Chemical Modification of Polyester Fiber Surfaces by Amination Reactions with Multifunctional Amines

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Synopsis

The feasibility of incorporating amine groups into the surface of polyester (PET) fibers by reaction with multifunctional amines was investigated. Reactions of diethylenetriamine (DETA), triethylenetetramine (TETTA), and tetraethylenepentamine (TTEPA) with PET monofilaments and with a multifilament yarn were studied. Microspectrophotometric examination of aminated fibers stained with an acid dye at low pH revealed the location and concentration of amine groups. Amination could be confined to the periphery and was found to be uniform on the fiber surface. The rate of the reaction, as revealed by acid dye staining, was characterized by an induction period followed by an autoaccelerated stage. Extent of incorporation of amine groups was found to be similar for the three amines. There is a significant improvement in water wettability due to surface amination, and the interfacial shear strength of TTEPA-treated PET monofilaments embedded in an epoxy resin matrix was almost doubled. As the amination reaction proceeds, there is a weakening of the reacted zone in the PET due to chain scission leading to a decrease in the interfacial shear strength. Scanning electron microscopy (SEM) studies revealed that failure occurred within the filament most probably between the reacted and unreacted zones. The tensile properties of the TTEPA-treated PET filaments were hardly affected at the investigated extents of amination.

INTRODUCTION

Polyester (PET) fibers generally exhibit low surface energy and limited chemical reactivity, resulting in poor wettability and weak adhesive bonding. When PET fibers are used as reinforcing elements in composites, appropriate treatment procedures must be followed to achieve adequate interfacial adhesion. The introduction of new functional groups by means of chemical modification reactions is one possible means for altering the physical and chemical nature of the fiber. By choosing the proper experimental conditions, it should be possible to restrict the chemical modification to the surface of the fiber, leaving the interior structure unchanged. The work described in this paper constitutes an initial study of the incorporation of amine groups into the surface molecules of polyester fibers.

The presence of amine groups should increase wettability, and should also provide potential sites for the formation of covalent chemical bonds with polymeric matrices as in a composite. Amine groups are able to react with expoxides, isocyanates, and methylol compounds, forming chemical bonds

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with epoxies, polyurethanes, and phenol- and resorcinol-formaldehyde resins. For example, the effectiveness of resorcinol-formaldehyde-latex (RFL) dip systems that are used in the case of reinforced rubber products·should be enhanced by the presence of amine groups at the PET surface.[1] Furthermore, the scope of possible chemical and physical surface modifications of PET can be broadened by subsequent alkylation and silation of the amine groups using appropriate reagents, as well as by graft polymerization.

Reaction of an amine with an ester group of the PET leads to chain scission at the reaction site and to amide formation:
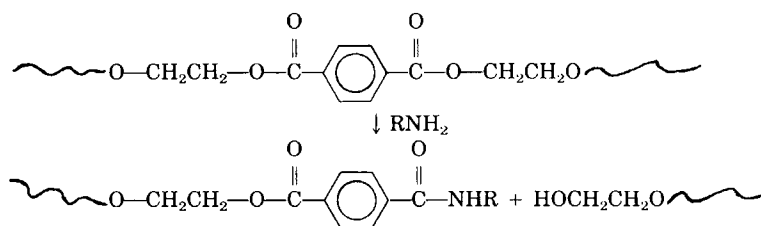
In the reaction of a multifunctional amine with PET, only one of the amine groups is consumed in the chain scission reaction, being converted to an amide group, while the remaining amine groups should be incorporated into the PET structure. Ideally the reaction sequence might be visualized as follows:
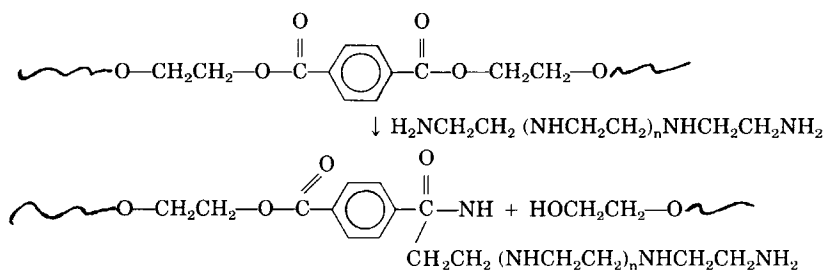
To prevent or minimize deterioration of fiber mechanical properties, successful incorporation of amine groups by reaction with multifunctional amines should seek minimal chain scission with a relatively high extent of amine group incorporation. Diffusion of the reacting amine into the PET fiber should be minimized or even totally eliminated so that reaction will be restricted to the fiber surface.

The first reports on the interaction of low-molecular weight amines with PET appeared in the early 1960s.[2–5] Most of the amines used were low-molecular weight monofunctional amines such as methylamine, ethylamine, n-propylamine, benzylamine, piperidine, and aniline. Attempts to react PET with bifunctional amines such as ethylenediamine and hexamethylenediamine also were reported.[3]

Differences in reactivity between different amines were observed.[3] Some amines caused complete degradation of the PET to the corresponding diamides of terephthalic acid, some caused the formation of mixtures of oligomers, and some hardly reacted at all. On reaction with hydrazine and benzylamine, the corresponding PET degradation products—terephthalicdihydrazide, terephthalic-*bis*-benzylamide, and *bis*-benzylamides of oligomers were obtained. On reaction with ethylenediamine, only a mixture of oligomeric *bis*-ethylenediamides was isolated. Reactions with hexamethylenediamine, piperidine, and aniline were not as vigorous, and no definite low-molecular weight PET degradation products were obtained.[3]

In a study of the reaction of PET with methylamine, Farrow et al.[2] reported that aminolysis of PET with 20% aqueous methylamine took place in three stages, reflecting the amorphous and crystalline regions of the fiber. Kurita[5] reported two stages for the degradation of PET in 70% aqueous ethylamine and also interpreted the results in terms of a rapid degradation of amorphous regions followed by a slower degradation of crystalline regions. Amine etching of PET by low-molecular weight, monofunctional amines has been shown to discriminate between crystalline and amorphous regions.[5-7] Such etching processes were used to investigate bulk morphology of PET fibers and films,[4, 8-10] and chemical stress cracking of PET fibers.[11]

In contrast to PET hydrolysis with aqueous sodium hydroxide, which is confined to the fiber surface, amines were reported to diffuse into the PET fibers leading to reaction throughout the fiber.[12-15] Reaction within the fibers affected their brittleness, flexural fatigue, and ultimate tensile properties more drastically than hydrolysis by aqueous sodium hydroxide.[13]
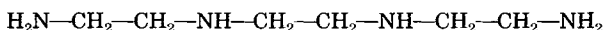
Few attempts to improve surface properties of PET fibers by amine treatments have been reported. PET fibers having a wool-like surface were prepared by first treating the fibers with ethylamine, and then saponifying the fibers with an alkali.[16,17] In a short communication it was reported that treatment of polyester fibers with 23% aqueous ethylenediamine solution in the presence of NaOH at pH 9–10 produced increased adhesion of the modified fibers which was attributed to the incorporation of amide groups in the PET chains.[18] An attempt to promote adhesion of PET to polyethylene by absorbing poly(ethyleneimine) (PEI) on PET fibers has also been reported.[19] Adsorption of 0.3–0.5% PEI on PET fibers appeared to increase the tensile strength of the composite.

Reported results indicate differences in the reactivity of amines with PET.[3] There are indications that an increase in amine functionality and molecular weight both lead to decreased reactivity toward PET. Such a decrease in reactivity should help in controlling the extent of the scission reaction. Higher amine functionality reduces the amount of scission needed to incorporate a desired concentration of amine groups; i.e., the required change in surface properties should be achievable at a lower extent of reaction. Furthermore, an increase in amine molecular weight should decrease diffusion into the PET fiber, allowing the reaction to be restricted to the fiber surface. Combinations of high molecular weight and multifunctionality exist in commercially available multifunctional amines derived from ethyleneimine. These multifunctional amines should be promising reagents for controlled surface amination of PET fibers.

In the present study, the reactions between PET and diethylenetriamine (DETA), triethylenetetramine (TETTA), and tetraethylenepentamine (TTEPA) are described.

$$H_2N-CH_2-CH_2-NH-CH_2-CH_2-NH_2$$

DETA

$$H_2N-CH_2-CH_2-NH-CH_2-CH_2-NH-CH_2-CH_2-NH_2$$

TETTA

$$H_2N-CH_2-CH_2-NH-CH_2-CH_2-NH-CH_2-CH_2-NH-CH_2-CH_2-NH_2$$

TTEPA

Differences in reactivity of the multifunctional amines, extent of reaction, location of the reaction in the PET fiber, and the effect of the presence of amine groups on wettability and on the interfacial shear strength between amine-treated PET filaments and on epoxy resin are discussed.

EXPERIMENTAL

Materials

PET monofilament (dia. = 0.256 mm) and a high tenacity PET multifilament yarn were used. In order to remove finishing agents from the monofilaments and the high tenacity yarns, samples were rinsed in 1,1,2-trichlorotrifluoroethane (4×) for 2 hr followed by rinsing in methanol (4×) and drying in air. Technical grade DETA, 95%, TETTA and TTEPA (Aldrich Chemical Co.), and a typical epoxy resin Epon 828 (Miller Stephenson Chemical Company) were used. A buffer solution of pH 2.7 was prepared from potassium hydrogen phthalate and hydrochloric acid.

Reaction of PET with Multifunctional Amines

In a typical procedure, PET monofilaments or yarns (0.5 g) were allowed to react at 85°C with the amine (15 mL) in a closed test tube. At the appropriate time the PET monofilaments were removed and excess unreacted amine was washed off with methanol. The multifilaments were further rinsed in methanol (20 mL, 6×) for 6 hr under constant agitation and were dried in air.

Staining of the Amine-Treated PET

Staining with Acid Fuchsin. Amine-treated specimens together with an untreated PET specimen were kept under constant agitation in 0.5% Acid Fuchsin in pH 2.7 buffer solution for 90 min at room temperature (liquor ratio = 0.37 L/g). The stained specimens were rinsed with pH 2.7 buffer solution (10 mL, 3×) for a total of one minute. Quantitative measurements of the depth into the filament of the reaction zone were made by embedding

the treated filaments in epoxy resin, microtoming to 10 μm thickness, staining, and inspecting under the microscope.

Absorbance Measurements. Absorbance of longitudinally viewed Acid Fuchsin-stained PET filaments was calculated from

$$A = \ln \frac{I_0}{I},$$

where A is the absorbance, and I_0 and I are the intensities of light transmitted through the unstained and stained filaments, respectively. The transmission for the unstained PET, I_0, was arbitrarily adjusted to 70%. For each condition of stained filaments, 15 to 20 transmission readings were taken at equal intervals along 2–4 cm of each of 3 to 5 fibers. The readings were always taken at the center of the fibers to assure a measurement of equal fiber thickness. The visible spectrum of the stained filaments showed a broad absorbance peak in the form of a plateau in the range of 510–560 nm. The transmission of the stained PET was determined at 535 nm using a Leitz MPV 1.1 microspectrophotometer.[20]

Quantitative Determinations. Acid Fuchsin in the stained PET filaments was extracted and spectrophotometrically determined. A linear relationship was established between the absorbance of the stained PET filaments and the extracted dye concentration, allowing calculation of the number of amine groups in the modified PET. In a typical extraction procedure, amine-treated PET filaments (0.15 g) were extracted with 2 N NaCl solution (5 mL) in the presence of 1 N NaOH solution (1 mL) for 1 hr, under constant agitation. Solution was acidifed with 1.1 N HCl solution (1 mL), and the absorbance was determined at 546 nm using a Beckman DU-6 spectrophotometer. The dye concentration was calculated from a standard calibration curve prepared at pH 2.7. This procedure was repeated several times to assure complete extraction.

Determination of Wettability

Wettability measurements were carried out using the TRI Wilhelmy scanning wetting force technique.[21]

Determination of Interfacial Shear Strengths

The interfacial shear strength was determined by a pull-out test. A washer, covered on one side with Teflon protective overlay film, was used as a container for the epoxy resin. The amine-treated PET filament was inserted through the Teflon protective overlay and was left hanging, protruding from both sides. Epoxy resin was prepared according to the manufacturer's instructions (100:12 w/w mixture of Epon 828 and TETTA), and poured into the washer and allowed to cure for 17 hr at 65°C. The force (F) required to pull the monofilament out of the epoxy resin was determined on an Instron tensile tester. The embedded length (l) of the fiber was determined by mea-

suring the width of the epoxy resin button, after the filament was pulled out. The interfacial shear strength τ was calculated from the relationship

$$\tau = \frac{F}{\pi dl},$$

where d = filament diameter.

Tensile Properties

Tensile properties were determined on individual untreated and amine-treated filaments on an Instron tensile tester at a 50% per minute rate of extension under standard conditions.

RESULTS AND DISCUSSION

Amination of PET with DETA, TETTA, and TTEPA

Since the solubility parameters of the three multifunctional amines, as calculated according to Hoy (Ref. 22) (10.73 for DETA, 10.76 for TETTA, and 10.78 for TTEPA), are close to that of PET, good interaction between the reagents and the polymer was to be expected, which should facilitate chemical reaction.[23] Amination of the PET should lead to a weight increase. On the other hand, as reaction progresses and the molecular weight of the PET decreases as a result of chain scission, oligomers and low-molecular weight PET fractions may be extracted, leading to a decrease in the PET mass. Thus the time dependence of the PET weight change during reaction is indicative of the interaction of the amine with the polymer involving the diffusion behavior of the amine, its reactivity toward the ester group, and the solubility and diffusivity of the low-molecular weight reaction products that are formed. The dependence of the weight change of PET monofilaments on reaction time is shown in Figure 1 for the three amines. In each case, the extent of amination was not enough to produce an initial net weight increase. Significant weight loss in the reaction with DETA, TETTA, and TTEPA first appeared after 30, 90, and 210 min, respectively. When TTEPA was allowed to react with the high tenacity PET yarn under the same experimental conditions (85°C) significant degradation did not take place until about 300 min (Fig. 2). This is a reflection of the higher orientation and crystallinity of the high tenacity multifilament yarn since the much higher surface to bulk ratio of the multifilament yarn would have been expected to cause a much faster weight loss once surface reaction and penetration had been initiated. Reaction with an undrawn amorphous yarn could be carried out under much milder conditions (21°C) to reveal the differences in the extent of interaction of the three amines with the polymer. The data shown in Table I indicate the large differences in interactive capability in the order: DETA >TETTA >TTEPA.
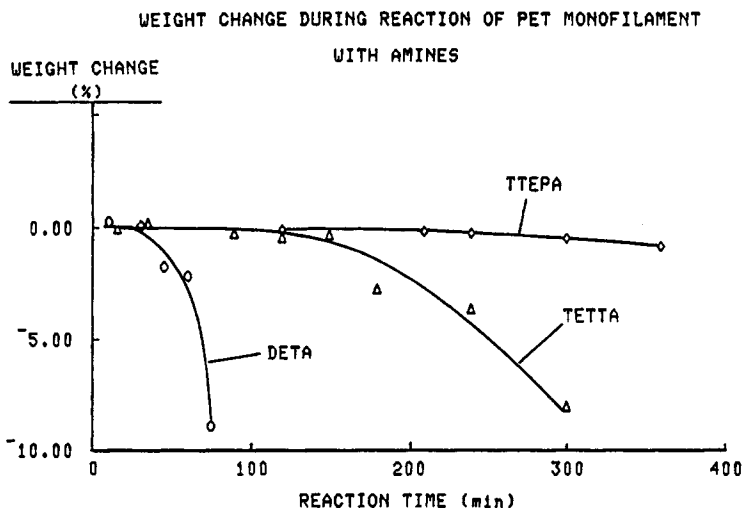
WEIGHT CHANGE DURING REACTION OF PET MONOFILAMENT
WITH AMINES

Fig. 1.   Weight change of PET monofilaments as a function of reaction time at 85°C with multifunctional amines.

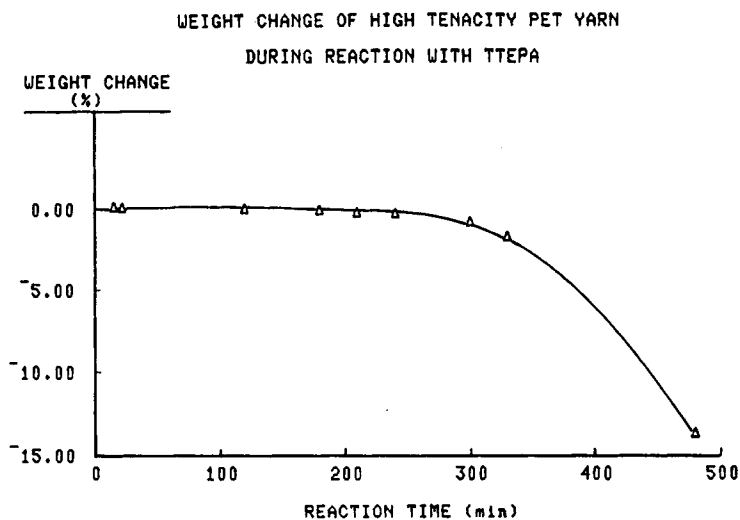WEIGHT CHANGE OF HIGH TENACITY PET YARN

DURING REACTION WITH TTEPA

Fig. 2.   Change in weight of a PET high tenacity yarn as a function of reaction time at 85°C with TTEPA.

TABLE I
Weight Loss During Reaction of Multifunctional Amines with Undrawn PET Yarn

Amine	Time to 1% weight loss (min)
DETA	7
TETTA	40
TTEPA	320

Detection of Amine Groups

The presence of amine groups in PET can be detected by selective staining to yield both qualitative and quantitative information about their location and concentration in the fiber. Staining with Acid Fuchsin in pH 2.7 water solution has been used successfully for the detection of amine groups in hydrolyzed Kevlar®.[24] At this pH all amine groups are protonated and are capable, by an anion exchange process, of electrostatic interaction with the acid dye anion.

Amine-treated PET monofilaments and yarns were stained with 0.5% Acid Fuchsin at pH 2.7 for 90 min at room temperature and longitudinally scanned using the MPV 1.1 microspectrophotometer at 535 nm, absorbance being proportional to the number of amine groups in the fiber. The possibility that true equilibrium staining is not achieved under these staining conditions has been explored. It is likely that the modification of the polymer in the reaction zone, especially for the short treatment times, is not sufficient to lower the glass transition temperature of the polymer to below room temperature. Diffusion of the dye into the fiber would then be extremely slow, and it is unlikely that stoichiometry between protonated amine groups and the Acid Fuchsin molecules can be assumed. However, deviations from true values of amine incorporation as determined by the staining method do not alter the overall shape of the curves in the subsequent figures. The reaction time dependence, in terms of absorbance of stained amine-treated filaments is shown in Figures 3, 4, and 5 and for DETA, TETTA, and TTEPA, respectively. Similar time dependence is observed for the reaction between TTEPA and the high tenacity multifilament yarn (Fig. 6) and TETTA with the undrawn yarn at 21°C (Fig. 7).

Reaction with the different amines is characterized by several stages, the significance of which appears to be unaffected by the kinetic considerations

REACTION OF PET MONOFILAMENT WITH DETA
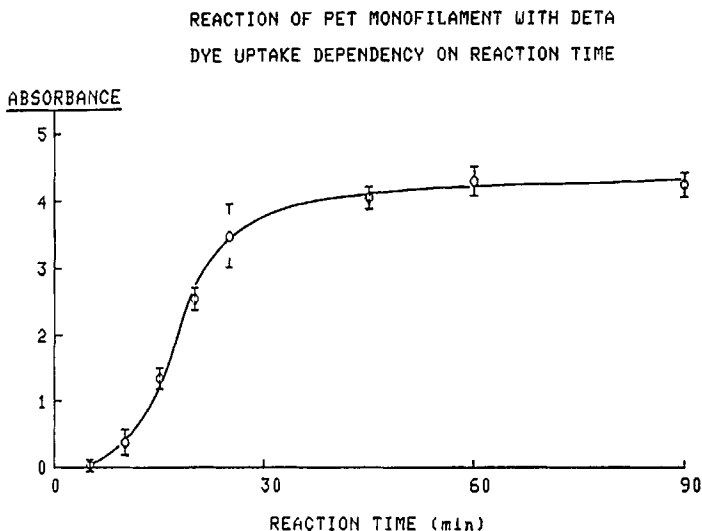
DYE UPTAKE DEPENDENCY ON REACTION TIME

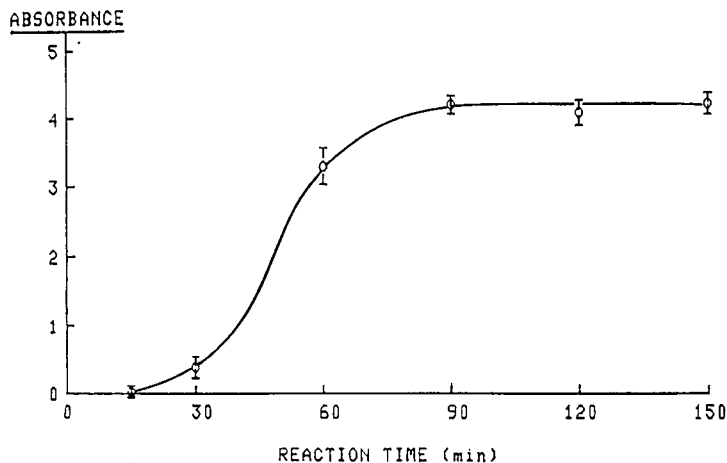Fig. 3. Absorbance of stained monofilaments as a function of reaction time at 85°C with DETA.

REACTION OF PET MONOFILAMENT WITH TETTA

DYE UPTAKE DEPENDENCY ON REACTION TIME

Fig. 4. Absorbance of stained monofilaments as a function of reaction time at 85°C with TETTA.

pointed out above with regard to the staining method. During the first stage no significant staining occurs, indicating minimal extent of reaction. This "induction period" is followed by a fast "autoaccelerated" reaction during which most of the chemical modification takes place. In the last stage reaction rate is decreased and a plateau in absorbance is approached. An increase in amine reactivity and diffusivity results in a shorter induction period. Reaction of PET with DETA and TETTA leads to similar maximum
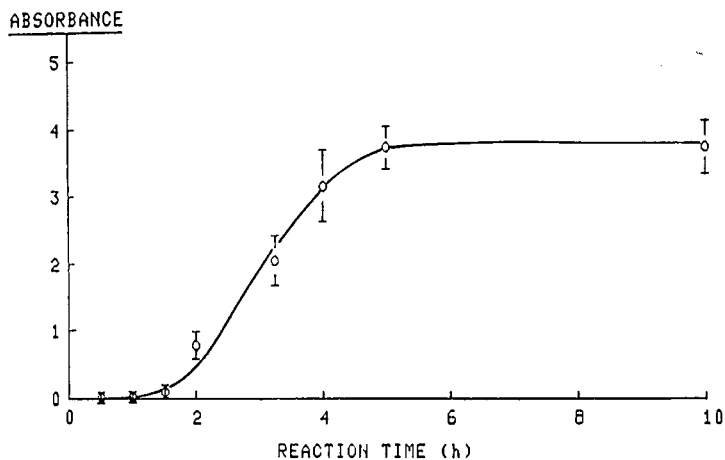
REACTION OF PET MONOFILAMENT WITH TTEPA

DYE UPTAKE DEPENDENCY ON REACTION TIME

Fig. 5. Absorbance of stained monofilaments as a function of reaction time at 85°C with TTEPA.

REACTION OF HIGH TENACITY PET YARN WITH TTEPA
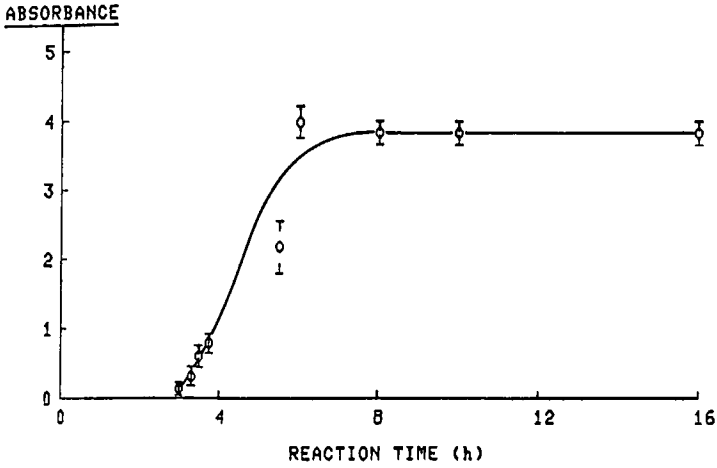
DYE UPTAKE DEPENDENCY ON REACTION TIME

Fig. 6.   Absorbance of filaments from a high tenacity PET yarn as a function of reaction time at 85°C with TTEPA.

absorbance values for the stained monofilaments while reaction with TTEPA leads to slightly lower values. Considering the fact that the TTEPA molecule has a higher amine content it appears that a lower extent of chain scission was required for the incorporation of TTEPA. Thus, of the three multi-functional amines TTEPA should be the most appropriate for the introduction of amine groups with minimal deterioration of the physical properties of the polymer.

REACTION OF UNDRAWN PET YARN WITH TETTA

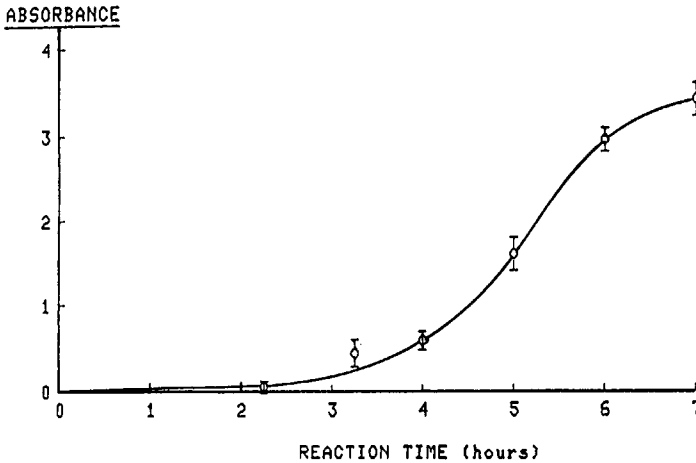DYE UPTAKE DEPENDENCY ON REACTION TIME

Fig. 7.   Absorbance of stained undrawn PET filaments as a function of reaction time at 21°C with TETTA.

The observed induction period is actually the first stage of the reaction in which the amine diffuses into the PET causing significant swelling and allowing the reaction to take place. Inspection of a cross section of Acid Fuchsin unstainable TTEPA-treated PET monofilament taken at the end of the induction period reveals a swollen periphery. As reaction proceeds and more amine groups are introduced, the accessibility of the modified PET and its reaction with the diffusing amine constantly increases, resulting in an accelerated reaction. Most probably, the fast reaction occurs mainly in the amorphous regions of the PET, while the final slow stage may be attributed to degradation of crystalline regions.[2,5] During this stage there is the onset of a significant weight decrease due to extraction of newly formed low-molecular weight PET.

Staining of the PET surface was uniform as revealed by longitudinal views (Fig. 8) in optical microscopy, and inspection of cross sections (Fig. 9) of stained PET filaments revealed that reaction was confined to the periphery. This was confirmed by separate examination of stained filament ends. The depths of the reaction zone at the beginning of the reaction and when maximum adsorbance of the aminated PET monofilaments is attained are reported in Table II. The depth of the reaction zone does not increase even though the extent of the reaction as indicated by the absorbance data increased by more than an order of magnitude. It is obvious that once the amine has penetrated and reacted with the PET, further reaction with already aminated PET is preferred over diffusion into and reaction with unreacted PET. As a result the reaction is confined to a clearly identifiable zone. The fact that the depth of the reaction zone is so shallow reflects the slow diffusion rate of the multifunctional amines into the PET structure. The combination of high-molecular weight and high amine functionality leads to an aggregation of amine molecules through intermolecular hydrogen bonding which limits the diffusivity of these multifunctional amines. Once reaction takes place, portions of the reaction surface layers separated from the unreacted underlayer which then proceeded to react as a freshly exposed surface. At very long reaction times, longitudinal parallel cracks developed, resembling the patterns observed in the degradation of oriented
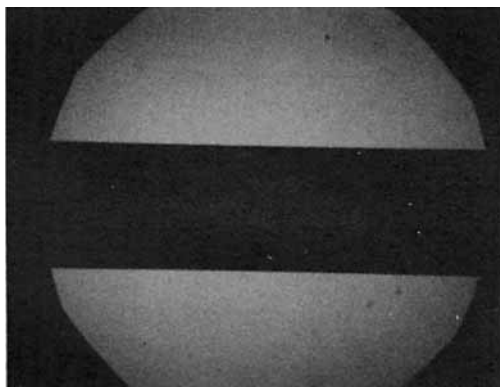

Fig. 8. Longitudinal view of a stained PET monofilament after reaction with a multifunctional amine.
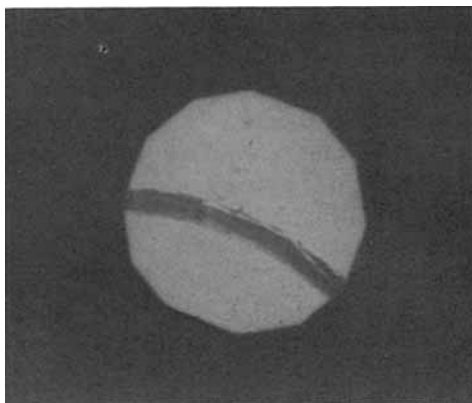
Fig. 9.   Cross-sectional view of a stained PET monofilament after reaction with a multi-functional amine.

PET film.[4] This longitudinal cracking was not observed in the case of aminated (TTEPA) high tenacity multifilament yarns even at very long reaction times. Such patterns were not observed during etching of PET multifilament yarns until recently.[10,11]

Under the assumption of stoichiometric interactions of the protonated amine groups and the Acid Fuchsin molecules, an approximate estimate of the concentration of the amine groups present in the treated PET can be made from the dye content. The dye present in the PET was extracted and its concentration determined spectrophotometrically using calibration curves obtained by standard methods. The lowest and highest amine group concentrations at the filament surface are reported in Table III. Since the depth of the reaction zone was found to be in the range of 4 μm, the values reported actually correspond to the amine groups present in this annular reaction zone. The presence of amine groups at much shorter reaction times has been confirmed by visual observation after iodine staining, but quantitative determinations of these groups from absorbance measurements could not be achieved due to sensitivity limits of the microspectrophotometer.

Changes in Wettability of Aminated PET

Incorporation of hydrophilic amine groups at the PET surface should change its surface energy. The water wettabilities of TTEPA-treated monofilaments

TABLE II
Aminated PET Monofilaments—Depth of Reaction Zone

Amine	Reaction time, min	Stained filament absorbance	Depth of reaction zone, μm
TTEPA	90	0.12 ± 0.03	2.32 ± 0.40
TTEPA	300	3.72 ± 0.24	2.56 ± 0.50
DETA	10	0.39 ± 0.13	3.78 ± 0.33
DETA	60	4.17 ± 0.15	3.85 ± 0.44

TABLE III
Amine Groups in Aminated PET

PET	Amine	Reaction time (min)	Absorbance of stained PET	Amine groups $\times 10^{-8}$ (mol/cm^2)
Monofilament	DETA	5	0.04	0.02
		60	4.3	1.8
Monofilament	TETTA	15	0.04	0.02
		90	4.2	1.8
Monofilament	TTEPA	30	0.03	0.01
		300	3.7	1.6
High tenacity multifilament yarn	TTEPA	180	0.15	0.07
		480	3.8	1.7

and single filaments from the high tenacity yarn as a function of reaction time are shown in Figures 10 and 11, respectively. The increase in cos θ_{adv} with reaction time indicates that most of the change in wettability is achieved within 10 minutes. Even though the amine groups present at this stage could not be detected by staining with Acid Fuchsin, they were present in sufficient quantity to cause a significant increase in wettability.

As more amine groups are introduced by the amination reaction, the wettability of the treated PET does not change. Comparing the effect of the three amines (Table IV) on wettability at the highest amine content obtained revealed no significant difference among the three products.
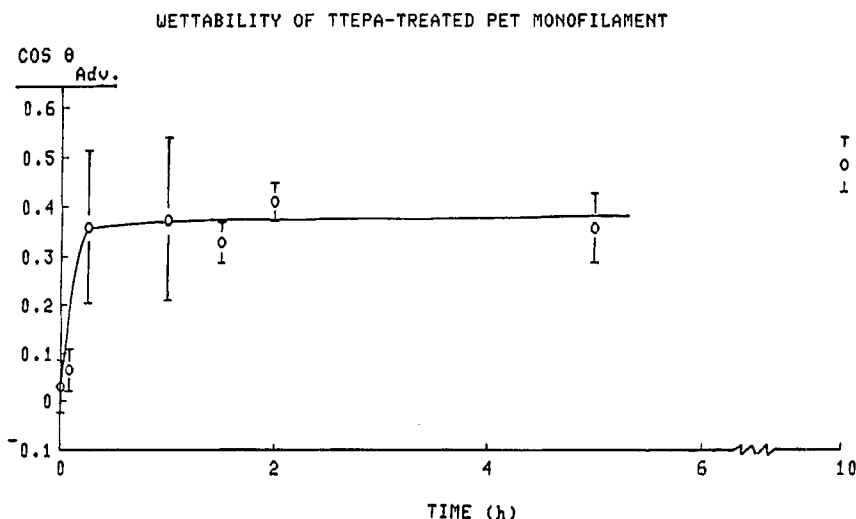

Fig. 10. Wettability of TTEPA-treated PET monofilaments as a function of reaction time at 85°C.
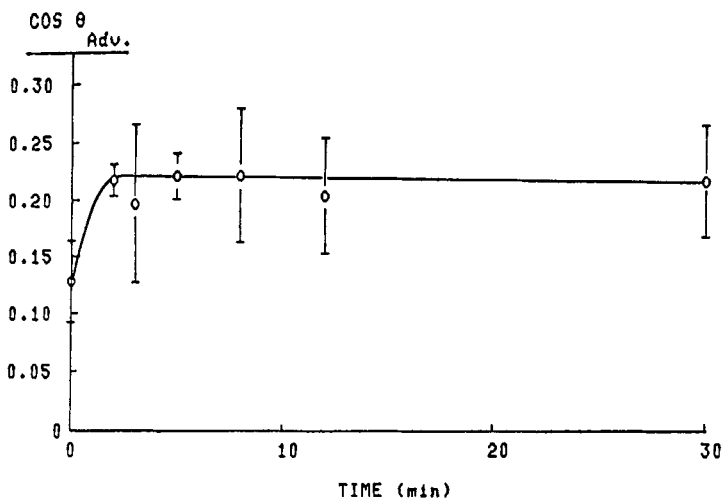
WETTABILITY OF TTEPA-TREATED PET YARN

Fig. 11. Wettability of filaments from a TTEPA-treated polyester yarn as a function of reaction time at 85°C.

Interfacial Shear Strengths

The interfacial shear strength is commonly determined in terms of the force needed to pull a single fiber out of a solid matrix. The presence of amine groups at the PET filament surface should enhance chemical interaction between an epoxy resin matrix and the PET. This enhancement should be in the form of covalent bond formation between the newly introduced terminal amine groups of the aminated PET and the epoxide groups of the epoxy resin. Increase in extent of amination should enable better chemical bonding between the fiber and the epoxy resin. On the other hand, an increase in extent of amination will lead to an increase in chain scission which should affect the strength of the reaction zone within the fiber. Thus, the interfacial shear strength should be influenced by two opposing effects.

Interfacial shear strength dependency on reaction time of PET monofilaments with TTEPA is shown in Figure 12. At short reaction times there is a significant increase in the interfacial shear strength, but this decreases again after longer reaction times. It seems that under these experimental

TABLE IV
Wettability of Aminated PET Monofilaments

Amine	Reaction time, min	Stained filament absorbance	cos θ_{adv}
—	0	0.00	0.033 ± 0.045
DETA	60	4.27 ± 0.15	0.313 ± 0.057
TETTA	90	4.18 ± 0.06	0.330 ± 0.032
TTEPA	300	3.72 ± 0.24	0.380 ± 0.041

EFFECT OF REACTION TIME ON INTERFACIAL SHEAR STRENGTH
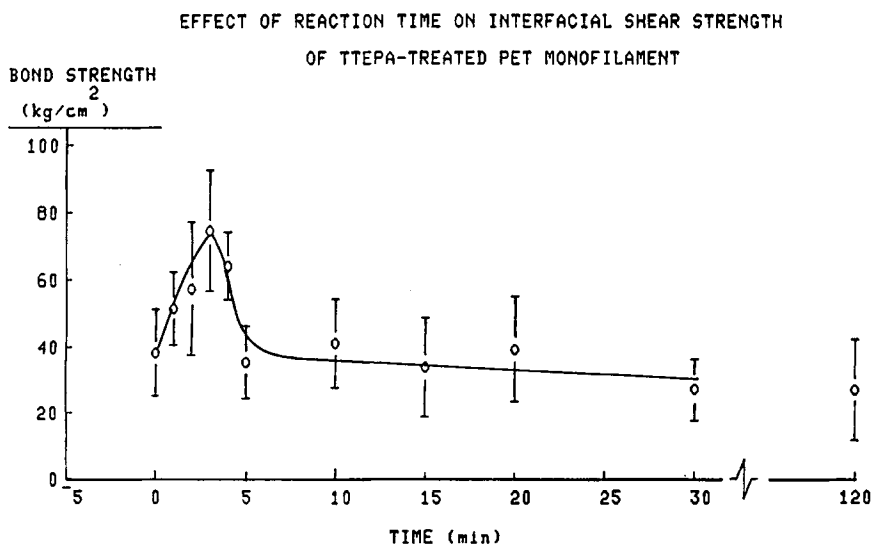OF TTEPA-TREATED PET MONOFILAMENT

Fig. 12.   Interfacial shear between an epoxy resin and TTEPA-treated PET monofilaments as a function of reaction time with TTEPA at 85°C.

conditions after 5 min of reaction time there is a weakening of the PET surface by chain scission which overcomes the enhancement of adhesion due to incorporation of amine groups. Support for this interpretation can be found by studying the mode of failure of aminated PET filaments embedded in an epoxy resin and subjected to a shearing force while cross-sectioning. In the case of aminated monofilaments, the intact fiber core frequently failed and was actually removed, while the reacted periphery remained attached to the epoxy matrix. A similar situation was observed in making cross sections of filaments from the high tenacity multifilament yarn treated with TTEPA for long time periods. Failure while exercising shearing force during cross-sectioning of fibers embedded in epoxy resin never occurred at the fiber surface. Failure was always within the fiber at a region close to the fiber surface, most probably occurring between the reacted and unreacted zones, as indicated in Figure 13.
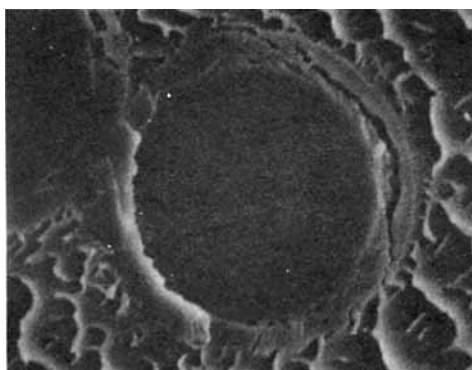

Fig. 13.   Cross-sectional view of a DETA-treated PET monofilament embedded in an epoxy resin after shearing during cross-sectioning.

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TABLE V
Tensile Properties of TTEPA-Treated Monofilament and High Tenacity PET Yarn

PET	Treatment time (min)	Initial modulus (GN/m²)	Extension to break (%)	Stress to break (GN/m²)
Monofilament	0	9.42 ± 1.50	14.8 ± 3.0	0.61 ± 0.07
	120	9.59 ± 0.96	12.3 ± 2.5	0.55 ± 0.05
	210	9.05 ± 0.42	11.6 ± 2.5	0.54 ± 0.07
	300	9.47 ± 0.84	11.4 ± 1.8	0.52 ± 0.07
High tenacity yarn	0	10.8 ± 1.9	16.3 ± 2.7	1.11 ± 0.04
	8	10.1 ± 1.8	14.9 ± 0.7	0.90 ± 0.12
	180	11.1 ± 1.0	15.3 ± 2.0	0.95 ± 0.14
	300	11.3 ± 0.4	14.3 ± 1.3	0.92 ± 0.06
	330	10.0 ± 1.5	14.6 ± 1.8	0.86 ± 0.06

Tensile Properties

The staining technique adapted through this work clearly indicates that reaction between the amine and the PET was confined to the fiber periphery. Nevertheless, due to the limited sensitivity of this technique at very low levels of amination, it is possible that some deeper penetration had occurred that could not be detected. Since reaction within the fiber would lead to some deterioration of internal structure, standard properties of TTEPA-treated filaments were determined. It can be seen from the data in Table V that tensile properties are modified to a minimal extent even at reaction times corresponding to high concentration of amine groups.

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