

Thermal stability of additivated isotactic polypropylene

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Received: 5 June 2002/Revised version: 10 August 2002/ Accepted: 12 September 2002

Summary

Isotactic polypropylene stabilised with fullerene [C60], its adduct with methyl levopimarate, carbon black, *p-t*-butylcalix[4]arene, *p-t*-butylcalix[6]arene, Irganox 1076 or Topanol OC was investigated by means of oxygen uptake method under isothermal (165°C) and isobaric (normal pressure) conditions. Oxidation investigations were performed in air as degradation environment. Additive concentration was 0.25 % (w/w). Kinetic parameters, oxidation induction and oxidation rate are compared with similar characteristics of additive-free i-PP. Effect of γ -irradiation on thermal oxidation is also presented. Three γ -exposure doses (50, 100 and 150 kGy) were selected. The influence of radiation treatment on the efficiency of studied compounds and some mechanistic aspects are also presented.

Introduction

Thermal stability of polymers is of a great importance for long term service of polymers. Great efforts are spent either for synthesis of new compounds or assessment of their antioxidant activity. The oxidative degradation of organic products is accelerated by the action of various factors, namely action of light and high energy radiation, extended mechanical stress, radical generator decomposition, transitional metal traces, attack of pollutants. Self-oxidation is propagated by peroxy radical formed as the result of reactions between free radicals and molecular oxygen [1-4]. The presence of stabilizers slows down the oxidation rate by reactions with intermediates, free radicals or peroxy radicals [3, 4].

Polypropylene presents thermal stability less than polyethylene and even than ethylene-propylene elastomers due to its high proportion of tertiary carbon atoms contained in molecular structure [5, 6]. Many authors [7-12] have investigated thermal stability of this polyolefin. Polypropylene systems stabilized with commercially available products have presented specific efficiency in retarding oxidation in correlation with protection activity of additives.

The present paper intends to prove the effectiveness of several additives that may be used in the manufacture of polypropylene articles.

Experimental

Materials and sampling

Isotactic polypropylene (Moplen[®], Himont, Italy) was previously purified by removing any amount of antioxidant. Polypropylene was boiled in *o*-xylene for 10 h and precipitated with cold methanol. Solid phase remained on filter was abundantly washed with acetone for removing residual *o*-xylene. In the end polypropylene was gently dried in air circulating oven at 30°C.

The additives studied in this paper were mixed in polymer substrate wetted with chloroform during vigorous grinding. To crude polypropylene each stabilising compound (fullerene [C60], its adduct with methyl levopimarate, carbon black, calix[4]arene, calix[6]arene, Irganox 1076, Topanol OC) was put in at the same concentration (0,25 % w/w).

Fullerene and its adduct with levopimaric acid were prepared by INETI-Lisbon (Portugal) [12]; carbon black were obtained from IFA-Bucharest (Romania) [13]; Irganox 1076 and Topanol OC were provided by Ciba Geigy (Switzerland); *p*-*t*-butylcalix[4]arene, was synthesized at ICECHIM-Bucharest (Romania), *p*-*t*-butylcalix[6]arene was manufactured by Merck (Germany). Molecular structures of studied antioxidants are presented in figure 1.

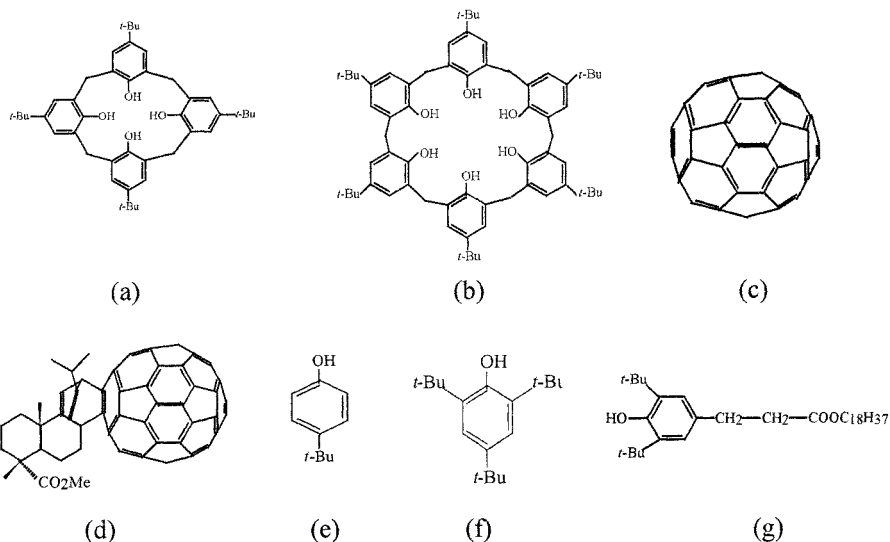


Figure 1. Structures of studied compounds: (a) calix[4]arene; (b) calix[6]arene; (c) fullerene [C60], (d) methyl [C60] fullerene adduct; (e) *p*-*t*-butylphenol; (f) Topanol OC; and (g) Irganox 1076.

Specimens of 20mg polypropylene were prepared. For easy handling i-PP powder samples were brought in thin film in an oven by heating at 150°C for 20 seconds.

Irradiation

Polymer samples were exposed to γ -radiation (¹³⁷Cs) in air at ambient temperature.

Irradiation was performed in GAMACELL facility (USA) by permanent rotation of samples in front of radiation beam. Dose rate was 0.4 kGy/h.

Measurement

Oxygen uptake investigations were carried out in a device designed in our laboratory [14]. Determinations were performed in air at 165^oC and normal pressure and promptly accomplish at the end of irradiation. The efficiency of additives must be checked for various structures of stabilizers and for different application conditions.

Results and discussion

Permanent action of aggressive environmental factors for example sunlight, heat, reagents and intensive or continuous mechanical stress requires improved stability of materials for long term operation [15]. The action of various antioxidants is very useful for polymers that contain notable concentration of reactive positions, such as double bonds, high number of methyl units or high-branched macromolecular chains. Thermal or radiation stability can be augmented by adding proper compounds that block free radicals towards other reactions or react selectively with peroxy radicals breaking chain propagation of oxidation degradation. The problem of antioxidative activity is the period on which additive acts efficiently in polymer protection. The hazardous agent, in the present study, heat and ionizing radiation, can not exhibit selectivity between host polymer and the oxidation retardant. The radiation resistance of additive represents an important factor that determines the duration of induction and influences oxidation rate over all steps of degradation according with the mechanism proposed by Bolland and Gee[1]. The inhibition of oxidation involving free radical has to solve first the question of structure preservation and, of course, the minimizing changes in material properties [16-19]. The detailed description of degradation reactions for various classes of polymers, including polyolefins is presented in [20].

Oxygen uptake measurements have provided the proof of antioxidant activity giving the possibility to evaluate the main kinetic parameters, namely oxidation induction time and oxidation rate. Figures 2 and 3 presents the dependencies of oxygen amount consumed on oxidation time. It may be noticed great differences between raw polymer and the stabilized material where studied compounds were added.

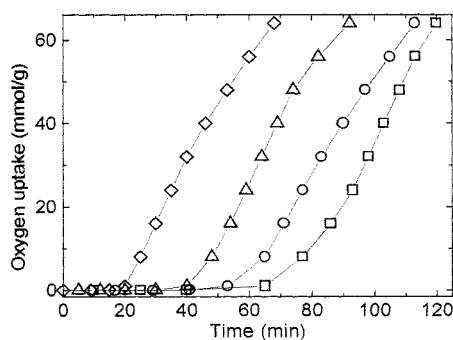


Figure 2. Oxygen uptake vs time curves obtained for purified isotactic polypropylene under various irradiation states: (□) unirradiated; (○) 50 kGy; (△) 100 kGy; (◇) 150 kGy.

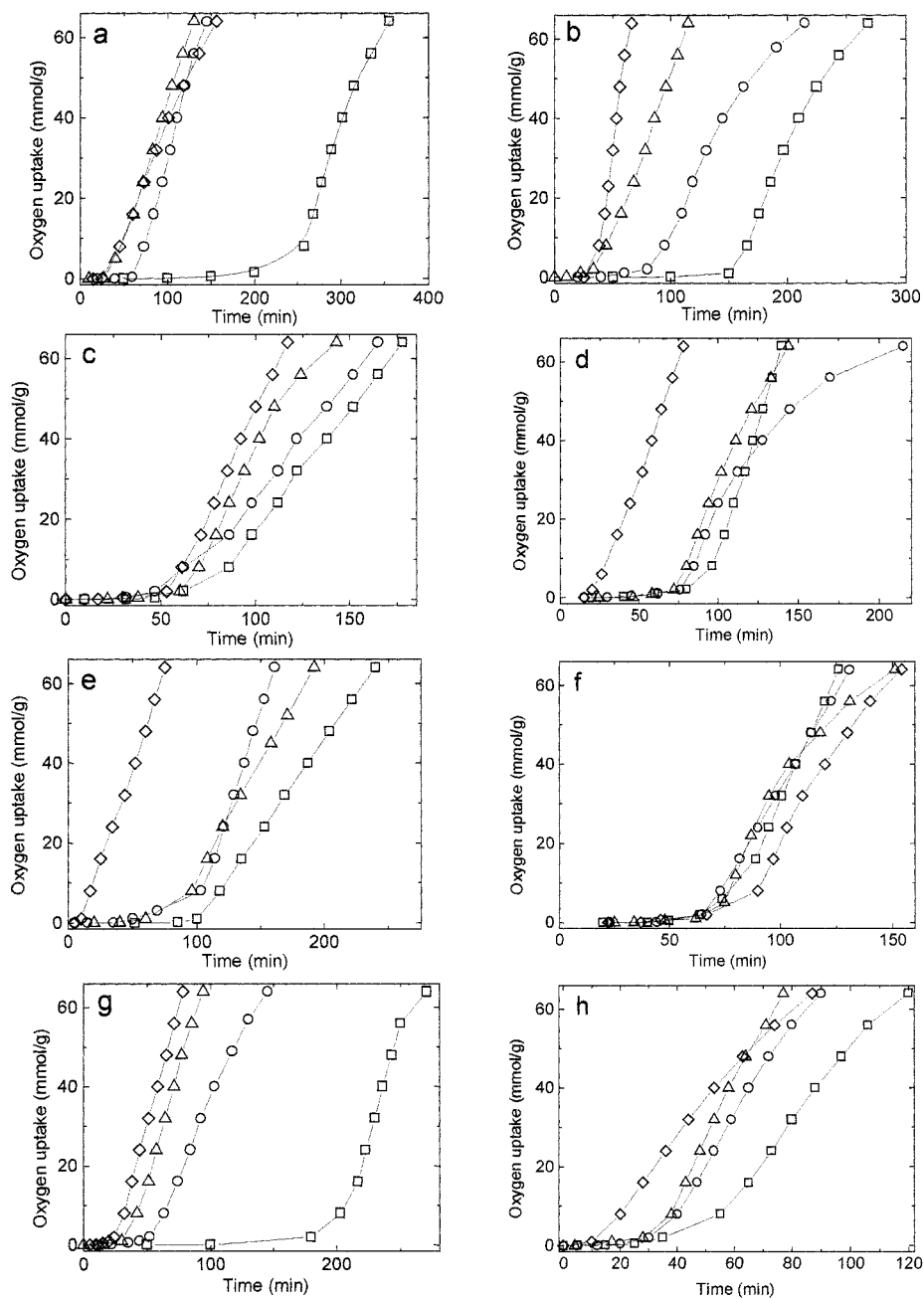


Figure 3. Time dependencies of oxygen uptake for various stabilized states of i-PP.

(a) calix[4]arena; (b) calix[6]arena; (c) fullerene [C60]; (d) methyl [C60] fullerepiramate adduct; (e) *t*-butylphenol; (f) Topanol OC; (g) Irganox 1076; (h) carbon black. (□) unirradiated; (○) 50 kGy; (Δ) 100 kGy; (◇) 150 kGy.

Figure 4 presents the most representative kinetic characteristics of radiation effects on thermal stability: oxidation induction time and oxidation rate on propagation stage. As it can be deduced from experimental data large differences between oxidation induction times of unirradiated samples are found when polypropylene was stabilized with calix[4]arene and Irganox 1076. In spite of their protection ability in unirradiated specimens these compounds do not exhibit peculiar capacity in the prevention of oxidation of low and medium γ exposed polypropylene matrix; it means that their low radiation stability does not ensure long-term antirad activity. It may be assumed that calix[4]arene is destroyed during irradiation and the remained amount does not exhibit satisfactory diameter of cage for efficient radical scavenging. On the other side, Irganox 1076 molecules contain large substituent which can be split easier than benzene ring. Under these circumstances phenolic unit will be not able to act as proton donor.

The presence of Topanol OC does not modify thermal stability of i-PP in unirradiated polypropylene. As it was previously proved [21] this stabilizer induces light changes in the accumulation of oxygenated products formed during radiochemical degradation. Somewhat larger distributed curves (figure 3c) that sustain its satisfactory inability in the association with oxidation precursors.

Outstanding results on the delay of thermal degradation were obtained by addition of calix[6]arene to polypropylene. It seems that the effect induced by the six phenol groups placed in the inner area of molecules and the spatial protection of double bond due to advanced delocalisation of π electrons correlated with the interaction between oxygen atom of HO units and trapped radical are the main explanations on the higher efficiency of this compound. It may not be ignored the possibility that oxygen atoms initially belonging to phenolic groups act as quinone oxygen.

Figures 3 c, 3d and 4 emphasize that [60]fullerene and the adduct of [60]fullerene with levopimaric acid derivative manifest relative larger availability to act as thermal antioxidant in comparison with [60]fullerene especially on the low dose range. Their ball structure confers to these compounds higher radiation stability in comparison with linear chain compound. In addition, the presence of substituent on the outer zone of "ball" modifies the homogeneity of electron distribution. Thus, reactive position may be generated and the activity regarding radical scavenging is promoted.

Carbon black (figure 3h and 4) worsens the thermal resistance of isotactic polypropylene. The low oxidation induction times at all selected doses prove the depletion of additive and involvement of oxidized carbon in the promotion of thermal degradation. It may be supposed that at a low dose range a competition between polymer and carbon black for oxygen allows formation of carbon oxide which can transport oxygen from gaseous phase onto polymer chain. This aspect is proved by the considerable decrease in oxidation induction time (figure 4). On the propagation stage when oxidative degradation depends on the diffusion of oxygen it is possible that a crosslinking of polymer would occur due to the depletion of oxygen. The oxidation rate of polypropylene containing carbon black is slow down because of the availability of free radicals to recombine to each other.

The low values of oxidation induction times at all selected doses prove the depletion of additive and involvement of oxidized carbon in the promotion of thermal degradation.

Similar results were obtained [22] studying thermal degradation of polypropylene in the presence of carbonic materials.

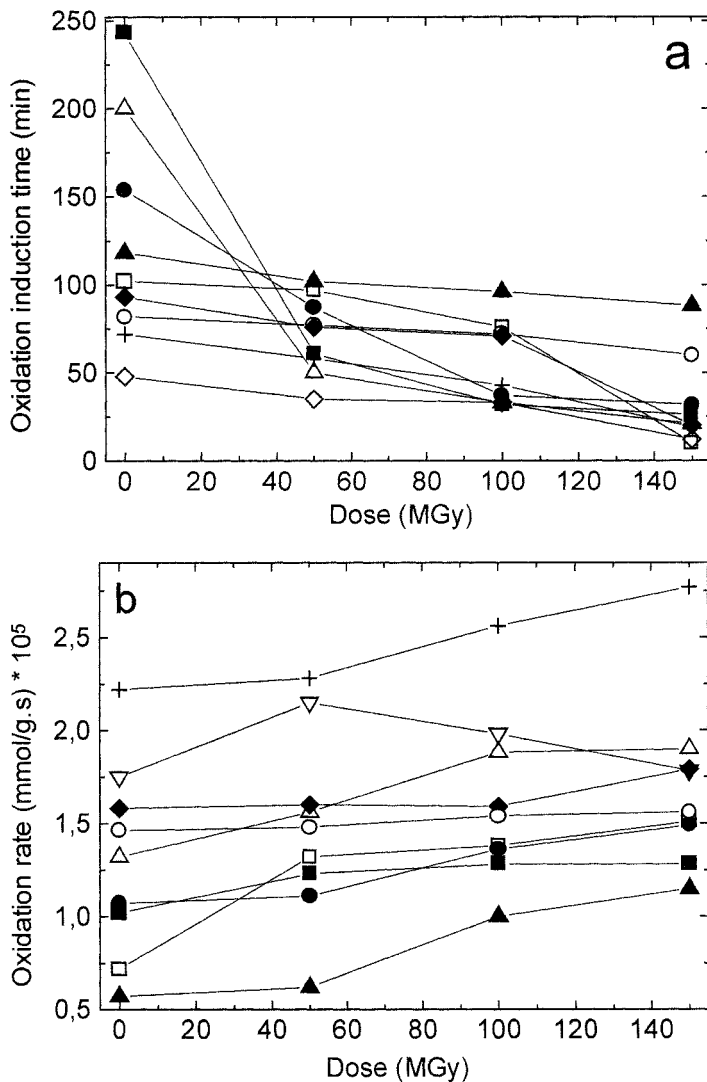


Figure 4. Dose dependencies of oxidation induction time (a) and oxidation rate (b) determined for stabilised i-PP samples.

(■) calix[4]arene; (●) calix[6]arene; (▲) [C60] fullerene; (◆) [C60] fullerepimarate; (□) *t*-butylphenol; (○) Topanol OC; (△) Irganox 1076 (◇) barbon black; (+) control.

From the present investigations it is clear that the differences between the thermal behavior of investigated systems are brought by the accessibility of various oxygenated intermediates to the reactive sites of macromolecules. In the same time the strength of temporary bridges formed during relative stabilization period determines the efficiency of additive.

In the case of HO containing antioxidants free radical mechanism may be successfully applied. Unfortunately, the mechanistic aspects of stabilization activity shown by [C60]fullerene is not reported yet.

The stabilisation capacity of calix[n]arene increases with the number of benzene rings because the probability of radical scavenging increases with the diameter of "basket" [23].

Conclusions

Through the compounds selected as antioxidants calix[4]arene, calix[6]arene and Irganox 1076 present satisfactory activity in the prevention of thermal degradation of isotactic polypropylene. Methyl [C60]fulleropyrimate adduct is more efficient in delaying oxidation than [C60]fullerene. Unfortunately, exposure of polypropylene to the action of high energy radiation that induces fast polymer degradation, and longer oxidation induction time does not offer satisfactory thermal stability by addition of [C60]fullerene adduct with methyl levopimarate.

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