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Melt stabilization of PE with natural antioxidants: Comparison of rutin and quercetin

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ABSTRACT

The stabilization effect of a flavonoid type natural antioxidant, rutin, was compared to that of quercetin in polyethylene. Additive concentrations changed between 0 and 500 ppm in several steps and also 1000 ppm Sandostab PEPQ phosphorus secondary stabilizer was added to each compound. Stabilization efficiency was determined by changes in vinyl group content, melt flow rate, oxygen induction time, color and the consumption of the secondary antioxidant during multiple extrusions. The results showed that rutin is as efficient melt stabilizer as quercetin used as reference. On the other hand, rutin has a deteriorating effect on the stability of the polymer at small concentrations and partially decomposes during processing. The comparison of bond dissociation enthalpies indicated that the substitution of the hydroxyl group in the ring C of quercetin by saccharide moieties increases their value, but the small increase does not influence the efficiency of the stabilizer. FTIR and DSC measurements indicated the interaction of the natural antioxidant and the phosphonite secondary stabilizer, and the development of interactions was confirmed by molecular modeling. Mainly hydrogen bonds and aromatic, π electron interactions develop between the hydroxyl groups in ring A and the POC group of the phosphonite, as well as between the aromatic rings of PEPQ and the flavonoids, but they do not influence the stabilization efficiency of the antioxidants.

1. Introduction

Plastics are exposed to heat, shear and oxygen during their processing and to various effects during their application that may result in degradation [1]. In order to prevent changes in their chemical structure and properties, they contain heat and/or light stabilizers practically always. Polyethylene is routinely protected against degradation during processing with the combination of a synthetic phenolic antioxidant and a secondary, processing stabilizer, usually a phosphorous compound. This simple stabilization package proved to be very efficient and cost effective thus very few new stabilizers appeared on the market in the last few decades. However, for various reasons, the interest turned towards natural antioxidants recently. The general concern of the politicians and the public about sustainable economy is one of the driving forces, while doubts about the possible environmental and health hazard [2] of the degradation products of phenolic antioxidants used routinely also may play a role in this increased interest. Consequently, the number of publications about the possible use of natural antioxidants for the stabilization of polymers increases continuously.

A considerable number of natural compounds proved to be beneficial for the human health because of their antioxidant, anti-inflammatory, antiviral or other effects and many of them are being used for therapy for a very long time. Natural antioxidants are used in increasing quantities also in food products [3,4]. Attempts have been made to apply various natural compounds for the stabilization of polymers, and specifically polyolefins as well. Vitamin E is a very efficient stabilizer [5–8] and it is presently used as antioxidant in ultrahigh molecular weight polyethylene implants [9–11]. Because of its polyaromatic structure and the number of phenolic hydroxyl groups in it, lignin has a stabilization effect in polymers, which was proved both in polyethylene and polypropylene [12–14]. Several attempts were reported in the literature to use flavonoids for the stabilization of

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polyolefins. Quercetin, a natural antioxidant, was explored as possible stabilizer both in food [15] and in polymers [16,17] and most of the results obtained confirmed its efficiency indeed. Dihydromyricetin, another flavonoid was also studied as stabilizer in both PE and PP and proved more efficient than the commercial stabilizers used as reference [18,19].

Among other groups, we also carried out experiments to explore the effect and efficiency of several natural compounds as stabilizer in PE. The antioxidant effect of curcumin [20,21], quercetin [22], dihydromyricetin [23] and silymarin [24] was studied in a Phillips type polyethylene in the presence of a phosphorous secondary stabilizer. Three of them are very efficient, their stabilization efficiency exceed that of the synthetic phenolic antioxidant used in the largest quantity in industrial practice. The stabilizers protected the polymer against degradation during processing already at the concentration of 50 ppm and provided sufficient residual stability at 250 ppm. Silymarin was less efficient, because of its slightly different chemical structure [24]. In this work we study the possible stabilization effect of rutin, [2-(3,4-dihydroxyphenyl)-5,7-dihydroxy-3-{[(2*S*,3*R*,4*S*,5*S*,6*R*)-3,4,5-trihydroxy-6-({[(2*R*,3*R*,4*R*,5*R*,6*S*)-3,4,5-tri-hydroxy-6-methyloxan-2-yl]oxy}methyl) oxan-2-yl]oxy}-4*H*-chromen-4-one], a natural antioxidant which belongs to the family of flavonoid glycosides. The compound is the glycoside of quercetin formed with the rutinose disaccharide. It can be found in numerous fruits, citruses, apple, buckwheat and Japanese acacia. It obtained its name from the flower *Ruta graveolens* that contains it in large quantities similarly to other yellow flowers [25]. Rutin has several beneficial effects on the human body; it protects the heart and the arteries, as well as the neural system, since as an antioxidant it neutralizes free radicals [26]. Research is going on to use it as an antidepressant [27] or to treat Alzheimer disease [28] and stroke [29] with it.

Most of the flavonoid type natural antioxidants investigated in the previous projects proved to be very efficient processing stabilizers for PE, but they all had some drawbacks like high melting temperature, limited solubility in the polymer and strong color. Consequently, the primary goal of this work was to try another member of the flavonoid family, rutin, as antioxidant in PE. Similarly to previous works [20–24], rutin was used in combination with a phosphorous secondary stabilizer to comply with industrial practice. The effect of the new antioxidant was compared to that of quercetin used as reference compound. Besides the effect of rutin on the processing stability of polyethylene, we paid more attention to mechanistic aspects and to the possible interaction of the primary and the secondary antioxidant, since previous results indicated that the two types of compounds, i.e. the flavonoids and the phosphonite, interact with each other and the developing interactions might affect their efficiency.

2. Experimental

2.1. Materials

The polymer used in the experiments was the Tipelin FS 471 grade ethylene/1-hexene copolymer (melt flow rate: 0.3 g/10 min at 190 °C, 2.16 kg; nominal density: 0.947 g/cm^3) polymerized with a Phillips catalyst (PE). The number average molecular weight of the polymer is 15.4 kg/mol, its polydispersity 7.6 and it contains 1.81 comonomer/1000 C. The additive free polymer powder was provided by MOL Group Ltd., Hungary. Both stabilizers, i.e. rutin and quercetin, were purchased from Sigma-Aldrich with 95 and 94% purity, respectively. The antioxidants were added to the polymer in various amounts, in 5, 10, 25, 50, 100, 250 and 500 ppm, to study the effect of additive content on stability. Each compound contained also 1000 ppm Sandostab PEPQ (PEPQ, Clariant) phosphonite secondary stabilizer.

2.2. Sample preparation

The polymer and the additives were homogenized in a high-speed mixer (Henschel FM/A10) at a rate of 500 rpm for 10 min. The necessary amount of quercetin was dissolved in 200 mL acetone and the solution was added to the PE powder in the mixer. The resulting powder was dried overnight to remove acetone. Rutin was added to the polymer together with PEPQ directly and homogenized in the high-speed mixer under the same conditions as described above. The dry blend was processed and pelletized in six consecutive extrusion steps at 50 rpm and barrel temperatures of 180, 220, 260 and 260 °C under normal laboratory conditions using a Rheomex S ¾″ type single screw extruder attached to a Haake Rheocord EU 10 V driving unit. Samples were taken after each extrusion step. For further studies, films of about 100 µm thickness were compression molded at 190 °C and 5 min using a Fontijne SRA 100 machine. Blends of the two stabilizers, i.e. the natural antioxidant and PEPQ, were prepared by mixing the components in various amounts in 2-propanol to study their interactions. The solvent was evaporated in a Büchi Rotavapor R-210 vacuum assisted rotary distillation apparatus in about 1 h at 40 °C, then the mixtures were dried further overnight at 100 °C, 200 mbar in a vacuum oven.

2.3. Characterization

The melt flow rate (MFR) of the polymer was determined according to the ASTM D 1238-79 standard at 190 °C with 2.16 kg load using a Göttfert MPS-D MFR tester. Residual thermo-oxidative stability was characterized by the oxidation induction time (OIT) measured at 200 °C in oxygen atmosphere with constant, 20 mL/min flow rate in open aluminum pans using a Perkin Elmer DSC-7 apparatus. The concentration of the unsaturated functional groups of polyethylene were determined by FTIR spectroscopy on the 100 µm thick compression molded films in transmission mode using a Tensor 27 (Bruker) spectrophotometer. Five spectra were recorded on each sample between 4000 and 400 cm^{-1} wavelengths at 2 cm^{-1} resolution and 16 scans. The concentration of vinyl groups were calculated from the absorption at 908 cm^{-1}. FTIR spectroscopy was used also for the determination of residual PEPQ content based on the absorption of the P(III)-O-C groups at 850 cm^{-1}. The color of the samples was described by the yellowness index (YI) and the optical L* parameter determined with a Hunterlab Colourquest 45/0 apparatus. The thermal behavior of rutin, that of its blends with PEPQ, and component interactions were studied by differential scanning calorimetry (DSC). The measurements were carried out in nitrogen atmosphere with constant, 20 mL/min flow rate in open aluminum pans, at a heating rate of 10 °C/min from 0 to 350 °C using a Perkin Elmer Diamond DSC-IC apparatus. The thermal stability of the two natural antioxidants was checked by thermogravimetry using a Perkin Elmer STA-6000 apparatus. Samples were heated from 30 °C up to 260 °C at 20 °C/min rate and then held there for 15 min. The measurements were carried out in oxygen atmosphere with constant, 20 mL/min, flow rate. The possible interactions of the components were estimated also by molecular modeling using the density functional theory (DFT). The details of the calculations are given in the respective section (Section 3.4). In figures, rutin is abbreviated as R, while quercetin as Q in order to increase clarity and help understanding.

3. Results and discussion

The results are reported in several sections. First, the characteristics of the two antioxidants are compared and based on their structure an attempt is made to predict their performance. The stabilization efficiency of the two compounds is presented in the next section. Mechanistic aspects and additive interactions are considered in the following two sections, while unresolved issues as well as consequences for practice are discussed in the final section of the paper.