Journal of Thermal Analysis, Vol. 46 (1996) 465-470

LIFETIME PREDICTION OF ABS POLYMERS BASED ON THERMOANALYTICAL DATA

L. Rosík[1]*, Jana Kovářová*[2] *and J. Pospíšil*[2]

[1]Kaučuk a.s., Synthetic Rubber Research Institute, 27852 Kralupy
[2]Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, 162 06 Praha 6, Czech Republic

Abstract

The service life of ABS polymer, stabilized by 2-(3,5-di-tert-butyl-4-hydroxyanilino)-4,6-bis(octylthio)-1,3,5-triazine and containing 50% of a modifying rubber component, was estimated from oxidative induction times measured by DSC in isothermal mode in the temperature interval 140–170°C. The lifetime of ABS powder at the actual temperature of drying was predicted by linear extrapolation according to Arrhenius. However, the extrapolated value was much longer than the real lifetime determined from the long-term oven aging tests at 70 and 90°C, simulating the industrial drying process. The effect of changes in the apparent activation energy of oxidation due to antioxidant consumption during polymer aging is discussed.

Keywords: ABS polymer, DSC, lifetime estimation, thermooxidation

Introduction

Diene polymers and copolymers are highly sensitive towards oxygen, even at ambient temperatures [1]. This feature is present also in rubber-modified styrenics containing the unsaturated rubber component dispersed in the form of small discrete particles within the polystyrene or SAN copolymer matrix (in high-impact polystyrene or ABS polymer, respectively). As for ABS polymer, containing as a rule 10–25% and in special cases up to around 50% of the rubber component (while part of SAN is grafted on the rubber particles), the reaction of polybutadiene with air oxygen is clearly seen in thermoanalytical evaluation as a pronounced exotherm on the DTA or DSC curves [2, 3]. Thermoanalytical measurement of ABS polymers can be used for thermo-oxidation studies and antioxidant efficiency evaluation, as well as for the prediction of service life [2–5].

Emulsion technology [6] in ABS usually produces the polymer in the form of a fine powder, the sensitivity of which towards oxygen is even more pronounced. In this respect, reliable lifetime predictions become essential e.g. for the determination of safe residence times of polymer powder in the drying

0368–4466/96/ $ 5.00

John Wiley & Sons, Limited
Chichester

equipment at various temperatures, for the estimation of the risk inherent in longer remaining deposits in dead spaces of the equipment, and for proper specification of shelf-life conditions.

Some types of ABS, manufactured specifically as intermediates for the production technology of blending either with SAN copolymer [6] or with PVC, may have an exceptionally high content of the polybutadiene component (up to 50%). For these types of ABS, there is obviously a much higher risk of spontaneous exothermal reaction of the powder polymer with air oxygen [7], representing in extreme cases a real danger for the production process.

Experimental

Long-term oven aging experiments at temperatures of 100, 90 and 70°C were performed with ABS in powder form containing 50% of the polybutadiene component and stabilized by 0.81% of 2-(3,5-ditert-butyl-4-hydroxyanilino)-4,6-bis(octylthio)-1,3,5-triazine (Irganox 565, Ciba Geigy). The test layer of ABS powder was about 1 cm thick, and was regularly homogenized during long-term experiments (1300 days). The extent of polymer degradation in relation to exposure time was evaluated using changes in the DSC curves (in both the isothermal and dynamic modes) supplemented by other types of analysis (evaluation of hydroperoxide and carbonyl group content and antioxidant consumption). The methods applied have been described in detail elsewhere [4, 5].

Results and discussion

Exploitation of thermoanalytical methods for aging studies of ABS powders is very straightforward applicable due to obvious heat evolution accompanying the thermo-oxidation of the polybutadiene component of ABS. Samples oven-aged at isothermal conditions and analysed after regular exposure time intervals typically show a gradual increase in the area and height of the exotherm (Fig. 1). It is essentially a manifestation of the observed consumption of the antioxidant as well as to the accumulation of polymer hydroperoxides [8, 9] (Fig. 2).

The exothermal effect reaches a maximum, in terms of time, when the antioxidant content in the polymer approaches zero, and the inhibited oxidation gives way to the autocatalytic process. This time is to be considered, from the practical point of view, as the end of polymer lifetime (approx. 500 days at 90°C, and approx. 1000 days at 70°C). Further continuation of isothermal aging leads to vigorous oxidation accompanied by accumulation of carbonyl groups in the polymer [8, 9] (Fig. 2). The thermoanalytical evaluation of these samples is characterized by a shift in the onset (T_i) of the residual exotherm to lower temperatures. At the same time, the magnitude of the exotherm (Δn) gradually

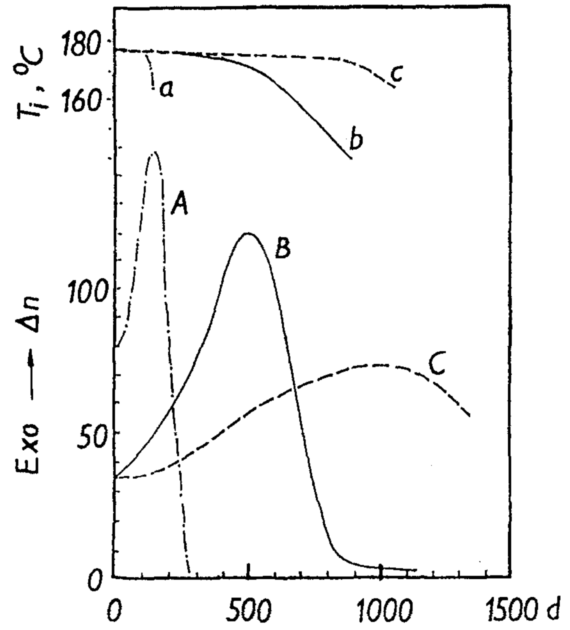

Fig. 1 Changes in thermoanalytical characteristics of ABS polymer in the course of oven aging. Thermooxidation (aging) at isothermal conditions of 100°C (curves a,A), 90°C (b,B) and 70°C (c,C) respectively. DSC measurements of oven aged samples performed on DuPont 900TA, sample weight 3 mg, heating rate 5°C min^{-1} in a static air atmosphere. T_i (°C) represents the onset temperature of exotherm peak (curves a, b, c). Δn characterises the amount of heat evolved in the exothermal process via the maximum height of the peak (the sensitivity of the recording: 1 unit of scale =0.002 mV)

becomes smaller because a substantial part of exothermal oxidation reaction has already taken place during the isothermal oven-aging. Eventually, the oxidation exotherm completely disappears and the polymer is totally destroyed. This state was reached after 300 days at 100°C, after 900 to 1300 days at 90°C, respectively. At 70°C, however, the time needed for complete destruction of the sample was much longer than the duration of the aging experiment, and thus only the extrapolated estimate of about 1800 days is given here.

We attempted to estimate lifetime of the ABS powder under the conditions simulating industrial drying (temp. interval 70–90°C). Linear extrapolation according to Arrhenius (using the OIT data from isothermal high-temperature DSC experiments, line A, Fig. 3) gave unrealistically optimistic data, substantially exceeding the real lifetime as ascertained in long-term drying test (line B, Fig. 3).

Generally, the reliability of lifetime prediction is the more limited the more distant is the temperature range of the actual measurement from the temperature

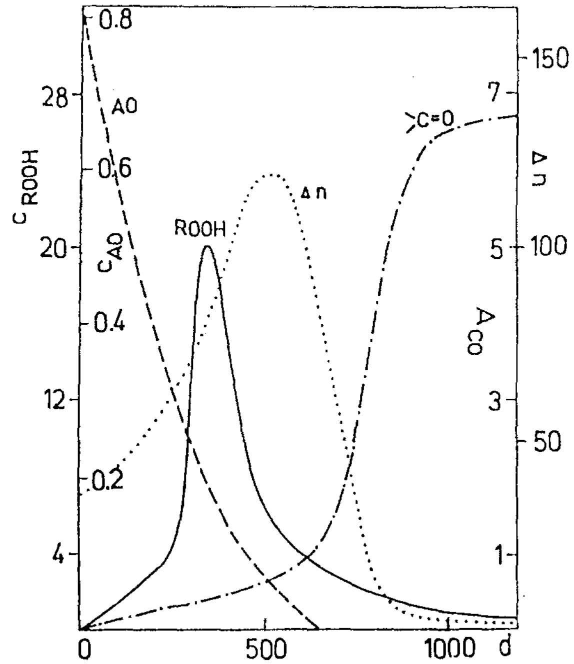

Fig. 2 Oxidation characteristics of ABS polymer in the course of oven aging at 90°C. Δ*n* is the same as in Fig. 1., C_{AO} (%) represents the residual content of applied antioxidant Irganox 565, $C_{ROOH}\cdot 10^3$ (mol kg^{-1}) =concentration of hydroperoxides and $A_{C=O} = A_{1733}/A_{2238}$ (carbonyl groups by IR spectroscopy)

of extrapolation. It has been stated [10, 11] that extrapolation should not exceed an interval of 20 to 25°C beyond the most extreme experimental point. For a variety of reasons it is not always possible to meet this demand [3, 4].

The linearity of the Arrhenius plot may not be fulfilled in cases when the extrapolation is made through the glass transition or polymer melting region [12], or when a change occurs in the mechanism of the oxidation or inhibition reaction. Previous model tests have revealed [5, 9] that a change in oxidation mechanism may be caused even by a low the antioxidant content in the polymer.

Table 1 E_A changes in the thermo-oxidative aging of ABS polymer at 90°C

Sample	Exposure time at 90°C $days^{-1}$	Residual content of Irganox 565/%	Residual τ_i at 140°C min^{-1}	E_A/kJ mol^{-1}
1	0	0 (unstab.)	1	$(110)^a$
2	0	0.81	1280	193
3	300	0.22	330	197
4	670	0	65	123

[a] ... Fig. 3, line D

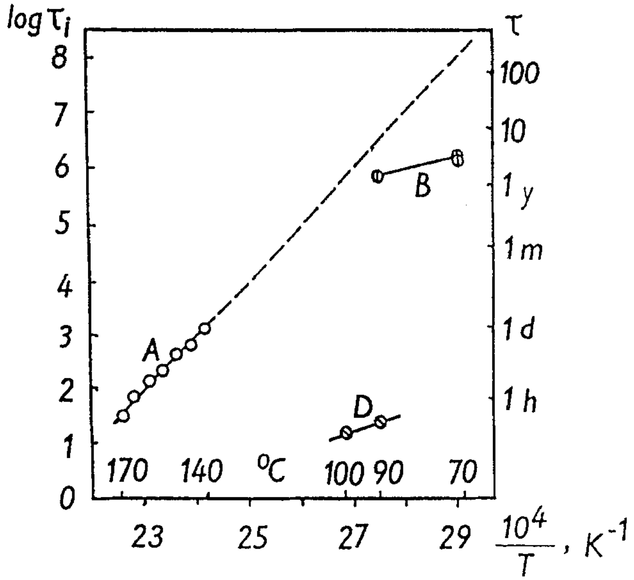

Fig. 3 Lifetime estimate of ABS polymer; A – extrapolation according to Arrhenius from inhibition periods of oxidation (OIT) measured by isothermal DSC in the temperature interval 140–170°C; B – real lifetime from long-term drying experiments (oven aging) at 90 or 70°C, respectively; D – lifetime of unstabilized ABS polymer from drying at 90 or 100°C, respectively

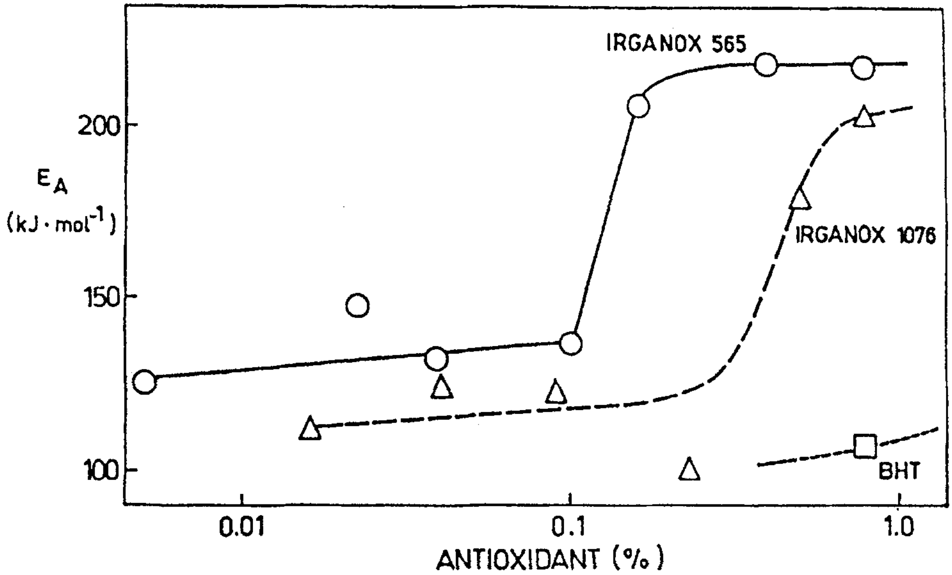

Fig. 4 Dependence of the apparent activation energy E_A/kJ mol^{-1} on the concentration of the applied antioxidant in ABS polymer

Comparing ABS powders containing decreasing concentration levels of Irganox 565, it was evident that at a certain critical concentration (cca 0.1%) the apparent activation energy of oxidation E_A suddenly dropped from around 200 kJ mol^{-1} to only 120–130 kJ mol^{-1} (Fig. 4). A similar drop in E_A was observed in the case of long-term isothermally aged samples where the decrease in antioxidant level was due to its natural consumption in the aging experiment (Table 1).

Obviously, the change in the apparent activation energy of oxidation E_A is to be connected here with the change in the mechanism of oxidation reactions taking place after the antioxidant level drops below the critical concentration. This fact has to be taken into account when extrapolating across a wider temperature interval, otherwise unacceptable error in the lifetime prediction is to be expected.

References

1 L. Rosík, Aging and Stabilization of Elastomers. In: J. Pech et al., Synthetic Rubber, SNTL Praha 1971, p. 414.
2 L. Rosík et al., VIII. Conference on Thermal Analysis Termanal 79, Vysoké Tatry 1979, Proc. Paper, p. 234.
3 L. Rosík, J. Kovářová and J. Pospíšil, IX. Conference on Thermal Analysis, Termanal 82, Vysoké Tatry 1982, Proc. Paper, p. 199.
4 L. Rosík, J. Kovářová and J. Pospíšil, Plasty Kauc., 19 (1982) 145.
5 J. Kovářová, J. Pospíšil and L. Rosík, Plasty Kauc., 24 (1987) 164.
6 L. Rosík, Toughness modification. In: P. Švec, L. Rosík, Z. Horák, F. Večerka, Styrene-based plastics and their modification, E. Horwood Ltd., Chichester 1990, p. 149.
7 L. Rosík, Durability modification. Ibid., p. 245.
8 J. Kovářová, L. Rosík and J. Pospíšil, Stabilization of thermooxidized ABS. In: Proc. of Symp. on Environ. Degrad. of Polym., 3rd North American Chemical Congress, Toronto, June 1988. See also: Polym. Mater. Sci. Eng. 58 (1988) 215.
9 J. Kovářová, L. Rosík and J. Pospíšil, Thermooxidative behaviour of ABS polymers. IUPAC Symposium on Macromolecular Chemistry, Kyoto, August 1988. Preprint p. 657.
10 IEEE Standards 1, 98, 101. The Institute of Electrical and Electronic Engineers Inc., New York. (R. R. Dixon: IEEE Trans. on Electr. Insul. E-1, No. 4, 1980).
11 N. Grassie and G. Scott, Polymer Degradation and Stabilization, Cambridge University Press, Cambridge 1985.
12 S. G. Kirjuškin et al., Vysokomol. Soyedin., A30 (1988) 2102.