

Electrical Conductivity and Mechanical Properties of Polyaniline/Natural Rubber Composite Fibers

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ABSTRACT: Electrically conducting elastomer fibers based on natural rubber (NR) and up to 10% w/w polyaniline (PANI) in its emeraldine base (EB) form were fabricated by a wet spinning process. The resulting fibers at various PANI contents were doped by immersion in aqueous HCl solution, which converted the PANI to the electrically conductive emeraldine salt (ES) form. The morphology of the composite fibers was studied by scanning electron microscopy (SEM). PANI particles were inhomogeneously distributed in the NR matrix. The electrical conductivity of the fibers increased with the increasing PANI-ES content

and leveled off at a value of around 10^{-3} S/cm at PANI-ES concentration of 5% w/w. The fibers retained most of their elasticity upon doping, while the tenacity was somewhat reduced. Gratifyingly, the electrical conductivity of the new elastomer fibers was preserved upon elongational deformation, even if strains as large as 600% were applied. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 4038–4046, 2007

Key words: polyaniline; natural rubber; electrical conductivity; elastomers; composites; fibers

INTRODUCTION

Since the discovery of electrical conductivity in π -conjugated polymers three decades ago,¹ these materials have become the focus of major research and development activities around the globe.^{2–4} The excitement for this new generation of polymeric materials reflects their potential to combine the processibility and outstanding properties of polymers with the exceptional, readily tailored electronic, and optical properties of functional organic molecules. Their potential use in technologically interesting applications such as electromagnetic shielding,⁵ antistatic coatings,⁶ corrosion protection,⁷ artificial muscles,^{8,9} light-emitting diodes,^{10–12} field-effect transistors,¹³ photovoltaic cells,¹⁴ and sensors^{15,16} has promoted the development of synthesis and processing methods of conjugated polymers with unique electronic properties.

Polyaniline (PANI) has emerged as one of the most promising electrically conducting polymers, because of its high electrical conductivity, relatively good environmental stability, and comparatively low cost.^{17–19} Unfortunately, the mechanical properties of pristine PANI are inferior compared with those of conventional plastics. One approach to overcome this problem is to fabricate the blends or composites of PANI with matrix polymers that provide the desired mechanical property matrix.^{20–22} Although the approach has been extensively applied for the development of comparatively rigid materials that involve semicrystalline or glassy amorphous host polymers, some studies have addressed the development of electrically conducting composites or blends that combine the elastomeric properties of a rubbery host polymer with the conductive properties of PANI. A number of such composite or blend materials were recently produced by introducing (small amounts of) PANI into several elastomers, including ethylene-propylene-diene monomer (EPDM) rubber,^{23,24} silicone rubber,²⁵ nitrile rubber,²⁶ polyisoprene,²⁷ polyurethane,²⁸ acrylonitrile-butadiene-styrene (ABS),²⁹ and natural rubber (NR).³⁰ With the notions that (i) PANI-containing fibers are of interest in a variety of applications^{31–34}; (ii) materials that combine high electrical conductivity and high elastic deformability are sought for a variety of devices that

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range from deformation sensors²² to actuators³⁵; (iii) NR is one of the technologically most important elastomers because of its unique combination of excellent elasticity, low swelling in water, large extension, good resilience, high abrasion resistance, and low cost³⁶; and that to our best knowledge no PANI/NR composite fibers have been studied, the problem of producing such materials was addressed. The fabrication and investigation of electrically conducting elastomer fibers based on NR at concentration up to 10% w/w PANI is reported here. The new composite fibers synergistically combine the elastic properties of the NR host with the conductive nature of the PANI filler and display a most desirable property matrix, which appears to be useful for a variety of applications.

EXPERIMENTAL

Materials

Centrifugated NR latex with a dry rubber content of 60% was provided by the Rubber Research Institute of Thailand, Bangkok, Thailand. Sodium alginate was purchased from Carlo Erba, Aniline (Merck), was purified by vacuum distillation and stored at 4°C before polymerization. Ammonium peroxodisulfate (AR grade, Merck) was used as an oxidizing agent, and aqueous ammonia (25%, Merck) was used as a dedoping agent. *N*-methyl-2-pyrrolidone (NMP, Merck), hydrochloric acid (37% AR grade, Labscan), and dehydrated calcium chloride (Labscan) were used as received. Commercial grade methanol and acetone were used without further purification.

Polyaniline synthesis

PANI was synthesized in its emeraldine base (EB) form according to the method described by Cao et al.³⁷ Freshly distilled aniline (20.4 g) was dissolved in aqueous HCl (1.5M, 230 mL), and the solution was cooled to below 5°C using an ice bath. After 30 min, a solution of (NH₄)₂S₂O₈ (25 g) in aqueous HCl (1M, 250 mL) was added dropwise over the course of 1 h. The solution was then vigorously stirred and maintained at a temperature of 0–5°C for 4 h. The dark green emeraldine salt (ES) form of PANI that had precipitated from the reaction mixture was collected by filtration under reduced pressure and washed repeatedly with a water/methanol mixture (80:20 v/v) until the filtrate was colorless and of neutral pH. The PANI-ES was converted into the EB form by stirring for 2 h in aqueous (NH₄)OH (3%, 300 mL). The resulting dark blue PANI-EB powder was filtered off and washed with water until the filtrate was colorless and had a neutral pH. The dark blue powder was dried under a vacuum for 48 h to yield

6.27 g (30.7%) of the product. The size of the PANI particles was measured with a Malvern Instruments. The average particle diameter of PANI was determined to be ~ 20.8 μm with a standard deviation of 0.12 μm.

Wet spinning of PANI/NR composite fibers

It was first attempted to adopt the protocol reported by Camillo et al.,³⁰ who prepared PANI/NR composite films by adding the PANI-EB solutions in NMP to the NR latex and casting the resulting mixtures into Petri dishes. Unfortunately, under the conditions used here, rapid gelation was observed when PANI solutions in NMP were mixed with the NR dope. It was next explored the possibility of simply dispersing the neat PANI-EB powder into the NR dope, but (rather expectedly) the mixture displayed poor miscibility. It was discovered, however, that the dispersion of the neat PANI-EB powder in the NR dope could be significantly improved if a small amount of a PANI-EB solution in NMP was added to the mixture. It appears that the dissolved PANI, perhaps in conjunction with the sodium alginate, acts as a surfactant for the PANI particles and helps to at least temporarily stabilize the latter. Note that the aggregation was observed if doped PANI-ES was used under similar conditions and, hence, all dopes were produced with dedoped PANI-EB.

The NR latex (37.5 g) was mixed with the surface-active agent sodium alginate (5% w/w aqueous solution) in a ratio of 75 : 25 (w/w) (total amount of sodium alginate added was 0.625 g) to produce a spinning dope, which had an appropriate viscosity.³⁸ After thoroughly mixing these components, dry PANI-EB was added (to prepare the 0.5, 1, 2, 5, and 10% w/w PANI/NR composites, 0.116, 0.234, 0.472, 1.217, and 2.57 g PANI were added). The dispersions were subsequently mixed mechanically for 15 min. During the mixing, 1.67 mL of a 1% w/w PANI solution in NMP was added dropwise to improve the PANI dispersion in the NR dope. In the case of the neat NR reference fibers (NR comprising sodium alginate without PANI), the spinning dope was prepared without NMP.

The spinning dopes thus prepared were extruded under nitrogen pressure (0.5 kg/cm²) through a spinneret (30 holes with a 0.20 mm diameter) into a first coagulation bath consisting of a solution of calcium chloride (which cross-links the sodium alginate) in methanol (5% w/v), and the coagulated fiber bundles were subsequently drawn through a second bath containing neat methanol. The resulting fibers were subsequently straightened by applying uniaxial tension before the fiber bundles were collected on a take-up roller. The exact wind-up speed was not known, but it was chosen such that only a

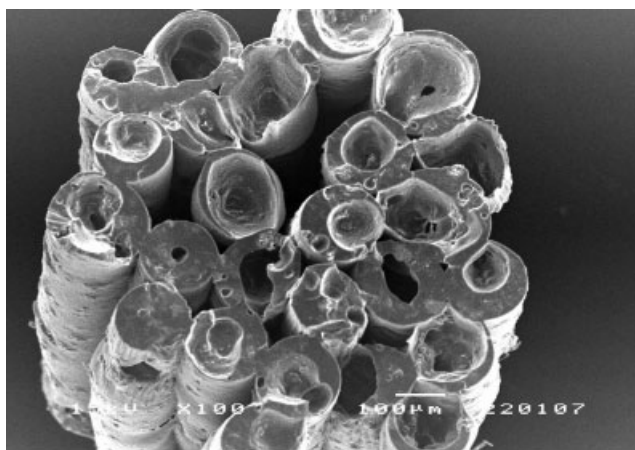


Figure 1 Scanning electron microscopy (SEM) image of the cross-section of a bundle of a PANI/NR composite fiber comprising 5% w/w PANI.

slight tensional force was exerted to the fiber in the coagulation bath, just to keep them straightened. Samples used for further investigation were collected by cutting the strands (before take up through the take-up roller) to a length of ~ 25 cm. The fiber bundles thus obtained were fixated on a glass frame to keep them straight while they were subsequently immersed in methanol bath for 24 h and then dried in air. The cross-sectional shape of the resulting fiber bundles is roughly circular as shown in Figure 1. The average fiber bundle diameter was 0.85 ± 0.04 mm, as determined from the SEM images of 90 selected fiber bundles with the help of image-analysis software (SemAfore 4.0). It should be noticed that for the determination of cross-sectional areas, voids or spaces in fiber bundles were neglected. To dope PANI, the dried fiber bundles were immersed for 24 h in an aqueous HCl solution (1M) and subsequently allowed to dry in air. Upon doping, the composite fiber bundles changed their color from blue to green, which is the characteristic color change associated with the doping of PANI³⁹; the color change was clearly visible in all samples, even those with low PANI content (0.5% w/w).

Characterization

Fourier transform infrared (FTIR) spectra of PANI, neat NR, and composite fibers were recorded with a Thermo Nicolet Nexus 670 FTIR spectrometer equipped with an attenuated total reflectance (ATR) crystal accessory operating at 32 scans at a resolution of 4 cm^{-1} .

Surface and cross-sectional morphological studies of the fibers were carried out with a JEOL JSM-5200 scanning electron microscope (SEM) operating at an accelerating voltage of 15 kV. For the cross-sectional morphology, the fiber bundles were fractured by

immersion in liquid nitrogen and then gold sputtered prior to microscopic analysis.

Thermal analyses were carried out on a Perkin-Elmer Pyris Diamond thermogravimetric–dynamic temperature analyzer (TG-DTA) at a heating rate of $10^\circ\text{C}/\text{min}$ in the temperature range of $30\text{--}700^\circ\text{C}$ and under nitrogen atmosphere.

The tenacity and elongation at break of fiber bundles fibers were measured according to ASTM D 2433 with an initial sample length of 20 cm. The measurements were carried out on a Lloyd Instruments model LR50K testing machine. The load cell used was 100 N, the displacement rate was 500 mm/min, and the gauge length was set at 50 mm. The values quoted are the averages values of 20 individual specimens.

DC electrical conductivity measurements were carried out with a two-point probe arrangement. Two grip probes were used to contact the ends of individual fiber bundles, and a circuit consisting of a power source that provided a constant voltage, and a current meter (Keithley, model 6517A) was used to measure the current through the sample. The specific conductivity σ (S/cm) was calculated according to eq. (1)^{40,41}:

$$\sigma = \frac{L_o I}{A_o V} \quad (1)$$

where L_o (cm) is the length of fiber between the two contacts (typically 2.50 cm), I (A) is the current driven through the sample, A_o (cm^2) is the cross-sectional area of the fiber (typically 0.0057 cm^2 for an average diameter of 0.085 cm), and V (V) is the applied voltage.

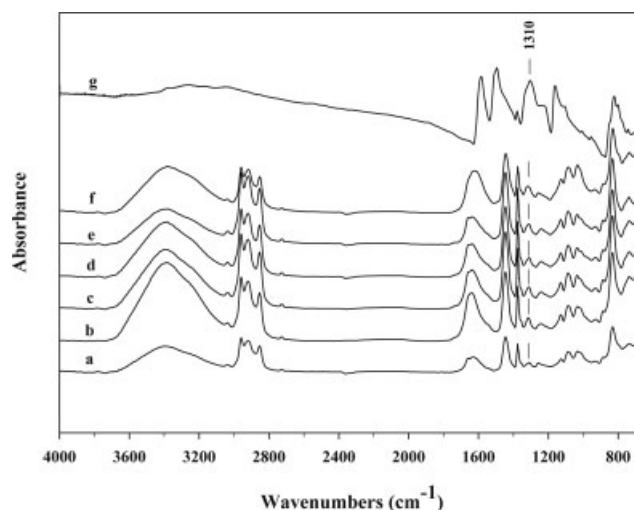


Figure 2 ATR-FTIR spectra of neat NR fiber bundles (a), undoped PANI-EB/NR composite fiber bundles containing (b) 0.5, (c) 1, (d) 2, (e) 5, and (f) 10% w/w of PANI, and an undoped PANI-EB pellet (g).

TABLE I
Wavenumbers (cm^{-1}) as Observed in the FTIR Spectra of NR, Sodium Alginate, Undoped PANI-EB and Undoped PANI-EB/NR Composite Fiber Bundles

Wavenumber (cm^{-1})	Vibration assignment	NR	Sodium alginate	PANI-EB	PANI-EB/NR composite
3373	O—H stretching		✓		✓
3300	NH stretching			✓	
2962	CH ₃ asymmetric stretching	✓			✓
2928	CH ₂ asymmetric stretching	✓			✓
2854	CH ₂ symmetric stretching	✓			✓
1663	C=C stretching	✓			✓
1629	C=O stretching		✓		✓
1586	Stretching vibration of C=N quinoid ring			✓	
1497	Stretching vibration of C=C quinoid ring			✓	
1447	CH ₂ deformation	✓			✓
1375	CH ₃ asymmetric deformation	✓			✓
1310	Stretching vibration of C—N quinoid ring			✓	✓
1161	Vibration mode of quinoid ring			✓	✓
1035	C—O—C stretching		✓		✓
838	C—H bending vibration of para-couple benzene ring			✓	
835	=C—H wagging	✓			✓

The strain-dependent conductivity experiment was carried out by the method reported by Chiang et al.⁴² Since the cross-sectional area of the fibers upon uniaxial deformation is inversely proportional to the length after stretching L (cm), the conductivity can be determined as a function of strain ($\epsilon = L/L_0 - 1$) by an experiment that is similar to the above and using eq. (2):

$$\sigma = \frac{L^2 I}{V L_0 A_0} \quad (2)$$

The equation is derived under the assumption that the final volume of the fiber does not change upon stretching.

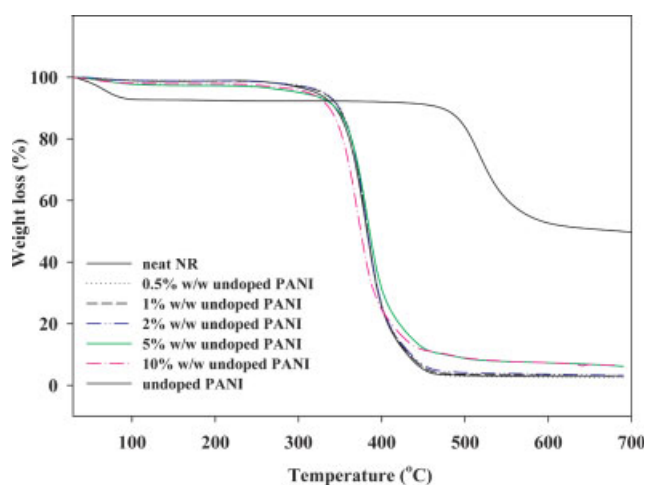


Figure 3 Thermogravimetric analysis (TGA) traces of undoped PANI-EB, bundles of neat NR fiber and the series of undoped PANI-EB/NR composite fibers. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

RESULTS AND DISCUSSION

Structural characterization of PANI/NR composite fibers

FTIR spectra was used to characterize the chemical structure of neat PANI-EB, neat NR fiber bundles (without PANI but with sodium alginate), and undoped PANI-EB/NR composite fiber bundles as shown in Figure 2. The spectrum of the NR fibers shows the main absorption peaks at 2928, 2962, 2851, 1663, 1447, 1375, and 835 cm^{-1} (Table I), which are the characteristic signals of the NR.^{43,44} Additional bands can be observed at 3373, 1629, and 1035 cm^{-1} , corresponding to the hydroxyl, the carbonyl, and the C—O—C stretching vibrations, associated with the

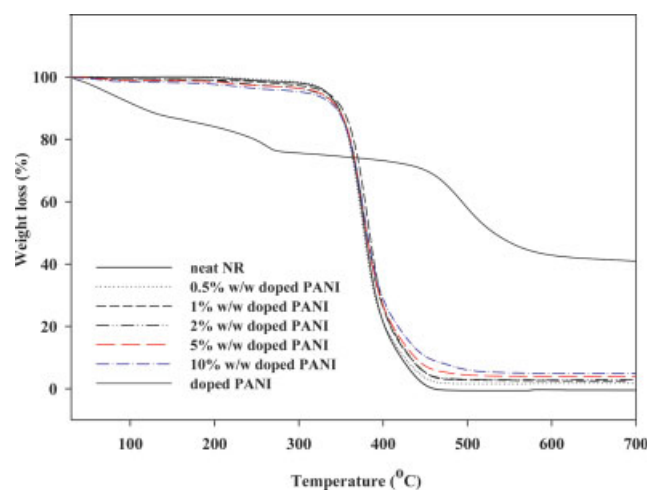


Figure 4 Thermogravimetric analysis (TGA) traces of HCl-doped PANI-ES, bundles of neat NR fiber, and the series of HCl-doped PANI-ES/NR composite fibers. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

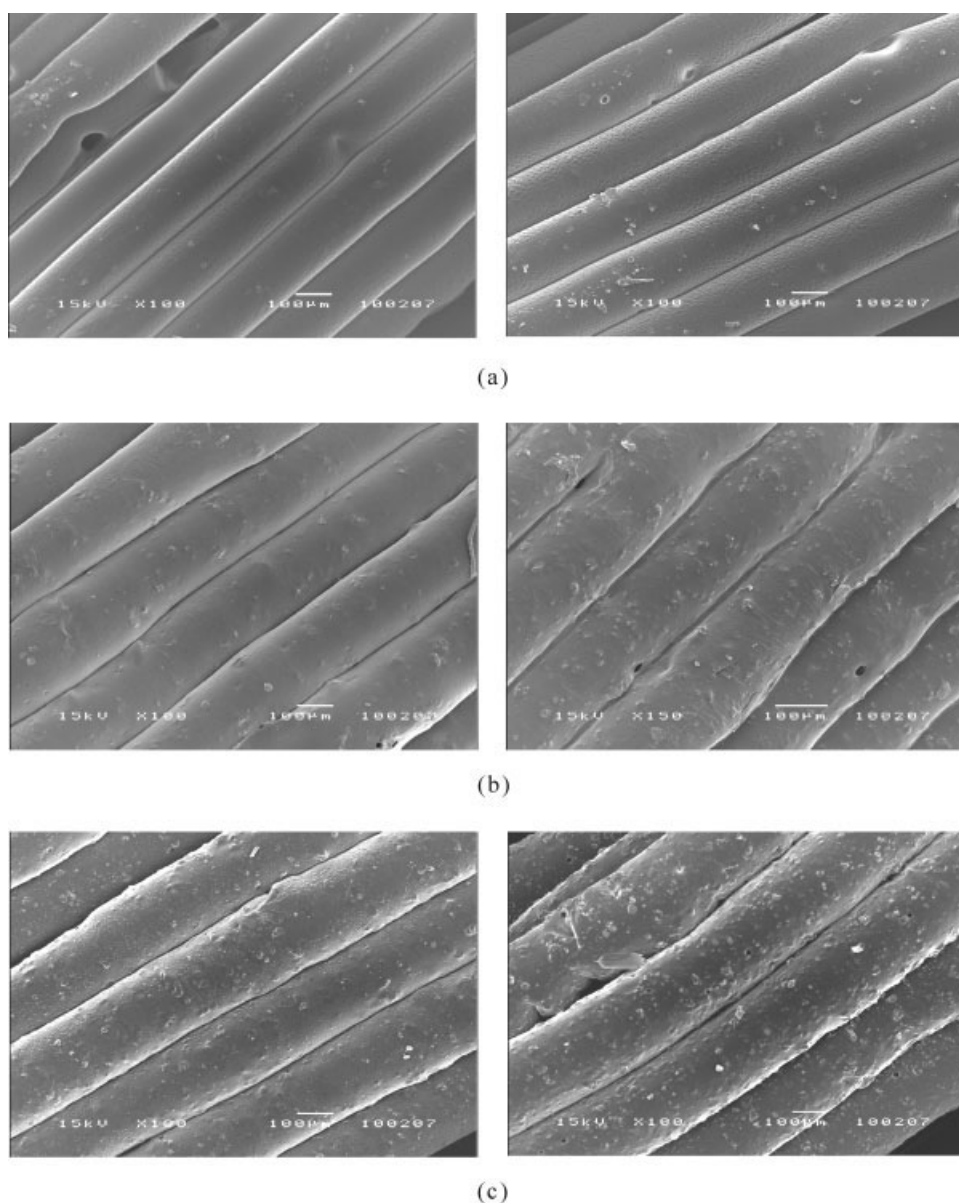


Figure 5 Scanning electron microscopy (SEM) images of the surface of bundles of undoped and HCl-doped PANI/NR composite fibers with PANI contents of (a) 0, (b) 5, and (c) 10% w/w; left column: undoped, right column: HCl-doped.

sodium alginate in the fibers (Table I).⁴⁵ The spectrum of the neat PANI exhibits absorption peaks that mirror those reported for the EB form (undoped) of PANI in the earlier studies.^{46,47} The main characteristic peaks are summarized in Table I. The characteristic absorption peaks of all three components (NR, sodium alginate, PANI) can also be found in the spectra of composite fibers with a PANI content of 0.5–10% w/w. Unfortunately, the signals of PANI cannot be unequivocally distinguished in the composites due to the low PANI content in the composites and overlap with NR and alginate signals. Nevertheless, the spectra of the PANI-EB/NR composite fibers show an increase of

the relative intensity of a peak around 1310 cm^{-1} with an increasing PANI content. This signal is assigned to the stretching of the C–N of the benzenoid structure of PANI⁴⁸ and is indicative for an increasing PANI concentration throughout the series.

Thermal stability

Thermogravimetric analyses (TGA) data for the series of composite fibers are shown in Figure 3 together with the reference data for the neat PANI-EB powder and the neat NR fiber bundle. The thermogram of the neat PANI-EB shows two discrete weight loss steps in the temperature ranges of 60–

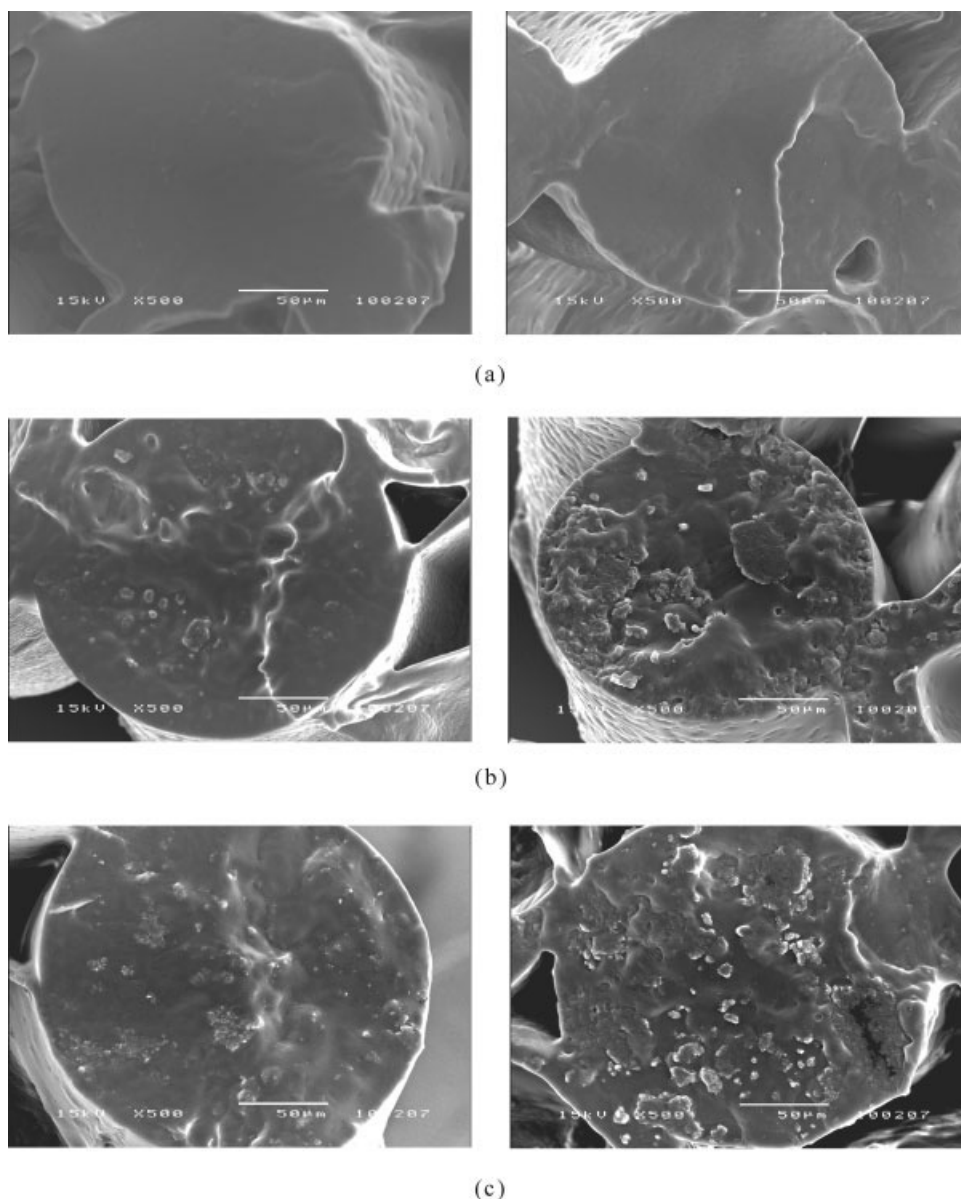


Figure 6 Scanning electron microscopy (SEM) images of cross-sections of bundles of fractured, undoped, and HCl-doped PANI/NR composite fibers with PANI contents of (a) 0, (b) 5, and (c) 10% w/w; left column: undoped, right column: HCl-doped.

100°C and 480–600°C, corresponding to the loss of water and the degradation of PANI, respectively.^{49,50} The thermogram of the neat NR fiber shows only one discrete weight loss step that is typical for the degradation of NR.⁵¹ The decomposition has an onset at ~ 320°C, is steepest around 370°C, and is complete around 475°C with a char yield of ~ 3%. The results show that the NR appears to degrade before PANI.^{51,52} All composite fibers show virtually identical behavior, and mirror largely the degradation behavior of the neat NR, most likely due to the small amount of PANI. It can be noted, however, that the char yield continuously increases, as expected, with increasing of PANI content in the

composites. The thermograms of the neat PANI-ES (powder), neat NR fiber, and the composite fibers after doping with HCl are shown in Figure 4. The thermogram of the doped PANI-ES exhibits three weight loss steps.⁵³ The first step in the range of 65–120°C is again explained with the loss of water. The second weight loss step between 120 and 280°C has been explained with the loss of low-molecular-weight polymer and unbound HCl.⁵⁴ The third weight loss step between 420 and 580°C is related to the degradation of PANI chains. Again, no remarkable change was observed in the thermal stability of the PANI/NR composite (Fig. 4), but it should be noted that the NR appears to degrade before the PANI.

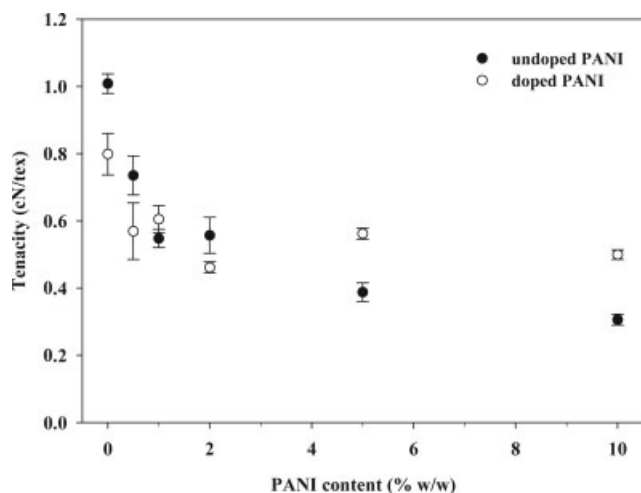


Figure 7 Tenacity of bundles of undoped and HCl-doped PANI/NR composite fibers with PANI contents of between 0 and 10% w/w.

Morphology

Surface scanning electron microscopy (SEM) images of undoped and HCl-doped NR/PANI composite fiber bundles containing 5 and 10% w/w PANI and of a NR reference without PANI are shown in Figure 5. The images illustrate that the roughness of the fiber surface increases somewhat with the increasing PANI content. The surface roughness of the nanocomposite fiber appears to increase upon doping with HCl and the size of the features matches with the dimensions of the PANI particles. To further explore the distribution of the PANI particles throughout the fibers, cross-sections of freeze-fractured PANI/NR composite fibers containing 5 or 10% w/w PANI and of a neat NR reference fiber were imaged by SEM (Fig. 6). In the case of the neat

NR fiber [Fig. 6(a)], a homogeneous morphology was observed. By contrast, the SEM images of the 5 and 10% w/w PANI-containing fibers show clear evidence of the presence of PANI particles. The images show a combination of well dispersed, isolated PANI particles, and agglomerates, which are typical for composites of ultimately rather incompatible components.⁵⁵ Rather interestingly, the images (particularly of the 5% w/w HCl-doped PANI/NR fiber) suggest an inhomogeneous distribution with high local PANI particle/agglomerate densities [Fig. 6(b), right]. It appears that the PANI preferentially resides at the surface of the fibers; this morphology may be the result of the very different polarities of the PANI and the NR and the coagulation process, which utilizes a polar solvent bath (methanol/CaCl₂, vide supra), providing a driving force for the migration of PANI to the fiber surface during this step.

Mechanical properties

The mechanical properties of the bundles of PANI/NR composite fibers were determined by the standard uniaxial tensile tests. The results are compiled in Figures 7 and 8. The neat NR fiber bundle displays a tenacity of about 1 cN/tex and an elongation at break of 820%; these values are typical for NR.⁵⁶ An introduction of undoped PANI particles leads to a reduction of both, tenacity (Fig. 7), and elongation at break (Fig. 8). The tenacity decreases in a nonlinear fashion with increasing PANI content to level at ~0.3 cN/tex (tenacity) at a PANI content of 10% w/w. At the same time, the elongation at break was reduced to 160%. Similar tendencies were found in the previous studies for PANI composites with ethylene-vinyl acetate⁵¹ and styrene-butadiene-styrene

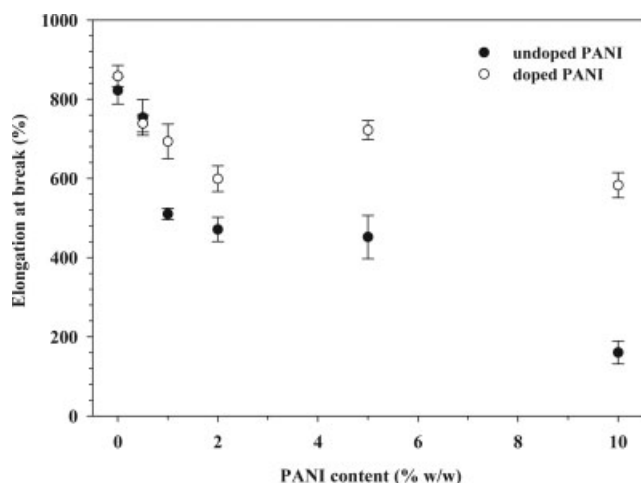


Figure 8 Elongation at break of bundles of undoped and HCl-doped NR/PANI composite fibers with PANI contents of between 0 and 10% w/w.

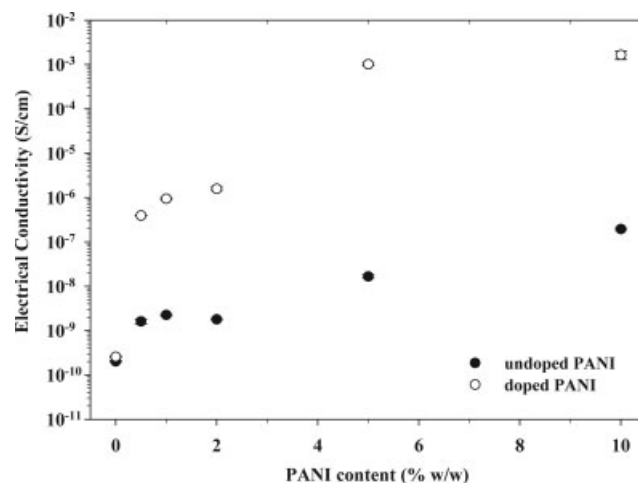


Figure 9 Electrical conductivity of undoped and HCl-doped PANI/NR composite fiber bundles as function of PANI content.

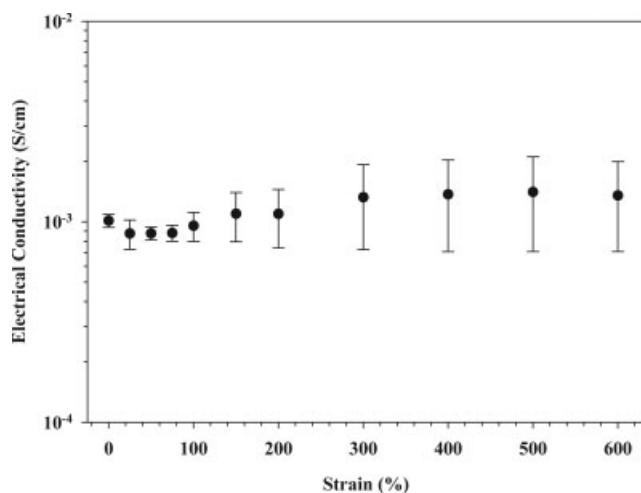


Figure 10 Electrical conductivity of HCl-doped PANI/NR composite fiber bundles comprising 5% w/w PANI as function of uniaxial strain.

triblock copolymers.⁵³ This situation may reflect the poor mechanical properties of PANI and limited mechanical interaction between the NR matrix and the PANI filler. Rather interestingly, in comparison with the undoped composite fiber bundles, the tenacity, and elongation at break of the PANI-containing samples increase again upon doping; in the case of the 10% w/w blend in a rather significant way to 0.5 cN/tex (tenacity) and 580% (elongation at break). The detailed mechanism of this fortunate effect is as of yet unclear, but it may be related to electrostatic interactions (enabled through HCl doping) between the protonated PANI and the alginate network.⁵⁷

Electrical conductivity

The DC electrical conductivity of the elastomeric PANI/NR composite fiber bundles was studied as a function of PANI concentration and doping level using a conventional two-point probe arrangement. The results are compiled in Figure 9. In the case of the undoped fibers, the electrical conductivity increases gradually from 10^{-10} S/cm (neat NR fiber bundle) to 10^{-7} S/cm (10% w/w PANI) with increasing PANI content. This finding is consistent with the findings by Camillo et al.³⁰ who reported that the NR latex itself was able partially to dope the PANI by either protonation from NR chains or imparting conformational changes to the PANI chains (which in case of the presently used PANI particles is rather unlikely).³⁰ Upon doping with HCl, the electrical conductivity increased sharply for all PANI-containing fibers (but not the NR reference) to reach a plateau of $\sim 1 \times 10^{-3}$ S/cm at a PANI content of 5% w/w. Further increase of the PANI concentration to 10% w/w increases the conductivity

only marginally to 1.7×10^{-3} S/cm (Fig. 9), suggesting that the percolation threshold is already reached at a PANI content of 5% w/w. We also explored the influence of mechanical deformation on the electrical conductivity of the new composite fibers. Figure 10 shows the electrical conductivity of the bundle of the NR/PANI composite fibers containing 5% w/w PANI as a function of uniaxial strain, $\varepsilon = L/L_0 - 1$. Gratifyingly, the conductivity remains virtually unchanged upon deformation. In the light of classical percolation theory, these results provide further support for the conclusion that in the PANI/NR composite fibers studied here the PANI particles migrate to the fiber surfaces, wherein their higher-than-statistical density leads to percolation.

CONCLUSIONS

In summary, we have shown that electrically conducting elastomer fibers based on NR and up to 10% w/w PANI in its EB form can be readily fabricated by a conventional wet-spinning process. The resulting fibers can be doped by immersion in aqueous HCl solution, which converts the PANI to the electrically conductive ES form. The composition of the new composite fibers was identified by the FTIR spectra. It appears that the PANI particles are inhomogeneously distributed in the NR matrix and preferentially migrated to the fiber surfaces. The electrical conductivity of the fibers increases with the increase in PANI content by more than seven orders of magnitude, and it levels off at a value of around 10^{-3} S/cm at a PANI concentration of 5% w/w. The fibers retained most of their elasticity upon doping, while the tenacity was somewhat reduced. Gratifyingly, the electrical conductivity can remain unchanged upon deformation to elongations up to 600%. Thus, the new composite fibers display a most desirable property matrix having properties that make them useful for applications in, for example, soft actuator applications.

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