Aminolysis of Poly(ethylene terephthalate) in Aqueous Amine and Amine Vapor

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SYNOPSIS

Poly(ethylene terephthalate) fibers were aminolyzed in *n*-butylamine vapor and aqueous *n*-butylamine. Both aminolysis reactions resulted in weight loss, reduction of molecular weight and tensile strength, and some increase in density. After extraction in chloroform, weight loss of the aminolyzed samples increased due to removal of oligomers which had not been removed during aminolysis or rinsing. Differences between vapor and aqueous aminolysis are discussed in terms of previously described stages of aminolysis. Scanning electron photomicrographs revealed that the surface of vapor-aminolyzed fibers developed axial cracks while the surface of aqueous-aminolyzed fibers contained cracks in the radial direction. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Liquid phase aminolysis of poly(ethylene terephthalate) (PET) fibers has been studied by many researchers, as described in an extensive literature review published recently.[1] The amine attacks the PET, breaking the polymer chain. One end of the broken chain will have an amide group and the other a hydroxyl group. It is known that the attack occurs throughout the fiber; molecular weight and tensile strength decrease, degree of crystallinity increases, and cracks are present on the aminolyzed fiber surface. As a finishing treatment, aminolysis renders textiles made of PET fibers more wettable, thereby increasing garment comfort. The strength decrease makes fabrics less likely to pill. In addition, aminolysis can improve the handle and dyeability of PET.

Generally, aminolysis is carried out in aqueous media, the solution being anywhere from 30 to 90% water. After treatment, the textile is rinsed in a large volume of water to terminate the reaction and to rinse away oligomers formed during the reaction. Both the amine solution and contaminated rinse water must be treated before disposal such that aminolysis of PET requires a large amount of energy for effluent treatment.

The cost of aminolysis in terms of energy requirements for effluent treatment and environmental contamination risks could be decreased by carrying out the reaction in the vapor phase—that is, exposing the PET to neat amine vapor in a closed container rather than immersing the textile in aqueous amine solution. The entire volume of amine could be used to treat the PET since it would not become contaminated with oligomers of PET. Effluent, therefore, would be reduced; only rinsing would generate effluent, rather than both treatment and rinsing, as is the case with liquid phase aminolysis.

The mechanism and location of attack of the aqueous amine are well established, as are the effects of aqueous phase aminolysis on fiber and fabric performance. Very little work on vapor phase aminolysis has been reported. Ethylenediamine vapor has been used to aminolyze PET, although analysis was limited to the effects of temperature and vapor concentration on amine group incorporation and tensile strength.[2,3] Thus, the objective of the present study is further understanding of vapor phase aminolysis by investigating the effects of *n*-butylamine vapor on the fine structure of PET fibers and comparing the results with those obtained using aqueous *n*-butylamine.

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EXPERIMENTAL

Materials

Bright PET yarns were provided by Hoechst Celanese, Charlotte, North Carolina. All chemicals used were of reagent grade.

Procedures

Aminolysis

All aminolyses were carried out at 21°C in screw-top glass jars. For the vapor treatments, neat liquid *n*-butylamine was placed in a crystallizing dish in the bottom of the glass jar. A ribbed watch glass holding the PET yarns was placed on top of the crystallizing dish. The aminolyzed yarns were rinsed in methanol followed by distilled water until neutral to litmus paper. For the aqueous treatments, PET yarns were immersed in 56% (v/v) aqueous *n*-butylamine. Mild mechanical action was used to provide agitation. After aminolysis, the yarns were rinsed in distilled water until neutral to litmus paper. All samples were air dried and conditioned to constant weight at 21°C and 65% relative humidity (RH). Portions of selected conditioned aminolyzed samples were Soxhlet extracted in chloroform for 8 h, dried in a fume hood overnight, and conditioned to constant weight.

Weight Loss

Percentage weight loss was calculated using the conditioned weights before and after aminolysis. Total weight loss after extraction was based on the conditioned weight before aminolysis.

Density

A density gradient column maintained at 23°C and prepared with tetrachloroethylene and mixed xylenes was used to measured density.

Viscosity Average Molecular Weight (M_v)

Relative viscosity was measured at 25°C in a 0.4% (w/v) solution of phenol/1,1,2,2-tetrachloroethane (3/2 v/v). Billmeyer's equation (3) (ref. 4) was used to calculate intrinsic viscosity, and M_v was calculated using the Mark-Houwink equation[5]:

$$[\eta] = KM_v^a$$

where $K = 7.44 \times 10^{-4}$ dL/g and $a = 0.648$.[6]

Tensile Strength

The breaking loads of 25 single fibers were measured at 21°C and 65% RH using a table model Instron Universal Testing Machine. Gauge length was 2.5 cm, and the constant rate of elongation was 4 cm/min.

Scanning Electron Microscopy

Samples were mounted with silver paint on aluminum specimen stubs and coated with a gold/palladium alloy. Photomicrographs were taken using a JEOL JSM-35C scanning electron microscope operating in the secondary mode.

RESULTS AND DISCUSSION

Weight Loss and M_v

Before Extraction in Chloroform

After aminolysis, all samples lost weight (Table I). Initially, weight loss decreased somewhat with increasing aminolysis time. Weight loss occurs due to chain scission and formation of oligomers that are removed during aminolysis and/or the rinsing process. At short treatment times, chain scission did occur and increased with treatment time, as evidenced by the decrease in M_v. It appears that the formation and removal of oligomers at low weight loss (<1%) were masked by the incorporation of the butylamine molecule, which adds weight to the broken chain. As aminolysis continued, weight loss again increased with time, as the effect of oligomers being formed and removed overwhelmed the effect of the extra weight due to the addition of butylamine to the PET chain.

Weight loss of the samples treated in amine vapor leveled off at a rather low value of approximately 4%, while weight loss of the aqueous aminolyzed samples did not level off at the treatment times used in this study (Table I). The low weight loss of the vapor aminolyzed fibers, however, is associated with a very low M_v, indicating that oligomers were formed but not removed. The higher weight loss of the samples treated in aqueous amine suggests that oligomers formed during that treatment were able to be removed. During the aqueous treatment, the fibers were immersed in butylamine solution, allowing the aminolysis products to diffuse out of the fibers and dissolve in the solution. This was not possible in the vapor treatment, although rinsing removed some products.

After Extraction in Chloroform

Subsequent Soxhlet extraction in chloroform confirmed the presence of many oligomers within the vapor aminolyzed, rinsed, and conditioned samples, as the weight loss of these samples after extraction increased dramatically (Table I). The weight loss of the fibers treated in aqueous amine also increased after extraction, although to a much smaller extent, indicating that some oligomers remained in these samples as well. After extraction, the shapes of the weight loss–aminolysis time curves for both treatments are very similar (Fig. 1). Thus it appears that butylamine vapor and aqueous butylamine attack the PET chain at comparable rates.

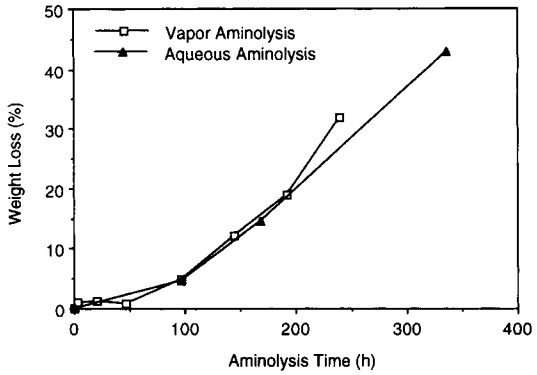

Figure 1 Weight loss–aminolysis time relationships for aminolyzed and extracted PET fibers.

Density

Density was measured as an indication of crystallinity. The density of the vapor-aminolyzed samples remained approximately constant until long treatment times, when a small increase was observed (Table II). These data, however, are likely obscured by oligomers remaining in the fiber. Chloroform crystallizes PET such that density measurements of extracted samples would not be useful. The density of the samples treated in aqueous amine increased at a shorter treatment time and eventually to a larger extent compared to the samples treated in amine vapor (Table II). This increase in density has been observed in other studies of aqueous aminolysis and is believed to be due to preferential attack and removal of amorphous regions.[1]

Tensile Strength

Tensile strength was measured before extraction in chloroform, as any oligomers present in the unex-

Table I Weight Loss and M_v of Aminolyzed PET Samples

Aminolysis Time (h)	Weight Loss (%)		M_v (g/mol)
	Before Extraction	After Extraction[a]	
Vapor Aminolysis			
Untreated	—	—	46894
3	0.53	1.08	46155
21	0.34	1.25	41693
47	0.16	0.76	37208
96	1.18	4.82	31059
144	2.65	12.13	11871
192	4.56	18.97	9143
240	4.07	31.76	2787
Aqueous Aminolysis			
Untreated	—	—	46894
4	0.45		41309
8	0.53		38485
16	0.33		34365
48	0.46		32045
96	2.48	4.72	26338
144	6.62		21082
168	9.76	14.50	19834
240	20.76		12315
336	36.48	42.88	6746

[a] Weight loss due to both aminolysis and extraction, based on conditioned weight before aminolysis.

Table II Density and Tensile Strength of Aminolyzed PET Samples

Aminolysis Time (h)	Density (g/cm^3)	Breaking Load (mN)	Relative Breaking Load
Vapor Aminolysis			
Untreated	1.399	327.1 (3.4)	1.00
3	1.398	320.3 (2.2)	0.98
21	1.397	273.7 (1.7)	0.84
47	1.399	217.7 (2.0)	0.67
96	1.397	151.3 (3.4)	0.46
144	1.399	82.2 (2.2)	0.25
192	1.403	61.8 (1.5)	0.19
240	1.405	— —	—
Aqueous Aminolysis			
Untreated	1.399	327.1 (3.5)	1.00
4	1.399	325.6 (2.1)	1.00
8	1.399	296.5 (2.5)	0.91
16	1.398	261.7 (2.5)	0.80
48	1.398	257.0 (1.7)	0.79
96	1.399	191.9 (2.5)	0.59
144	1.403	141.0 (1.7)	0.43
168	1.403	143.5 (0.9)	0.44
240	1.401	— —	—
336	1.415	— —	—

Standard error in parentheses.

tracted samples were not expected to be load-bearing material. The breaking load of both sets of samples decreased with increasing aminolysis time (Table II). For the vapor-aminolyzed samples, the decrease was more rapid. At very long treatment times, both aminolyses resulted in products too fragile to be tested.

When breaking load is considered as a function of M_v, it is revealed that at a given M_v, the fibers treated in butylamine vapor were weaker than those treated in aqueous butylamine (Tables I and II), suggesting different mechanisms for the two types of aminolyses. The interfibrillar extended-chain tie molecules are believed to be the strongest phase of melt-spun fibers[7]; the unoriented intrafibrillar amorphous regions of PET fibers are not considered to be the principal load-bearing entities. Chain scission of the tie molecules, therefore, would result in a more rapid decrease in breaking load at a given M_v compared to chain scission in the unoriented amorphous regions. It is thus hypothesized that in vapor aminolysis, preferential attack of the tie molecules occurred, while attack by the aqueous butylamine primarily occurred in the unoriented amorphous regions. It is likely that in aqueous aminolysis, the butylamine molecule hydrogen bonds with water, causing it to be too large to penetrate the relatively more ordered interfibrillar regions occupied by extended-chain tie molecules; such regions appear to be accessible to the smaller vapor butylamine molecule.

Stages of Aminolysis

Aqueous aminolysis has been described as a selective reaction, initially and more rapidly occurring in unoriented, amorphous regions of the PET fiber.[1] As many as four stages have been identified in aqueous aminolysis of PET depending on the amine used and the fine structure of the untreated fiber[8]: (1) attack of unoriented amorphous regions with little change in weight or crystallinity and a decrease in molecular weight; (2) continued attack of unoriented amorphous regions accompanied by increased weight loss; (3) attack of oriented amorphous regions and crystallite edges associated with a considerable decrease in tenacity; (4) slower attack of both crystalline and amorphous regions, as indicated by slowing of the reaction rate.

Stage 1 seems to be present for both types of aminolysis and appears to proceed through a treatment time of 47 or 48 h. Until these times,

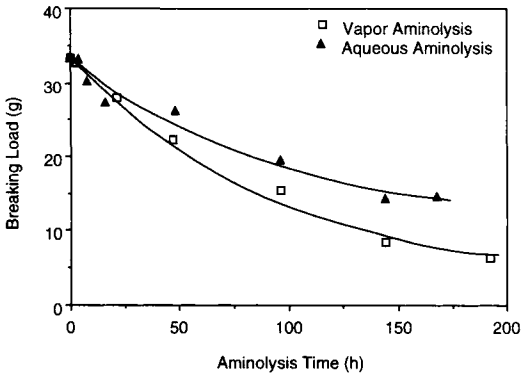

Figure 2 Breaking load–aminolysis time relationships for aminolyzed PET fibers.

weight loss was small before and after extraction, M_v decreased, and density remained approximately constant (Tables I and II). Beginning with the sample aminolyzed for 96 h in either butylamine vapor or aqueous butylamine and considering just weight loss data, stage 2 is apparent; weight loss increases rather steadily. However, the decrease in breaking load is also fairly steady over all aminolysis times (Fig. 2), making it difficult to assess the onset of stage 3. Collins et al.[8] are the only workers to associate considerable loss in strength with a separate stage. In the present work, stage 2 and stage 3 seem to occur simultaneously. Nonetheless, the vapor amine-treated fibers lost strength more quickly and showed a different breaking load–M_v relationship than the fibers aminolyzed in aqueous amine, as previously discussed. Stage 4 does not appear to be present in either set of samples, as there are no indications of the reaction slowing if the weight loss of the vapor-aminolyzed samples before extraction is not considered.

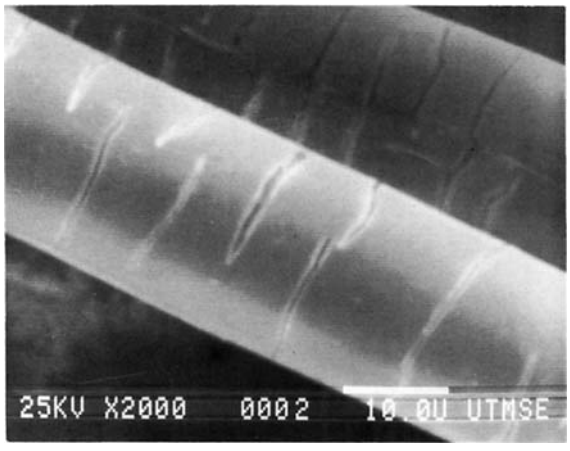

Figure 3 Scanning electron photomicrograph of PET fibers aminolyzed in aqueous butylamine for 144 h.

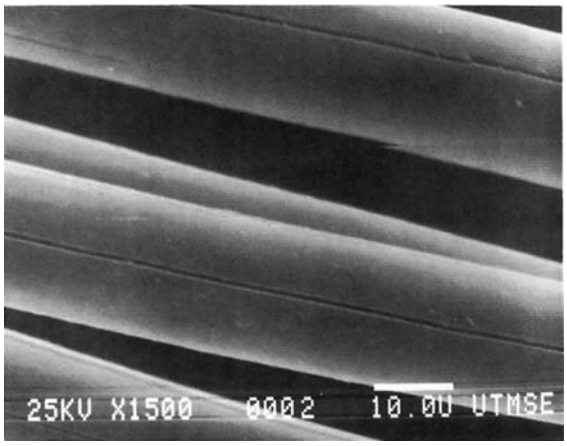

Figure 4 Scanning electron photomicrograph of PET fibers aminolyzed in butylamine vapor for 144 h.

Scanning Electron Microscopy

Scanning electron microscopy revealed different types of surface cracks for the two sample sets. Radial cracks were apparent on the fibers treated in aqueous butylamine (Fig. 3), consistent with previous studies of aqueous aminolysis.[1] In contrast, aminolysis in butylamine vapor resulted in axial cracks (Fig. 4). These oppositely oriented cracks provide further support of differences in the location of attack by the amine vapor versus the aqueous amine. Specifically, the unoriented amorphous regions hypothesized to be attacked by the aqueous butylamine have greater dimension in the direction of the fiber radius, while the extended tie molecules wherein attack by the vapor butylamine is believed to have occurred are oriented in the direction of the fiber axis. The relationship between crack geometry and tensile failure of these samples is considered elsewhere.[9]

CONCLUSIONS

To a degree, vapor aminolysis and aqueous aminolysis affect PET fibers similarly. Both treatments resulted in reductions in fiber weight, molecular weight, and tensile strength and an increase in density. Aminolysis in butylamine vapor resulted in the formation of many more oligomers remaining in the fibers after treatment compared to aminolysis in aqueous butylamine. Finally, differences in the geometry of surface cracks on the

aminolyzed fibers were observed. Further study of the effects of vapor aminolysis on the performance properties of fabric composed of PET fibers is planned.

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