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Structural and morphological changes during UV irradiation of the *trans*-planar form of syndiotactic polypropylene

Liberata Guadagno*, Carlo Naddeo, Marialuigia Raimondo, Vittoria Vittoria

Dipartimento di Ingegneria Chimica e Alimentare, Università di Salerno, Via Ponte Don Melillo 1, 84084 Fisciano – Salerno, Italy

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Abstract

Syndiotactic polypropylene films, obtained in the *trans*-planar mesophase, were exposed to accelerated weathering in a UV device at 45 °C for increasing times. A different series of films, characterized by the same structural organization, was annealed at 45 °C for the same times, to discern the thermal effects from those due to UV irradiation. The influence of UV irradiation and thermal treatments on the structural changes in terms of phase composition, crystallite sizes, and chain conformations was studied. Diffractometric and thermal analyses show that UV radiation causes a strong increase of helical crystallinity (189% with respect to the initial value), leaving the *trans*-planar mesophase unchanged. The mesophase domains have a higher rigidity and hinder the oxygen diffusion slowing down the photooxidative degradation.

The chain scission in the amorphous phase produces a higher mobility, allowing crystallization. The crystallinity also increases in the thermally treated samples, but the increase is limited to the first 48 h and reaches about 89% of the initial value. Both in the thermally treated and UV irradiated samples the crystallite coherence length perpendicular to the 200 planes increases with time. The amorphous chains do crystallize at the beginning near the already formed crystals, thus increasing their dimensions. The carbonyl index shows an induction period of 48 h, before a rapid increase which apparently is inversely proportional to the percentage of mesomorphic and crystalline phases of the irradiated samples, indicating that the photooxidative reactions took place mainly in the amorphous region. A comparison with data already published on the photooxidative behavior of samples crystallized in form I shows that the presence of compact domains in *trans*-planar mesophase led to an increase in the induction period and to a greater stability of the material in the first 150 h of UV treatment.

Keywords: Syndiotactic polypropylene; Photooxidation; *Trans*-planar mesophase; Morphological changes

1. Introduction

Syndiotactic polypropylene (sPP) has been obtained with high molecular weight and high tacticity in recent years, using a new class of metallocene catalysts [1–3]. Following extensive research aimed at clarifying the complex polymorphic behavior of this new polymer [4–18], attention is currently devoted to its physical properties in view of innovative applications.

Besides the unusual elasticity shown by the oriented samples of sPP, the electrical properties have been recognized as superior to those of the isotactic isomer [19–21]. In particular a better resistance to pulse breakdown, combined with a higher toughness, would make sPP particularly suitable for insulation in electrical machinery. It has also been shown that sPP is a good candidate for manufacturing of insulating cables for electrical wiring and therefore could be used to substitute conventional cross-linked polyethylene (XLPE) which requires complex cross-linking using peroxide for successful welding. However, in the study of the physical properties, scarce attention is generally given either to the polymorphism or to the morphology of differently processed samples. On the contrary, the macroscopic properties depend indeed on many factors, often hardly correlated, such as phase composition, features of the amorphous component, crystallite size and perfection, morphology and polymorphism. These considerations are particularly relevant in the case of syndiotactic polypropylene

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* Corresponding author. Fax: +39 089 964057.
E-mail address: lguadagno@unisa.it (L. Guadagno).

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(sPP), a polymer exhibiting highly variable mechanical properties, depending on chain conformation, orientation, crystallinity and polymorphism.

Four crystalline forms of sPP have been described so far. Forms I and II are characterized by chains in $(T_2G_2)_n$ helical conformation [4,10], whereas forms III and IV present chains in *trans*-planar and $(T_6G_2T_2G_2)_n$ conformations [8,9], respectively. Form I is the stable form of sPP obtained under the most common conditions of crystallization either from the melt state or from solution as single crystals [4–7]. Different kinds and amounts of disorder of the crystalline phase, depending on the degree of stereoregularity and the mechanical and thermal history, were described in rapidly crystallized samples [22]. In samples kept from the melt in a cold bath at 0 °C for many days, the presence of a *trans*-planar mesophase [11,17–18] was recognized and described. Stretching either the helical form I or the *trans*-planar mesophase, the crystalline form III with the chains in *trans*-planar conformation is obtained when the sample is fixed, whereas the starting conformations are again formed when the tension on the sample is relaxed [15–16,18].

We have already described the influence of the morphology on some of the physical properties of sPP [23, 24]. Moreover, for potential and specific applications, the degradation studies are of topical and relevant interest. Since these properties also have to be strictly correlated to the sample morphology which plays an integral part in the course of photooxidation, we have undertaken a wide study to correlate the photooxidative degradation to the structural organization of sPP samples of very well controlled morphology. In a previous paper [25] we have shown the effect of an accelerated weathering on the morphological changes of a sPP sample crystallized in the disordered form I, having the chains in helical conformation, and containing a small fraction of chains in *trans*-planar conformation. We have found that the irradiative treatment determines a complex structural and morphological reorganization in terms of crystallinity, crystal dimensions, and phase composition.

In this paper we present the structural changes due to the degradation of sPP solidified at low temperature into a mesophase with the chains in *trans*-planar conformation. The *trans*-planar mesophase shows, besides a different chain conformation, a morphological organization very different from form I helical samples, and therefore is worth of investigation in light of correlating morphology and properties. The photooxidative degradation is carried out by exposing the films to UV-A radiation, reproducing the ultraviolet component of solar radiation which strikes the earth's surface. This irradiative treatment has been realized in the presence of oxygen and humidity. The results of the present paper are compared with the degradation behavior of samples crystallized in the helical form I.

2. Experimental section

2.1. Materials

For this work, the same syndiotactic polypropylene used for studying the photooxidative degradation of samples crystallized in the disordered form I [25] was used.

Polymer pellets formulated without slip and antiblock, were bought from Aldrich Polymer Products. The molecular weight, polymer density, and melt index were respectively, 127,000, 0.900 g/mL, and 4.5 g/10 min (ASTM 1238). ^{13}C NMR spectra was recorded on an AM Bruker spectrometer operating at 62.89 MHz, by dissolving 30 mg of polymer into 0.5 mL 1,1,2,2,-tetrachlorodideuterioethane. Hexamethyldisiloxane (HMDS) was used as internal chemical shift reference. Our sample showed 89% syndiotactic pentads.

sPP pellets were molded in the hot press (Carver Inc.), at 170 °C, forming a 70 ± 5 μm thick film, and was rapidly quenched in an ice-water bath at 0 °C. This film was left in the cold bath for three days and analyzed at room temperature (M0 sample).

Sample M0 films were UV irradiated, at different times, in a accelerated photoaging device Q-Panels (Model QUV/spay) equipped with medium pressure mercury lamps at a temperature of 45 °C which glass envelope filters out light at $\lambda < 290$ nm. The UV irradiance times were 1 h (M1UV), 2 h (M2UV), 3 h (M3UV), 6 h (M6UV), 10 h (M10UV), 24 h (M24UV), 33 h (M33UV), 48 h (M48UV), 100 h (M100UV), 170 h (M170UV), 200 h (M200UV), 250 h (M250UV) and 340 h (M340UV). Others samples were subjected for the same times only at thermal treatment of 45 °C. These last samples were denominated with the abbreviation " MtT" where "t" is the heat treatment time (in hours) as in the lines above.

In this paper, the abbreviation AtUV will be also used for syndiotactic polypropylene films, in the most usual crystallographic modification [25] (form I) exposed to the UV radiation for "t" time, where "t" is the UV irradiance time in hours.

2.2. Methods

Wide-angle X-ray patterns (WAXD) were obtained using a Philips PW 1710 Powder diffractometer (Cu K_α-Ni filtered radiation) with a scan rate of $1°(\vartheta)$/min.

Differential scanning calorimetry (DSC) was carried out using a thermal analyzer Mettler DSC 822/400 equipped with DSC cell purged with nitrogen and chilled with liquid nitrogen for sub-ambient measurements. Temperature range was −50 °C/250 °C at a heating rate of 20 °C/min.

The infrared spectra were obtained in absorbance mode using a Bruker IFS66 FTIR-spectrophotometer with a 2 cm^{-1} resolution (64 scans collected). The absorbances of the *trans*-planar conformational bands at 831 and 1132 cm^{-1} and of the helical bands at 812, 977, and 868 cm^{-1}, were normalized with the absorbance of the band at 2724 cm^{-1}. Also the carbonyl index and the absorbance of −OH group were calculated normalizing the absorbance of the bands at 1712 cm^{-1} (C=O group) and 3432 cm^{-1} (O−H group) with the absorbance of the band at 2724 cm^{-1}; obtaining the ratio $I_{C=O} = A_{1712}/A_{2724}$ and the ratio $R_{O-H} = A_{3432}/A_{2724}$.

All the bands composed of different vibrational modes, were decomposed into the different components, using a complex fitting in which a Lorentzian and a Gaussian contribution were considered in the form: