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# Effect of carboxylic end groups on thermooxidative stability of PET and PBT

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## Abstract

A series of poly(ethylene terephthalate) and of poly(butylene terephthalate) samples containing different amounts of carboxyl end groups were prepared by chain-extension reaction with diepoxides. The effect of the carboxyl content on thermooxidative degradation was studied, using as criteria the induction period of oxidation and the stabilisation coefficient, both obtained by differential scanning calorimetry during isothermal or dynamic heating of the samples under air and nitrogen atmosphere. It was found that as the carboxyl content decreases the thermooxidative stability increases. However, in some more chain extended (crosslinked) samples the thermooxidative stability degraded. This abnormal behaviour was attributed to the lower degree of crystallinity of these samples. © 1999 Elsevier Science Ltd. All rights reserved.

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## 1. Introduction

Thermal stability of thermoplastic engineering polyesters such as poly(ethylene terephthalate) (PET) and poly(butylene terephthalate) (PBT) is of great technological importance. The deterioration of these polyesters can take place during their life cycle, starting from their production, during product formulation, moulding, end use of the product and especially when all these steps are accompanied by an oxygen atmosphere and a higher temperature.

Thermal degradation takes place mainly during the polycondensation stage due to the high temperatures used (280–300°C for PET and 250–280°C for PBT). This is the reason for the relatively low molecular weight of these polyesters 15,000–25,000. The mechanism for this degradation involves a random alkyl-oxygen chain scission of the  $\beta$ -hydrogen type. Acetaldehyde, water, carbon dioxide and carboxyl end groups are the main products of thermal degradation of PET [1], while butadiene and carboxyl end groups are produced from PBT [2]. The kinetic parameters of this thermal degradation have been also studied [3,4].

From very early studies, it was found that the main factors affecting the thermal degradation are the catalysts which are used in the first stage of the polyester production (transesterification stage) [5]. A mechanism for their promoting action was proposed by Zimmermann et al. [6] in which a complex formation between the metal and the carbonyl group takes place. In order to prevent this action, phosphite and phosphate [7–9] as well as phosphonate [10,11] compounds were used after the completion of transesterification stage.

The degradation of PET and PBT in the presence of air proceeds through a free radical mechanism. The thermooxidative degradation takes place mainly during the product formulation in injection machines or during the extrusion of the polymer melt (moulding). In these procedures there is a critical time period for polymer melt which cools down and finally solidifies. During this period the polymer can be affected by air and the results are in general the same as in the case of thermal degradation. This leads to a decrease of the molecular weight and the formation of undesirable products. All these can significantly affect the properties of the end products.

According to the free radical mechanism of thermooxidative degradation, a free macroradical is generated by heat, radiation or stress. This reacts readily with oxygen to yield a peroxy radical. The peroxy free radical abstracts hydrogen from another polymer molecule

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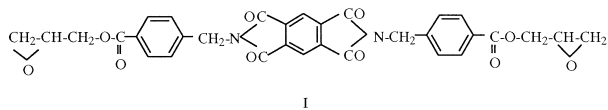
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creating a new macroradical and a hydroperoxide. Then the hydroperoxide decomposes to two new free radicals which are also initiators of the chain reaction. This decomposition in this case is accelerated by the same metal ions derived from the transesterification catalyst. Hindered phenols, aryl phosphites, phosphates and phosphonates are the most effective antioxidants [12,13] and they are often used at about 0.05–1 wt% [14]. Some other phosphorous compounds can also inhibit the thermooxidative degradation of PET by deactivating the zinc acetate, the most common transesterification catalyst [15].

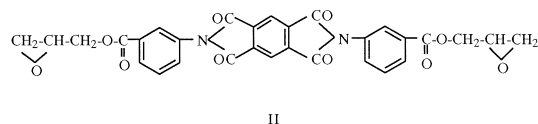
As it is obvious from all the above, a great amount of research has been done on the thermal and thermooxidative stabilisation of PET, but some questions are still unanswered. One of them is: how does the carboxyl content affect the thermooxidative stability of polyesters? For this purpose PET and PBT samples, with different amount of carboxyl content were prepared by using a diepoxide chain-extension reaction and their thermooxidative stability was evaluated by high temperature DSC measurements.

## 2. Experimental

The virgin PET and PBT samples, having intrinsic viscosity of 0.60 and 0.84 dl/g, respectively, were kindly supplied by Du Pont de Nemours (Luxembourg). The carboxyl content was 42 for PET and 44 eq/10<sup>6</sup> g for PBT. The preparation of polyesters containing lower carboxyl content than the virgin one (blank) is described in our previous papers [16,17]. The PET samples were taken from the chain extension reaction carried out at 280°C ± 1 with diepoxide I:



and the PBT samples at 250°C ± 1 with diepoxide II:



Both diepoxides were used in different amounts (half, theoretical and double) and for different times of reaction (5, 10, 15, 20, 30 and 60 min) under an inert atmosphere. The theoretical amount of the chain extender to be added to the polyesters was calculated from Eq. (1)

$$W\% = \frac{M_w \times CC_0}{2 \times 10^4} \quad (1)$$

where  $M_w$  is the molecular weight of the chain extender and  $CC_0$  the carboxyl content of the initial polymer. As theoretical amount we mean the quantity of chain extender which is needed, so that a mole of chain extender reacts with 2 moles of polyester, assuming that only the carboxyl groups will be the reactive groups of this process.

Both diepoxides were synthesized in our laboratory and they are not commercially available. They worked successfully and in the same manner, i.e. they increased the initial molecular weight of PET and of PBT about three times, as was found by intrinsic viscosity measurements [16,17] and decreased their carboxyl content as is shown in Figs. 1 and 2.

For the thermooxidative study of the polyesters, a Perkin-Elmer differential scanning calorimeter model DSC-2 was used. All the samples were fine milled and the particle size fraction  $-0.40 + 0.16$  mm was used. To prevent any hydrolytic degradation during heating, the samples were dried before the study in a vacuum oven at 110°C for 24 h.

For the isothermal study,  $10 \pm 0.01$  mg of each sample were placed in an aluminium pan and the cover was simply placed on the sample, without sealing. The samples were heated in an air atmosphere (flow rate 1.5 l/h) with heating rate 20°C, up to the desired temperature (240°C for PET and 210°C for PBT). After reaching the appropriate temperature the sample remained isothermal until completion of the oxidation (exothermic peak). From the thermograms obtained the induction period was determined, as the time required for the appearance of aforementioned thermooxidative exothermic peak [15].

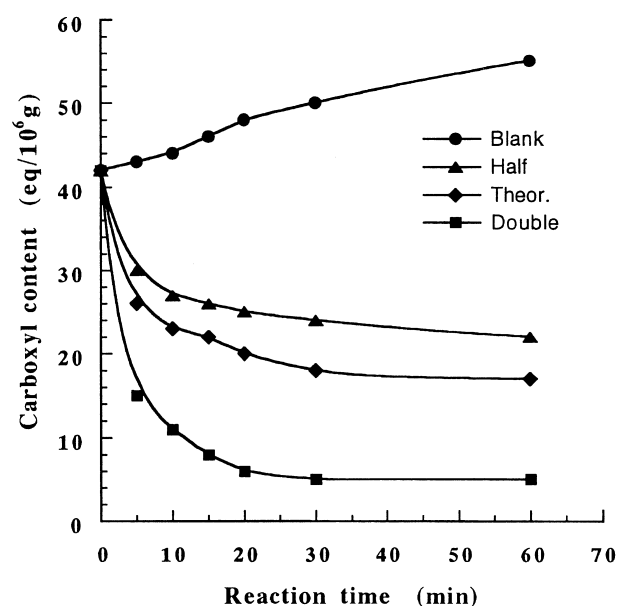


Fig. 1. Variation of the carboxyl end groups of PET samples with chain extension reaction time and different amounts of diepoxide I.

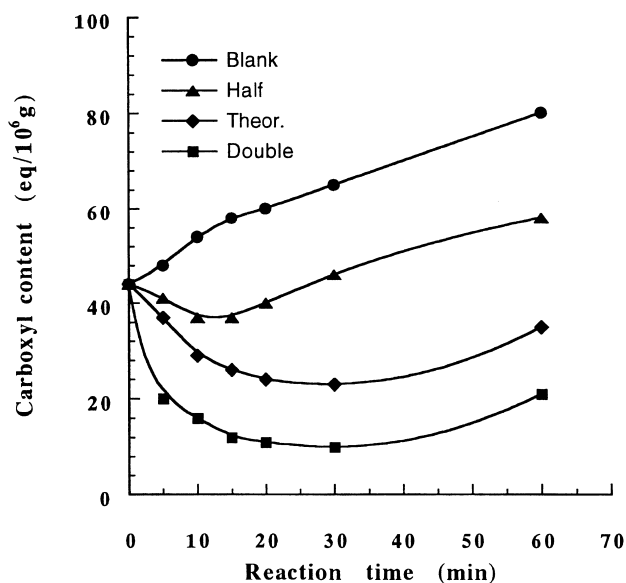


Fig. 2. Variation of the carboxyl end groups of PBT samples with chain extension reaction time and different amounts of diepoxide II.

For the dynamic treatments  $10 \pm 0.01$  mg of each sample were placed in an aluminium pan as described before. These were first heated in an inert atmosphere (nitrogen) with a heating rate of  $5^\circ\text{C}/\text{min}$  and flow rate  $1.5$  l/h, up to temperatures about  $30^\circ\text{C}$  higher from the melting point of each polyester ( $250^\circ\text{C}$  for PBT and  $290^\circ\text{C}$  for PET). After that, a new amount of the same sample was heated in an air atmosphere, under the same conditions. As comparison factor was taken the stabilisation coefficient [18] ( $C_{st}$ ) which represents the heat of fusion in nitrogen ( $H_N$ ) and the heat of fusion in air ( $H_A$ )  $C_{st} = H_N/H_A$ . This can take values between 0 in the case that no melting peak appears in the air atmosphere (only oxidation peak) and 1 in the case that no oxidation peak appears (only melting peak).

### 3. Results and discussion

The catalytic effect of the carboxyl end groups on the hydrolysis of PET has been mentioned by Buxbaum [19] and later some other researchers have studied this effect [6,20]. This catalytic effect is the main reason, for polyester producers to offer polyesters with carboxyl content less than  $10\text{--}15$  eq/ $10^6$  g, but PET and PBT, apart from the high susceptibility to hydrolysis at temperatures close to their melting points [21,22], can also be oxidized very easily in the presence of small quantities of air. This oxidation is affected by many parameters such as temperature [23], catalysts, diethyleneglycol content [24], etc. However, the role of the carboxyl end groups in the thermooxidative stability of PET and PBT remained unknown until now. For this reason samples containing different amounts of carboxylic end groups were

prepared. This was realized by adding different amounts of diepoxide compounds to the polyester melts and allowing them to react with the carboxyl end groups for different time periods. To prevent oxidation, the reaction took place under argon atmosphere. The carboxyl content of PET and PBT samples was determined according to Pohl's method [25], and is presented in Figs. 1 and 2.

From Figs. 1 and 2 we can see the clear increase of the blank run without diepoxide of both polyesters, that is from 42 to 55 and 44 to 80 eq/ $10^6$  g for PET and PBT respectively. In the case of PET the variation of the carboxyl content is relatively small. On the contrary, for PBT sample the amount of the carboxylic groups almost doubled during the same time period. The above mentioned increase is due to the thermal degradation of the polyesters that takes place during heating [26–28] and of course is higher at prolonged heating times. When the diepoxides are added, there is a continuous reduction of the carboxyl groups during the reaction time. This happens due to the reaction of the glycidyl groups of the diepoxides with the carboxyl end groups of polyesters. Thus, it can be said that the addition of diepoxides besides the molecular weight increase (which was the main reason of their use) also results to a sufficient control of the undesirable carboxylic groups. Furthermore, as the amount of diepoxides increases the carboxyl end groups decrease even more. This is more prominent in the case of PET in which the carboxyl content became 5 eq/ $10^6$  g after 60 min of thermal treatment by doubling the amount of the diepoxide used.

#### 3.1. Thermooxidative stability of PET samples

The thermooxidative stability of PET samples was estimated in the solid state as well as in the melt. For the first study the induction period was chosen as a criterion. The temperature of  $240^\circ\text{C}$  was chosen, because the oxidation rate increases with increasing temperature and for the solid state it has its maximum value near the melting point. The induction periods for the PET samples are shown in Fig. 3.

The induction periods for the blank samples are almost the same and lie between 17 and 18 min. It seems that the small increase of carboxyl end groups that was observed in these samples (8 eq/ $10^6$  g for the sample of 30 min of heating) does not affect their oxidation rate. Since the differences on the carboxylic groups are very small in these samples, their real effect upon oxidation, is obscure. Only in the sample heated for 60 min where the highest increase in carboxyl groups is observed (13 eq/ $10^6$  g), a small decrease of the oxidative stability (about 4 min) is recorded. In contrast, in the chain-extended samples there is an increase in the induction periods and this happens in all the samples up to 30 min

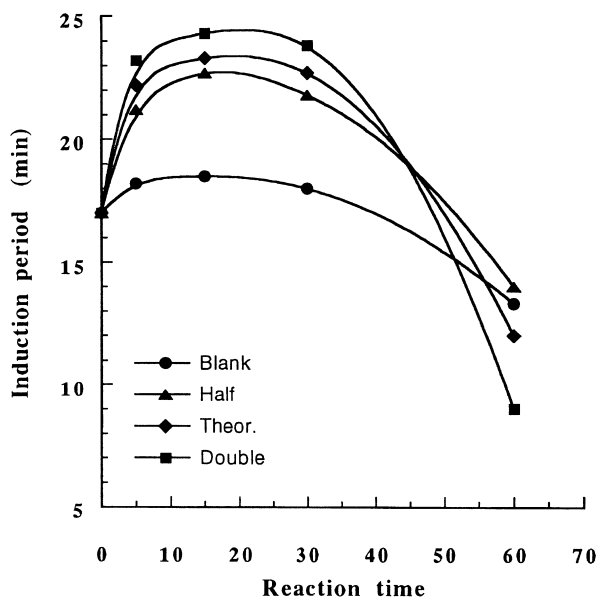


Fig. 3. Induction periods of thermooxidative degradation of chain-extended PET samples.

of reaction time. These induction times lie between 21 and 24 min. We can generally say that these samples are more resistant to oxidation than the corresponding blank samples by about 4–6 min. The highest increase appeared in the samples of 5 min and afterwards there is a small stabilisation. This is in good agreement with the variation of the carboxylic groups at these samples. From Fig. 1 it can be seen that the highest decrease in carboxylic groups, due to the effect of chain extension, appears within the first 5 min of the reaction and afterwards the decrease rate becomes lower.

The above findings demonstrate that the carboxyl end groups have a promoting effect on the oxidation of PET, so their decrease in chain extended samples had as a result an increased thermooxidative stability, but in order to have an appreciable effect, the differences in the carboxyl content must be more than  $10 \text{ eq}/10^6 \text{ g}$ . A similar promoting effect of the carboxylic groups was also found in the thermooxidative degradation of polymers derived from lactams [29] and of LDPE [30]. The mechanism is not clear but this promotion can be ascribed to the ease of the abstraction of the carboxylic hydrogen in the presence of free radicals. From a previous study [31] in model compounds, it was found that the rate of this carboxyl hydrogen abstraction from peroxy radicals ( $\text{ROO}\cdot$ ) lies between 50 and  $500 \text{ l/mol.s}$ . The same rate for methylene ( $-\text{CH}_2-$ ) hydrogen is about  $1-5 \times 10^{-4} \text{ l/mol.s}$ , while the abstraction rate of the  $\alpha$ -hydrogen adjacent to a double bond ( $-\text{C}=\text{C}-\text{CH}_2-$ ) is  $0.1-1 \text{ l/mol.s}$ .

It is of particular interest that the most chain-extended samples, e.g. those after 60 min of reaction time, showed the lowest induction periods. These samples gave an insoluble residue, when we tried to prepare

solutions for viscosity measurements [15,16], attributed to crosslinking. For this reason they also showed lower melting points [32]. Consequently, they were less crystalline or better more amorphous; this is the reason of the lower thermooxidative stability.

If the lower melting point was really the main reason for this peculiar behaviour, we should find another criterion to elucidate this fact. The stabilization coefficient ( $C_{\text{st}}$ ) is the second criterion, which was used in this study, and it is referred to the thermooxidative stability of polyester in the melt. Thus the melting point is not involved.

As can be seen from Fig. 4 the variation of  $C_{\text{st}}$  shows about the same trend as in the case of induction period. There is also a clear and similar increase of the stability for all chain extended samples (up to 30 min of reaction time). In contrast, in the samples of 60 min, the stabilisation coefficient is lower and very close to the corresponding blank sample. This is clear evidence that in this case the decrease of the thermooxidative stability is affected by the crosslinking rather than by the melting point.

### 3.2. Thermooxidative stability of PBT samples

The research studies concerning the thermooxidative stability of PBT are fewer compared to PET. PBT is used mostly for electronic and electrical equipment housings. In the last case, the temperatures which PBT is exposed to, are often very high. Thus, inorganic fillers or glass fibers are added to ensure form stability. To estimate the thermooxidative stability in the solid state a temperature of  $210^\circ\text{C}$ , which is quite close to its melting point, was chosen. The induction periods of the oxidation of PBT samples are presented in Fig. 5.

From Fig. 5 it can be seen that the induction period for the blank samples decreases continuously with

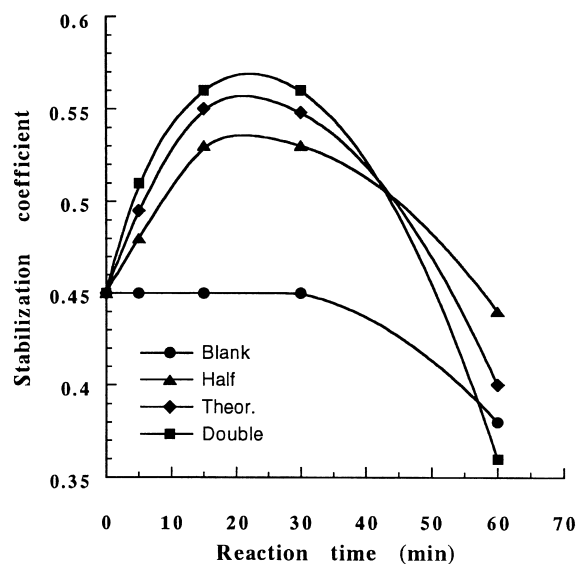


Fig. 4. Stabilization coefficient of chain-extended PET samples.

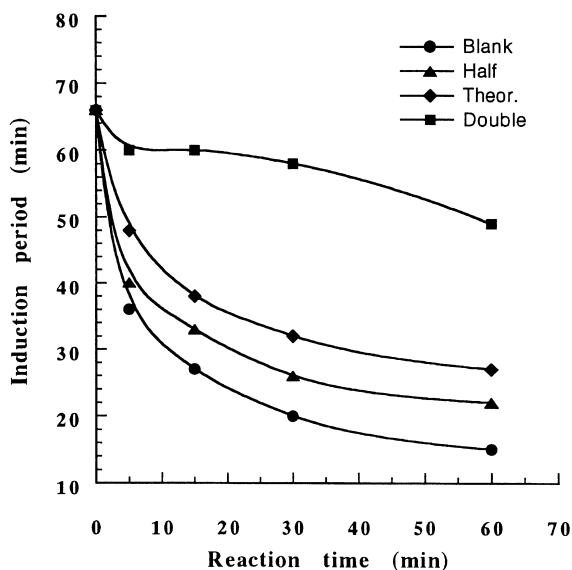


Fig. 5. Induction periods of thermooxidative degradation of chain-extended PBT samples.

increasing the reaction time (thermal treatment of PET sample without chain extender). Surprisingly, the virgin PBT sample seemed to be very stable, since its induction period (about 65 min) is much higher than that of PET. This must be attributed to the presence of some antioxidant, which was added during its production. This is a very common practice among all polymer manufacturers. The decrease, which appears thereafter, can be attributed to the promoting effect of the carboxylic groups that are produced from the thermal decomposition of PBT during heating (Fig. 2). Thus, the samples with the higher carboxyl content showed the lower induction periods (30 and 60 min of heating time). From these findings, it is concluded that the role of an antioxidant is not permanent. That is after its partial or complete consumption the oxidation rate increases again. Something like that should have happened in the initial PBT sample. The increased amount of the carboxylic groups on prolonged exposure times has as a result the production of more free radicals which consumed the antioxidant.

In contrast, the decrease of carboxylic end groups of all chain-extended samples had as a result an increased induction time compared with the corresponding blank ones. Examining more carefully the results it can be seen that there is a clear trend for increasing the induction period, which was not detected in the case of PET samples. As the added amount of diepoxide increases, the induction time shifts to the higher values and the samples become more stable against air oxidation.

It is worthwhile noting that the most chain extended PBT samples (60 min and double amount of chain extender) showed an improved thermooxidative stability in relation to the blank one of the same heating time (60 min). This behaviour must be attributed to

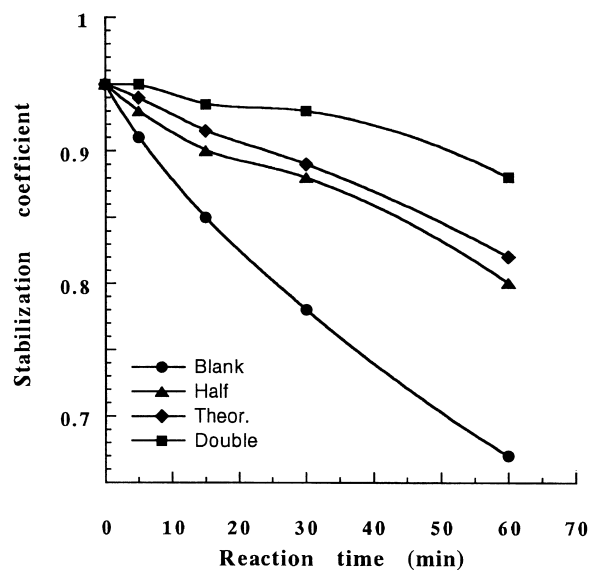


Fig. 6. Stabilization coefficient of chain-extended PBT samples.

the easier crystallization of PBT compared to that of PET.

The stabilization coefficient can also be a very good criterion (Fig. 6) and in this case, the values of this parameter showed the same trend with those mentioned for the induction period, but the curves derived from these values (Fig. 6) have a slightly different shape. The high value of the stabilization coefficient for the virgin sample, 0.95 which is close to 1, verifies the assumption that this sample contains a high amount of antioxidant. Afterwards, a continuous decrease is observed up to the sample of 60 min and the coefficient becomes about 0.66. All chain extended samples have a higher thermooxidative stability than the corresponding blank ones. This behaviour is found in good agreement with that observed by the induction period.

#### 4. Conclusions

From this study, it was concluded that polyester carboxyl end groups have a promoting effect on thermooxidative degradation. Thus, it is worth noting that a further benefit is given to polyester from chain extension reaction with diepoxides, because in addition to molecular weight increase, an improvement in the thermooxidative stability is produced. On the other hand, crosslinking negates this effect to some extent.

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