



## Melt stabilization of polyethylene with dihydromyricetin, a natural antioxidant



B. Kirschweng<sup>a</sup>, K. Bencze<sup>a</sup>, M. Sárközi<sup>a</sup>, B. Hégyel<sup>c,d</sup>, Gy. Samu<sup>c,d</sup>, J. Hári<sup>a</sup>,  
D. Tátraaljai<sup>a,b</sup>, E. Földes<sup>a,b</sup>, M. Kállay<sup>c,d</sup>, B. Pukánszky<sup>a,b,\*</sup>

<sup>a</sup> Laboratory of Plastics and Rubber Technology, Department of Physical Chemistry and Materials Science, Budapest University of Technology and Economics, H-1521, Budapest, P.O. Box 91, Hungary

<sup>b</sup> Institute of Materials and Environmental Chemistry, Research Centre for Natural Sciences, Hungarian Academy of Sciences, H-1519, Budapest, P.O. Box 286, Hungary

<sup>c</sup> Spectroscopy Laboratory, Department of Physical Chemistry and Materials Science, Budapest University of Technology and Economics, H-1521, Budapest, P.O. Box 91, Hungary

<sup>d</sup> MTA-BME Lendület Quantum Chemistry Research Group, Department of Physical Chemistry and Materials Science, Budapest University of Technology and Economics, H-1521, Budapest, P.O. Box 91, Hungary

### ARTICLE INFO

#### Article history:

Received 5 July 2016

Received in revised form

23 August 2016

Accepted 29 August 2016

Available online 30 August 2016

#### Keywords:

Polyethylene

Processing stabilization

Long chain branching

Natural antioxidants

Dihydromyricetin

Solubility

Color

### ABSTRACT

Experiments have been carried out to compare the stabilization effect of two flavonoid type natural antioxidants, dihydromyricetin (DHM) and quercetin (Q) in polyethylene (PE). Additive concentrations changed between 0 and 500 ppm in several steps and 1000 ppm Sandostab PEPQ phosphorus containing secondary stabilizer was also added to each compound. Both antioxidants are very efficient stabilizers for PE, sufficient melt stability was achieved already at 50 ppm DHM content. At small concentrations dihydromyricetin proved to be more efficient melt stabilizer and it protected the secondary antioxidant better than quercetin. In spite of its better efficiency in melt stabilization, polymers containing DHM had the same residual stability as those prepared with quercetin. Accordingly, the larger efficiency does not result from the larger number of active phenolic hydroxyls in the molecule, but from interactions with the phosphorous secondary stabilizer that is stronger or at least different for DHM than quercetin. In spite that DHM is a white powder, it gave the polymer a brownish color which became deeper with increasing number of extrusions and additive content. Nevertheless, both natural antioxidants can be used efficiently for the stabilization of polymers in applications in which color is of secondary importance.

© 2016 Elsevier Ltd. All rights reserved.

### 1. Introduction

Polyethylene (PE) is exposed to heat, shear, and oxygen during its processing and use. Adequate stabilization is essential to protect the polymer already during the manufacture of the final product and hinder degradation which usually results in the deterioration of properties. Synthetic antioxidants (AO) are used for stabilization in industrial practice, but sometime ago questions emerged regarding the effect of their reaction products on human health [1]. Most of these questions have not been answered satisfactorily yet. As a consequence, more and more attempts are made to find new

solutions including the use of natural antioxidants for the stabilization of food [2–4], but also of polymers [5–15]. These compounds usually can be found in vegetables and fruits, are often used as spices and are known to have beneficial effect on the human health.

Several compounds with different chemical structures have been studied as potential stabilizers in polymers and also in polyethylene. Vitamin E, i.e.  $\alpha$ -tocopherol, is a natural phenolic compound which was shown to be a very efficient antioxidant [5–8] and it is used in practice for the stabilization of hip replacements prepared from ultra-high molecular weight polyethylene (UHMWPE). Attempts were made to use lignin, a natural polyphenol, as stabilizer and it proved to have some antioxidant effect indeed [9–11]. Recently, the stabilization of PE with another natural compound, curcumin, was studied in detail [16] and it was found that its melt stabilizing efficiency is superior to that of the synthetic

\* Corresponding author. Laboratory of Plastics and Rubber Technology, Department of Physical Chemistry and Materials Science, Budapest University of Technology and Economics, H-1521, Budapest, P.O. Box 91, Hungary.

E-mail address: [bpukanszky@mail.bme.hu](mailto:bpukanszky@mail.bme.hu) (B. Pukánszky).

antioxidant extensively used in industrial practice. The effect of the antioxidant was further enhanced by the addition of a phosphorus containing secondary stabilizer. The study has shown that besides its phenolic –OH groups, also the linear linkage between the two methoxyphenyl rings participates in stabilization reactions leading to a unique reaction route and increased efficiency.

Quercetin, i.e. [2-(3,4-dihydroxyphenyl)-3,5,7-trihydroxy-4H-chromen-4-one] (Q), is also a natural antioxidant found in fruits, vegetables, leafs and seeds in nature. The compound is a flavonol type flavonoid, which has proven antioxidant, antiviral and anti-inflammatory effect in the human body. It was already used for the stabilization of polyolefins [17,18], and also as a component of active packaging materials [19–22]. Quercetin was added to polyethylene [17], polypropylene [18] and an ethylene vinyl alcohol copolymer and it proved to be an efficient stabilizer in all cases. However, quercetin was applied at concentrations of 2000–3000 ppm [17,18] or at even larger quantities in most studies, which raises the question of solubility, efficiency and price.

Although the studies cited above [17,18] proved that quercetin is a very efficient stabilizer in various polymers, several questions remained open. Quercetin is a polar compound with a melting temperature of around 320 °C, thus its solubility in the polymer is limited. Its efficient homogenization is questionable under the usual conditions of polyolefin processing, since the additive does not melt. The concentrations used in previous studies also seemed to be quite large [17,18]. In a recent study the melt stabilization effect of quercetin was investigated in a Phillips type polyethylene at much smaller concentrations, in the range of 5–1000 ppm [23]. It proved to be very efficient and prevented the formation of long chain branches already at a concentration as small as 50 ppm, while its dosage at 250 ppm provided the polymer sufficient residual stability. There were indications that quercetin interacted with the phosphonite secondary stabilizer used and that the mechanism of stabilization might differ from that of hindered phenolic stabilizers routinely used in practice. However, besides the advantages of quercetin, its very high melting temperature, limited solubility in polyethylene and strong yellow color are definite drawbacks for this compound.

The disadvantages mentioned in the previous paragraph might be overcome by the use of another flavonoid type natural antioxidant dihydromyricetin (2R,3R)-3,5,7-trihydroxy-2-(3,4,5-trihydroxyphenyl)-2,3-dihydrochromen-4-one) (DHM). The compound is very similar to quercetin, but it is colorless and has a lower melting temperature. According to our knowledge only two attempts were made to use DHM as a stabilizer in polymers and both were done by the same group [24,25]. Chen et al. added DHM to polyethylene [24] and polypropylene [25] at 2000 ppm and without any secondary antioxidant. According to the authors the additive is more efficient than the commercial stabilizers used as reference. They explained the large efficiency with the position and the large number of hydroxyl groups in the molecule, but did not offer any information about melt stability, color, the effect of concentration or stabilization mechanism. As a consequence, the goal of this study was to explore the possibility of using DHM as stabilizer in polyethylene. The effect of the compound was compared to that of quercetin discussed above. Stabilization was studied as a function of composition at much smaller amounts than that used by Chen et al. [24,25]. Special attention was paid to processing stability, solubility and color in the study.

## 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<sup>3</sup>) polymerized by a Phillips catalyst. The additive-free polymer powder was provided by Tisza Chemical Ltd. (TVK), Hungary. Quercetin (Sigma-Aldrich, 95%) and dihydromyricetin (Y&L Biotech Co., Ltd., China, 98%) were added to the polymer in various amounts, at 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. DHM 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 3/4" 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.

### 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. The residual thermo-oxidative stability of the polymer was characterized by the oxidation induction time (OIT) measured at 200 °C in oxygen atmosphere with constant, 20 ml/h flow rate in open aluminum pans using a Perkin Elmer DSC 2 apparatus. The functional groups (methyl, unsaturated and carbonyl) 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 parallel measurements were carried out on each sample between 4000 and 400 cm<sup>-1</sup> wavelengths at 2 cm<sup>-1</sup> resolution by 16 scans. Concentration of methyl, trans-vinylene and vinyl groups were calculated by absorptions at 1378 cm<sup>-1</sup>, 965 cm<sup>-1</sup> and 908 cm<sup>-1</sup>, respectively. Amount of carbonyl groups were measured by calculating the peak area between 1780 and 1680 cm<sup>-1</sup>. FTIR spectroscopy was used also for the determination of residual PEPQ content based on the absorption of P(III)-O-C groups at 850 cm<sup>-1</sup>. The color of the samples was described by the yellowness index (YI) and the optical L\* parameter measured on a Hunterlab Colourquest 45/0 apparatus. The UV–VIS spectra of reaction products of quercetin and dihydromyricetin were predicted by Time-Dependent Density Functional Theory (TDDFT) calculations at PBE0/6-311++G\*\* [27] level. Geometries were optimized for these calculations in three steps. First conformations with the lowest energies were identified by molecular mechanics using the Merck molecular force field (MMF94) [28] from 2D structures drawn by using the MarvinSketch (ChemAxon) program, then the selected conformers were optimized by DFT calculations at the PBE0/6-311++G\*\* level with Gaussian09 [29]. The obtained geometries were optimized again after manually orienting hydrogens towards possible intramolecular hydrogen bonds resulting in lower energies. Finally, vibrational frequencies of the resulting conformers were calculated by the same DFT method ensuring their correspondence to local minima.

Download English Version:

<https://daneshyari.com/en/article/5200962>

Download Persian Version:

<https://daneshyari.com/article/5200962>

[Daneshyari.com](https://daneshyari.com)