

Material Properties

Effects of solar irradiation on the properties of ethylene-norbornene composites containing solvent dyes

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ABSTRACT

This study investigates the effects of irradiation with artificial solar light on the resistance to aging of ethylene-norbornene (EN) copolymer with different solvent dyes and commercial stabilizers. The mechanical properties of the samples were measured before and after ageing using tensile tests. FTIR spectroscopy was used to evaluate the carbonyl index as a measure of photooxidation after irradiation. It was found that the carbonyl index of the samples depended on the type of additive in the composite. Secondary ion mass spectrometry (TOF-SIMS) was used to analyze the chemical composition of the sample surfaces. The degree of oxidative aging was evaluated by measuring the intensities of secondary $C_xH_yO_z^+$ type ions. Samples containing anthraquinone solvent dyes, such as Solvent Blue 97 or Solvent Green 28, showed the most significant improvements in durability in an aging test. Some of the applied solvent dyes showed much greater ability than the studied stabilizers to protect EN films exposed to the full solar spectrum.

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1. Introduction

The stability of polymer materials is an important issue for both the polymer industry and the potential user. Polymers and polymer composites are increasingly being used in a wide range of applications where long-term service in hostile environments is required. One of the disadvantages of polymers is that they undergo an aging process when used in high temperatures or in outdoor conditions [1–5]. The aging of polymers is mainly induced by environmental factors like oxygen, ozone, light or high temperature and leads to undesired changes in their physico-chemical properties, such as discoloration or loss of mechanical strength [6–9]. Apart from the environmental factors, other parameters, such as the polymer itself, and the use of additives such as plasticizers, fillers, dyes, pigments etc. affect the rate of degradation. Nevertheless, some additives may affect the aging process and act as a stabilizer or photodegradant in polymer materials [10–12]. For that reason, when selecting additives for polymer blends it is necessary to know the effect of the additive on both the polymer matrix and its other components. Organic dyes and pigments are mainly used

in polymer materials to impart color, however they can have also a significant impact on photostability [13–20].

Only a small group of dyes is suitable for coloring hydrophobic polymers (PP or PE). Such colorants must fulfill a number requirements such as good solubility in non-polar or slightly polar media, light resistance, resistance to chemicals and high thermal stability under processing [21,22].

Solvent dyes is relatively a new group which almost fully meet these requirements. They are inexpensive, have very good solubility in non-polar media, excellent color strength and transparency as well as high heat and light stability. Despite this group of dyes being of great interest to industry, there is still no information about the effects of these dyes on the properties and aging process of the final polymer materials.

In the present research, solvent dyes with different types of chromophores were employed to obtain colored polymer films characterized by enhanced aging resistance. The effects of solvent dyes on the properties of the dyed ethylene-norbornene EN copolymer were compared to a reference and samples with stabilizers that are commonly used in polymer technology.

2. Materials and sample preparation

Dyes: Solvent Blue 97 1,4-bis [2,6-diethyl-4-methylphenyl]

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amino] anthracene-9,10-dione (Keystone, USA), Solvent Green 28 (1,4-bis [(4-*n*-butylphenyl)amino-5,8-dihydroxy] anthracene-9,10-dione (Keystone, USA), Solvent Red 149 6-(cyclohexylamino)-3-*N*-methylantrapyridone (Keystone, USA), Solvent Red 52 3H-naphtho [1,2,3-*de*]quinoline-2,7-dione, 3-methyl-6-[(4-methylphenyl) amino] (Keystone, USA), Solvent Yellow 98 2-octadecyl-1H-thioxantheno [2,1,9-*def*]isoquinoline-1,3(2H)-dione, Solvent Green 5 3,9-perylenedicarboxylic acid (Keystone, USA).

Stabilizers: Tinuvin 234 2-(2H-benzotriazol-2-yl)-4,6-bis(1-methyl-1-phenylethyl) (Ciba, Switzerland), Chimassorb 81 [2-hydroxy-4-(octyloxy)phenyl]phenyl (Ciba, Switzerland), Tinuvin 1577 2-(4,6-diphenyl-1,3,5-triazin-2-yl)-5-[(hexyl)oxy]-phenol (Ciba, Switzerland). Structures of the studied dyes and stabilizers are shown in Table 1.

Ethylene norbornene random copolymer (EN) - Topas Elastomer 140 (40 wt% bound norbornene content, TOPAS Advanced Polymers, Germany) was used as a polymer matrix. The ethylene-norbornene EN mixtures were prepared by homogenization of the EN copolymer and dyes or stabilizers in an internal mixer (Brabender Measuring Mixer N50).

The formulations of the EN compounds consisted of the following: ethylene-norbornene copolymer (100 phr), dye (0.2 phr) or stabilizer (0.2 phr). The polymer mixtures were processed at a rotor speed of 50 rpm and an initial temperature of 120 °C. Samples with a thickness of 1 mm were obtained by pressing the compounds between steel plates at 100 °C for 10 min.

3. Methods

The solubility parameters of the solvent dyes and stabilizers were predicted according to Krellen's method from the group contributions (dispersion forces δ_d , polar forces δ_p , hydrogen-bonding forces δ_h , V - molar volume) using the following equations [23]:

$$\delta_d = \frac{\sum F_{di}}{V} \quad (1)$$

$$\delta_p = \frac{\sqrt{\sum F_{pi}^2}}{V} \quad (2)$$

$$\delta_h = \frac{\sqrt{\sum E_{hi}}}{V} \quad (3)$$

The differences in the solubility parameters ($\Delta\delta$) between the polymer and additives (solvent dyes, stabilizers) were calculated using equation (4).

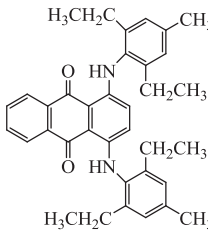
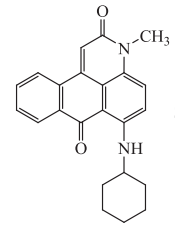
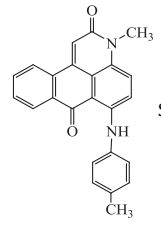
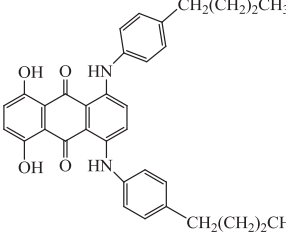
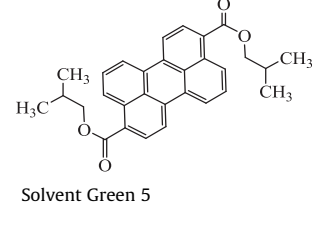
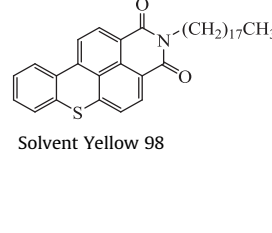
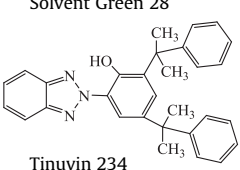
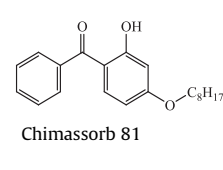
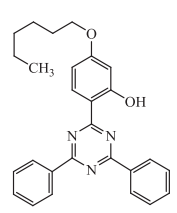
$$\Delta\delta = \left[(\delta_{d,P} - \delta_{d,D})^2 + (\delta_{p,P} - \delta_{p,D})^2 + (\delta_{h,P} - \delta_{h,D})^2 \right]^{\frac{1}{2}} \quad (4)$$

The thermal stability of the powders was studied using a TGA/DSC1 (Mettler Toledo, Italy) analyzer. The samples were heated from 25 °C to 500 °C in an argon atmosphere (60 ml/min) at a rate of 10 °C/min.

The UV-Visible absorption measurement were studied with a Jasco V-670 spectrophotometer (Japan) using standard quartz cuvettes. The absorption spectra were recorded over a wavelength range of 200–800 nm. The dyes and stabilizers concentrations were 1×10^{-5} M (in chloroform) for all the samples. Attenuated total reflection Fourier transform infrared (ATR-FTIR) spectra were recorded on a Thermo Scientific Nicolet 6700 FTIR spectrometer (USA), equipped with a diamond crystal, at room temperature with a 32-scan signal from 600 to 4000 cm^{-1} in absorbance mode. Each result was the average from 3 different places on the sample and averaged.

DSC measurements (Q 200 DSC, TA Instrument, USA) of samples were performed at a heating rate of 10 °C min^{-1} in the temperature range –80 to 180 °C under a nitrogen atmosphere.

Table 1
Chemical composition of the dyes and stabilizers studied.

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