

Effect of Volatilization of Stabilizers and Oxidation Products on Polypropylene Lifetimes*

M. BLUMBERG, C. R. BOSS, and J. C. W. CHIEN, *Hercules Research Center, Wilmington, Delaware*

Synopsis

Three methods of measuring thermal oxidative stability of polypropylene have been compared. The oxygen absorption and the sealed tube tests give comparable results. The polymer lifetimes in circulating oven-aging tests differ significantly from those obtained by the first two methods. The oven-aging lifetime is apparently influenced to a large extent by the volatilization of the added stabilizer and of the oxidation products, the former decreases whereas the latter increases the polymer lifetime. The optimum composition of a synergistic stabilizer system was found to vary with the test method.

INTRODUCTION

The thermal oxidative stability of polyolefins is usually measured by either oven-aging and/or by oxygen absorptions. The results of these measurements cannot be readily correlated. Furthermore, the reproducibility of a given method is poor. For example, the round-robin studies of ASTM D-20 oven-aging of 125-mil polypropylene specimens gave results which vary by more than $\pm 20\%$. Also the oxygen absorption method does not always yield the same results for different workers.^{1,2}

Recently, Forsman³ determined some of the factors, such as sample thickness, temperature, and air-flow rate, which affect oven-aging lifetimes. In this paper, results are presented which show the importance of volatilization of oxidation products and of antioxidants upon the oxidation characteristics of polypropylene.

A recognized art in the stabilization of polyolefins is the use of a synergistic system consisting of a phenolic antioxidant and a sulfur-containing additive. This synergistic effect has been ascertained by some workers⁴⁻⁷ but was found to be absent by others.² Some of the experimental variables, which influence this synergistic phenomenon, were studied.

EXPERIMENTAL

Sealed-Tube Tests

Without Desiccant. A tube 20 mm. in outside diameter and 15 cm. long containing a 10-mil polypropylene film weighing 0.1 g. was attached to the

* Presented at the annual conference of the Plastics Institute of America, Hoboken, New Jersey, November 1965.

vacuum line. After 1 hr. of evacuation at a pressure of 1μ , oxygen was admitted at the desired pressure. The tube was then sealed off and placed in the oven. The onset of oxidation was signified by the appearance of droplets of condensate on the film surface; within a few hours the film broke into minute pieces when the tube was shaken vigorously. There was no visible discoloration of the sample. The degradation was followed by the decrease in η_{sp} measured at 135°C . in Decalin.

With Desiccant. In these experiments, 0.2 g. each of Linde 5A sieve, calcium oxide, Drierite, and Ascarite were first introduced into the tube. On top of the desiccants was placed a wad of glass wool which had been cleaned with boiling nitric acid, thoroughly washed and dried. The polypropylene sample was placed on top of the glass wool. The tube was filled with oxygen and sealed.

In contrast to the experiments without desiccant, the samples in experiments with desiccants developed spots of local crazing and/or discoloration. There was no indication that these spots were formed on parts of the film which were in contact with the glass wool. Within a period of several hours, the whole film was crazed and discolored.

Oven-Aging Test

Polypropylene films (10 mil) were suspended from glass hooks in a circulating-air oven. The samples were periodically examined for crazing and discoloration.

Oxygen Absorption

The apparatus and the procedure for oxygen absorption measurement has been described elsewhere.⁸ All results of this test and others of this section were averages of two to four experiments.

Materials

The phenolic antioxidants used in this work are commercial products which are probably not pure compounds. The detailed structures of these antioxidants are unknown to us. However, we will summarize below the information regarding these materials as given to us by the manufacturers.

A-2246, obtained from American Cyanamid Company, is a bisphenol condensate of 2-*tert*-butyl-4-methylphenol and formaldehyde. A-80 is a linear trisphenol analog of A-2246.

SPR, a product of Monsanto, is similar to A-2246, except that butyraldehyde is used instead of formaldehyde.

Ionox 330 is made by Shell Development Company by the condensation of formaldehyde with 2,6-di-*tert*-butylphenol and mesitylene. It is probably a very bulky molecule of trisphenol, in contrast to other linear condensation products.

ICI's Topanol is made from 3-methyl-6-*tert*-butylphenol and crotonaldehyde. It is believed to be a mixture of about 20% bisphenol and 83% trisphenol adducts.

Dilauryl thiodipropionate (DLTDP) was purchased from American Cyanamid Company.

From the information above, the antioxidants may be arranged in the following order according to their relative vapor pressures and diffusivities: DLTDP \approx A-2246 \approx SPR $>$ A-80 \approx Topanol $>$ Ionox 330.

RESULTS

Comparison of Aging Methods

The lifetimes of polypropylene as determined by oven-aging, sealed tube, and oxygen absorption are summarized in Table I. To compare these results, the differences in oxygen pressure and antioxidant concentration need to be corrected. In the previous paper,⁸ it was shown that t_{ind} varies inversely with the first power of oxygen pressure. Therefore, the lifetimes found in sealed tube and by oxygen absorption are multiplied by 8.3 and 5.0, respectively. Several workers^{5,9,10} have shown that the induction period of inhibited oxidation varies linearly with the concentration of antioxidant. A factor of five was used here to compensate the results of oxygen absorption measurements made on samples containing only 0.1% of antioxidant.

TABLE I
Comparison of Polypropylene Aging Tests^a

Type of Test	Oxygen Pressure cm.	[Anti-oxidant] Wt.-%	Time to failure at 140°C., days ^b				
			A-2246	SPR	A-80	Topanol	Ionox 330
Oven	15 (air)	0.5	2	2	16	31	111
Sealed tube ^c	125	0.5	5 (41) ^c	5 (41)	6 (49)	3 (25)	5 (41)
O ₂ Absorption	76	0.1	—	1.4 (35)	—	0.8 (20)	1.7 (42)

^a 10-mil polypropylene film.

^b Numbers in parenthesis are days to failure corrected to an oxygen pressure of 15 cm. and [antioxidant] = 0.5%. See text for these corrections.

^c Without desiccant.

Comparison of corrected lifetimes reveals that the results of oxygen absorption and of sealed-tube tests are comparable. Furthermore, different antioxidants appear to protect polypropylene to about the same extent. In contrast, the oven-aging lifetimes are shorter for A-2246, A-80, and SPR, and longer for A-80, Topanol, and Ionox 330 when compared with the results of the other aging tests.

Effect of Oxygen Pressure on Polypropylene Lifetime

The effect of oxygen pressure on the lifetime of polypropylene in the sealed tube was studied in two formulations: (A) with 0.5% of A-2246 and, (B) with 0.5% of A-2246 and 0.5% of DLTDP. In the previous paper,⁸

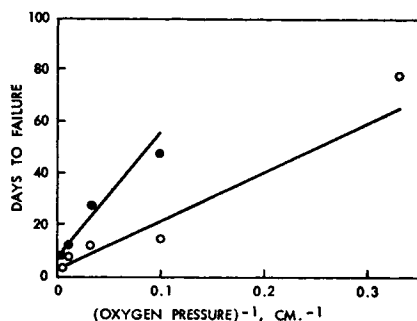


Fig. 1. Variation of polymer lifetime with oxygen pressure at 140°C. in the presence of desiccant: (O) 0.5% A-2246; (●) 0.5% A-2246 + 0.5% DLTDP.

the t_{ind} of unstabilized polypropylene was found to vary inversely with the first power of oxygen pressure. The same relationship appears to be valid here (Fig. 1).

Synergistic Effect

Samples containing synergistic stabilizer systems were compared in sealed-tube and in oven-aging tests. The compositions of the synergistic systems were varied systematically. The results are summarized in Tables II and III.

DISCUSSION

The intrinsic activity of a phenolic antioxidant depends upon several factors. It has been often stated¹⁰⁻¹² that each phenolic OH group can terminate two chain-carrying radicals. The phenolic antioxidants used in this work have nearly the same number of OH groups per unit weight of antioxidant. Studies of antioxidant efficiency versus structure by Baum and Perun¹³ and by Scott¹⁴ indicate that the antioxidants used here have

TABLE II
Sealed-Tube Lifetimes of Polypropylenes Stabilized by Synergistic Systems, in Days to Failure at 140°C.^a

Phenolic antioxidant	Time to Failure at various ratios of DLTDP to phenolic antioxidant, days ^b			
	0	1:1	3:1	10:1
None	1	1	1	1
A-2246	4	9	28	16
SPR	7	16	9	7
A-80	7	8	28	16
Topanol	4	10	18	14
Ionox 330	14	19	16	9

^a Aged in the presence of desiccants.

^b Total weight of phenolic antioxidant plus DLTDP was maintained at 1%.

TABLE III
Oven-Aging Lifetimes of Polypropylenes Stabilized
by Synergistic Systems, in Days to Failure at 140°C.

Phenolic antioxidant ^a	Time to failure at various Ratios of DLTDP to phenolic antioxidant, days			
	0	1:1	3:1	10:1
None	—	7	7	33
A-2246	7	16	40	40
SPR	6	31	40	41
A-80	19	22	37	43
Topanol	31	40	37	43
Ionox 330	>140	126	108	105

^a Total weight of phenolic antioxidant plus DLTDP was maintained at 1%.

similar reactivity. The efficiency of an antioxidant is thought to depend to some extent upon its ability to diffuse and to intercept radicals. This factor is unimportant for the antioxidants studied here because the observed induction periods are the same in polypropylene and in squalane. At 140°C., and 0.1% of SPR, Topanol, and Ionox 330, the induction periods for squalane oxidation are 1.4, 1.0, and 1.2 days, respectively. The corresponding induction periods for polypropylene oxidation are 1.4, 0.8, and 1.7 days (Table I).

The results of sealed-tube and oxygen absorption tests are in fair agreement with each other. These results indicate that A-2246, SPR, A-80, and Ionox 330 have equivalent reactivities in these tests. There is some inexplicable variation of the efficiency of Topanol; its efficiency is in general lower than that of the other additives.

In contrast, the oven-aging lifetimes are very different from those of the other tests. These differences may be attributed primarily to the volatilization of both antioxidants and of oxidation products in the circulating air oven. Appreciable losses of A-2246 and SPR, due to their relatively high vapor pressure, are assumed. Vapor pressures of several mono- and bisphenols have been reported.¹⁵ On the other hand, the losses of A-80 and Topanol were probably much less, whereas loss of Ionox 330 may be assumed to be negligible. These considerations could account for the short lifetimes of samples stabilized by A-2246 and SPR.

The long lifetimes of polypropylenes stabilized by Ionox 330 in oven-aging may be attributed to the volatilization of oxidation products. The oxidation of polypropylene is characterized by the formation of low molecular weight hydroperoxides and oxidation products.¹⁶ The latter enhance oxidation either by catalyzing the decomposition of hydroperoxides or by acting as reactive substrates. It is reasonable to postulate that in sealed-tube and in oxygen absorption tests, the desiccants, because of equilibration, are not completely effective in the removal of oxidation products, whereas elimination is more complete in the circulating-air oven.

The sulfur-containing compounds have been conclusively established^{5,7,8} as precursors to some active species which decompose hydroperoxides via a polar mechanism. There is a further indication⁴ that this decomposition can be effected catalytically by the active species. On the other hand, the results of Shlyapnikov et al.⁵ appear to indicate a 1:1 ratio as the optimum composition for the synergistic components.

Our results in Tables II and III suggest that the optimum ratio depends upon the relative volatility of the constituents and upon the test method. In the sealed-tube test, the optimum ratio appears to lie between 1:1 and 3:1 of DLTDTP to phenolic additives. On the other hand, in oven-aging tests, the optimum requirement for DLTDTP increases with increasing volatility of the phenolic components.

These results can be understood in a qualitative way. The long lifetimes of polypropylene stabilized by Ionox 330 are not enhanced by the presence of DLTDTP which is highly volatile at 140°C. Addition of DLTDTP with simultaneous reduction of Ionox 330 content causes a steady decrease in oven-aging lifetime. As the volatility of the phenolic component increases, the beneficial effect of DLTDTP becomes evident. For bisphenols, samples containing the most DLTDTP have the longest oven-aging lifetimes.

The above interpretation of data is probably oversimplified. For example, the oxygen diffusion limitation must differ in the circulating-air oven and in the sealed-tube tests. In the former, the turbulent flow of air, which decreases the thickness of the laminar layer where equilibrium conditions exist, causing increased volatilization, must also provide more ready access of oxygen to the sample; as contrast to the thicker stagnant layer, which probably exists in the sealed tube. More experiments designed specifically to bring out the effects of these variables are indicated.

References

1. Russell, C. A., and J. V. Pascale, *J. Appl. Polymer Sci.*, **7**, 959 (1963).
2. Bell, G. W., Jr., and C. E. Heyd, *SPE Trans.*, **4**, 39 (1964).
3. Forsman, J. P., *SPE Trans.*, in press.
4. Hawkins, W. L., and H. Sautter, *J. Polymer Sci.*, **A1**, 3499 (1963).
5. Shlyapnikov, Yu A., V. B. Miller, M. B. Neiman, and Ye. S. Torsuyeva, *Vysokomol. Soedin.*, **5**, 1507 (1963).
6. Cain, M. E., and J. I. Cunneen, *J. Chem. Soc.*, **1962**, 2959.
7. Bateman, L., M. E. Cain, T. Colclough, and J. I. Cunneen, *J. Chem. Soc.*, **1962**, 3570.
8. Boss, C. R., and J. C. W. Chien, *J. Polymer Sci.*, in press.
9. Ingold, K. U., *J. Inst. Petrol.*, **45**, 244 (1959).
10. Boozer, C. E., G. S. Hammond, C. E. Hamilton and C. Peterson, *J. Am. Chem. Soc.*, **77**, 3233, 3238 (1955).
11. Ingles, T. A., and H. W. Melville, *Proc. Roy. Soc. (London)*, **A218**, 163 (1953).
12. Bolland, J. L., and P. ten Have, *Trans. Faraday Soc.*, **43**, 201 (1947).
13. Baum, B., and A. L. Perun, *SPE Trans.*, **2**, 1 (1962).
14. Scott, G., *Chem. Ind. (London)*, **1963**, 271.
15. Spacht, R. B., W. S. Hollingshead, H. L. Ballard, and D. C. Wills, *Rubber Chem. Technol.*, **37**, 210 (1964).
16. Bevilacqua, E. M., *J. App. Polymer Sci.*, **8**, 1029, 1691 (1964).

Résumé

On a comparé trois méthodes de mesure de la stabilité thermique du polypropylène à l'égard de l'oxydation. La méthode par absorption d'oxygène et celle aux tubes à essais scellés fournissent des résultats comparables. Les durées de vie des polymères déterminés au cours d'essais de vieillissement diffèrent notablement de celles obtenues par les deux premières méthodes. La durée de vie déterminée par vieillissement est apparemment influencée en grande partie par la volatilisation du stabilisant ajouté et des produits d'oxydation; dans le premier cas la durée de vie diminue, dans le second cas elle augmente. La composition optimale d'un système stabilisant synergique varie suivant la méthode d'essais.

Zusammenfassung

Drei Methoden zur Messung der thermischen Oxydationsbeständigkeit von Polypropylen wurden verglichen. Sauerstoffabsorption und Tests im zugeschmolzenen Rohr liefern vergleichbare Ergebnisse. Die Lebensdauer des Polymeren bei Alterungstests im Zirkulationsofen unterscheidet sich wesentlich von den nach den ersten beiden Methoden erhaltenen. Die Lebensdauer bei der Ofenalterung wird offenbar in starkem Ausmass durch die Verflüchtigung des zugesetzten Stabilisators und der Oxydationsprodukte beeinflusst; ersteres setzt die Lebensdauer herab, während letzteres sie vergrössert. Die optimale Zusammensetzung eines synergistischen Stabilisatorsystems erwies sich als von der Testmethode abhängig.

Received June 7, 1965

Revised July 16, 1965

Prod. No. 1244