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Course of the changes in thick and thin isotactic polypropylene samples subjected to natural aging

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ABSTRACT

The course of degradation in natural environment of polypropylene items was studied with DSC and thermogravimetric techniques. The enthalpic patterns of the materials vary with time of exposure. Measurements of the melting enthalpies in comparison with the heats of crystallization enabled to assess the evolution of crystallinity during exposure of plates and films of iPP. The induction time before the photochemical attack is of 800 h regardless of the thickness.

The plates lose all practical mechanical properties after 4800 h of exposure, the film only after 2000 h. At the end of exposure, the plate provides a brittle and cracked material that includes a volatile phase and a heat resistant share due to crosslinking reactions. Some hypotheses on the degradation mechanism are presented.

1. Introduction

In previous works [1–3] we studied the natural outdoor aging of isotactic polypropylene (iPP) samples having different thickness. Investigations were performed mainly by means of differential scanning calorimetry (DSC) measures and using other techniques as infrared spectroscopy (FT-IR and ATR), thermogravimetry (TGA), scanning electron microscopy (SEM) and mechanical tests. The experimental findings showed the behavior in real conditions of a material that, unlike the laboratory experiments with artificial radiation, is subjected, among others, to day–night thermal cycles that mean meaningful temperature changes during each season in a temperate climate. This can result in phenomena of natural annealing. Furthermore the weathering can be affected by other outdoor elements as wind, rain, atmospheric dust and pollutants. As a matter of fact some authors confirm that the results obtained with the artificial degradation are not comparable to the natural aging [4,5]. Moreover most of the artificial aging has a relatively short duration, often because the energy levels, so it becomes very difficult to follow in detail the DSC peak changes occurring already in the induction time, referred to as the one that precedes the photooxidation start.

Our previous investigations have not enabled to define the course of the natural degradation as a function of the polymer thickness and to understand the changes in crystallinity with the progress of exposure time. However the natural aging we have studied emphasized clear variations in the shape of DSC peaks from the beginning of exposure and therefore also in the induction period; such variations are roughly characteristics of the degradation type. Moreover the hypothesis of a solid state reaction in the absence of a predominantly photooxidative mechanism could be proposed in the study of thick layers [3].

Literature shows that DSC techniques are able to provide insights into the behavior of macromolecular materials [6] and DSC tests have been widely used in order to follow the polymer changes while increasing the weathering process [7,8].

This work presents the results of DSC tests of natural aged iPP samples with a detailed assessment of the fusion and solidification peaks. The previous data were integrated with those obtained by means of a new experimental procedure, able to assure a better control of heat exchanges by running the DSC curves. The study was supported by data from other techniques used in the preceding works. The degradations of specimens having different thickness were compared in order to define and explain trends and characteristics of the natural aging process.

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2. Materials and methods

Experiments were carried out on polypropylene films and plates not stabilized to light, having the following characteristics: biaxially oriented films of average thickness = 26 μm and of average molecular weight M_w = 328,000 Da [1]; cast films of average thickness = 50 μm and of average molecular weight M_w = 231,000 Da [2]; compression molded plates of average thickness = 2 mm and of average molecular weight M_w = 441,000 Da [3].

All the samples were exposed in Messina, Italy (38° 11′ 20″ north, 15° 33′ 30″ east, 59 m from sea level). The samples were mounted on wooden frames inclined at 45° with respect to the horizon and were exposed facing southwest on a terrace at about 20 m above the ground.

The crystallinity was evaluated on the basis of the melting and crystallization heats measured by DSC. DSC curves were obtained on a DSC-2 Perkin–Elmer instrument using aluminum pans under nitrogen. Indium was used as the standard for calibrating the temperature axis and the enthalpy output. Preliminary tests showed that it is not possible to obtain realistic and reproducible samples of each region of the plate (through the thickness) in the quantities required for the DSC tests. Therefore the sampling was done by cutting a cross-section of the plate including both the surfaces that the inside. So these data are indicative of the average morphology of the whole plate. Each enthalpy value is the average of ten measurements performed on different specimens having the same exposure time. In order to provide faultless thermal contact with the DSC pans many runs were carried out with a new technique: the weighed sample (5–8 mg) was tightly wrapped in an aluminum foil, closed into an aluminum non-hermetic pan and heated under nitrogen at 2.5 deg min^{-1}. For comparison a flat DSC baseline was obtained with an empty aluminum foil closed into an aluminum non-hermetic pan. This modified technique resulted in a higher sensitivity, as confirmed by the detection of the solid phase transition (see Results and discussion) in good agreement with the results of an other modified DSC technique based on an improved thermal transfer [9].

The weight loss of the plate (cross-section) during aging was obtained by dynamical thermogravimetric analysis (TGA) with a TGS-2 Perkin–Elmer thermo-balance in air with a heating rate of 20 deg min^{-1} in the range 323–1223 K.

Scanning electron microscopy experiments have been carried out with a Zeiss DSM 490 instrument. Attenuate total reflection (ATR) infrared spectra have been recorded with a Nicolet Magna 560 interferometer, using a 45° shaped KRS5 ATR crystal. Absorption infrared experiments have been carried out on powder scratched from the thick samples and dispersed in KBr pellets and on films. Mechanical tests have been performed on an Instrom tensile testing machine 1115 at a traction rate of 500 mm/min, at 25° and 50% humidity.

Other experimental details about TGA, SEM, FT-IR, ATR and mechanical tests were reported elsewhere [1–3].

3. Results and discussion

Fig. 1 shows the typical DSC pattern of pure iPP (2 mm thick plate). This curve was obtained by optimizing the thermal exchanges as described in the experimental part and displays two thermal phenomena, important for the characterization of the material:

In the temperature range between 384 K and 402 K is shown a weak exotherm ($\Delta H = -3.2$ J g^{-1}). It is attributable to the solid phase transition of mesomorphic crystal structures into the monoclinic, in agreement with the results of a recent work based on the control of heat exchanges [9].

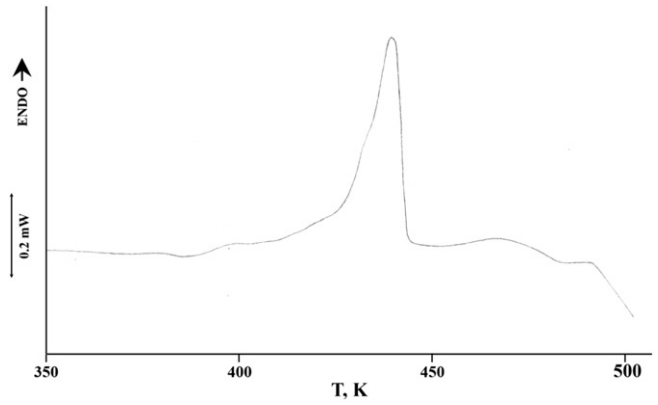

Fig. 1. Typical DSC curve of pristine iPP (2 mm thick plate) with improved thermal transfer: sample wrapped in aluminum foil, closed into an aluminum non-hermetic pan and heated under nitrogen at 2.5 deg min^{-1}.

The melting peak ranges from 407 K to 444 K and has the initial part characterized by small irregularities and a slight shoulder. The temperature corresponding to the maximum of the peak (T_{max}) is 439 K and the melting ΔH is 92.5 J g^{-1}.

3.1. Induction period

Many papers [1–3,10–12] highlight that at an early time of the natural or artificial aging of polypropylene there is no evidence of those oxygenated products that afterwards are visible and growing. So it is called the induction time. Until now no meaningful change in DSC curves or other phenomena able to characterize and clarify the induction time have been reported.

The induction time is about 800–1000 exposure hours in a temperate climate. Since the duration of induction does not change with the thickness, as the exposure of films and plates at the same site has proved [2,3], this period is mainly influenced by the chemical nature of the material, i.e. by the surface radical activity below a critical level before reactions with oxygen.

Fig. 2 shows the heat given by the solid phase transition of thick iPP plates vs. outdoor exposure time, in DSC measurements. The exothermic effect is very low, but the average of many measures suggests a believable decrease from the beginning of the exposure, indicating that some unstable crystallites of the starting plates become monoclinic because of the ambient temperature in the induction time. Contemporaneously the original shoulder of the melting peak becomes more prominent and the height of the main peak decreases (Fig. 3). These shape changes are already visible in

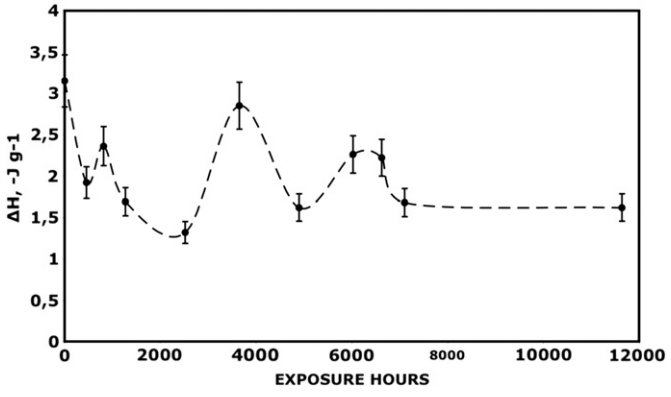

Fig. 2. Enthalpy of the solid phase transition of thick iPP plates vs. outdoor exposure time, in DSC measurements with improved thermal transfer.