Polymer Degradation and Stability 94 (2009) 2128–2133

Contents lists available at ScienceDirect

Polymer Degradation and Stability

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

Abiotic and biotic degradation of oxo-biodegradable foamed polystyrene

Telmo Ojeda [a], Ana Freitas [a], Emilene Dalmolin [b], Marcus Dal Pizzol [c], Leonardo Vignol [c], José Melnik [d], Rodrigo Jacques [e], Fátima Bento [f], Flávio Camargo [a,*]

[a] Department of Soil, Faculty of Agronomy, UFRGS, mailbox 776, Porto Alegre, RS, Brazil
[b] GSI Agromarau, Highway RS 324 Km 80, 99150-000 Marau, RS, Brazil
[c] Innova, III Pólo Petroquímico, 95853-000 Triunfo, RS, Brazil
[d] SpumaPac Ind. Emb., Juscelino Kubitschek Ave., 1726/82, 04543-000 São Paulo, Brazil
[e] Department of Soil, Center of Rural Sciences, Federal University of Santa Maria, 97105-900 Santa Maria, RS, Brazil
[f] Department of Microbiology, Institute of Biosciences, UFRGS, Sarmento Leite St., 500, 90050-170 Porto Alegre, RS, Brazil

ARTICLE INFO

Article history:
Received 10 August 2009
Received in revised form
8 September 2009
Accepted 24 September 2009
Available online 9 October 2009

Keywords:
Abiotic and biotic degradation
Oxo-biodegradable polystyrene
Pro-oxidant additives
Accelerated weathering
Respirometry

ABSTRACT

An alternative for improving the degradability of polyolefins and polystyrene is the addition of pro-oxidant substances to their formulations. The materials obtained are then called oxo-biodegradable. This work aimed to assess the biotic and abiotic degradation of atactic polystyrene (PS), utilising as test material foamed PS plates used in the manufacture of trays, formulated with Co- and Mn-based pro-oxidant additives. The plates were exposed to artificial weathering (ultraviolet radiation and heat) and were periodically analysed for changes in structural properties. The oxidised surface residues detached from the samples were incubated in a stabilised compost of urban waste (58 °C) or in an aqueous mineral medium (25 °C), the latter being inoculated with urban waste compost and also with a microbial consortium. It was found that the molar masses of the eroded materials from the pro-oxidant activated samples were significantly lower than the initial sample molar masses, with simultaneous incorporation of oxygen into the chains during the accelerated weathering. These samples underwent biodegradation and gave mineralisation values of 2–5% over 2–3 months of incubation in compost and perlite or in mineral aqueous medium. Biodegradation of the residues from the samples not containing pro-oxidant additives was also observed, but at levels which were lower than those obtained for oxo-biodegradable samples.

1. Introduction

Polystyrene (PS) is widely used today because of its good mechanical properties and the ease with which it is processed, as well as because of its relatively low cost [1]. As a result of its chemical stability and ubiquitous abundance, a large amount of plastics, including PS, have accumulated in the environment, causing a phenomenon termed "white pollution" [2]. In order to reduce the accumulation of PS in the environment, new alternatives should be sought. Among them is the possibility of converting PS into a more easily biodegradable material, though this is a challenge for the materials and microbiological sciences. Although PS is hardly crystalline, its molecules have high molar masses and are nonpolar, existing in the glassy state at room temperature; as such, enzymatic attacks are very difficult [3]. Moreover, the phenyl side groups, which are distributed in space in a disordered manner, are biodegraded very slowly [4].

A strategy in development for increasing the biodegradability of PS is to promote its oxidative degradation, in order to break the molecules into smaller fragments containing hydrophilic oxygenated groups. These fragments still biodegrade slowly, but at much higher rates than does the PS polymer [5]. The degradation of this polymer under the actions of electromagnetic, thermal or mechanical energy occurs via a chain reaction mechanism, with the intermediate formation of free radicals, which give multiple reaction possibilities. As such, this is a less selective process than other types of chemical degradation [6]. Antioxidant additives added to a resin hinder these oxidative degradation reactions and must be previously consumed so that those reactions can occur. In the case of PS, the weak sites of the polymer chain are the tertiary carbon atoms attached to the phenyl groups, which are vulnerable to the attack by free radicals. Here, a series of chemical reactions can lead to cleavage of the chain and start formation of carbonyl groups [7,8]. The presence of carbonyl groups, as well as moieties capable of forming free radicals, such as

* Corresponding author. Tel.: +55 51 3308 7466; fax: +55 51 3308 6023.
E-mail address: fcamargo@ufrgs.br (F. Camargo).

0141-3910/$ – see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymdegradstab.2009.09.012

peroxides, accelerates this degradation [2,9]. Similarly, trace amounts of metals with variable oxidation states, such as Co, Mn, Fe, Cu and Ni, considerably increase the rate of oxidative degradation [10].

Although the hydrocarbon chains of PS are only biodegraded by oxygenase enzymes, the oxidised fragments, in principle, can be biodegraded by a much larger number of enzymes capable of degrading the following moieties: carbonyls, ethers, esters, peroxides, aldehydes, alcohols, carboxylic acids and others [4].

PS foams made with pro-oxidant materials were recently released on the market. So far, there is little information regarding the effect of these additives on the acceleration of the degradation rate of this material. The need to validate these polymers as an economic and environmentally-friendly alternative has been the goal of this work, in which the abiotic degradation of PS, accelerated by ultraviolet (UV) A + B radiation and heat was evaluated, followed by the assessment of the biotic degradation of the polymer in a mature compost of urban wastes.

2. Experimental

2.1. Experimental conditions and materials

Atactic polystyrene homopolymer samples with weight average molar masses (Mw) of 270,000 g mol^{-1} (sample without pro-oxidant additive) and 286,000 g mol^{-1} (sample with pro-oxidant additive) were extruded and foamed in the form of plates (300 × 300 × 3.6 mm), by the Spumapac™ Company (Brazil). The samples were prepared as follows: with no pro-oxidant additive; with a cobalt-based salt additive; and with a manganese-based salt additive. The additives used were d_2w™ from Symphony Environmental, at 5% on total formulation, containing a very small amount of the transition metal. For the evaluation of the samples' densities and fractions of open and closed cells, a Quantachrome Ultrapycnometer 1000 was utilised. For the observation of the structural cells formed, an optical microscope with incident light was utilised. The carbon content of the samples was determined by dry combustion (Perkin–Elmer 2400 CHN Elemental Analyzer). The stabilised compost used as an inoculum for the biodegradation tests was purchased from the urban waste composting plant of Porto Alegre, RS (Brazil), and had the following characteristics: pH value (compost:water of 1:1) = 7.8; organic C (dry combustion) = 230 g kg^{-1}; N (dry combustion) = 17.5 g kg^{-1}, P (acid digestion and inductively-coupled plasma - optical emission spectroscopy, or ICP-OES) = 4.2 g kg^{-1}. The expanded perlite, used as a porous medium for biodegradation, was acquired from Schumacher/Multiquim, with average particles size of approximately 2 mm, and was washed 5 times with distilled water and dried for 24 h at 110 °C. Microcrystalline cellulose, used as the positive standard in the biodegradation, was purchased from Macherey–Nagel (MN301, powder, min. 98% particles <32 μm, 4.5% moisture). Corn starch, also used a positive standard, was purchased from Duryea (Maizena). The microbial consortium used as an inoculum for the biodegradation was obtained from the petrochemical sludge landfarming in the Petrochemical Complex of Triunfo (RS, Brazil). Briefly, in a previous study [11], soil samples were collected from this landfarming site, which received petrochemical sludge from a petroleum refinery and a petrochemical complex for 20 years. From this soil, six bacterial species (Mycobacterium fortuitum, Bacillus cereus, Microbacterium sp., Gordonia polyisoprenivorans, Microbacteriaceae bacterium and Naphthalene-utilising bacterium) and one fungal species (*Fusarium oxysporum*) were isolated, collectively showing the capacity to biodegrade aliphatic and aromatic hydrocarbons in culture medium and in soil. The inoculation with the mixture of these seven species of microorganisms in the culture medium with PS, as described below, resulted in the microbial consortium. The Tanner mineral medium, used as a biodegradation medium, was prepared according to the procedure of Shuttleworth and Cerniglia [12], with the following nutrients (g dm^{-3} of deionised water): 0.040 $CaCl_2.2H_2O$; 0.100 KH_2PO_4; 0.800 NaCl; 1.000 NH_4Cl; 0.200 $MgSO_4.7H_2O$; 0.100 KCl; and micronutrients (mg dm^{-3} of deionised water): 0.100 $CoCl_2.6H_2O$; 0.425 $MnCl_2.4H_2O$; 0.050 $ZnCl_2$; 0.015 $CuSO_4.5H_2O$; 0.010 $NiCl_2.6H_2O$; 0.010 $Na_2MoO_4.2H_2O$; 0.010 $Na_2SeO_4.2H_2O$.

2.2. Abiotic degradation

Three groups of PS samples were subjected to degradation by ultraviolet radiation and heat over three different time periods. The first two groups were made of PS foam plates with or without the cobalt salt-based additive. The third group consisted of foamed PS plates with or without the manganese salt-based additive. Samples were taken periodically from the accelerated weathering tests and were stored at −20 °C in darkness until the day of their analysis.

The first group of samples was exposed to UV A + B radiation via a Comexim apparatus for accelerated weathering, with 8 Philips TL40W12/RS lamps at a controlled temperature of 60 °C. The UV lamps used in this study emitted most of their energy at wavelengths between 280 and 340 nm. The procedure recommended by ASTM [13,14] was adopted. The plates followed a rotation inside the apparatus, as described by the standards referenced above. A spray of distilled water was applied every 75 h to half of the samples in order to remove the oxidised surface layer. Thus in the other half the oxidised layer remained, protecting the internal layers of the samples from ultraviolet radiation. Photographs were taken every 100 h. During the exposure period, samples were taken at 0, 150, 300, 450 and 600 h of weathering for analyses of oxidative degradation, through the techniques described below: a) Visual inspection with photographs (for observation of cracks, fragmentation and yellowing) and measurement of the thickness (average of 12 values); b) Analysis of molar masses by size exclusion chromatography (SEC) in a Waters 2410 gel permeation chromatograph, with a refraction index detector, 4 Styragel HR5E 7.8 × 300 mm columns, and THF as the solvent, at 38 °C. Calibration was performed with monodispersed PS standards. c) Analysis of chemical structure through Fourier transform infrared spectroscopy (FTIR) in a Nicolet Avatar 370 DTGS/Avatar 360 ESP instrument. PS samples were analysed in the form of films with a thickness of approximately 80 μm, pressed at 170 °C for 1 min, or in the form of a powder pressed between KBr disks, in the case of eroded oxidised residues. The incorporation of oxygen into the PS molecules was analysed through a "carbonyl index", calculated by the ratio of the carbonyl band (1640–1841 cm^{-1}) to the reference band (1564–1631 cm^{-1}).

The second group of samples was irradiated with UV and heated under the same conditions used for the first group for a total period of 450 h. However, the goal here was the collection of the oxidised particles, which were easily detached from the surface of the irradiated plates. These particles were removed every 75 h with a soft paintbrush and accumulated in sufficient quantities for SEC and FTIR analyses, as well as for biodegradation tests via respirometry.

The third group of samples was irradiated for 500 h at 40 °C, with particles removed every 125 h for respirometry tests.

2.3. Biodegradation

Biodegradability tests of the foamed PS samples, both with and without pro-oxidant additives, were carried out with the three sample groups described above. Plates from the first group of samples, with or without the pro-oxidant additive and with or without being subjected to periodic washing by water spray, were selected for the biodegradation tests after 600 h of irradiation.