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DIFFUSION OF ANTIOXIDANTS IN SHEETS AND PLATES OF ISOTACTIC POLYPROPYLENE MEASURED BY ISOTHERMAL DIFFERENTIAL-THERMAL-ANALYSIS

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The diffusion of the phenolic antioxidant 1,3,5-tris(3,5-ditert. butyl-4-hydroxybenzyl)mesitylene (IRGANOX 1330) in compressed sheets of isotactic polypropylene (iPP) was investigated over the temperature range from 80 °C 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 stabilizer.

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.

The same method was employed to measure the diffusion coefficient of IRGANOX 1330 in compression-molded plates of iPP.

The influence of the morphological structure of iPP on the diffusion process was investigated by measuring the cristallinity degree of iPP-films and -plates and the determination of the dimensions of the spherulites.

Introduction

To protect polyolefins and other plastic materials against thermo-oxidative degradation it is necessary to add small amounts of antioxidants to the polymers.

The effecitiveness of such an antioxidant depends not only on the chemical nature of this antioxidant, but also on its mobility in the polymer, 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/Miller/

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/Neimann/Shlyapnikov [1], Jackson/Oldland/Pajaczkowski [2], Westlake/Johnson [3], Dubini/Cicchetti/Vicario/Bua [4,5] and others.

Klein and Briscoe [6,7,8] 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/Poos/Guillet [10].

The method of isothermal differential-thermal-analysis (DTA) is similar to the thermogravimetric technique of Roe/Bair/ /Gieniewski [11,12] and is based directly on the effect of the additives on the thermo-oxidative stability of the plastic materials.

Experimental

Materials

An unstabilized film grade of iPP powder produced by ICI (MFI/230/2,16-3g/10 min) was used for making the films for this present investigation.

The antioxidant (Fig. 1), 1,3,5 (3,5-ditert.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 %, 0,10 % and 0,20 % 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 plates were compression-molded at 240 °C for 5 minutes to a thickness of 2,7 mm.

The preparation of the iPP granules with different levels of antioxidant, the extrusion of the films and the compression-molding of the plates were done by CIBA-GEIGY AG.

IRGANOX 1330

Antioxidant by CIBA GEIGY AG

1,3,5,-Tris(3,5,-ditert.butyl-
-4-hydroxybenzyl)mesitylene

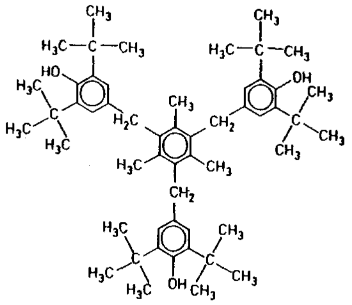

Fig. 1: Antioxidant used for measurements

Procedure

Isothermal DTA experiments werde 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 aluminium 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 thermo-oxidative 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 ist shown in Fig. 2. 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 level (Table 1).

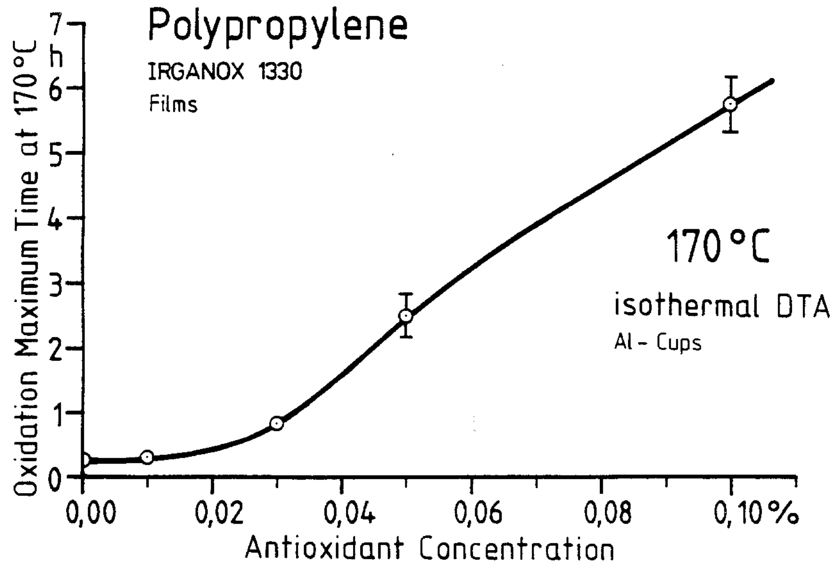

Fig. 2: Oxidation maximum times at 170 °C of iPP-sheets as a function of antioxidant concentration (isothermal DTA).

Table 1 Oxidation maximum times of iPP-sheets and -plates

OMT at 170 °C [h] iPP-sheets	Antioxidant concentration [%]	OMT at 170 °C [h] iPP-plates
0,27 ±0,05	0,00	0,37 ±0,11
0,31 ±0,03	0,01	0,27 ±0,06
0,83 ±0,12	0,03	0,59 ±0,14
2,50 ±0,32	0,05	2,85 ±0,73
5,77 ±0,38	0,10	5,61 ±0,72

Table 1 shows, that iPP-films have a higher thermal stability than microtomous slices of iPP-plates at low antioxidant concentrations, whereas the thermo-oxidative stability is nearly the same at higher concentrations (0,10 %).

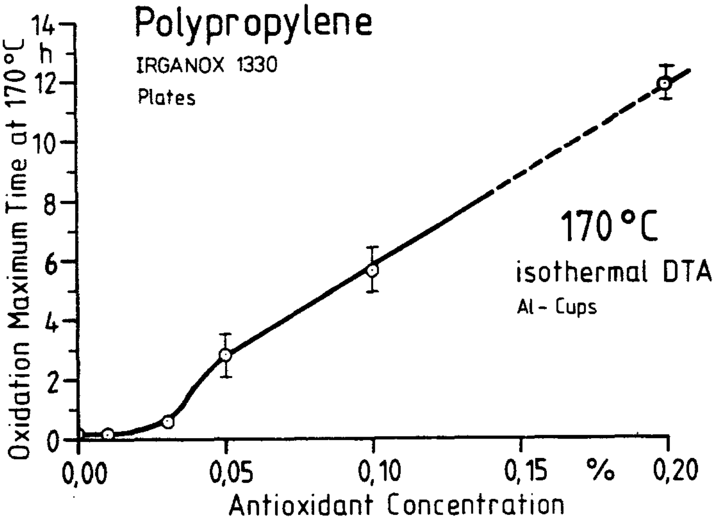

Fig. 3: Oxidation maximum times at 170 °C of iPP-plates as a function of antioxidant concentration (isothermal DTA).

Generally, the standard deviations of the oxidation maximum times of the plates are higher than that of the films, which is caused by the different processing operations.

The calibration curve of the plates is shown in Fig. 3. Each point in this figure is the average of ten measurements carried out on 40 µm thick microtomous slices of the plates with the specific antioxidant concentration.

Measurement of Diffusion

Films of iPP with 0,03 and 0,10 % antioxidant levels were chosen to understand the influence of thermo-oxidative degradation during storage of the materials in the circulating-air oven. The plot of reciprocal temperature of the DTA-oven versus the OMT for the unstabilized and stabilized iPP sheets is shown in Fig. 3. 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 thermo-oxidative degradation and the loss of added antioxidant.

IPP films having the dimension 15 mm² x 100 µm with an antioxidant level of 0,03 % and 0,10 % were chosen for the diffusion measurements. Fifteen films having 0,03 % antioxidant concentration were stacked togehter and placed over fifteen films with 0,10 % antioxidant concentration and the whole stack of 30 sheets was kept tightly in the center of a diffusion device (two blocks of aluminium with steel bolts) [21]. This unit was placed in a 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 thermo-oxidative stability is determined after storage in the oven.

Two iPP-plates of the dimensions 25 mm x 15 mm x 2,7 mm and an antioxidant level of 0,03 % and 0,10 % were stacked together and kept in the diffusion device. This unit was placed in a circulating-air oven for one week (168 h) at 120 °C.

At the end of the run, two blocks of the dimension of 15 mm x 3 mm x 2,7 mm were cut out of the plates. These blocks were separated in microtomous slices (15 mm x 3 mm x 40 µm), which were tested at 170 °C by isothermal DTA.

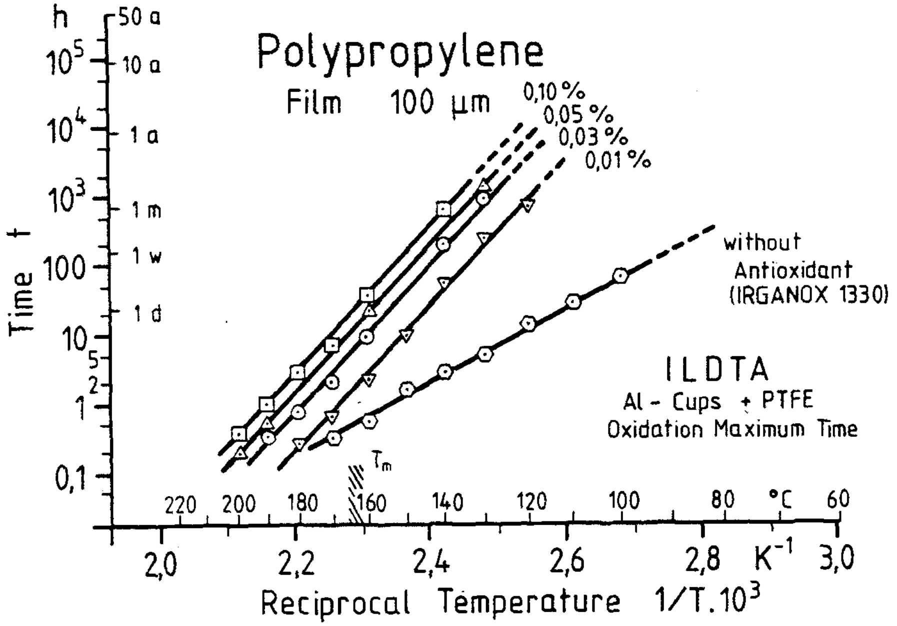

Fig. 4: Logarithms of oxidation maximum times of isotactic polypropylene with different antioxidant concentrations as a function of reciprocal temperature (isothermal DTA).

Results and Discussion

After having stored a stack of iPP-sheets for 48 hours at 120 °C in a circulating-air oven, the residual stability time of each sheet of this stack was determined.

Fig. 5 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 Fig. 2 the concentration profile can be determined (Fig. 6).

For the iPP sheets (48 h, 120 °C) Fig. 7 shows the different graphs of residual stability time and antioxidant concentration as a function of the thickness of the film stack.

Fig. 8 shows the residual stability time of the microtomous slices of the plates which were stored one week (168 h) at 120 °C in a circulating-air oven.

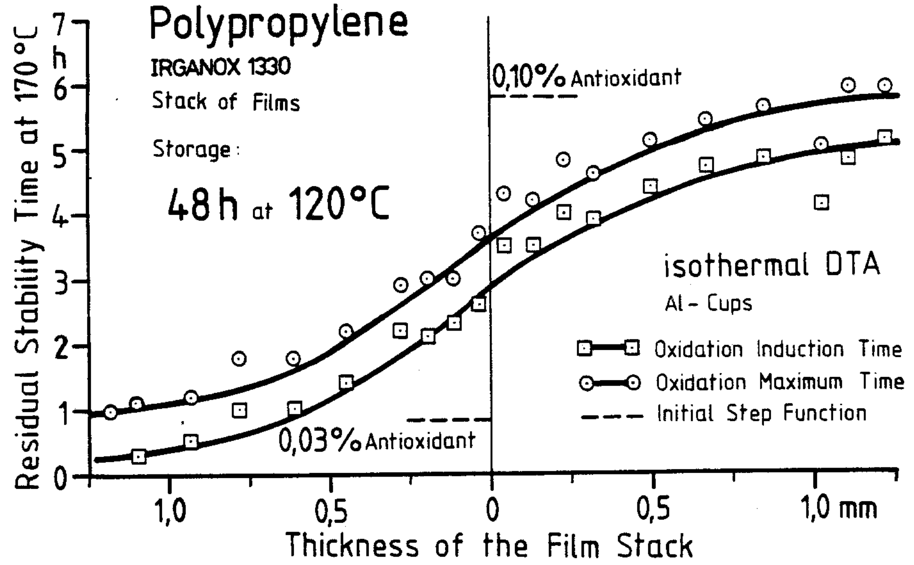

Fig. 5: Residual stability time (OMT and OIT) at 170 °C of iPP-sheets after storage of 48 h at 120 °C as a funktion of the thickness of the film stack (isothermal DTA)

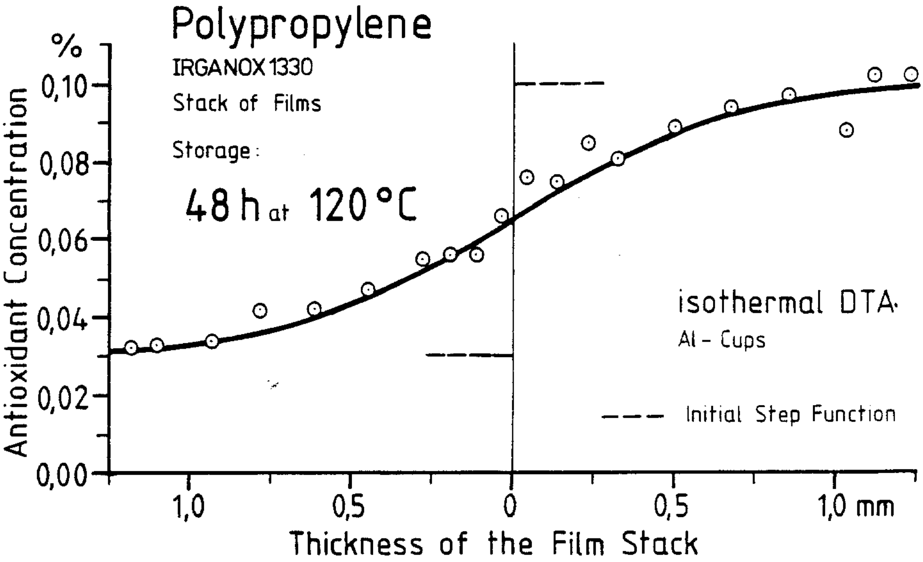

Fig. 6: Antioxidant concentration of iPP-sheets after storage of 48 h at 120 °C as a function of the thickness of the film stack

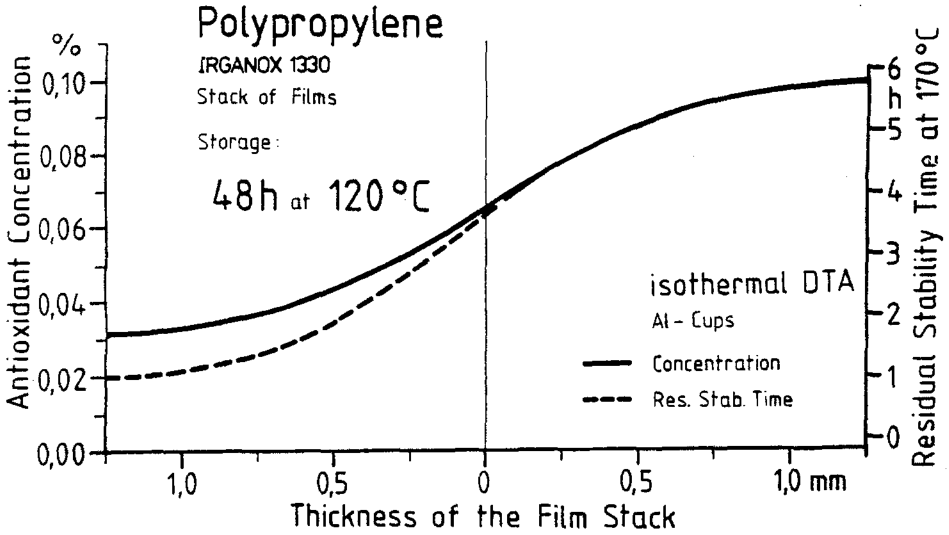

Fig. 7: Antioxidant concentration and residual stability time after storage of 48 h at 120 °C as a function of the thickness of the film stack

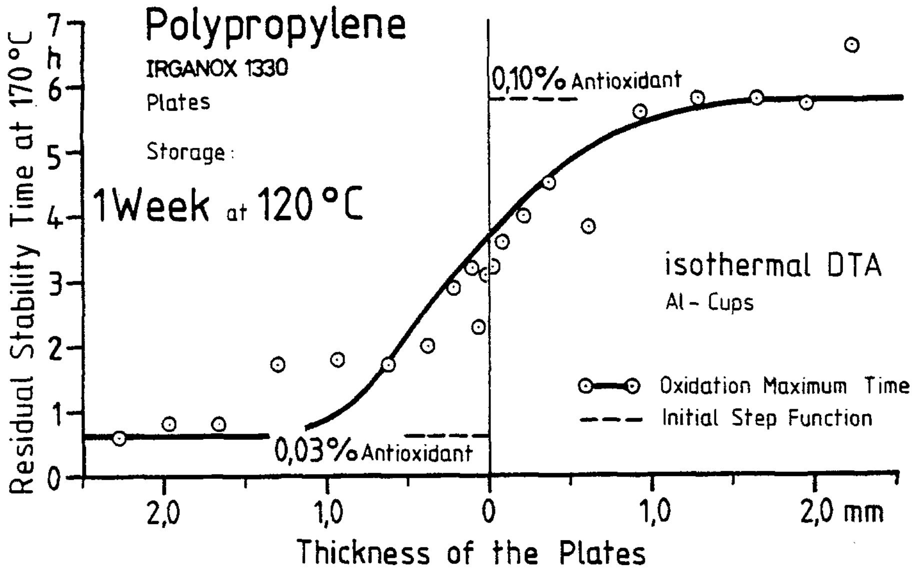

Fig. 8: Residual stability time (OMT) of Microtomous slices of iPP-plates after storage of 1 week (168 h) at 120°C as a function of the thickness of the plates (isothermal DTA)

The concentration profile belonging to this measurement is presented in Fig. 9.

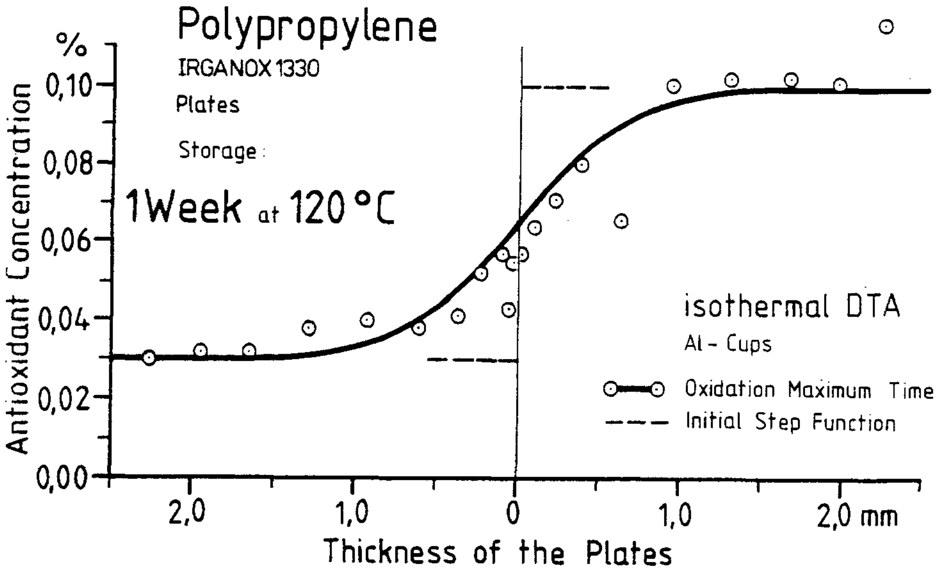

Fig. 9: Antioxidant concentration of microtomous-slices of iPP-plates after storage of 1 week (168 h) as a function of the thickness of the plates

The differences in the graphs of residual stability time of iPP-sheets and -plates (Fig. 5 and Fig. 8) are caused by the different calibration curves (Fig. 2 and Fig. 3).

Calculation of diffusion coefficient

Under the above described conditions the solution of Fick's diffusion equation (22) is

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

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 coefficent 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 and -plates at various temperatures are presented in Table 2.

Table 2 Diffusion coefficients of IRGANOX 1330 in isotactic Polypropylene

Temperature [°C]	Diffusion coefficient iPP-sheets [cm²/s]	Diffusion coefficient iPP-plates [cm²/s]
80	$1{,}4.10^{-10}$	-
100	$7{,}7.10^{-10}$	-
110	$2{,}8.10^{-9}$	-
120	$8{,}4.10^{-9}$	$2{,}2.10^{-9}$

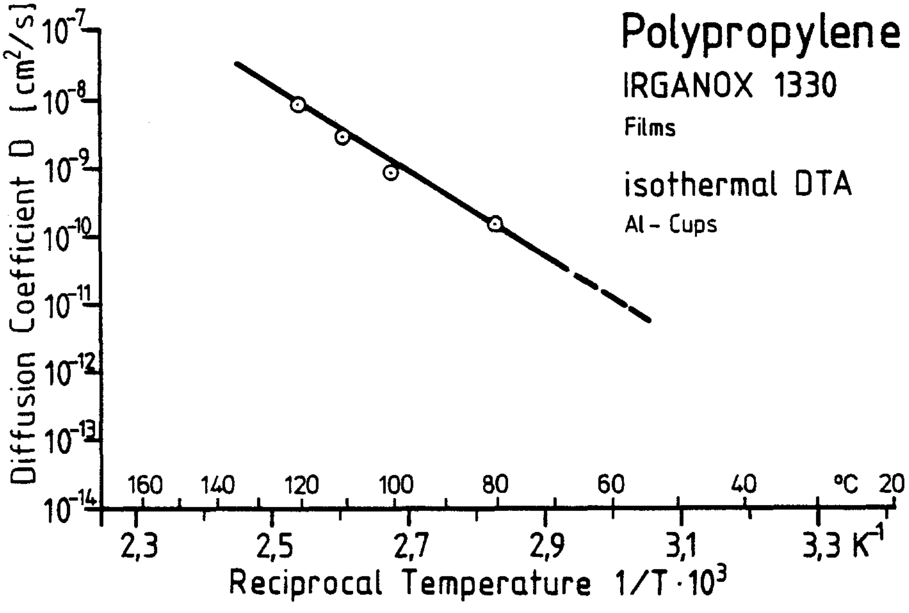

Fig. 10: Temperature dependence of the diffusion coefficient for IRGANOX 1330 in isotactic polypropylene (Arrheniusplot)

In Fig. 10 the logarithms of diffusion coefficients are plotted against reciprocal temperatures.

In general, stabilizer diffusion obeys the Arrhenius law

$$D = D_o \exp(-E_d/RT), \qquad (2)$$

where e_d is the activation energy of diffusion and D_o is the preexponential factor.

For the present investigations values of E_d = 117 kJ/mol and $D_o = 2{,}5.10^7$ cm²/s can be calculated.

Table 3 shows diffusion parameters of stabilizers which have a similar diffusivity to IRGANOX 1330.

Table 3 Diffusion Parameters for some stabilizers

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

IONOX 330: 1,3,5-tris(3,5-ditert. butyl-4-hydroxybenzyl)mesytilene

PHENOL A: 1,1,3 Tri(2-methyl-4-hydroxy-5-(tert-butyl-phenyl) butane

Influence of the morphological structure on diffusion.

Table 3 shows that the diffusion coefficient of iPP-sheets is 4 times higher than the diffusion coefficient of iPP-plates at 120 °C.

The differences are caused by processing - extrusion and compression-molding - because both materials, the film strips and the plates, are of the same grade of iPP-powder.

Moisan [24] and Mucha [25] have studied the influence of the morphological structure to diffusion processes. Both have measured that diffusion coefficients decrease with the degree of cristallinity.

The degrees of cristallinity of the iPP-sheets and iPP-plates are 41 % respectively 42 % - both determined by dynamic DTA. This minimal difference of 1 % cristallinity cannot be the reason for such a great difference of diffusion coefficients.

But the morphological structure of semicristalline thermoplastic materials - such as isotactic polypropylene is - depends not only on the degree of cristallinity but also on the size of the sperulites.

The sizes of the sperulites were determined on 20 µm thick microtomed slices over the thickness of the sheets and plates by a polarization microscope. At an amplification factor of 62 the microtomous slice of the sheets has no visible spherulites, whereas the plates have an average spherulitic size of 40 µm at the same amplification. This might be a possible explanation of the different diffusion coefficients of sheets and plates:

Semicristalline polymers have two amorphous phases, which are located both between spherulites and inside spherulites - the interspherulitic and intraspherulitic phase.

The antioxidant cannot diffuse through the cristalline parts of the polymer, also the antioxidant cannot diffuse through the intraspherulitic amorphous phases of the polymer. So the antioxidant molecules which are solved in the intraspherulitic amorphous phases cannot diffuse out of the sperulites, and so the diffusion coefficient must decrease with increasing spherulite size.

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 % to 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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References

1 B.A. Gromov, V.B. Miller, M.B. Neumann and Yu.A. Shlayapnikov, Intern. J. Appl. Radiation Isotopes, 13 (1962) 281.

2 R.A. Jackson, S.R.D. Oldland and A. Pajaczkowski, J. Appl. Polym. Sci., 12 (1968) 1297.

3 J.F. Westlake and M. Johnson, J. Appl. Polym. Sci., 19 (1975) 319.

4 M. Dubini, O. Cicchetti, G.P. Vicario and E. Bua, Europ. Polym. J., 3 (1967) 473.

5 O. Cicchetti, M. Dubini, P. Parrini, G.P. Vicario and E. Bua, Europ. Polym. J., 4 (1968) 419.

6 J. Klein and B.J. Briscoe, Polymer, 17 (1976) 481.

7 J. Klein and B.J. Briscoe, J. Polym. Sci. Phys. Ed., 15 (1977) 2065.

8 J. Klein and B.J. Briscoe, Proc. Roy. Soc., Lond. A, 365, (1979) 53.

9 B. Andress and P. Rohl, Amn. Rep. Conf. Electr. Insul. Dielectr. Phenomena, Whitehaven, Pennsylvania, 26-28, 10, (1981) 333.

10 J.M. Braun, S. Poos and J.E. Guillet, J. Polym. Sci. Letters, 14 (1976) 257.

11 R.J. Roe, H.E. Bair and C. Gieniewski, Polym. Reprints, Amer. Chem. Soc., Div., Dpolym. Chem., 4 (1973) 530.

12 R.J. Roe, H.E. Bair and C. Gieniewsky, J. Apl. Polym. Sci., 18 (1974) 843.

13 R. Gächter and H. Müller, "Kunststoffadditive" 2. Auflage, Carl Hanser Verlag München, Wien (1983).

14 E. Kramer and J. Koppelmann, Kunststoffe 73, 11 (1983) 714.

15 E. Kramer, Österr. Kunststoff.-Z. 15, 3/4 (1984) 32.

16 E. Kramer and J. Koppelmann, Polym. Degrad. and Stab., 14 (1986) 333.

17 E. Kramer and J. Koppelmann, Polym. Degrad. and Stab., 16 (1986) 261.

18 E. Kramer and J. Koppelmann, Polym. Eng. Sci., 27 (1987) 945.

19 G. Steiner and J. Koppelmann, Kunststoffe, 77 (1987) 286.

20 G. Steiner and J. Koppelmann, Polym. Degrad. and Stab., 19 (1987) 307.

21 T. Schwarz, "Diffusionsmessungen von Antioxidantien in isotaktischem Polypropylen mittels isothermer DTA". Diplomarbeit am Institut für Chemische und Physikalische Technologie der Kunststoffe, Montanuniversität Leoben (1986).

22 J. Crank, "The Mathematics of Diffusion", Second Edition, Oxford University Press (1975).

23 C. Jastings, Jr., "Approximations for digital computers", Princeton University Press (1955).

24 J.Y Moisan, Effects of Oxigen Permeation and Stabiliser Migration on Polymer Degradation, in "Polymer Permeability", Edited by J. Comyn, Elsevier Applied Science Publischers Ltd. (1985).

25 M. Mucha, J. Coll. and Polym. Sci., 264 (1986) 113.

Zusammenfassung

Die Diffusion des phenolischen Antioxidanten 1,3,5-Tris (3,5-ditert.butyl-4-hydroxybenzyl)mesitylen (IRGANOX 1330) in zusammengepreßten, isotaktischen Polypropylenfolien wurde mittels isothermer Differentialthermoanalyse (DTA) über einen Temperaturbereich von 80 °C bis 120 °C untersucht.

Die isothermen DTA-Messungen zeigten einen klaren Zusammenhang zwischen Oxidationsinduktionszeit und Oxidationsmaximumszeit und der Konzentration des Antioxidanten.

Über die Bestimmung der Oxidationsmaximumszeiten von Folienstapeln aus isotaktischem Polypropylen war es möglich, die Diffusionskonstanten und Aktivierungsenergie der Diffusion von IRGANOX 1330 in iPP zu bestimmen.

Um den Einfluß der Kristallstruktur auf die Diffusion von Stabilisatoren zu ermitteln, wurdedie gleiche Methode bei gepreßten Platten angewendet. Die Gefügestruktur (Kristallinitätsgrad und Sphärolithgröße) der Platten und Folien wurde mittels dynamischer DTA und Polarisationsmikroskop untersucht.

Резюме – Методом изотермического ДТА в интервале температур 80-120° изучена диффузия фенольного антиокислителя 1,3,5-трис-/3,5-ди-трет.бутил-4-оксибензил/мезитилена /Игранокс 1330/ в пресованных листах изотактического полипропилена / и-ПП/. Измерения показали ясную зависимость между индукционным временем окисления и максимальным временем окисления / оба определяются изотермическим ДТА / и концентрацией стабилизатора. Путем измерения максимального времени окисления через стопку пластин изотактического полипропилена, представилось возможным вычислить коэффициенты диффузии и энергию активации процесса диффузии антиокислителя в и-ПП. Этот же самый метод был использован для измерения коэффициентов диффузии антиокислителя Игранокс 1330 в прессовано-отлитых пластинах изотактического полипропилена. Влияние морфологической структуры и-ПП на процесс диффузии был изучен путем измерения степени кристалличности пленок и пластин изотактического полипропилена и определения размера сферулитов.