Polymer Bulletin 57, 729–735 (2006)
DOI 10.1007/s00289-006-0628-x

Polymer Bulletin

Stabilized polyethylene on the sterilization dose range

T. Zaharescu[1] (✉), S. Jipa[1,2], B. Gigante[3]

[1] INCDIE, ICPE CA, 313 Splaiul Unirii, P. O. Box 149, Bucharest 030138, Romania
[2] “Valahia” University of Târgovişte, 1 Carol I Av., Târgovişte, Romania
[3] INETI, DTIQ, Estrada do Paço do Lumiar, 1649-038 Lisbon, Portugal

E-mail: zaharescut@gw-chimie.math.unibuc.ro, Fax: 0040-21-346-8299

Received: 1 November 2005 / Revised version: 11 June 2006 / Accepted: 15 June 2006

Summary

This paper presents the effect of gamma irradiation on polyethylene stabilized with two derivatives of carnosic acid. LDPE-stabilized samples were subjected to high energy radiation on three doses (5, 10 and 20 kGy) on the sterilization range of polymers. The stability of radiochemically degraded LDPE was achieved by oxygen uptake at 190^{0}C under isothermal and isobaric conditions. Antioxidant concentration of 0.25 % w/w was selected to demonstrate the availability of these compounds for delaying oxidative degradation under hard service circumstances. The influence of substitution in antioxidant molecules on the kinetic parameters of thermal stabilization is discussed. Some mechanistic aspects in relation to the intermediates of additives are assumed.

Introduction

The radiation sterilization of polymer materials is an advantageous procedure through which biological contaminants are totally inactivated by the exposure to the action of high energy radiation. It is obviously recognized that in polymers the accelerated electron, γ- or X-rays induce bond scission, which is followed by certain chemical modifications [1-4]. In spite of beneficial aspects of the efficiency of radiochemical treatment, the radiation sterilization causes either a slight variation in molecular weight, or degradation. In any case, the presence of an active antioxidant is required for the prevention of oxidation during irradiation processing.

Even though considerable research effort has been devoted to the study on the stabilization of polymers, high number of papers is issued [for example, 5-9] on this topic. After the application of radiation treatment, exposed material becomes more reactive to oxygen due to the activity of new formed free radicals. The addition of efficient compounds, which can delay the start of oxidation, is the most convenient solution for the extension of material lifetime.

According to the international standards applied in the area of radiation sterilization [10-12] the conditions and requirements under which this operation must be practiced have to follow certain recommendations. The application of these regulations on the preservation of high stability on oxidation is the goal of several academic papers [for example 13-15], where the authors have emphasized the practical advantages offered by this kind of processing. The investigations on radiation resistance of polymer must be depicted because this property represents the most important characteristic that determines the durability of products. In this paper the capability of low density polyethylene stabilized with two carnosic acid derivatives is discussed.

Experimental

Materials and sampling

Low density polyethylene, K322 sort, was provided by Brazi Chemical Enterprise (Romania). This pristine material presents some characteristics, which are listed in Table 1.

Table 1. The main characteristics of pristine low density polyethylene

Density	0.920
Crystallinity	45.5 %
Number of CH_3 per 100 carbon atoms	3.1

LDPE was previously purified by sohxlet boiling for 10 hours in *o*-xylene, followed by the precipitation with cold methanol. The separation of supernatant was done when the system was still hot in order to prevent the adsorption of the any trace of antioxidant, which would exist in liquid phase. The raw polyethylene was dried in an air-circulating oven at 30^0C till the solvent was totally removed.

The compounds used as antioxidants are the derivative of carnosic acid. Their structures are presented in Figure 1. Their preparation was previously reported [16] being commercially named CS 84 and AM 138.

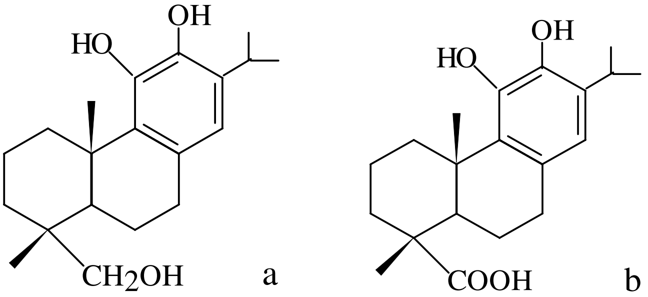

Figure 1. Molecular structures of studied additives. (a) CS 84 and (b) AM 138.

The addition of antioxidants at a concentration of 0.25 % w/w was performed by vigorous grounding in a mortar of CH_3Cl-wetted and fresh polyethylene, till a high homogeneity was attended. The obtained powder was also dried at room temperature.

Aliquots of 20 mg were taken for further steps of investigation (irradiation and thermal characterization).

Irradiation

γ-Exposure ageing of modified and control LDPE specimens were done in air at room temperature in an irradiator GAMMATOR 220 (USA) provided with ^{137}Cs source. Dose rate was 0.4 kGy/h; the selected total doses were 5, 10, 20 kGy. All the oxygen uptake determinations were promptly done, because it must avoid any errors brought about by the storage of samples.

Measurement

Oxygen uptake investigations on various sample formulations consisting of control – and modified – low density polyethylene were carried out in a device designed in our laboratory [17]. Determinations were performed in air as oxidant environment at 190^{0}C and normal pressure. This temperature was properly chosen, because the oxidation takes place to an appropriate rate and it is usually applied in several manufacture technologies of polyethylene-made products. However, the thermal stability investigation on polyethylene samples would not be performed on solid-phase material due to the too long experiments (several weeks).

Results and discussion

The radiochemical consequence of the high energy radiation exposure of LDPE is the formation of free radicals on the first stage of irradiation [18]. The lifetime of radiolyzed materials depends on the behavior of radicals [19]. It is generally accepted that polyethylene belongs to the class of radiation crosslinkable polymers, which exhibits a satisfactory radiochemical stability [20]. However, the reaction of free radicals with molecular oxygen occurs, but at a minimal level. The appearance of peroxyl radicals denotes the start of oxidation and they will initiate a subsequent degradation by a chain process. The presence of antioxidants minimizes the probability of the early beginning of oxidation [21, 22]. The higher the efficiency of radical protection by scavenging of a radical, free hydrocarbon moiety or peroxyl intermediate, the longer the durability of polymer. The oxidative degradation must be stopped on the first stage by chain breaking antioxidants, because any peroxyl radical becomes further an oxidation promoter.

The oxidation behavior of purified low density polyethylene is illustrated in figure 2 by the progress of oxygen consumption (a) and the change in the oxidation rate (b) of LDPE free of antioxidant.

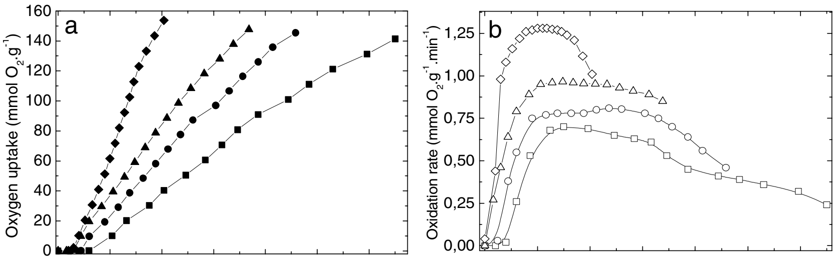

Figure 2. The dependencies of oxygen uptake (a) and of oxidation rate (b) obtained for purified LDPE at various doses. (■, □) unirradiated sample; (●, ○) 5 kGy; (▲, Δ) 10 kGy; (♦, ◊) 20 kGy.

The accumulation of oxygenated intermediates occurs faster at higher doses, because the local energetic transfer is larger and, consequently, the specific number of split bonds is greater in the absence of oxidation inhibitor. From the figure 2b, it is easy to remark that the increase in the rate of oxidation for purified LDPE happens at the start of thermal oxidation; it means that the long life radicals previously trapped in the crystalline phase (45.5 %) are involved in the fast oxidation of radiation sterilized polyethylene. If the unirradiated LDPE specimen attends a pseudoplateau on the dependence of oxidation rate on time for the first 50 minutes, the unstabilized LDPE sample irradiated at 20 kGy reaches a maximum oxidation rate after first 30 minutes. The maximum oxidation rate may be attended faster, if the dose rate will be higher due to the higher rate of bond scission, followed by oxidation of radical intermediates. The diffused oxygen provided from the outer layers toward the inner part of polyethylene bulk will be faster consumed and the degradation of radiation-processed material will be happened earlier. The oxidation curves (figure 2a) present various oxidation induction times for the different irradiation doses absorbed by LDPE powder patterns. However, they are not so unlike that the oxidation rates are, because on the first step of degradation (initiation) the concentration of free radicals does not determine sharply propagated oxidation.

The addition of antioxidants brings about a significant improvement of oxidation resistance for similar irradiation doses. Figures 3 and 4 illustrate the oxygen consumption and the modification occurred in oxidation rates for the both stabilized formulations of low density polyethylene samples.

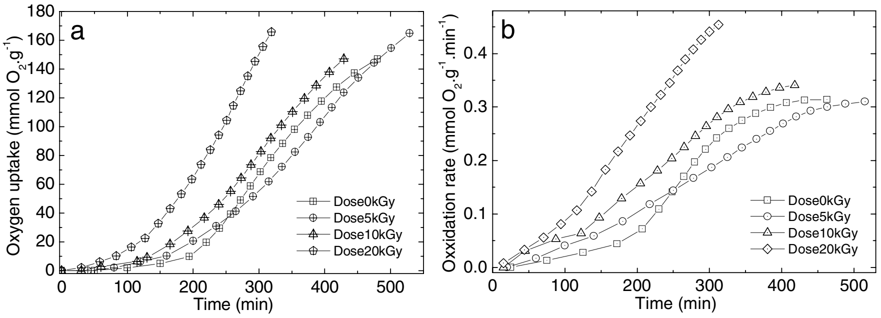

Figure 3. Oxidability curves (a) and the dependencies of oxidation rate (b) on degradation time for LDPE stabilized with AM 138.

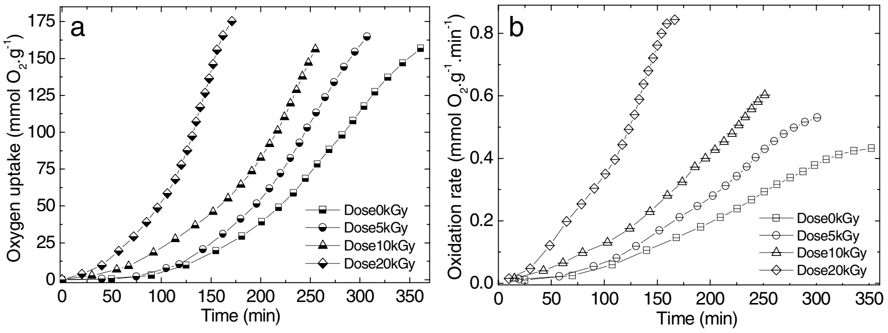

Figure 4. Oxidability curves (a) and the dependencies of oxidation rate (b) on degradation time for LDPE stabilized with CS 84.

Though a certain initial amount of molecular oxygen pre-exists in polyethylene material from manufacturing step, the presence of antioxidant does not allow material to be fast degraded. On the initial stages of thermal degradation in γ-irradiated LDPE, the antioxidant activity is more efficient in the presence of AM 138 than it has been observed in the case of CS 84 (figures 3a and 4a). After the propagation step is attended, the thermal degradation of the two modified LDPEs advance differently. This aspect may be explain by the differences in the chemical reactivities of initial structures and, may be, of the antioxidant intermediates that are formed on various moments of investigations. The oxidation induction time, which defines, in the first approximation, the thermal stability of irradiated specimen [23] is the most relevant kinetic parameter that characterizes the sensitivity of polymer materials to oxidation. Because of the very low concentration of peroxyl radicals, it is difficult to evaluate accurately the start moment of oxidation. But, by the intercept of the tangent drawn at the uptake curve on the propagation stage, it can be established the theoretical term of induction. The ratios between the oxidation induction times (OIT) for stabilized and control LDPE samples illustrate suggestively the high efficiency of studied antioxidants in the thermal stabilization of LDPE (Table 2).

Table 2. The OIT ratios for irradiated and control samples at various doses

Dose (kGy)	$\tau_{\text{stabilized LDPE}}/\tau_{\text{virgin LDPE}}$	
	Antioxidant	
	AM 138	CS84
0	5.62	3.91
5	6.04	4.67
10	5.90	5.20
20	6.00	4.82

These results can be evaluated as a proof of the possibility for the formation of intermediates. Previous research on the oxidative protection activity of these compounds has suggested this hypothesis [24]. On this basis, a mechanism of the antioxidant action of the derivatives of carnosic acid may be presumed (figure 5).

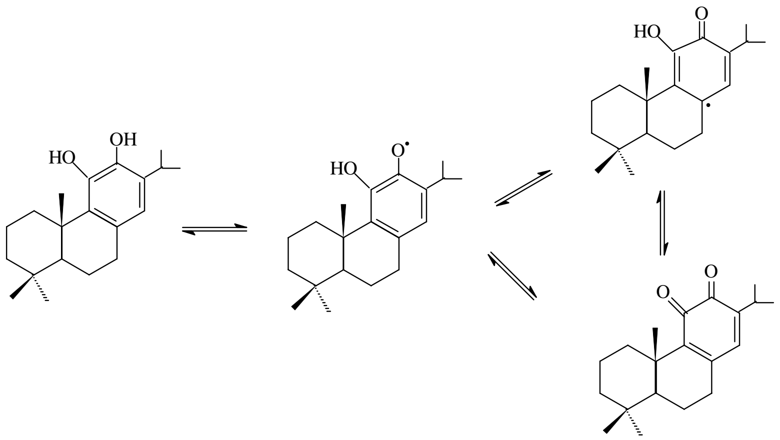

Figure 5. Suggested mechanism involved in the stabilization action of the derivatives of carnosic acid.

The tested compounds would present quinone intermediates, whose stabilizing activity was demonstrated for the hindered phenolic antioxidants [25]. The reactive site is influenced by the substitutant on C16 and the stability of this structure is ensured by the participation of delocalized electrons belonging to benzene ring. As the result of this kind of coupling, the electronic density is not significantly modified, but a radical position is created by the neighbor units: the benzene ring and the saturated cycle.

The experimental results demonstrate the satisfactory efficiency in the stabilization of radiation-sterilized polymers that are degraded through a mechanism based on radical intermediates like polyethylene. The high testing temperature, which is usually chosen for the processing of polyethylene (extrusion or pressing) is additional argument by which the these compounds can be considered very good antioxidants for polyolefins.

Conclusion

This study on the prevention of oxidative degradation initiated by free radicals presents the high efficiency of carnosic acid derivatives. On the dose range that is characteristic for radiation sterilization, the oxidation induction periods of irradiated LDPE are more than four times longer than the controls investigated under similar conditions. The propagation rate of oxidation is also significantly diminished due to the capability for the formation of alternative structures, which present certain antioxidant activity.

Due to the existence of this derivative in nature, being used as curative agent in cancer treatment, it may be emphasized that these derivatives are proper antioxidants for ecologica stabilization of low dose irradiated polyethylene without any dangerous consequences.

Acknowledgement. The authors thank IAEA for including this work through the investigations in the frame of CRP "Controlling of degradation effects in radiation processing of polymers”.

References

1. Woods R, Pikaev A (Eds) (1994) Applied Radiation Chemistry: Radiation Processing, ch. 9, Wiley, New York
2. Suwanprateev J, Trongton P (2003) J Mater Sci, Mater Medicine 14:851
3. Dalai Siqion, Wenxiu Chen (2003) J Appl Polym Sci 86:1296
4. Stojanović Z, Kačarević-Popović Z, Galović S, Miličević D, Suljovrujić E (2005) Polym Degrad Stabil 87:279
5. Schwetlick K, Habicher WD (2002) Polym Degrad Stabil 78:35
6. Tzenoglou CJ, Kartalis CN, Papaspyrides CD, Pfendner R (2002) Adv Polym Technol 21:260
7. Zaharescu T, Jipa S, Setnescu R, Santos C, Gigante B, Gorghiu LM, Mihalcea I, Podină C (2002) Polym Bull 49:289
8. Bottino FA, Cinquegrani AS, Di Pasquale G, Leonardi L, Orestano A, Pollicino A (2004) Polym Testing 23:779
9. Zaharescu T, Kaci M, Setnescu R, Jipa S, Touati N, Polym Bull in press (PB_05_0327_R2)
10. American Standard “Sterilization of health care products – Radiation sterilization”, ANSI/AAM/ISO 11137-1994
11. European standard “Sterilization of medical devices. Validation and routine control of sterilization by irradiation”, EN 552 (1994)

12. *** IAEA 1987 Guideline for industrial radiation sterilization of disposable medical products. ^{60}Co gamma irradiation
13. Fengmei Li, Ying Wang, Xiaoguang Liu, Baoyu Yang (2000) Rad Phys Chem 57:435
14. Zimek Z, Kaluska I (2002) Radiat Phys Chem 63:673
15. Woo Lecon, Sanford CL (2002) Radiat Phys Chem 63:845
16. Gigante B, Santos C, Silva AM, Curto, MJM Nascimento, MSJ Pinto E, Pedro M, Cerqueira F, Pinto MM, Duarte MP, Laires A, Rueff J, Gonçalves J, Pegado MI, Valdeira ML (2003) Bioorg. Med. Chem 11:1631
17. Zaharescu T, Mihalcea I (1994) Mater Plast (Bucharest) 31:139
18. Singh A (1999) Radiat Phys Chem 56:375
19. von Sonntag C, Bothe E, Ulanski P, Adhikary A (1999) Radiat Phys Chem 55:599
20. Chapiro A (Ed) (1962) Radiation Chemistry of Polymer Systems, Interscience Publishers, New York
21. Pentimalli M, Ragni P, Righini G, Capitani D (2000) Radiat Phys Chem 57:385
22. Albano P, Perera R, Silva P, Sáncez Y (2003) Polym Bull 51:135
23. Pospíšil J, Horák Z, Pilař J, Billingham NC, Zweifel H, Nešpůrek (2003) Polym Degrad Stabil 82:145
24. Wenkert E, Fuchs A, McChesney JD (1965) J Org Chem 30:2931
25. Pospíšil J, Klemchuk P (Eds) (1990) Oxidation Inhibition in Organic Material, CRC Press, Boca Raton