Laurolactam as a stabilizer against the thermo-oxidative degradation of poly(ether-esters)[☆]

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Abstract

In this study we examined the influence of laurolactam on the thermo-oxidative degradation of a copolymer of poly(butylene terephthalate) and polybutylene glycol and of di(ethyleneglycol) dibenzoate, used as model compound. The degradation was followed by measurement of the oxygen uptake, FTIR and ^{1}H-NMR spectroscopy and measurement of the intrinsic viscosity changes during degradation. A stabilizing effect of laurolactam on the thermo-oxidative degradation could be observed, as an induction time was defined in which hydroperoxides were not formed and molecular weight was kept constant. After this period the oxygen uptake, hydroperoxide formation and polymer conversion increased more slowly.
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1. Introduction

Polymers are very different as far as their inherent sensitivity to oxidation is concerned. Generally, differences in stability arise from a variety of chemical structures, manufacturing processes and polymer morphology [1]. Poly(ether-esters) are very sensitive to oxidative degradation due to the ether soft segment. The mechanism of the thermo-oxidative degradation of these polymers involves a radical chain process with formation of hydroperoxides at the carbon adjacent to the ether oxygen. The hydroperoxides undergo further reactions leading to new esters and to oxidized products formed after chain scission, such as formates, acids and alcohols [2,3].

By the addition of radical scavengers, such as phenolic antioxidants and aromatic amines the long term heat stability of poly(ether-esters) can be increased [4]. Recently, the interaction of a phenolic antioxidant and an aromatic amine, was studied using poly(tetramethylene oxide) as a mimicking solvent [5,6]. Besides, with well known antioxidants it is also possible to increase the long term heat stability of poly(ether-esters) with compounds containing an amide functionality [7,8]. It is suggested that these amides function by scavenging formaldehyde or formic acid and, in this way, preventing acidolysis [7] or by deactivation of antioxidants [8]. To get a better understanding of the mechanism of action of amides in poly(ether-esters), in this paper results are presented on the degradation of this polymer and one of its model compounds (DEGDB) in the presence of laurolactam, an aliphatic amide. As degradation methods oxygen uptake, hydroperoxide formation, intrinsic viscosity measurements and changes in the FTIR and NMR spectra during ageing were used [9].

2. Experimental

Laurolactam ($C_{12}H_{23}NO$) was obtained from FLU-KA chemicals and used as received. Diethyleneglycol dibenzoate (DEGDB) was supplied by Aldrich (structure in Fig. 1). The polymer studied was a block copolymer of poly(butylene terephthalate) and poly-butylene glycol (PBT/PBO) supplied by DSM. Laurolactam was mixed with DEGDB at a 4% (w/w) concentration. The polymer film was immersed in a saturated solution of laurolactam in pure methanol for 24 h. All samples were vacuum dried for 24 h before degradation.

Degradation experiments were carried out in an oil bath at 100 °C in a closed vessel filled with oxygen, as described elsewhere [10]. Two experiments have been carried out independently and the results obtained in both cases were reproducible. The oxygen uptake was calculated from the pressure drop and thus, not corrected for the evolution of gases, a procedure that proved to be unnecessary for oxygen uptake values below 1800 mmol/kg [11]. At various degradation times samples were taken and characterized using the analytical techniques indicated below.

^{1}H-NMR spectra were recorded on a Varian 300 MHz spectrometer using deuterated chloroform as solvent and tetramethylsilane as internal standard. FTIR spectra were recorded on a Bomen spectrophotometer. The absorptions were corrected for baseline variations by subtracting the absorption at 2500 cm^{-1}. The intrinsic viscosity was determined using an Ubbelohde capillary viscometer with 5 mg ml^{-1} solutions in chloroform at 25.0 ± 0.5 °C.

3. Results and discussion

3.1. Model compound

Interruption of the experiment for sampling had no effect on the course of the oxidation, in agreement with the results obtained by Gijsman et al. [11]. Oxygen uptake results for the model compound are shown in Fig. 2. An induction period of *ca.* 24 h was observed for the stabilized model compound, while for the unstabilized model compound oxygen is consumed right from the beginning. After the induction period a significant
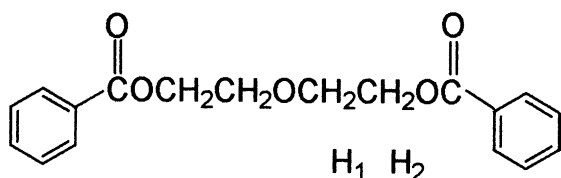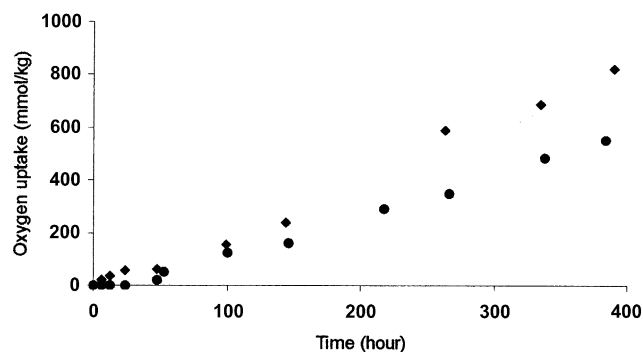
Fig. 2. Oxygen uptake of diethyleneglycol dibenzoate thermo-oxidized at 100 °C vs. time: (●) stabilized; and (♦) unstabilized.

difference in the oxygen uptake rates for the unstabilized (2.12 mmol kg^{-1} h^{-1}) and stabilized model compound (1.53 mmol kg^{-1} h^{-1}) was observed.

In spite of the effectiveness of laurolactam in reduction of the oxygen consumed, yellowing of the stabilized samples was observed after 266 h at 100 °C. This can be explained in terms of the formation of an active chromophore after oxidation of laurolactam. The molecular structure of yellowing products could not be assessed on the basis of NMR and FTIR spectroscopy due to the lack of sensitivity of these techniques [12].

The ^{1}H-NMR spectra of stabilized and unstabilized DEGDB degraded for 338 h are shown in Figs. 3a,b, respectively. The signals at δ 3.90 and 4.52 ppm correspond to the H_1 and H_2 protons, respectively. The observed decrease in the intensity of both peaks is higher for the unstabilized sample, being more evident for the H_1 protons in both cases. Besides, for the stabilized sample, new peaks associated with oxidation products show lower intensities. This is true for the signals at δ 4.56 and 4.91 ppm corresponding to the main oxidation products, previously identified as a formate and a new ester, respectively [10]. These results are consistent with the previously postulated mechanism for the thermo-oxidative degradation of poly(ether-esters).

Fig. 4 shows the conversion of the model compound, calculated from the ratio of the intensities of the H_1 signals of degraded and non-degraded samples, at δ 3.90 ppm. After the induction period, the conversion for the stabilized compound was always lower than that of the unstabilized compound, in agreement with the oxygen uptake curve (Fig. 2). Moreover, for the same oxygen uptake, the stabilized compound shows lower conversions.

3.2. Polymer film

The oxygen uptake curves for the polymer film are shown in Fig. 5. For the stabilized polymer film an
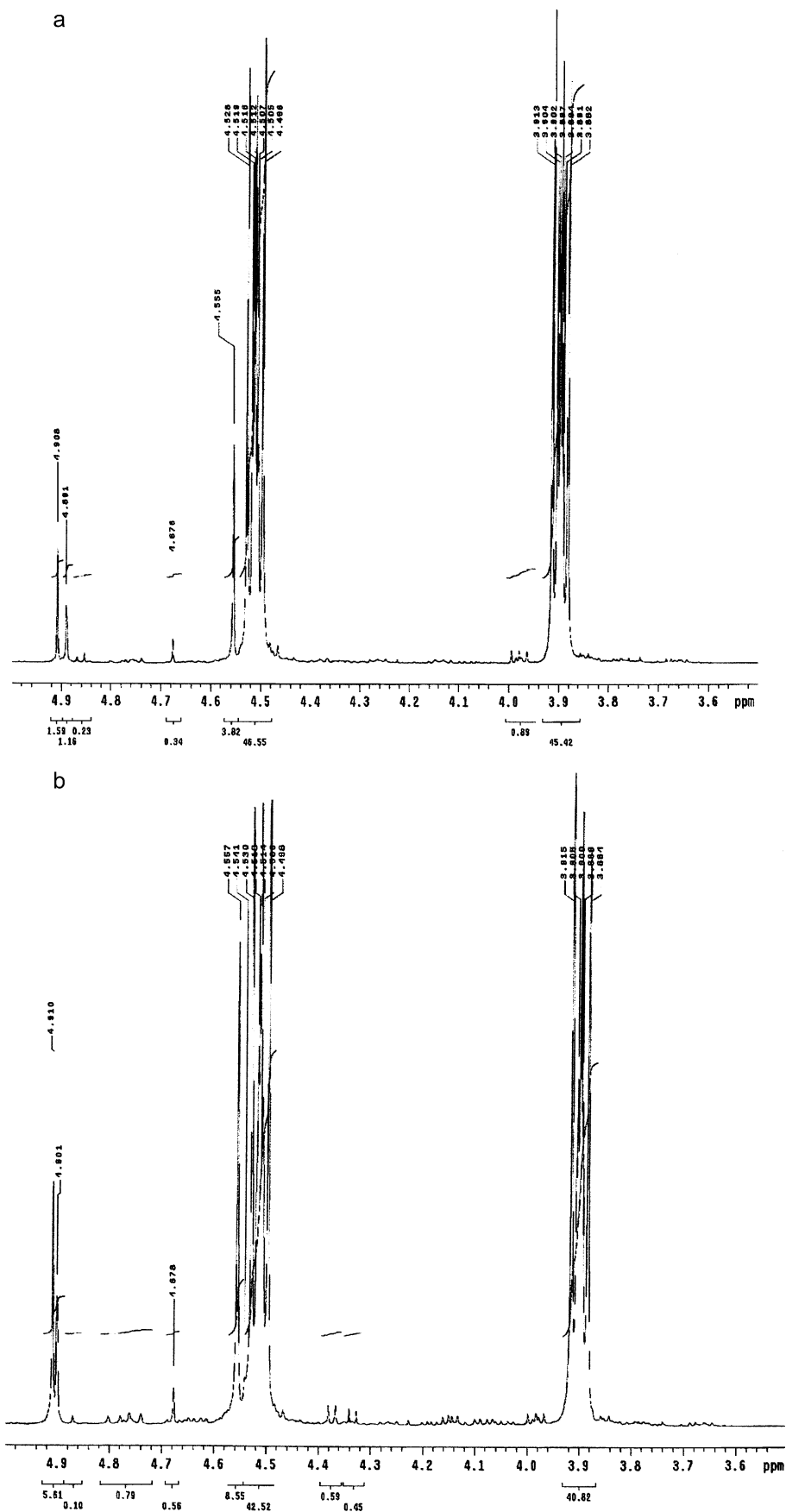
Fig. 1. Structure of the model compound DEGDB.

Fig. 3. ^{1}H-NMR in CDCl$_3$ of diethyleneglycol dibenzoate thermo-oxidized during 338 h at 100 °C: (a) stabilized; and (b) unstabilized.
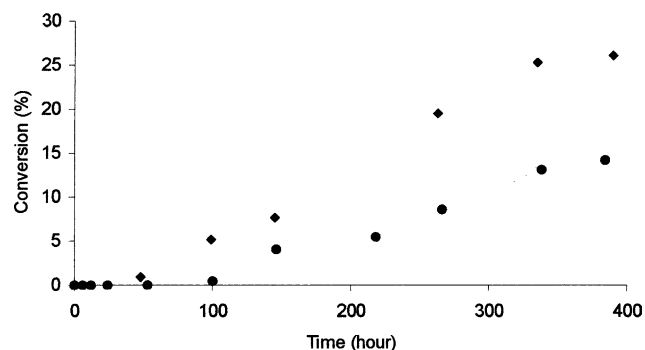
Fig. 4. Conversion of diethyleneglycol dibenzoate thermo-oxidized at 100 °C vs. time: (●) stabilized; and (◆) unstabilized.
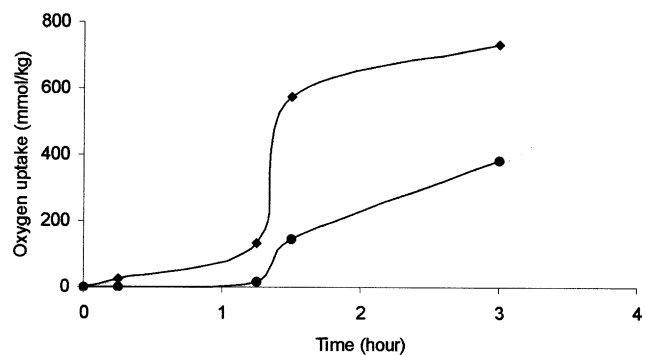

Fig. 5. Oxygen uptake of the polymer film thermo-oxidized at 100 °C vs. time: (●) stabilized; and (◆) unstabilized.

induction period of *ca.* 1.25 h was observed and the oxygen uptake rate was much lower than that of the unstabilized polymer film. The same was previously observed for the model compound (Fig. 2).

It is known that, degradation of poly(ester-ethers) leads to the formation of secondary hydroperoxides [10,13] that are intermediates in the mechanism leading

to other oxidation products, such as aromatic carboxylic acids, formates and alcohols [2]. Figs. 6a,b show the FTIR spectra, in the 4000–2000 cm^{-1} region, of the stabilized and unstabilized polymer films, respectively. The formation of hydroperoxides is demonstrated by the increasing absorptions observed in the 3600–3100 cm^{-1} region and previously confirmed by the nitric
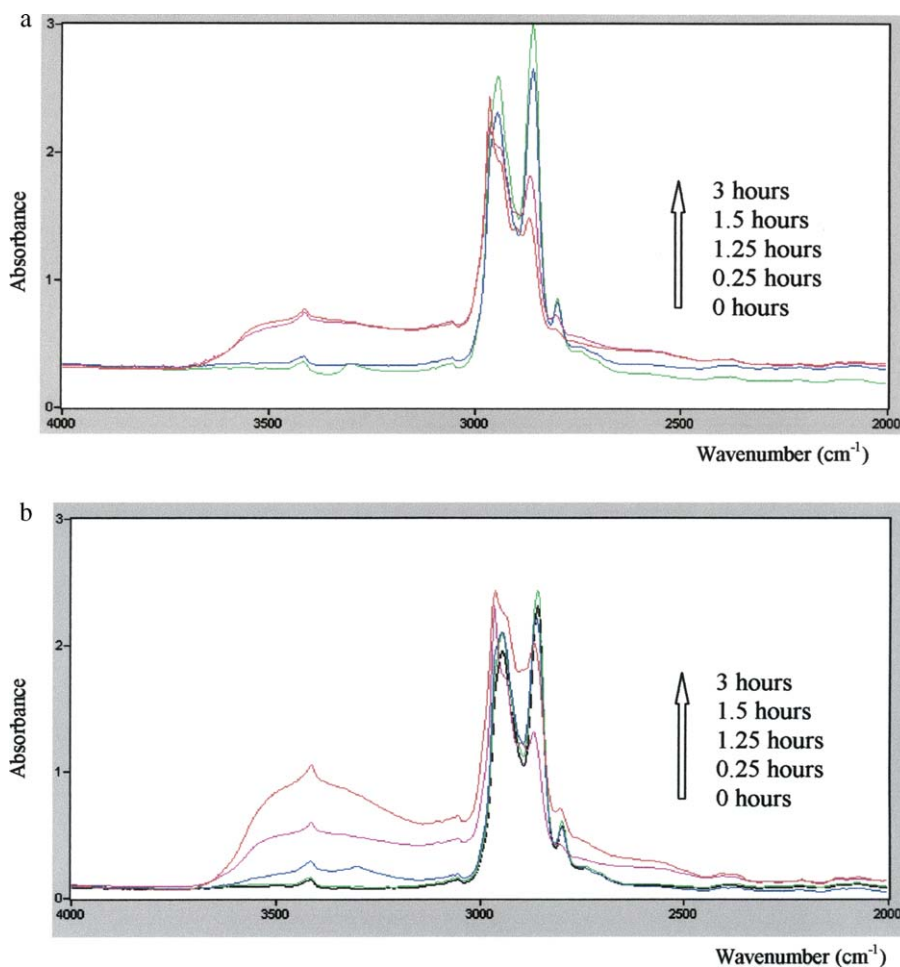

Fig. 6. FTIR spectra of the polymer film: (a) stabilized; and (b) unstabilized.
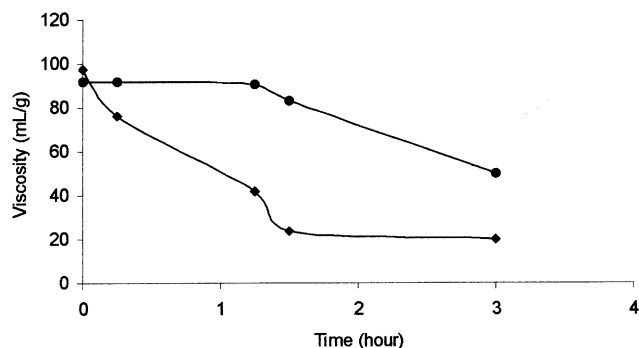
Fig. 7. Intrinsic viscosity of the polymer film thermo-oxidized at 100 °C vs. time: (●) stabilized; and (♦) unstabilized.

4. Conclusions

The results described herein show clearly that laurolactam has a stabilising effect on the thermo-oxidative degradation of poly(ether-esters). Amides in poly(ether-esters) do not function by preventing acidolysis or deactivation of stabilizers. In the presence of laurolactam an induction period could be observed. Concomitantly, hydroperoxides are not formed and no changes in the molecular weight are observed. After that period the oxidation rate, as well as hydroperoxide formation are reduced. The results reveal that laurolactam is able to prevent the polymer from oxidation.

oxide treatment [14]. Fig. 6a shows that no changes in the spectra were observed up to 1.25 h and that the absorbance after 3 h oxidation was *ca.* 0.613. In Fig. 6b an increase in the absorption is observed from the beginning reaching an absorbance of 0.928 after 3 h. So, when laurolactam is present an induction period is observed and less hydroperoxide is formed in the same time period.

The occurrence of chain scission or cross-linking during degradation was evaluated by measurements of the intrinsic viscosity of the stabilized and unstabilized polymer films with different degradation times. The results are shown in Fig. 7. For the unstabilized polymer film the observed decrease in intrinsic viscosity indicates that chain scissions occur from the beginning of the degradation. For the stabilized polymer film a constant value of the intrinsic viscosity could be observed, for 1.25 h, prior to a significant decrease. However, the value obtained after 3 h is higher than that obtained for the unstabilized polymer film. As could be expected, the change of the intrinsic viscosity along degradation follows that of the oxygen uptake. No chain breaking is observed before hydroperoxides could be formed.

In this study no other stabilizers were present, which means that the mechanism postulated by Hoeschele [8] (deactivation of antioxidants) cannot explain the mechanism of action of laurolactam in this study. Preventing acidolysis can also not explain the present results because this should only be visible for the viscosity measurements and not for the oxygen uptake and hydroperoxide data. From this study it is clear that amides function by preventing the polymer from oxidation.

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