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Diffusion and Copolymerization of Polyacrylic Acid in Nylon 66 Fibers

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ABSTRACT

Polyacrylic acid (PAA) was applied to a plain-weave nylon 66 fabric from solution at an elevated temperature and pressure. Excess solution was squeezed out and the fabric was oven-dried, heat-cured, and hot water-scoured. The weight of PAA, up to 6% fixed to the nylon, varied inversely with the pH of the PAA solution. Cured fabric with 6% fixed PAA, when converted to the sodium and potassium salts, had moisture regain values comparable to those for cotton. The calcium salt increased the melting temperature of the nylon.

Cross sections, of yarns teased from this fabric, stained with a cationic dye revealed that PAA had penetrated the individual fibers. This type of polymer diffusion has not been reported previously.

The PAA-nylon product isolated from the cured fabric differed from the reactants in solubility, thermal characteristics, and ir absorption. These facts suggest that the PAA had reacted chemically with the nylon. Less PAA reacted when the amine end groups of nylon were blocked, indicating that, in addition to a block copolymer, a graft copolymer formed.

KEYWORDS

Nylon 66 fabric; polyamide fabric; acetic anhydride; polyacrylic acid; Malachite Green; cationic dye. Acetylated nylon 66 fabric; chemically modified nylon 66 fabric. Triton X-100(TN); surfactant; delusterant; TiO_2. Time; temperature; pressure; pH. Add-on; copolymer (polyacrylic acid and nylon 66); block copolymer; graft copolymer; copolymers; diffusion; regain; solubility; thermal behavior. Copolymerization; sulfamation; reactions (chemical); microscopy.

Introduction

The grafting of polyacrylic acid (PAA) on nylon 66 offers a potential means of increasing the relatively low moisture regain and melting point of nylon 66 which are undesirable properties in some consumer end uses. This technique was suggested by the fact that acrylic-acid monomer grafts as the sodium salt are significantly hydrophilic and as the calcium salt have a higher than usual melting point [8].

While a variety of techniques has been described for grafting acrylic acid monomer on nylon 66 and similar polyamides [1–7, 9, 13, 16, 17], very little has

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been reported on the reaction (grafting) of PAA on these substrates.

Nuessle and his associates [10–12] showed that, when a commercial PAA (MW = 50,000) was heat-set on nylon 66, a very durable crisp finish was produced. This PAA was applied by padding a solution of 5 or 10% solids, drying, and heating to temperatures of 149–218°C. Higher temperatures and longer heating times increased the extent of reaction. Ronzoni *et al.* [15] reported similar heat-fixation results; however, very little data were given to explain the reaction mechanism.

Chemical combination of PAA on the surface of nylon fiber was suggested by Nuessle [10–12] because a gossamer-like residue remained after the nylon was extracted with boiling benzyl alcohol. This residue contained both nitrogen and unreacted carboxyl groups. Rupture of nylon amide groups and formation of a new amide group with the PAA was considered to be the most plausible reaction sequence for this combination. Other possible routes were amide or imide formation between a PAA carboxyl group and either a nylon amine end group or an amide nitrogen, respectively.

Data obtained in this laboratory under different experimental conditions also suggested that a PAA-nylon reaction took place and, in addition, showed that penetration of PAA into the nylon fiber occurred. The latter appears significant because penetration of a polymer from solution into a fibrous polymer has not been reported before and, indeed, has been thought not to occur except with polymers containing very few monomer units [12].

Experimental

Materials

A plain-weave nylon 66 fabric weighing 6.74 oz/yd^2 and containing 38 ends and 36 picks of spun staple yarn was used. Before use, the fabric was purified by intensive scouring in a jig with an alkaline nonionic surfactant solution for 2 hr at 79°C. The solution contained 0.05% Triton X-100 [1] by weight and sufficient sodium carbonate to obtain a pH of 11. This scour was followed by repeated rinsing to a neutral pH, hydroextraction, and drying. Microscopic cross sections of the scoured material showed that the yarns contained fibers of different diameters and also some pigment-delustered fibers. The pigment was a titanium compound, as indicated by emission spectroscopy.

Acetylated nylon 66 fabric was prepared by modifying the procedure of Peters [14] to further insure complete acetylation and thorough removal of the acid anhydride solution after acetylation. Quadruplicate 2 × 12-in. samples of nylon 66 fabric, each weighing approximately 14 g, were dried at 105°C for 2 hr. After drying, the samples were placed in a 1-l. reaction flask equipped with a reflux condenser vented with a drying tube. The samples were then boiled at 86°C for 112 hr in a solution of 140 ml acetic anhydride in 450 ml benzene. Removal of unreacted acetic anhydride was accomplished by boiling for 1 hr and rinsing twice in anhydrous ether. This procedure was followed by two cold-water rinses and a 30-min boil water rinse with overnight cooling.

A PAA solution [2] having 28% aqueous solids, an amber color, a density of 1.09 g/ml, and a pH of 1.6 was used. According to the manufacturer, the molecular weight of the PAA was 15,000–20,000.

Fixation Procedure

A 2 × 12-in. fabric sample was heated to constant weight at 105°C. The dried and weighed sample was immersed in 50 ml of the 28% PAA solution at a specific pH in an unsealed 8-in.-long test tube. Caustic-soda flake was used to adjust the pH, as required. Blank or control solutions were prepared in the same manner, substituting distilled water or dilute sulfuric acid for the PAA solutions.

Several tubes were heated simultaneously at 121°C for 2 hr in an autoclave, approximately 25 min additional time being allowed for slow exhaustion of the autoclave chamber. The fabric samples were taken from the tubes and the surface solution was removed from each sample by passing it through two nips of a laboratory pad. Drying was accomplished collectively for 20 min at 100°C. Finally, the samples were cured at 177°C for 10 min.

Removal of Unfixed PAA

Unfixed PAA was removed from each sample individually by extraction with hot water in a glass extraction thimble in a beaker. Extraction thimbles (Pyrex, size B) were used to assure retention of loose yarn fragments. Each sample was rolled inside a weighed thimble and two thimbles were placed together in a 400-ml beaker containing 275 ml water, so that the samples were completely immersed. The water was heated to 95°C on a steam bath, held at this temperature for 15 min, and then drained. Each sample was subsequently rinsed with distilled water. This initial scouring and rinsing procedure was repeated twice more. Samples, still in the thimbles, were then passed through three extended cycles of scouring at 95°C for 1 hr and rinsed.[3] Each sample and thimble was then dried to constant weight at

[1] Rohm & Haas Company. Citation of this and subsequent trade names does not constitute an official endorsement by the U. S. Army.

[2] An experimental solution furnished by American Cyanamid Company.

[3] A preliminary study showed that the third 1-hr scour gave a minimum weight loss. Additional scourings gave small erratic weight losses which were apparently due to degradation resulting from extended heating to dryness at 105°C.

105°C as before and the sample weight gain determined by difference. Finally, the percent fixation was calculated based on the original sample weight. The samples produced in this manner were tan in color.

Removal of Unreacted Nylon 66

Both unreacted nylon 66 and accompanying titanium pigment were removed from the water-extracted samples by 2,2,2-trifluoroethanol (TFE) extraction in a Soxhlet equipped with a cellulose-extraction thimble (size 33 mm × 80 mm, Whatman No. 2, double thickness) and a drying tube. As the nylon 66 dissolved during extraction, titanium pigment therein was released and carried away by the TFE solvent. Since the pigment had a small particle size, it passed through the cellulose-extraction thimble and slowly settled to the bottom of the extraction flask. The extraction was continued for 6 hr (24 extractions) with the solvent at 65°C within the thimble. At this time, the product was free of nylon 66. This was indicated, first, when no precipitate formed on diluting the last TFE extract with water and, second, when the differential scanning calorimeter (DSC) plot of the dried residue was found to be completely free of a characteristic nylon 66 endotherm at 259°C.

Thermal Analysis of Isolated Reaction Product

A Perkin-Elmer DSC-1 [18] equipped with a Honeywell Electronic 19 recorder was used. The instrument was operated with nitrogen as the purge gas. Dried PAA control samples were placed in open platinum cups to insure that no reaction took place with residual H_2SO_4 from the PAA solution of pH 1.6. To verify whether any melting occurred with the nylon 66 control, one sample was examined in an uncovered aluminum cup. Closed aluminum cups were used, as usual, with other samples.

Cross-Sectioning and Staining

Seven yarns of each fabric sample were cross-sectioned in a Schwarz Fiber Microtome [4] after being embedded in Mico Lac [4] mounting media. Six cross sections, 20 microns thick, were cut from each sample and were stained at room temperature by immersion for 4 hr in a 30-ml bath of 0.0010% aqueous Malachite Green (91% pure) buffered at pH 7.0. They were then rinsed in water and dried. Cross sections of the untreated nylon were also prepared unstained to serve as a standard for assessing the degree of staining.

The resulting cross sections were examined under a microscope at 440×, using mineral oil as a supplemental mounting media. Photomicrographs of selected significant slides were made at 680×, using 5-sec exposure times with Polaroid type 58 color film.

[4] Mico Instrument Company.

Characterization of Treated Fabric

Nylon 66 was treated as described above to achieve 6% added weight of PAA after scouring. The material was converted to the sodium and calcium salts by boiling for 1 hr with one percent solutions of sodium carbonate and calcium acetate, respectively, at 25 to 1 bath ratios. This was followed by rinsing until the wash water was neutral to litmus and then drying. Moisture regain values were determined on the original free-acid form and the sodium and calcium salts at 70°F and 50% RH. The melting point of the calcium form was measured in the DSC. The sample was housed in an aluminum cup with a lid having a small viewing hole. This cup was inserted in the sample chamber which also contained a viewing port. The chamber was purged with nitrogen while the temperature was elevated.

Discussion and Results

The PAA was chosen because it had the relatively low molecular weight of 15,000–20,000. Selection was based on a desire to obtain maximum penetration into nylon fibers and minimum stiffening of the treated nylon fabric. Both of these specific properties were observed, the former as discussed below, and the latter in a series of fabric samples treated with varying molecular weights (15,000–300,000) of PAA. Other properties observed and/or obtained during the unique treatment process with the low molecular-weight PAA include a fabric color change from white to light tan. This was not considered a serious matter at this stage of the research, even though it is recognized that some dyed shades cannot be achieved with a tan substrate.

Moisture regain values measured on the treated material, after converting it to the sodium and calcium salts, were 5.5 and 4.8%, respectively. These values, measured at 70°F and 50% RH, were higher than the 4.5% regain value usually measured for cotton under identical conditions. The regain value of the free-acid form of the treated material was 2.5%, almost unchanged from that of the original nylon. A marked improvement in thermal properties was shown, as the calcium salt of the material maintained a fabric structure at temperatures much higher than the nylon mp of 258°C. Slight fabric darkening occurred at 340°C, increasing gradually as the temperature was raised. At 375°C, the fabric structure was still intact, but traces of melted material, assumed to be unmodified nylon, were evident; the fabric was nearly black at 385°C.

The amount of PAA fixed to the nylon substrate by this elevated-pressure and temperature method ranged from 0 to 6% [5] and varied inversely with the pH of the treatment solution (Table I). Specifically,

[5] Approximately three times this amount of unfixed PAA was retained by the nylon before scouring.

TABLE I. Relationship of pH to fixation of polyacrylic acid on nylon 66.

Treatment solution	pH	Ave. PAA fixation, %[a]
PAA	5.5	−0.6
PAA	5.2	−0.3
PAA	4.5	−0.4
PAA	4.0	0.5
PAA	3.5	0.7
PAA	3.0	2.1
PAA	2.5	3.8
PAA	2.0	5.9
PAA	1.6	5.7
Water (control)	5.2	−0.8
H_2SO_4 (control)	3.0	−0.7
H_2SO_4 (control)	1.6	−0.7

[a] Average increase in weight of sample after repeated scouring in 95°C. water.

less than 1% fixation was obtained above pH 3.5, while the fixation increased rapidly below this pH. The low pH of the treatment solution was due partly to PAA and partly to sulfuric acid originating in the PAA preparation. For this reason, controls at different pH's were studied to determine the effect of acidity on the nylon under identical temperature and pressure conditions. As shown in Table I, there was a small loss in weight (0.7–0.8%) in the samples under these conditions. The magnitude of this loss was only slightly higher than that for the PAA solution at higher pH. It was, therefore, concluded that the effect was relatively small and constant. No attempt was made, however, to use the control as a correction factor, although it indicated that the amount of PAA reacted might be somewhat higher than observed.

The inverse relationship between the amount of PAA fixed to the fabric and the pH of the PAA solution initially applied appears to depend on the extent of PAA diffusion into the nylon 66 fibers prior to reaction *in situ*. This diffusion is possibly a function of the following several factors, all of which are influenced by pH.

(a) Reduced hydrogen bonding between adjacent nylon 66 molecules could increase their intermolecular distances and thereby generate larger diffusion channels.

(b) Reduced hydrogen bonding between adjacent PAA molecules may give a narrower configuration for diffusion.

(c) Reduced hydrogen bonding between adjacent PAA and nylon 66 molecules might eliminate an obstacle to diffusion.

(d) PAA in solution at pH values greater than four exists as the ionized free acid in the uncoiled molecular configuration; at lower pH values where the ionization is suppressed, the coiled molecular configuration predominates and may have an overall geometry which is more compatible with diffusion.

Diffusion of PAA was shown to occur in the reacted materials by examining stained microscopic cross sections of an untreated nylon control, a sulfuric acid-treated nylon control, two PAA-treated nylon samples (pH 1.6 and 3.0), and two PAA-treated nylon samples previously acetylated with acetic anhydride (Table II). The carboxyl groups of the fixed PAA presumably provided a site for dye fixation and an intense staining of the reacted fiber. The unreacted nylon control did not stain significantly nor did the sulfuric acid-treated nylon control. Both of these had a faint green tint, as shown in Figures 2 and 3, respectively, with the latter somewhat darker. Unstained and untreated nylon is shown for comparison in Figure 1.

TABLE II. Staining results for nylon 66.

Treatment	PAA Fixation, %	Degree of staining	Figure no.
None (control)	0	None (unstained)	1
None (control)	0	Trace	2
pH 1.6 H_2SO_4 (control)	0	Very slight	3
pH 1.6 PAA	5.5	Very heavy	4
Acetylation and pH 1.6 PAA	3.9	Very heavy	—
pH 3.0 PAA	2.1	Very heavy	—
Acetylation and pH 3.0 PAA	0.9	Very heavy	—

The slightly greater staining after H_2SO_4 treatment can probably be explained by the formation of a sulfamic-acid derivative of the nylon which provided additional sites for cationic dye reaction. All of these cross sections show that the fibers varied in diameter, and the unstained control shows that some fibers were pigment-delustered. The pigment, as shown by emission spectroscopy, was a titanium compound and was assumed to be TiO_2, the delusterant normally used for textile fibers. However, these factors did not seem to prevent PAA fixation or penetration. Figure 4 shows the stained PAA-treated cross section, where staining deep into the center has taken place, indicating PAA penetration. As expected, the smaller-diameter fibers were more completely penetrated, but none of the fibers were merely stained at the periphery. The sizes of these fibers can be determind by the 0.1-mm bench marks on these figures. This is the first reported observance for penetration phenomenon of this type. Obviously, the optimum penetration conditions are yet to be achieved, since all the fibers were not stained completely. However, it is felt that this can be improved not only by changing the heat and pressure conditions, but also by using PAA of lower molecular weights.

At attempt was made to determine the mechanism of the fixation reaction by acetylating the amine end groups of the nylon fabric before treatment with PAA. Acetylation was carried out under stronger than nor-

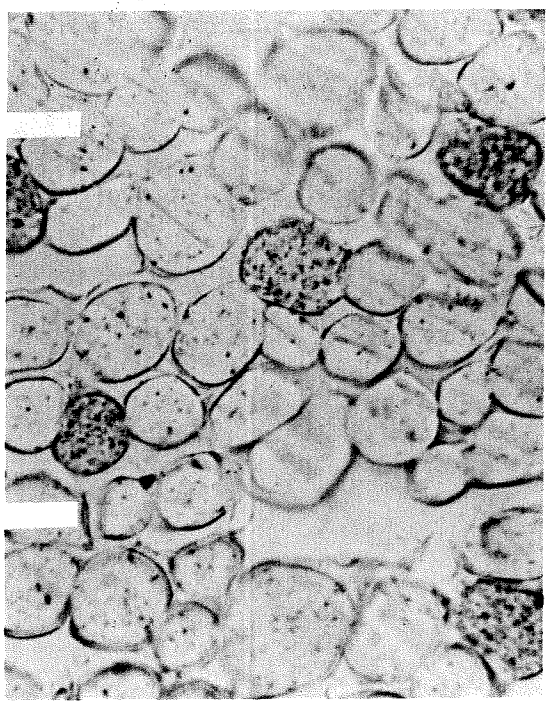

Fig. 1. Unstained untreated nylon 66 control.

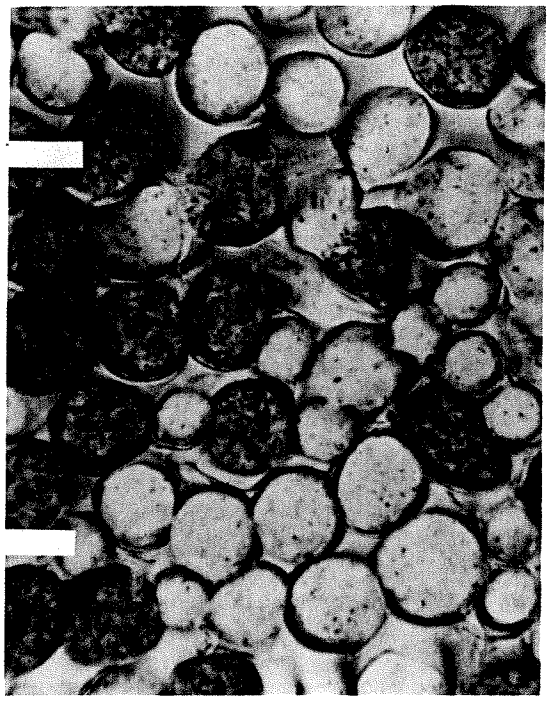

Fig. 2. Stained untreated nylon 66 control.

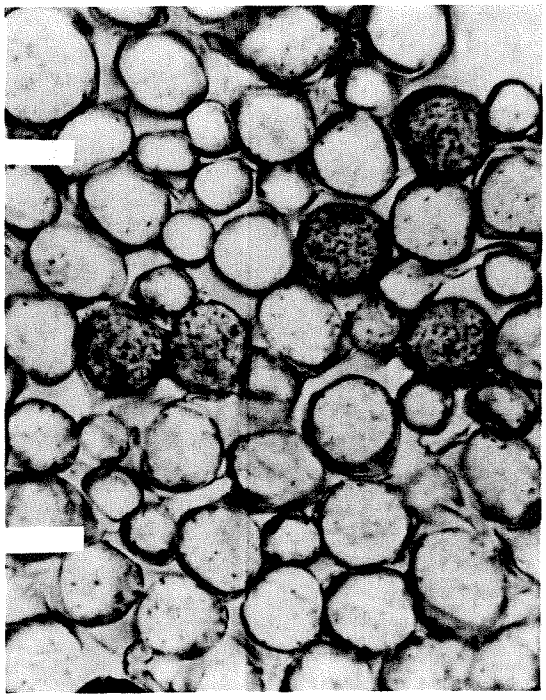

Fig. 3. Stained acid-treated nylon 66 control.

Fig. 4. Stained PAA-treated nylon 66.

mal conditions in an attempt to mask all of the amine groups. The results of treatments at pH 1.6 and 3.0 show a significant reduction in the amount of PAA fixed. In a similar experiment, the nylon was treated with sulfuric acid to effect sulfamation of at least part of the amine end groups. When this material was treated with PAA in the usual manner at pH 3.0, a reduction in the amount of fixation was also obtained. These data are shown in Table III. It thus appears that the mechanism of the PAA reaction involves the amine end groups of nylon, presumably by amide formation with a carboxyl group of the PAA. This mechanism is not considered exclusive at this time, insofar as only a partial reduction in PAA fixation was achieved. Other mechanisms such as transamidation or imide formation are also possible, as suggested by Nuessle [10–12].

TABLE III. Fixation of PAA on acetylated and sulfamated nylon 66.

Treatment	pH	Average PAA fixation, % Nylon 66	Sulfamated Nylon 66	Acetylated Nylon 66
PAA	1.6	5.7	...	4.4
PAA	3.0	2.2	1.4	0.8

Isolation of the PAA-nylon reaction product was accomplished by removal of unreacted nylon with TFE. Preliminary attempts at extracting the nylon with boiling benzyl alcohol, as described by Nuessle, were unsuccessful, since our PAA-fixed material completely dissolved in this solvent. This solubility difference was attributed to the low molecular weight of the PAA used in this work. Other solvents, o-chlorophenol and m-cresol, were also satisfactory for extracting the nylon but were not preferred because of their toxicity.

The product obtained by this procedure behaved differently from the unreacted nylon and PAA, as expected. It was insoluble in water (a PAA solvent) and TFE (a nylon 66 solvent). Its DSC curve had a moderate endotherm peak at 230°C and a strong endotherm peak at 337°C, but it did not melt at these temperatures. Also, there was no endotherm peak at 259°C, characteristic of unreacted nylon 66. This indicated not only that the material had changed composition in the PAA-fixation process, but also that the product was free of unreacted nylon. Similarly, there was no unreacted PAA present, since the broad endotherm characteristic of PAA above 130°C was also absent.

The infrared spectrum [6] of the isolated product showed a carbonyl peak at 1730 cm^{-1}, indicating the presence of carboxyl groups along with the normal nylon 66 amide absorption peaks at 1650 cm^{-1} and 1550 cm^{-1}.

[6] Spectra were obtained in a Beckman Model IR 9 Spectrophotometer using KBr pellets.

Conclusions

Diffusion and copolymerization of PAA prepolymer in nylon 66 fibers has been attained, as indicated by examination of stained fiber cross sections and isolation of reacted material. The mechanism of the reaction appears to involve not only the amine end groups of the nylon by formation of a block copolymer, but also additional sites on the nylon backbone by formation of a graft copolymer. Of particular significance is the fact that penetration of the PAA into the nylon fiber can be achieved.

This diffusion and copolymerization process is advantageous, insofar as it can be accomplished in conventional textile wet-processing equipment. It has the further advantage that the molecular weight of the copolymers can be controlled up to a point by the molecular weight of the PAA prepolymer. Also, it yields a fabric with increased moisture sorption capacity and thermal radiation resistance.

One disadvantage of the process at present is its relatively low efficiency. The degree of fixation varies up to 6% after scouring. Since the weight increase before scouring is considerably higher, much of the PAA originally applied is unreacted. This unreacted PAA could presumably be recovered and recycled to prevent losses and increase the process efficiency. A better approach to this problem would be to obtain further penetration into the fibers and thus further fixation by lowering the PAA molecular weight and varying the process conditions.

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