

Surface Modification of Polyacrylonitrile Staple Fibers via Alkaline Hydrolysis for Superabsorbent Applications

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Received 28 February 2003; accepted 23 August 2003

ABSTRACT: The alkaline hydrolysis of polyacrylonitrile staple fibers was investigated for evaluation as superabsorbent materials. Studies were performed to analyze the hydrolysis of fibers and the quantification of the developed functional groups, such as carboxyl and amide groups as well as changes in the nitrile content by means of Micro-ATR. Dyeing of the samples with methylene blue was carried out to monitor the carboxyl groups formed during the hydrolysis. A gradual decrease in the nitrile groups and built up of the carboxyl and the amide groups was observed during the hydrolysis. Microscopic investigation carried out

to investigate the surface structure of hydrolyzed fibers. Hydrolysis led to surface nonhomogeneity and erosion that was dependent on the hydrolysis conditions. The fibers showed good water retention behavior, making them superabsorbent materials. The dyeing showed more intense coloration in the surface region of the modified fibers. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 3127–3133, 2004

Key words: polyacrylonitrile; superabsorbent; surface characterization; FTIR (Micro-ATR)

INTRODUCTION

Acrylic fibers occupy a prominent position in the family of synthetic fibers and have replaced wool in many respects.¹ They have extensive applications in apparel as well as in related industrial sectors. They are mainly used for bulk yarn production and pullovers. In recent years, a broad range of acrylic products have become available for a number of application areas, such as water-absorbent, antistatic fibers, conducting fibers, ion-exchange fibers, and antimicrobial fibers.² Superabsorbent materials have an important role to play in today's world. The most popular superabsorbent polymers exist in the form of a sodium salt of polyacrylic acid, available as powder or in granular form and used mainly in personal care products such as baby diapers.^{3,4} The limitations of using superabsorbents in granular form lie in migration in the superabsorbent core, pinhole formation in the waterproof backsheet of a diaper, and harmfulness in contact with eyes and skin of the baby. All these aspects motivate the application of superabsorbents in fibrous materials instead of using the powder form. By virtue of the presence of nitrile groups along the fiber backbone, it offers multidirectional approaches to modify fibers for specific applications.

The modification of fibers and fabrics, without deterioration in the bulk properties, is an interesting domain. It is necessary to optimize reaction conditions to achieve required characteristics in the fiber. The alkaline hydrolysis of polyacrylonitrile (PAN) has been employed as an alternative way of superabsorbent polymer processing.⁵ On alkaline hydrolysis, PAN fibers undergo some chemical and color changes during reaction.^{6,7} Initially, the alkali modifies the surface and then penetrates inside the fiber structure. The final chemical change in hydrolyzed PAN gives the sodium salt of carboxylic acid along the polymer backbone. This polyacrylate salt is responsible for the superabsorbency of the hydrolyzed PAN.

Alkaline hydrolysis of PAN to produce superabsorbents has been studied by several workers.^{8–11} However, extensive studies on controlled modification of the fiber or the fabric form of PAN have not been conducted. Moreover, the reaction mechanism is still not clear.^{6,7} Therefore, in this study an attempt has been made to study the modification of acrylic fiber under alkaline conditions for enhancing its water absorptivity.

EXPERIMENTAL

Material

PAN Staple fibers (Dolanit) supplied by Acordis (Kelheim, Germany) were used for the hydrolysis. The specifications of fibers are as follows: comonomer, methyl acrylate, 0.5%; fiber molecular weight, 2.1×10^5 g/mol.

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Dimethylformamide (DMF) and sodium hydroxide were received from Fluka. Deionized water was used for all experiments. Methylene Blue was supplied by Fluka.

Alkaline treatment

Acrylic fiber was placed in a glass tube containing the required amount of sodium hydroxide solution. The tube was subsequently placed in a water bath maintained at a constant temperature of 95°C. After hydrolysis, samples were washed with deionized water and dried under vacuum.

Nitrogen estimation by Kjeldahl method

Nitrogen content determination was carried out by the Kjeldahl method using a Buechi (B-343) machine. Nitrogen digestion was carried out using 98% H₂SO₄. Two observations for each sample were taken and averaged. Two blank readings were taken before analyzing samples. Titration of the distilled ammonia was carried out against 1 mol/L hydrochloric acid. Nitrogen content was obtained as per the following equation:

$$\% \text{ Nitrogen} = (\text{volume of HCl} - \text{blank reading}) \times 14 / (\text{fiber weight})$$

Carboxylic group content determination

Carboxyl group estimation was carried out using the methylene blue coloration method.¹² The dye was extracted by dissolving the dyed fibers in DMF and absorbance was recorded on a UV/visible spectrophotometer (Perkin-Elmer) at wavelength maximum of 664 nm. Carboxyl groups were calculated as mmol/g of the fiber.

Micro-attenuated total reflectance (μ -ATR) spectroscopy

The micro-ATR accessory was a germanium crystal (A 529-P/Q model, Bruker Optics, Germany), and Windows NT OPUS (Optics User Software) was used for the analysis. The bulk FTIR spectra of samples were taken using KBr pellets. The ratios of peaks for nitrile, amide, and carboxyl groups with respect to the —CH₂ peak were determined.

Scanning electron microscopy (SEM)

SEM studies were carried out on a LEO DSM962. Single fibers were mounted on a SEM sample holder by using a Leit-Tab. The sample was then sputtered with Au/Pd in an Edwards Sputter Coater S 150 B.

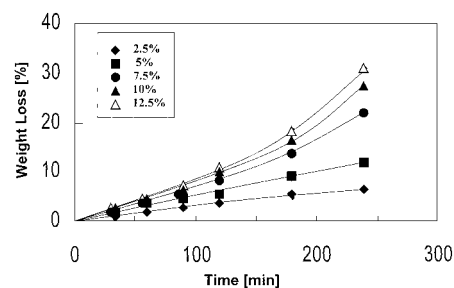


Figure 1 Weight loss as a function of treatment time at various alkali concentrations: temperature, 95°C.

Water retention capability

Samples were dried for 1 h at 105°C and weighed. Subsequently, fibers were placed in distilled water for 20 min. Samples were removed and placed in a glass tube, centrifuged for 15 min at 1500 rpm, and then weighed. Water absorption was determined as the increase in the weight of the fiber.

Transmission light microscopy

A hank of dyed fibers was prepared and embedded on a cardboard frame. The embedding medium was LR white, produced by Agar Scientific. Cross sections were made using a Jung microtome, model MINOT. The thickness was adjusted to 10 microns. Pictures were taken on a ZEISS Axioplan microscope in transmission light microscopy. Images were recorded by a digital camera and imaging system, DC 200 from Leica.

RESULTS AND DISCUSSION

The hydrolysis of acrylic fiber was carried out for different periods using alkali concentrations in the range of 2.5–12.5%. The results are presented in Figure 1. Results show a gradual loss in the weight of the fiber with the increase in the reaction time. The weight loss is more pronounced for the higher alkali concentrations. It seems that chains, which are shorter and are loosely packed within the polymer matrix, are quickly converted into water-soluble products and lead to the weight loss. As the reaction progresses with time, alkali travels gradually from surface to the core of the fiber and subsequently converts these shorter chains into water-soluble products. With the increasing sodium hydroxide concentration, the hydrolysis of the polymer chains becomes vigorous and therefore higher weight loss is observed. It is interesting to observe autocatalytic behavior beyond 90 min during hydrolysis, which is, in fact, more pronounced at higher alkali concentration. Once hydrolysis starts, it makes the fiber more hydrophilic, which enhances the aqueous alkali imbibition in the fiber and enhances

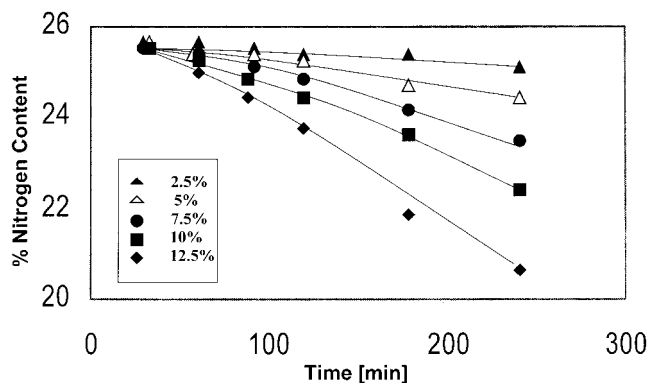


Figure 2 Variation of nitrogen content with the treatment time at various alkali concentrations: temperature, 95°C.

the hydrolysis and hence the weight loss in the fiber that is observed.

Figure 2 shows the nitrogen content of samples treated under various reaction conditions. The nitrogen content in the original PAN staple fiber was 25.6% as compared to the theoretical value of 26.4%. This was also verified by elemental analysis of PAN original fiber. The hydrolysis led to a gradual decrease in

the nitrogen content with the reaction time. This is an indication that nitrile groups are transformed into other functional groups. The most likely groups are amide and carboxyl groups, as observed in earlier studies.¹¹ The higher loss of nitrogen at higher alkali concentration is well in line with the assumption that the transformation of nitrile is more pronounced.

The hydrolysis of PAN fiber is evident from the FTIR-ATR of samples at different hydrolysis periods (Fig. 3). The original fiber shows a peak at 2245 cm^{-1} for the $-\text{CN}$ group and at 1743 cm^{-1} for the ester group. The hydrolysis leads to the development of peaks at 1550 cm^{-1} and 1688 cm^{-1} , which indicates the presence of $-\text{COONa}$ and $-\text{CONH}_2$ groups in the modified fiber. The nitrile content, and its transformation into amide and carboxyl groups as obtained from FTIR- μ -ATR, is presented in Figure 4. Nitrile groups decrease with the time of hydrolysis. At the same time, the formation of amide and carboxyl groups takes place. It is important to see that the nitrile groups decrease and the amide as well as carboxyl groups increase and reach equilibrium at 1 h of hydrolysis time. However, a slight decrease in the carboxyl and amide groups is observed at higher re-

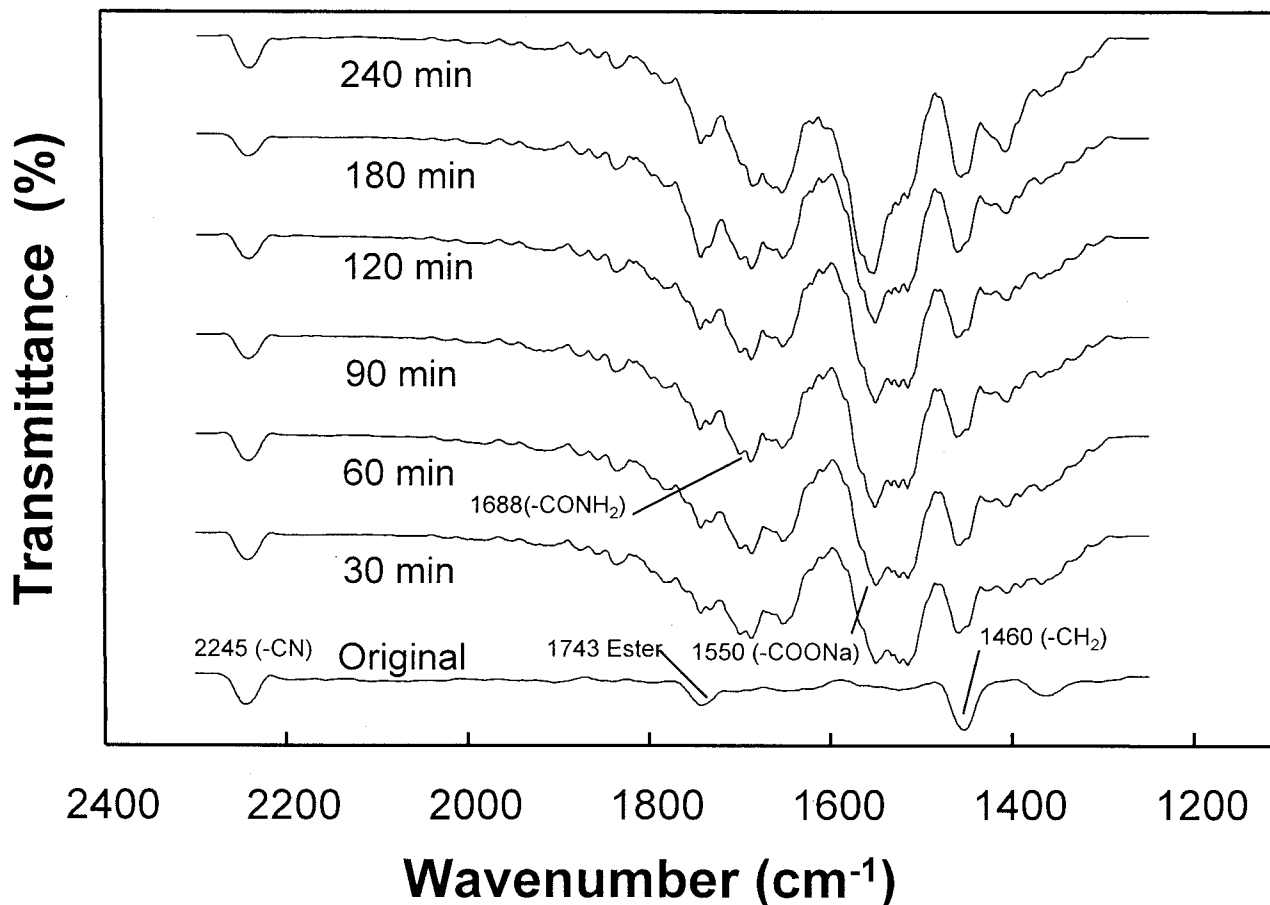


Figure 3 μ -ATR of PAN samples hydrolyzed at various periods: alkali concentration, 7.5%; temperature, 95°C.

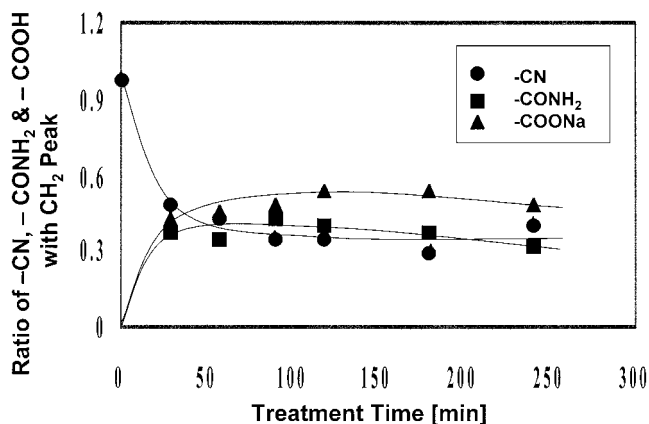


Figure 4 Variation of nitrile, carboxyl, and amide groups by FTIR with hydrolysis time: alkali concentration, 7.5%; temperature, 95°C.

action time indicating deactivation of groups most probably by the crosslinking reaction.

Considering the net result of nitrile hydrolysis as the formation of amide and carboxyl groups, assessment of carboxyl groups was carried out via dyeing with methylene blue (Fig. 5). It can be observed that methylene blue absorption by the alkali treated fibers increases with the hydrolysis time up to ~100 min and then tends to decrease, subsequently. These observations may be explained in terms of the dyeing mechanism of fibers that depends on the carboxylic content present in the polymer system, but also on the permeability of the dye within the fiber. It was observed that, with higher treatment times (> 150 min), fiber loses its physical structure because its surface dissolves almost completely and subsequently, gel formation takes place and the fiber has no more identity in terms of length, individuality, and thickness. On increasing treatment time, crosslinking involving carboxyl groups increases. The availability of carboxylic groups for the bulky dye molecules, therefore, reduces signif-

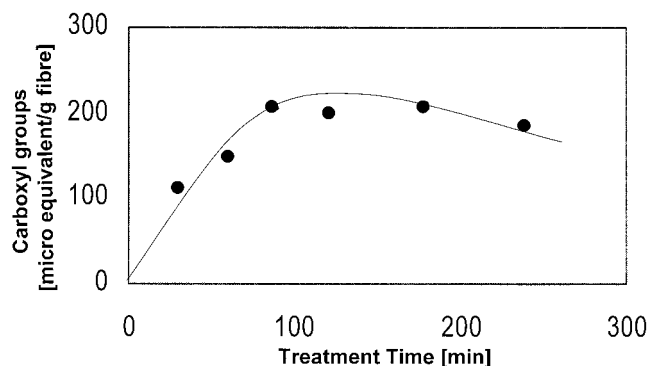


Figure 5 Carboxylic group content in hydrolyzed PAN fibers by methylene blue absorption: sodium hydroxide, 7.5%; temperature, 95°C.

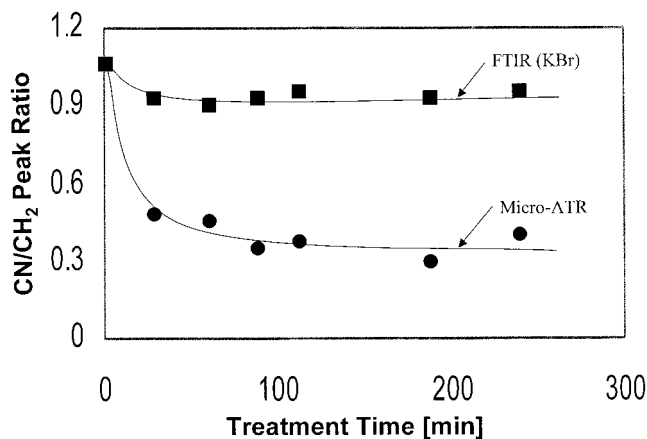


Figure 6 Quantification of nitrile content on Surface and bulk by FTIR and ATR of samples: sodium hydroxide, 7.5%; temperature, 95°C.

icantly because carboxylic groups also take part in crosslinking.

The μ -ATR of fibers, hydrolyzed at different reaction times, showed a progressive loss in the nitrile peak at 2245 cm^{-1} and the evolution of peaks at 1550, 1480, and 1405 cm^{-1} , which are characteristic of the carboxyl and amide groups. In order to investigate the gradient in the nitrile functionality across the fiber matrix, both the μ -ATR and FTIR of samples were monitored (Fig. 6). Although the trend in the nitrile variation was identical for both the methods, the FTIR showed almost 10% loss in the nitrile content right in the beginning and remained constant for the whole period of the hydrolysis. μ -ATR, on the other hand, showed much higher loss (~66%) in the nitrile content for similar treatment time. These results are indicative of the higher degree of transformation of nitrile groups at the surface of the fiber as compared to the bulk matrix.

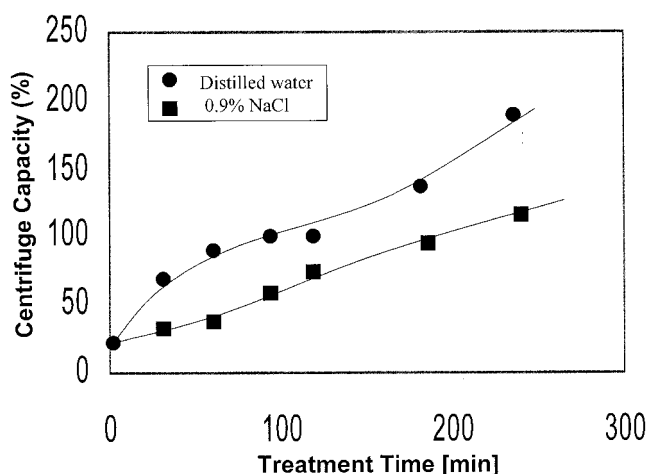


Figure 7 Centrifuge capacity of PAN fiber with treatment time: sodium hydroxide, 7.5%; temperature, 95°C.

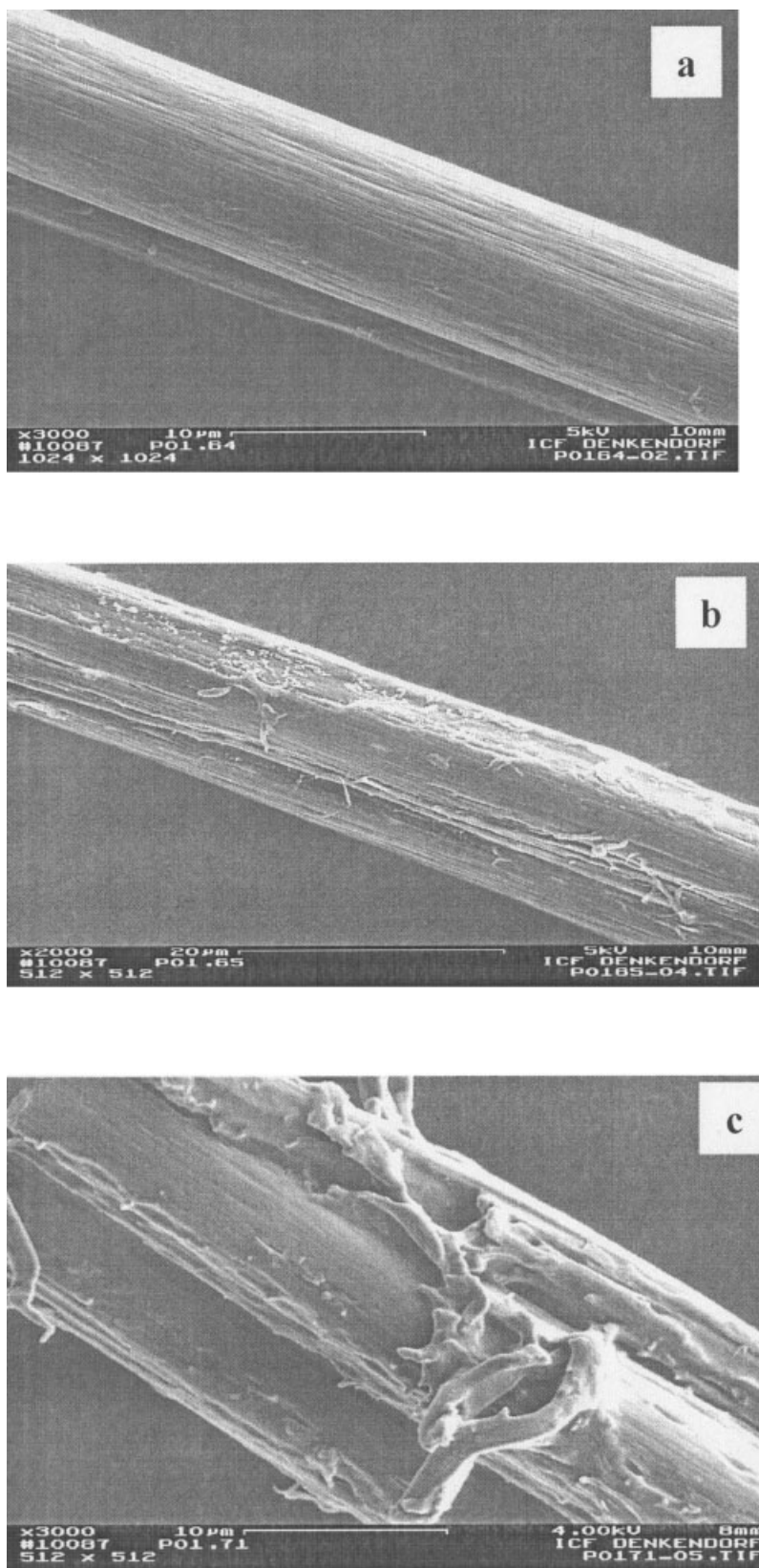


Figure 8 SEM photograph of (a) untreated PAN fiber and (b) alkali treated fiber, 2.5% sodium hydroxide for 3 h; (c) alkali-treated fiber, 10% sodium hydroxide for 2 h.

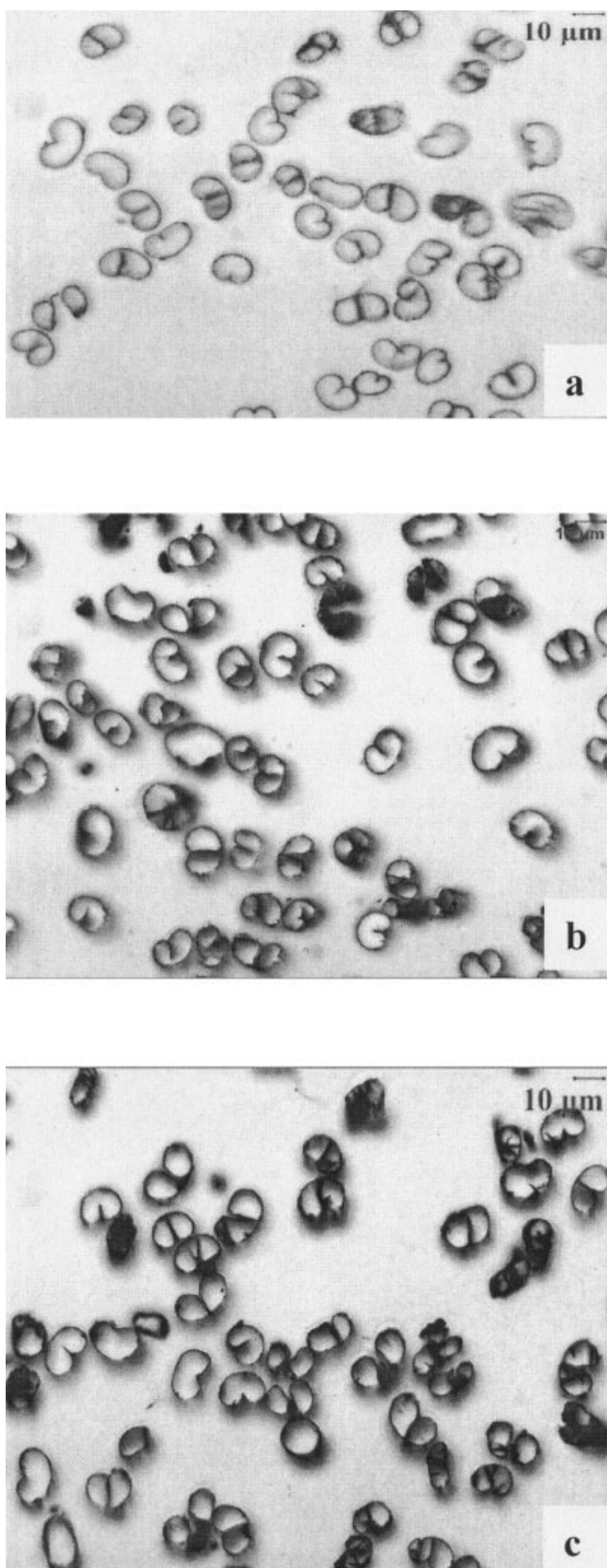


Figure 9 Cross-sections of (a) untreated dyed PAN fiber and (b) dyed PAN fiber, 7.5% NaOH for 1 h; (c) dyed PAN fiber, 7.5% NaOH for 2 h.

The swelling behavior of fibers with the time of hydrolysis is presented in Figure 7. The water retention capacity of the fiber increases considerably as compared to the original fiber. The presence of the salt in water reduces the swelling, significantly. The higher the hydrolysis time, the higher is the water uptake. This behavior is associated with the increase in the hydrophilic functionality such as carboxyl and amide groups. As the hydrolysis progresses, the hydrophilic functionality increases and leads to higher water uptake.

The surface morphology of the fibers was evaluated by scanning electron microscopy. The original fiber shows a smooth surface (Fig. 8). However, hydrolysis makes the surface nonhomogeneous: the surface roughness is more pronounced at higher alkali concentration. The results indicate that the alkali treatment of the fiber leads to surface erosion and detachment of fibrils. This loosening of the structure originates due to the loss of intermolecular interaction between the chains. These fibers were dyed with methylene blue to study the influence of the hydrolysis. The cross section analysis of dyed fibers [Fig. 9(a–c)] shows that in the surface modified samples (low treatment time) dye is confined mostly on the surface, while in case of bulk modified samples (higher treatment time) dye penetrates into the fiber as well.

CONCLUSION

During alkaline hydrolysis of polyacrylonitrile staple fibers, nitrogen content in the sample decreases gradually, while the formation of amide and carboxyl groups follows smoothly. It seems that some crosslinking takes place during the hydrolysis reaction so that the hydrophilic groups are deactivated partially and their content does not increase anymore. Methylene Blue absorption results provide an idea about cross linking in the product as well as severe deterioration in the physical structure of the fiber. Scanning Electron Micrographs study confirms the layer-by-layer degradation. Also the small molecular chains loosely packed in the polymer system dissolve continuously with the treatment time and this degradation becomes faster with the increase in the NaOH concentration. Cross section analysis of dyed fibers shows that, in the surface modified samples, dye is mostly on the surface, while in case of bulk modified samples dye penetrates into the fiber also. This is the indication that the polyacrylonitrile fiber structure is transformed into a structure where dye diffusion is enhanced so that the dye-carboxyl site interaction is facilitated.

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