Conducting Nylon fibers were prepared by in situ polymerization of aniline on to the fiber surface, after providing a chemical etching treatment to the fibers using chromic acid. The properties of the etched and polyaniline coated fibers were evaluated using scanning electron microscopy, X-ray photoelectron spectroscopy, infrared spectroscopy, X-ray diffraction, thermogravimetry and differential scanning calorimetry. Though the etching process caused a marginal decline in the mechanical properties of the fiber, it provided a reasonably rough surface for PANI adhesion and enhanced the conductivity of the fiber. The conductivity increased from $4.22 \times 10^{-2}$ S/cm to $3.72 \times 10^{-1}$ S/cm at an etching time of 4 h.

Chapter 2

Polyaniline coated short Nylon fiber*

2.1 Introduction

Conductive polyaniline (PANI)/polymer fibers can be produced either by inclusion of PANI or by in situ oxidative polymerization of aniline monomer. Owing to low thermal stability and insolubility of PANI, the former method is hardly acceptable for producing conductive composite fabrics. Therefore, most studies have focused on in situ polymerization route to produce conductive fabrics. This method does not require destruction of the substrate and provides reasonably good conductivity and

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- International Conference POLYCHAR-16, World Forum of Advanced Materials, Feb 17-21, 2008, World Unity Convention Center, Lucknow, India
- 17th AGM of Materials Research Society of India, AGM-MRSI, Feb 13-15, 2006, University of Lucknow, India
- National Conference on Frontiers in Polymer Science and Technology, POLYMER 2006, Feb 10-12, 2006, Indian Association for the Cultivation of Science, Kolkata, India
produces modified polymer matrices with a PANI layer at their surface. The thickness and conductivity of the layers depend on the method of modification and on the time of contact of the solid matrix with the reaction medium. The surface conductivity obtained may range, from semiconductor level up to the conductivity of pure PANI. Even a simple dipping method resulted in conductivity of 1-5 S/cm and transmittance of 80% at 450-650 nm for a 0.5 µm PANI layer [1]. Apparently, this method is not technically suitable for sheet materials, because it requires the use of polymer matrixes with a good adhesion to PANI. Moreover, it produces pure PANI deposits having poor mechanical properties. At the same time, for fibers and textile materials with a well-developed reactive surface, it may lead to the production of conducting fibers and fabrics with PANI grafted on the surface and inside the pores.

Genies et al. have reported the impregnation of PANI onto glass textiles [2]. Chemical polymerization of polypyrrole on poly(ethylene terephthalate) fabric was reported by Kim et al. [3]. Aniline can be polymerised on the fabrics from the aqueous solution [4-6] or the vapor phase [7] using appropriate oxidizing agents. The use of peroxosalts as oxidants causes a graft copolymerization of aniline and its derivatives onto a polymer matrix [8]. Anbarasan and co-workers investigated the kinetics of this grafting onto rayon [9], wool [10] and PET [11] fibers and proposed a possible mechanism of graft and homo polymerization of aniline. Specifically, they carried out oxidative chemical polymerization of aniline using peroxydisulfate and peroxomonosulfate as the sole initiator in an aqueous acidic medium in the presence of the fibers. This resulted in the chemical grafting of PANI onto the fibers, confirmed by Fourier Transform Infrared spectroscopy (FTIR), cyclic voltammetry, weight loss study, and conductivity measurements. The authors proposed a probable mechanism involving graft polymerization of aniline through interaction of the oxidant with the fiber surface, inducing the formation of radical sites at the fiber surface, followed by grafting aniline with its subsequent participation in a typical aniline oxidative polymerization. The conductivity of such fabrics depended on deposition of conductive polymer on the surface or in the interstices of the fabric [4, 12]. A PANI layer bonded strongly to the fiber surface is required for better conductivity.
and durability. This can be achieved by improving the adhesion of PANI on the fiber surface.

Two methods to obtain electrically conductive fabrics by *in situ* polymerization of aniline were compared by Oh and coworkers [13]. These materials were prepared by immersing the Nylon fabrics in pure aniline or an aqueous hydrochloride solution of aniline followed by initiating the successive direct polymerization in a separate bath (DPSB) or in a mixed bath (DPMB) of oxidant and dopant solution with aniline. They showed that the DPMB process produced higher conductivity in the composite fabrics, reaching $0.6 \times 10^{-1}$ S/cm. Moreover, this process induced a smaller decrease in the degree of crystallinity than the DPSB process. The PANI/Nylon composite fabrics displayed a good serviceability. Thus, no important changes in the conductivity were observed after abrasion of the composite fabrics over 50 cycles and multiple acid and alkali treatment. The stability of the conductivity decreased by less than one order after exposure to light for 100 h, but it was significantly decreased after washing with a detergent.

In another work, the same authors attempted plasma treatment of the fabrics to improve the surface adhesion between PANI and Nylon fabric and hence the serviceability, conductivity and durability [14]. But this is an expensive method. An alternate, less expensive method is chemical etching of the fiber surface. The monomer and the oxidant are adsorbed on the surface of the fiber instead of diffusing into the fiber. Therefore, it is expected that the fabric conductivity and adhesion of the polymer on the fiber surface can be improved with an increase in the surface energy and surface area. This can be achieved by the chemical etching process. In this work, we have explored the possibility of using chromic acid for improving the adhesion properties and conductivity of Nylon fibers. Optimization of chromic acid concentration and etching time and the electrical properties of the PANI deposited etched Nylon fiber are presented. Surface characteristics of the etched fibers were analyzed using scanning electron microscopy, X-ray photoelectron spectroscopy, infrared spectroscopy and X-ray diffraction analysis. The thermal characterization of the coated fibers is also presented.
Chapter 2

2.2 Experimental

2.2.1 Materials

Nylon-6 fibers (1680/2D) were obtained from Sri Ram Fibers Ltd., Chennai, India. Aniline, ammonium peroxydisulfate, hydrochloric acid and chromium trioxide were supplied by S. D. Fine Chemicals Ltd., Mumbai, India.

2.2.2 Preparation of polyaniline

An aqueous solution of ammonium peroxydisulfate (1.62 M) was added drop wise to a solution of 0.0219 M aniline in 50 ml, 1 N hydrochloric acid at ambient temperature. After complete addition, the reaction was left to proceed for 4 h. The precipitate formed was then filtered, washed with acetone till the filtrate became colorless, followed by a wash with dilute hydrochloric acid and finally with water. The PANI formed was then dried in an air oven at 60 °C.

2.2.3 Etching treatment

1 g of the chopped Nylon fibers (5 mm) were immersed in 250 ml of aqueous chromic acid solution of a specified concentration at 60-65 °C with continuous stirring for a specified time. The etched fibers were subsequently filtered and washed with distilled water till the washings were free from coloration and then dried at 60 °C in an air oven.

2.2.4 In situ polymerization

0.5 g of the etched fiber was soaked in 10 ml of aniline for 24 h at room temperature. The excess aniline was then drained off and the fibers were blotted with tissue paper. The weight of the fiber before and after soaking was noted. The percentage of aniline absorption was determined to be 23.8 %. The soaked fibers were then added to a solution of 0.0219 moles of aniline in 50 ml, 1 N hydrochloric acid. The polymerization was carried out for 4 h at room temperature using an aqueous solution of ammonium peroxydisulfate (1.62 M). These were then filtered, washed with water till the washings became colorless and further dried.
2.2.5 Characterization

2.2.5.1 Tensile strength

The mechanical properties of the fibers were studied using a Shimadzu Universal Testing Machine (UTM model AG I) with a load cell capacity of 10 kN. The gauge length between the grips at the start of each test was adjusted to 50 mm. The fibers of 254 mm length were held between the two grips and a uniform rate of grip separation (cross-head speed) of 20 mm/min was applied. The strength was evaluated after each measurement automatically by the microprocessor and presented on a visual display. Average of at least six sample measurements were taken to represent each data point.

2.2.5.2 Scanning electron microscopy (SEM)

Scanning electron microscopy is a very useful tool to gather information about topography, morphology, composition and micro structural information of materials. In a typical SEM, electrons are thermionically emitted from a tungsten or lanthanum hexaboride (LaB$_6$) cathode and are accelerated towards an anode; alternatively, electrons can be emitted via field emission. The electron beam, which typically has an energy ranging from a few hundred eV to 100 keV, is focused by one or two condenser lenses into a beam. Characteristic X-rays are emitted when the primary beam causes the ejection of inner shell electrons from the sample and are used to tell the elemental composition of the sample. The back-scattered electrons emitted from the sample may be used alone to form an image or in conjunction with the characteristic X-rays. These signals are monitored by detectors (photo multiplier tubes) and magnified. An image of the investigated microscopic region of the specimen is thus observed in cathode ray tube and is photographed.

The SEM images of the short fibers were obtained using a Cambridge Instruments S 360 stereo scanner (version V02-01). The fibers were mounted on a metallic stub and an ultrathin coating of electrically conducting material (gold) is deposited by low vacuum sputter coating. This is done to prevent the accumulation of static electric fields at the specimen due to the electron irradiation during imaging. Another reason
for coating, is to improve contrast. The SEM is capable of producing high-resolution images of a sample surface.

### 2.2.5.3 X-ray photoelectron spectroscopy (XPS)

For each and every element, there will be a characteristic binding energy associated with each core atomic orbital i.e. each element will give rise to a characteristic set of peaks in the photoelectron spectrum at kinetic energies determined by the photon energy and the respective binding energies. The presence of peaks at particular energies therefore indicates the presence of a specific element in the sample under study. Furthermore, the intensity of the peaks is related to the concentration of the element within the sampled region. The shape of each peak and the binding energy can be slightly altered by the chemical state of the emitting atom. Hence XPS can provide chemical bonding information as well. XPS is not sensitive to hydrogen or helium, but can detect all other elements. Thus, X-ray photoelectron spectroscopy is a quantitative spectroscopic technique that measures the elemental composition, empirical formula, chemical state and electronic state of the elements that exist within a material. XPS is also known as ESCA, an abbreviation for Electron Spectroscopy for Chemical Analysis.

The phenomenon is based on the photoelectric effect. XPS spectra are obtained by irradiating a material with a beam of aluminum or magnesium X-rays while simultaneously measuring the kinetic energy and number of electrons that escape from the top 1 to 10 nm of the material being analyzed. XPS requires ultra-high vacuum conditions. Commercial XPS instruments use either a highly focused 20 to 200 µm beam of monochromatic aluminum K-alpha X-rays or a broad 10-30 mm beam of non-monochromatic Mg X-rays.

The surface of the fibers was analyzed using an X-ray induced photoelectron VG Scientific ESCA-3000 spectrometer using a non-monochromatic Mg Kα radiation (1253.6 eV). First a general scan was recorded from 0-1000 eV at steps of 1 eV to confirm the presence of C, N and O in the sample. Then, narrow scans were done for C1s, N1s and O1s at steps of 0.1 eV. To correct for possible deviations caused
by electric charge of the samples, the C$_{1s}$ line at 285 eV was taken as internal standard.

2.2.5.4 Infrared spectroscopy (IR)

Infrared spectroscopy is the absorption measurement of different IR frequencies (400-4000 cm$^{-1}$) by a sample positioned in the path of an IR beam. Infrared spectroscopy exploits the fact that molecules have specific frequencies at which they rotate or vibrate corresponding to discrete energy levels. These resonant frequencies are determined by the shape of the molecular potential energy surfaces, the masses of the atoms and, by the associated vibronic coupling. In order for a vibrational mode in a molecule to be IR active, it must be associated with changes in the permanent dipole. The frequency of the vibrations can be associated with a particular bond type.

The infrared spectrum of a sample is collected by passing a beam of infrared light through the sample. Examination of the transmitted light reveals how much energy was absorbed at each wavelength. This can be done with a monochromatic beam, which changes in wavelength over time, or by using a Fourier Transform instrument to measure all wavelengths at once. From this, a transmittance or absorbance spectrum can be produced, showing at which IR wavelengths the sample absorbs. Analysis of these absorption characteristics reveals details about the molecular structure of the sample. This technique works almost exclusively on samples with covalent bonds.

Infrared spectra of the fibers were recorded on a Bruker FTIR spectrophotometer model Tensor 27 (spectral range of 7500 cm$^{-1}$ to 370 cm$^{-1}$ with standard KBr beamsplitter) in attenuated total reflectance (ATR) mode. It uses zinc selenide as the crystal material with high sensitivity DLATGS detector with KBr window.

2.2.5.5 X-ray diffraction (XRD)

X-rays are electromagnetic radiation of wavelength about 1 Å, which is about the same size as an atom. X-ray diffraction has been in use in two main areas, for the fingerprint characterization of crystalline materials and the determination of their
structure. Each crystalline solid has its unique characteristic X-ray powder pattern which may be used as a "fingerprint" for its identification. Once the material has been identified, X-ray crystallography may be used to determine its structure, i.e. how the atoms pack together in the crystalline state and what the interatomic distance and angle are, etc. X-ray diffraction is one of the most powerful characterization tools used in solid state chemistry and materials science. We can determine the size and the shape of the unit cell for any compound most easily using the diffraction of X-rays.

X-ray diffractograms of the fibers were recorded using a Bruker AXS D8 Advance Diffractometer using CuKα radiation (λ = 1.54 Å) at 35 kV and 25 mA with a smallest addressable increment of 0.001°. XRD results were obtained in the range 2θ = 3° to 80° at a scan rate of 4°/min.

2.2.5.6 Thermogravimetric analysis (TGA)

Thermogravimetric analysis is a type of testing that is performed on samples to determine changes in weight in relation to change in temperature. Such analysis relies on a high degree of precision in three measurements: weight, temperature, and temperature change. TGA is commonly employed in research and testing to determine characteristics of polymers, to determine degradation temperatures, absorbed moisture content of materials, the level of inorganic and organic components in materials, decomposition points of explosives, solvent residues and composition of blends and composites. The analyzer usually consists of a high-precision balance with a pan loaded with the sample. The sample is placed in a small electrically heated oven with a thermocouple to accurately measure the temperature. The atmosphere may be purged with an inert gas to prevent oxidation or other undesired reactions. A computer is used to control the instrument. Analysis is carried out by raising the temperature gradually and plotting weight against temperature.

Thermogravimetric studies lend a hand in determining the thermal stability of the fibers. The TGA instrument produces a continuous record of weight as a function of temperature. TGA studies were carried out on a Q-50, TA Instruments
thermogravimetric analyzer (TGA) with a programmed heating of 20 °C/min from ambient to 800 °C. The chamber was continuously swept with nitrogen at a rate of 90 ml/min. The onset temperature of degradation was recorded and temperature at maximum degradation was taken as the peak degradation temperature. The weight percentage of the samples remaining at 800 °C was recorded as the residue.

### 2.2.5.7 Differential scanning calorimetry (DSC)

Differential scanning calorimetry is a technique for measuring the energy necessary to establish a nearly zero temperature difference between a substance and an inert reference material, as the two specimens are subjected to identical temperature regimes in an environment heated or cooled at a controlled rate. Both the sample and reference are maintained at nearly the same temperature throughout the experiment. The basic principle underlying this technique is that, when the sample undergoes a physical transformation such as phase transitions, more (or less) heat will need to flow to it than the reference to maintain both at the same temperature. Whether more or less heat must flow to the sample depends on whether the process is exothermic or endothermic. By observing the difference in heat flow between the sample and reference, differential scanning calorimeters are able to measure the amount of heat absorbed or released during such transitions.

Differential scanning calorimetry was employed to determine the degree of crystallinity, heat of fusion and melting temperature of the fibers. The measurements were conducted using a DSC Q-100, TA Instruments calorimeter having a temperature accuracy of ± 0.1 °C. Analyses were done in nitrogen atmosphere using standard aluminum pans. The samples were exposed to a heating rate of 10 °C/min from ambient to 300 °C. The peak temperature of the melting endotherm was taken as the melting temperature; $T_m$, and the heat of fusion; $\Delta H_f$, was determined from the area of the melting endotherm. The degree of crystallinity; $\chi_c$, was determined by normalizing the observed heat of fusion of the sample to that of a 100 % crystalline sample of Nylon, which is available from literature [15, 16].
2.2.5.8 DC electrical conductivity

The DC electrical conductivity of the fibers was measured by a two-probe method using a Keithley 2400 source-measure unit, which is a fully programmable instrument capable of sourcing and measuring voltage or current simultaneously with accuracy. A constant current source was used to pass a steady current through one of the probes and the voltage across the other was measured. The measurements were done at room temperature. The conductivity of the sample was calculated by the following formula:

\[ \sigma (S/cm) = (I/V) \times (l/A) \]  

(2.1)

where, \( \sigma \) is the electrical conductivity, \( I \) is the current through the probe in amperes, \( V \) is the voltage across the probe in volts, \( l \) is the spacing between the probes in centimeters and \( A \) is the area of contact of the probes with the sample in centimeter square.

2.3 Results and discussion

2.3.1 Characterization of polyaniline

2.3.1.1 Scanning electron microscopy

The SEM micrograph of pristine PANI can be seen in fig. 2.1. It shows aggregated granular form and lacks macroscopic molecular orientation. Several reports on such a granular morphology of PANI are available in the literature [17]. Especially, such morphology is obtained in the absence of a surfactant [18]. The shape of the chemically polymerized polyaniline particles is generally difficult to be controlled in a bulk polymerization process. PANI aggregates are made of small grains comprised of a collection of small spheres, which in turn, is comprised of smaller spheres built from still smaller primary particles. These primary particles have a metallic core surrounded by an amorphous non-metallic shell. Haba and coworkers calculated the average size of the DBSA doped primary PANI particles to be 18.7 nm using Small angle X-ray scattering (SAXS) [19]. These primary particles generate aggregates,
which further cluster into agglomerates. These agglomerates, about 50 µm in size, are located within gel-like units, which are structured due to the formation of hydrogen bonds between free DBSA molecules. The granular morphology obtained for PANI is presumed to be due to the characteristic feature of the hydrochloric acid dopant used in the preparation. There are reports which state that the dopant size and its nature affect the surface morphology of the composite. Oh et al. synthesized PANI with various acidic dopants with an electrochemical method and found that the dopants had a great influence on the morphology of PANI [20].

Fig. 2.1 Scanning electron micrograph of pristine PANI

2.3.1.2 Infrared spectroscopy

Fig. 2.2 presents the IR spectrum of pristine PANI. The absorption at 3235 cm$^{-1}$ is assigned to the NH$^+$ group and indicates the protonated PANI salt. There were no features in the spectra between 2800 cm$^{-1}$ and 1650 cm$^{-1}$, because no functional groups of PANI showed vibration absorption peaks in this region. The peaks at 1569 cm$^{-1}$ and 1492 cm$^{-1}$ are due to the C=C stretching in the quinoid ring and benzenoid ring, respectively [21-23]. The peak at 1299 cm$^{-1}$ is due to the C-N stretching of the secondary amine of the PANI backbone. A strong band characteristically appears at 1146 cm$^{-1}$ which has been explained as an electronic band or a vibrational band of nitrogen quinone, an in-plane bending vibration of imino-1,4-phenylene, and has been reported to be associated with the electrical conductivity of PANI [22-25].
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The -C-H aromatic out of plane bending mode is a key to identify the type of substituted benzene. For PANI, this mode is observed as a single band at 817 cm\(^{-1}\), which falls in the range 800-860 cm\(^{-1}\) and is reported for 1, 4 disubstituted benzene [26-28].

![Fig. 2.2 IR spectrum of pristine PANI](image)

**Fig. 2.2 IR spectrum of pristine PANI**

### 2.3.1.3 X-ray diffraction analysis

The XRD pattern of pristine PANI was obtained as shown in fig. 2.3.

![Fig. 2.3 XRD spectrum of pristine PANI](image)

**Fig. 2.3 XRD spectrum of pristine PANI**

Pristine PANI gives diffraction peaks at \(2\theta \approx 11^\circ, 15^\circ, 17.5^\circ, 21^\circ, 26^\circ\) and \(30^\circ\). Poughet et al. also have reported similar diffraction peaks for PANI [29]. Ram and
coworkers reported sharp peaks at $\theta \approx 9^\circ$, $20^\circ$, $25^\circ$, $30^\circ$ and $35^\circ$ [26]. Moon et al. reported that the peak at $\theta \approx 10^\circ$ arises from scattering with momentum transfer approximately parallel to the polyaniline chains [30].

2.3.1.4 Thermal analysis

The TGA trace of pristine PANI is presented in fig. 2.4. PANI shows three degradations. The first one is due to the loss of moisture, which ends at $139^\circ$ C. The second degradation, which starts at $15\circ$ C, ends at $295^\circ$ C and corresponds to a weight loss of 7.4 % is due to the dopant evolution. The final one in the range 342-689 $^\circ$ C is due to degradation of the PANI chain [31]. About 70 % weight loss occurs during this degradation. This is the general thermal behavior of PANI [32]. PANI doped with DBSA too exhibited similar degradations [33]. The possibility of stable carbonaceous char formation is greater in the case of aromatic compounds and hence PANI leaves a residue of 5.19 %.

![Fig. 2.4 TGA trace of pristine PANI](image)

The DSC curve of PANI is shown in fig. 2.5. The PANI powder shows two endotherms; the first one between 100 $^\circ$ C and 190 $^\circ$ C due to deprotonation and the second one due to the PANI backbone degradation starting at about 200 $^\circ$ C.
2.3.2 Etching of Nylon fiber

Chemical etching treatment using chromic acid can be an effective method to increase aniline deposition and polymerization on Nylon fiber. The etching conditions were optimized with reference to concentration of chromic acid and time of etching. Nylon fibers were treated with chromic acid of differing concentrations and to different time durations.

2.3.2.1 Strength of the fiber

Effect of etching conditions on the strength of the fiber was determined as a function of acid concentration and time of etching. Fig. 2.6 shows the strength of the fiber etched with different concentrations of chromic acid for a period of 6 h. There is a regular decrease in the strength of the fiber on etching. This may be attributed to the possible degradation of the Nylon fibers. Higher concentrations drastically reduce the strength of the fiber. Hence the concentration of chromic acid was optimized at 0.012 N for further studies.
PANI coated short Nylon fibers

Fig. 2.6 Variation of the strength of Nylon fiber with chromic acid concentration

The strengths of the fiber etched to different extents of time are depicted in fig. 2.7. There is a major drop in the strength of the fiber during the initial one hour, after which the fall slows down and, stabilizes at 4 h. Beyond this, the strength further drops. Hence the optimum time of etching is found to be 4 h.

Fig. 2.7 Variation of strength of Nylon fiber with etching time

2.3.2.2 Surface characteristics

The morphology changes in the Nylon fiber surface on etching with chromic acid were observed with SEM. Fig. 2.8 shows the scanning electron micrographs of virgin fiber and fiber etched with 0.012 N chromic acid for 4 h. Clean and smooth surface is
observed for virgin Nylon fiber. The etched fiber shows an irregular surface with minor cracks, probably arising from the hydrolysis of the fiber surfaces in the acidic medium. Such irregularity in the fiber surface is expected to help in the physical anchoring and to improve adhesion of PANI on the fiber.

![Fig. 2.8 Scanning electron micrographs of (a) virgin fiber and (b) etched fiber](image)

The general scan in the XPS spectra of the virgin and etched fibers show the presence of C, N and O. Individual scans were done for C, N and O. The peak in the XPS spectrum of the virgin fiber is at 406.2 eV and that of the etched fiber is at 399.4 eV (fig. 2.9). This change in the peak position might be due to the difference in the environment of the N-H bonds. The peak at 406.2 eV in the virgin fiber may be due to that of N-H bond and the peak at 399.4 eV is due to the H-N-H bond. This means that as a result of etching, hydrolysis of the amide linkage has taken place changing the amide NH to primary amine. The intensity of the N-H peak is decreased in the case of etched fibers as the amide group hydrolyses to yield NH₂ groups.
PANI coated short Nylon fibers

Fig. 2.9 XPS spectra of (a) virgin fiber and (b) etched fiber

The infrared spectra of the virgin and etched fibers are presented in fig. 2.10.

Fig. 2.10 IR spectra of (a) virgin fiber and (b) etched fiber

The absorption at 3297 cm\(^{-1}\) is due to the N-H stretching; peak at 2928 cm\(^{-1}\) is due to the C-H stretching; peaks at 1634 cm\(^{-1}\) and 1538 cm\(^{-1}\) can be assigned to C=O stretching in the amide and N-H bending in secondary amide (-N-H), respectively, and the peak at 1415 cm\(^{-1}\) is assigned to the C-N stretching of amide group in Nylon [32, 34]. The ratio of intensities of absorption corresponding to N-H and C-H vibrations (N-H/C-H intensity ratio) of the etched fiber increased to 1.625 from 1.109 of the virgin fiber, indicating that hydrolysis of the amide linkage has taken place during etching. The N-H bonds change to NH\(_2\) during hydrolysis. Since there are
more number of H atoms per N atom in the NH$_2$ bonds, the intensity of the N-H peaks will be higher. This indicates that the etching process induces hydrolysis of the amide linkages in the Nylon fiber.

Fig. 2.11 presents the XRD patterns of the virgin and etched fibers. The virgin fiber shows maxima at $2\theta = 20.2^\circ$ and $23.5^\circ$, which are reasonably close to the values assigned by previous researchers for the $\alpha_1$ and $\alpha_2$ peaks, respectively [13, 35]. The etched fibers showed maxima at $2\theta = 20.3^\circ$ and $23.6^\circ$. Upon etching, the intensity of the $\alpha_1$ peak reduces slightly due to the slight decrement in the percentage crystallinity as confirmed by the DSC measurements. Oh et al. have also reported such a decrement in intensity owing to a decrease in the percentage crystallinity [13].

![Fig. 2.11 X-ray diffraction patterns of (a) virgin fiber and (b) etched fiber](image)

### 2.3.2.3 Thermal characteristics

The TGA traces of the virgin and etched fibers are given in fig. 2.12 and the thermal degradation characteristics are presented in table 2.1. The thermograms show only one major weight loss attributed to the structural decomposition [25] starting at $\sim 340^\circ$C for the virgin fiber and $\sim 330^\circ$C for the etched fiber. The onset temperature of degradation, the peak degradation temperature and the temperature at 50 % weight loss decrease on etching pointing to the decreased thermal stability of the etched fiber. But the etched fiber gives a lesser weight loss during the degradation and higher amount remains at the peak degradation temperature.
Fig. 2.12 TGA traces of (a) virgin fiber and (b) etched fiber

Table 2.1 Thermal decomposition data of the virgin and etched fibers

<table>
<thead>
<tr>
<th></th>
<th>Virgin fiber</th>
<th>Etched fiber</th>
</tr>
</thead>
<tbody>
<tr>
<td>Onset temperature (°C)</td>
<td>342.9</td>
<td>331.9</td>
</tr>
<tr>
<td>Peak degradation temperature (°C)</td>
<td>461.1</td>
<td>452.9</td>
</tr>
<tr>
<td>Weight loss (%)</td>
<td>94.9</td>
<td>92.4</td>
</tr>
<tr>
<td>Weight remaining at Peak degradation temperature (%)</td>
<td>33.4</td>
<td>37.7</td>
</tr>
<tr>
<td>Temperature at 50 % weight loss (°C)</td>
<td>453.5</td>
<td>447.1</td>
</tr>
</tbody>
</table>

The melting temperature, heat of fusion and degree of crystallinity of the fibers were determined by differential scanning calorimetry and are presented in table 2.2. Fig. 2.13 shows the DSC curves of the virgin and etched fibers. All these parameters decrease upon etching, as expected. This decrease may be attributed to the degradation of the fiber surface during the etching process.
Fig. 2.13 DSC curves of (a) virgin fiber and (b) etched fiber

Table 2.2 Melting temperature, heat of fusion and degree of crystallinity of the virgin and etched fibers

<table>
<thead>
<tr>
<th>Fiber</th>
<th>Melting temperature, ( T_m ) (°C)</th>
<th>Heat of fusion, ( \Delta H_f ) (J/g)</th>
<th>Degree of crystallinity, ( \chi_c ) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Virgin</td>
<td>219.4</td>
<td>64.5</td>
<td>28.0</td>
</tr>
<tr>
<td>Etched</td>
<td>215.8</td>
<td>57.8</td>
<td>25.1</td>
</tr>
</tbody>
</table>

2.3.3 PANI coated Nylon fiber

2.3.3.1 Strength of the fiber

The effect of etching time on the strength of PANI coated fiber was evaluated by etching the fiber to different time durations at 60-65 °C with 0.012 N chromic acid, and subsequently effecting *in situ* polymerization as explained in section 2.2.4. The breaking load of the PANI coated fibers was plotted against the time of etching as shown in fig. 2.14. Generally, PANI is known as a very rigid material, and the tensile strength of most PANI blends or composites has a decreasing tendency as the concentration of PANI increase [36, 37]. This trend is seen in our case also. An increase in etching time leads to better surface etching, enhancing the physical adsorption of aniline molecules on the fiber surface. This result in the formation of
more amount of PANI on the fiber surface leading to a better coating of PANI layer strongly bonded to the surface. There is a sudden fall in the strength of the fiber during the first hour, after which there is a gradual decrease and it stabilizes at an etching time of 4 h. Beyond 4 h, again, the strength shows a drastic decrease. Comprehending fig. 2.7 and fig. 2.14, it can be inferred that the PANI coating does not affect the fiber strength significantly up to an etching time of 4 h, beyond which there is a rapid fall.

![Graph showing the variation of breaking load of PANI coated fiber with etching time](image)

**Fig. 2.14 Variation of breaking load of PANI coated fiber with etching time**

### 2.3.3.2 DC electrical conductivity

Fig. 2.15 presents the variation of conductivity of PANI coated fibers with time of etching. The conductivity of the PANI coated virgin Nylon fiber is $4.22 \times 10^{-2}$ S/cm (log conductivity of -1.37 S/cm). An etching time of 1 h itself increases the conductivity to $1.73 \times 10^{-1}$ S/cm. i.e. A four-times increase in conductivity is observed for the fibers that have been given etching treatment for 1 h compared to the unetched ones. The conductivity increases almost steadily to $3.72 \times 10^{-1}$ S/cm at 4 h. As the etching time is again increased, there is a further increase in conductivity. Obviously, the conductivity should increase on increasing the etching time as the amount of PANI formed on the surface increases. Since the strength of the fiber decreases beyond 4 h, and a reasonable conductivity is obtained at 4 h, the optimum time of etching is deduced to be 4 h. At an etching time of 4 h, the fiber conductivity
is $3.72 \times 10^{-1}$ S/cm (log conductivity of -0.42 S/cm), approximately 8 times than that of the unetched fibers. Genies and co-workers prepared conducting materials made with polyaniline and glass textiles [2]. The glass textiles were given a chemical treatment with 20% sulphuric acid solution for 6 h before giving the PANI coating, to wash off the glass of any surface agents. They could achieve only a conductivity in the range of $1.5 \times 10^{-3}$ to $5.2 \times 10^{-2}$ S/cm. By plasma treatment, Oh et al. reports only a fabric log conductivity of $-2.2$ to $-1.6$ S/cm [14]. Thus, chemical etching is effective in giving improved surface adhesion and better coating of PANI, resulting in improved conductivity than the expensive plasma treatment method.

**Fig. 2.15 Variation of conductivity of the PANI coated fibers with time of etching**

### 2.3.3.3 Scanning electron microscopy

Figs. 2.16(a) and (b) show the micrographs of PANI coated etched fibers and PANI coated virgin fibers, respectively. PANI particles grown on the fiber surface are visible. Such globular deposits have been observed in several reports on PANI and polypyrrole films produced on fibers or micro particles [14, 38-41]. Pud et al. also reported the morphology of PET/PANI composites with atomic force microscopy (AFM), and they observed that PET and the undoped form of the PET/PANI composite exhibited comparatively flat surfaces, whereas doping led to the emergence of mountainous features [42]. With etched fibers, better deposition of PANI on the fiber surface is obtained. Thus, etching is effective in increasing the deposition of PANI.
2.3.3.4 Infrared spectroscopy

The spectra of PANI coated etched fiber and PANI coated virgin fiber are presented in figs. 2.17(a) and (b), respectively.

The N-H/C-H intensity ratio reduced from 1.63 to 0.388 for PANI coated etched fiber, which can be attributed to the shielding of the Nylon fibers as a result of the PANI coating on the fiber surface. We expect the ratio to be higher for PANI coated etched fiber since more N-H bonds are formed during etching. On the contrary, the PANI coated virgin fiber gives a value of 0.802, which is higher than that of the
PANI coated etched fiber. The increase is due to the lesser shielding of the Nylon fibers as compared to the latter, as there is a lesser amount of PANI coating on the unetched fibers.

### 2.3.3.5 X-ray diffraction analysis

The X-ray diffraction patterns of the PANI coated fibers (fig. 2.18) differ from the uncoated Nylon fibers (fig. 2.11) suggesting that PANI coating affects the crystal structure of Nylon fiber. In the XRD spectrum of the PANI coated fibers, in addition to the peaks of the fiber, diffraction peaks of PANI at \( \theta \approx 17.5^\circ, 27^\circ \) and \( 30^\circ \) can be seen. The intensity of the \( \alpha_1 \) and \( \alpha_2 \) peaks of the uncoated Nylon fibers (fig. 2.11) reduces upon PANI coating (fig. 2.18) due to a decrease in the percentage crystallinity of the fiber. Oh et al. too have reported such a decrease in the intensity of the peaks after PANI coating [13]. The \( \alpha_1 \) and \( \alpha_2 \) peaks can be seen at \( \theta \approx 20.1^\circ \) and \( 23.6^\circ \) for the PANI coated etched fiber. These are seen at \( \theta \approx 20.5^\circ \) and \( 24.1^\circ \) for the PANI coated virgin fiber. The \( \alpha_2 \) values slightly shifted to higher side after PANI coating, in comparison to the virgin and etched fibers.

![X-ray diffraction patterns](image)

**Fig. 2.18 X-ray diffraction patterns of (a) PANI coated etched and (b) PANI coated virgin fiber**

### 2.3.3.6 Thermal stability

The thermal degradation characteristics of PANI and PANI coated fibers as extracted from TGA data is given in table 2.3. The TG curves are presented in fig. 2.19. The
PANI coated fibers exhibit a lower onset decomposition temperature than the virgin fiber, but the slope of the decomposition curve is more gentle [25]. The peak degradation temperatures of the etched and PANI coated etched fibers are 453.4 °C and 452.5 °C, respectively, and that of the virgin fiber and PANI coated virgin fiber are 460.9 °C and 460.5 °C, respectively (tables 2.1 and 2.3). This indicates that the PANI deposition does not affect the thermal stability of the fiber. The onset temperature, weight loss during degradation, weight remaining at peak degradation temperature and the temperature at 50 % weight loss of the PANI coated, etched and virgin fibers does not show variation. Even though etching causes a reduction in the thermal stability of the fibers, PANI coated fibers does not show much variation in the thermal characteristics. The thermal characteristics of the PANI coated fibers do not show the significant improvement in thermal stability that has been reported for other conductive polymer composite systems [43, 44]. Similar results in the case of PANI/Nylon composite systems have been reported elsewhere [32]. Abraham and coworkers reported poor thermal stability of PANI/Nylon composite films when compared to pristine Nylon film [45]. PANI coated etched fibers leave slightly more residue than the PANI coated virgin fibers showing that PANI deposition is higher on the former.

*Table 2.3 Thermal decomposition data of the PANI coated fibers*

<table>
<thead>
<tr>
<th>Fiber</th>
<th>PANI coated etched</th>
<th>PANI coated virgin</th>
</tr>
</thead>
<tbody>
<tr>
<td>Onset temperature (°C)</td>
<td>293.5</td>
<td>291.5</td>
</tr>
<tr>
<td>Peak degradation temperature (°C)</td>
<td>452.9</td>
<td>460.0</td>
</tr>
<tr>
<td>Weight loss (%)</td>
<td>92.3</td>
<td>93.2</td>
</tr>
<tr>
<td>Weight remaining at Peak degradation temperature (%)</td>
<td>33.4</td>
<td>33.9</td>
</tr>
<tr>
<td>Temperature at 50 % weight loss (°C)</td>
<td>444.8</td>
<td>452.2</td>
</tr>
<tr>
<td>Residue (%)</td>
<td>2.57</td>
<td>2.43</td>
</tr>
</tbody>
</table>
Fig. 2.19 TG curves of (a) PANI coated etched fiber and 
(b) PANI coated virgin fiber

Fig. 2.20 presents the DSC curves of the PANI coated fibers.

Fig. 2.20 DSC curves of (a) PANI coated etched fiber and 
(b) PANI coated virgin fiber

The melting temperature, heat of fusion and degree of crystallinity are presented in table 2.4. PANI coating on the Nylon fiber reduces the degree of crystallinity and heat of fusion. The melting temperature also shifts to a slightly lower value. This can be visualized in the DCS curves too. This means that the crystalline regions are partly destroyed by the formation of PANI on the fiber surface. Similar observations have been reported by Oh et al. [13, 14] and Byun et al. [25]. Diffusion of aniline
into the Nylon fiber presumably disturbs the crystalline regions and decreases its thermal properties. The aniline diffused into the Nylon fibers localizes in the amorphous regions and acts a plasticizer, disturbing the orientation and arrangement of Nylon macromolecular segments [46].

Table 2.4 Melting temperature, heat of fusion and degree of crystallinity of PANI coated fibers

<table>
<thead>
<tr>
<th>Fiber</th>
<th>Melting temperature, ( T_m ) (°C)</th>
<th>Heat of fusion, ( \Delta H_f ) (J/g)</th>
<th>Degree of crystallinity, ( \chi_c ) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PANI coated etched</td>
<td>218.0</td>
<td>61.5</td>
<td>26.7</td>
</tr>
<tr>
<td>PANI coated virgin</td>
<td>211.8</td>
<td>58.7</td>
<td>25.5</td>
</tr>
</tbody>
</table>

2.4 Conclusions

Electrically conducting fibers were prepared by in situ polymerization of aniline on Nylon fibers. Chemical etching of Nylon fibers using chromic acid prior to in situ polymerization is found to be effective in improving the adhesion of PANI to the fiber surface and conductivity. The etching process involves hydrolysis of the amide linkages. The crystallinity and thermal stability of the fiber reduces upon etching. The etching process roughens the fiber surface and slightly reduces the strength of the fiber. PANI deposition on the etched fibers does not further lower its strength and thermal stability. Better deposition of PANI on the fiber and improved conductivity is attained by the etching treatment of the fibers. By giving an etching treatment for 4 h, 8 times increase in conductivity is attained. The crystallinity of the fiber reduces on PANI coating.

References

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PANI coated short Nylon fibers
