Hydrolytic Degradation of Poly(1,4-butylene terephthalate-*co*-tetramethylene oxalate) Copolymer

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ABSTRACT: Experimentally synthesized poly(1,4-butylene terephthalate-*co*-tetramethylene oxalate) (PBT–PTMO) monofilaments were evaluated for hydrolytic stability in salt water (SW) and distilled water (DW) at temperature below and above glass transition temperature (T_g), along with commercially available poly(hexamethylene adipamide) (NY), poly(ethylene terephthalate) (PET), and polypropylene (PP) monofilaments. There was no decrease in mechanical properties in case of NY, PET, and PP in either DW or SW below their T_g. The breaking strength, ultimate elongation, and thermal shrinkage of the PBT–PTMO, however, decreased as the ageing time increased. Total strength loss occurred after approximately 300 days at 25°C in either DW and SW. This can be attributed to the chain scission that occurs in the PBT–PTMO copolymer chain. The poor hydrolytic stability of the PBT–PTMO may be attributed to the higher moisture regain. The salinity of water did not have a significant effect on the breaking strength loss of the materials. The mode of hydrolytic degradation of aged PBT–PTMO polymer was confirmed by the increasing generation of the acid carbonyl and hydroxyl groups with concomitant increasing consumption of ester groups, regardless of ageing conditions. Above T_g, the hydrolytic rate constant (k'_H, day^{-1}) of the PBT–PTMO, estimated by the rate of formation of acid carbonyl groups, is greater at a higher ageing temperature. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 921–936, 1999

Key words: hydrolytic degradation; PBT–PTMO copolymer; salt water; ageing and monofilament

INTRODUCTION

Since the 1960s, there has been an awareness that discarded plastic materials pose a threat to the environment, not only on land but also in the sea. Improper disposal of waste plastic from commercial fishing activities has become increasingly urgent since it is directly or indirectly responsible for the death of a number of sea animals and birds. Two major approaches to solving environmental pollution due to plastic waste have been proposed.[1–4] One involves product design using readily recyclable polymers; the other is the development of environmentally degradable polymeric materials, because the marine environment properties of photo- or biodegradability are of no benefit in fishing net, lines, or traps remaining under water. Development of hydrolytically degradable polymers, however, would be highly appropriate for marine applications.

In this study, the hydrolytic degradability of experimental PBT–PTMO copolymer in distilled water and salt water was examined in comparison to commercial homopolymers, poly(hexamethylene adipamide), poly(ethylene terephthalate), and polypropylene. The hydrolytic degradation of the PBT–PTMO was evaluated in terms of changes in

Table I   Characterizations of Monofilaments

	NY	PBT–PTMO	PET	PP
Linear density (d) (g/9000)	615 $\pm$ 22	1178 $\pm$ 28	997 $\pm$ 15	850 $\pm$ 67
Breaking loads (g)	4792 $\pm$ 145	3340 $\pm$ 127	4780 $\pm$ 117	5148 $\pm$ 234
Tenacity (g/d)	7.8 $\pm$ 0.4	2.9 $\pm$ 0.1	4.8 $\pm$ 0.1	6.1 $\pm$ 0.5
Ultimate elongation (%)	35.3 $\pm$ 2	24.2 $\pm$ 1	65.3 $\pm$ 3	25.7 $\pm$ 2
Moisture regain (%)[a]	4.1	6.1	0.4	0.05
T_g (°C)	55	28	69	−10
T_m (°C)	250	195	265	175
Weight loss (%)[b]	—	30.7	—	—

[a] 65% RH at 20°C.
[b] 700 days ageing in distilled water.

tensile properties, intrinsic viscosity, and thermomechanical properties. The mechanism of degradation due to ageing was confirmed via Fourier transform infrared (FTIR) measurement of end-group analysis. The effects of ageing temperature and saltwater on the rate of hydrolytic degradation of PBT–PTMO monofilaments were also studied.

EXPERIMENTAL

Materials

Monofilament PBT–PTMO was obtained from Professor Bernard Gordon III, Department of Materials Science and Engineering, Pennsylvania State University, University Park, PA 16802. The experimentally synthesized poly(1,4-butylene terephthalate-*b*-tetramethylene oxalate) PBT–PTMO monofilament is a block copolymer with composition ratio of 90 : 10 (*w/w*). The melting point and the glass transition temperature of PBT homopolymer are 225 and 40°C, respectively. The melting point and the glass transition temperature of PTMO (aliphatic polyester) used as a comonomer are 105 and 4.5°C, respectively.[5–7] The intrinsic viscosity of the PBT–PTMO polymer

measured at 30°C is 0.433 dL/g. Its melting point and glass transition temperature determined using the thermomechanical analysis are 195 $\pm$ 5 and 28 $\pm$ 5°C, respectively. Monofilaments of PP, PET, and NY, commonly used as fishing lines, were obtained from commercial sources. The characteristics of the monofilaments used are given in Table I. The repeating units of the polymers in this study are shown in Figure 1.

Ageing of Monofilaments

The average salinity of seawater is 3.4% (*w/w*) with 2.4% (*w/w*) sodium chloride as the major constituent.[8] In this study, water containing 2.4% (*w/w*) sodium chloride was prepared to simulate the effect of seawater on the hydrolytic degradation of monofilaments. The selected ageing temperatures, 25, 40, and 50°C, were below and above the glass transition temperature of the PBT–PTMO. 200-cm filaments of NY, PBT–PTMO, PET, and PP were aged in plastic vials containing 1-L of distilled water at pH 6.9 or 1 L of saltwater at pH 6.7, respectively, in constant-temperature ovens at 25°C, at various time intervals (days). Monofilament samples were also aged in the same media at 40 and 50°C in order to

-[-CH₂-CH(CH₃)-]ₙ-

poly(propylene)

-[-NH(CH₂)₆NHCO(CH₂)₄-CO-]ₙ-

poly(hexamethylene adipamide)

-[-O(CH₂)₂OCO-⬡-CO-]ₙ-

poly(ethylene terephthalate)

-[-O(CH₂)₄OCO-⬡-CO-]ₙ-b-[-O(CH₂)₄OCO-CO-]ₘ-

poly(1,4-butylene terephthalate-co-tetramethylene oxalate)

Figure 1   Repeating units of polymers.

Table II   Completely Randomized Block Design for Ageing of Monofilaments

| Bath Temp (°C) | Monofilaments NY, PBT–PTMO, PET, and PP | | | | | |
| | Distilled Water | | | Saltwater | | |
	25°C	40°C	50°C	25°C	40°C	50°C
Ageing time (days)	60	6	2	60	16	8
	120	10	6	120	24	10
	180	12	10	180	32	12
	210	14	—	210	—	—
	270	—[a]	—	270	—	—
	300	—	—	300	—	—

[a] A dash indicates "not aged."

delineate the effect of ageing temperature on the rate of hydrolytic degradation. The pH of the ageing solutions, both the distilled water and the saltwater, was not adjusted during the ageing process. As shown in Table II, a completely randomized block design was used for ageing of monofilaments. For this design, all the plastic vials were prepared at the same time and placed in an oven at a designated temperature.[9] Plastic vials were randomly removed from the oven according to the ageing time intervals. The aged monofilaments were dried in air at $21 \pm 1°C$ and 65% relative humidity (RH) for 24 h before further testing.[10]

Performance Evaluations

The control monofilaments, which were not aged either in distilled water or saltwater, were periodically examined by mechanical testing for signs of degradation during storage in air. For the mechanical testing, 10 specimens of each aged or control monofilament were tested to obtain the average value of breaking loads and ultimate elongation using an Instron tester (Model 1130, Instron Corp., USA) per ASTM Standard Test Method: D-2256-90.[10] The gauge length was 10

cm. Double-sided tape (Scotch™) was used to prevent slippage of the filament during testing.

Thermomechanical analysis (TMA) (Perkin–Elmer, Model TMS-1) was used to measure the deformation characteristics of the aged PBT–PTMO polymer on heating. In TMA, a 0.4-cm sample was placed between a vitreous silica platform and a movable silica rod and were subjected to a constant load. Its displacement (extension or shrinkage) was recorded as a function of temperature. The chart speed and the heating rate was 4 cm/min and 20°C/min, respectively. TMA curves, plotted with extension and shrinkage on the vertical axis and temperature on the horizontal axis, were obtained. The maximum thermal shrinkage, the glass transition temperature and the melting point (T_m) of the PBT–PTMO were derived from these curves,[11–13] providing a measure of the structural changes associated with the hydrolytic degradation.

The intrinsic viscosity of the aged and control PBT–PTMO monofilaments was determined by a viscometer (Cannon–Ubbelohde Four Bulb Shear Dilution Viscometer, 100 mL-S209, Cannon Instrument Co., USA) at $30 \pm 0.02°C$.[13–17] A known weight of the PBT–PTMO polymer sample was

Table III   Breaking Loads (g) of Monofilaments in Air

In Air	NY	PBT–PTMO	PET	PP
0 (control)	4792 ± 145 (100)[a]	3340 ± 127 (100)	4780 ± 117 (100)	5148 ± 234 (100)
180 days	4580 ± 45 (96)	3533 ± 97 (105)	4620 ± 84 (97)	5460 ± 69 (106)
300	4693 ± 71 (98)	3596 ± 32 (107)	4731 ± 21 (99)	5221 ± 31 (101)
Avg $\pm$ std	4668 ± 106 (97)	3489 ± 133 (104)	4710 ± 81 (99)	5271 ± 163 (102)

[a] Retention (numbers shown in parentheses) is the percentage of the initial value.

Table IV Ultimate Elongation (%) of Monofilaments in Air

In Air	NY	PBT–PTMO	PET	PP
0 (control)	35.3 ± 2 (100)[a]	24.2 ± 1 (100)	65.3 ± 3 (100)	25.7 ± 2 (100)
180 days	40.6 ± 3 (115)	24.8 ± 1 (102)	60.3 ± 4 (92)	28.2 ± 3 (109)
300	38.2 ± 1 (108)	23.9 ± 1 (99)	63.2 ± 2 (98)	26.7 ± 1 (104)
Avg ± std	38.0 ± 2 (107)	24.3 ± 1 (100)	62.9 ± 3 (96)	26.8 ± 1 (104)

[a] Retention (numbers shown in parentheses) is the percentage of the initial value.

dissolved in 10 mL of a phenol–1,1,2,2-tetrachloroethane (60/40, *w/w*) (Adlich Chemical Co.) mixture at room temperature in a stoppered test tube.[15,16] The tube was agitated gently until the polymer dissolved. No heat was employed during the sample preparation. Viscosity measurements were repeated until three timings agreed within ±0.2 s. The intrinsic viscosity [η] (dL/g) of the PBT–PTMO polymer was obtained from the limiting value of the specific viscosity (η_{sp}) extrapo-

lated to concentration (g/dL) at zero ($c = 0$),[13] as given in the following equation:

$$[\eta] = \lim_{c \to o} \frac{\eta_{sp}}{c} \tag{1}$$

FTIR measurements were made on PBT–PTMO samples in order to detect the consumption and generation of functional groups during ageing. A

Table V Breaking Loads (g) of Monofilaments Aged at 25, 40, and 50°C in DW

	NY	PBT–PTMO	PET	PP
Control	4792 ± 145 (100)[a]	3340 ± 127 (100)	4780 ± 117 (100)	5148 ± 234 (100)
@25°C				
60 days	4574 ± 110 (95)	3273 ± 68 (98)	4753 ± 123 (99)	5160 ± 447 (100)
120	4630 ± 47 (96)	3088 ± 96 (93)	4657 ± 97 (97)	5422 ± 41 (105)
180	4553 ± 76 (95)	2225 ± 198 (67)	4531 ± 263 (95)	5429 ± 41 (105)
210	4333 ± 115 (90)	1973 ± 66 (59)	4588 ± 110 (96)	5368 ± 257 (104)
270	4420 ± 44 (92)	628 ± 143 (19)	4355 ± 234 (91)	5042 ± 415 (98)
300	4262 ± 212 (88)	562 ± 98 (16)	4470 ± 124 (93)	5344 ± 152 (103)
Ave ± std	4509 ± 182 (94)	2167 ± 1213 (65)	4590 ± 152 (96)	5273 ± 154 (102)
@40°C				
6	4597 ± 96 (96)	3418 ± 107 (98)	4780 ± 100 (100)	5474 ± 106 (106)
10	4560 ± 95 (95)	3229 ± 94 (97)	4774 ± 100 (100)	5412 ± 105 (105)
12	4565 ± 93 (95)	3213 ± 93 (96)	4694 ± 96 (98)	5382 ± 104 (105)
14	4564 ± 95 (95)	3094 ± 90 (93)	4700 ± 100 (98)	5380 ± 99 (105)
16	4505 ± 94 (94)	2828 ± 82 (85)	4720 ± 98 (99)	5356 ± 104 (104)
20	4557 ± 95 (95)	2745 ± 80 (82)	4805 ± 100 (101)	5420 ± 105 (105)
30	4656 ± 160 (95)	1513 ± 44 (45)	4850 ± 101 (101)	5589 ± 108 (109)
36	4340 ± 114 (91)	198 ± 5 (6)	4522 ± 94 (95)	5336 ± 103 (104)
Ave ± std	4560 ± 115 (95)	2623 ± 1078 (78)	4736 ± 94 (99)	5388 ± 117 (104)
@50°C				
2	4442 ± 231 (92)	2772 ± 73 (83)	4530 ± 208 (95)	5340 ± 196 (104)
6	4877 ± 78 (102)	2404 ± 600 (72)	4951 ± 90 (104)	5758 ± 228 (112)
10	4489 ± 117 (94)	1657 ± 498 (50)	4596 ± 103 (96)	5091 ± 238 (99)
12	4457 ± 190 (93)	970 ± 487 (29)	4689 ± 76 (98)	5144 ± 292 (100)
14	4440 ± 89 (93)	380 ± 413 (11)	4569 ± 142 (96)	5298 ± 297 (103)
16	4475 ± 205 (93)	40 ± 123 (1)	4567 ± 200 (96)	5394 ± 199 (105)
Ave ± std	4565 ± 186 (95)	1739 ± 1537 (52)	4668 ± 151 (97)	5130 ± 227 (103)

[a] Retention (numbers shown in parentheses) is the percentage of the initial value.

Table VI   Breaking Loads (g) of Monofilaments Aged at 25, 40, and 50°C in SW

	NY	PBT–PTMO	PET	PP
Control	4792 ± 145 (100)[a]	3340 ± 127 (100)	4780 ± 117 (100)	5148 ± 234 (100)
@25°C				
60 days	4605 ± 120 (96)	3292 ± 43 (98)	4656 ± 350 (97)	4992 ± 183 (97)
120	4578 ± 68 (95)	2944 ± 159 (88)	4544 ± 371 (95)	5492 ± 132 (106)
180	3970 ± 97 (83)	1928 ± 151 (57)	4445 ± 60 (93)	5083 ± 396 (98)
210	4040 ± 294 (84)	1780 ± 178 (53)	4502 ± 110 (94)	5080 ± 268 (98)
270	3908 ± 82 (81)	509 ± 96 (15)	4386 ± 275 (91)	5071 ± 130 (98)
300	4220 ± 205 (88)	408 ± 85 (12)	4445 ± 295 (93)	5410 ± 74 (105)
Ave ± std	4301 ± 352 (90)	2028 ± 1235 (61)	4536 ± 137 (95)	5182 ± 190 (101)
@40°C				
16	4717 ± 136 (98)	2555 ± 888 (76)	4670 ± 194 (98)	5190 ± 409 (101)
24	4767 ± 136 (99)	2490 ± 589 (75)	4829 ± 130 (101)	5220 ± 439 (101)
32	4460 ± 151 (93)	110 ± 191 (3)	4743 ± 97 (99)	5450 ± 232 (106)
Ave ± std	4684 ± 152 (98)	2123 ± 1396 (64)	4755 ± 67 (99)	5252 ± 135 (102)
@50°C				
8	4633 ± 175 (96)	2356 ± 589 (71)	4700 ± 21 (98)	5576 ± 91 (108)
10	4467 ± 196 (93)	1110 ± 746 (33)	4651 ± 111 (97)	5328 ± 301 (104)
12	4614 ± 121 (96)	710 ± 550 (21)	4675 ± 90 (98)	5178 ± 429 (101)
16	4310 ± 155 (90)	280 ± 274 (8)	4683 ± 130 (99)	4943 ± 826 (96)
Ave ± std	4656 ± 182 (95)	1559 ± 1261 (46)	4697 ± 49 (98)	5234 ± 235 (101)

[a] Retention (numbers shown in parentheses) is the percentage of the initial value.

NIC Nicolet 5DXC FTIR spectroscope (Nicolet Instrument Corp., USA) programmed by MCO-LETDX V 5.07 was used with a 25 × 4 mm NaCl window plate (Perkin–Elmer). A dry casting film technique was used to prepared the FTIR sample.[13] A known weight of the aged PBT–PTMO monofilament was dissolved in phenol–1,1,2,2-tetrachloroethane (60/40, *w/w*) mixture at room temperature, and 40 μL of the solution was deposited directly on the NaCl plate. No heat was employed for sample preparation. The polymer films were dried in a vacuum oven at 20°C for 24 h to prevent interference of hydroxyl groups from moisture in the air and from the solvent, and to avoid any further degradation of the aged PBT–PTMO sample during drying. The average absorption spectrum of the PBT–PTMO measured in three different positions by rotating the NaCl window was obtained. Peaks of the spectrum were assigned to functional groups by reference to a correlation chart.[18] The absorption of the ester carbonyl group of PBT–PTMO monofilaments was identified at 1713 cm^{-1}. Acid carbonyl groups, hydroxyl groups and —C—H— in the backbone of PBT–PTMO polymer were identified at 1769, 3418, and 2963 cm^{-1}, respectively.[12,13,18,19] The functional group index (FGI) in the following equation was used to make the comparative quantitative determination.

$$\text{FGI} = \frac{\text{absorbance of examined group}}{\text{absorbance of —C—H—}} \quad (2)$$

Using the FGI avoids the necessity of obtaining a uniform film thickness. The absorbance value of —C—H— stretching in the backbone of the PBT–PTMO copolymer chain was used as the internal standard since its intensity is practically independent of the initial morphology.[13,19,20] It is also because the number of —C—H— bond remains unchanged as if chain scission occurs at the ester linkage of PBT–PTMO copolymer (i.e., acyloxygen cleavage).

RESULTS AND DISCUSSION

Strength and Viscosity

During the course of this study, the average values of breaking load and ultimate elongation of all control monofilaments kept under ambient conditions (in air) were periodically examined. They are given in Tables III (breaking load) and IV (ultimate elongation) and show essentially no change up to 300 days, i.e., no degradation occurred in the control monofilaments on storage in air. The breaking loads of monofilaments aged in

(a)

(b)

Figure 2 Breaking loads as a function of ageing time on monofilaments aged at 25°C in (a) DW and (b) SW.

both DW and SW aged at 25, 40, and 50°C are given in Tables V and VI, respectively. Figures 2(a) and (b) depict the retention of breaking load as a function of ageing time in DW [Fig. 2(a)] and SW [Fig. 2(b)] at 25°C. In Table V, the PP and PET monofilaments aged at 25°C retain more than 96% of their original breaking load over 300 days ageing, whereas NY retains 94%. These data indicate that hydrolytic degradation was negligible in these materials. The fluctuation of breaking loads is probably because of the existence of a distribution of chain lengths and, therefore, the degree of polymerization and molecular weight,

Table VII   Intrinsic Viscosity [η](dL/g) of PBT–PTMO Polymer

Control	DW 0.43249 (100)[a]	SW 0.43249 (100)
@25°C		
60 days	0.42557 (98)	0.41692 (96)
120	0.40740 (94)	0.37799 (87)
180	0.32090 (74)	0.28847 (66)
210	0.30274 (70)	0.27419 (63)
270	0.24868 (57)	0.18294 (42)
300	0.23743 (54)	0.16607 (38)
@40°C		
6	0.42989 (99)	—[b]
12	0.40610 (93)	—
16	0.35939 (83)	0.37064 (85)
24	—	0.29063 (67)
30	0.26944 (62)	—
32	—	0.25170 (58)
36	0.23830 (55)	—
@50°C		
2	0.40264 (93)	—
6	0.36804 (85)	—
8	—	0.32955 (76)
10	0.34901 (80)	0.32134 (74)
12	0.27030 (62)	0.30836 (71)
14	0.23873 (55)	—

[a] Retention (numbers shown in parentheses) is the percentage of the initial value.
[b] A dash indicates "not aged."

rather than polymer degradation. However, as shown in Figure 2(a), PBT–PTMO retains about 93% of its breaking strength during the first 120

Figure 3 Correlation between intrinsic viscosity and breaking loads on PBT–PTMO copolymer aged at 25°C.

days exposure, after which it shows a consistent decline up to 300 days (16%). After 180 days ageing, the PBT–PTMO monofilaments started to show brittleness. In fact, after 300 days, the PBT–PTMO monofilaments were so brittle that it was difficult to handle the specimens during tensile testing.

The effect of ageing in saltwater is illustrated in Figure 2(b). As in distilled water, the PP and PET largely retain breaking strength in saltwater. The nylon filament, however, shows a comparatively greater decrease in retained breaking load over the ageing period (90%). The PBT–PTMO shows a dramatic decrease in the breaking strength (12% at 300 days), just as in distilled water. The salinity of water does not seem to have significant effect on the breaking strength loss of this material (Tables V and VI). The breaking load retention of PBT–PTMO monofilament aged both in DW and SW at 25°C is approximately less than 5% after 300 days. Such a significant decrease in the breaking load of the PBT–PTMO

polymer directly implies that a hydrolytic degradation (chain scission) occurred during ageing.

The hydrolytic stability of the monofilaments aged at 25°C in both DW and SW was observed in the order of PP ≥ PET ≥ NY ≫ PBT–PTMO. The difference in the hydrolytic stability of the aged monofilaments can be explained in terms of water absorption ability of the polymers. For a significant hydrolytic degradation to occur in the polymer matrix, water must be adsorbed at the surface and then penetrate into the amorphous regions of the polymer structure. Once the water is absorbed into the amorphous regions, if water-reactive (hydrophilic) groups are present in the chains, hydrolytic degradation may occur.[17,21]

As shown in Figure 1, the hydrophobic nature of the PP and PET give very little affinity or access to water molecules; therefore, little polymer degradation occurs. The absence of polar groups in PP imparts high hydrolytic stability during the ageing. In the case of PET homopolymer, although hydrolyzable ester groups are

Table VIII   Ultimate Elongation (%) of Monofilaments Aged at 25, 40, and 50°C in DW

Control	NY 35.3 ± (100)[a]	PBT–PTMO 24.2 ± 1 (100)	PET 65.3 ± 3 (100)	PP 25.7 ± 2 (100)
@25°C				
60 days	44.9 ± 3 (127)	22.4 ± 1 (93)	60.8 ± 3 (93)	24.4 ± 3 (95)
120	46.1 ± 1 (130)	20.2 ± 1 (83)	61.4 ± 7 (94)	27.2 ± 3 (105)
180	39.6 ± 3 (112)	17.2 ± 2 (71)	63.6 ± 5 (97)	27.7 ± 2 (107)
210	38.8 ± 2 (109)	16.5 ± 1 (68)	62.1 ± 6 (95)	25.2 ± 4 (98)
270	45.8 ± 3 (129)	4.0 ± 1 (17)	60.8 ± 4 (93)	24.4 ± 3 (95)
300	40.7 ± 5 (115)	3.5 ± 2 (14)	63.4 ± 1 (97)	25.4 ± 2 (98)
Ave ± std	41.6 ± 4 (117)	15.4 ± 8 (63)	62.4 ± 2 (96)	25.7 ± 1 (100)
@40°C				
6	49.0 ± 2 (139)	25.0 ± 1 (103)	65.1 ± 4 (100)	26.0 ± 2 (101)
10	43.4 ± 4 (123)	22.7 ± 2 (94)	64.2 ± 2 (98)	26.9 ± 2 (105)
12	47.4 ± 4 (134)	22.5 ± 1 (93)	58.9 ± 3 (90)	28.3 ± 3 (110)
14	46.2 ± 3 (131)	21.9 ± 1 (90)	62.3 ± 4 (95)	26.1 ± 2 (102)
16	45.1 ± 5 (128)	20.5 ± 1 (85)	60.8 ± 2 (93)	26.5 ± 2 (103)
20	46.6 ± 3 (132)	20.2 ± 4 (83)	62.4 ± 3 (96)	25.7 ± 6 (100)
30	48.3 ± 4 (137)	3.1 ± 1 (13)	61.4 ± 3 (94)	25.5 ± 3 (99)
36	41.8 ± 4 (118)	0.9 ± 0.1 (4)	58.0 ± 5 (89)	25.4 ± 2 (99)
Ave ± std	44.8 ± 4 (126)	17.8 ± 9 (73)	62.0 ± 3 (95)	26.3 ± 1 (102)
@50°C				
2	45.7 ± 7 (130)	26.0 ± 1 (107)	62.1 ± 6 (95)	25.7 ± 3 (100)
6	44.0 ± 3 (125)	18.6 ± 3 (77)	63.3 ± 3 (97)	25.7 ± 3 (100)
10	44.2 ± 4 (125)	15.2 ± 6 (63)	61.5 ± 2 (94)	25.3 ± 5 (98)
12	47.1 ± 4 (133)	13.2 ± 7 (55)	62.4 ± 3 (96)	26.2 ± 4 (102)
14	46.3 ± 3 (131)	4.3 ± 5 (18)	59.6 ± 3 (91)	25.3 ± 3 (98)
16	45.6 ± 4 (129)	1.0 ± 3 (4)	59.1 ± 6 (91)	25.7 ± 2 (100)
Ave ± std	44.0 ± 4 (124)	14.6 ± 9 (60)	61.9 ± 2 (94)	25.4 ± 5 (99)

[a] Retention (numbers shown in parentheses) is the percentage of the initial value.

Table IX   Ultimate Elongation (%) of Monofilaments Aged at 25, 40, and 50°C in SW

Control	NY 35.3 ± 2 (100)[a]	PBT–PTMO 24.2 ± 1 (100)	PET 65.3 ± 3 (100)	PP 25.7 ± 2 (100)
@25°C				
60 days	39.7 ± 3 (112)	23.9 ± 1 (99)	65.3 ± 3 (93)	24.9 ± 2 (97)
120	46.4 ± 1 (131)	20.8 ± 1 (86)	60.7 ± 7 (97)	26.8 ± 1 (104)
180	33.5 ± 2 (95)	17.8 ± 1 (74)	63.1 ± 5 (96)	27.8 ± 2 (108)
210	42.3 ± 7 (119)	16.5 ± 1 (68)	62.7 ± 6 (94)	24.8 ± 4 (96)
270	34.3 ± 2 (98)	3.3 ± 1 (14)	61.3 ± 4 (96)	24.9 ± 3 (96)
300	40.9 ± 2 (116)	2.2 ± 1 (9)	63.1 ± 6 (97)	25.1 ± 2 (97)
Ave $\pm$ std	38.9 ± 5 (110)	15.5 ± 9 (64)	62.7 ± 1 (96)	25.7 ± 1 (100)
@40°C				
16	41.6 ± 5 (118)	19.2 ± 1 (79)	60.5 ± 4 (93)	22.4 ± 4 (87)
24	43.2 ± 3 (122)	14.7 ± 6 (61)	63.2 ± 3 (97)	23.8 ± 4 (93)
32	48.3 ± 6 (136)	0.9 ± 0 (3)	63.6 ± 4 (97)	23.7 ± 2 (92)
Ave $\pm$ std	42.1 ± 5 (119)	14.7 ± 10 (60)	63.1 ± 2 (97)	23.9 ± 1 (93)
@50°C				
8	49.0 ± 6 (139)	18.3 ± 3 (76)	61.5 ± 2 (94)	25.7 ± 2 (100)
10	47.0 ± 4 (133)	10.6 ± 7 (44)	59.2 ± 4 (90)	25.1 ± 2 (97)
12	50.8 ± 6 (144)	7.0 ± 6 (29)	63.3 ± 4 (96)	24.4 ± 4 (95)
16	46.5 ± 6 (132)	1.8 ± 7 (7)	62.4 ± 3 (95)	25.3 ± 1 (98)
Ave $\pm$ std	45.7 ± 6 (129)	12.3 ± 8 (51)	62.3 ± 2 (95)	25.4 ± 5 (98)

[a] Retention (numbers shown in parentheses) is the percentage of the initial value.

present, stiffening aromatic groups in the backbone significantly tend to reduce water accessibility to amorphous regions and, consequently, low water absorption (Table I). The amide groups in the main chain of NY homopolymer are susceptible to water attack and the relatively higher moisture absorption leads to the slightly greater hydrolysis. PBT–PTMO copolymer has a much high affinity for water due to hydrophilicity of the ester groups in the aliphatic hydrolyzable segments (PTMO). Also, a lower degree of crystallinity, due to the added flexibility in the chain (i.e., PTMO segment's disturbance to the chain regularity of PBT–PTMO) tends to increase the water absorption. PBT–PTMO monofilament has a higher moisture regain than the other materials studied in Table I. Hence, during ageing, the hydrolyzable aliphatic segments PTMO significantly influence the water absorption, which can accelerate its hydrolytic degradation.

For polydisperse polymers, the intrinsic viscosity $[\eta]$ is related to the molecular weight, given by the Mark–Houwink–Sakurada relation, $[\eta] = kM^a$, where k and a are constant as a function of temperature and solvent.[13] The molecular weight of linear polymers directly affects their properties, strength, and other mechanical properties generally increasing with increasing molecular weight.[13,15] The intrinsic viscosities of the PBT–PTMO monofilaments and their retention (%) over time are given in Table VII. Intrinsic viscosity (IV) decreased as the ageing time increased at all the temperature. The loss of strength of the PBT–PTMO monofilaments was presumably due to chain scission. This is confirmed by a plot of the intrinsic viscosity retention with retained breaking load (Fig. 3), showing that the reductions in tensile properties of aged monofilaments correspond with the changes in intrinsic viscosity.

Elongation and Thermal Shrinkage

Changes in ultimate elongation, that is, elongation at break are also indicative of some degradation process.[20] The ultimate elongations of monofilaments aged in both DW and SW aged at 25, 40, and 50°C are given in Tables VIII and IX, respectively. Figures 4(a) and (b) describe the change in the retention of the ultimate elongation due to the DW [Fig. 4(a)] and SW [Fig. 4(b)] ageing. Data show very small changes in the ultimate elongation for PP and PET monofilaments over 300 days ageing in both DW and SW at 25°C. This indicates that PP and PET monofilaments were very stable in both DW and SW and that hydrolytic degradation was negligible. In contrast, the ultimate elon-

(a)

(b)

Figure 4 Ultimate elongation as a function of ageing time on monofilaments aged at 25°C in (a) DW and (b) SW.

gation of NY shows an increase over the same ageing period. This difference in mechanical response of NY may be attributed to the swelling effect of water on the NY structure, resulting in the increased volume of the amorphous regions. Retention of the ultimate elongation for the PBT–PTMO monofilaments is less than 14% at 300 days. Such a decrease in ultimate elongation again indicates that polymer degradation occurs in the PBT–PTMO monofilament.

As discussed previously, hydrolytic degradation as measured by decrease in IV reduces the mechanical properties and eventually leads to

mechanical failure. Changes in thermomechanical properties of the aged polymer, such as shrinkage (contraction), extension, or melting point, may reveal structural changes in polymer matrix during the ageing. Shrinkage usually results from a relaxation of the stress introduced during previous processing, such as spinning and subsequent drawing.

On heating, the PBT–PTMO monofilament initially extended, and then an irreversible shrinkage gradually occurs due to the presence of the rubbery state (Fig. 5). The maximum thermal shrinkage (MTS) of the PBT–PTMO polymer may be used to determine the extent of polymer degradation. The MTS determined for PBT–PTMO samples aged at 25, 40, and 50°C at various ageing periods are presented in Table X. The MTS of a control PBT–PTMO monofilament was 17.9%. The MTS of the aged PBT–PTMO decreases as the ageing time and temperature increase. At 25°C, the MTS declined to 36% in DW and 30% in SW of its initial value after 270 days. This indicates that the recovery force, which is from the extended state to the original state, was weak due to the chain scission and, therefore, reduced the thermal shrinkage for the degraded polymer.

Figure 5 also shows the changes in thermal shrinkage as a function of temperature. The crystalline melting point (T_m), determined by the point at which the MTS occurred, was 195 ± 5°C. The melting point of aged PBT–PTMO monofilaments did not significantly change with ageing time or ageing temperature (Table X). The crys-

Figure 5 Thermomechanical curves of PBT–PTMO monofilament.

Table X Shrinkage and Melting Point of PBT–PTMO Monofilaments

Control	Shrinkage (%) DW	Shrinkage (%) SW	T_m (°C) DW
	17.9 (100)[a]	17.9 (100)	195
@25°C			
60 days	16.5 (92)	15.9 (89)	190
120	14.9 (86)	13.8 (77)	190
180	9.2 (51)	8.7 (48)	190
210	7.5 (41)	6.2 (34)	190
270	6.6 (36)	5.4 (30)	190
@40°C			
6	15.0 (83)	—[b]	190
10	13.3 (74)	—	190
12	11.6 (64)	—	190
14	10.0 (55)	—	190
16	9.5 (52)	10.3 (57)	190
20	9.8 (54)	—	190
24	—	5.8 (32)	190
30	5.6 (31)	—	195
32	—	3.2 (0.2)	190
36	1.2 (0.1)	—	190
@50°C			
2	13.5 (75)	—	190
6	9.87 (55)	—	190
8	—	9.37 (52)	195
10	3.45 (19)	5.85 (33)	190
12	3.63 (20)	4.10 (23)	190
14	3.76 (21)	—	190
16	3.52 (20)	2.27 (13)	185

[a] Retention (numbers shown in parentheses) is the percentage of the initial value.
[b] A dash indicates "not aged."

talline melting point (T_m) is given by $T_m = \Delta H_m / \Delta S_m$.[22] The melting point of a polymer crystal will be high with a high heat of fusion (ΔH_m) (i.e., high intermolecular forces) or if the entropy of fusion (ΔS_m) is small. In other words, chains that are strongly bonded in a crystal lattice have a high heat of fusion and will have a high melting point. In this respect, the melting point of the aged monofilament would only change if the degree of crystallinity changed during the ageing (degradation) process. Since degradation (chain scission) occurs only in the accessible amorphous region, it would not significantly change the degree of crystallinity of the aged monofilament. Therefore the melting point would be expected to remain unchanged, as observed in Table X. This is consistent with the argument that the chain scission in the amorphous region results in de-

creased molecular entanglement. The overall volume of the amorphous region and the associated free volume decrease as molecular chains decrease in size and tend to collapse. The strong correlation observed between the MTS and the ultimate elongation of the aged samples, as shown in Figure 6, would further support this argument.

Mode of Hydrolytic Degradation

Ester hydrolysis is the reverse of the mechanism involved in ester formation. It has been suggested that the hydrolytic degradation of polyester proceeds with the chain scission at the ester linkage,[21,23] involving several steps to form the alcohol and acid. The mechanism of ester hydrolysis of polyester [—RC(O)OR′—] proceeds via protonation of carbonyl oxygen. The protonation (H^+) makes the carbonyl group more susceptible to nucleophilic attack by water, which occurs at the electron-deficient carbonyl carbon of the ester, resulting in the substitution of the —OR′ group by the —OH of water. Consequently, acid [RC(O)OH] and alcohol [R′(OH)] groups are formed. FTIR spectroscopy was used to detect the ester carbonyl groups, acid carbonyl group and hydroxyl groups in order to confirm the above described mode of hydrolytic degradation in case of PBT–PTMO samples.

The FGI of functional groups of the PBT–PTMO are given in Table XI. FTIR spectra of the control and PBT–PTMO monofilaments aged at

Figure 6 Correlation between ultimate elongation and shrinkage of PBT–PTMO monofilament aged at 25°C.

Table XI   Functional Group Index (FGI) of PBT–PTMO Monofilaments

	Ester Carbonyl Group @1712.5 cm^{-1}	Acid Carbonyl Group @1768.5 cm^{-1}	Hydroxyl Group @3418.7 cm^{-1}
Control	0.8866 (100)[a]	0.2799 (100)	0.2095 (100)
@25°C & DW			
60 days	0.7073 (80)	0.2704 (96)	0.2433 (116)
180	0.4490 (51)	0.2832 (101)	0.2736 (130)
270	0.4664 (53)	0.3003 (107)	0.2718 (129)
300	0.4571 (51)	0.3038 (108)	0.2840 (135)
@25°C & SW			
60	0.3879 (44)	0.3016 (107)	0.2771 (132)
180	0.3796 (43)	0.3085 (110)	0.2876 (137)
270	0.3802 (43)	0.3292 (117)	0.2907 (138)
300	0.3757 (42)	0.3172 (113)	0.2921 (139)
@40°C & DW			
6	0.7227 (82)	0.2600 (92)	0.2361 (112)
10	0.6533 (74)	0.2894 (103)	0.2375 (113)
12	0.5497 (62)	0.2973 (106)	0.2462 (117)
20	0.5137 (58)	0.3181 (113)	0.2478 (118)
36	0.4893 (55)	0.3395 (121)	0.2960 (141)
@40°C & SW			
16	0.5403 (61)	0.3029 (108)	0.2620 (125)
24	0.4764 (54)	0.3272 (116)	0.2839 (135)
32	0.4739 (53)	0.3216 (114)	0.2930 (139)
@50°C & DW			
2	0.6458 (73)	0.2944 (105)	0.2280 (105)
10	0.4445 (50)	0.3057 (109)	0.2439 (116)
12	0.4071 (46)	0.3042 (108)	0.2441 (116)
14	0.3859 (43)	0.3087 (110)	0.3083 (147)
16	0.3439 (39)	0.3291 (117)	0.3198 (152)
@50°C & SW			
8	0.4203 (47)	0.3012 (107)	0.2675 (127)
10	0.4026 (45)	0.3113 (111)	0.2864 (136)
12	0.3815 (43)	0.3048 (108)	0.2850 (136)

[a] Retention (numbers shown in parentheses) is the percentage of the initial value.

25°C in DW for 180 days and 270 days are compared in Figure 7. These show that with increase in ageing time, the absorption of ester carbonyl groups at 1712.5 cm^{-1} decreases and the absorption of acid carbonyl groups at 1768.5 cm^{-1} increases. The consumption of the ester carbonyl groups along with the generation of hydroxyl and acid carbonyl groups on PBT–PTMO ageing at 25°C are shown in Figure 8(a) for DW and in Fig. 8(b) for SW. The replacement of ester group with carbonyl acid and alcohol groups is clear. This trend supports the mechanism[16,21,23,24] of hydrolytic degradation involving scission of ester linkage in PBT–PTMO copolymer. The correlation between the loss of ester carbonyl groups and intrinsic viscosity is shown in Figure 9, both implying the chain shortening occurring in hydrolysis, regardless of the ageing temperature.

Figure 7   FTIR spectra of PBT–PTMO copolymer.

(a)

(b)

Figure 8 Functional groups versus ageing time on PBT–PTMO copolymer aged at 25°C in (a) DW and (b) SW.

Figure 9 Correlation between ester carbonyl group and intrinsic viscosity of PBT–PTMO copolymer aged in DW.

Effect of Ageing Temperature

The breaking load and ultimate elongation at three distinct ageing temperatures, 25, 40, and 50°C, in DW and SW was also assessed for PP, PET, NY, and PBT–PTMO. Data in Tables V, VI, VIII, and IX show that the tensile properties of NY, PET, and PP monofilaments aged at 40 and 50°C in DW and SW were not significantly different from those aged at 25°C in DW and SW, indicating no significant effect of ageing temperature on NY, PET, and PP, at below T_g and the times studied. The change in intrinsic viscosity of the PBT–PTMO follows a similar trend; the decline in intrinsic viscosity is higher for samples aged at 40 and 50°C than at 25°C (Fig. 10). The breaking load of the PBT–PTMO also correlated with the intrinsic viscosity at these higher ageing temperatures (Fig. 11). The trend was similar for both distilled and saltwater conditions previously noted in Figure 4. It is also shown in Figure 12 that the effect of ageing temperature on the rate of the consumption of ester carbonyl group increased with increasing the ageing temperature.

The effect of ageing temperature on the rate of hydrolytic degradation can be explained in terms of the chain mobility and the facility of diffusion of water into the polymer matrix affected by the glass transition temperature.[11] The rise in the relative free volume with increasing temperature above T_g leads to the higher volume expansion coefficient in amorphous regions and, therefore,

Figure 10 Effect of temperature on intrinsic viscosity on PBT–PTMO copolymer aged in DW.

Figure 11 Correlation between intrinsic viscosity and breaking loads on PBT–PTMO copolymer aged in DW.

contributes to an increase in water absorption. Below T_g, NY, PET, and PP monofilaments have hydrolytic stability during ageing. The T_g of PBT–PTMO monofilament, determined using TMA, is $28 \pm 5°C$. The ageing temperatures, 40 and $50°C$ (above T_g), may contribute to hydrolytic instability of PBT–PTMO by increasing the accessibility of water molecule into the amorphous regions of PBT–PTMO polymer matrix. The probability of the ester hydrolysis reaction therefore increases since the rate of reaction is dependent on the concentration of the

Figure 12 Effect of temperature on consumption of ester carbonyl groups of PBT–PTMO copolymer aged in DW.

(a)

(b)

Figure 13 Fractional changes in carboxyl end groups of PBT–PTMO copolymer aged in (a) DW and (b) SW.

reactants (water and ester carbonyl groups available in amorphous regions). This accounts for the rapidly increase in the rate of hydrolytic degradation of PBT–PTMO monofilament at higher temperature.

The hydrolysis reaction of PBT–PTMO copolymer in this experiment was autocatalyzed by the carboxyl end groups of PBT–PTMO polymer[23] since no acid or base was added to the bath; and if a chain cleavage occurs at ester links and re-esterification is negligible as in the following,

Table XII   Average of Apparent Hydrolytic Rate Constant of PBT–PTMO Monofilaments

Ageing Temp (°C)	Rate Constant (k_H')(day^{-1})		
	DW	SW	Average
25	5.1538×10^{-4}	5.8121×10^{-4}	5.4830×10^{-4}
40	4.3403×10^{-3}	5.2820×10^{-3}	4.8115×10^{-3}
50	8.6711×10^{-3}	1.1013×10^{-2}	9.8421×10^{-3}
Average	4.5089×10^{-3}	5.6254×10^{-3}	

$$R—C \overset{O}{\underset{OR'}{\diagdown}}$$

$$+ H_2O \leftrightarrows R—C \overset{O}{\underset{OH}{\diagdown}} + R'O—H \quad (3)$$

the proposed ester hydrolysis reaction[23,24] can be described by the following overall rate equation;

$$d[COOH]/dt = k_H[COOH] [H_2O] [Ester] \quad (4)$$

The terms [COOH], [H$_2$O], and [Ester] are concentrations of carboxyl groups, water, and ester groups in the polymer, respectively, and k_H is the hydrolytic rate constant. As long as the extent of chain cleavage remains small, both [H$_2$O] and [Ester] can be assumed to be constant. Equation (4) can be simplified to a pseudo first-order kinetics,

$$d[COOH]/dt = k_H'[COOH] \quad (5)$$

where $k_H' = k_H [H_2O]$ [Ester], since water was present in such excess that its concentration remained practically constant during the degradation.[1,24,25] The integrated form of Eq. (5) describes the changes in the carboxyl end-group concentration with degradation time (t), as follows.

$$[COOH]_t = [COOH]_o \exp(k_H't) \quad (6)$$

The term [COOH]$_o$ is the initial carboxyl end-group concentration, [COOH]$_t$ is the carboxyl end-group concentration with degradation time (t), and (k_H') is the apparent hydrolytic rate constant of PBT–PTMO polymer. The apparent hydrolytic rate constants (k_H', day^{-1}) of the PBT–PTMO were obtained by taking logarithms of Eq. (6) [i.e., slop of ln([COOH]$_t$/[COOH]$_o$) versus time (t) in the following equation

$$\ln([COOH]_t/[COOH]_o) = k_H't \quad (7)$$

which are shown in Figures for DW [Fig. 13(a)] and SW [Fig. 13(b)]. The apparent hydrolytic rate constants, and their average values are summarized in Table XII.

Figures 13(a) and (b) show that the rate of formation of the acid carbonyl group is faster at a higher temperature than at a lower temperature, and the hydrolytic degradation (ester hydrolysis reaction) in this experiment was well fitted with the pseudo first-order kinetics since the simple regression showed a straight line. In Table XII, the average apparent rate constant (k_H', day^{-1}) is regardless of bath conditions, greater at a higher ageing temperature. Also, the result of F-test testing the null hypothesis (H_o) that there is no effect of bath condition (A), no effect of temperature (B), and no interaction (AB) on the apparent hydrolytic rate constant indicates the temperature significantly affects the rate of hydrolytic degradation of PBT–PTMO at 95% confidence level (Table XIII). However, the salt did not significantly affect the rate constant since the hypothesis was accepted. This means there were no significant differences in the hydrolytic degradation rate of PBT–PTMO monofilaments aged in either DW or SW. Schwartz and Sampathkumar[26] also has reported the salt-effect of saltwater immersion on the ultimate tensile strength of aramid braids (used for optical cable and fishing lines) aged in distilled water and saltwater for 30 days. There were no differences in strength of braids taken from either DW or SW.

Table XIII   2-Factor ANOVA on Hydrolytic Rate Constant of PBT–PTMO Monofilaments

Source	df^a	E of Sum of Square	E Mean of Square	F-test^b
DW & SW (A)	1	1.8709×10^{-6}	1.8709×10^{-6}	2.8
Temp (°C) (B)	2	8.6572×10^{-5}	4.3286×10^{-5}	65.7^c
AB	2	1.3181×10^{-6}	6.5907×10^{-7}	1
Error^b	2	1.3181×10^{-6}	6.5907×10^{-7}	—

^{a} df is the abbreviation for the degree of freedom (df).
^{b} By the expected mean square (EMS) rule.
^{c} Significant at a 95% confidence level.

CONCLUSIONS

The effect of hydrolytic degradation of experimentally synthesized PBT–PTMO monofilament aged at various times and temperatures was evaluated in both DW and SW and compared with that of PP, PET, and NY. Results indicated that there was no significant hydrolytic degradation in case of PP, PET, and NY in either DW or SW. The tensile properties of PBT–PTMO monofilament, however, decrease as the ageing time increases. This can be attributed to the chain scission that occurs in the PBT–PTMO copolymer chain. The consequent decrease in intrinsic viscosity and loss of ester groups were recorded. A higher moisture regain may contribute to the poor hydrolytic stability, due to the presence of a flexible and hydrolyzable segment of poly(tetramethylene oxalate) in the PBT–PTMO block copolymer and, therefore, significantly increases its susceptibility to hydrolysis. Thermomechanical analysis (TMA) spectra did not show any change in the melting point of aged PBT–PTMO monofilament. This is consistent with the discussion that the hydrolytic degradation occurred only in the amorphous regions of the polymer matrix.

The mode of hydrolytic degradation of aged PBT–PTMO copolymer was confirmed from the formation of hydroxyl and acid carbonyl groups simultaneous with the ester carbonyl groups. The acid carbonyl and hydroxyl groups increased with increasing consumption of ester groups, regardless of ageing conditions. The FTIR results clearly show that the chain scission of PBT–PTMO copolymer at the ester linkage is the basic model of degradation during hydrolysis. The ageing temperature has a significant effect on the hydrolytic degradation rate at temperatures above T_g. The apparent hydrolytic rate constant (k'_H, day^{-1}) of the PBT–PTMO, estimated by the rate of formation of acid carbonyl groups, is greater at a higher ageing temperature. No significant effect of ageing temperature on the rate of degradation of PP, PET, and NY was observed at below T_g and the times studied.

It has been noted that it takes more than 50 or 100 years (total strength loss) for most thermoplastic polymer to be degraded under normal environmental conditions. The study indicates that in air, the PBT–PTMO monofilament has good mechanical stability. On immersion in water, the stability of the PBT–PTMO dramatically decreased due to hydrolytic chain scission. Total strength loss occurred after about 300 days at 25°C either in DW and SW. The use of hydrolytically degradable PBT–PTMO monofilament in marine applications can significantly mitigate environmental pollution currently caused by nondegrading plastic materials.

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