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The potential of quercetin as an effective natural antioxidant and indicator for packaging materials

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ABSTRACT

Quercetin was studied as an antioxidant and environmentally-friendly coloured indicator of ageing time in a Topas cyclo-olefin copolymer (ethylene-norbornene). Derivatives of flavonoids may be interesting alternatives to the use of hindered amines or other synthetic stabilizers. Our research shows that quercetin prolongs the oxidation induction time of the Topas copolymer and increases its thermo-oxidative stability and resistance to high-energy radiation (UVA, $\lambda = 340$ nm). Topas composites containing quercetin have anti-fungal properties. Flavonoids are natural plant pigments that, when added to polymer materials significantly change the colour of the final product. Moreover, the colour of the material changes as a function of time and climatic factors. By examining the colour, one can determine the lifetime, e.g., packaging.

1. Introduction

Polymers in use are subject to changes over time. These changes are largely due to degradative factors such as radiation (mainly UV in the range of 340 nm) as well as water or high temperatures. Stabilizers can slow the deterioration of the polymers. Current polymer technology uses synthetic polyphenols, amines or phosphate derivatives as stabilizers. A current concern is the migration of additives into the environment during polymer use. It is therefore important that polymer additives be environmentally friendly and non-toxic Currently, intensive research is ongoing into new natural antioxidants that are effective in polymers (AlMalaika, Ashley, & Issenhuth, 1994; Arrigo et al., 2015; Delprat, Duteurtre, & Gardette, 1995; Hussein et al., 2015; Lopez-de-Dicastillo, Alonso, Catala, Gavara, & Hernandez-Munoz, 2010; Soroka, 2002; Tumwesigye, Oliveira, & Sousa-Gallagher, 2016). One obstacle is the adequate dispersion of these compounds in the polymer matrix, in addition to concerns about price, which must be competitive with the prices of stabilizers currently used in industry. There are several key issues when introducing new stabilizers, including solubility in the polymer, diffusion, and migration, lability of the polymer. Stabilization time and anti-ageing efficiency are also crucial, and these abilities are determined by several parameters of the antioxidant. Flavonoids are a widely distributed group of natural heterocyclic antioxidants (Cerrutia et al., 2011; Fearon, Bigger, & Billingham, 2004). They have been widely studied in the fields of biotechnology, medicine and chemistry, indicating that they form a highly effective group of antioxidants. In our manuscript we propose the use of a compound derived from a group of flavonoids as an environmentally-friendly stabilizer and a colour indicator of ageing time (Ambrogia et al., 2011; Masek, Chrzescijanska, & Zaborski, 2014a, 2014b; Masek, Chrzescijanska, Zaborski, & Piotrowska, 2014; Samper, Fages, Fenollar, Boronat, & Balart, 2013), because quercetin is a plant-derived pigment, we have found that it can colour polymer composites. Moreover, we found that oxidation of the polymer changes the molecular structure of quercetin, which also changes its colour. Thus, the controlled colour change of quercetin may yield detailed information regarding the shelf life of materials. The proposed antioxidant flavonoid group may function not only as natural anti-ageing stabilizers but also as colourimetric indicators of ageing. In our paper examines the free radical scavenging activity of quercetin. We used ABTS (2,2′-azinobis-(3-ethylbenzothiazoline-6-sulfonic acid) and DPPH (2,2-diphenyl-1-picryl-hydrazyl-hydrate) radicals for this purpose and examined the ability of quercetin to reduce iron ions, which are a common cause of polymer degradation. Topas is a cyclo-olefin, which, due to these polymers' advantages such as high purity, glass-like texture, transparency, and very low permeability to water and gas, are often used in packaging materials for foods or cosmetics and pharmacy. (Brocca, Arvin, & Mosbaek, 2002; Cerrutia et al., 2011; Gitonga Giteru et al., 2015; Tank, Oliveira, & Sousa-Gallagher, 2015; Zenkevich et al., 2007; Zheng, Zhao, Xiao, Zhao, & Su, 2016). Packaging used in these areas is subject to large insignia indicating the ecological character of the packing material as well as its stabilizer-modified properties. In the case of these packages of hindered

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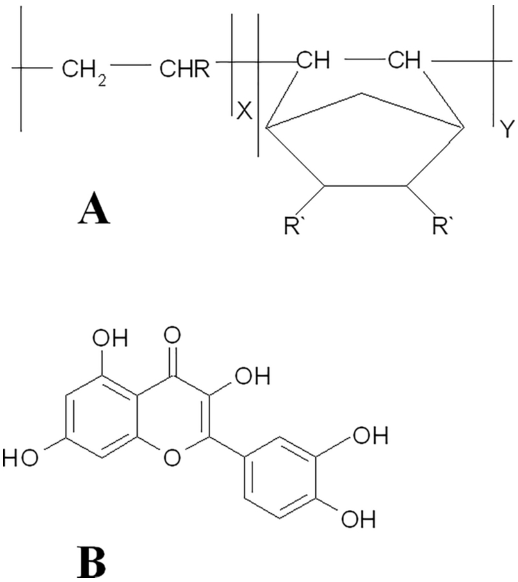

Fig 1. (A) Structure of ethylene-norbornene copolymer (Topas E-140). (B) Structure of quercetin.

amines, use in polymer technology is inadmissible because of their potentially negative effects on human health. Our approach presents a step forward in the stabilization of polymers and aligns with current goals related to environmental and human health (Makris, & Rossiter, 2000; Masek, Zaborski, & Chrzescijanska, 2011; Moure et al., 2001; Ramadan 2012; Ozgen, Reese, Scheerens, & Miller, 2006; Osman, 2011; Wu, Xu, Héritier, & Adlauer, 2012).

2. Experimental

2.1. Materials

We used a cyclo-olefin copolymer (COC)/TOPAS E-140 provided by Ticona (Germany). It was used as granules or as 3.25-mm thick plates (Fig. 1 A, inset).

Pure quercetin ($C_{15}H_{10}O_7 \cdot 2H_2O$) (2-(3,4-Dihydroxyphenyl)-3,5,7-trihydroxy-4H-1-benzopyran-4-one dehydrate, MW = 338.27) was obtained from a commercial source (Sigma-Aldrich, Germany) and used as received (Fig. 1B).

3. Measurement methods

3.1. Measurement methods of antioxidant activity

3.1.1. Scavenging of DPPH radicals

The antioxidant activity of quercetin towards DPPH radicals was evaluated. An ethanol solution of DPPH (2.0 mL) at a concentration of 40 mg/mL (0.1 mM) was added to 0.5 mL of an ethanol solution (70% ethanol) containing 0.02 mg/mL of quercetin. After mixing, the absorbance of the solutions was determined at 516 nm using a UV–vis Spectrometer. As a blank, 70% ethanol was used. The inhibition level (%) of DPPH was calculated by using the following equation:

$$\text{Inhibition (\%)} = [(A_o - A_1)/A_o] \times 100 \quad (1)$$

where A_o was the absorbance of the control, and A_1 was the absorbance in the presence of quercetin (Dudonné, Vitrac, Coutière, Woillez, & Mérillon, 2009; Masek & Chrześcijańska, 2015; Podsędek, Sosnowska, Redzynia, & Koziołkiewicz, 2008).

3.1.2. Scavenging of ABTS radicals

The antioxidant activity of quercetin was evaluated using the ABTS $\cdot^+$ method. ABTS was dissolved in water (6 mM) and reacted with 2.45 mM potassium persulfate. The mixture was left in the dark at room temperature for 15 h before use. The radical was stable in this form for more than two days when stored in the dark at room temperature. The ABTS$\cdot^+$ solution was diluted with ethanol to an absorbance of 0.70 ± 0.02 at 734 nm. After mixing the diluted ABTS$\cdot^+$ solution (4.0 mL) with a 40 μL aliquot of each investigated solution (2 mg/mL) or Trolox in ethanol, the absorbance was measured at 734 nm after 2 min at room temperature. Solvent blanks were run in each assay. The inhibition level (%) of absorbance was calculated using the standard curve prepared with Trolox (% inhibition level – μM Trolox). The effect of quercetin on scavenging ABTS$\cdot^+$ is referred to as the Trolox equivalent antioxidant capacity (TEAC) (Masek, & Chrześcijańska, 2015; Podsędek, Redzynia, Klewicka, & Koziołkiewicz, 2014; Re et al., 1999).

3.1.3. FRAP (Ferricion reducing antioxidant power)

Various concentrations of tannic acid (15–45 mg/mL) in 1.0 mL of distilled water were mixed with sodium phosphate buffer (sodium phosphate buffer; 2.5 mL, 0.2 M, pH 6.6) and potassium ferricyanide (hexacyanoferrate (III) potassium), $K_3[Fe(CN)_6]$ (2.5 mL, 1%). The mixture was incubated for 20 min at 50 °C. Aliquots (2.5 mL) of trichloroacetic acid (10%) were added to the mixture. The upper layer solution (2.5 mL) was mixed with distilled water (2.5 mL) and $FeCl_3$ (0.5 mL, 0.1%), and the absorbance was measured at 700 nm. Increased absorbance of the reaction mixture indicates an increase in reduction capacity (Büyükokuroğlu, Gülçin, Oktay, & Küfrevioğlu, 2001; Gülçin, Huyut, Elmastaş, & Aboul-Enein, 2010).

3.2. Measurement methods of the topas composite with quercetin

3.2.1. Preparation and measurement of ethylene-norbornene copolymer

Blends of ethylene-norbornene copolymer (thermoplastic polyolefin elastomer) with natural antioxidant (0.5–2 parts quercetin per 100 parts polymer) were prepared using a laboratory mixer (Brabender Measuring Mixer N50, 2007, Germany) with a front-roll rotation speed of V_p = 60 rpm and friction of 1.1. The average temperature in the Brabender mixer was approximately 110 °C, and the mixing time was 30 min. Composites with a thickness of 1 mm were obtained by pressing the compounds between steel plates at 100 °C for 11 min (Masek, 2015).

3.2.2. Colour measurement

The colour of the obtained vulcanizates was measured using a CM-3600d spectrophotometer (Konica Minolta Sensing, Inc, Japan). The radiation source consisted of four xenon tube pulses. The spectral range of the apparatus was 360–740 nm, and the change in colour dE*ab was calculated as follows:

$$dE^*ab = \sqrt[2]{(\Delta \boldsymbol{L})^2 + (\Delta \boldsymbol{a})^2 + (\Delta \boldsymbol{b})^2} \quad (2)$$

The CIE-Lab scale is a system of coordinates showing the colour space. The CIE-Lab colour space is presented in a cube form. The L‘ axis passes through the coordinate system from top to bottom. The maximum value for L‘ is 100, which represents an ideally reflecting diffuser. The minimum value for L‘ is zero, which corresponds to the colour black. The a* and b* axes are not limited to special units. A positive value for a* is red; a negative a* is green; a positive b* is yellow; and a negative b* is blue (Hunter Associates Laboratory, Inc, 1996; Masek, 2015).

3.2.3. The oxygen induction time (OIT)

The OIT test was performed on a Mettler Toledo differential scanning calorimeter (DSC1, Mettler Toledo, Italy, 2001). Samples (4 mg) were heated from room temperature to the test temperature, 220 °C, at a rate of 20 °C/min under a nitrogen atmosphere. After 5 min at 220 °C,