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Natural and artificial photo-aging of non-stabilized and pigmented, hindered-amine stabilized propylene–ethylene copolymers

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Abstract

This paper describes the chemical evolution of two propylene–ethylene copolymer formulations, non-stabilized and carbon black filled – HALS stabilized, exposed to a range of natural and artificially accelerated weathering techniques, commonly used in the field of material testing. With the non-stabilized formulation, a fairly good representation of weathering in outdoor conditions was demonstrated with any of the accelerated exposures through the recognition of similar chemical changes at the molecular level. In contrast, the additives in the stabilized matrix induced very different chemical evolutions depending on the weathering techniques employed. This variability has been used to critically characterize those techniques on a scientific basis.

Keywords: Polypropylene; HALS; Photooxidation; Weathering; Artificial; Accelerated

1. Introduction

Aside from the conventional approach used to evaluate the weatherability and durability of polymeric materials, relying on the measurement of material macroscopic properties, a more fundamental approach to the weathering phenomenon at the molecular level is available [1,2]. Indeed, far from being merely a black box exhibiting property changes, any polymer exposed to environmental stresses can be seen as a photochemical reactor undergoing complex chemical reactions where a few, known as the photooxidation mechanism, actually account for the loss of material properties. As will be shown, hereafter, a thorough knowledge of such a mechanism can be used as a powerful tool to scientifically evaluate the relevance of any type of accelerated weathering technique to any outdoor reference weathering.

The photooxidation mechanism of polypropylene has been thoroughly investigated for nearly 40 years and is now fairly well understood [3–8]. The main route accounting for chain scissions involves the primary hydroperoxidation of the tertiary carbon atom and leads to the build-up of the final photoproduct, an α-methyl carboxylic acid, which is mostly found as a dimeric form absorbing at $1713 \pm 3\ \text{cm}^{-1}$ in the infrared range (Fig. 1) [9–11]. Therefore, measuring the intensity of this band in the course of PP photooxidation can be substituted for the use of mechanical tests, provided that the relation between the acidic final product concentration and the variation of the mechanical property has been previously determined. Aside from acids, intermediate and final photoproducts such as hydroperoxides, esters, peresters, ketones, alcohols and lactones are also formed, absorbing between 3700 and 3000 cm^{-1} and between 1780 and 1700 cm^{-1} [12–14].

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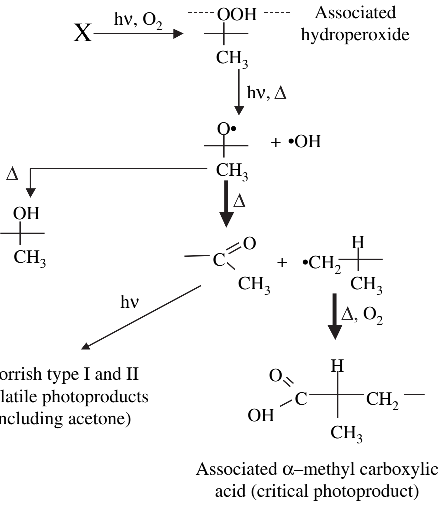

Fig. 1. Main photooxidation route of polypropylene.

2. Experimental

2.1. Materials

Two formulations based on propylene–ethylene copolymer (containing 16% PE), non-stabilized and carbon black filled – HALS stabilized were provided by Targor in the form of 3 mm thick samples. The matrix consisted of nodules of poly (propylene–ethylene) rubber dispersed in a phase of isotactic PP. FT-IR analyses presented in Section 3.2 showed that a combination of monomeric and oligomeric/polymeric HALS was used, at a concentration of 0.3–0.4%. The carbon black concentration was such that at least 99% of the UV daylight (290–390 nm) was filtered out within a path length of 35 μm, as determined from UV–vis spectrophotometry.

2.2. Weathering techniques

2.2.1. Outdoor weathering exposures

Two locations were chosen for outdoor weathering. In Clermont–Ferrand, France, samples were mounted on a rack tilted at 45° facing south. Although no standard practice is associated with this natural exposure location, it has been chosen as a characteristic temperate climate in Western Europe. The second location, at the DSET laboratories in Arizona is a benchmark site for natural exposures in desert conditions. Samples were fastened on open- and plywood-backed racks tilted at 5° facing south, meeting the ASTM G7 standard procedure requirements [15].

2.2.2. Accelerated weathering exposures

EMMA® and EMMAQUA® Atlas instruments use the concentrated daylight as the light source, through its reflection by 10 flat mirrors onto specimens mounted on the target board of the device. Those instruments are operated exclusively at the DSET laboratories, Arizona, according to the ASTM G90 standard cycle 1 (8 min wet/52 min dry, EMMAQUA) and cycle 2 (dry conditions, EMMA) [16].

2.2.3. Accelerated artificial aging exposures

Two accelerated artificial techniques were used. The Weather-Ometer Ci4000 Atlas unit was operated according to the ISO 11341 standard recommendations [17]. The light source is a xenon-arc lamp filtered by a combination of two borosilicate filters ensuring the removal of any wavelengths shorter than 290 nm.

The SEPAP 12/24 Atlas unit, originally designed in 1979 by the Laboratoire de Photochimie Macromoléculaire et Moléculaire in Clermont–Ferrand [18], uses four medium pressure vapour mercury arc lamps filtered by a borosilicate envelop to remove any wavelength shorter than 290 nm, located in the geometrically equivalent corners of the square chamber, operating at a irradiance level of about 80 W m^{-2} between 295 and 385 nm at the specimen level. Samples were mounted on a revolving rack (4 rpm) located in the centre of the chamber. The temperature of the exposed surface was controlled by a thermocouple placed at the back of a film of the same colour and chemical nature as that of the samples, ensuring control at 60 ± 0.3 °C. Neither dark cycles nor water spray was used. Measurement of the relative humidity level performed at the laboratory has shown an average relative humidity level of about 10%.

2.3. Analytical techniques

Various FT-IR spectrophotometers were employed, depending on the geometry of the sample and the examined degradation process. Two transmission modes were available, the macromode for film analysis (Nicolet 510 FT-IR spectrophotometer) and the micromode for very small zones of a film (few thousandths of μm^2) on a Nicolet 800 FT-IR spectrophotometer equipped with a Nic-Plan IR microscope. Photoacoustic analyses were conducted on a Nicolet 800 FT-IR spectrophotometer equipped with an MTEC 200 cell manufactured by Spectra-Tech. This surface analysis technique (FT-IR PAS) is based on the transformation of modulated infrared radiation to a mechanical vibration. The incident IR beam is absorbed by the sample, which results in a thermal transfer from the sample to a surrounding gas (helium in our case). The gas expands to give small pressure fluctuations detected by a sensitive microphone. This acoustic signal is further transformed into an interferogram from which the IR spectrum of the sample is calculated by the application of Fourier transform [19,20].

While the FT-IR PAS provides information regarding the chemical changes at the surface of a sample, the use of the transmission FT-IR spectrophotometry gives access to the profile of a product concentration within the thickness of a sample (e.g. the acid photoproduct to characterize the oxidation profile). This is achieved in two possible ways: either thin films are frontally microtomed (Jung RM2055, Leica) from the exposed surface of a thick sample and individually analyzed by classical transmission FT-IR spectrophotometry [21,22] or a thin film (ca. 30 μm) is cut normally to the exposed surface, so that this cross-section encompasses all the elementary layers from the exposed side to the rear of the sample [23].