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Eco-friendly elastomeric composites containing Sencha and Gun Powder green tea extracts

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ABSTRACT

A permanent increase in the demand for polymers is closely related to the issue of their degradation. Typically, aromatic amines or phenol derivatives are used to protect materials against ageing. In our studies, we propose to use natural pro-ecological substances, such as polyphenols extracted from green tea leaves, to protect elastomers against ageing. Several extracts from Sencha and Gun Powder green tea leaves were incorporated into ethylene-propylene rubbers (EPM, Dutral CO-054). The vulcanizates of EPM samples containing the anti-oxidants under investigation were then subjected to UV radiations and climatic and thermal ageing processes. The changes in deformation energy, colour, and crosslinking density of the EPM vulcanizates were then measured before and after each ageing process. Based on the investigations performed, it is has been found that both the Sencha and Gun Powder green tea extracts display anti-oxidative properties that can protect EPM rubbers against the action of climatic factors.

1. Introduction

The development of new engineering techniques promotes the finding of new technologies that increase product quality [1]. Due to their increased consumption, materials have to meet stringent requirements to comply with current ecology principles [2,3]. Toxic substances, such as derivatives of aromatic amines that are potentially carcinogenic, should, therefore, be avoided in commercial production [4–7]. Amino compounds are currently incorporated into polymeric materials to obtain anti-ageing compounds. In the past years, there have been no significant changes in polymer stabilisation methods [8,9]. Most investigations have focused on structural improvements to increase the effectiveness of the Hindered Amine Light Stabilisers (HALS)-type anti-oxidants used [10,11]. In our study, we decided to propose natural anti-oxidants obtained in the form of natural extracts from plants, such as green tea leaves. Green tea leaves are the richest source of various polyphenolic compounds, with up to 36% of these compounds being flavonids [12–14], which are known as strong anti-oxidants [15–18]. Polyphenols can be obtained by standard extraction in an organic solvent or by innovative extraction methods, e.g., in supercritical carbon dioxide [19–21]. The addition of natural anti-oxidants to polymers may eliminate hazardous substances from technological processes (Scheme 1).

2. Materials and methods

2.1. Reagents

The object of this study was ethylene-propylene rubber (EPM, Dutral CO-054, manufacturer: Montedison Ferrara–Italy). Dicumyl peroxide (DCP; Fluka), 1,3,5-Triallyl-1,3,5-triazine-2,4,6 (Sigma Aldrich Chemie GmbH), hexadecyltrimethylammonium bromide (CTBA; Sigma Aldrich Chemie GmbH), and Areosil 380 silica (Degussa) were

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1. Initiation as radical formation:

   $R^{\cdot}$, $RO^{\cdot}$, $ROO^{\cdot}$

2. Increase in the reaction chain:

   $R^{\cdot} + O_2 \longrightarrow ROO^{\cdot}$

   $ROO^{\cdot} + RH \longrightarrow ROOH + R^{\cdot}$

3. Chain branching

   $ROOH \longrightarrow RO^{\cdot} + HO^{\cdot}$

   $RO^{\cdot} + RH \longrightarrow ROH + R^{\cdot}$

   $HO^{\cdot} + RH \longrightarrow HOH + R^{\cdot}$

4. Chain termination

   $2R^{\cdot} \longrightarrow$
   $2ROO^{\cdot} \longrightarrow$
   $R^{\cdot} + ROO^{\cdot} \longrightarrow$ } inactivated forms

   R - alkyl

Scheme 1. Mechanism of polymer degradation.

used as a cross-linking agent, a cross-linking co-agent, a dispersing agent, and a filler, respectively.

Extracts from green teas were used as anti-ageing substances. More specifically, dried leaves of Chinese Sencha (S) and Gun Powder (GP), which were purchased from Natur-Vit, Poland, were used. The anti-oxidant properties of their extracts were compared with that of a commonly used hydroxybenzophenone UV stabiliser, Chimassorb81 (commercial-type anti-oxidant [Ciba]). The compositions of the elastomer blends are given in Table 1.

2.2. Preparation and measurement methods

The extraction of the green tea leaves was performed in an 80% ethanolic solution using an OMC SER 148 apparatus from Envag consisting of three extraction columns and three containers with thimbles, in which samples of disintegrated and dried tea leaves were placed. The process was carried out for 6 h at the boiling point of ethanol, 78.5 °C.

Rubber blends were prepared using a laboratory mixing mill with rolls of the following dimensions: length $L = 330$ mm, diameter $D = 140$ mm. The speed of rotation the front roll was $V_p = 20$ rpm, the friction was 1.1, and the average temperature of the rolls was of about 40 °C.

The vulcanization of rubber blends was carried out using steel vulcanization molds placed between the plates of an electrically heated hydraulic press. Teflon films were used as spacers to prevent adherence of the blends to the press plates. Samples were vulcanised for 30 min at a temperature of 160 °C and under a pressure of 15 MPa. The vulcanization process of EPM rubber followed according to Scheme 2.The density of crosslinks in the vulcanizates was determined by the method of equilibrium swelling. More specifically, the vulcanizates were subjected to equilibrium swelling in toluene for 48 h at room temperature. The swollen samples were then weighed on a torsion balance and dried to a constant weight in a dryer at a temperature of 60 °C; they were reweighed after 48 h. The cross-linking density was determined using the Flory-Rehner's equation:

$$\vartheta_e = -\frac{1}{V_0} \cdot \frac{\ln(1 - V_r) + V_r + \mu V_r^2}{\left(V_r^{\frac{1}{3}} - \frac{V_r}{2}\right)} \quad (1)$$

for elastomer-solvent interactions amounting to $\mu = 0.501 + 0.273\,V_r$, where V_r is the volume fraction of the elastomer in the swollen gel.

The tensile strength (TS) of the vulcanizates was tested according to the standard method described in PN-ISO 37:1998 using a ZWICK tester (model 1435) and a w-3 dumbbell. Ageing characteristics were determined according to the standard method described in PN-82/C-04216. More specifically, samples were subjected to the action of air at an elevated temperature (353 K) for 7 days in a dryer with thermo-circulation. UV ageing was performed using an UV 2000 apparatus from Atlas. The measurements lasted for 120 h and involved repetition of consecutive day and night segments with the following parameters: day segment (radiation intensity: 0.7 W m^{-2}, temperature: 60 °C, duration: 8 h), night segment (no UV radiation, temperature: 50 °C, duration: 4 h). Climatic ageing was carried out using a Weather-Ometer (Atlas; Ci4000). The test was based on two variable segments simulating day and night conditions, and the samples were subjected to two different cycles of thermal shocks. During the first cycle, they were subjected to a temperature of 120 °C for 10 min, and during the second cycle, they were kept at a temperature of −50 °C for 10 min. The whole ageing process consisted of 450 cycles. The ageing coefficient S was calculated according to the relationship: $S = [TS_A \times Eb_A]/[TS_B \times Eb_B]$, where TS corresponds to the tensile strength; Eb to the elongation at break; and TS_A and Eb_A correspond to the values of the TS and elongation at break after ageing, respectively. The color of the

Table 1
Composition of ethylene-propylene rubbers (EPM) elastomer blends containing extracts of tea.

Composition	M1 (phr)	M2 (phr)	M3 (phr)	M4 (phr)
EPM	100	100	100	100
DCP	2.00	2.00	2.00	2.00
CTBA	2.00	2.00	2.00	2.00
1,3,5-Triallyl-1,3,5-triazine	0.5	0.5	0.5	0.5
A380	30	30	30	30
Chimassorb81		1.25		
Gun Powder			1.25	
Sencha				1.25

DCP: Dicumyl peroxide; CTBA: hexadecyltrimethylammonium bromide.