UV Irradiation and Weathering Effects on Amine-Stabilized Polypropylene

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An assay on the thermal stability of isotactic polypropylene stabilized with Sanduvor PR 31, a hindered amine (O1-(1,2,2,4,6,6-hexamethyl-4-piperidyl) O3 - (1,2,2,6,6-pentamethyl-4-piperidyl) (2Z) – 2 - [(4-methoxyphenyl) methylene] propanedioate, was performed. The oxidability of modified polymer previously subjected to weathering treatment or UV irradiation was investigated in air by isothermal (155⁰C) and isobaric (normal pressure) oxygen uptake. The exposure time was sufficient enough to attend a slow degradation rate (281 days for weathering test and 550 h for accelerated UV ageing). The main kinetic parameters, oxidation induction time and oxidation rate, were determined from the dependencies of chemically consumed oxygen on testing time. Comparative results on reference samples (control or stabilized polypropylene) and degraded materials are analyzed for depicting the influence of ageing factors on the polypropylene durability.

Keywords: polypropylene, UV degradation, weathering, oxygen uptake, Sanduvor PR 31

Numerous applications of polypropylene sheets, especially for the covering of greenhouses or for product package require detailed investigations on long-term stability. There were reported several papers that have been dedicated to the susceptibility of polypropylene to oxidation, most of them offer the peculiar features suggested by experimental conditions [for example, 1-5]. However, the durability of polymer materials must be investigated under certain conditions that simulate closely real circumstances [6]. The degradation factors, i. e. heat, radiation, mechanical stress, bring about structural modifications in material at different degradation rates. The synergistic action of these factors is depicted conclusively by weathering exposure. The understanding on the progress of degradation under simultaneous action of heat, UV radiation and humidity allows the manufacturers and customers to evaluate the quality of polymer materials.

For polypropylene claddings, the key of long life service is the efficiency offered by stabilization additives. It was demonstrated by various studies that hindered amines (HAS) are the most efficient inhibitors of oxidation that occurs by artificial UV radiation [8-10]. HASs form nitroxyl radicals, which may be coupled with free radicals in order to prevent degradation [10]. Their ability in the reducing of oxidation rate was confirmed with model compounds like decalin and squalen, which behave similarly with polypropylene [11, 12].

Polypropylene, whose degradation takes place by a radical mechanism, needs hindered amines for attending a long period of stabilization against the natural ageing. This kind of antioxidant reacts preferentially with the free radicals formed on the initiation and propagation stages of degradation, but they would also combine with aldehydes that represent one of the final products of oxidation [9]. The effectiveness of hindered amines on the delaying the material degradation depends on the system in which they are incorporated; the fast degradation of polypropylene can be diminished in a large extent by the addition of different HAS compounds [13]. The absence of any amount of protection compound will cause a premature ageing of polypropylene sheets due to the "competition" between different energetic suppliers.

In this paper an analysis on the oxidation resistance of isotactic polypropylene stabilized with an efficient antioxidant, Sanduvor PR31, is presented. The consequences of natural degradation are compared with the results obtained by accelerated process under artificial UV exposure.

Experimental part

Materials

The present investigations were carried out on isotactic polypropylene provided by Exxon Mobil Chemical (Saudi Arabia) as BK-160-4102 sort. The melt flow index (MFI) of the polymer was 3 g/10 min, according to ASTM D1238L. Sanduvor PR 31, a hindered amine (*O1-(1,2,2,4,6,6-hexamethyl-4-piperidyl) O3 - (1,2,2,6,6-pentamethyl-4-piperidyl) (2Z) – 2 - [(4-methoxyphenyl) methylene] propanedioate*, fig. 1) was produced by Clariant Company (Huningue, France). The concentration of stabilizer in polymer samples was 0.3 % (w/w).

Sample preparation

Films of 130 μm thickness were obtained by extrusion using Bargman Aktiengese US Chaft D-42895 device having L/D ratio of 24 and 3.2 mm diameter. The temperature inside the barrel of extruder, as well as in die, was maintained constantly at 230⁰C, while the screw speed was fixed at 35 rpm. The residence time was approximately 5 min. The film was stretched in air after leaving the die at a pulling speed of 5 m.min^{-1}.

Ageing conditions

The natural weathering of polypropylene specimens (free of antioxidant or modified with Sanduvor PR 31, fig. 1) was carried out according to ASTM D 1435. The sheets in the tape form were mounted on racks that are placed with the exposure side to South. The natural exposure was performed on the Eastern coast of Algeria starting over the period April - June 2003. The exposure times were: 15, 45, 63, 72, 100 days.

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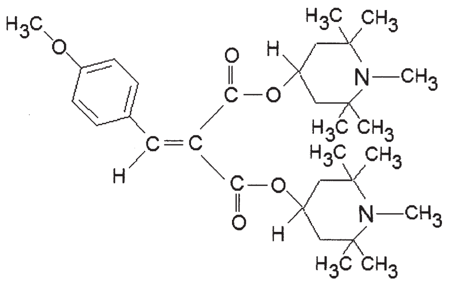


Fig. 1. Molecular structure of Sanduvor PR 31

Other polypropylene samples were subjected to an accelerated test using Suntest CPS (Atlas Model) at a constant temperature of about 30°C. This device is equipped with a 1500 W Xenon lamp provided with cooling loop. The energy distribution was maintained at 270 $W.m^{-2}$ in the interval 300-800 nm. The exposure times were: 40, 80, 100, 160, 250, 400, 500 and 550 h.

Oxygen uptake determination

The oxidability measurements were accomplished under isothermal (155^{0}C) and isobaric pressure (1 atm) in air environment. This low value of temperature was selected, because it allowed the fast reaction to be followed with high accuracy either for unstabilized, or aged specimens. Each polymer sample was cut in small pieces (surface of 1 cm^2), which had 2 mg in weight. Before starting each experiment, the samples were weighted to allow the evaluation of consumed-oxygen quantity relative to mass unity. The equipment used for oxidability investigation was built up in our laboratory. The flowsheet of equipment and the determination procedure were presented in an earlier paper [14].

Results and discussion

The antioxidant potential of Sanduvor PR 31, previously demonstrated for thermal oxidation of polyethylene [10], is revealed from the oxidability measurements performed on nondegraded polypropylene films (control and modified materials). Figure 2 presents the progress in thermal oxidation of these two samples. The large discrepancies between the oxidation induction periods (fig. 2a) and the rates of oxidation (fig. 2b) are the strong proof for the appropriate stabilizing activity of tested hindered amine. The oxidation induction time exhibited by the stabilized polypropylene is five times longer than the control one, while the oxidation rate ratio of stabilized to control samples is about 5.2.

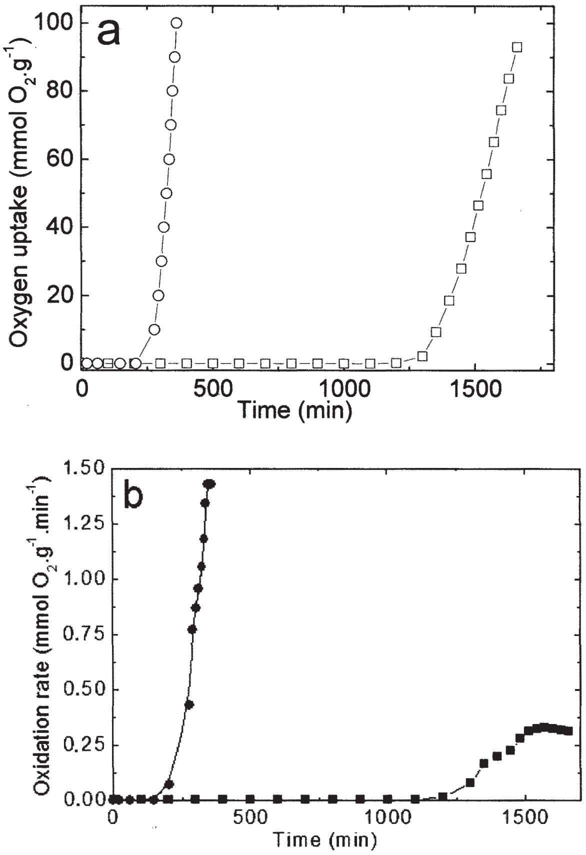


Fig. 2. Oxygen uptake (a) and oxidation rate (b) dependencies on time for initial i-PP samples (o,□) neat film; (•,■) stabilized i-PP

The exposure of neat isotactic polypropylene to artificial UV radiation reveals a sharp decrease in the oxidation induction period even from the start of process. The severe drop in oxidation resistance of polypropylene is the result of the higher concentration in free radicals. In unexposed polymer the start of oxidation occurs smoothly, because the distribution of oxidation initiators, the peroxyl radicals, is somewhat homogenous. The polypropylene films, which are crossed by radiation, contain peroxyl radicals gathered along the track before the thermal investigation. The

Table 1

THE KINETIC PARAMETERS OBTAINED FOR ARTIFICIAL UV-EXPOSURE DEGRADATION OF i-PP

Initial PP			Modified PP		
Exposure time (h)	Induction time (min)	Maximum oxidation rate (mmol O_2•g^{-1}.•min^{-1})	Exposure time (h)	Induction time (min)	Maximum oxidation rate (mmol O_2•g^{-1}.•min^{-1})
0	252	0.95	0	1348	0.28
10	36	0.93	40	465	
20	32	0.95	80	422	0.37
30	29	1.08	100	385	0.42
40	25	1.22	160	320	0.64
50	18	1.42	300	236	0.85
70	14	1.63	400	179	0.98
90	8	1.76	500	148	1.02
110	5	1.98	550	119	1.10

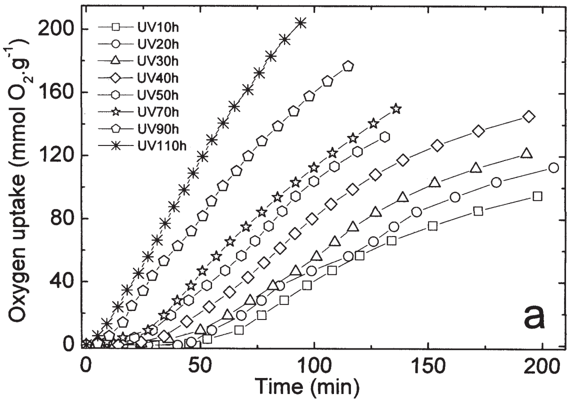
Table 2
FIRST ORDER DEPENDENCIES OF KINETIC PARAMETERS OBTAINED FOR ARTIFICIAL UV-EXPOSURE DEGRADATION OF CRUDE i-PP

Kinetic parameter	Relationship	Correlation factor
Crude polypropylene		
Induction period	$\tau_i = 37.74 - 0.32\ t$	0.986
Maximum oxidation rate	$v_{ox}^{max} = 0.78 + 0.011\ t$	0.991
Stabilized polypropylene		
Induction period	$\tau_i = 574.5 - 0.65\ t$	0.978
Maximum oxidation rate	$v_{ox}^{max} = 0.30 + 0.0015\ t$	0.985

clusters of intermediates placed around the track of radiation represent the regions with the highest concentrations of oxidation initiators. They cause a slower oxidation due to the diffusion in the bulk of samples. After the spreading of $RO_2^{\cdot}$ it may be considered that the progress in the thermal oxidation of i-PP takes place similarly in the whole volume. Table 1 lists the kinetic parameters that characterize the oxidative degradation of polypropylene. The decrease in the oxidation induction period seems to follow a linear relationship on exposure time. The same result was obtained for the increase of oxidation rate. From table 2 it can be remarked that the decrease in oxidation rate is smoother that the reduction of oxidation induction time. This behaviour can be explained by the movement of intermediates before the collision with the next radicals with which they react on the propagation step of oxidation. It is well known that the oxidation rate exceeds the crosslinking rate for polypropylene due to the existence of tertiary carbon atoms, which are the most reactive sites on the PP chains.

The comparison between the progress in oxidation of neat and stabilized polypropylene subjected to various periods of UV exposures (fig. 3) emphasizes the contribution of stabilizer to the increased stability of polymer. The significant longer induction period is demonstrated by the similar values of oxidation induction time for two sample that exhibit different degradation state: the initial PP and stabilized specimen previously exposed 300h to accelerated ageing. The analysis of equations that present the evolution of kinetic parameters as the time of accelerated treatment lengthens allow to underline two main aspects:

- the slope of function v_{ox}^{max} vs time for crude PP is greater than the similar parameter for stabilized polymer due to the contribution of additive on the exposing period;
- the decrease in oxidation induction time (τ_i) for more degraded PP is faster in the case of the presence of Sanduvor PR31 because of longer exposure times and the generation of a higher concentration of free radicals in the polymer matrix.



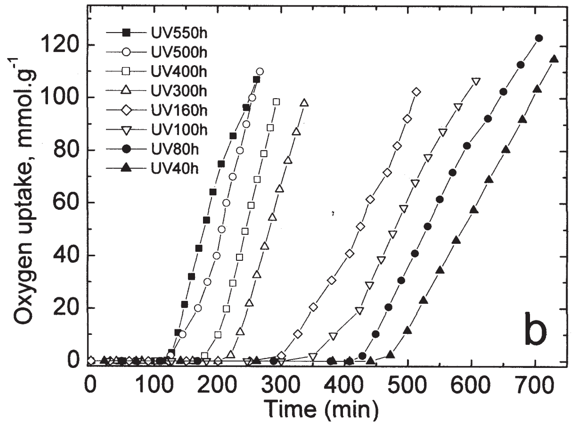


Fig. 3. Oxidation curves for i-PP subjected to artificial UV irradiation (a) unstabilised samples; (b) modified samples

The weathering treatment of polypropylene is a very hard appliance for the thermal strength determination and usage. The addition of antioxidant prolongs the lifetime of material and allows maintaining the material integrity for a long time. Figure 4 presents the oxidability curves drawn for the polypropylene samples subjected to climatologic stress. The shortest exposure, 15 days, causes the generation of low amount of oxidation initiators due to the presence of the stabilizer and the smallest received energy. This feature may also be noticed at the similar unprotected polypropylene. The very slow increase in the oxygen-consumed amount demonstrates that the added antioxidant is efficient for this kind of protection. At longer exposure times, this performance is diminished smoothly for the modified polypropylene samples, but disappears at crude material. The depletion of antioxidant is accentuated by the advanced reaction with free radicals and, partially, by the self-decomposition [15].

Table 3 lists the values of kinetic parameters for weathered polypropylene. The contribution of additive to the prolonged durability and the material integrity is demonstrated by the longer period of induction in comparison with the crude material. It may be noticed that smooth increase in oxygen-consumed amount is present for all stabilized samples (Figure 4b), while this feature is observed only for the shortest (15 days) outdoor exposure.

An overview on these results leads to general remarks concerning the similitude between the two procedures of degradation involving UV light. The artificial ageing, which

Table 3
THE KINETIC PARAMETERS OBTAINED FOR WEATHERING DEGRADATION OF **i-PP**

Initial PP			Modified PP		
Exposure time (d)	Induction time (min)	Maximum oxidation rate (mmol O_2•g^{-1}•min^{-1})	Exposure time (d)	Induction time (min)	Maximum oxidation rate (mmol O_2•g^{-1}•min^{-1})
15	191	0,63	15	671	0.54
45	88	0,83	45	556	0.59
63	64	0,96	71	424	0.66
72	62	1,18	100	381	0.72
100	55	1,27	160	289	0.79
			221	232	0.86
			281	188	0.93

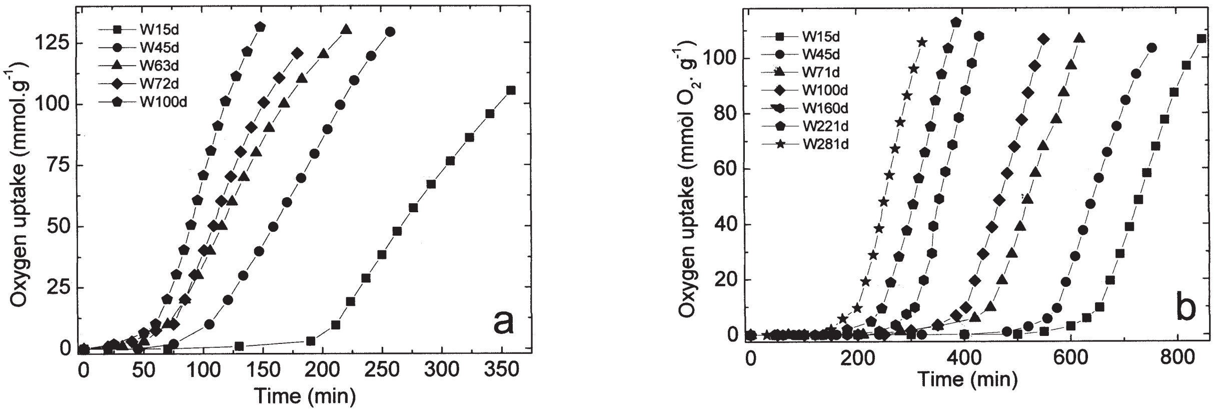


Fig. 4. Oxidation curves for i-PP subjected to outdoor degradation
(a) unstabilised samples; (b) modified samples

would simulate real conditions when UV lamp is used as light source, provides constant irradiance than it is happening during weathering testing. The energetic factor plays a decisive role in the material damaging, because it determines the rate of bond scission, namely the concentration of free radicals. A sustained exposure during artificial degradation transfers more energy on testing materials than natural weathering. The sunlight brings about significant modifications in polymer structure. The presence of antioxidant minimizes the irradiation consequences improving the material quality.

Conclusion

In this paper, a satisfactory stabilization efficiency of Sanduvor PR 31 antioxidant was obtained. The accelerated degradation promoted by artificial UV exposure and the weathering treatment of isotactic polypropylene were inhibited by this hindered amine. The oxygen uptake measurements applied to crude and stabilized polypropylene revealed the benefit of polymer modification with this compound. The long oxidation induction times and low oxidation rates obtained from oxidability investigations on i-PP modified with Sanduvor PR 31 emphasizes the beneficial contribution of additive to the improvement of material durability. The formulation that was tested in this study represents a good alternative for PP-cladding manufacturers. This material can be used successfully in the worm climate areas as greenhouse covers or other outdoor applications.

The follow up of these experiments will deal with the energetic conditions under which the antioxidative protection is accomplished in isotactic polypropylene by Sanduvor RP 31.

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Manuscript received: 19.03.2009