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Radiation stability of poly (ethylenevinylacetate) stabilized with natural extract of rosemary

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The evaluation of oxidation stability of poly(ethylenevinylacetate) (EVA) samples stabilized with rosemary extract under accelerated oxidative degradation by the action of gamma radiation is presented. The FTIR and UV investigations pointed out the efficiency of natural stabilized in the EVA products used for the manufacture of drug packaging, medical wear, blood preservation. The efficiency of additive is spectrophotometrically attributed.

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1. Introduction

Phenolic compounds show antioxidant activity mainly by reaction with free radicals that are formed during material service, or even the products are stored. The benefit of the added stabilizer in the delay of oxidation with the direct consequence on the durability of materials justifies the great attention paid to the improvement of lifetime of polymer products.

Several studies on the thermal stability of ethylenevinylacetate have pointed out the certain ability of this material to resist against the attack of oxygen under thermal stress [1 – 3]. However, the accelerated degradation has revealed the behavior of this material under certain hard service conditions, when EVA exhibited a significant resistance under the action of ionizing radiation [3 – 6]. The stability of polymer materials depends not only on their molecular structure: the presence of unsaturation, electronic effects, spatial hindering, but also on the formulation, when the convenient amount of antioxidant delays the effective start of oxidative degradation. Several classes of stabilizing compounds are known, but the most important categories of oxidation protectors include hindered phenols and amines [7 – 10]. The addition of antioxidants is one of the manner through which polymers may work for a long time in oxidative environments. The material durability represents the most important characteristic that determines the quality of products [11]. The concentration of any stabilizer plays an important role in the progress of degradation, because this factor involves the quantitative reaction with free radicals [12]. These intermediates may be oxidized by molecular oxygen or may react to each other for promoting crosslinking. The former process is inhibited by the radical scavenger in the favor of later process. On this way, the oxidative degradation is delayed and the initial properties of material remain somewhat constant. The nature of oxidation inhibitor influences the kinetic parameters of degradation: the oxidation induction period and the rate of oxidation [13, 14]. On the other hand, a strong accent is put on natural antioxidants, because the synthesis compounds generate undesirable structures for human health. The present paper, a continuation of a previous assay on the antioxidant effects on polymer stabilization [15 – 17] proposes an extension of application area of rosemary extract onto the manufacture of high temperature resistant products starting from EVA and destined to various economical branches: drug packaging, medical wear, blood-preserving bottles, etc. This stabilized material can be used in the manufacture of electrical insulations.

2. Experimental

Poly(ethylenevinylacetate) containing 28 % vinylacetate was provided by ARPECHIM Piteşti (Romania). The neat material was pressed in thin films (thickness of 100 μm) for 10 minutes at 100 atm between electrical heating plates. Rosemary solid extract was prepared by Soxhlet procedure carried out at low temperature. Three kinds of films were obtained: EVA free of additive, EVA + 0.25% or 0.50% rosemary extract. Accelerated degradation was performed by the exposure of films in an irradiator GAMMATOR M-38-2 (USA) having a ^{137}Cs source. The dose rate was 0.4 kGy/h. Spectral investigations were run using JASCO 4200 FTIR spectrometer and JASCO V 650 spectrophotometer for UV/VIZ/NIR determinations.

3. Results and discussion

The FTIR spectra of the three types of EVA films are presented in Fig. 1.

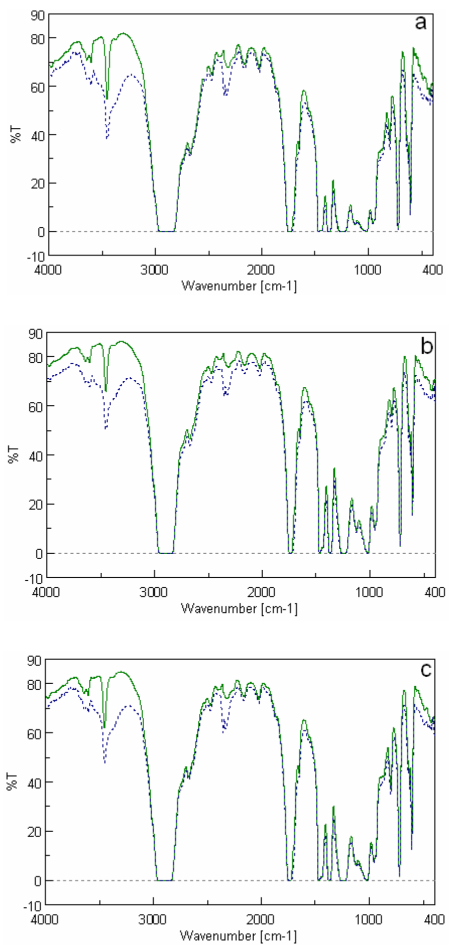

Fig. 1. FTIR spectra recorded on neat EVA (a), EVA + 0.25% rosemary extract (b) and EVA + 0.50% rosemary extract (c). Solid lines: unirradiated films; dot lines: samples which received 60 kGy.

From Fig. 1 it may be observed that on the region of the vibration of OH, there were recorded two peaks at 3450 cm^{-1} and 3650 cm^{-1}, which can be ascribed to the hydroperoxides and unassociated OH, respectively. The changes in transmittance values depend on the content of rosemary extract. The greater content of rosemary extract, the higher the material stability. Because the basic material was EVA, the characteristic peak at 1720 cm^{-1} was not evaluated. However, the residual double bonds that exist in the neat polymer are consumed and the shoulder at 1650 cm^{-1} is diminished. It means that the generation of oxygenated radiolysis products is the result of several reactions between free radicals formed during irradiation (energetic damage) and molecular oxygen and the attack of oxygen on the present unsaturation. The evolution of the 3450 cm^{-1} band may be assessed not only by the discussion on the enlargement of it as it is recorded in fig. 2. It can be easy remarked that the presence of rosemary extract causes the diminution of oxidation rate due to a proper antioxidant activity.

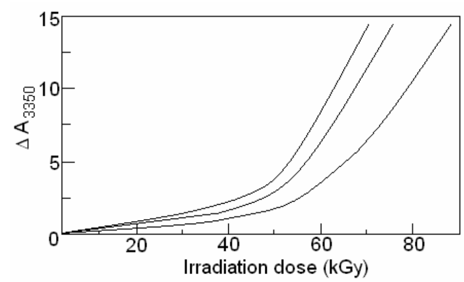

Fig. 2. Variation in the 3350 cm^{-1} band estimated from FTIR spectra for EVA/rosemary samples

From Fig. 2 some characteristic features of studied materials may be revealed:

- the degradation on the low exposure doses occurs slowly, because the remarkable resistance of EVA upon the action of ionizing radiation;
- the remarkable difference in the absorbance of stabilized samples is noticed at higher doses, where the antioxidant efficiency is relevant;
- the natural antioxidants present a good antioxidant activity due to their phenolic structures

The UV recorded spectra (fig. 3) reveal the contribution of rosemary extract on the radiochemical stability of the sampled prepared with poly(ethylenevinylacetate) – based material. The accumulation of degradation products causes the increase in the sample absorbance. The polymer sample without rosemary extract presents a larger dispersion curves. On the spectral range between 230 and 300 nm several compounds containing chromophore units C=O are present. It denotes that polyphenols that are active compounds of additive hinder the oxidation degradation that is promoted by the incident radiation. The carbonyl compounds are visualized by means of this spectral procedure demonstrating the accumulation of this structure during irradiation.

4. Conclusions

The natural antioxidants are suitable compounds for the stabilization of polymer materials that are in the direct contact with people. Due to their activity conferred by OH groups, rosemary extract is an efficient stabilizer for thermoplastic materials and the unpleasant effects of various degrading factors such as heat, UV light, humidity may be avoided by the scavenging process through which the protector acts. The stabilization efficiency is the consequence of additive activity, which may characterize the long term usage of polymer items. The vegetal extracts have a great advantage in comparison with the synthesis compounds that are manufactured on large scale: the perfect compatibility with human body and the secondary sequences that are favorable for human health. The production of this kind of stabilizers would ensure larger areas of applications in the benefit of people. A large variety of natural extracts that exhibit antioxidant properties is required for the manufacture of "clean" products, which eliminate the disease probability, but promote healthy products for medical and pharmaceutical purposes.

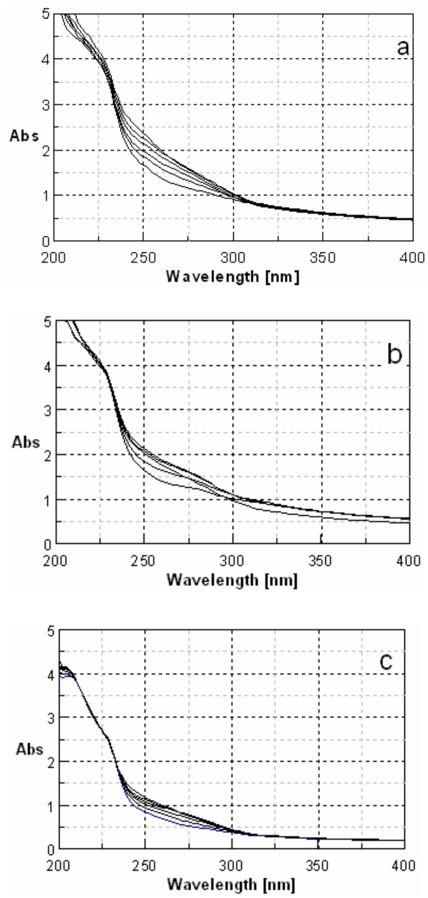

Fig. 3. UV spectra recorder on neat EVA (a), EVA + 0.25% rosemary extract (b) and EVA + 0.50% rosemary extract (c). Exposure dose increases from the bottom to the top of figure. The films have similar thicknesses.

References

[1] N. S. Allen, M. Edge, C. M. Rodriguez, E. Fontain, Polym. Degrad. Stabil., **68**, 363 (2000).
[2] M. Giurginca, L. Popa, T. Zaharescu, Polym. Degrad. Stabil., **82**, 463 (2003).
[3] A. J. Krűger, A. T. Tolmay, J. Appl. Polym. Sci., **84**, 806 (2002).
[4] S. J. Dutta, A. K. Bhowmick, P. G. Mukundu, T. K. Chaki, Polym. Degrad. Stabil., **50**, 75 (1995).
[5] S. Chattopadyay, T. K. Chaki, A. K. Bhowmick, Radiat. Phys. Chem., **59**, 510 (2000).
[6] S. Jipa, T. Zaharescu, M. Mărcuță, R. Setnescu, L. M. Gorghiu, C. Dumitrescu, Nuclear Instrum. Meth., **B236**, 567 (2005).
[7] T. Zaharescu, M. Giurginca, S. Jipa, Polym. Degrad. Stabil., **63**, 245 (1999).
[8] H. Bergennudd, P. Eriksson, C. DeArmitt, B. Stenberg, E. Malmstrőm-Jonsson, Polym. Degrad. Stabil., **76**, 503 (2002).
[9] F. Gugumus, Polym. Degrad. Stabil., **77**, 157 (2002).
[10] S. Jipa, T. Zaharescu, L. M. Gorghiu, C. Dumitrescu, R. Setnescu, M. A. Esteves, B. Gigante, J. Appl. Polym. Sci., **95**, 1571 (2005).
[11] J. Pospišíl, Z. Horák, J. Pilař, N. C. Billinghan, H. Zweifel, S. Nešpůrek, Polym. Degrad. Stabil., **82**, 145 (2003).
[12] V. Dinoiu, L. M. Gorghiu, I. Mihalcea, S. Jipa, T. Zaharescu, C. Dumitrescu, R. Olteanu, Mater. Plast. (Bucharest), **40**, 149 (2003).
[13] T. Zaharescu, S. Jipa, R. Setnescu, C. Santos, B. Gigante, L. M. Gorghiu, I. Mihalcea, C. Podină, Polym. Bull., **49**, 289 (2002).
[14] S. Jipa, T. Zaharescu, L. M. Gorghiu, C. Dumitrescu, R. Setnescu, Rev. Chim. (Bucharest), **55**, 514 (2004).
[15] S. Jipa, T. Zaharescu, R. Setnescu, W. Kappel, J. Optoelectr. Adv. Mater. **9**, 1623 (2007).
[16] A. Mihai, T. Zaharescu, S. Jipa, L. Andrade e Silva, C. Oros, J. Optoelectr. Adv. Mater. **9**, 1626 (2007).
[17] S. Jipa, T. Zaharescu, W. Kappel, M. Lungulescu, R. Olteanu, Adv. Mater. **10**, 837 (2008).
[18] J. L., Bolland, G. Gee, Trans. Faraday Soc., **42**, 236 (1946).

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