

Properties and Performance of Polypyrrole (PPy)-coated Silk Fibers

Alessandra Boschi, Cristina Arosio, Iliaria Cucchi¹, Fabio Bertini¹,
Marinella Catellani¹, and Giuliano Freddi*

Silk Research Institute, 20133 Milan, Italy

¹*CNR-ISMAR, Institute for Macromolecular Studies, 20133 Milan, Italy*

(Received February 23, 2008; Revised July 17, 2008; Accepted August 8, 2008)

Abstract: Different silk substrates in form of spun silk tops, nonwoven web, yarn, and fabric were coated with electrically conducting doped polypyrrole (PPy) by *in situ* oxidative polymerization from an aqueous solution of pyrrole (Py) at room temperature using FeCl₃ as catalyst. PPy-coated silk materials were characterized by optical (OM) and scanning electron (SEM) microscopy, FT-IR spectroscopy, and thermal analysis (DSC, TG). OM and SEM showed that PPy completely coated the surface of individual silk fibers and that the polymerization process occurred only at the fiber surface and not in the bulk. Dendrite-like aggregates of PPy adhered to the fiber surface, with the exception of the sample first polymerized in the form of tops and then spun into yarn using conventional industrial machines. FT-IR (ATR mode) showed a mixed spectral pattern with bands typical of silk and PPy overlapping over the entire wavenumbers range. DSC and TG showed that PPy-coated silk fibers attained a significantly higher thermal stability owing to the protective effect of the PPy layer against thermal degradation. The mechanical properties of silk fibers remained unchanged upon polymerization of Py. The different PPy-coated silk materials displayed excellent electrical properties. After exposition to atmospheric oxygen for two years a residual conductivity of 10-20 % was recorded. The conductivity decreased sharply under the conditions of domestic washing with water, while it remained essentially unchanged upon dry cleaning. Abrasion tests caused a limited increase of resistance. PPy-coated silk tops were successfully spun into yarn either pure or in blend with untreated silk fibers. The resulting yarns maintained good electrical properties.

Keywords: Silk, Polypyrrole, Composite, Conductive textile

Introduction

Natural and synthetic fibers represent an ideal starting material for applications where high surface-to-mass ratios, good mechanical performance, resistance to chemicals and harsh environmental conditions, flexibility, and ability to be shaped in various forms able to fit end-use requirements are needed. Since conventional fibers are not intrinsically conductive, incorporation of conductive fillers into the fiber structure, for example during melt or electrostatic spinning, or coating with metals or thin films of conductive polymers represent a good approach. Direct polymerization of conductive conjugated polymers on fibers may provide useful tools for producing new conducting materials which allow us to overcome some limitations in the use of conducting polymers alone, such as poor mechanical properties and lack of processability. Various conducting polymers are suitable to this purpose, such as polypyrrole, polyaniline, and polythiophene. Their conductive form could be utilized in applications such as antistatic materials, heat generation, electromagnetic shielding, actuators, and biosensors. Different polymerization methods can be applied, i.e. in solution, in vapor phase, under supercritical conditions [1], via admicellar polymerization with a surfactant template [2].

Various natural and synthetic fibers have been subjected to polymerization of pyrrole and other aromatic conductive monomers for the production of conductive textiles. A great deal of work has been carried out on synthetic fibers, especially

polyester [1-3], which takes the leading position in the world fiber market in terms of fiber production and consumption. Comparatively less attention has been paid to other man-made fibers, such as polyamide [1] or cellulose-based regenerated fibers, like viscose, cupro, and lyocell [4,5]. As far as natural fibers are concerned, cotton [2,6,7] and, more recently, wool have attracted a great deal of attention [8-10].

Varesano *et al.* [8,9] recently reported the *in situ* oxidative polymerization of pyrrole on wool with the aim to produce electrical conductive textiles for apparel and technical end-uses. Shrink resist treated fibers were found more suitable than untreated wool fibers as substrate for pyrrole polymerization. Conductive wool-based textiles retained the high flexibility and elasticity typical of wool, showing enhanced thermal properties. The level of conductivity was satisfactory even after treatments simulating use and maintenance operations, like light exposure, domestic washing, dry cleaning, and surface abrasion.

Comparatively lower attention has been dedicated to silk as substrate for deposition of conductive polymers [6,11,12]. In a recent study Cucchi *et al.* [13] reported the coating of silk fabrics with electrically conducting doped polypyrrole (PPy) by *in situ* oxidative polymerization from an aqueous solution of pyrrole (Py) at room temperature, by using FeCl₃ as catalyst. The amount of polymer deposited on the fabrics increased up to 22 % with increasing the reaction time or the concentration of Py in the reaction system. Polymerization occurred at the fiber surface and not in the bulk. The intrinsic crystalline structure and the molecular conformation of silk were not affected by the polymerization. PPy-coated silk fabrics displayed a significantly higher thermal stability and

*Corresponding author: freddi@ssiseta.it

excellent electrical properties. Optimum reaction time and Py concentration able to ensure good conductivity were 3 h and 1 g/l, respectively. Due to the Joule effect, the temperature of PPy-coated silk fabrics increased as a function of the electrical potential applied and of the amount of PPy.

The decay of the electrical properties may become a critical factor for the application of PPy-coated silk fibers. Decrease of conductivity may occur for various reasons, such as environmental aging due to exposition to light or to the oxidative action of oxygen. Khedkar and Radhakrishnan [14] reported a detailed investigation of the stability of PPy films on aging. PPy is comparatively more stable than other conductive polymers.

However, there are changes in the conductivity of PPy with the time. In particular, the rate of the decrease of conductivity was found to be dependent on the polymerization method, i.e. electrochemical or vapor phase, on the concentration of the dopant, and on fine details of the structure of the deposited PPy film. Loss of electrical properties of PPy-coated textile fibers can be caused not only by environmental aging of the PPy coating but also by the chemical or mechanical stresses related to conventional textile processing, from spinning to weaving, dyeing, and finishing, by the end-use conditions of the textile products comprising the conductive fibers, as well as by the treatments carried out to maintain the products, typically washing. Varesano *et al.* [8] studied the decay of the electrical properties of PPy-coated wool fibers and reported that conductivity decreased sharply on washing, probably due to the alkali dedoping of the conductive PPy film, while an excellent stability was observed under the conditions of conventional dry cleaning. A moderate increase of resistance was observed on exposition to light and temperature, as well as after extensive abrasion cycles simulating the conditions of use of the textile material.

In this study various silk materials in form of loose fibers (tops, nonwoven web), yarn or fabric were coated with PPy by oxidative polymerization in aqueous solution. The fibrous materials were then characterized by morphological, spectroscopic, thermal, and tensile analyses. Electrical conducting properties were investigated with the aim to evaluate their stability to environmental aging and to study their decay under the conditions of end-use and maintenance of the conductive textile goods.

In order to assess the processability of PPy-coated silk fibers with conventional industrial machines a sample of spun silk tops was subjected to oxidative polymerization of PPy and then was spun into yarn either pure or in intimate blend with untreated silk fibers. Properties of this industrially processed sample are here reported.

Experimental

Materials

The degummed silk fabric (weight: 60 g/m²) was purchased

from Società Ausiliari Tessili s.r.l. (Milano, Italy). The raw silk yarn (trame, 4 ends, 80-82 den) was purchased from Clerici Tintoria Filati S.p.A. (Como, Italy) and degummed with water in autoclave at high-temperature (120 °C) for 40 min. Degummed silk yarn and fabric were preliminarily cleaned by Soxhlet extraction with hexane in order to remove impurities before the polymerization reaction with pyrrole. The spun silk tops was purchased from Cascami Seta, Division of Gruppo Botto (Tarcento, Ud., Italy). Before polymerization with pyrrole, the fiber mass was cleaned in an industrial dry-cleaning machine with 1,2-tetrachloroethylene in order to remove sizing agents and impurities. The silk nonwoven web was produced from the spun silk tops by the carding-needling technique.

To produce the spun silk yarn suitable amounts of untreated and PPy-coated spun silk tops were mechanically intersected using industrial machinery and then spun into yarns of 308 den. Intimate blends containing 100 w%, 60 w%, and 30 w% PPy-coated silk fibers were thus obtained.

Analytical grade pyrrole (Py) was purchased from Aldrich and distilled before use. Iron (III) chloride hexahydrate (catalyst), and anthraquinone-2,6-disulfonic acid disodium salt (dopant) were purchased from Fluka and used without any further purification.

Polymerization of Py

The lab scale polymerization of Py was carried out as reported elsewhere [13]. Briefly, samples of fabric, yarn, nonwoven web, and tops were soaked in an aqueous solution of Iron (III) chloride hexahydrate (catalyst) and anthraquinone-2,6-disulfonic acid disodium salt (dopant) for 30 min, then the Py monomer was added (Py concentrations of 1 g/l). The weight ratio among monomer, catalyst, and dopant was 1:9:1.67 w/w, respectively. The polymerization was carried out at room temperature, for 3 h, with a material-to-liquor ratio of 2 g/l. After polymerization the silk samples were thoroughly washed with water in order to remove the polymer excess.

The pilot scale polymerization of Py onto the spun silk tops was performed under slightly different conditions. Namely, the material-to-liquor ratio and the Py concentration were 20 g/l and 5 g/l, respectively, resulting in a silk:Py ratio of 4:1, as compared to 2:1 for the lab scale trials. Other reaction conditions were the same.

Weight Increase

The amount of polypyrrole (PPy) deposited onto the silk substrates was determined by weighing the silk samples before and after the polymerization reaction under standard conditions of temperature (20 °C) and relative humidity (65 %). The percentage weight increase ($W\%$) was calculated as follows:

$$W\% = [(W_f - W_i) / W_i] \times 100$$

where W_i and W_f are the initial and final weight, respectively.

Optical (OM) and Scanning Electron Microscopy (SEM) Analyses

To prepare cross-sections for OM observation, silk fibers were included in an epoxy resin and thin slices (10 μm) were cut with a Supercut microtome (Reichert-Jung) and examined under an optical microscope Mod. BX51 (Olympus).

SEM characterization was performed by using a LEO Stereoscan model 440 microscope, at an acceleration voltage of 15 kV and 15 mm working distance. Samples were mounted onto aluminium specimen stubs by means of double-sided adhesive tape and sputter-coated with a thin gold layer under rarefied Argon atmosphere, using a BAL-TEC MED 020 Coating System, with a current of 30 mA for 180 s.

Fourier Transform-infrared (FT-IR) Spectroscopy

FT-IR spectra were obtained with a Thermo Nicolet Nexus spectrometer equipped with the attenuated total reflection module (ATR Smart Performance) and a ZnSe crystal. Spectra were recorded in the range 4000-700 cm^{-1} by accumulating 64 scans at a resolution of 4 cm^{-1} .

Thermal Analysis

Differential scanning calorimetry (DSC) was performed with a Mettler DSC 30 instrument, calibrated by an Indium standard. The calorimeter cell was flushed with 200 ml/min of N_2 . Sample weight was about 3 mg and Al crucibles were used. The temperature range scanned was 25-500 $^\circ\text{C}$, at a heating rate of 10 $^\circ\text{C}/\text{min}$.

Thermogravimetric Analysis (TG) was performed with a TGA Q500 instrument (TA Instruments), from room temperature to 600 $^\circ\text{C}$, at a heating rate of 20 $^\circ\text{C}/\text{min}$, on 3 mg samples. The cell was swept with N_2 during the analysis.

Tensile Properties

Tensile properties of silk yarn were measured by means of an Instron tensile testing machine mod. 4501, at 25 mm gauge length and 25 cm/min crossbar rate. Measurements were performed under standard conditions of temperature (20 $^\circ\text{C}$) and humidity (65 %). Breaking strength, elongation at break, modulus, and energy values are the average of 20 individual measurements.

Electrical Properties

Electrical measurements were recorded by means of an electrical circuit composed by a Hewlett Packard 6634B System DC Power Supply and a digital Hewlett Packard 34401A Multimeter. PPy-coated silk fabrics were cut to the size of 6 \times 6 cm and placed in an electrical circuit with 6 equidistant terminals and voltage was progressively increased up. For the samples subjected to washing tests the size was 8 \times 4 cm, while round samples (diameter 5 cm) were used for the abrasion tests. To measure the electrical properties of PPy-coated silk yarns, the samples were fixed to the screw clamps of a twist counter

(tension applied: 16.7 cN) and placed in contact with two Al electrodes at the distance of 0.5 cm. A silver conductive paint (RS Component) was used to improve the contact between the yarn and the electrodes.

Electrical measurements were made on samples as prepared (t_0) and after different times of aging (t_x , x =days), up to two years. Samples were stored in air and protected from light.

Fastness Tests

Domestic and commercial washing fastnesses were evaluated according to EN ISO 105-C06:1997. Fastness to organic solvents was assessed with the same apparatus according to EN ISO 105-X05:1997, using 1,2-tetrachloroethylene extra pure (C_2Cl_4). Abrasion tests (based on UNI 4818-15:1992) were performed using a Cesconi abrasion and pilling tester, with a load of 12 kN.

The increase of resistance of PPy-coated silk fabrics following washing, solvent, or abrasion treatments was evaluated from the resistance ratio R_0/R ratio, where R_0 is the resistance at t_0 and R is the resistance at t_x (x =days). The resistance is proportional to the resistivity ρ ($\rho=R \times \text{section}/\text{length}$), which is the inverse of the conductivity σ ($\sigma=1/\rho$), so that: $R_0/R=\rho_0/\rho=\sigma/\sigma_0$, which provides an evaluation of the final conductivity of the material with respect to the initial one.

Results and Discussion

Morphological Properties of PPy Coated Silk Samples

The optimum conditions for the polymerization of Py onto silk fibers were reported in a previous study [13]. A Py concentration of 1 g/l and a reaction time of 3 h at room temperature allowed to prepare PPy-coated silk samples with resistance values suitable for employment as conductive textile materials in applications aimed at EMI shielding and static charges dissipation. By using the same reaction conditions, Py was polymerized onto the different silk substrates object of this study, i.e. fabric, yarn, nonwoven web, and spun silk tops. The polymerization resulted in black silk substrates, meaning that the polymer completely coated the fibrous materials. The amount of polymer was evaluated by measuring the weight increase of the silk samples. The weight increase values of fabric, yarn, nonwoven web, and spun silk tops were 13.5 %, 16.8 %, 18.7 %, and 42.0 %, respectively. The looser the fibrous structure, the higher the yield of polymerization owing to the better accessibility of the substrate to the monomer and the reagents. The surprisingly high yield of the spun silk tops can be attributed to the difficulty to completely wash out the loosely bound PPy particles which remained trapped into the fiber mass.

The morphological analysis of PPy-coated silk samples was performed by means of OM and SEM. OM pictures of fiber cross-sections (Figure 1) show the presence of a continuous

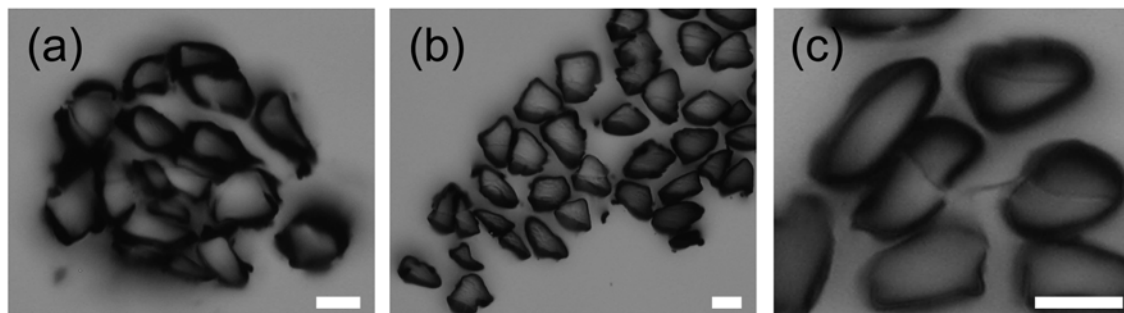


Figure 1. Cross-sections of PPy-coated silk fibers from silk yarn and fabric; (a) silk yarn, weight increase 16.8 %, (b) warp thread taken from the silk fabric (weight increase 13.5 %), and (c) close-up of (b). The magnification bar is 10 μm .

PPy layer covering the surface of individual fibers. These findings confirm that Py could diffuse into the compact texture of silk yarns and fabrics and that the polymerization proceeded smoothly, resulting in the formation of a continuous layer of polymer around the individual fibers, in good agreement with the results previously reported [13].

Another interesting feature is that the polymerization occurred only at the surface level and not in the bulk. Actually, silk behaved like synthetic fibers, polyester, and polyamide, which showed the formation of an outer layer of conductive polymer [1]. In the case of wool, another protein fiber like silk, a partial penetration of the polymer inside the fiber matrix was observed [8] because the scaled surface structure of wool allows paths for penetration and diffusion of relatively small molecules like the Py monomer [15]. When cellulose-based regenerated fibers like viscose and Lyocell were used as substrate, the polymerization proceeded in the bulk of the fiber, owing to the easy penetration of the monomer into the fiber matrix during the initial step of the

process [4,5]. These results provide strong evidence of the key role played by morphological and structural features of the fiber substrates in determining the nature and extent of the PPy-fiber interaction, which may range from nanodispersion of PPy into the fiber matrix, as in the case of cellulose fibers, to formation of a skin-core composite structures, as for silk and synthetic fibers. In the case of silk, the extremely smooth surface lacking any gap to the inside coupled with the highly oriented and crystalline structure of the fiber probably caused a marked slow down of the rate of monomer penetration and diffusion, resulting in the deposition of layers of polymer onto the fiber surface. Hence, PPy-silk composites with a skin-core structure were obtained, with the protein fiber forming the core and the conjugated polymer the external layer.

SEM pictures of PPy-coated silk fabric and nonwoven web are shown in Figure 2. Fibers appear homogeneously coated with a film of PPy. The smooth and longitudinally striated surface of natural silk fibers is no more visible. Dendrite-like

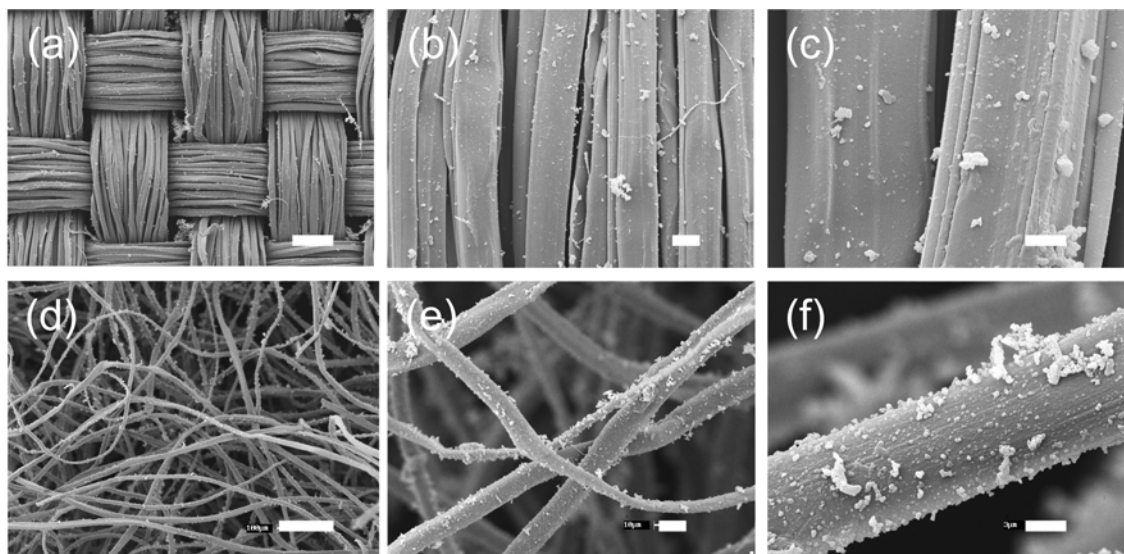


Figure 2. SEM pictures of PPy-coated (a-c) silk fabrics with 13.5 % weight increase and (d-f) silk nonwoven web with 18.7 % weight increase. Magnification bars: (a) and (d) 100 μm ; (b) and (e) 10 μm ; (c) and (f) 3 μm .

structures loosely attached to the fiber surface can be observed. These are more abundant at the crossover of warp and weft threads of the fabric. In the nonwoven web the polymer particles are distributed all along the surface of the individual fibers. Their amount seems slightly higher than in the fabric, which accounts for the higher weight gain (18.7% against 13.5%). A stronger washing cycle would have probably caused their more efficient removal. Interestingly, in all PPy-coated silk substrates individual fibers did not stick to each other but remained well separated. This feature is clearly demonstrated not only by SEM, but also by OM observations (Figure 1).

Figure 3 shows the SEM pictures of the spun silk yarns produced in a pilot scale industrial trial by mixing different amounts of untreated and PPy-coated silk tops. The two types of fibers, i.e. uncoated and PPy-coated, are homogeneously distributed in the final yarn. It is interesting to note that there are no traces of the loosely bound polymer aggregates previously observed onto the fiber surface of fabric or nonwoven web (Figure 2). The strong mechanical stresses caused by the industrial machines resulted in an almost complete removal of the loosely bound particles. The granular surface morphology of PPy-coated silk fibers is due to the

aggregation of small-sized polymer particles which formed a compact and dense PPy layer.

FT-IR Spectroscopy Analysis

Figure 4A shows the FT-IR spectra of untreated and PPy-coated silk yarn. The spectrum of untreated silk is characterized by strong vibrations of the peptide group falling in three well-defined ranges, namely amide I at 1626 cm^{-1} (shoulder at 1699 cm^{-1}), amide II at 1520 cm^{-1} , and the bimodal amide III with peaks at 1232 and 1263 cm^{-1} [16]. All these IR bands are conformationally sensitive. Their position and intensity are consistent with the prevailing β -sheet molecular conformation of the silk fibers [17]. The spectrum of pure PPy is characterized by a series of broad absorptions comprising various stretching modes at about 1520 cm^{-1} (C=C), 1450 cm^{-1} (C-C), and 1298 cm^{-1} (C-N), and different C-H bending modes falling at about 1140 and 1030 cm^{-1} [4]. The band at 1036 cm^{-1} is characteristic of the dopant, being attributable to the vibration of the aryl sulfonate salt. The band at 960 cm^{-1} has been assigned to a fraction of PPy free from the influence of the dopant [9]. The spectrum of the PPy-coated silk yarn with 16.8% weight increase showed a FT-IR pattern closely similar to pure PPy, with a very weak

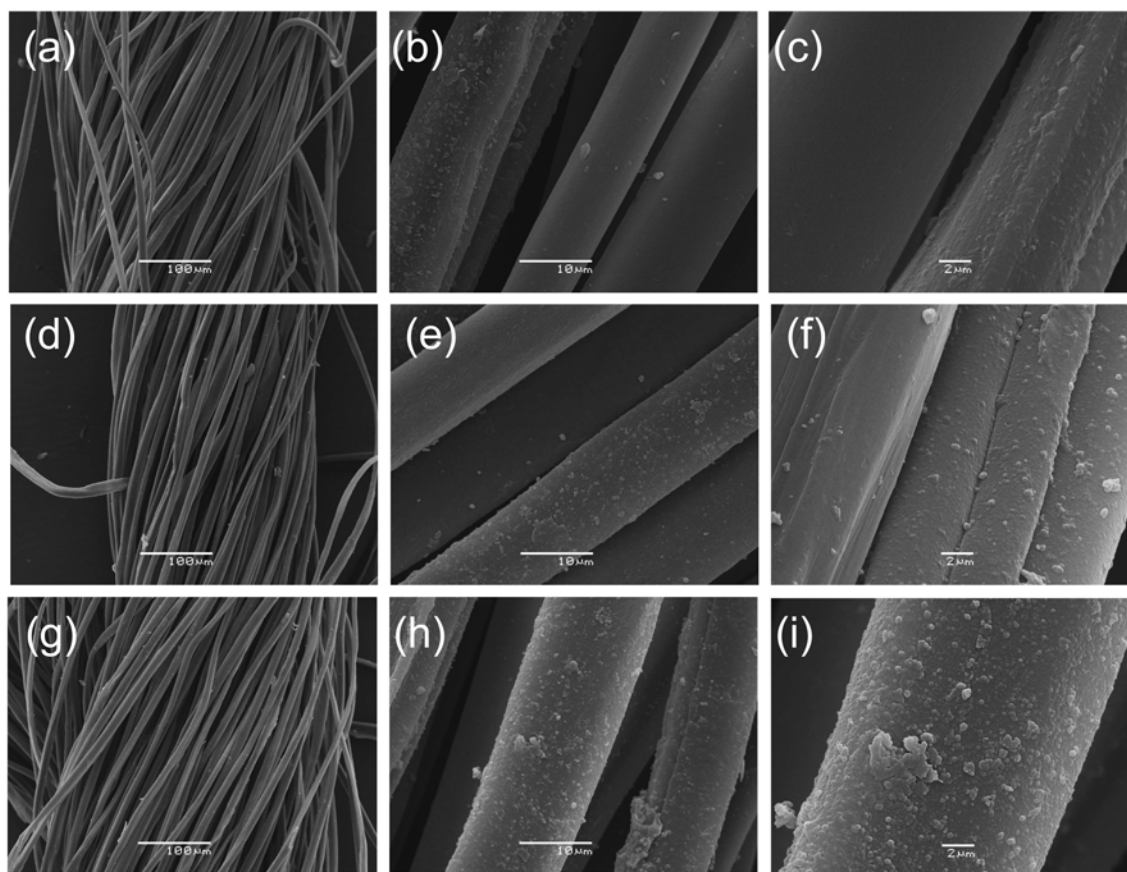


Figure 3. SEM pictures of spun silk yarns containing different amounts of PPy-coated silk fibers: (a-c) 30 w%, (d-f) 60 w%, and (g-i) 100 w%. Magnification bars: (a), (d), and (g) 100 μm ; (b), (e), and (h) 10 μm ; (c), (f), and (i) 2 μm .

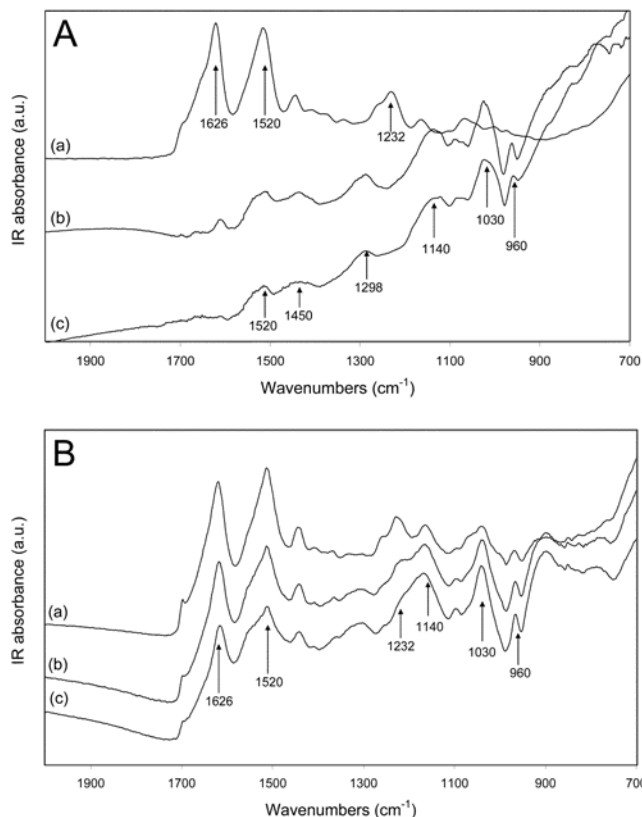


Figure 4. (A) FT-IR spectra of (a) untreated silk yarn, (b) PPY-coated silk yarn with 16.8 % weight increase, and (c) pure PPY. (B) FT-IR spectra of spun silk yarns with (a) 30 w%, (b) 60 w%, and (c) 100 w% PPY-coated fibers.

absorption in the amide I range at 1626 cm^{-1} attributable to silk. This behavior is due to the ATR technique which explores the most external surface layers of the sample. The thicker the PPY layer, the weaker the contribution of silk to the FT-IR signal, because the incident radiation could not reach the fibrous core of the composite [13].

The FT-IR spectra of the spun silk yarns containing different amounts of PPY-coated silk fibers displayed a mixed pattern, with bands of silk and PPY overlapping in the $2000\text{--}700\text{ cm}^{-1}$ range (Figure 4B). With increasing the amount of the PPY-coated fibers the relative intensity of the bands typical of silk gradually decreased. The spun silk yarn produced by using the 100 w% PPY-coated silk tops still showed quite intense silk bands, suggesting that the PPY layer was thinner than that of the PPY-coated yarn. This feature can be attributed either to the slightly different conditions adopted for the polymerization of Py onto the spun silk tops or to the strong cleaning action exerted by the spinning machines which removed the excess polymer loosely bound and left the fraction strongly bound to the fiber surface in place.

Thermal Properties

The thermal behavior of silk fibers was significantly

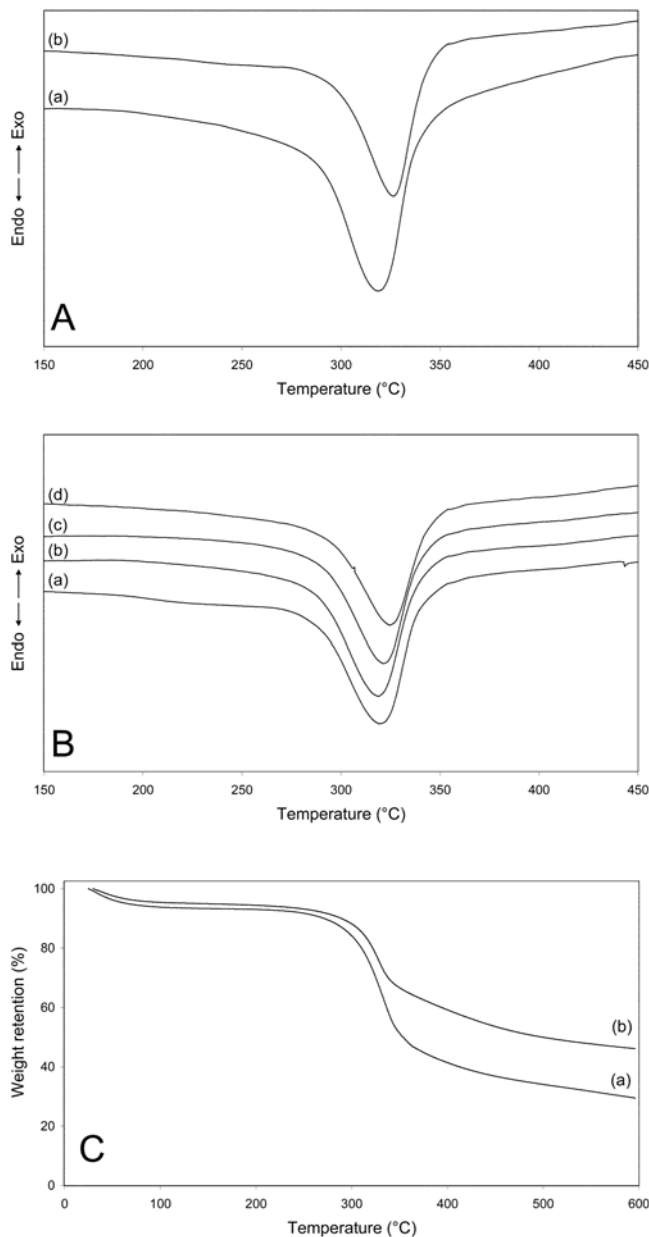


Figure 5. (A) DSC curves of (a) untreated silk yarn and (b) PPY-coated silk yarn with 16.8 % weight increase. (B) DSC curves of spun silk yarns with (a) 0 w%, (b) 30 w%, (c) 60 w%, and (d) 100 w% PPY-coated fibers. (C) TG curves of (a) untreated silk yarn and (b) PPY-coated silk yarn with 16.8 % weight increase.

affected by the polymerization of Py, as evidenced by the DSC curves (Figure 5A). Untreated silk fibers are characterized by an intrinsically high thermal stability. The intense DSC endothermic peak at above 300 °C is characteristic of the thermal degradation of silk fibroin with well oriented β -sheet crystalline structure [18]. Coating with PPY enhanced the thermal stability of silk, whose degradation peak shifted to higher temperature of about $6\text{--}11\text{ °C}$ depending on the sample (Table 1).

Table 1. Peak temperature of the DSC decomposition endotherm of different untreated and PPy-coated silk substrates

| | Untreated silk substrates (°C) [A] | PPy-coated silk substrates (°C) [B] | Temperature difference (°C) [C = B - A] |
|-------------------|---------------------------------------|--|--|
| Spun silk tops | 318.8 | 325.3 | +6.5 |
| Silk yarn | 319.1 | 326.5 | +7.4 |
| Silk fabric | 310.5 | 321.5 | +11.0 |
| Spun silk yarn: | | | |
| 30 w% PPy-coated | - | 319.0 | +0.2 |
| 60 w% PPy-coated | - | 321.7 | +2.9 |
| 100 w% PPy-coated | - | 324.7 | +5.9 |

The same effect was observed for the samples of spun silk yarn containing different amounts of PPy-coated silk fibers (Figure 5B). The extent of high temperature shifting of the decomposition peak of silk was related to the content of PPy-coated silk fibers, i.e. the higher the amount, the larger the shift. It is interesting to note that blend yarns displayed a unique endothermic peak. No peak broadening or splitting was observed, whatever the content of PPy-coated silk fibers.

TG analysis (Figure 5C) showed that upon polymerization of Py the onset of weight loss moved to higher temperature of about 10-15 °C and the weight retention at 500 °C increased from 35 % of the untreated sample to 50 % for the sample coated with PPy, thus confirming the protective effect of the PPy layer against thermal degradation [12]. Actually, the PPy-coated silk fibers have a composite structure with an outer PPy layer and a fiber core. The PPy layer, being more external and more resistant to heat, acted as a barrier and protected silk fibers from degradation until a threshold was reached above which silk was attacked as well.

Electrical Properties

The overall electrical properties of PPy-coated silk substrates were reported in a previous study [13]. The current vs. voltage (C/V) curves, measured on samples obtained at different polymerization times, showed a linear fit. The longer the reaction time, the higher the current increment and the better the conductivity, due to the increased amount of PPy loaded onto the fibers. Accordingly, the resistance (R) decreased exponentially with increasing either monomer concentration in the polymerization bath or reaction time. Interestingly, the R curves showed an opposite trend as compared to that of the corresponding weight increase curves. These observations pointed out that the amount of PPy plays a key role in determining the ultimate electrical properties of conductive silk substrates. Electrical measurements also allowed us to fix the optimum reaction conditions for the production of PPy-coated silk substrates with electrical resistance suitable for EMI shielding and static charges dissipation applications.

To evaluate the decay of the electrical properties on exposition to atmospheric oxygen as a function of time, PPy-

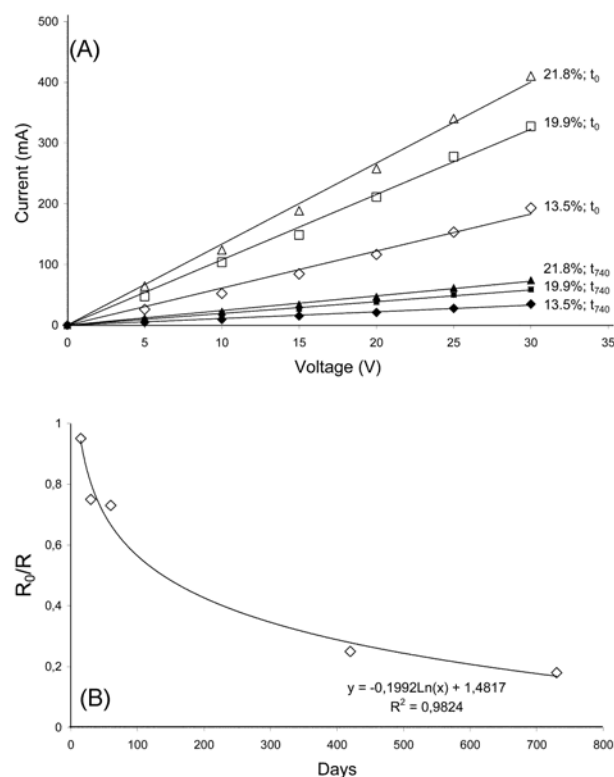


Figure 6. (A) Current vs. voltage curves of PPy-coated silk fabrics with different amounts of PPy (13.5 %, 19.9 %, 21.8 %) measured on samples as prepared (t_0) and after two years of storage (t_{740}). (B) Time course of the resistance ratio of the PPy-coated silk sample with 13.5 % weight increase.

coated silk fabrics were kept in air, protected from light, for different times up to two years. Figure 6A shows the C/V curves of three PPy-coated silk fabrics with different weight increase values measured at t_0 and t_{740} . The C/V curves displayed a linear fit. The higher the amount of PPy is, the higher the slope of the curve is. The residual conductivity after two years of exposition to atmospheric oxygen was in the range of 10-20 % of the initial value for all the samples, irrespective of the amount of polymer loaded. Figure 6B shows the time dependence of the decay of conductivity for

Table 2. Mechanical properties of untreated and PPy-coated silk yarn

| | Untreated yarn ^a | PPy-coated yarn ^b |
|----------------------------|-----------------------------|------------------------------|
| Tenacity (g/den) | 3.99±0.16 | 4.09±0.15 |
| Elongation (%) | 13.7±1.3 | 13.2±1.1 |
| Modulus (g/den) | 90.3±4.9 | 85.5±6.3 |
| Energy (gxmm) ^c | 6536±1015 | 6222±703 |

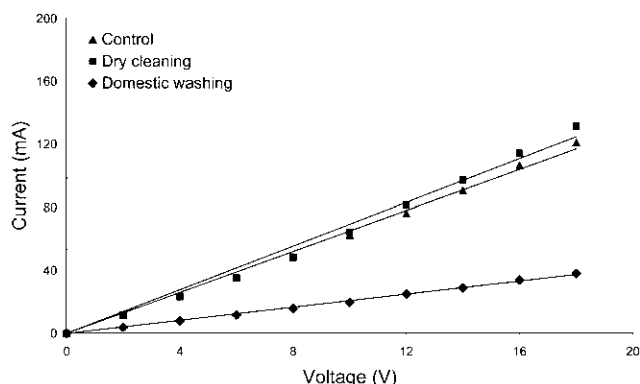
^a66.1 den, ^b77.9 den, and ^cenergy is the area underneath the stress-strain curve and expresses the toughness of the material, i.e. the energy the material can absorb prior to rupture.

the PPy-coated sample with 13.5 % weight increase. The experimental data points fit a logarithmic curve ($R^2=0.982$). Likewise other PPy-coated fibrous systems, the loss of conductivity is larger at the beginning and then tends to stabilize with increasing the time of aging. It is worth to note that, after two years, the PPy-coated silk substrate still exhibits conductivity suitable for static charge dissipation application.

Tensile Properties and Technological Performance of PPy-coated Silk Fibers

To assess whether the polymerization of PPy had any effect on the mechanical properties of silk fibers, tensile measurements were made on silk yarn before and after reaction with Py. From the results listed in Table 2, it is possible to observe that silk fibers displayed closely similar values of the tensile parameters before and after polymerization. The polymerization process did not affect the overall tensile performance of silk fibers. Following Py polymerization a polymer layer was built around the fibers. As a consequence, their transverse size was increased by about 10 %. However, since the polymer layer is expected to have poor mechanical properties, its contribution to the response to tensile stresses may be very low or none, as confirmed by the results here reported. These results are of technological significance because they demonstrate that untreated and PPy-coated silk fibers can be processed together in the same spinning, weaving, or knitting machines without any drawback in terms of resistance to mechanical stresses.

To assess the durability of conductive silk textiles to use and maintenance treatments, samples of PPy-coated silk fabrics were subjected to washing and dry cleaning cycles according to well established standard methods. From the C/V curves of Figure 7 it is possible to observe that domestic washing caused a large decrease of conductivity, which dropped to about 30 % of that of the control samples, as estimated from the R_0/R ratio. The conductivity of the sample subjected to dry cleaning with C_2Cl_4 remained essentially unchanged, in good agreement with the results reported for PPy-coated wool fibers [8]. The decrease of conductivity on washing can be attributed to solvation of chlorine ions by

**Figure 7.** Current vs. voltage curves of PPy-coated silk fabrics untreated, and subjected to domestic washing and dry cleaning cycles.**Table 3.** Resistance ratio of silk fabrics subjected to abrasion cycles

| | Weight loss (%) | R_0/R |
|-------------------|-----------------|---------|
| 2000 cycles-2 kg | 1.84 | 0.93 |
| 2000 cycles-1 kg* | 1.22 | 0.78 |
| 4000 cycles-1 kg | 1.52 | 0.87 |
| 6000 cycles-1 kg | 2.71 | 0.85 |

*The fabric sample was abraded on both sides.

water. The extent of doping of PPy was decreased and the conductivity of the polymer, especially of its most external layers, decreased as well.

Table 3 lists the R_0/R values of PPy-coated silk fabrics subjected to different abrasion cycles. Despite the weight loss and the surface damage induced by abrasion the resistance ratio remained quite high. Indeed, a good level of conductivity was ensured by the fact that during polymerization the PPy layer effectively grew around the individual fibers even in the innermost part of the yarn.

To assess the processability of PPy-coated silk fibers, 1.5-2 kg of silk tops were treated with Py and then spun into yarn, either in pure form or mixed at 60 w% and 30 w% with untreated silk fibers derived from the same lot of spun silk tops. Figure 8 shows pictures of the spun silk yarns produced in the industrial trial. The excess of polymer trapped into the fibrous mass, which was not removed by washing, caused some problems during the initial step of industrial processing, i.e. tops opening, homogenizing, and mixing before being spun into yarn. This suggests that the scale up of Py polymerization from grams to kilos of silk fibers needs further optimization in order to avoid processing drawbacks like fiber sticking, entanglement or production of excess dust. Nevertheless, it has been possible to produce yarns even from 100 % PPy-coated silk fibers. The blend yarns at 60 w% and 30 w% of PPy-coated fibers showed a characteristic melange grey colour due to the mixing of coated and uncoated silk fibers. Figure 9 compares the electrical properties of the three



Figure 8. Pictures of spun silk yarns with (a) 30 w%, (b) 60 w%, and (c) 100 w% PPy-coated silk fibers.

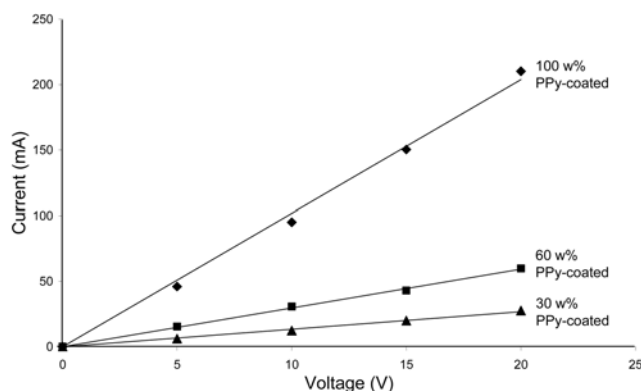


Figure 9. Current vs. voltage curves of spun silk yarn with different amounts of PPy-coated silk fibers (intimate blend).

kinds of yarns. As expected, the yarn containing 100 w% of PPy-coated silk fibers exhibited the highest conductivity, which decreased by about 70 % and 85 % of the maximum value when the amount of uncoated fibers was 30 w% and 60 w%, respectively. Assuming a circular cross-section for the yarns, with a diameter of about 180 μm , it has been estimated that the value of resistance falls in the range of 1-10 Ωm , a value suitable for static charge dissipation applications.

Conclusion

The oxidative polymerization of Py onto silk fibers in aqueous solution, under mild reaction conditions, allowed us to produce technical conductive silk-based textiles which combine the outstanding chemical and physical properties of silk fibers with good levels of electrical and thermal performance. PPy displayed high affinity for degummed silk and formed a homogeneous polymer layer around the individual fibers. The conductivity of PPy-coated silk materials can cover a wide range of applications, from static charges dissipation to EMI shielding and heat generation.

The intrinsic structural and mechanical properties of silk were not affected by Py polymerization. Any form of silk material, i.e. loose fibers, nonwoven web, yarn, or fabric, can be subjected to the reaction. The treatment was also carried out on loose fibers, like the spun silk tops, which

were then successfully blended with untreated fibers, thus opening the possibility to produce a large variety of textile materials with intrinsic conductive properties incorporated during conventional processing.

The conductivity of PPy-coated silk fibers decayed on exposition to environmental conditions but over a quite long period of time (two years). Treatments simulating the maintenance and end-use conditions of textiles gave good results for dry cleaning, which did not affect the electrical properties, while domestic washing in water resulted in a drastic drop of conductivity. These results are important because they may address the possible application of conductive silk-based textiles from apparel to technical uses, including the most advanced field of knowledge-based multifunctional materials.

Acknowledgements

The work was carried out in the framework of the project “New fibers from renewable resource: Fibers on demand” (2003.1583/10.8441) funded by Fondazione Cariplo, Milan, Italy. Authors would like to express their gratitude to Mr. Matteo Hary of Filatura di Trivero (Gaglianico, Italy) for the spun silk yarn processing.

References

1. A. Harlin, P. Nousiainen, A. Puolakka, J. Pelto, and J. Sarlin, *J. Mater. Sci.*, **40**, 5365 (2005).
2. P. Lekpittaya, N. Yanumet, B. P. Grady, and E. A. O’Rear, *J. Appl. Polym. Sci.*, **92**, 2629 (2004).
3. E. Hakansson, A. Amiet, and A. Kaynak, *Synth. Met.*, **156**, 917 (2006).
4. L. Dall’Acqua, C. Tonin, R. Peila, F. Ferrero, and M. Catellani, *Synth. Met.*, **146**, 213 (2004).
5. L. Dall’Acqua, C. Tonin, A. Varesano, M. Canetti, W. Porzio, and M. Catellani, *Synth. Met.*, **156**, 379 (2006).
6. S. N. Bhadani, M. Kumari, S. K. Sen Gupta, and G. C. Sahu, *J. Appl. Polym. Sci.*, **64**, 1073 (1997).
7. S. Subianto, G. D. Will, and S. Kokot, *Int. J. Polym. Mater.*, **54**, 141 (2005).
8. A. Varesano, L. Dall’Acqua, and C. Tonin, *Polym. Degrad.*

- Stab.*, **89**, 125 (2005).
9. A. Varesano, A. Aluigi, C. Tonin, and F. Ferrero, *Fiber Polym.*, **7**, 105 (2006).
 10. S. S. Najar, A. Kainak, and R. C. Foitzik, *Synth. Met.*, **157**, 1 (2007).
 11. A. M. White and R. C. T. Slade, *J. Mater. Chem.*, **13**, 1345 (2003).
 12. S. H. Hosseini and A. Pairovi, *Iran. Polym. J.*, **14**, 934 (2005).
 13. I. Cucchi, A. Boschi, C. Arosio, F. Bertini, G. Freddi, and M. Catellani, *Synth. Met.*, in press.
 14. S. P. Khedkar and S. Radhakrishnan, *Polym. Degrad. Stab.*, **57**, 51 (1997).
 15. F. J. Wortmann, G. Wortmann, and H. Zahn, *Text. Res. J.*, **67**, 720 (1997).
 16. S. Krimm and J. Bandekar, *Adv. Protein Chem.*, **38**, 181 (1986).
 17. R. D. B. Fraser and T. P. MacRae, "Conformation in Fibrous Proteins and Related Synthetic Polypeptides", pp.293-343, Academic Press Inc., NY, 1973.
 18. T. Arai, G. Freddi, R. Innocenti, and M. Tsukada, *J. Appl. Polym. Sci.*, **89**, 324 (2003).