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Novel dyed ethylene-norbornene composites with enhanced aging resistance



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Stability

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ABSTRACT

The current research investigated the effects of anthraquinone solvent dyes and commercial stabilizers on the aging resistance properties of ethylene-norbornene (EN) composites subjected the aging in the full solar-spectrum for various time periods. During irradiation, the mechanical properties were measured by low and high degrees of deformation using dynamic mechanical analysis (DMA) and tensile tests until break, respectively. Changes in the color and surface defects in the investigated composites were evaluated using spectrophotometry and scanning electron microscopy (SEM). An accelerated aging test revealed that the application of solvent dyes with anthraquinone chromophores significantly prolonged the lifetimes of the EN composites during aging. The best improvement in durability was found in the EN samples that contained dyes, such as Solvent Blue 97, Solvent Blue 104, Solvent Blue and Solvent Green 28. Moreover, the ability of solvent dyes to protect EN composites against harmful effects of solar radiation was found to be much greater comparing to those of the investigated, commonly used stabilizers.

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1. Introduction

Dyes and pigments are widely used in the coloration of polymer materials for many commercial applications [1,2]. Although pigments and dyes are primarily used to impart color to the particular polymer and make it attractive for consumers, they can also have a dramatic effect on the polymer photostability [3–9]. For example, anatase form of titanium dioxide (TiO₂) is markedly photosensitive in degrading polymers [10]. Literature data showed that both organic and non-organic pigments generally improve the light stability and weathering resistance of polymeric materials [11–14]. Favorable pigment influences on the polymer light stability is most likely due to screening or selective absorption of harmful radiation, and deactivation of polymer photoexcited species. Among organic pigments, phthalocyanine blue and green pigments were identified as the most useful in this regard, because they exhibit strong absorption in UV range [15–17].

Dyes as opposed to pigments, are soluble and transmit light in

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http://dx.doi.org/10.1016/j.polymdegradstab.2015.11.013 0141-3910/© 2015 Elsevier Ltd. All rights reserved. the media being colored. Out of the wide variety of dyes only a small group of them is suitable for coloring polymers especially non polar like PP or PE. They must fulfill a number of requirements such as good solubility in non-polar or slightly polar media, light resistance, resistance to chemicals and high thermal stability under processing [18,19]. Some of the colorants which almost fully meet these requirements are solvent dyes being the subject of this study.

Recently a new group of solvent dyes with anthraquinone chromophores, characterized by exceptional good heat and light resistance has been developed. They are relatively inexpensive, have very good solubility in non-polar medium, excellent color strength, transparency as well as high heat and light stability. Moreover, a full range of colors, with similar solubilities and stabilities, can be developed by changing the pendants on the anthraquinone molecule [20,21]. Nevertheless, in the literature there is no information about the effects of such type of dyes on the aging process of polymer materials.

In the current research solvent dyes with anthraquinone chromophores and different types of auxochromes, were employed to obtain colored elastomer composites characterized by enhanced aging resistance and good mechanical strength. The effects of



solvent dyes on the properties of the tested composites were compared to a reference sample and stabilizer-based composites of ethylene-norbornene EN, which are commonly used in polymer technology.

2. Materials and sample preparation

Dyes: Solvent Blue 97, 1,4-bis[(2,6-diethyl-4-methylphenyl) amino] anthracene-9,10-dione (Keystone, USA), Solvent Blue, 104 1,4-bis[(2,4,6-trimethylphenyl)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 207, 1,5-bis[(3-methylphenyl)amino]anthracene-9,10-dione (Keystone, USA). Solvent Blue dye, 1,4-bis[(4-n-butylphenyl) amino] anthracene-9,10-dione has been synthesized according to formulas described in the literature [21].

Commercial stabilizers: Tinuvin 234, phenol, 2-(2H-benzotriazol-2-yl)-4,6-bis(1-methyl-1-phenylethyl) (Ciba, Switzerland), Chimassorb 81, methanone [2-hydroxy-4-(octyloxy)phenyl]phenyl Switzerland (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 copolymers (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), solvent 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 80 °C. Samples with a thickness of 1 mm were obtained by pressing the compounds between steel plates at 100 °C for 10 min.

3. Method

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) with a heating 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 for all the samples.

Attenuated total reflection Fourier transform infrared (ATR-FTIR) spectra were recorded on a Thermo Scientific Nicolet 6700 FT-IR 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 taken from 3 different places of sample and averaged.

DSC measurements (DSC1 Mettler Toledo, Italy) of samples were performed at a heating rate of 10 °C min⁻¹ in the temperature range -50 to 200 °C under a nitrogen atmosphere. The glass transition temperatures (T_g) were determined at the midpoint of the step.

Tensile properties were characterized with ZWICK 1435 tensile testing machine of Zwick Roell Group (Germany). Tensile strength (TS) and elongation at break (Eb) were measured at room temperature with a crosshead speed of 500 mm/min. For testing, type 2 dumb-bell specimens were prepared according to the ISO-37-2005 standard. Five different dumbbell-shaped specimens were tested, and the average value for each formulation was reported. Measurement error was in the range of $\pm 1-3$ MPa for TS values and for

 \pm 5–15% for Eb values. The aging coefficient S was calculated according to the following relationship: S = [TS_A × Eb_A]/[TS_B × Eb_B], where TS corresponds to the tensile strength, Eb to the elongation at break, and TS_A and Eb_A correspond to the values of the TS and Eb after aging, respectively.

Dynamic mechanical analysis (DMA) was performed on a TA Instruments Q 800 Dynamic Mechanical Analyzer (USA) operating in tension mode at a frequency of 10 Hz. Testing was conducted over the temperature range of -80 to $100 \degree$ C with a heating rate of 2 °C/min.

The color of the obtained composites was measured using a CM-3600d spectrophotometer from Konica Minolta Sensing, Inc. (Japan). The instrument provided the color in the terms of the CIE L*a*b* color space system. In this color space, L represented the lightness (or brightness), a and b were color coordinates, where $+a^*$ was the red direction, $-a^*$ was the green direction, $+b^*$ was the yellow direction, and $-b^*$ was the blue direction. Moreover, changes in individual components allowed to estimate the total change of color E. The spectral range of the apparatus was 360–740 nm, where the change of color ΔE was calculated by the equation below (1):

$$\Delta E = \sqrt[2]{(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2}$$
⁽¹⁾

 ΔL corresponds to the difference in the brightness intensity between light and dark, Δa corresponds to the difference of intensity between green and red, Δb corresponds to the difference of intensity between blue and yellow, and the Δ symbol implies the difference in the colors of the samples before and after aging.

Weather aging of samples that contained dyes or stabilizers was performed with light radiation of $\lambda = 280-3000$ nm using a Solar Climatic 340 instrument. The test was based on two variable periods that simulated day and night conditions. The test timeline had the following parameters: day period – solar irradiation, temperature 70 °C, humidity 50%, duration 8 h; night period – temperature –20 °C, humidity 60%, duration 4 h. The length of the test was 1400 h.

4. Results and discussion

4.1. Thermal stability of dyes and commercial stabilizers

Thermal analysis plays an important role in the study of the stability of polymer additives. To be suitable for application, the dyes and stabilizers must be able to withstand the polymer processing conditions and the subsequent environmental conditions. Table 2 shows the thermal stability data of the dyes and stabilizers as determined by thermogravimetric analysis (TGA). The nature and position of the substituents in the anthraquinone dves influence the color and other properties. The heat and chemical stabilities vary considerably for different substituted pendants on the base anthraquinone chromophore. It is known that α -substituents increase the molar extinction coefficients and enhance the technical performance, especially the lightfastness, of dyes because of their participation in intramolecular hydrogen bonding with the carbonyl groups. Generally, the heat stability of 1,4-disubstituted anthraquinone dyes, increases with the polarity of the substituent group [22,23].

Solvent Green 28 has the highest heat resistance of the anthraquinone dyes with different substituents. The presence of hydroxyl groups in the 5- and 8-positions in the molecule of Solvent Green 28 increases its thermal stability compared to Solvent Blue. On the other hand, the alkyl butyl chain attached to the aromatic ring in Solvent Blue provided better heat stability than the

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