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# Improvement in the degradation resistance of LDPE for radiochemical processing

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## HIGHLIGHTS

- ·Rosemary extract is a good antirad agent.
- ·LDPE is highly stabilized by rosemary extract.
- The extension of its application to other irradiated polyolefins would be beneficial for human health.
- The descendants of basic components such as rosemary active compounds also present antioxidant activities.
- Radiation processing of LDPE protected with rosemary extract does not affect the oxidation state of material.

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## ABSTRACT

The effect of rosemary extract on radiochemical stability of low density polyethylene was studied by chemiluminescence, FT-IR spectroscopy and differential scanning calorimetry after $\gamma(^{137}Cs)$-irradiation at processing low doses (10 and 20 kGy) in respect of pristine material. The additive concentrations (1, 2 and 5 wt%) induced a significant improvement in radiation stability, especially at high temperatures, for example 200 °C, which is proved chiefly by lower values of chemiluminescence intensities. The comparison of neat and rosemary-modified LDPE samples has revealed the protection action of this natural extract, which delays efficiently the propagation of oxidative degradation in $\gamma$-exposed polyethylene. The most evident proof for antioxidative protection efficiency promoted by rosemary is the smooth changes in hydroxyl and carbonyl indexes calculated on LDPE/5 wt% rosemary samples at all exposure doses.

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## 1. Introduction

The critical behavior of polymers along their life is determined by the oxidative degradation. It causes the shortening service periods (Briskman and Tlebaev, 2005; Celina and Clough, 2006). The radiochemical degradation mechanism involving the formation of peroxyl radicals (Czvikovszky, 2003) illustrates the formation of a large number of oxygenated compounds (Sugimoto et al., 2013). Polyethylene, which is the most commercialized polymer, is subjected to degradation during radiation processing, even though it belongs to the category of crosslinkable polymers. The rate of oxidation depends on the material formulation and the irradiation conditions (absorbed dose, dose rate, exposure environment, processing temperature). Numerous studies have analyzed the amplitude of oxidative degradation in pristine polyethylene (Abdel-Fattah et al., 1998; Suarez et al., 2002; Khelidj et al., 2006; Cheng et al., 2009; Galovic et al., 2012; Murrey et al., 2012).

The limitation of oxidation may be achieved by the addition of suitable stabilizers, which delay the start of oxidation and diminish the radiation degradation rate due to the scavenging of free radicals formed during polymer radiolysis (Zaharescu et al., 2006; Ghaffari and Ahmadian, 2007; Ferreto et al., 2012; Zaharescu and Jipa, 2013a, 2013b).

Natural antioxidants are the remarkable alternatives for the improvement of radiolytic stability of polyethylenes (Lee et al., 2005, 2012; Suhaj et al., 2006; Harisson and Were, 2007; Kim et al., 2008; Zaharescu et al., 2010, 2013). The manufacture of stabilized polymers with this kind of protectors offers the possibility to deliver friendly behaved products in respect of human health especially for radioprotection (Samarth et al., 2008; Mariş et al., 2010). The important advantage of rosemary, as well as many other antioxidant natural extracts, which act as oxidation protector, is the further involvement of its descendants the delaying of oxidation by their antioxidant activities (Jipa et al., 2005; Mariş et al., 2010). Rosemary extracts contain carnosic acid (Fig. 1) as the major active component. By a cascade scheme (Gorghiu et al., 2004) during stabilization, it turns into other related structures exposing oxidation prevention activities

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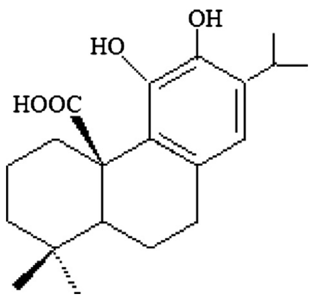


**Fig. 1.** Molecular structure of carnosic acid.

and the stabilization is going on, even though initial molecules of carnosic acid are decayed.

The main goal of this study is to provide information on the behavior of rosemary extract under $\gamma$-irradiation and on the induced effect of descendants on LDPE stability, as an example for polyolefins. Certainly, high concentration of additive is required, because regularly added amounts of 0.25–0.50 wt% would be not conclusive.

## 2. Experimental

Low density polyethylene (LDPE, B 21/2 type) provided by ROMPETROL PETROCHEMICALS Piteşti (Romania) had the following initial characteristics: density $-0.9077$ g cm$^{-3}$, crystallinity $-18\%$, melting index $-3.25$ g/10 min (190 °C/2.16 kg), and number of $CH_3$ per 100 carbon atoms $-3.05$.

Rosemary extract was processed in our laboratory by solvent extraction with ethanol in Soxhlet unit and, finally, precipitated by addition of water into the collected liquid. The yellow greenish powder fell down suddenly. It was further dried in an electrically heated oven for an hour by gentle heating at 50 °C. The powder was stored in a desiccator avoiding the absorption of moisture.

The thermal stability of rosemary extract is very attractive, because it resists for many hours at 185 °C (Lalas and Dourtoglu, 2003). Our previous investigations on the activity of rosemary loaded in paraffin were accomplished at 160 °C, when an induction time of oxidation (423 min) was obtained in contrast with 16 min OIT for control.

Polymer samples were obtained by intimate mixing in a Brabender unit of low density polyethylene powder with rosemary extract at different concentrations of additive (1, 2 and 5 wt%). Plaques with thickness of 0.5 cm were obtained by pressing at 150 °C for 15 min from which small chops were obtained. Under the same conditions thin films (100 μm) were also prepared. Though stabilizers are usually added at the concentrations up to 1%, the extension of concentration domain would be applied for attaining long period service.

FTIR spectra were recorded on a JASCO 4000 spectrometer with a resolution of 4 cm$^{-1}$ after 48 scans. Carbonyl indexes (CI) were calculated according to a previously reported method (Roy et al., 2007); hydroxyl indexes (HI) were obtained applying the relation presented by Jia et al. (2007).

Chemiluminescence (CL) spectra were obtained with LUMIPOL 3 (SAS – Bratislava); temperature was measured with an error of ±0.2 °C. The investigation temperature range was scanned from room temperature up to 230 °C. The selected heating rate was 2 °C/min for all nonisothermal measurements. The procedures were described earlier (Rychlý et al., 2009). Samples of about 2 mg were placed on aluminum trays. The specific CL intensity expressed in Hz g$^{-1}$ was preferred for the assessment of oxidation stability. Because of the proportionality between the CL emission intensities the oxidation process can be watched effectively (Zaharescu and Jipa, 2013a).

DSC curves were recorded on a DSC-823 type METTLER-TOLEDO apparatus. The weighted samples were sealed in 40 μl aluminum crucibles with a small hole in the lids. Heating rate of 10 °C/min was applied. Before measurements this device was previously calibrated with indium standard.

## 3. Results and discussion

### 3.1. FTIR

According with the oxidation mechanism, free radicals react with oxygen and further peroxyl intermediates initiate degradation chains through which oxygen-containing products are generated (Fig. 2). The recorded spectra of pristine and stabilized LDPE with rosemary extracts allow the evaluation of the main chemical modifications in polymer structure: carbonyl and hydroxyl indexes (Fig. 3), whose values reflect the cumulative actions of antagonistic processes: degradation and stabilization. The build-up of oxidation radiolysis products containing mainly C=O and C-OH groups is described by these indexes and occurs according to the chain reaction mechanism accepted for the oxidative degradation of

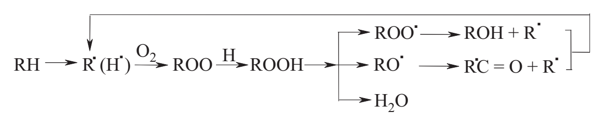


**Fig. 2.** General scheme of oxidative degradation.

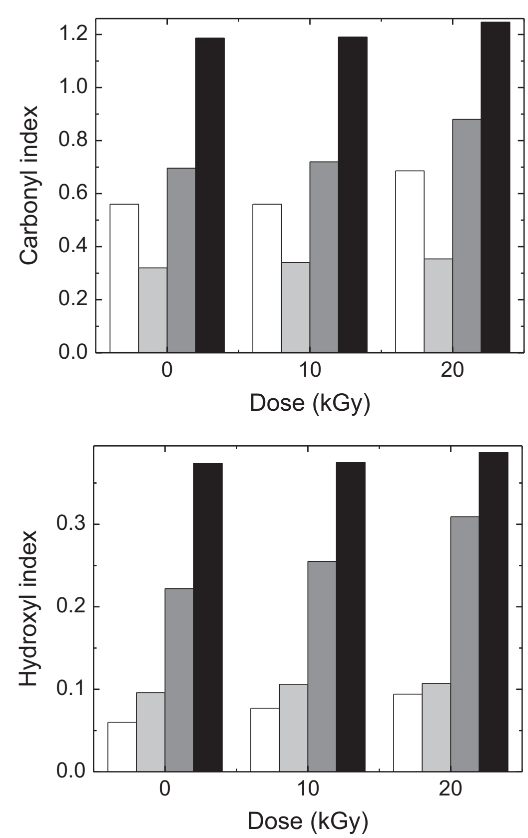


**Fig. 3.** Modification of carbonyl (a) and hydroxyl (b) indexes in LDPE stabilized with rosemary extract: (white) pristine LDPE; (light gray) LDPE/rosemary extract 1 wt%; (dark gray) LDPE/rosemary extract 2 wt%; (black) LDPE/rosemary extract 5 wt%.

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