

OXIDATION STABILITY OF CROSSLINKED POLYETHYLENE.
ISOTHERMAL DTA METHOD.

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Isothermal differential thermal analysis has been used to study the thermooxidative stability of two grades of crosslinked polyethylene in the temperature range from 120 °C to 230 °C. Induction times of thermooxidative degradation were measured from 2 minutes up to 3590 hours. Oxidation Induction time and mechanical failure in oven ageing experiments coincided over the measured temperature range. The degree of crosslinking was not strongly affected by the oxidative reaction. The Arrhenius-plots of DTA results showed curvature at 150 °C, so straight line extrapolations from short-term experiments at elevated temperatures to low temperatures and long times are not possible. Thermoanalytically measured residual thermooxidative stability decreased linearly with ageing time and showed great scattering of the results.

Introduction

The methods used for evaluating oxidation stability of plastics materials have been object of great interest during the past few years. Oxidation has been studied extensively by thermal analysis in the isothermal method and even by running DTA [1-9]. In the isothermal experiments so called oxidation induction times of thermooxidative degradation were measured as the times from start of the isothermal DTA experiments to the beginning of exothermal decomposition. Lifetime estimations based on the results of short-term experiments at higher temperatures were not reliable, because the activation energy of thermooxidative degradation changes in the temperature region of 150 °C [5,10] and most isothermal DTA experiments were done at higher temperatures.

The purpose of the present investigation was to determine how isothermal long-term DTA experiments up to several 100 or 1000

hours correspond to the mechanical properties and gel content of oven aged samples of crosslinked polyethylene. Further on the decrease of residual thermooxidative stability in the course of oven ageing experiments was investigated.

Experimental

Materials

The samples used for the present investigations were taken from industrially produced pipes with an outside diameter of 20 mm and a wall thickness of 2 mm. The pipes of peroxide crosslinked polyethylene had been produced by Wirsbo Pex in an Engel process. The samples differed in their concentration of stabilizer and their degree of crosslinking.

XPE-I samples were prepared from a 20 x 2,0 mm pipe with a highly effective antioxidant system. The gel content measured in xylene was 90 %.

XPE-II was provided with a less effective antioxidant system, although the gel content of 87 % was comparable to that of XPE-I. The pipe dimension of 20 x 2,0 mm also corresponded to those of XPE-I.

Procedure

Isothermal DTA experiments were carried out partly in a Mettler TA system, partly in self constructed DTA cells under normal atmospheric conditions. The samples were quickly inserted into the preheated cells and no purge gas was used. The shortest measurable oxidation induction time was about 2 minutes, the more interesting results were obtained after some 100 or 1000 hours.

Samples for the DTA experiments were cut from the described pipes to a thickness of 50 μm using a microtome. The average sample weight of the slices was 4 mg. They were inserted into conventional DTA cups in a manner that sufficient gas exchange was ensured.

Tensile bars according to DIN 53455 type 4 were punched out of pipes of crosslinked polyethylene and oven aged at 140 °C to 180 °C in forced air ovens. The tensile bars were 2 mm thick, 80 mm long and 4 mm wide in the gauge section. Tensile properties were measured at 10 mm/min in accordance with DIN 53455.

The gel content of the peroxide crosslinked polyethylene was measured in xylene at 140 °C according to DIN 16892. The solvent was stabilized by 1 weight- % of Irganox 1330.

Results and Discussion

A survey over the isothermal DTA experiments on XPE-I is given in Fig. 1. It shows the heat flow of the oxidation reaction over a temperature range from 200 °C to 130 °C in a logarithmic time scale. The oxidation induction time at 200 °C is 1 h; the exothermal peak at 130 °C shows an oxidation induction time of 3256 h. In the case of XPE-II (Fig.2) the crosslinked polyethylene of lower effective stabilization and with polypropylene [11] we were successful in measuring the autooxidative degradation of polyolefins in the solid state by isothermal DTA. XPE-II showed an oxidation induction time of 3590 h at 120 °C.

Fig. 2 shows the Arrhenius plot of the results of both grades of crosslinked polyethylene. The logarithm of oxidation induction time is plotted against the reciprocal absolute temperature. The oxidation induction time in Fig. 2 was determined as the time from the beginning of the experiment to the moment of the first deviation from the baseline which indicated the beginning of the exothermal reaction.

Within the limitations of experimental accuracy the curves for XPE-I and XPE-II are parallel over the measured temperature range. The more effective stabilization of XPE-I causes an extension of oxidation induction times by a factor of 5 compared to XPE-II. As the activation energies for thermal decomposition are similar for both materials over all measured temperatures, the factor of 5 in the oxidative stability is found at every experimental temperature.

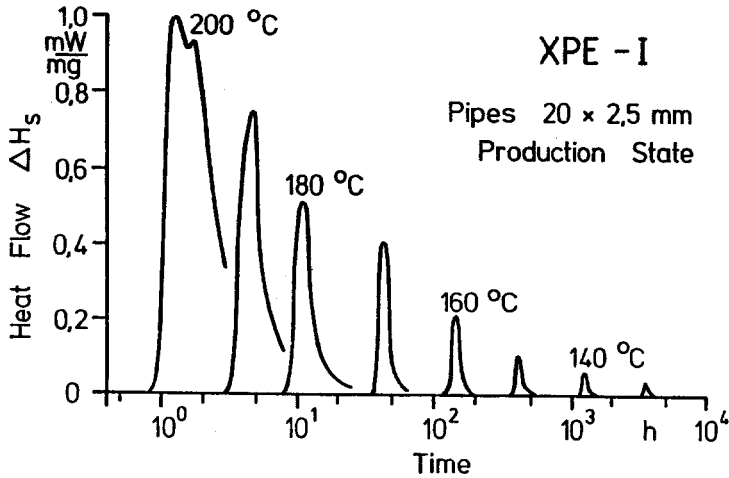


Fig.1. Isothermal DTA thermograms of crosslinked polyethylene XPE-I at various temperatures.

As Fig. 2 shows the logarithm of oxidation induction time plotted against the reciprocal absolute temperature does not give a straight line for both grades of crosslinked polyethylene. The knees at 150 °C indicate that different degradation processes with different activation energies are occurring above and below this temperature. This curvature shows that straight line extrapolation from short-term experiments at high temperatures may give wrong results if the long-term behaviour of the material is unknown. Only by extension of the isothermal DTA experiments to long times up to several 1000 hours and the use of low testing temperatures, can extrapolations to lower service temperatures and long times become more reliable

The apparent activation energies of thermooxidative decomposition are found to be about 220 kJ/mol in the temperature range from 200 °C to 220 °C for both grades and about 140 kJ/mol in the more interesting temperature range from 130 °C to 140 °C. A slight knee in the curve of XPE-II is observed when the crystallite melting range is crossed, so straight

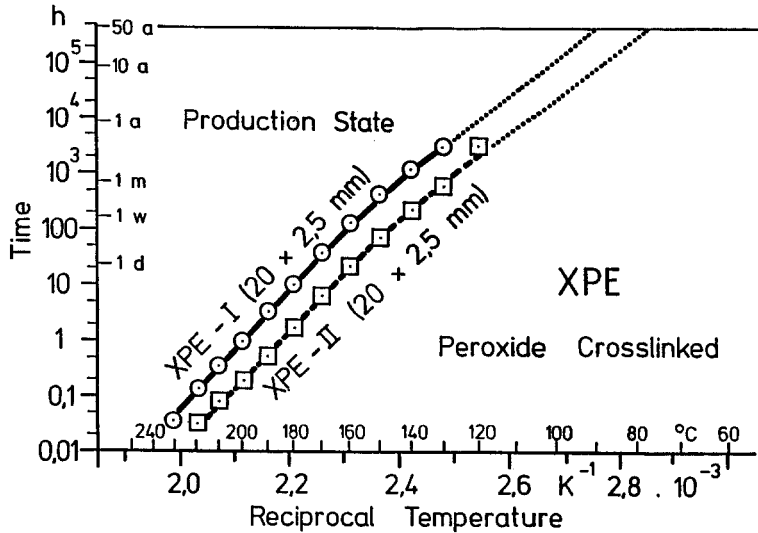


Fig. 2 Logarithms of oxidation induction times of different grades of crosslinked polyethylene as a function of reciprocal temperature.

line extrapolations based on the results of experiments above the crystallite melting temperature may give misleading results, although it could be ensured for polypropylene, that the activation energy of thermal decomposition is the same above and below the melting temperature [12]. The extrapolations to lower temperatures which may be expected in practical application are indicated in Fig. 2.

Another aim of the present investigation was to find a correlation between isothermal DTA experiments and measurements of mechanical properties. We used isothermal DTA to measure the thermooxidative stability of polyolefins and compared the results with oven ageing experiments carried out with the same material. Characteristic results for these experiments are compiled in Fig. 3. The oxidation induction time of XPE-I at 180 °C is 9,4 h. The DTA graph of a ring shaped sample at 180 °C is represented in a linear time scale. The oxidation induction time found by isothermal DTA experiments coincide with a sudden breakdown of mechanical properties in the oven

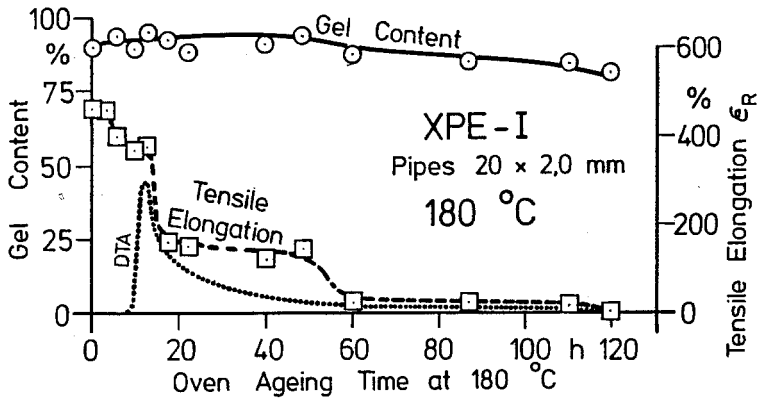


Fig. 3 Effect of oven ageing at 180 °C on the tensile elongation of crosslinked polyethylene XPE-I and comparison with gel content and DTA results.

ageing experiments of the same material. The oven ageing experiments at longer exposure times, beyond the oxidation induction time, revealed that mechanical properties are not entirely lost in the initial stages of oxidative processes. The elongation at break drops to a value of about 100 % after 15 hours of oven ageing at 180 °C and decreases continuously until the material is totally decomposed, so that no more tensile strength can be measured after 120 hours of oven ageing at 180 °C. The degree of crosslinking measured as the gel content is in no phase of oven ageing affected by the degradation processes. It remains unchanged after the beginning of exothermal decomposition.

Fig. 4 shows the effect of oven ageing at 180 °C on the mechanical properties and the degree of crosslinking for XPE-II. The sudden breakdown of tensile elongation again coincides with the beginning of the exothermal DTA peak. The gel content increases during the induction period of thermooxidative degradation to a value of 95 % and drops as soon as mechanical failure and exothermal DTA peak occur.

Experiments at lower temperatures such as 160 °C also show coincidence of oxidation induction time and breakdown of mecha-

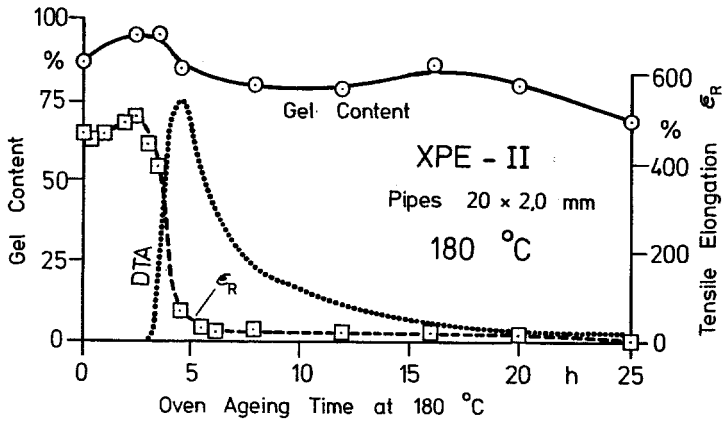


Fig.4 Effect of oven ageing at 180 °C on the gel content and tensile elongation of crosslinked polyethylene XPE-II and correlation with DTA experiments.

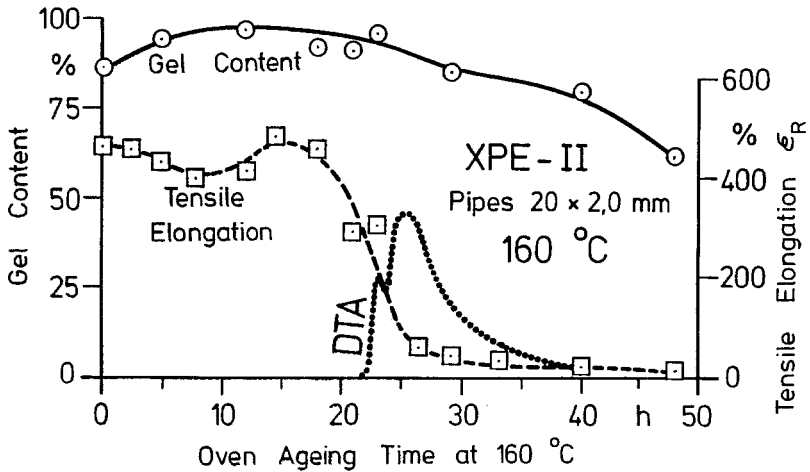


Fig.5 Effect of oven ageing at 160 °C on the tensile properties and gel content of crosslinked polyethylene XPE-II and comparison with DTA results.

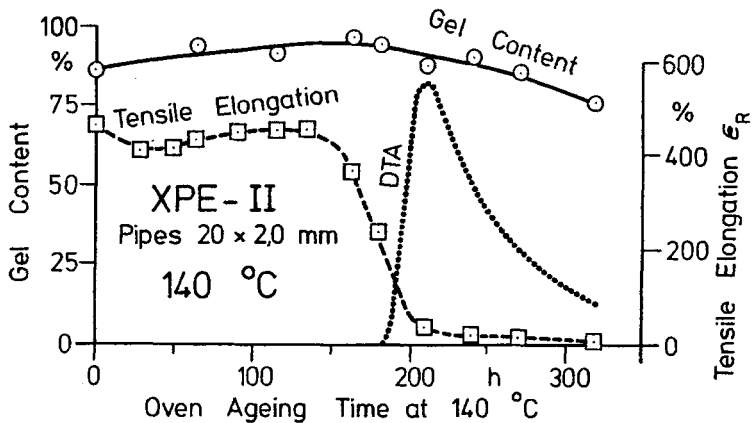


Fig.6 Effect of oven ageing at 140 °C on the gel content and tensile elongation of crosslinked polyethylene XPE-II and correlation with DTA experiments.

nical properties (Fig.5). The oxidation induction time of XPE-II at 160 °C is 22 h, the reaction maximum occurs at 25,5 hours. The beginning of the decrease of tensile elongation can be observed 2 hours prior to the first measurable exothermal DTA signal. The tensile elongation reaches a level of 100 % at the time of the reaction maximum.

Fig. 6 shows the results of the comparable experiments at 140 °C. The oxidation induction time of XPE-II at 140 °C is 180 hours. The onset of mechanical breakdown can be measured 30 hours prior to the exothermal decomposition. The gel content is - similar to the results at 160 °C - not seriously affected by the oxidation reaction.

As an illustration of the coincidence of thermooxidative degradation observed by isothermal DTA and the loss of mechanical properties in oven ageing experiments, results for XPE-II, the less effective stabilized grade of crosslinked polyethylene, are compiled in Fig. 7. The lower curve in the Arrhenius plot shows the beginning of the decrease of tensile elongation in the temperature range from 140 °C to 180 °C. The intermediate curve marks the oxidation induction times of

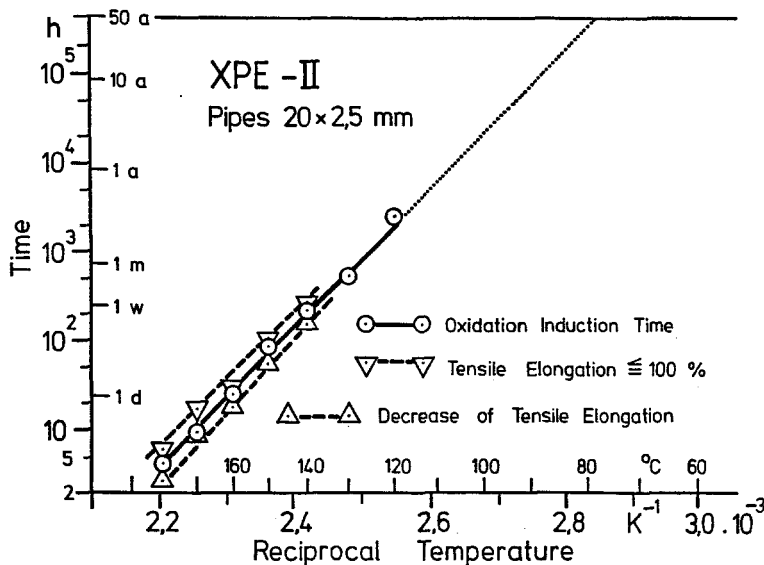


Fig. 7 Logarithms of oxidation induction times of crosslinked polyethylene XPE-II as a function of reciprocal temperature, compared with the results of oven ageing experiments.

XPE-II as they are known from Fig. 2. The upper curve in Fig. 7 indicates a tensile elongation of 100 % in the oven ageing experiments. The straight line for the beginning of the decrease of tensile elongation lies parallel to the oxidation induction times over the measured temperature range, so that that extrapolation of mechanical failure in this case may be replaced by extrapolation of DTA results, which can be obtained more easily.

The first decrease of tensile elongation in oven ageing experiments of crosslinked polyethylene is not accompanied by any visible change in the material's appearance, but its technical applicability is lost by thermooxidative degradation processes. Measurements of gel content cannot reveal the state of deterioration of the material during the induction period of thermooxidation. Short-term DTA measurements of residual lifetime can be carried out without excessive expense and can also help to estimate the degree of thermooxidative decom-

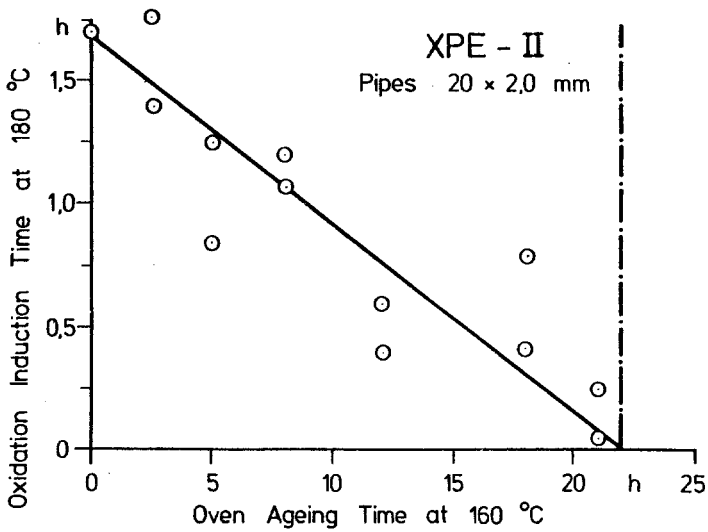


Fig. 8 Oxidation induction time of crosslinked polyethylene XPE-II at 180 °C as a function of oven ageing time at 160 °C.

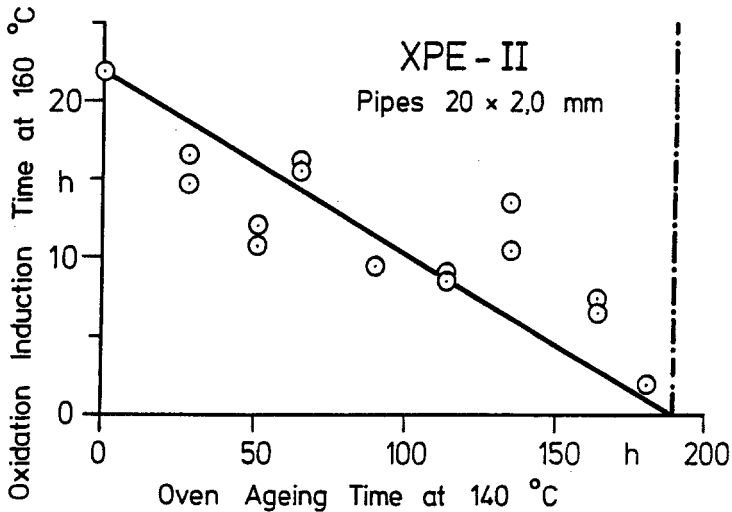


Fig. 9 Oxidation induction time of crosslinked polyethylene XPE-II at 160 °C as a function of oven ageing time at 140 °C.

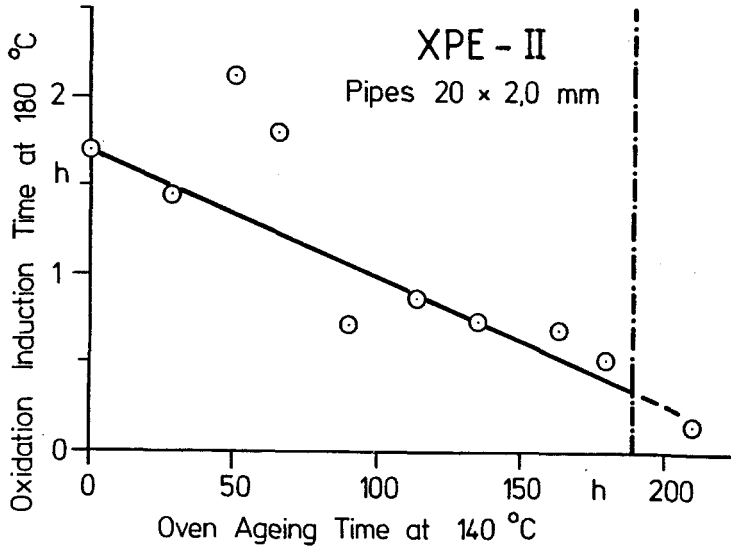


Fig.10 Oxidation induction time of crosslinked polyethylene XPE-II at 180 °C as a function of oven ageing time at 140 °C.

position before the breakdown of mechanical properties.

Fig. 8 shows the decrease of residual lifetime of XPE-II in DTA experiments at 180 °C in the course of oven ageing at 160 °C. In the initial state the material shows an oxidation induction time of 22 hours at 160 °C. After this time the mechanical properties decrease rapidly, but before the catastrophic breakdown no indication for the end of the material's applicability can be found by measuring the mechanical properties or the gel content.

In Fig. 8 it can clearly be seen that the residual lifetimes in the DTA experiments decrease nearly linearly with time. The scattering of the measured values in Fig. 8 is caused by the inhomogeneity of stabilizer distribution [9].

The end of the material's durability can be predicted by measurement of the residual lifetime and comparing it with the oxidation induction time of the initial state. Fig. 8 shows that short term measurement of residual lifetime by by iso-

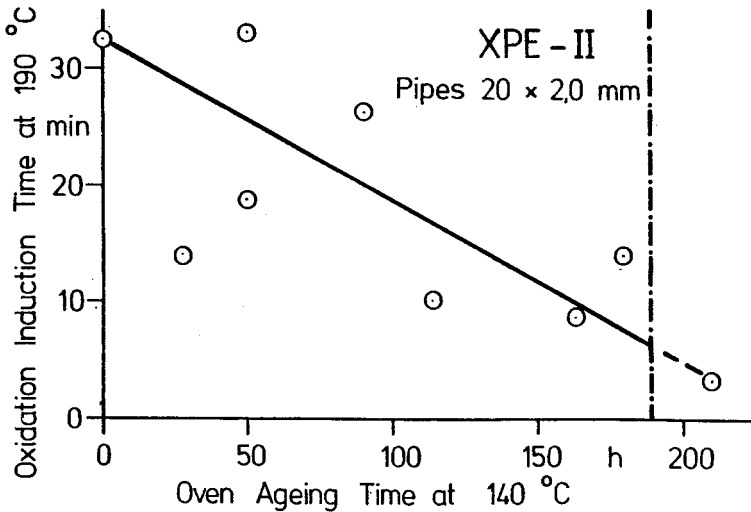


Fig.11 Oxidation induction time of crosslinked polyethylene XPE-II at 190 °C as a function of oven ageing time at 140 °C.

thermal DTA is an appropriate method of estimating the state of thermooxidative degradation of polyolefins before their mechanical failure.

Fig. 9 shows that the oxidation induction time at 160 °C decreases linearly with oven ageing time at 140 °C. A similar linear accumulation of deterioration can also be found in isothermal DTA experiments at higher temperatures (Fig. 10). Short-term tests, as illustrated in Fig. 10, bring more scattering in the results than DTA measurements at lower temperatures.

If information about the state of thermooxidative deterioration is required within short times, the temperature in the isothermal DTA experiments has to be raised as high as possible. Fig. 11 shows that in this case the scattering of the results increases but a linear decrease of residual lifetimes may be assumed similar to the DTA experiments at lower testing temperatures.

Conclusions

It has been demonstrated that isothermal long-term DTA is an appropriate method of testing the effectiveness of stabilizer systems in a simple isothermal apparatus. Oxidation induction times can be registered from small amounts of polyolefin samples. With the results of these DTA experiments it is possible to calculate the activation energies of thermooxidative decomposition for polyolefins in different temperature regions. The Arrhenius plots of DTA results are not straight lines over wide temperature ranges. For reliable lifetime estimations it is necessary to extend DTA experiments to some 1000 hours.

The oxidation induction time of the exothermal peak coincides with a sudden breakdown of mechanical properties in oven ageing experiments at the same temperature. So extrapolations for the loss of mechanical properties can be replaced by extrapolations of DTA results. Residual thermooxidative stability measured by isothermal DTA at elevated temperatures shows a linear decrease with ageing time during the induction period of thermooxidative degradation, while mechanical properties remain unchanged. The deterioration of the material during ageing experiments can be determined by measurement of residual lifetime and comparison with the oxidation induction time of the initial state.

Acknowledgements

The Austrian Fonds zur Förderung der Wissenschaftlichen Forschung and Jubiläumsfonds der Nationalbank are gratefully acknowledged for supporting this research. The authors would also like to thank Mr. Imgram (Wirsbo Pex, Heusenstamm) for the supply of materials and Dr. K.W.Leu (Ciba Geigy) for helpful discussion.

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Zusammenfassung

Die isotherme Differentialthermoanalyse ist als Methode zur Abschätzung der thermooxidativen Beständigkeit von Polyolefinen seit längerem bekannt. In der vorliegenden Arbeit wird über isotherme DTA-Messungen an Proben aus vernetztem Polyäthylen im Temperaturbereich von 230 °C bis 120 °C berichtet, wobei Oxidationsinduktionszeiten bis zu 3590 Stunden gemessen wurden. Die Auftragung der Oxidationsinduktionszeiten in Arrhenius-Diagrammen zeigte für vernetztes Polyäthylen keine für Extrapolationszwecke geeignete Linearität des Logarithmus der Oxidationsinduktionszeiten über der reziproken absoluten Temperatur über weitere Bereiche der Meßzeiten bzw. Prüftemperaturen. Die thermoanalytisch bestimmten Oxidationsinduktionszeiten stimmten mit dem Steilabfall der Reißdehnung in Ofenalterungsversuchen überein während der über den Gelgehalt ermittelte Vernetzungsgrad vom thermooxidativen Abbau nicht signifikant beeinflusst wurde. Somit können aufwendige Ofenalterungsversuche durch experimentell einfache isotherme

DTA-Versuche ersetzt werden. Die Messung der thermooxidativen Restbeständigkeit im isothermen DTA-Versuch bei erhöhter Prüftemperatur ermöglicht einen wesentlich deutlicheren Einblick in den thermooxidativen Schädigungszustand eines Polyolefins während der Induktionsperiode des thermooxidativen Abbaus als die Messungen des Vernetzungsgrades oder der Reißdehnung. Die Abnahme der thermooxidativen Restbeständigkeit erfolgt im Fall des vernetzten Polyäthylens in allen Fällen linear über der Alterungszeit.

Резюме – Методом изотермического ДТА изучена термоокислительная стабильность двух видов сшитого полиэтилена в температурном интервале 120–230°. Времена индукции термоокислительного разрушения полимера были измерены в интервале от 2 минут до 3590 часов. Индукционное время окисления и механическое повреждение в опытах по старению совпадали во всем измеренном температурном интервале. Степень сшивания не сильно затрагивалась окислительной реакцией. Аррениусовские графики данных ДТА показали перегиб при 150°, в связи с чем не представилось возможным провести экстраполяцию от кратковременных опытов при повышенных температурах до низких температур и более длинных периодов времени. Термоаналитически измеренная остаточная термоокислительная стабильность уменьшалась линейно с временем старения и показала большое расхождение результатов.