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Thermal stability evaluation of polypropylene protected with grafted amine

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Summary

Polypropylene containing a grafted amine as oxidation protector was subjected to γ-irradiation for the evaluation of thermal stability. Several formulations were prepared containing hindered amine, Sanduvor PR 31 (0.1, 0.2 and 0.3 % w/w) and $CaCO_3$ (0.6 % w/w). The stability assessment was carried out in air by oxygen uptake procedure under isothermal and isobaric conditions (165°C and normal pressure, respectively). The exposure doses were placed in the range from 0 to 70 kGy. The changes appeared in the main kinetic parameters (oxidation induction time and oxidation rate) evaluated for thermal degradation of irradiated PP specimens are presented and the stability analysis is explained starting from the behaviour differences of various formulations of radiation processed polypropylene. On the low dose range, the drop in thermal stability of modified polypropylene films occurs more abrupt than it was observed for the samples irradiated at higher doses.

Introduction

The radiation processing of polymers is generally used for industrial purposes [1,2], but the exposure to high energy radiation is a proper procedure to assess material quality under hard operation conditions [3]. The material structure and formulation plays an important role in the investigations on durability [4]. A special attention of researchers and polymer manufacturers has been paid to the stabilization efficiency of antioxidants. The stabilizer activity depends on several factors, through which concentration and the nature of active functions must be emphasized. The commercialized antioxidants belong usually to sterically hindered phenols and amines, but other peculiar compounds like triazines [5], elementary selenium [6], fullerenes [7] present satisfactory activity in the slowing down of polymer degradation.

The prevention of polymer degradation is required for long-term service of material. The stressing of polymers under the action of natural or artificial factors demands detailed study. Several papers were concerned to phenolic antioxidants in polyolefins

(Pospíšil and Nešpurek [8]), while the effect of hindered amines was reported by Gugumus [9], Shamshad and Basfar [10] and Zaharescu et al [11].

Like polyethylene, polypropylene has gained a large usefulness in various branches of activities. The stabilized material quality must remain unchanged for a long time, because it determines the product lifetime. The enormous amounts of polypropylene are used for greenhouses, medical wear, commodities, plastic tissues and many other practical products. They are continuously exposed to sunlight, especially in the low latitude lands. The fast degradation would be produced, if polypropylene is not protected with suitable compounds. Some papers have been dedicated to the topic of weathering [12-15], but an accelerated investigation was not presented in detail.

The main aspects of the stabilization activity of amines include the primary oxidation of amine to a stable nitroxyl radical, reactions involving this radical and alkyl entities and regeneration of alkoxy radicals. Smoliak and Prokopchuk [16] have presented the estimation of parameters that correlate molecular structure of hindered amines with their stabilizing efficiency for polyethylene. Now, the current practice in the polymer stabilization by antioxidant couples regards meaningfully the simultaneous action of phenolic antioxidant and amine protector [17].

Under γ-irradiation, polypropylene is quickly degraded in the presence of air [18]. The analogy of degradation processes caused by heat and ionizing radiation allows estimating the contribution of stabilizers to the prevention of oxidation reactions; while radical reactions depend on the polymer morphology itself, the oxidation reactions can be controlled by the incorporation of certain oxidation protectors. The light conditions gathered during storage do not rise many problems concerning the increase in the oxidation degree of the most polymers, but the radiation sterilization and hard weathering exposure promote fast damage of material. The radiation degradable polymers like polypropylene call for attentive accelerated studies on their potential to avoid modifications for periods as long as possible. The appropriate testing procedure can provide significant information on the long-term service following the standard requirements under real conditions [19].

The mechanism of polypropylene oxidative degradation is based on Bolland and Gee model [20]. The involvement of hydroperoxyl intermediates demands a stabilization solution, which anticipates an efficient reaction between these radicals and stabilizer molecules with satisfactory results on material integrity. A kinetic modeling approach on the thermal degradation of polypropylene [21] underlines that a heterogeneous distribution of oxidation products exists in polypropylene under stationary condition and the oxidation becomes diffusion-limited process after the consumption of initial amount of oxygen initially trapped in polymer.

This paper presents the behaviour of polypropylene subjected to γ-radiation as various formulation films. The effects of hindered amine stabilizer and the additional contribution of calcium carbonate to the hindering in thermal degradation of polypropylene are discussed.

Experimental

Materials and sampling

Polypropylene was manufactured by Exxon Mobil Chemical (Saudi Arabia) with trade mark BK-160-4102. The melt flow index of raw material was 3 g/10 min. The stabilizer, Sanduvor PR 31, an amine compound, was produced by Clariant Company

(Huningue, France). The molecular structure of this oxidation inhibitor is presented in figure 1.

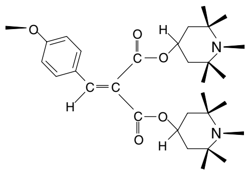

Figure 1. Structure of studied amine (Sanduvor PR 31).

The addition of oxidation preventing additive and/or calcium carbonate modified polypropylene. Thus, a series of three concentrations of stabilizer (0.1, 0.2 and 0.3 % w/w), $CaCO_3$ (0.6 % w/w) and a combination (0.3 % w/w Sanduvor PR 31 + 0.6 % w/w $CaCO_3$) were selected for improving the thermal stability of polypropylene support. Analytical grade calcium carbonate (finely ground material) was dried before mixing in polypropylene. The grafting of stabilizer on polypropylene macromolecules was previously performed by γ-radiation exposure [22]. Grafted Sanduvor PR 31 has shown stable structure for long time. After the reaction of hindered amine and PP a UV absorbing unit was detected at 308 nm in the UV spectrum whose absorbance increased as the concentration of stabiliser grew in the polymer matrix [23].

Films of 130 μm thickness were prepared by an extrusion process using a Bargmag Akteiengese US Charf D-42895 extruder with the length/diameter ratio of 24. The temperature barrel of the extruder, as well as the die, was maintained at 230°C. The screw speed was fixed at 35 rpm. The residence time was approximately 5 min. The films were stretched in air after leaving the die at a pulling speed of 5 $m.min^{-1}$. Specimens of 20mg polypropylene were prepared.

Irradiation

γ-Exposure ageing of modified and control PP specimens was done in air at room temperature in an irradiator GAMMATOR 220 provided with ^{137}Cs source. Dose rate was 0.4 kGy/h; the selected total doses were 10, 20, 30, 50 and 70 kGy.

Measurement

Oxygen uptake investigations on various sample formulations consisting of grafted PP and similar matrix modified with 0.3 % of calcium carbonate were carried out in a device designed in our laboratory [24]. Determinations were performed in air at 165°C and normal pressure and promptly accomplish after the end of irradiation. The efficiency of additives must be checked for various structures of stabilizers and for different application conditions.

Results and discussion

The functionality of polymers can be improved by correct addition of stabilizers that prevent oxidation, the unavoidable reason for the ageing of materials. The formulations would be correlated with the purpose of material. In the case of our study, polypropylene would be destined to the fabrication of foils for covering of greenhouses, and for manufacture of fibers. The choice of the additives: antioxidant, Sanduvor PR 31 and filler, calcium carbonate, are justified by their contribution to the minimization of photodegradation simultaneously with thermal stabilization, and the amelioration of processability by temperature reduction, respectively.

As it was reported earlier [11] Sanduvor PR31 presents a good stabilizing activity for polyethylene. The oxygen uptake investigation on its efficiency in the delay of thermal degradation of polypropylene confirms the availability of this compound for the retardation of oxidation. Figure 2 displays the oxygen uptake dependencies on irradiation time for polypropylene with 0.3 % Sanduvor PR31 at various doses. In comparison with free PP, which does not resist to the action of high energy radiation, this formulation is a good alternative for production of improved-resistance PP sheets. The oxidation induction time of raw polypropylene was only 18 min, similar with the PP samples containing $CaCO_3$, but too short in comparison with improved material. The long induction periods for thermal oxidation of polypropylene in the presence of antioxidant prove the light accessibility of the two-substituted amine position to the interaction with free radicals. Table 1 lists the oxidation induction periods for all irradiated PP samples. Irradiation caused a sharp decrease in the stability of polymer matrix. This behaviour may be related by the separation of grafted antioxidant from PP backbone. The joint of antioxidant on the PP macromolecules would be done by the substitution of methyl moiety from phenolic position. Irradiation would easy split the C-O bond than C=C double bond that is coupled with the π electrons belonging to benzene ring. The hard figures demonstrate the synergistic effect of Sanduvor PR 31 and calcium carbonate in the inhibition of oxidation.

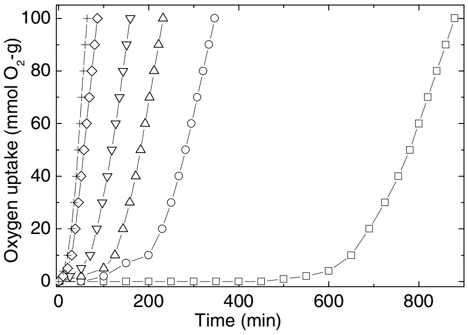

Figure 2. Oxidability curves for the irradiated polypropylene/0.3 % Sanduvor PR 31.

Table 1. Oxidation induction times for modified and irradiated polypropylene.

Dose (kGy)	Oxidation induction time (min)				
	PR 31 0.1 %	PR31 0.2 %	PR 31 0.3 %	$CaCO_3$ 0.6 %	PR 31 0.3 % + $CaCO_3$ 0.6 %
0	449	560	**660**	**63**	**820**
10	101	128	**145**	**54**	**227**
20	78	95	**118**	**50**	**185**
30	48	54	**70**	**42**	**140**
50	33	34	**36**	**28**	**122**
70	12	17	**21**	**8**	**53**

Under aerobic irradiation, polypropylene is quickly damaged, if the material is not previously stabilized. The methyl units are facilely removed from initial molecules and the oxidation of polymer occurs fast. The decay curves in antioxidant activity for different types of samples look similar for the specimens containing only Sanduvor PR 31 (figure 3a). The analogy of scavenging process occurred in irradiated polypropylene by the pair of additives (stabilizer and filler) confirms the favourable contribution of calcium carbonate (figure 3b).

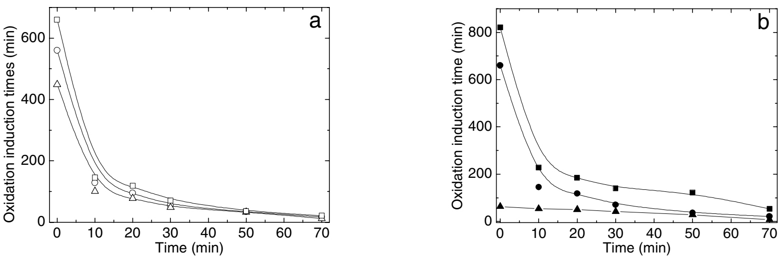

Figure 3. Decay curves for irradiated polypropylene stabilised with Sanduvor 31.
(a) (□) 0.3% PR 31, (○) 0.2 % PR 31, (Δ) 0.1 % PR 31;
(b) (●) 0.3 % PR 31 (▲) 0.3 % PR 31 + 0.6 % $CaCO_3$, (■) 0.6 % $CaCO_3$.

In addition, this compound offers a convenient condition to the protection of polypropylene (figure 4). Besides the lack of negative effect of this inorganic filler, calcium carbonate and Sanduvor PR 31 form a pair with synergistic activity (table 1). All irradiated PP samples containing this combination of compounds show co-operation factor exceeding unit. The cooperation between two compounds seems to be explainable by the assumption on surface activity of calcium carbonate grains, where oxygen may be retained.

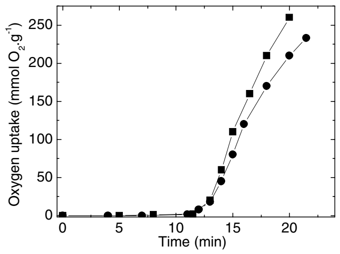

Figure 4. Oxygen uptake curves drown for initial polypropylene (■) and modified material with $CaCO_3$, 0.6 % (●).

The kinetic parameters regarding to the thermal oxidation of unirradiated PP (oxidation induction time and oxidation rate) would be expected to follow a first order dependency on the amount of additive. The deviation from linearity for oxidation rate (figure 5) suggests the possibility that grafted antioxidant to be detached from the connection place allowing to migrate more easily in the polymer bulk. The linear variation of oxidation time with additive concentration (figure 6) implies the lack of interaction between fixed stabilizer molecule and the polymer matrix. The sloping of these lines decreases with dose, because the generation of polar products during irradiation probably induces a peculiar dependence and a diminution of protector amount by radiolysis damage.

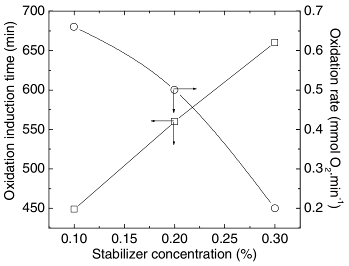

Figure 5. Changes in kinetic parameters of thermal oxidation of unirradiated PP with additive concentration.

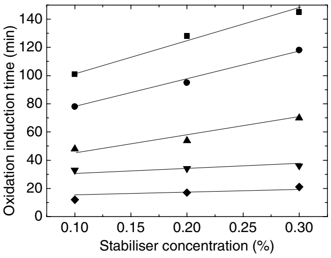

Figure 6. Dependency of oxidation induction times on antioxidant concentration for various doses. (■) 10 kGy, (●) 20 kGy, (▲) 30 kGy, (▼) 50 kGy (◆) 70 kGy.

The oxidation rates differ significantly to each other samples (figures 3, 4 and 7). This aspect indicates the fast consumption of antioxidant. However, the most important parameters that must be considered as milestones for stability of polymers are induction period and oxidation rate, when the initiators of oxidation, peroxyl radicals, start to appear. The propagation step of oxidation will determine the progress of material damage, which strongly influences the durability.

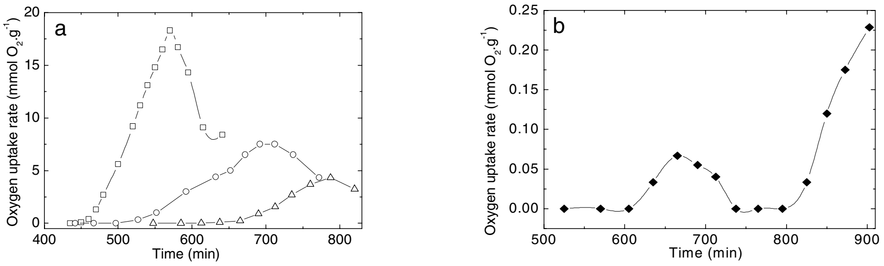

Figure 7. Change in the rate of oxidation for initial PP samples.
(a) HAS concentration: (□) 0.1 %, (○) 0.2 %, (Δ) 0.3 %. (b) HAS 0.3 % + $CaCO_3$ 0.6 %.

In spite of the sharp decrease of thermal stability of irradiated polypropylene, oxidation induction times reveal satisfactory values. This peculiarity assures that Sanduvor PR 31 may be successfully applied for manufacture of medical wear, because it confers good radiochemical stability for this kind of products subjected to radiation sterilization.

Conclusions

The stabilization of polypropylene with Sanduvor PR 31 represents a proper choice for various foreseen applications. Under the hard conditions of radiochemically accelerated degradation, polypropylene exhibits long oxidation induction times with beneficial consequence on product durability. The interpretation of the experimental results offers an advantageous combination between an amine oxidation protector, Sanduvor PR 31, and calcium carbonate. This pair exhibits a synergistic effect on the attack of oxygen on irradiated polypropylene. The improved polypropylene by the action of Sanduvor PR 31 show even at 50 kGy oxidation induction periods longer than unirradiated and unmodified PP. The addition of 0.3 % Sanduvor PR 31 together with 0.6 % $CaCO_3$ to polypropylene induces higher OIT 2.5 times in comparison with virgin material at 70 kGy. After irradiation at 10 kGy, this pair of additives delays oxidation with a period ten times longer than fresh polymer.

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