

## DTA INVESTIGATION OF INHIBITED AND CATALYZED OXIDATION OF POLYETHYLENE

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Differential thermal analysis (DTA) and infrared (IR) spectroscopy have been used to investigate the effects of an antioxidant (neozone D) and an oxidation catalyst (dispersed copper) on polyethylene melt oxidation under nonisothermal conditions (samples were heated at a constant rate). An increase in the content of the antioxidant or the oxidation catalyst gives similar results: a decrease in the thickness of the oxidized surface layer and accordingly in the total amount of oxidation in polyethylene samples. This is due to an increase in the rate of oxidation of the polymer.

Most papers concerning investigations into the oxidation of polyethylene melts deal with samples oxidized under isothermal conditions [1-10]. Of greater interest, however, is the investigation of polyethylene melt oxidation under nonisothermal conditions, for in the course of polyethylene item production (injection molding, powder coating, extrusion plating, etc.) oxidation takes place at varying temperatures. The derivatograph allows observation of oxidation in polymers under conditions similar to those applied in practice to the material. DTA curves for polyethylene free of antioxidant show a distinct peak in the range of 425 to 525 K, due to oxidation reactions in the polymer [11]. Thermogravimetric (TG) curves exhibit a peak in the same temperature range as a consequence of two competing processes: a mass increase due to oxygen absorption by the polyethylene, and a mass decrease in the oxidized polyethylene due to evaporation of the products of oxidative destruction of macromolecules. DTA and TG do not reveal peaks in the curves for preliminarily oxidized polyethylene in the above-mentioned temperature range [12, 13]. When a layer of 50 to 150  $\mu\text{m}$  is removed from polyethylene oxidized under isothermal and nonisothermal conditions, DTA and TG curves again show peaks [13]. These and some other data [14, 15] indicate that polyethylene resists oxidation into the depth of the sample. The distribution of the degree of oxidation (optical density of carbonyl groups in the IR spectrum of the polyethylene) through the sample thickness is described by an exponential function [13]. Polypropylene follows a similar law [16]. For isothermal oxidation of a polyethylene melt at 423 K, IR spectroscopy shows the thickness of the oxidized surface layer to be about 1.6 mm [13]. Increasing the oxidation temperature decreases the thickness of the oxidized surface layer [13, 15]. Filling polyethylene with substances which cause variations in the rate of the oxidation reactions may

shift the commencement of polyethylene oxidation (under nonisothermal conditions) to lower or higher temperatures. As the thickness of the oxidized layer in polyethylene samples depends on the oxidation temperature, one would expect that incorporation of antioxidants and oxidation catalysts into polyethylene would cause variations in the thickness of the oxidized surface layer, and consequently in the overall rate of oxidation of the polyethylene samples when heated at a constant rate, i.e. when DTA is applied.

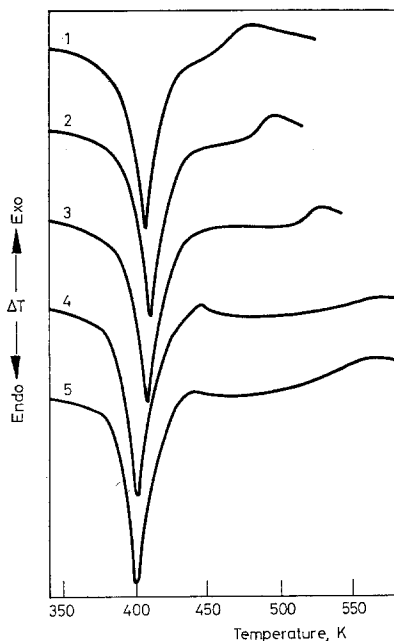


Fig. 1. DTA curves for original polyethylene (1); polyethylene containing 0.125 wt.% (2) and 0.75 wt.% (3) of neozone D; and polyethylene containing 0.5 vol. % (4) and 1.5 vol. % (5) of powdered copper

The purpose of the present work was to investigate by DTA the melt oxidation of polyethylene containing an antioxidant or an oxidation catalyst.

Powdered high-density polyethylene having a melt flow index of 7.5 g/10 min, the antioxidant neozone D and powdered copper with a particle size of 50 to 70  $\mu\text{m}$  were used in the experiments. The antioxidant was incorporated into the polymer by treating the polymer powdered with a solution of the antioxidant in acetone, followed by drying to constant mass. Copper was introduced into the polyethylene mechanically by stirring a mixture of the polymer powder and copper. Oxidation of the polymer under nonisothermal conditions was studied by an OD-102 derivatograph (0.7 g polymer samples) and by IR spectroscopy (UR-20

spectrophotometer). The heating rate in both cases was  $1/30$  °/sec. In the case of thermal samples of the above compositions were made in a special compression mold which had the shape of the crucible. Compression molding was performed at room temperature. For IR spectroscopy,  $100\ \mu\text{m}$  thick films were prepared by compressing samples between polytetrafluoroethylene films at 410 to 415 K. The films obtained were placed onto the KBr crystal surface in the thermocell of the spectrophotometer, and subjected to oxidation by heating at a given rate in air. The amount of polyethylene film oxidation was expressed as the optical density of the band corresponding to the vibrations in the carbonyl groups ( $1720\ \text{cm}^{-1}$ ).

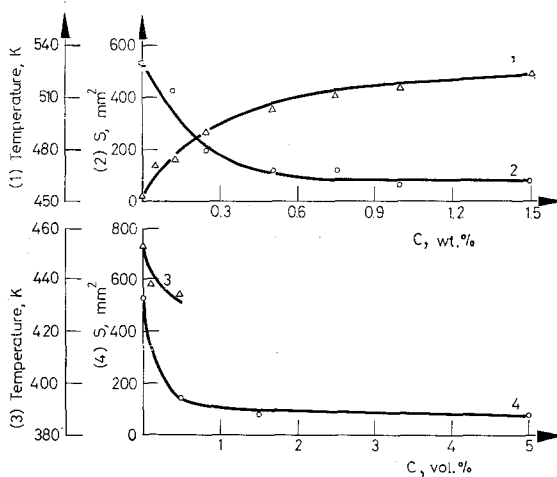


Fig. 2. Dependences of the temperature of commencement of oxidation ( $T$ ) (curves 1 and 3) and the area of the exothermic oxidation peak ( $S$ ) (curves 2 and 4) on the concentrations ( $C$ ) of antioxidant neozone D (curves 1 and 2) and powdered copper (curves 3 and 4) in polyethylene (DTA curves)

Figure 1 shows DTA curves for unmodified polyethylene (1), and polyethylene containing 0.125 wt. % (2) and 0.75 wt. % (3) of the antioxidant. After the antioxidant has been introduced into the polyethylene, oxidation starts at a higher temperature; the DTA curves show that the peak related to the polyethylene oxidation shifts to higher temperatures, and the area under the exothermic oxidation peak decreases. The dependence of this area, together with the temperature of commencement of the oxidation, on the antioxidant content in the polyethylene is shown in Fig. 2 (curves 1 and 2). The thickness of the oxidized polyethylene surface layer decreases from 1.6 mm to 0.5–0.3 mm when 0.25 wt. % of antioxidant is introduced. On increasing the antioxidant content in the polyethylene the oxidation area undergoes a higher localization in the surface layer.

The liquid-phase oxidations of low and high molecular weight substances show a number of similarities [2, 17, 18]. However, there are significant differences. For both cases the oxidation rate is higher in the surface layers; the oxidation products

either evaporate or diffuse into the bulk liquid. With low molecular weight substances, unoxidized molecules diffuse from the bulk to the surface (oxidation zone), simultaneously with diffusion of the oxidation products into the bulk liquid, i.e. self-mixing of the liquid takes place. The lower the molecular weight of the substance, the higher the self-diffusion coefficient, and the faster the mixing process. The oxidation products are distributed more or less uniformly in the bulk liquid. In the case of high molecular weight melts the diffusion of macromolecules from the bulk to the oxidation zone may be neglected because of an extremely low coefficient of self-diffusion. In fact, no diffusion mixing occurs in the polymer melt. When the oxidation causes no destruction in the macromolecules, an oxidized layer is rapidly formed on the melt surface. Deeper layers undergo oxidation only due the oxygen diffused into the polymer. As the concentration of oxygen decreases rapidly with the distance from the surface [13], the melted polymer sample oxidizes through a relatively small depth, and the deeper layers in thick samples remain unoxidized. On increasing the temperature and hence the rate of polyethylene oxidation, the depth of the oxidation zone decreases, for the diffusing oxygen governs the process, and the oxidation reaction is localized in the surface layer. It should be noted that the distribution of oxygen-containing groups through the sample depth i.e. variations in the extent of oxidation, (e.g. as revealed with an IR spectrophotometer) may not correspond to the variations in the concentration of oxygen molecules through the depth of the unoxidized sample. Firstly, the diffusion coefficient for oxygen varies with the oxidation of the substance; secondly, the oxidation products containing oxygen also diffuse into the bulk sample. When molecules of the polymer undergo crosslinking on oxidation, the oxidation process is still more localized in the surface layer. Chemical bonding of the macromolecules inhibits the diffusion processes by decreasing their mobility. This is the case for polyethylene when the oxidation temperatures are lower than that of the intensive thermal destruction of the macromolecules. On increasing the oxidation temperature, the intensity of structure-forming of polyethylene macromolecules increases [15]. Unlike polyethylene, when 3.3-bis(chloromethyl)oxacyclobutane is subjected to oxidation mainly destruction of macromolecules occurs. Here, unoxidized macromolecules are exposed due to evaporation as well as to diffusion of low molecular weight oxidation products into the melt; these macromolecules undergo oxidation and as a result the oxidation zone is continuously moving (the sample thickness decreases). With 3.3-bis(chloromethyl)oxacyclobutane, the depth of the region under the oxidation reaction (the thickness of the surface layer of the oxidized macromolecules) does not exceed 100 to 200  $\mu\text{m}$ , and the oxygen-containing low molecular weight products of oxidation are observed at a depth of 1.5 to 2.5 mm.

When powdered copper is introduced into polyethylene, the peak corresponding to oxidation in the DTA curves shifts to lower temperatures (Fig. 1, curves 1, 4 and 5). This indicates the catalysis of polyethylene oxidation in the presence of copper. Simultaneously, a decrease in the oxidation peak area is observed which indicates an increase in the total amount of oxidation of the samples. The latter is

connected with a decrease in the thickness of the oxidized surface layer of polyethylene. DTA curves give the dependences of the temperature of commencement of oxidation and the oxidation peak area on the copper content (Fig. 2, curves 3 and 4).

DTA results support the IR spectroscopy results. The temperature of commencement of nonisothermal oxidation of polyethylene increases, as does the oxidation rate, when the antioxidant content is increased (Fig. 3). When copper is introduced into polyethylene, the temperature of commencement of nonisothermal oxidation decreases (Fig. 3, curves 1 and 4).

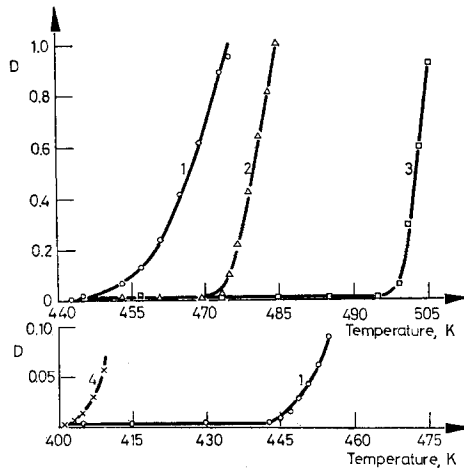


Fig. 3. Accumulation of carbonyl groups in polyethylene films oxidized under non isothermal conditions at a heating rate of  $1/30$  °/sec (1) original polyethylene; (2–3) polyethylene containing 0.1 and 0.4 wt. % of neozone D, respectively; (4) polyethylene containing 1.5 vol. % of powdered copper

Thus, when substances inhibiting polyethylene oxidation are introduced into polyethylene, similar results are obtained under nonisothermal oxidation, i.e. the total amount of sample oxidized decreases. This does not mean, however, that when copper (oxidation catalyst) and antioxidant (oxidation inhibitor) are introduced simultaneously into polyethylene, the compensating effect may not occur under nonisothermal oxidation.

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RÉSUMÉ — Etude par ATD et par spectroscopie infrarouge (IR) de l'effet de la teneur en antioxydant (Néozone D) et en catalyseur d'oxydation (cuivre dispersé) sur l'oxydation du polyéthylène fondu, en conditions non isothermiques (échauffement des échantillons à vitesse constante). L'augmentation de la teneur en antioxydant ou en catalyseur d'oxydation donne des résultats similaires, c'est-à-dire une diminution de l'épaisseur de la couche superficielle oxydée, et, par suite, de la quantité oxydée totale des échantillons de polyéthylène. Ceci est dû à l'augmentation de la vitesse de l'oxydation du polymère.

ZUSAMMENFASSUNG — Differentialthermoanalyse (DTA) und Infrarotspektroskopie (IR) wurden zur Untersuchung der Wirkung des Gehaltes an Antioxidantien (Neozone D) und Oxidierungskatalysator (dispergiertes Kupfer) auf die Oxidation von Polyäthylenschmelze unter nicht-isothermischen Bedingungen (unter Aufheizung der Proben mit konstanter Geschwindigkeit) eingesetzt. Die Zunahme des Gehaltes an Antioxidanz oder Oxidierungskatalysator ergibt ähnliche Ergebnisse, d. h. Herabsetzung der Stärke der oxidierten Oberflächenschicht und, dementsprechend, der Gesamtoxidationsmenge in den Polyäthylenproben. Dies ist der Zunahme der Oxidationsgeschwindigkeit des Polymers zuzuschreiben.

Резюме — Дифференциальный термический анализ (DTA) и инфракрасная спектроскопия (IR) были использованы для исследования влияния содержания антиокислителя (неозон D) и катализатора окисления (диспергированная медь) на окисление расплава полиэтилена в неизотермических условиях (образцы были нагреты при постоянной скорости). Увеличение содержания антиокислителя или катализатора окисления дает одинаковые результаты, главным образом, уменьшение толщины окисленного поверхностного слоя и, согласно этому, уменьшение общего количества окисленного продукта в полиэтиленовых образцах. Это обусловлено увеличением скорости окисления полимера.