Polymer Degradation and Stability 96 (2011) 703–707

Contents lists available at ScienceDirect

Polymer Degradation and Stability

journal homepage: www.elsevier.com/locate/polydegstab

Degradability of linear polyolefins under natural weathering

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ARTICLE INFO

Article history:
Received 13 April 2010
Received in revised form
17 November 2010
Accepted 8 December 2010
Available online 16 December 2010

Keywords:
HDPE
LLDPE
PP
Polyolefin weathering and degradation
Antioxidant and pro-oxidant additives

ABSTRACT

High density polyethylene (HDPE), linear low density polyethylene (LLDPE), and isotactic polypropylene (PP) containing antioxidant additives at low or zero levels were extruded and blown moulded as films. An HDPE/LLDPE commercial blend containing a pro-oxidant additive (i.e., an oxo-biodegradable blend) was taken from the market as supermarket bag. These four polyolefin samples were exposed to natural weathering for one year during which their structure and thermal and mechanical properties were monitored. This study shows that the real durability of olefin polymers may be much shorter than centuries, as in less than one year the mechanical properties of all samples decreased virtually to zero, as a consequence of severe oxidative degradation, that resulted in substantial reduction in molar mass accompanied by a significant increase in content of carbonyl groups. PP and the oxo-bio HDPE/LLDPE blend degraded very rapidly, whereas HDPE and LLDPE degraded more slowly, but significantly in a few months. The main factors influencing the degradability were the frequency of tertiary carbon atoms in the chain and the presence of a pro-oxidant additive. The primary (sterically hindered phenol) and secondary (phosphite) antioxidant additives added to PP slowed but did not prevent rapid photo-oxidative degradation, and in HDPE and LLDPE the secondary antioxidant additive had little influence on the rate of abiotic degradation at the concentrations used here.

1. Introduction

Polyolefins are a class of polymers synthesised by addition reactions of unsaturated monomers (alkyl-ethylenes), of which high density polyethylene (HDPE), linear low density polyethylene (LLDPE) and polypropylene (PP) are good representatives. HDPE, LLDPE and PP differ structurally in the number and length of branches, whose presence tends to reduce the amount and size of crystals, as well as their melting and crystallisation temperatures [1,2]. While HDPE has molecules with a very low number of short and long branches (typically <2 CH_3 groups/1000 C atoms), LLDPE has more short branches (10–30 CH_3/1000 C), obtained through the introduction of one or more co-monomers to ethylene such as 1-butene, 1-hexene and 1-octene [1]. As a result of these branches, HDPE has a high degree of crystallinity (typically 60–80%) and a high melting temperature of ~135 °C, while LLDPE has lower crystallinity (40–60%) and melting temperature (~125 °C) [1]. Isotactic PP contains one methyl branch per monomer unit (333 CH_3/1000 C), but the spatial organisation of these branches results in degrees of crystallinity of 40–60% and a melting temperature of ~163 °C [2]. The tertiary carbon atoms that are present at the branch sites are more susceptible to attack by free radicals, because they form more stable radicals when they lose a hydrogen atom. Some structural defects such as unsaturation and carbonyl and hydroperoxide groups may also be present in all polymers, formed during polymerisation and subsequent processing, but are present at very low levels [3–5].

Polyolefins are the most produced and consumed synthetic polymers worldwide, with many uses such as packaging, toys, appliances, and disposable items. Although chemical and biological inertness was originally seen as an advantage, the high stability of these compounds and resistance to degradation has led to their accumulation in the environment, considerably increasing visible pollution and contributing to the clogging of drains during heavy rains, among other problems [6–8]. Biodegradation represents a solution for the treatment of packaging and disposable items

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doi:10.1016/j.polymdegradstab.2010.12.004

wastes with low thicknesses, which are usually difficult to recycle. However, the principle of microbial infallibility formalised by Alexander [9] has serious limitations when it comes to xenobiotics consisting of polyolefin polymers, which are resistant to biodegradation (recalcitrant) for a number of reasons: they are hydrophobic and have high molar masses, dramatically reducing their bioavailability; they usually form crystals, which are less vulnerable to degradation; and they usually have varying amounts of branches, increasing the recalcitrance of these materials by blocking the action of enzymes of the β-oxidation route on the fatty acids formed by abiotic and biotic oxidation of hydrocarbons [10].

Physical and chemical treatments leading to polymer oxidation (abiotic degradation) can be effectively used as a pretreatment strategy before subjecting the material to biodegradation (biotic degradation) [11,12]. Natural weathering, which includes solar radiation, wind and ambient temperature leads to the formation of free radicals, which may combine with oxygen at the surface and form peroxides and hydroperoxides, following the known reactions of oxidative degradation. As a consequence, alkanes, alkenes, ketones, aldehydes, alcohols, carboxylic acids, keto-acids, linear esters and lactones are formed [13], decreasing the polymer hydrophobicity and molar mass, thus increasing the bioavailability and biodegradability of the polymer [3]. Some branching and crosslinking reactions may also occur, but chain scission dominates over crosslinking for all materials [8,14,15]. Abiotic degradation can be magnified by certain organic salts of transition metals (Co, Mn, Fe, Ni, Cu, etc.), which participate in redox reactions, generating free radicals on the hydrocarbon chains or decomposing previously formed hydroperoxides. Such compounds may be purposely added to the polymer as pro-oxidant additives or may be present as catalytic residues or impurities [2,8,16,17]. The polymeric materials containing pro-oxidant (or pro-degrading) substances are known as oxo-biodegradable polymers [18].

On the other hand, antioxidant additives are usually added to slow the abiotic degradation of polyolefins, and these additives can be generally classified as primary and secondary [19]. Primary antioxidants work efficiently at ambient temperature (and at processing temperatures in synergism with secondary antioxidants), providing protection during the polymer's service life (long-term thermal stability). These are free radical scavengers such as sterically hindered phenols, and are added at levels of about 200–1000 mg kg^{-1} of polymer. Secondary antioxidants act efficiently at the high processing temperatures (melt-processing stability). These are hydroperoxides decomposers, and are mainly certain phosphites, phosphonites and thioesters, and are added at levels of about 400–2000 mg kg^{-1} of polymer. In addition to these additives, there are UV stabilisers, including the UV absorbers that shield the polymer from UV light, and the sterically hindered amine light stabilisers (HALS) that scavenge the radical intermediates formed in the photo-oxidation process. Abiotic degradation only becomes significant after the consumption of the antioxidant additives, and results in the breakdown of the polyolefin molecules into smaller segments and in the incorporation of oxygenated groups, significantly increasing the bioavailability and biodegradability of the polymer [2,17,18].

Considering the enormous and growing worldwide consumption of linear polyolefins and the worrying pollution caused by their accumulation in the environment, this study aimed to assess the abiotic degradability of HDPE, LLDPE and PP extruded blown films with low or zero concentrations of antioxidant additives, as well as an HDPE/LLDPE blend containing a pro-oxidant additive (oxo-biodegradable blend), during one year of natural weathering. Another objective was to understand how the different chemical structures of the polyolefins studied here affect their abiotic degradability.

2. Materials and methods

2.1. Experimental conditions and materials

HDPE was obtained directly from the polymerisation reactor output (Braskem, Spherilene technology). The HDPE used here had melt indices [20] of 0.35 (190 °C, 5.0 kg) and 8.5 dg min^{-1} (190 °C, 21.6 kg), with <2 CH_3/1000 C atoms and a density of 0.947 g cm^{-3} (23 °C). The virgin resin was mixed with 0, 100 and 300 mg kg^{-1} of tris (2,4-di-tert-butylphenyl) phosphite (Irgafos 168, Ciba, a secondary antioxidant) and blown extruded into films (Carnevalli CHD 60 extruder) with a thickness of 25 ± 5 μm. LLDPE, an ethylene-1-butene copolymer (15 CH_3/1000 C atoms), was taken from the reactor (Braskem, Unipol technology) with a melt index of 0.70 dg min^{-1} (190 °C, 2.16 kg) and a density of 0.921 g cm^{-3}, and was mixed with 0, 100 and 300 mg kg^{-1} of Irgafos 168 prior to being blown extruded into films with a thickness of 80 ± 5 μm. Isotactic PP was taken from the reactor (Braskem, Spheripol technology) with a melt index of 7.0 dg min^{-1} (230 °C/2.16 kg) and a density of 0.905, and was mixed with 0, 100 and 300 mg kg^{-1} of Irganox B-215 (a blend of 2 mass parts of Irgafos 168 and 1 part of Irganox 1010, from Ciba). Irganox 1010 is tetrakis [methylene (3,5-di-tert-butyl-4-hydroxyhydrocinnamate)] methane, a primary antioxidant. Subsequently, these mixtures were extruded to form 70 ± 5 μm thickness films. Unlike PE resins, PP always needs primary and secondary antioxidants, because it is extremely sensitive to oxidative degradation under environmental conditions, due to its high content of tertiary carbon atoms. PE bag samples (HDPE/LLDPE – around 70/30 in mass) containing a pro-oxidant additive (d_2w additive from Symphony, at approximately 80 mg cobalt per kg of resin), with 15 μm thickness and 3.66 ± 0.05 g each bag were obtained in supermarkets in São Paulo, Brazil. These bags were painted on one side. In this work, the priority was to obtain films with thicknesses of normal market applications for each resin, using the process of blown film extrusion, which was recommended for all resins used.

2.2. Abiotic degradation

The blown extruded films were inserted into transparent polypropylene envelopes as rectangular samples of approximately 75 × 35 cm. The exposure of the samples to natural weathering was conducted from February, 2007 to February, 2008 on platforms built with an angle of 30° to the ground, facing the equator, in Porto Alegre, RS (Brazil), 30°02′S; 51°12′W. The envelopes used to support the samples on the platform for sun exposure were made of polypropylene, and they were prepared by blown film extrusion, with a wall thickness of 50 ± 5 μm, containing anti-blocking and antioxidant additives but no light stabiliser. The envelopes were changed monthly to avoid losses in transparency and mechanical properties. The transmittances of the envelopes to visible and ultraviolet radiation were higher than 90% in the 285–800 nm range. The transparencies of the film samples used in this work followed the order: PP >> LLDPE > HDPE > > HDPE/LLDPE blend (opaque, painted). The supermarket bag films were exposed with the side without ink to the sun. The envelopes were opened weekly for several hours of aeration. At regular intervals up to 280 days, the exposed samples were analysed as follows. a) Visual inspection of fragmentation, documented by photography. b) Molar masses were determined by size exclusion chromatography (SEC) in a gel permeation chromatograph model Waters GPC 150C with trichlorobenzene as the solvent at a temperature of 140 °C with refraction index detection. c) Changes in chemical structure were monitored through Fourier transform infrared spectroscopy (FTIR) with a Nicolet 470 Nexus instrument. The samples were pressed