



Analysis method

Determination of antioxidants in polyolefins by pressurized liquid extraction prior to high performance liquid chromatography

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ABSTRACT

The effect that a high amount of mineral filler might have on the extraction process of antioxidants from polyethylene and polypropylene was investigated. Extraction of Irganox 1010, Irganox 1076 and Irgafos 168, along with its oxidation product 2,4-di-*tert*-butylphenol, from freeze ground polyethylene-based (PE-based) and polypropylene-based (PP-based) mineral concentrates of 85 w/w calcium carbonate (CaCO₃) and 75 w/w talc was carried out by pressurized fluid extraction (PLE) prior to high performance liquid chromatography (HPLC). Results indicate that 85 w/w CaCO₃ did not affect the extraction process from PE or PP. For talc concentrates, additive recovery from PE and PP was considerably lower. The relation of recovery yield and mixing time was investigated for the talc concentrates and it was concluded that the presence of talc seemed to accelerate the rate of antioxidant consumption during sample processing, thus, less antioxidant was left to be extracted from the polyolefin; rather than talc has limited the extraction process. The method developed in this work has been applied to determine these compounds in several commercial samples.

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1. Introduction

It is well known that adding mineral fillers to polymers offers the possibility to enhance some mechanical properties, to improve manufacture efficiency and help offset any rising resin costs [1,2], while lowering the environmental impact of the end product [3]. For these reasons, it is becoming more common for manufacturers to add mineral fillers in their processes, reaching values as high as 50 w/w for a given application [4]. A practical way for a manufacturer to introduce mineral fillers into a plastic article is by using mineral concentrates in their processes. These products consist, generally, of 70–80 w/w of mineral filler, e.g. calcium carbonate (CaCO₃) or talc, loaded in a polyolefin carrier resin.

Just as conventional polyolefins, the polymer used as carrier in mineral concentrates, is vulnerable to oxidation and can experience a substantial loss of mechanical and optical properties, and more importantly, of processability when oxidized. The addition of antioxidants is the most commonly used method to prevent or inhibit polymer oxidation, and this is also the case for the polymer used as a carrier resin in mineral concentrates [5]. Currently, over 50% of

antioxidants used in the plastics industry are destined for polyolefins. Among the most important and widely used antioxidants are the primary antioxidants Irganox 1010, Irganox 1076 or Irganox 1330, and hydroperoxide decomposers, or secondary antioxidants, namely Irgafos 168, Irgafos P-EPO, Irgafos 38, and others [6].

The determination of the amount of additives in polymers has a major role in quality control and research and development as well as for regulatory reasons. In general, additive determination involves an initial step of extraction from the polymer matrix. Traditionally, the extraction has been carried out by Soxhlet extraction [7], or dissolution of the polymer followed by re-precipitation [8]. Although these methods imply rather simple and inexpensive equipment, they are time and solvent consuming [9]. More recent methodologies involve microwave assisted extraction (MAE) [10–12], supercritical fluid extraction (SFE) [13,14] and pressurized liquid extraction (PLE) [15–17] which, in turn, offer the possibility to extract at high pressure and temperature, resulting in a considerably lower extraction time and less solvent usage [7,9]. In a second step, the extracted additives are quantified by high performance liquid chromatography (HPLC) in both reversed [18] and normal phase [19].

As mentioned above, several methods have been proposed for the extraction and quantification of a variety of antioxidant

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additives in polyolefins, nonetheless, the effect that a high amount of mineral filler might have on the extraction process has not yet been considered. The aim of this work is the development of a method for extraction and quantification of the primary antioxidants Irganox 1076 and Irganox 1010 and the secondary antioxidant Irgafos 168, along with its oxidation product tri[2,4-di-*tert*-butylphenyl]phosphate, in polyethylene-based (PE-based) and polypropylene-based (PP-based) mineral concentrates of CaCO₃ and talc, and compare the recovery yields with those obtained for polyolefins without mineral fillers. The method combines one first step of extraction by PLE and subsequent direct determination by liquid chromatography with diode array detection (LC – DAD).

2. Experimental

2.1. Materials and reagents

The solvents for pressurized liquid extraction used in this work were HPLC gradient grade *iso*-propanol (J.T. Baker, Deventer, Holland) and cyclohexane for pesticide residue analysis (VWR, Leuven, Belgium). Solvents used for sample preparation and LC analysis were HPLC gradient grade methanol, dichloromethane, tetrahydrofuran (all from J.T. Baker, Deventer, Holland) and ultra pure water with 18 MΩ cm (Veolia Water Technologies, Sant Cugat del Vallès, Spain).

Irganox 1010 (CAS-number: 6683-19-8), Irganox 1076 (CAS-number: 2082-79-3) and Irgafos 168 (CAS-number: 31570-04-4) were obtained from BASF SE (Ludwigshafen, Germany).

Individual stock solutions of 1000 mg L⁻¹ were prepared in methanol/dichloromethane (50/50, v/v) for Irganox 1010, Irganox 1076 and Irgafos 168. A mix solution of 200 mg L⁻¹ was prepared weekly, also in methanol/dichloromethane (50/50, v/v). More dilute solutions were prepared on a daily basis using the same solvents. According to Garde et al. [20] fully oxidized Irgafos 168 can be obtained after 24 h of dissolution in THF. Oxidized Irgafos 168 was obtained by preparing a standard solution of 500 mg L⁻¹ of Irgafos 168 in THF, the efficiency was calculated by HPLC. For calculations, the reported recovery of Irgafos 168 was the resultant of the sum of the recoveries of Irgafos 168 and oxidized Irgafos 168.

The polyolefins used in this work were a 0.920 g cm⁻³ lineal low density polyethylene and a homopolymer polypropylene, supplied by Dow Chemical Ibérica (Tarragona, Spain) and Ineos (Frankfurt/Main, Germany), respectively. The mineral fillers were high purity and fine particle size grades of surface treated CaCO₃ of 1.6 μm mean particle size, obtained from Omya (Oftringen, Switzerland), and talc of 9 μm mean particle size, from Imerys Talc (Toulouse, France).

2.2. Instrumentation

Chromatographic analyses were performed on an Agilent Series 1100 HPLC system equipped with vacuum degasser, binary pump and UV-DAD (all from Agilent, Palo Alto, CA, USA). The analytes were separated using a Kromasil stainless steel column 150 mm × 4.6 mm ID, packed with Symmetry C₁₈ and 5 μm particle size (Eka Chemicals, Bohun, Sweden).

A pressurized liquid extractor ASE 350 (Dionex, Sunnyvale, CA, USA) with a solvent controller and equipped with 10 mL stainless steel extraction cells was used in all the extractions.

PE and PP reference samples, without mineral fillers, and PE-based and PP-based mineral concentrates were prepared using a Haake PolyLab QC modular torque rheometer equipped with four temperature sensors and a mixing chamber of 310 cc (Thermo

Fisher Scientific, OH, USA).

2.3. Sample preparation

For this work, the following samples were considered: reference samples of PE and PP (without mineral filler) spiked with 500 μg g⁻¹ of each additive, and PE-based mineral concentrates of 85 w/w of CaCO₃ and 75% w/w talc, both of them spiked with 500 μg g⁻¹ of each additive. The PP-based were obtained with the same conditions. The added quantity of each material was calculated in order to fill 70% of the mixing chamber volume (according to the apparent density at 25 °C of each material). The reference samples were prepared by blending 120 g of PE or PP and 60 mg of each additive. The PE–CaCO₃ and PP–CaCO₃ concentrates were prepared by mixing 306 g of CaCO₃, 54 g of the corresponding polyolefin and 180 mg of each additive. PE–talc and PP–talc concentrates were prepared by blending 150 g of talc, 50 g the corresponding polyolefin and 100 mg of each antioxidant.

The preparation of the PE reference sample and PE-based mineral concentrates was carried out at 160 °C and involved a pre-mix step at 25 rpm for 1.5 min followed by a mix step at 150 rpm for 2.5 min. The PP reference sample and PP-based mineral concentrates were obtained at 185 °C after a pre-mix step at 25 rpm for 1.5 min followed by a mix step at 75 rpm for 1 min. Such conditions were selected to guarantee good dispersion with short mixing times in order to prevent polymer oxidation during sample preparation. For sample preparation, all components were added simultaneously to the mixing chamber which was already pre-heated at the mixing temperature. After preparation, each sample was cut into small pieces and allowed to cool down in water at room temperature.

2.4. Extraction conditions

Before extraction, all samples were ground by means of an ultracentrifugal mill, after freezing with liquid nitrogen, and sieved to obtain ≤1 mm particle size using a 1 mm mesh sieve.

The extraction on the PE reference sample and PE-based mineral concentrates was carried out on 1 g of ground sample using a mix of *iso*-propanol and cyclohexane as extraction solvent (92.5/7.5, v/v), a pressure of 10.3 MPa (1500 psi) and a temperature of 105 °C. One cycle of static extraction of 15 min, a flush volume of 50% of cell volume and 60 s of purge were used.

The extraction on the PP reference sample and PP-based mineral concentrates was carried out on 0.2 g of ground sample using *iso*-propanol as extraction solvent, a pressure of 10.3 MPa and a temperature of 130 °C. One cycle of static extraction of 5 min, a flush volume of 50% of cell volume and 60 s of purge were used.

All extracts were evaporated at 40 °C and reconstituted in a 10 mL solution of methanol/dichloromethane (50/50, v/v). Solutions were filtered through a 0.45 μm PTFE syringe filter prior to HPLC analysis.

2.5. HPLC conditions

Separations were carried using a binary gradient of water and methanol. The initial conditions of the mobile phase gradient were methanol/water at 50/50, v/v. Then, the methanol fraction was increased to 100% from 0 to 5 min, maintained for 18 min and returned to initial conditions in 3 min. The flow of the mobile phase was 1.0 mL min⁻¹. The column was kept at a temperature of 30 °C throughout the analysis. The injection volume was 20 μL and the wavelength was 276 nm.

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