Copolyesters. III. Thermal Degradation of Poly(butylene Terephthalate-co-Adipate)s

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Synopsis

The copolyesters of poly(butylene terephthalate) and poly(butylene adipate) were prepared by melt polycondensation of 1, 4-butanediol, terephthalic acid, and adipic acid. The thermal stability was important for their use a shot melt adhesives. The thermal degradation of these copolysters and homopolyesters was determined through TGA, change of acid number, IR, GPC, and NMR analyses. It was found that the thermal stability of the copolysters in oxygen decreased as the content of butylene adipate increased at temperature above and below T_m. Thermal degradation occurred in oxygen even at temperature lower than T_m, so that degradation would also occur at room temperature in air and embrittlement was found for these copolysters for long term service.

INTRODUCTION

The copolyesters of poly(butylene terephthalate) (PBT) and poly(butylene adipate) (PBA) with low content of BA (butylene adipate units) had been considered to be used as hot melt adhesives.[1-4] We found that these copolyesters became brittle for long term service. It was thought to be due to degradation of the copolyesters in air. The thermal degradation of terephthalate polyesters has been studied by some researchers[5-11]; only thermal stability at temperature higher than T_m (melting point) was discussed in detail. There was little investigation on the degradation of the copolyesters of PBT and PBA at temperature below T_m. In this paper, the degradation of these copolyesters in oxygen at temperature lower than T_m was studied. The influence of composition on the thermal degradation of the copolyesters of PBT and PBA in oxygen above and below T_m is also presented.

EXPERIMENTAL

The copolyesters of PBT and PBA were prepared by melt polycondensation of 1,4-butanediol, terephthalic acid, and adipic acid with tetrabutyl orthotitanate (Merck reagent grade) as the catalyst followed by a method described by Droke and co-workers.[12]

The T_m of the polyesters was determined by Perkin-Elmer DSC-2 at heating rate of 20°C/min. The weight loss as a function of temperature was monitored by Perkin-Elmer TGA-2 at oxygen flow rate of 20 mL/min, and the heating rate was 20°C/min. The isothermal weight loss of the polyesters at

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250°C was also measured by TGA at oxygen flow rate of 20 mL/min. The isothermal weight loss of A30 (30 mol % BA content) at 250°C at nitrogen flow rate of 20 mL/min was also measured for comparison.

The polyesters were conditioned at 170°C in oxygen, and, at a time interval of 2 h, samples were taken out for analysis. For a blank test, A30 was conditioned at 170°C in nitrogen for comparison. The molecular weight of the samples before and after heat treatment for 12 h was measured by a Water Associates GPC II using m-cresol/chloroform (1/3 vol/vol) as the eluent followed by a method described in a previous paper.[13] The carboxyl content of the sample (dissolved in benzyl alcohol) was determined by titrating with KOH/benzyl alcohol standard solution, with phenol red as the indicator.[10] The proton nuclear magnetic resonance (NMR) spectra of samples of copolyester A30 before and after heat treatment at 170°C in oxygen for 12 h was determined by a Bruker AM 400 NMR. The IR spectra of A30 before and after heat treatment in oxygen at 170°C for 12 h were determined by a Perkin-Elmer IR spectrophotometer.

RESULTS AND DISCUSSION

The charged composition and intrinsic viscosity of the polyesters are listed in Table I. The intrinsic viscosity of each polyester was greater than 0.6 dL/g (weight average molecular weight greater than 30,000), the molecular weight was rather high, and the effect of molecular weight on the thermal stability could be considered to be small as compared to that of composition.

The thermogravimetric curves of the polyesters in oxygen are shown in Figure 1. In oxygen, significant weight loss of PBA occurred at considerably lower temperature than PBT. Obviously, the thermal stability of PBA in oxygen was lower than that of PBT. This would be contributed to the presence of adipate unit in PBA. As shown by Figure 1, the thermal stability of the copolyesters in oxygen decreased as the BA content increased.

The isothermal weight loss of the polyesters in oxygen at 250°C is shown in Figure 2. A blank test was also carried out for comparison. The weight loss of A30 at 250°C in nitrogen was very small as compared to that of all the polyesters in oxygen at the same temperature. Only 1% weight loss was found for A30 at 250°C in nitrogen for 2 h. Thus, there was much less thermal degradation at 250°C in inert gas. Considerable thermal degradation occurred at 250°C in oxygen as shown in Figure 2. The thermal stability of PBA at

TABLE I
T_m and Charged Composition of the Polyesters

	Mol % of adipic acid based on diacids	Intrinsic viscosity[a] (dL/G)	T_m (°C)	T_g (°C)
PBT	0	0.68	225	30
A20	20	0.60	196	10
A30	30	0.76	178	−1
PBA	100	0.92	73	−50

[a]Determined in phenol/syn-tetrachloroethane (60/40 wt/wt) by a Ubbelohde viscometer at 30°C.
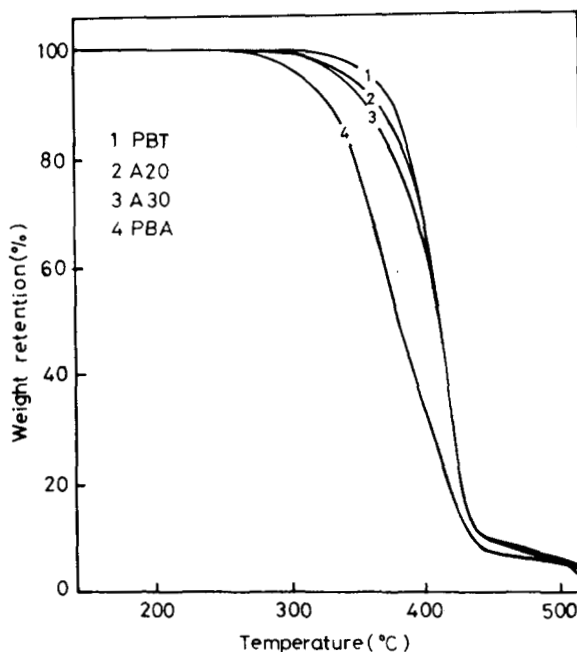
Fig. 1. The thermogravimetric curves of the polyesters in oxygen.

250°C in oxygen was considerably lower than that of PBT. As shown in Figure 2, the rate of isothermal weight loss of the copolyesters in oxygen at 250°C increased as the BA content increased, and the thermal stability under such a condition decreased as BA content increased. The aliphatic butylene adipate unit would be more easily degraded at 250°C in oxygen, so that the copolyester with higher BA content was less thermal stable in oxygen.
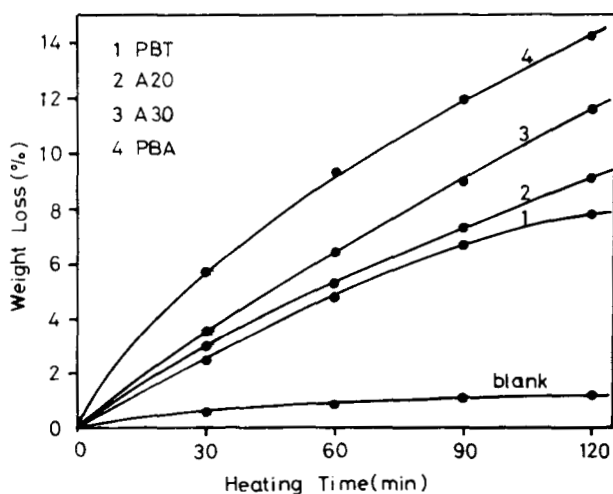

Fig. 2. The isothermal weight loss of the polyesters in oxygen at 250°C (the blank curve shows the case of A30 in nitrogen).

TABLE II
The Change of Molecular Weight Before and After
Heat Treatment at 170°C in Oxygen for 12 h

	PBT	A20	A30	PBA	Blank[a]
$\overline{M}_w$ initial	33,100	31,600	34,200	35,800	34,200
$\overline{M}_w$ after heat treatment	31,200	7200	4900	2700	33,800
$\overline{M}_n$ initial	12,500	9100	13,200	13,400	13,200
$\overline{M}_n$ after heat treatment	11,400	2400	1600	1000	13,900

[a] The case of A30 conditioned in nitrogen for 12 h as comparison.

The thermal stability of the polyesters in oxygen below T_m would be worth noting. The T_m of the copolyesters and homopolyesters was determined by DSC. Table I shows the results. The T_m's of PBT, A20, and A30 were found to be 225, 196, and 178°C respectively, and that of PBA was 73°C. The heat treatment at 170°C in oxygen could be considered as an accelerated test condition for PBT, A20, and A30. Although T_m of PBA was below 160°C, the heat treatment of PBA was also carried out for comparison.

First, the thermal degradation of the polyesters conditioned in oxygen at 170°C for 12 h was monitored by GPC measurement of molecular weight. The $\overline{M}_w$ (weight average molecular weight) and $\overline{M}_n$ (number average molecular weight) of the polyesters before and after heat treatment are listed in Table II. All the polyesters showed significant molecular weight loss after heat treatment in oxygen. Obviously, thermal degradation occurred even at temperatures lower than T_m in oxygen. The loss in molecular weight increased as the BA content increased, and the thermal stability of the copolyesters under such conditions also decreased as the BA content increased. The molecular weight change of A30 in nitrogen rather than in oxygen seemed interesting. There was no significant loss in molecular weight for A30 after heat treatment at 170°C in nitrogen for 12 h. Obviously, the presence of oxygen rendered a significant increase in the thermal degradation rate of the copolyesters.

The influence of heat treatment in oxygen at 170°C for 12 h on the IR spectra of A30 is shown in Figure 3. Since the polyesters would absorb moisture (about 0.3 wt % determined by the Karl Fischer method), a small broad peak at 3400 cm^{-1} corresponding to acid end group plus water was found for A30 before heat treatment. After heat treatment, a very broad peak located in the region from 2400 to 3500 cm^{-1} was found. Obviously, significant amounts of acid group were formed after heat treatment. There was no other significant change in characteristic peaks before and after heat treatment. It has been shown that the thermal degradation of some polyesters involved hydrolysis and oxidation.[5] Some hydroxy end groups might be formed together with the acid group due to hydrolysis, but could not be detected by IR.

The formation of significant amounts of acid group could be verified by the analysis of change of carboxyl content of the polyesters under heat treatment in oxygen. The change of carboxyl content vs. heating time at 170°C in oxygen for the polyesters is shown in Figure 4. All the polyesters show a significant increase in carboxyl content after heat treatment in oxygen. The increase in carboxyl content of PBA was greater than that of PBT under heat treatment
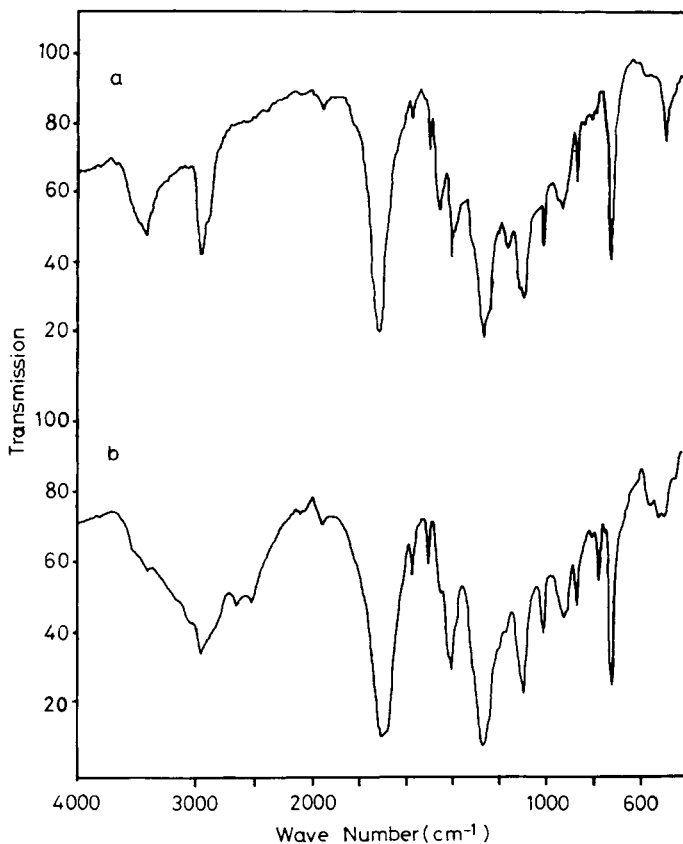
Fig. 3.   The IR spectra of A30 before and after heat treatment in oxygen at 170°C for 12 h.

in oxygen. Under such conditions, the carboxyl content increased to a greater extent for the copolyester with a higher BA content. The change of carboxyl content of A30 under heat treatment at 170°C in nitrogen is also shown in Figure 5. As described above, the degradation rate of A30 in nitrogen was much less than that in oxygen, so that there was no significant change in carboxyl content for A30 at 170°C in nitrogen within 12 h.

The NMR spectra of A30 before and after heat treatment in oxygen at 170°C for 12 h are shown in Figure 5. The assignments and relative peak area (integrated intensity) are shown in Table III. The relative peak areas of A30 before heat treatment were consistent with the chemical structure. From peak 1 and peak 4, or peak 2 and peak 3 (peak area ratio = 100 : 41), the mol % of adipic acid (based on diacids) was found to be 29 mol % and was close to the charged value.

The NMR spectrum of A30 after heat treatment showed additional small peaks (3.17, 3.05, and 2.58 ppm). Thus, the chemical structure was changed to some extent after heat treatment. Although only qualitative results could be obtained from these additional small peaks, the peak area ratio of peaks 2 and 3 gave interesting information. Peak 3 was due to the resonance of α-methylene protons in butylene unit linked with terephthalate unit, and peak 2 was due to that linked with adipate unit as shown in Figure 5. The ratio was equal
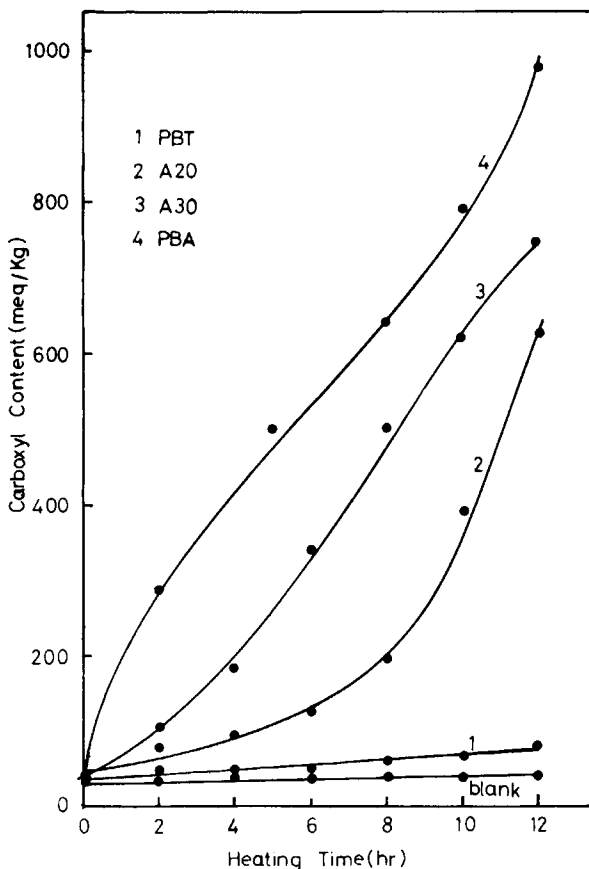
Fig. 4. The change of acid value of the polyesters vs. heating time at 170°C in oxygen (the blank curve shows the case of A30 in nitrogen).

to 100:41 for A30 before heat treatment and 100:29 for A30 after heat treatment. This indicated that more adipate units were lost after heat treatment. Thus, the butylene adipate unit was more readily attacked under such treatment, and thus the thermal degradation occurred at a faster rate as the BA content increased.

Comparing the molecular weight and carboxyl content data before and after heat treatment at 170°C in oxygen for 12 h, the sample with higher carboxy content had greater molecular weight loss. If the degradation had begun from the chain end, the molecular weight should have been changed to much less an extent for such values of carboxy content. Thus the degradation should be a main chain scission process. The NMR data indicated that the butylene adipate unit was more easily attacked, which is more evidence of a main chain scission process. For a degradation process only from chain ends, the thermal stability would have been less dependent on the composition.

T_g data are shown in Table I. T_g's of the two copolyesters are below room temperature. As described above, thermal degradation would occur at temperature lower than T_m in oxygen. For long-term application in air at room temperature, the copolyesters would be attacked by moisture and oxygen
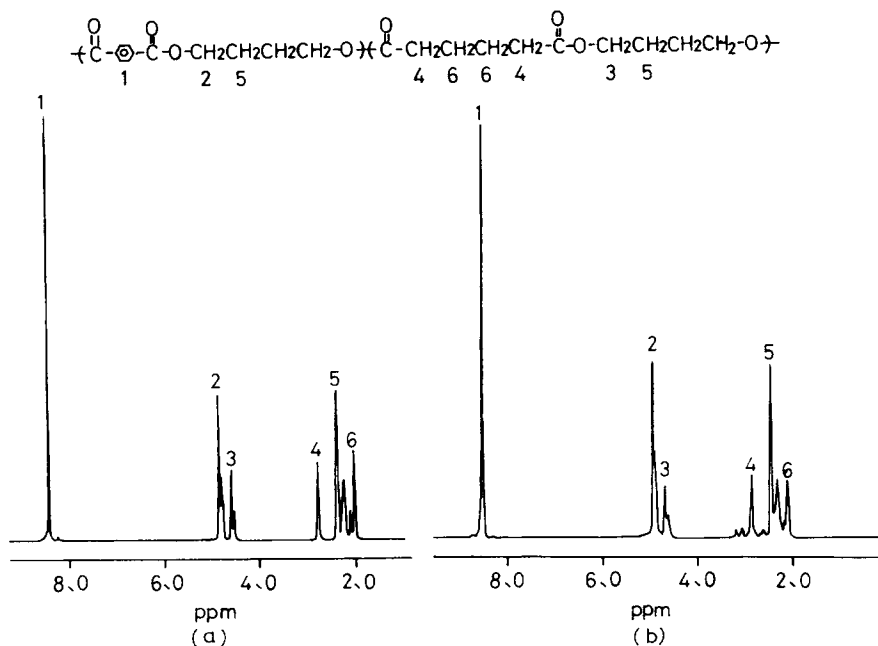
Fig. 5. The NMR spectra of A30 before (a) and after (b) heat treatment in oxygen at 170°C for 12 h.

TABLE III
The Assignment of Protons and the Relative Peak Area of A30
Before and After Heat Treatment in Oxygen at 170°C for 12 h

Protons (indicated in Fig. 5)	1	2	3	4	5	6
Chemical shift (ppm)	8.47	4.85 4.79	4.58 4.51	2.82	2.41 2.29 2.12	2.03
Relative peak area before heat treatment	100	100	41	41	143	41
Relative peak area after heat treatment	100	100	29	33	128	30

slowly, and degradation by hydrolysis and oxidation[5] would occur, so that embrittlement would be observed.

CONCLUSION

The thermal stability of the copolyesters of PBT and PBA was studied. In oxygen, the thermal stability of copolyesters was found to decrease as the BA content increased, as indicated by thermogravimetric analysis. At a temperature of 250°C in oxygen, the isothermal weight loss rate of the copolyesters decreased as the BA content increased. Much less weight loss was found for a copolyester at 250°C in inert gas; thus oxygen would enhance considerably the thermal degradation of the copolyesters. At 170°C (a temperature lower than

T_m) in oxygen, the copolyesters also showed significant degradation as indicated by the decrease of molecular weight and increase of acid number. The thermal stability under such a condition also decreased as the BA content increased. The analysis by NMR spectra showed that the adipate unit would be more readily attacked, and thus thermal stability of the copolyesters in oxygen in oxygen decreased as the BA content increased.

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