiff bases of 2,5-dimercapto-1,3,4-thiadiazole compounds was investigated. The PMMA films containing concentration of complexes 0.5% by weight were produced by the casting method from chloroform solvent. The photostabilization activities of these compounds were determined by monitoring the hydroxyl index with irradiation time. The changes in viscosity average molecular weight of PMMA with irradiation time were also tracked (using benzene as a solvent). The quantum yield of the chain scission (Φ_{cs}) of these complexes in PMMA films was evaluated and found to range between 4.19×10^{-5} and 8.75×10^{-5} . Results obtained showed that the rate of photostabilization of PMMA in the presence of the additive followed the trend:

[1] > [2] > [3] > [4] > [5].

According to the experimental results obtained, several mechanisms were suggested depending on the structure of the additive. Among them, UV absorption, peroxide decomposer, and radical scavenger for photostabilizer mechanisms were suggested.

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1. Introduction

Ultraviolet light stabilizers are used widely in plastics, cosmetics, and films. The main purpose of UV-stabilizer is to prevent polymers from photodegradation or photocrosslinking caused by ultraviolet light presented in sunlight and artificial light source. Ultraviolet light stabilizers are divided into inorganic UV-stabilizers, organic UV-stabilizers, and otherkinds. Inorganic UV-stabilizers, such as iron oxide, titanium oxide, chromic oxide, and carbon black, usually cannot evenly distribute in the plastic substrate so much as incompatible with the polymer matrix. The final effects depend on the particle size and concentration (Zhao and Dan, 2006). These drawbacks

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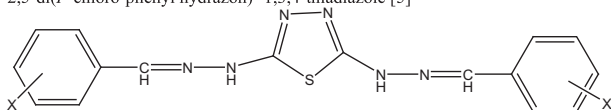
limit the application of inorganic UV-stabilizers. Organic UV-stabilizers, generally with small molecular weight, include fluorescent compounds, phenyl-ester of benzoic acid, hydroxybenzophenone, benzotriazoles, etc. In the addition of these stabilizers to plastic materials, problems such as migration, incompatibility, volatility, and solvent extraction will inevitably occur. It leads to a strong diminution of the materials' utilization. To resolve such problems, many approaches have been developed, such as preparing reactive UV-stabilizer, (Yousif et al., 2009; Grassie and Scott, 1985) introducing compatible side chains, or chemically anchoring of the additive to the polymer backbone, etc (Andrady et al., 1988). Among these methods, preparing high molecular weight UV-stabilizer is a highlight because, for most of the polymer materials, blending is the first choice to enhance their UV-resistance. Meanwhile, different high molecular weight UV-stabilizers can be prepared by the copolymerization of a reactive UV-stabilizer with other monomers. In this point, it is very convenient to ameliorate the compatibility between UV-stabilizer and plastic matrix by preparing suitable high molecular weight UV-stabilizer (Harper et al., 1974). As part of our on-going research on the photostabilization of polymers, the photostabilization of PMMA was studied using Schiff bases of 2,5-dimercapto-1,3,4-thiadiazole compounds.

2. Experimental

2.1. Materials

The Schiff bases of 2,5-dimercapto-1,3,4-thiadiazole compounds were all prepared by the method previously described by Salimon et al. (2010).

- 2,5-di(*O*-hydroxyl-phenyl hydrazon) -1,3,4-thiadiazole [1]
 2,5-di(*P*-nitro-phenyl hydrazon) -1,3,4-thiadiazole [2]
 2,5-di(*P*- dimethylamino -phenyl hydrazon) -1,3,4-thiadiazole [3]
 2,5-di(*P*-methyl-phenyl hydrazon) -1,3,4-thiadiazole [4]
 2,5-di(*P*-chloro-phenyl hydrazon) -1,3,4-thiadiazole [5]



where X = *O*-OH, *P*-NO₂, *P*-N(CH₃)₂, *P*-CH₃ or *P*-Cl.

3. Experimental techniques

3.1. Films preparation

Commercial PMMA was re-precipitated from chloroform solution by alcohol several times and finally dried under vacuum at room temperature for 24 h. Fixed concentrations of PMMA solution (5 g/100 ml) in chloroform were used to prepare polymer films with 40 μm thickness (measured by a micrometer type 2610 A, Germany). The prepared complexes (0.5% concentrations) were added to the films starting at 0 concentrations (blank). It was necessary to control the hygrometry and the rate of evaporation of solvent during casting to maintain good optical quality and very limited turbidity. The film transmission should be greater than 80% in the near-UV range. The films were prepared by evaporation technique at room temperature for 24 h. To remove the possible residual chloroform solvent, film samples were further dried at room

temperature for 3 h under reduced pressure. The films were fixed on stands especially used for irradiation. The stand is provided with an aluminium plate (0.6 mm in thickness) supplied by Q-panel company.

3.2. Irradiation experiments

3.2.1. Accelerated testing technique

Accelerated weather-meter Q UV tester (Q panel, Company, USA), was used for irradiation of polymers films. The accelerated weathering tester contains stainless steel plate, which has two holes in the front side and a third one behind. Each side contains a lamp (type Fluorescent Ultraviolet Lights) 40 W each. These lamps are of the type UV-B 313 giving spectrum range between 290 and 360 nm with a maximum wavelength 313 nm. The polymer film samples were vertically fixed parallel to the lamps to make sure that the UV incident radiation is perpendicular on 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.

3.3. Photodegradation measuring methods

3.3.1. Measuring the photodegradation rate of polymer films using infrared spectrophotometry

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 hydroxyl absorption is specified at 3430 cm⁻¹ (Rabek and Ranby, 1975).

The progress of photo-degradation during different irradiation times was followed by observing the changes in hydroxyl peak. Then hydroxyl index (*I*_{OH}) was calculated by comparison of the FTIR absorption peak at 3430 cm⁻¹ with reference peak at 1450 cm⁻¹, respectively. This method is called band index method which includes (Rabek and Ranby, 1975):

$$I_s = \frac{A_s}{A_r} \quad (1)$$

where *A*_s is the absorbance of peak under study, *A*_r is absorbance of reference peak, and *I*_s is the 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 (Rabek and Ranby, 1975).

3.3.2. Determination of average molecular weight \bar{M}_v using viscometry method

The viscosity property was used to determine the average molecular weight of polymer, using the Mark–Houwink relation (Mark, 2007)

$$[\eta] = K\bar{M}_v^\alpha \quad (2)$$

where $[\eta]$ is the intrinsic viscosity, *K* and α are constants depend 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 (g/100 ml) and the flow times of polymer solution and pure solvent are *t* and *t*₀, respectively. Specific viscosity (η_{sp}) was calculated as follows:

$$\eta_{re} = \frac{t}{t_0} \quad (3)$$

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