Measurement of Diffusion of Antioxidants in Isotactic Polypropylene by Isothermal Differential Thermal Analysis

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Synopsis

The diffusion of the phenolic antioxidant 1,3,5-tris(3,5-di *tert*-butyl-4-hydroxybenzyl)mesitylene (IRGANOX 1330) in extruded sheets of isotactic polypropylene (iPP) was investigated over the temperature range from 80 to 120°C by isothermal differential thermal analysis (DTA). The measurements showed a clear relation between oxidation induction time and oxidation maximum time (both determined by isothermal DTA) and the concentration of the stablizer. It was possible to calculate the diffusion coefficients and the activation energy of diffusion of IRGANOX 1330 in iPP by measuring the oxidation maximum times across stacks of isotactic polypropylene sheets.

INTRODUCTION

To protect polyolefins and other plastic materials against thermooxidative degradation, it is necessary to add small amounts of antioxidants to the polymers. The effectiveness of such an antioxidant depends not only on the chemical nature of this antioxidant, but also on its mobility in the polymers, generally known as diffusion. The diffusion of small molecules in polymers has been extensively studied in the past. Several well-established techniques for such studies exist and the most known one is the radio tracer technique, which was used by Gromov et al.,[1] Jackson et al.,[2] Westlake and Johnson,[3] Dubini et al.,[4,5] and others.

Klein and Briscoe[6-8] have plotted concentration profiles by moving the samples in the beam of an infrared spectrophotometer. The wavelength was selected at a specific absorption band of the diffusing molecules. In contrast, Andress and Rohl[9] obtained the concentration profile of phenolic antioxidants using ultraviolet spectrophotometry. Gas chromatography was used by Braun et al.[10]

The method of isothermal differential thermal analysis (DTA) is similar to the thermogravimetric technique of Roe et al.[11,12] and is based directly on the effect of the additives on the thermooxidative stability of the plastic materials.

EXPERIMENTAL

Materials

An unstabilized film grade of iPP powder produced by ICI (MFI/230/2.16–3 g/10 min) was used for making the films for this present investigation. The antioxidant 1,3,5, (3,5-di *tert*-butyl-4-hydroxybenzyl)mesitylene (IRGANOX 1330, Ciba-Geigy AG, molecular weight = 774 g/mol, melting point 245°C) was added to the iPP powder in different concentrations, viz., 0.00, 0.01, 0.03, 0.05, and 0.10% and was granulated at 230°C.

The film strips were made by extrusion of the granules at 260°C into a water bath (45°C) and was found to have a width of 50 mm and a thickness of 100 μm. The preparation of the iPP granules with different levels of antioxidant and the extrusion of the films were done by Ciba-Geigy AG.

Procedure

Isothermal DTA experiments were carried out in a Mettler measuring instrument, System TA 2000. The average weight of the specimens was 2 mg. The specimens were placed on conventional aluminum DTA cups in such a way that sufficient gas exchange was ensured. The samples were quickly inserted into the preheated cells and no purge gas was used.

Analysis of Antioxidant Concentration in Polypropylene by Isothermal DTA

For quantitative determination of the concentrations of antioxidants in polypropylene that are required for the analysis of diffusion data, an isothermal DTA technique was developed that directly uses the effect of antioxidants on the thermooxidative stability of the polymers. Especially at elevated temperatures and in the presence of oxygen, polyolefines undergo thermooxidative degradation which follows a radical mechanism.[13]

The time from the start of an isothermal DTA experiment to the beginning of exothermal decomposition is the so-called oxidation induction time (OIT). After this period, which depends on the antioxidant concentration, effectiveness, and temperature used, autocatalytic oxidation produces an exothermal peak.[14–19]

The time from the start of the test to the maximum of this peak is the so-called oxidation maximum time (OMT)[20] means the complete consumption of antioxidants and the loss of thermal stability of polymer. At elevated test temperatures, corresponding to short reaction times, it was difficult, or even impossible, to determine the OIT in the usual manner. For that reason OMT was chosen. The calibration curve, the OMT of iPP as a function of antioxidant concentration at 170°C DTA temperature, is shown in Figure 1. Each point in this figure is the average of ten measurements carried out on iPP films with the specific antioxidant concentration. From the calibration curve it is obvious that at low levels of antioxidant concentration in the iPP film, the standard deviation is minimum. But at higher levels of the antioxidant concentration, slight deviations are noted but they are within the acceptable
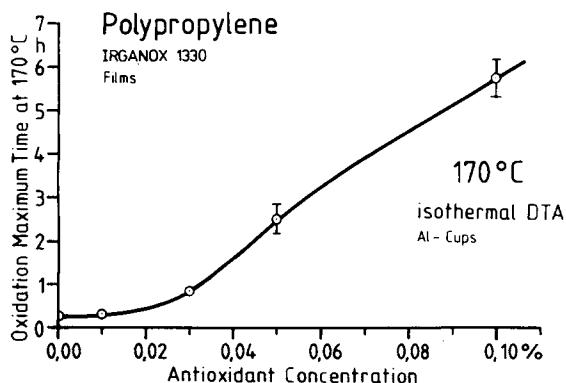
Fig. 1. Oxidation maximum times at 170°C of iPP sheets as a function of antioxidant concentration (isothermal DTA).

level (iPP film with 0.05% Irganox 1330: OMT = 2.50 ± 0.32 h; iPP film with 0.10% Irganox 1330: OMT = 5.77 ± 0.38 h).

Measurement of Diffusion

Sheets of iPP with 0.03 and 0.10% antioxidant levels were chosen to understand the influence of thermooxidative degradation during storage of the materials in the circulating-air oven. The plot of reciprocal temperature of the DTA oven vs. the OMT for the unstabilized and stabilized iPP sheets is shown in Figure 2. For an iPP sheet with 0.03% antioxidant concentration, the OMT is about 2000 h at 120°C. So the diffusion of the antioxidant in the iPP film can be measured at 120°C for a period of 48 h without the influence of the thermooxidative degradation and the loss of added antioxidant.

iPP films having the dimensions 15 mm × 15 mm × 100 μm with antioxidant levels of 0.03% and 0.10% were chosen for the diffusion measurements. Fifteen films having 0.03% antioxidant concentration were stacked together and placed over 15 films with 0.10% antioxidant concentration, and the whole
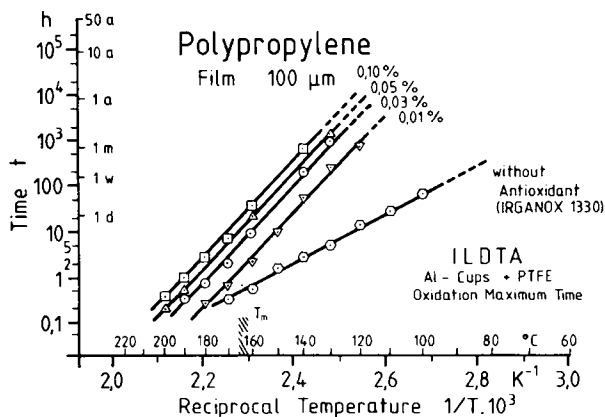

Fig. 2. Logarithms of oxidation maximum times of isotactic polypropylene with different antioxidant concentrations as a function of reciprocal temperature (isothermal DTA).
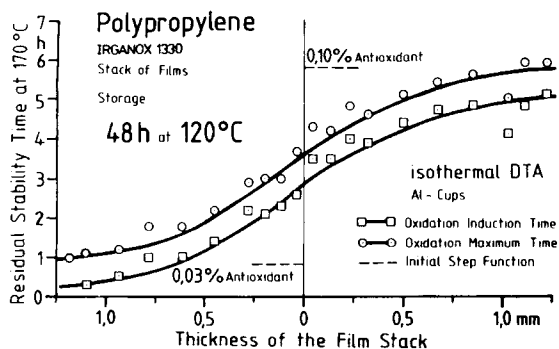
Fig. 3. Residual stability time [OMT (⊙) and OIT (□)] at 170°C of iPP sheets after storage of 48 h at 120°C as a function of the thickness of the film stack (isothermal DTA): (- - -) initial step function.

stack of 30 sheets was kept tightly in the center of a diffusion device (two blocks of aluminum with steel bolts).[21] This unit was placed in circulating-air oven for several predeterminated time intervals at a constant temperature. Some experiments were performed at different isothermal conditions, viz., 80, 100, 110, and 120°C.

At the end of the run, the iPP sheets were separated and samples out of the center of each sheet were analyzed at 170°C by isothermal DTA. This procedure is the measurement of residual stability time because the thermooxidative stability is determined after storage in the oven.

RESULTS AND DISCUSSION

After having stored a stack of iPP sheets for 48 h at 120°C in a circulating-air oven, the residual stability time of each sheet of this stack was determined. Figure 3 shows the residual stability time at 170°C (OIT and OMT) as a function of the thickness of the film stack. It is clear that both curves, OMT and OIT, are of the same shape.

Using the calibration curve shown in Figure 1, the concentration profile can be determined (Fig. 4). For the iPP sheets (48 h, 120°C), Figure 5 shows the
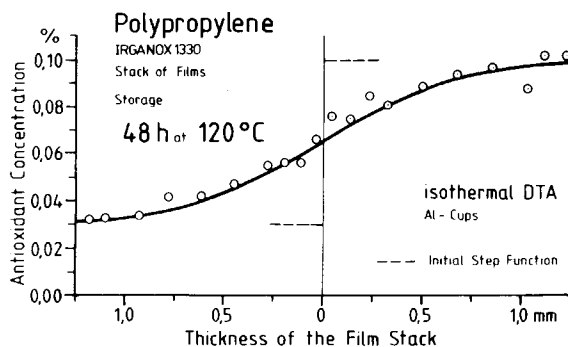

Fig. 4. Antioxidant concentration of iPP sheets after stroage of 48 h at 120°C as a function of the thickness of the film stack: (- - -) initial step function.
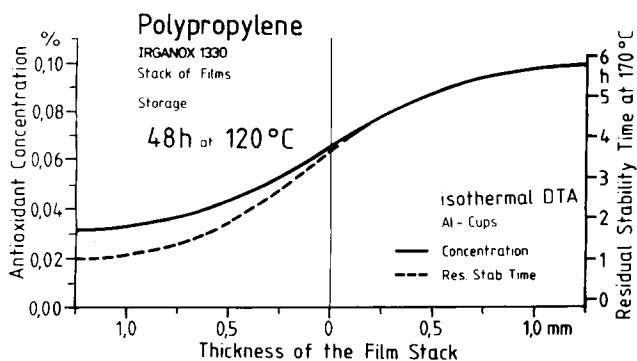
Fig. 5.   Antioxidant concentration (—) and residual stability time (- - -) after storage of 48 h at 120°C as a function of the thickness of the film stack.

different graphs of residual stability time and antioxidant concentration as a function of the thickness of the film stack.

Calculation of Diffusion Coefficient

Under the above-described conditions, the solution of Fick's diffusion equation[22] is

$$c(x, t) = \tfrac{1}{2} \cdot (c_1 - c_2)\mathrm{erfc}\left[x/2(Dt)^{1/2}\right] + c_2 \tag{1}$$

where erfc is referred to as the error-function complement, c_1 and c_2 are the concentrations of the initial step function at time $t = 0$ ($c_1 = 0.10\%$, $c_2 = 0.03\%$), and the diffusion coefficient D is independent of antioxidant concentration. This equation was solved numerically by a rational approximation based on Hastings.[23]

The diffusion coefficients of Irganox 1330 in stacks of iPP sheets at various temperatures are presented in Table I. In Figure 6 the logarithms of diffusions coefficients are plotted against reciprocal temperatures.

In general, stabilizer diffusion obeys the Arrhenius law

$$D = D_0 \exp(-E_d/RT), \tag{2}$$

where E_d is the activation energy of diffusion and D_0 is the preexponential factor. For the present investigations values of $E_d = 117$ kJ/mol and $D_0 = 2.5 \times 10^7$ cm^2/s can be calculated.

TABLE I
Diffusion Coefficients of Irganox 1330 in Isotactic Polypropylene

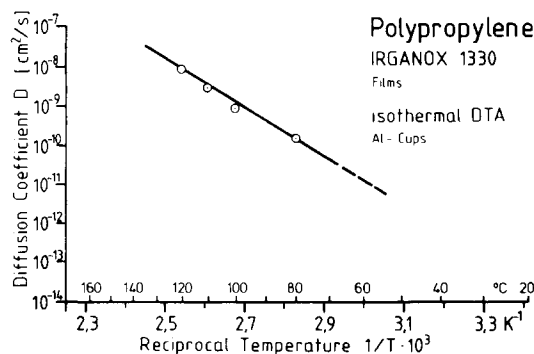| Temperature (°C)	Diffusion coefficient (cm^2/s)
80	$1,4 \times 10^{-10}$
100	$7,7 \times 10^{-10}$
110	$2,8 \times 10^{-9}$
120	$8,4 \times 10^{-9}$

Fig. 6. Temperature dependence of the diffusion coefficient for Irganox 1330 in isotactic polypropylene (Arrhenius plot).

TABLE II
Diffusion Parameters for Some Stabilizers[a]

Stabilizers	Polymer	log D_0	E_d (kJ/mol)	References
Irganox 1330	iPP	7.39	117	This work
Ionox 330	LDPE	6.43	93.6	24
Phenol A	iPP	4.2	93.3	1
Phenol A	LDPE	−0.30	51.0	1

[a] Ionox 330: 1,3,5,-tris(3,5-di tert-butyl-4-hydroxybenzyl)mesytilene. Phenol A: 1,1,3tri(2-methyl-4-hydroxy-5-(tert-butyl-phenyl **n**) butane.

Table II shows diffusion parameters of stabilizers which have a similar diffusivity to Irganox 1330.

CONCLUSIONS

Isothermal differential thermal analysis is an appropriate method for testing antioxidant diffusion in isotactic polypropylene. Only small amounts of sample materials are required to obtain the oxidation maximum time of the specimen, as an indicator for the antioxidant concentration.

A great advantage of isothermal DTA technique is that concentration profiles can be measured at very small amounts of stabilizer (0.03–0.10%). This is important because the investigated antioxidant Irganox 1330 is industrially used at these concentrations.

The measured concentration profiles show good agreement with the Fickian laws and the values of diffusion coefficient and activation energy are similar to that determined by other methods.

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