

Thermochromic Polyolefin Foils

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ABSTRACT: Novel polyethylene and polypropylene foils were prepared by incorporating a thermochromic composite into the polymer matrices by extrusion technology. The composite is homogeneously embedded in the polymer. Detailed investigations on the optical and surface properties of the prepared Polyolefin foils are reported. The investigations include the concentration and temperature dependence of the ultraviolet–visible spectra as well as the determination of the surface tension

by contact-angle measurements. A linear relationship between the concentration of the composite and the absorption intensity of the foil has been found. In contrast to polyethylene in polypropylene no migration process was observed under the used condition. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 1789–1792, 2005

Key words: extrusion; functionalization of polymers; tension; UV-vis spectroscopy

INTRODUCTION

In recent years several novel thermochromic polymer materials were reported whereby either the polymer itself possesses thermochromic properties or thermochromic pigments were incorporated into the polymer matrices.^{1,2} Polymers which can exhibit thermochromic properties themselves are conjugated polymers like polyacetylenes, polythiophenes and polyanilines as well as chiral liquid-crystalline polymers.^{3,4} Thermochromic pigments for the use in polymer matrices are e.g. microencapsulated materials like leuco dye systems or cholesteric liquid crystals.^{5,6} However, none of these thermochromic polymer systems has entered the mass market so far. Neither thermochromic polymer foils nor thermochromic plastic articles produced by injection molding are commercially available. In our opinion the main reason for this seems to be the high requirements on temperature and mechanical stability during the extrusion process on one side and the selection of the starting substances on the other side.

The aim of our work was to prepare thermochromic foils composed of commercial products. For this purpose novel thermochromic polymers and adapted extrusion processes were developed. Starting from Polyolefins and well known temperature

sensitive composites composed of dyes, developers and sensitizers thermochromic Polyolefin foils were obtained. Detailed investigations on the optical properties of the thermochromic foils as a function of concentration and temperature are presented and possible influences of the composite on the surface tension (γ) are discussed.

EXPERIMENTAL

Foil preparation

The thermochromic composite was prepared according to the well-known procedure described *in extenso* in the literature.^{1,5}

Polyethylene (PE; Lupolen 1800S) and polypropylene (PP; Moplen HP510M) were purchased from Basell (Rotterdam, The Netherlands). The raw polymers were mixed with the thermochromic composites in concentrations of 1.25, 2.5, 3.75, and 5.0 wt %. Then, these mixtures were used to prepare the thermochromic polymer foils by extrusion processes. For this purpose, an extrusion line (Dr. Collin GmbH, Ebersberg, Germany) consisting of an E 25 M extruder, a 200-mm slot die, and a CR 136/350 chill roll was used. The thermochromic PE foils were prepared at an extrusion temperature of 150°C, a slot-die temperature of 170°C, a chill-roll temperature of 55°C, and a screw speed of 40 rpm; this led to a dwell time of the polymer in the extruder of about 8 min. The respective parameters for the preparation of the analogous PP foils were an extrusion temperature of 230°C, a slot-die tempera-

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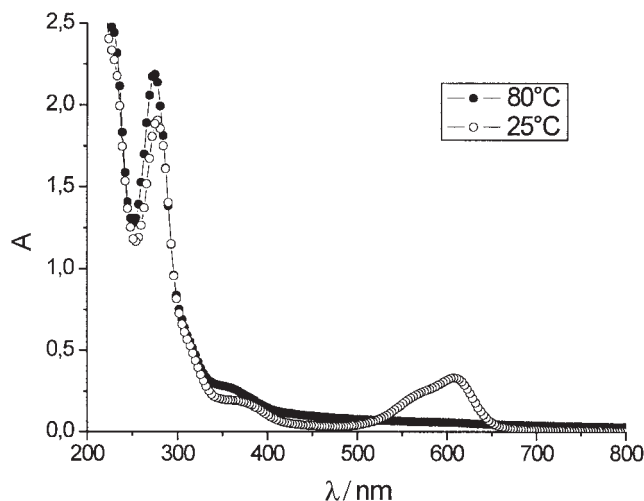


Figure 1 Absorption spectra of a PE foil (thickness = 100 μm , concentration of the thermochromic composite = 5 wt %) at 25 and 80°C. A is the absorption, and λ is the wavelength.

ture of 240°C, a chill-roll temperature of 35°C, and a screw speed of 40 rpm.

Ultraviolet–visible (UV–vis) spectroscopy

The temperature dependence of the optical properties of the thermochromic foils were determined with a PerkinElmer Lambda 18 UV–vis spectrometer in a dry atmosphere. All measurements were carried out against a foil of the raw polymer in the reference beam. Before spectra was taken, the samples were kept at the respective temperature for about 20 min to achieve an equilibrium state.

Surface tension

Contact-angle measurements were carried out with Krüss G1 equipment (Krüss GmbH, Hamburg, Germany). For these investigations, two liquids, water (bidistilled) and methylene iodide, were used. All measurements were carried out immediately after foil preparation. The relationship between the contact angle (Θ) of a liquid on a substrate surface and the three interface tensions (γ_S , γ_L , and γ_{SL}) is given by the Young equation [eq. (1)]. Fowkes divided γ into dispersive and polar components [γ^d and γ^p , respectively; eq. (2)].⁷ For liquid/solid systems with only dispersive forces between the two phases, Fowkes proposed eq. (3):

$$\gamma_S - \gamma_{SL} = \gamma_L \cos \Theta \quad (1)$$

$$\gamma = \gamma^d + \gamma^p \quad (2)$$

$$\gamma_{SL} = \gamma_S + \gamma_L - 2\sqrt{\gamma_S^d - \gamma_L^d} \quad (3)$$

Through the combination of eqs. (1) and (3), it becomes possible to determine γ^d and γ^p on the substrate surface [eq. (4)].⁸

$$\frac{\gamma_L(1 + \cos \Theta)}{2} = \sqrt{\gamma_S^d - \gamma_L^d} \quad (4)$$

RESULTS AND DISCUSSION

The UV–vis spectra of a 100- μm -thick thermochromic PE foil at 25 and 80°C are shown in Figure 1. In this temperature region, the investigated PE foil switches from blue to colorless. At 25°C, two absorption maxima appear in the spectrum, one in the visible region at 608 nm and the other one in the UV region at 276 nm. The absorption at 608 nm causes the blue color of this foil at room temperature. Increasing the temperature to 80°C leads to a complete disappearance of the absorption band at 608 nm, and thus the foil appears colorless at this temperature. Simultaneously, the intensity of the second band at 276 nm increases.

This behavior agrees with the model of a reversible ring-opening/ring-closing reaction of the leuco dye as the origin of the thermochromic effect.⁹ The dye used in this system is crystal violet lactone (CVL). CVL is one of the best investigated phthalide dyes; its ring-opened and ring-closed structures are displayed in Figure 2. The color formation in a CVL/developer system and the two main synthetic routes for CVL are described in detail in ref. 1. In comparison to the ring-closed state, which absorbs in the UV region (276 nm), the ring-opened zwitterionic state has an enlarged chromophoric group, and so the absorption takes place at a longer wavelength (608 nm). The reversible ring-opening/ring-closing mechanism can be observed in the thermochromic polymer foil too.

To investigate the influence of the polymer matrix on the thermochromic effect, we carried out analo-

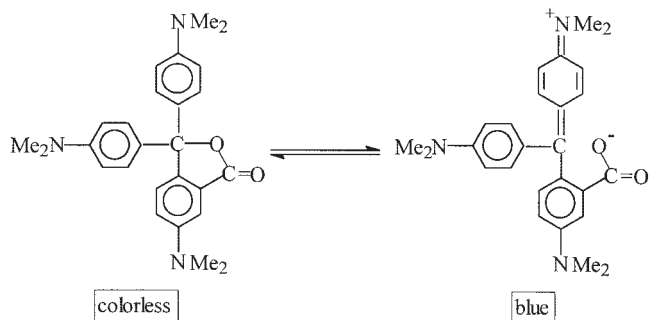


Figure 2 Molecular structures of the ring-opening/ring-closed forms of CVL.

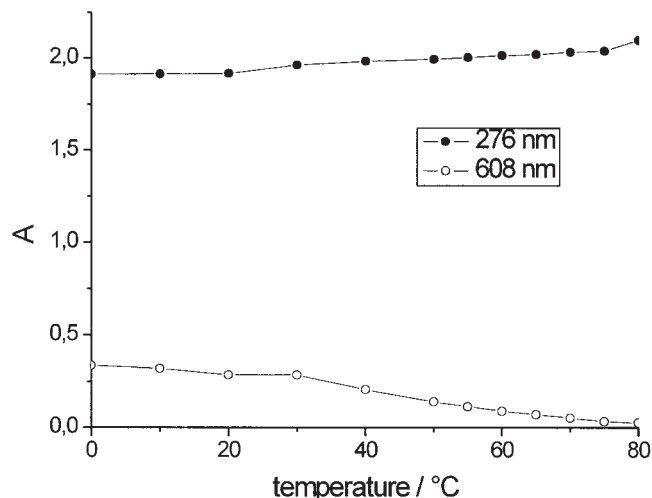


Figure 3 Intensity of the two absorption maxima of a PP foil (thickness = 100 μm , concentration of the thermochromic composite = 5 wt %) as a function of the temperature. A is the absorption.

gous experiments with PP as a carrier material. When the polymer matrix is changed from PE to PP, neither the maximum wavelength of the two absorption peaks nor the form of the bands changes. When the temperature is increased to 80°C, again a disappearance of the absorption band at 608 nm occurs, whereas the intensity of the absorption band at 276 nm simultaneously increases. In Figure 3, the temperature dependence of the intensities of both absorption maxima is displayed in more detail. Within the investigated temperature range, the absorption band at 608 nm decreases continuously with increasing temperature. To investigate potential interactions between the polymer and composite, we prepared foils with different composite contents.

Figure 4 shows the intensity of the two absorption bands at 276 and 608 nm of thermochromic PP foils with different composite contents. At all concentrations, the relation between the intensities of both bands is equal. This is an indication that the equilibrium between the ring-opened/ring-closed structure of the dye is not influenced by the concentration within the investigated concentration range. Moreover, a linear relationship between the absorption intensity and concentration of the thermochromic composite can be observed. This behavior agrees with Beer's law. Obviously, the interactions between the components of the composite are stronger than the polymer-composite interactions. No dye aggregate phenomena or novel structures induced by polymer-composite interactions exist in this concentration range. Analogous investigations with PE have led to the same results. It can be concluded that the composite is embedded as a separate phase in the polymer

foil. Obviously, a new ordered structure based on a specific interaction between the polymer carrier material and composite is not built up.

Considering the influence of the thermochromic composite on the surface properties of the foil, we have characterized γ in detail. γ is known as a suitable parameter for determining the relationship between polar and dispersive molecular structures. The results are summarized in Table I. With 30.5 mN/m, the determined γ value of PE is in good agreement with ref. 10. The deviation between the measured γ value of PP of 24.8 mN/m and the literature value of 30.0 mN/m may have its origin in the different types of PP investigated. With the addition of the thermochromic composite to the polymer foils, no specific differences in γ_s are found. Thus, the values for pure PP with 24.8 mN/m and doped PP with 24.6 mN/m and for pure PE with 30.5 mN/m and doped PE with 31.7 mN/m are within the range of experimental errors. Hence, the composite must be predominantly incorporated into the polymer bulk. For PP foils with and without the composite, even γ^d and γ^p are nearly equal. A comparison of the thermochromic PE foil and the pure material shows that γ^p increases with the addition of the composite. This can be an indication of an incipient diffusion of the composite materials to the surface. The different behaviors of the two thermochromic foils can be explained by a significantly slower migration of the composite materials in PP in comparison with that in PE.¹² Because all 10 measuring points are in very good conformance, it can be assumed that no concentration gradient of the composite exists. These results additionally support the assumption that the thermochromic composite is

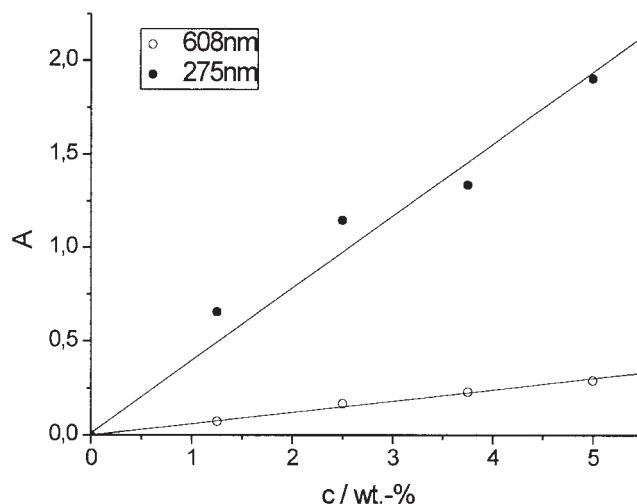


Figure 4 Intensity of the absorption maxima at 275 and 608 nm of PP foils (thickness = 100 μm) as a function of the concentration of the thermochromic composite. A is the absorption, and c is the concentration.

TABLE I
Surface Tension Parameters (mN/m) of the Investigated Foils

Polymer	γ_s (mN/m)	γ_s^d (mN/m)	γ_s^p (mN/m)
PE			
Pure	30.5 ^a	29.0	1.5
With thermochromic composite	31.7	21.2	10.5
PP			
Pure	24.8 ^b	24.6	0.2
With thermochromic composite	24.6	22.8	1.8

^aPE $\gamma_s = 30.8$.¹⁰

^bPP $\gamma_s = 30.0$.¹¹

very well homogeneously incorporated into the polymer foil.

CONCLUSIONS

Novel thermochromic polyolefin foils based on thermochromic composites have been prepared by extrusion technology. A linear relationship between the concentration of the thermochromic composite and the absorption intensity has been found, and it indicates that the interactions between the components of the composite dominate. When PE is exchanged for PP, there are no differences in the temperature-dependent absorption spectra. Furthermore, migration processes are much stronger in PE than in PP.

Further investigations for characterizing the interaction of the thermochromic composite with the polymer environment in detail, on the one hand, and possible migration processes with respect to a long period, on the other hand, are necessary to generalize the reported results. In particular, with

more polar polymers such as polyester and polycarbonate, continuative knowledge should be obtained.

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