Antioxidant and pro-oxidant activity of phenolic stabilizers during photooxidation of polyolefins

V. Gajdošová[1*], I. Šloufová[2], A. Rakitina[1], Z. Starý[1], T. Müller[3], J. Pilař[1], M. Šlouf[1]

[1]*Institute of Macromolecular Chemistry, Czech Academy of Sciences, Heyrovského nám. 2, 16206 Praha 6, Czech Republic*
[2]*Charles University, Faculty of Science, Department of Physical and Macromolecular Chemistry, Hlavova 2030, 128 40 Prague 2, Czech Republic*
[3]*Leibniz-Institut für Polymerforschung Dresden e.V. (IPF), Hohe Str. 6, 01069 Dresden, Germany*
**gajdosova@imc.cas.cz*

Phenolic stabilizers are employed in the stabilization of polymers during the processing to prevent thermooxidation [1]. They are also applied in medical applications to protect the polymers against biooxidation (in vivo oxidation) [1,2]. We investigated photodegradation processes in polymer plaques made of bulk polyolefin (HDPE or UHMWPE or COC) prepared by melt-mixing with or without phenolic natural (α-tocopherol) or synthetic (Irganox®1010) stabilizers and spin trapping agent (TTBNB; 2,4,6-Tri-tert-butylnitrosobenzene). The photodegradation was initiated either by non-ionizing radiation (wavelengths corresponding to terrestrial range of solar UV radiation) or ionizing radiation (high-energy electron beam).

In this contribution, we summarize our results concerning the comparison of the degradation processes in selected polyolefin after non-ionizing and ionizing radiation. The samples were characterized IR microspectroscopy, ESR spectroscopy including ESRI imaging, LM and SEM microscopy, and microindentation hardness testing. Both non-ionizing and ionizing radiation have generated polymer radicals in the whole volume of the irradiated samples, albeit by different mechanisms. The low-energy non-ionizing radiation is expected to split C-C bonds indirectly, through the formation of hypothetical chromophores, while high-energy ionizing radiation splits C-C bonds directly. Nevertheless, the resulting alkyl radicals might be assumed to undergo analogous reactions, regardless of their origin. However, our study has demonstrated clearly that the stability/reactivity of the generated radicals (and the concentration of the subsequently generated radical-induced oxidation products) depended on the mechanism of the radical generation together with the dynamics of polymer chains inside the studied polymers, which is closely related to their glass transition temperature. Moreover, the results have documented that the natural phenolic stabilizer exhibited both antioxidant and prooxidant activity depending on the degradation type: (i) antioxidant activity during thermooxidation, (ii) prooxidant activity during exposure to non-ionizing radiation, and (iii) antioxidant activity during exposure to ionizing radiation. The synthetic phenolic stabilizer Irg1010 showed similar, but not entirely identical behavior.

In summary, the activity of phenolic stabilizers depended not only on the degradation type (thermooxidation, non-ionizing or ionizing radiation), but also on type of polyolefin (low-Tg polyethylenes vs. high-Tg COC) and on the exact type of the stabilizer (α-Toc vs. Irg1010). Finally, the addition of TTBNB spin trapping agent enabled us to catch short-living and unstable radicals in HDPE, which could not be detected in the previous studies.

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References

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