Characterization of Aminated Poly(ethylene terephthalate) Surfaces for Biomedical Applications

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ABSTRACT: Aminated poly(ethylene terephthalate) (PET) surfaces were characterized for their use as substrates for the attachment of biologically active molecules. Amines of different chain lengths, tetraethylenepentamine, triethylenetetramine (TTETA), and diethylenetriamine (DETA), were investigated. X-ray photoelectron spectroscopy was used to show that each amine introduced a comparable amount of nitrogen (5 atom %) to the PET surface. Contact-angle and titration analyses indicated that the amination reaction was not restricted to the surface, with evidence of diffusion into the polymer by TTETA and DETA. As a result, degradation of the PET substrate, evidenced by mass loss, was observed to occur. Annealing of the PET films before amination at a temperature of 200°C reduced the extent of degradation without producing a decrease in the nitrogen content produced.
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Key words: annealing; biomaterials; polyesters

INTRODUCTION

Poly(ethylene terephthalate) (PET) has been demonstrated, in a series of long-term studies, to be biocompatible.[1] Although PET possesses the appropriate mechanical properties for use as a biomedical material, in use as a biomaterial substrate, it does have the drawback of poor chemical reactivity toward biologically active molecules such as proteins and growth factors. PET has a fairly inert surface and does not contain any functional groups that are available to react with protein molecules, so very little attachment of protein molecules is expected to occur on a virgin PET surface. To improve the attachment of biomolecules, the PET surface must be chemically modified.

In this study, nitrogenous functional groups were used to treat PET surfaces. The effectiveness of protein attachment to aminated surfaces has been demonstrated by a number of authors.[2–8] The initial modification step in other reported methods has often involved the attachment of nitrogenous functionalities via plasma and silane treatments. Although these methods have been quite effective in introducing nitrogen-based groups to the PET surface, they are quite complex and require specialized reaction conditions or expensive apparatus. In this study, we concentrated on the development and optimization of a simpler method of attaching nitrogenous groups to the polymer surface through the use of amine reagents.

One approach to the introduction of nitrogen-containing groups to the surface of PET is aminolysis, that is, the formation of amide groups by the reaction of a polyester with an amine. This method has already been identified as a simple approach to the surface modification of PET.[9–12] Unacceptable degradation to the PET, as a result of the treatment, was observed when primary amines were used. As a result, multifunctional amines have been used by some researchers to reduce the severity of the aminolysis reaction.[13,14]

A study in our laboratories demonstrated that nitrogenous groups can be introduced into the surface of PET films with tetraethylenepentamine (TTEPA) and that the effectiveness of the treatment improves with reaction time.[15] However, characterization of the treated films demonstrated that some degradation could still be observed in the film with the use of TTEPA. Environmental scanning electron microscopy (ESEM) data suggested that the amine reagent attacked the PET at the lamellae boundaries where tie molecules were present.[16] Thus, if the morphology could be suitably altered to reduce the amount of space between the lamellae, the extent of degradation and subsequent change in the mechanical properties should be minimized. One method that may be used to modify the morphology of PET is preannealing.[17] The effect of different annealing treatments on the PET film before treatment with TTEPA is reported in this article. Once an effective thermal treatment of PET before the reaction with amines

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was established, the effect of treatment with two other multifunctional amines with different chain lengths, triethylenetetraamine (TTETA) and diethylenetriamine (DETA), was also examined.

The extent of amination by TTEPA at the surface of PET was successfully identified in an earlier study with a range of techniques.[16] In this study, X-ray photoelectron spectroscopy (XPS) was used to determine the amount of nitrogen introduced to the PET surface as a result of the amine treatment. The types of nitrogen-containing groups incorporated were also determined. Dynamic contact analysis (DCA) was used to assess changes to the acid–base properties of the PET as a result of the different treatments, which reflected the effectiveness of the treatment. In addition, the degree of surface amination was compared with that of the bulk polymer with a titration method.

EXPERIMENTAL

Materials

Film samples (40 mm × 50 mm) with a thickness of 100 μm (Goodfellows, Cambridge, England) were cut from biaxially oriented PET film. The preannealing of PET films (25 mm × 25 mm) was carried out under a small flow of nitrogen for short annealing times or in a vacuum oven at 1 Torr for all other samples. After annealing, the films were allowed to cool for several minutes in a reduced oxygen environment. Samples were washed before surface treatment in a shaking water bath with a 0.1% aqueous solution of Teepol Gold detergent (Shell Corp., Melbourne, Australia) at 60°C for 30 min and then washed with distilled water for 10 min; this was followed by a wash with ethyl acetate (analytical-reagent-grade; BDH Chemicals, Poole, England) at 60°C for 30 min. The samples were dried to a constant weight in a 60°C oven before they were weighed. No swelling of the film was observed at any time during the washing procedure.

Amination of the PET films

Cleaned PET films were separately treated with TTEPA (technical-grade; Sigma Aldrich, Milwaukee, WI), TTETA (technical-grade; Sigma–Aldrich), and DETA reagents (98%; Sigma–Aldrich).[14] The washed PET was immersed in the preheated amine reagent held at 85°C for the required reaction time (15–210 min). The aminated samples were washed in three 500-mL aliquots of methanol (analytical-reagent-grade; BDH Chemicals) for 90 min and then dried at 60°C for 30 min before they were weighed.

XPS

The XPS spectra were recorded with a Vacuum Generators XPS system (Sussex, England). The X-rays were generated from a monochromatic Al Kα source and operated at 10 kV (10-mA emission current). A takeoff angle of 45° relative to the sample surface was used for all analyses. The pressure in the analyzer chamber was of the order of 1.33×10^{-6} Pa. Low-resolution scans were collected at an energy of 50 eV with a step size of 0.5 eV. High-resolution scans were collected at an energy of 20 eV with an increment of 0.05 eV. The films were mounted onto the sample probe with double-sided tape. The spectra were curve-fit with a Gaussian program function with Microcal Origin software (Northhampton, MA), and the atomic percentage values were calculated with integrated peak areas. Replicate analyses showed that the error in these values was on the order of 0.4%.

DCA

DCA measurements were carried out with a Cahn DCA-322 dynamic contact-angle analyzer (Cahn Instruments). The films were tested with three probe liquids: double-distilled water, formamide (>99.5%; Sigma–Aldrich, Madison, WI), and diiodomethane (99%; Sigma–Aldrich). A stage speed of 220 μm/s was used to immerse and remove the samples from the probe liquid. Contact angles were determined according to a method described in the literature,[16] and the values were corrected according to Adamson.[18] The contact angles reported are an average of four measurements for each probe liquid. Surface tension component theory was also applied to the contact-angle data according to the method described Nissen et al.[16]

Determination of the total nitrogen content

The total N content (the atoms available for protonation, not necessarily all of the N in the film) of the films was determined with back-titration with 0.01*M* aqueous HCl. The titrations were carried out immediately after drying. The samples (25 mm × 25 mm) were added to 20 mL of 0.01*M* HCl and allowed to react for 2 h at room temperature. After the reaction, the mixture was titrated against 0.01*M* NaOH with a methyl red indicator. The N content reported is the average of six measurements across two films.

ESEM

ESEM was used to establish changes in the surface morphology of the PET samples. ESEM micrographs were obtained with a Phillips XL 500 ESEM instrument, operated in the wet mode with a chamber

pressure of 1 Torr. An accelerating voltage of 8 kV and a spot size of 4 were used to collect the images.

Profilometry

The surface profiles of the samples were obtained with an Alpha-Step 100 Profilometer (Tencor Instruments, Mountain View, CA). A minimum of 10 profiles were collected for each sample.

RESULTS AND DISCUSSION

Annealing effects

The mass loss values obtained for PET annealed at five temperatures for 10 min and 10 h before treatment with TTEPA are listed in Table I. At 10 min, the mass loss values obtained at 120 and 140°C were on the order of twice that for nonannealed films, whereas films annealed at 160 and 170°C were comparable to that for a film without annealing. The sample annealed at 200°C showed the lowest mass loss, which was half that obtained for nonannealed films.

The mass loss results may be connected to the nature of the PET morphology produced on annealing. Pecorini and Hertzberg[17] investigated the morphology of PET annealed at different temperatures, and they observed that at lower temperatures, PET crystallized according to a Hoffman Regime III morphology. In the Regime III morphology, the crystals form when the polymer chains freeze into place due to a combination of fast nucleation rates and slow diffusion of the chains. Because very few molecules are folded, a greater number of tie molecules are present, which increases the amorphous volume between the lamellae. We propose that at annealing temperatures of 120 and 140°C for 10 min, PET crystallized according to a Hoffman Regime III morphology, which resulted in a greater number of tie molecules. ESEM was used to show that TTEPA reacts with PET at the tie molecules present between the crystalline lamellae.[16] It appeared that at 120 and 140°C, there were a greater number of sites for the TTEPA reagent to react with the film, which resulted in a greater mass loss than for films that were not annealed.

TABLE I
Mass Loss Measurements for the Annealed Films

Annealing temperature (°C)	Mass loss (%)	
	10 min	10 h
120	5.1 ± 1.5	0.9 ± 0.2
140	3.7 ± 0.4	0.6 ± 0.2
160	1.7 ± 0.5	0.8 ± 0.1
170	1.9 ± 0.7	2.1 ± 0.3
200	1.0 ± 0.1	2.0 ± 0.1
Reference	1.9 ± 0.4	1.9 ± 0.4

Pecorini and Hertzberg[17] also reported a transition from Regime III to Regime I/II morphology at approximately 165°C. For Regime I/II morphology, the crystallization of PET is limited by low nucleation rates so crystalline structures are produced as a result of chain folding. Under such conditions, an entire polymer chain can fold into a single lamella. As a result, films crystallized in this range contain a higher degree of crystallinity with fewer tie molecules between the lamellae. Needles and Park[19] also noted that the crystallites in PET fibers with a Regime I/II morphology were much smaller, which resulted in less accessible space between the lamellae. At 160°C, the temperature of the PET film in this study was close the Regime III transition temperature, so it is possible that this film contained regions that contained fewer tie molecules as a result of molecular folding. Hence, the mass loss for these samples was expected to be lower than that for films annealed at 120 and 140°C for 10 min. The film annealed at 170°C was also predicted to contain both morphologies, and so a similar mass loss value was obtained for films treated at the higher temperature. The fact that the mass losses obtained for these samples was the same as that for a supplied film suggests that the original PET contained a mixture of Regime I/II and III morphologies.

The annealing of samples at 200°C for 10 min was predicted to produce a film predominantly containing a Regime I/II morphology and so containing a greater number of folded molecules and very few tie molecules between the lamellae. The mass loss for films annealed at 200°C was approximately half that of the supplied films, as these films contained the fewest number of reaction sites. This result also suggests that the original film contained regions with Regime III morphologies.

For the samples annealed for 10 h, the samples annealed at 120, 140, and 160°C had much lower mass loss values than the supplied film. According to the Hoffman regime, these samples would be expected to contain the most tie molecules and, therefore, exhibit the greatest mass loss. ESEM imaging (not shown) of films annealed at these temperatures showed crystals that were much longer than those of the supplied film (420 μm compared with 180 μm in the supplied film). Thus, the amount of space available for reaction with TTEPA was reduced, which resulted in fewer reactions and a lower degree of mass loss. No obvious etching of the crystal boundaries in these samples was observed for the profilometry analysis, which suggested that the extent of amine diffusion had also decreased.

At annealing temperatures of 170 and 200°C, the mass loss showed a value slightly greater than that

TABLE II
XPS Surface Composition Values (±0.4 atom %) for the Annealed PET Films

Annealing temperature (°C)	C (%)		N (%)		O (%)	
	10 min	10 h	10 min	10 h	10 min	10 h
120	73.7	73.7	4.1	4.1	22.2	22.2
140	74.5	74.5	4.0	4.0	21.5	21.5
160	71.3	71.3	4.6	4.6	24.0	24.0
170	74.7	74.7	3.8	3.7	21.5	21.6
200	75.4	72.5	4.5	4.0	21.1	23.5
Reference	75.7	75.7	3.3	3.3	21.2	21.2

obtained for the supplied film. At these temperatures, films were predicted to contain fewer tie molecules and so should have produced a lower mass loss. Goschel[20] reported that there was significant increase in the molecular order of PET films at temperatures above 160°C. At 170 and 200°C, the length of the crystals decreased to a value similar to that of the supplied film (210 μm), which resulted in a greater extent of reaction and mass loss.

Table II lists the XPS results obtained for samples annealed at five temperatures for 10 min and 10 h, followed by treatment with TTEPA. The atomic percentage of nitrogen introduced into the surface appeared to be independent of the annealing temperature. These results suggest that either the same number of TTEPA molecules reacted with the PET film at all of the annealing temperatures investigated or that they reacted in a different manner so as to cause changes in the degree of mass loss. Another possibility is that there was a more extensive reaction between TTEPA and the PET samples annealed at 120 and 140°C, with any extra nitrogen introduced at levels deeper than that detected by XPS. As a result of the increase in the number of tie molecules in the films annealed at 120 and 140°C, the TTEPA molecules may have looped and reacted with another tie molecule instead of branching out of the film. Thus, with these films, one molecule of TTEPA reacted with two tie molecules, whereas a TTEPA molecule reacted with one tie molecule in the supplied film. Pittman et al.,[21] who carried out a study of chemically modified carbon fibers with TTEPA, found that substantial looping of the amine occurred at the carbon fiber surface. Films in which TTEPA molecules have folded would be expected to contain a similar amount of nitrogen to a twofold increase in mass loss. If a greater number of TTEPA molecules did react with films annealed at 120 and 140°C, the extra nitrogen atoms could have been present at a depth beyond the scope of XPS and could have resulted in a similar composition to that obtained for the supplied film. It has been shown that the TTEPA reagent diffused into the PET film, with profilometry measurements showing that the amine penetrated several micrometers into the film, 1000-fold deeper than the sampling depth of XPS.

The fact that the composition of the annealed films investigated was similar to that of films that were not annealed suggests that annealing at high temperatures such as 200°C did not influence the degree of reaction occurring between PET and TTEPA at the film surface. Therefore, a Regime I/II morphology could be used to minimize film degradation while maintaining the level of surface nitrogen introduced. The annealing at temperatures between 120 and 200°C for 10 h did not influence the surface nitrogen content, and the surface composition of the annealed film was not significantly different than that of the supplied film. Thus, any changes that occurred within the crystalline structure of the PET as a result of annealing did not appear to affect reactions at the outermost layer.

The results of contact-angle analysis carried out on the annealed films are shown in Table III. The data presents the water-advancing contact-angle values obtained for films annealed for 10 min and 10 h followed by treatment with TTEPA for 120 min and for the supplied film. Annealing at different temperatures over 120–200°C for 10 min had no effect on the advancing contact angle. This demonstrated that the degree of polarity introduced into the PET film by the chemical attachment of TTEPA was reasonably constant across the range of annealing temperatures investigated. Because contact-angle analysis could not detect TTEPA molecules that diffused into the PET film, this trend implies that the same degree of reaction occurred between PET and TTEPA, regardless of pretreatment, and so the number of TTEPA molecules present was the same for all of the samples investigated. Furthermore, the fact that the advancing contact angle for each of the annealed samples was the same as that for the supplied film showed that annealing did not influence the total extent of reaction. Hence, one could minimize the degree of mass loss by annealing at higher temperatures (200°C) while maintaining the polarity content.

The water contact angle of the films annealed at 120, 140, and 160°C for 10 h was a few degrees higher than that obtained for the aminated film and

TABLE III
Contact Angles for the Annealed PET Films

Annealing temperature (°C)	Water contact angle (°)	
	10 min	10 h
120	70.5 ± 1.7	76.7 ± 2.0
140	75.2 ± 2.4	77.9 ± 1.8
160	68.9 ± 2.1	80.8 ± 0.3
170	72.1 ± 1.8	72.9 ± 1.5
200	70.1 ± 1.2	71.9 ± 1.8
Reference	73.7 ± 0.8	81.9 ± 0.9

TABLE IV
Total Nitrogen Content for the Annealed Films

Annealing temperature (°C)	Nitrogen content (μg/cm^2)	
	10 min	10 h
120	25.0 ± 4.5	3.7 ± 1.4
140	22.8 ± 3.7	3.8 ± 1.4
160	17.8 ± 2.9	3.1 ± 1.1
170	23.2 ± 4.6	6.1 ± 1.3
200	28.2 ± 2.3	6.7 ± 1.0
Reference	26.6 ± 4.3	26.6 ± 4.3

was close to that measured for the reference film. At 170 and 200°C, the water contact angle of the aminated films decreased to a value obtained for the reference film. The lower water contact angle suggested that at a higher annealing temperature, there was a greater degree of reaction between TTEPA and PET. This demonstrated that the crystal structure produced by annealing at 170 and 200°C for 10 h was similar to that present in the untreated film.

To establish whether annealing influenced the mass of nitrogen present, the annealed samples were titrated with HCl. The amount of nitrogen measured by titration reflects the total amount present, not just the level of surface nitrogen. Table IV lists the nitrogen mass detected per unit area of film for the annealed films. The titration results show that none of the short annealing treatments carried out appeared to have significantly affected the total amount of nitrogen detected. Furthermore, the different kinds of crystal morphologies present in the annealed samples did not appear to affect the nitrogen mass introduced into the PET. Although the value obtained for the film annealed at 160°C was slightly lower than those obtained for the other annealed samples, it could not be differentiated. This suggests that the changes in crystal morphology introduced from a 10 min annealing treatment did not affect the number of TTEPA molecules that reacted with the film. Thus, an annealing step at 200°C before amine treatment could minimize the degree of degradation and maintain the surface and total nitrogen content of the modified film.

For PET films subjected to long annealing treatments, there was a more than sixfold decrease in the total nitrogen content for those samples annealed at 120, 140, and 160°C compared with the supplied film. These results agree with both the mass loss and contact-angle analysis. The fact that the total amount of nitrogen detected by titration was lower in the samples suggests that the overall degree of amination decreased despite the lack of effect on the surface reaction. A nearly twofold increase in the nitrogen content was observed in samples annealed at 170 and 200°C, which was also in agreement with the mass loss and contact-angle data and supported the finding of a greater extent of amination in these samples.

Amination with TTETA

Figure 1 illustrates the mass loss obtained for PET films treated with TTETA for times up to 120 min. Similar to the TTEPA treatment, the relationship between mass loss and reaction time was nonlinear with the amination reaction occurring via several stages. The onset of the different stages could be determined from reaction-rate calculations. At a reaction time of 30 min, the reaction rate reached 0.015% mass loss/min and remained constant up to a reaction time of 60 min. For the following 30 min, the reaction rate almost doubled, increasing to 0.026%/min. This increase in reaction rate indicated that a second stage of reaction began at 60 min. The extent of mass loss was lower than that reported for TTEPA[16] and reflected the effectiveness of the annealing treatment. At 120 min, the reaction rate increased to 0.038%/min. Although this value was greater than that reported for the previous 30 min, the degree of increase slowed from 100 to 50%, which indicated an overall slowing of the reaction. This decrease may have been due to the increased crystallinity of the lamellae at greater depths within the film. A similar trend for mass loss was observed by Avny and Rebenfeld,[14] who treated PET fibers with TTETA.

The degree of surface amination at reaction times of 60, 90, 120, and 150 min was determined with XPS. Figure 2 illustrates the high-resolution N1s peak obtained for the film treated with TTETA for 60 min and shows that treatment introduced two types of carbon–nitrogen bonding to the surface. The lower binding energy component appearing at 399.7 eV was assigned to C—N bonding.[22,23] The higher component at 402.6 eV was attributed to the amide bond; however, this peak may have possibly arisen from quaternary amide groups that formed when the amine groups within TTETA reacted with protons that were present during the intermediate stage of the aminolysis reaction.[24]

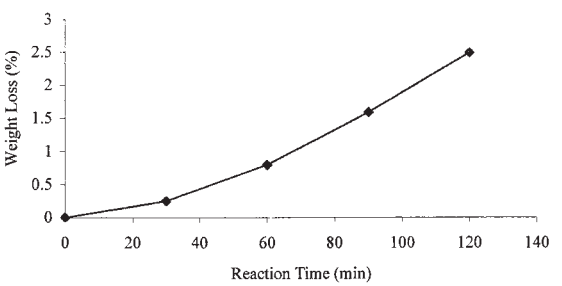

Figure 1 Mass loss as a function of time for TTETA-treated PET.

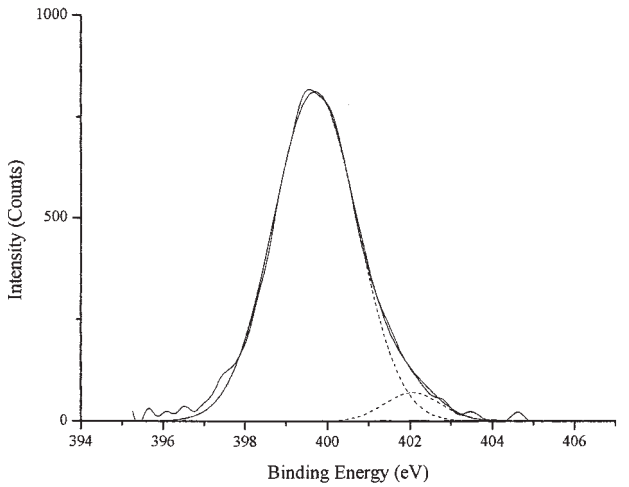

Figure 2 XPS N1s peak for PET treated with TTETA for 60 min.

The atomic composition after TTETA treatment was also determined with XPS (Table V). TTETA introduced approximately 3 atom % N at the film surface, and this value was 65% of that obtained with TTEPA treatment. Although a lower result may have been expected with TTETA because it contains fewer nitrogen atoms, if TTETA treatment was as effective as TTEPA, we would have expected that 75% nitrogen would be found at the surface. Thus, TTETA appeared to be a less effective surface treatment. The surface nitrogen remained constant up to 150 min, and a similar trend was observed for TTEPA.

Table VI lists the water contact angles obtained for PET films treated with TTETA for periods of 60–150 min. At 60 min, a 7° decrease in the contact angle was noted compared with the untreated film, which indicated the corrosive nature of TTETA. As the treatment time increased, the water contact angle decreased further, which indicated that more polar amine groups were introduced to the film surface at longer reaction times. An overall decrease of 18° relative to the untreated film was observed for the 150-min study, compared with a 16° decrease observed for the same experiment with TTEPA. This suggested that a similar N content was introduced by TTETA treatment, and so 20% more TTETA molecules were introduced to the film surface compared with TTEPA for the same treatment duration.

The degree of polarity introduced to the surface at different reaction times was determined from surface tension calculations. Table VII lists the surface energy components determined for films treated with TTETA. The percentage polarity introduced to the surface increased more than fivefold over the first 60 min. This increase was higher than that observed for the initial stages of the reaction with TTEPA, where a fourfold increase was observed, which reflected the greater reactivity of TTETA. As the reaction time increased, the percentage polarity remained approximately constant over the range of reaction times. Although the base component increased by 95% over the 150-min period because of the incorporation of basic amine groups, the more dominant dispersion component also increased, and this was ascribed to the long hydrocarbon chain present in TTETA. A similar trend was also observed for samples treated with TTEPA for up to 120 min.

An indication of the total amount of nitrogen introduced to the TTETA-treated films at each of the reaction times was determined with titration analysis (Table VIII). The total nitrogen content rose approximately threefold as the reaction time increased from 60 to 150 min. The relationship between total nitrogen content and reaction time was nonlinear, which reflected the fact that the reaction between TTETA and PET occurred in several stages. It appeared that the most significant stage of the reaction occurred between 90 and 120 min. The value obtained at 150 min was about 40% greater than the highest nitrogen content determined for the TTEPA experiments. As with contact-angle analysis, these data suggest that a greater number of TTETA molecules reacted with the PET film.

Amination with DETA

Figure 3 illustrates the mass loss for films treated with DETA at various times between 5 and 45 min. As observed for TTEPA treatment, four different rates of mass loss were observed over the range of

TABLE V
XPS Surface Composition Values (±0.4 atom %) for the PET Films Treated with TTETA

Reaction time (min)	C (%)	N (%)	O (%)
60	74.1	3.0	22.0
90	74.8	3.1	22.1
120	75.5	3.0	21.5
150	74.8	2.6	22.6

TABLE VI
Contact Angles for the PET Films Treated with TTETA

Reaction time (min)	Water contact angle (°)
0	81.9 ± 0.9
60	75.4 ± 3.0
90	71.9 ± 0.7
120	69.4 ± 0.5
150	63.7 ± 3.2

TABLE VII
Surface Tension Components for the PET Treated with TTETA

Treatment time (min)	γ^{TOT} (mJ/m^2)	γ^{LW} (mJ/m^2)	γ^{AB} (mJ/m^2)	γ^+ (mJ/m^2)	γ^- (mJ/m^2)	Polarity (%)[a]
0	40.1	39.6	0.5	0.03	2.1	1.2
60	42.1	39.3	2.8	0.67	2.9	6.6
90	43.9	40.6	3.3	0.76	3.6	7.5
120	46.3	43.8	2.5	0.39	4.1	5.4
150	54.8	50.7	4.1	1.1	3.9	7.5

γ^{TOT}, total surface tension component; γ^{LW}, dispersion surface tension component; γ^{AB}, acid-base surface tension component; γ^+, acid surface tension component; γ^-, base surface tension component.
[a] Polarity = $100\% \times \gamma^{AB}/\gamma^{TOT}$.

treatment times, which suggested that a similar mechanism operated for the two amines. At times up to 15 min, the reaction proceeded relatively slowly with an initial rate of mass loss of 0.15%/min. However, this initial rate was more than 10-fold higher than that observed for treatment with either TETTA or TTEPA. This reflected the more corrosive nature of the shorter chained DETA. At reaction times between 15 and 30 min, the degree of mass loss doubled with the reagent continuing to etch around the crystal boundaries. This resulted in a greater number of chain scissions and enhanced the dissolution of smaller molecular weight fragments.[14] The most significant mass loss, however, was observed between 30 and 45 min, where a three-fold increase suggested that the outer layer of crystalline lamellae was removed at this time. We could not determined whether this rate was the maximum mass loss per unit time for the reaction because of the highly corrosive nature of DETA. A longer treatment time of 60 min was also investigated; however, the poor mechanical properties of this sample made handling difficult.

Films treated with DETA were also characterized with XPS. Figure 4 illustrates the high-resolution C1s peak obtained for the PET film treated with DETA for 30 min. Six components were observed for the peak. Two of these components were introduced by DETA, with the components at 286.15 and 286.95 eV assigned to C—N and O=C—N bonding, respectively.[23,25] Figure 4 also illustrates the high-resolution N1s peak. Amide bonding was evident from this peak. The presence of O=C—N bonding showed that the reaction between DETA and PET involved the formation of amide bonds and was expected to follow the same reaction path as both TTETA and TTEPA. The presence of amide bonding was also detected by Gelinas et al.,[23] who treated carboxyl-terminated magnetic particles with DETA.

XPS was also used to determine the atomic percentage of nitrogen introduced at the surface for the reaction times investigated (Table IX). The nitrogen reached approximately 3 atom % and remained constant up to a reaction time of 30 min. This trend was similar to that obtained for films aminated with TTETA and TTEPA and indicated that the reaction time did not influence the amount of nitrogen present at the nanometer level. At 45 min, the nitrogen decreased by more than 50%, which suggested that a longer treatment time may have reduced the extent of surface reaction. However, the outer layers of this sample appeared fragmented in the surface region because of the highly corrosive nature of the DETA reagent, and consequently, the XPS spectra were not reproducible. Loss of crystals would result in a lower N signal, especially if the second, more crystalline layer of lamellae were not aminated to the same degree as the outer layer. Therefore, it could not be concluded from XPS whether the reaction

TABLE VIII
Total Nitrogen Content for the Films Treated with TTETA

Reaction time (min)	Nitrogen content (μg/cm^2)
0	0
60	13.3 ± 3.1
90	16.2 ± 1.2
120	26.8 ± 0.6
150	42.9 ± 2.8

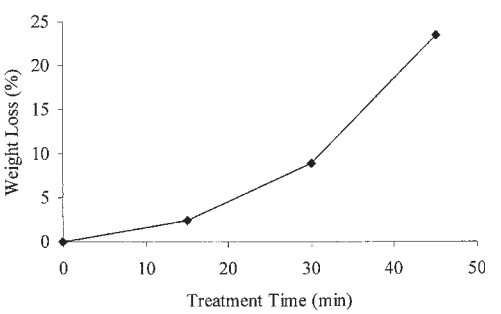

Figure 3 Mass loss as a function of time for DETA-treated PET.

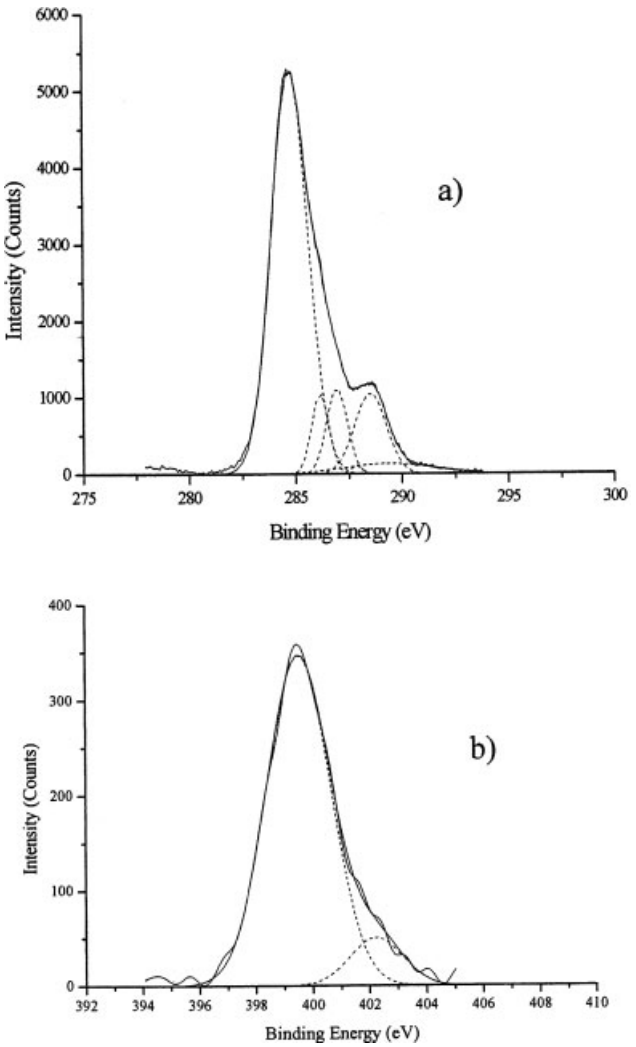

Figure 4 XPS (a) C1s and (b) N1s peaks for PET treated with DETA for 30 min.

time influenced the chemical composition of DETA-treated PET films.

Contact-angle analysis was used to characterize the PET films treated with DETA, and Table X lists the advancing contact angles obtained for the films treated with DETA up to 45 min. The 15-min treatment produced a 10° decrease in the water contact angle compared with the clean PET film. This observation supported the view that polar nitrogenous functional groups were introduced into the film as a result of DETA treatment. Interestingly, the initial change in water contact angle obtained was slightly higher than that obtained with TTETA and TTEPA, which suggested that a greater initial reaction occurred between DETA and PET relative to the two other amines. In fact, the most significant decrease in water contact angle for the DETA-treated films occurred within the first 15 min, which suggested that most of the reaction occurred during this period. This contradicts the mass loss results, which show a maximum reaction rate between 30 and 45 min. The reason for this discrepancy is uncertain; however, the loss of aminated crystals could have resulted in a less than expected reduction in contact angle at the longer reaction times. As the reaction time increased to 45 min, the water contact angle decreased further to 65°, which showed that an increase in reaction time produced a more polar surface. This result suggests that the absence of outer-layer PET crystals influenced the surface nitrogen content because the lowest content was obtained for the 45-min sample. The water contact angle obtained for the 45-min sample was the same as those values obtained for films treated with TTETA and TTEPA for 15 min, even though DETA contained half the amine groups of the other amines. This implied that twice as many DETA molecules were introduced into PET at 45 min as TTETA or TTEPA at 150 min. This increased extent of reaction with DETA was also reflected in the mass loss measurements.

Further information regarding the changes in surface chemistry with DETA treatment was obtained from surface tension components. Table XI lists the surface tension component values determined for PET films treated with DETA for up to 45 min. Treatment with DETA for 15 min produced a sevenfold increase in the degree of polarity of the film surface. This was slightly higher than the initial fivefold increase observed for TTETA-treated samples, indicating that DETA was more effective at introducing polar nitrogen groups into the PET surface. As with other amines, the extent of polarity after the initial 15 min remained constant for up to 30 min. Although the base component increased by nearly 30% over the second 15-min period, the dispersion

TABLE IX
XPS Surface Composition Values (±0.4 atom %) for the PET Films Treated with DETA

Reaction time (min)	C (%)	N (%)	O (%)
15	73.1	3.0	23.9
30	76.3	2.5	21.2
45	76.8	1.3	21.9

TABLE X
Contact Angles for the PET Films Treated with DETA

Reaction time (min)	Water contact angle (°)
0	81.9 ± 0.9
15	71.4 ± 3.0
30	67.9 ± 0.8
45	65.4 ± 0.1

TABLE XI
Surface Tension Components for the PET Films Treated with DETA

Treatment time (min)	γ^{TOT} (mJ/m^2)	γ^{LW} (mJ/m^2)	γ^{AB} (mJ/m^2)	γ^{+} (mJ/m^2)	γ^{-} (mJ/m^2)	Polarity (%)[a]
0	40.1	39.6	0.5	0.03	2.1	1.2
15	43.2	39.5	3.7	0.92	3.8	8.6
30	45.4	41.2	4.1	0.97	4.5	9.1
45	48.5	45.4	3.1	0.47	4.9	6.3

γ^{TOT}, total surface tension component; γ^{LW}, dispersion surface tension component; γ^{-}, base surface tension component.
[a] Polarity = $100\% \times \gamma^{AB}/\gamma^{TOT}$.

component also slightly increased, and this caused the extent of polarity to remain constant at different reaction times. At 45 min, the degree of polarity decreased by about 30%, but this was expected to be influenced by the loss of aminated crystals.

Titration analysis was used to determine the nitrogen present in the DETA-treated films (Table XII). A threefold increase in the total nitrogen content of the films was obtained when the reaction time was tripled, so a linear relationship was observed. This trend was quite different than those observed for films treated with TTETA or TTEPA. This relationship appeared to contradict the mass loss data, which showed several different rates of loss over a 45-min period. Titration analysis was also performed on a sample treated with DETA for 5 min, but an accurate value could not be obtained for this sample because of the low nitrogen content. The total amount of nitrogen detected in the PET film treated with DETA for 45 min was comparable with that measured in samples treated with TTETA or TTEPA for periods of 150 and 180 min, respectively. Similar to the DCA results, this implied that a greater number of DETA molecules were present at this treatment time relative to the other amines.

CONCLUSIONS

Annealing treatments were used to minimize the degradation of PET films treated with TTEPA. Annealing for 10 min produced a significant change in the crystal structure, with large variations in mass loss observed across the range of temperatures investigated. Films annealed at 120 and 140°C exhibited a significant increase in mass loss, but no increase in the total nitrogen content was observed. This was ascribed to the TTEPA molecules folding at the film surface. At higher temperatures, the degree of mass loss decreased, with the lowest value obtained by annealing at 200°C for 10 min before amination. Annealing for 10 h at low temperatures (<160°C) resulted in a reduced mass loss and degree of amination.

TABLE XII
Total Nitrogen Content for the Films Treated with DETA

Reaction time (min)	Nitrogen content (μg/cm^2)
0	0
15	15.2 ± 3.1
30	32.1 ± 1.7
45	44.6 ± 2.8

XPS was used to show that treatment with each of the three amines investigated produced amine and amide bonding at the PET surface. The presence of these types of bonds indicated that chemical attachment of the amines to PET did in fact occur and that the reaction occurred at the ester group. Treatment with TTETA and DETA produced films with lower surface nitrogen contents, as determined by XPS, compared with TTEPA. However, the total amount of nitrogen introduced to the PET surface was comparable for all three amines. This suggested that a greater degree of diffusion into the film surface occurred with the shorter chained TTETA and DETA.

The aminated PET surfaces characterized in this article are being further developed as potential biomaterials by the investigation of linker molecules, including gluteraldehyde. Such molecules may improve the attachment between nitrogen-containing PET surfaces and biologically active molecules.

References

1. Cenni, E.; Granchi, D.; Ciapetti, G.; Verri, E.; Cavedagna, D.; Gamberini, S.; Di Leo, A.; Pizzoferrato, C. Biomaterials 1996, 17, 2071.
2. Godjevargova, T.; Dimov, A. J Membr Sci 1992, 67, 283.
3. Wojciechowski, P. W.; Brash, J. L. Biointerfaces 1993, 1, 107.
4. Malstem, M.; Johansson, J. A.; Burns, N. L.; Yasuda, H. K. Colloids Surf B 1996, 6, 191.
5. Dekker, A.; Reitsma, K.; Beugling, T.; Bantjes, A.; Feijen, J.; van Aken, W. G. Biomaterials 1991, 12, 130.
6. Tang, L.; Wu, Y.; Timmons, R. B. J Biomed Mater Res 1998, 42, 156.
7. Walker, A. K.; Qu, H.; Wu, Y.; Timmons, R. B.; Kinsel, G. R. Anal Biochem 1999, 271, 123.
8. Khoklova, T. D.; Mchedlishvili, B. V. Colloid J 1996, 58, 793.
9. Farrow, G.; Ravens, D. A. S.; Ward, I. M. Polymer 1962, 3, 17.

10. Sweet, G. E.; Bell, J. P. J Polym Sci Polym Phys Ed 1978, 16, 1935.
11. Adams, G. C. Polym Eng Sci 1976, 16, 222.
12. Holmes, S. A. J Appl Polym Sci 1996, 61, 255.
13. Fukatsu, K. J Appl Polym Sci 1992, 45, 2037.
14. Avny, Y.; Rebenfeld, L. J Appl Polym Sci 1986, 32, 4009.
15. Nissen, K. Ph.D. Thesis, University of Technology, 2004.
16. Nissen, K. E.; Stevens, M. G.; Stuart, B. H.; Baker, A. T. J Polym Sci Part B: Polym Phys 2001, 39, 623.
17. Pecorini, T. J.; Hertzberg, R. W. Polymer 1993, 34, 5053.
18. Adamson, A. W. Physical Chemistry of Surfaces; Wiley-Interscience: New York, 1967.
19. Needles, H. L.; Park, M. J. J Appl Polym Sci 1996, 59, 1683.
20. Goschel, U. Polymer 1996, 37, 4049.
21. Pittman, C. U.; He, G. R.; Wu, B.; Gardner, S. Carbon 1996, 35, 333.
22. Gerenser, L. J.; Grace, J. M.; Apai, G.; Thompson, P. M. Surf Interface Anal 2000, 29, 12.
23. Gelinas, S.; Finch, J. A.; Vreugdehill, A. J. Colloids Surf A 2000, 164, 257.
24. Uchida, E.; Ikada, Y. J Appl Polym Sci 1996, 61, 1365.
25. Petrat, M.; Wolany, D.; Schwede, B. C.; Widermann, L.; Benninghoven, A. Surf Interface Anal 1994, 21, 274.