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Electrical properties and fractal behavior of polyurethane elastomer/polyaniline composites under mechanical deformation

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Abstract

Present work reports on electrical properties of polyurethane elastomer/polyaniline (PU/PANI–HCl) composite films under tensile deformation. Two types of surface-modified and one type of volume-modified composite of PU and PANI–HCl were prepared. Surface modification of PU film was performed by swelling the parent film in aniline followed by its contact with the acidified oxidant solution to polymerize aniline and form PANI–HCl distributed inside surface/subsurface layer of the film. Volume-modified PU was prepared by mixing of the polymer components in a joint solution and then solution casting. Nonlinear current–voltage characteristics were observed for surface-modified samples while linear ones were typical of volume-modified samples. Deformation of the polymer composites caused partially reversible decrease of their conductivity characteristics, which could be described mathematically with a power law function of the strain with an exponent being dependable on the type of PU modification. Such behavior was interpreted in terms of deformation of a fractal percolation network formed in the system during its formation and chemical synthesis.

Keywords: Polyurethane—polyaniline composites; Percolation network; Non-linear electrical properties

1. Introduction

During the last decade intrinsically conductive polymers (ICPs) became an efficient alternative to inorganic conductors in many practically important applications. In particular, composites based on common polymers and ICPs often possess electrical characteristics (especially being represented as specific ones, i.e., normalized to the material's specific gravity) highly competitive to those of traditional conductive composite materials in applications as electrode active mass of lightweight batteries, electromagnetic interference shielding, corrosion protection coatings, etc. [1–4]. Due to the occurrence of additional environmentally dependable properties (smart materials) for some ICPs they can be employed in modern sensor, electrochromic or electro-mechanical actuator devices [5–8]. High electrical conductivity [9], nonlinear electrical or piezo-electric responses [10–12] have been also demonstrated for such composites.

These and other publications stressed the crucial role of the morphology, microstructure and type of the matrix polymer on the electrical behavior of conductive polymer composites. For example, as has been demonstrated for PVDF based composites current–voltage (*I*–*V*) characteristics were switching from linear type for the case of ICP component distributed within the volume of the composite film to essentially nonlinear type for the case of surface modification (formation of PANI–HCl via polymerization of aniline in a thin surface

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layer of PVDF) [12]. Similar effects have been observed for elastomer/PANI composites [11]. The latter systems are also interesting as examples of materials suitable for electromechanical sensor applications as their I–V characteristics are sensitive to externally applied mechanical stresses. Wu et al. [13] have developed conducting polypyrrole coated wearable strain gauges based on nylon fabric (Lycra) to be used for biomechanical monitoring. Another study [14] points out the importance of conductive filler concentration in the composite system during mechanical deformation. The suggested mechanism of the observed unusual variation of conductivity under extension of the composite involves two stages. In the first stage, conductivity increased due to increased number of contacts of conductive polymer clusters. This is induced by orientation of extended chains and the stretching of soft segments of the matrix when under increasing strain and thus reducing the hindrance between conductive polymer clusters. In the second stage, further extension leads to a relative displacement of the conducting clusters resulting in lower probability of their contacts and thus reduction of conductivity of the composite material. Certainly, there is a higher probability of the initial conductivity increase at high concentrations of the conductive polymer filler in the composite under extension than at lower concentrations approaching percolation threshold where conductive paths among clusters can be disrupted by the extension more easily. Naturally, the magnitude of such conductivity variation is related to the number of conductive paths formed in the composite system.

In this publication we report on variation of the electrical conductivity of PU/PANI–HCl composite films under tensile deformation depending on their morphology and distribution of the conductive component. PU parent films that were surface or volume-modified with PANI–HCl, showed dissimilar electrical behavior, the former being nonlinear and the latter being typical ohmic behavior. Decrease in conductivity under tensile deformation was observed for three different types of composite systems and interpreted in terms of affine deformation of a fractal percolation network created in the system during its formation and chemical synthesis.

2. Experimental

Polyurethane elastomer (see Fig. 1 for the chemical structure) was synthesized via a prepolymer method [15]. As a typical example, 0.0130 mol of poly(oxypropylene glycol) with molecular mass 2075 g/mol and 0.0196 mol of hexamethylenediisocyanate with a small amount of dibutyl tin dilaurate catalyst (Aldrich) were mixed at 80 °C for 1 h under dry nitrogen atmosphere. Prepared urethane prepolymer with NCO group content of 1.71% was then dissolved in dimethylformamide (DMF) and then 1,3-phenylene diamine was added. The mixture was stirred for $\sim$2 h at 60 °C until complete consumption of the isocyanate groups. The final product, poly(urethane urea), was precipitated with water, washed with ethanol, and dried for 24 h at 40–45 °C. PU elastomer films of the thickness $\sim$300 μm were prepared by dissolving of the elastomer in DMF ($\sim$20% concentration) followed by casting this solution on a glass plate, and subsequent drying in vacuum for 48 h. The prepared PU elastomer had $M_w = 29{,}750$ g/mol and $M_w/M_n = 1.27$ (gel permeation chromatography, Waters Breeze 1500 System, DMF solution), amorphous structure (differential scanning calorimetry, Perkin–Elmer DSC Pyris 1, 20–300 °C, atomic force microscopy Autoprobe CP, tapping mode) and the Young's modulus of $\sim$3 MPa (Instron, tensile deformation).

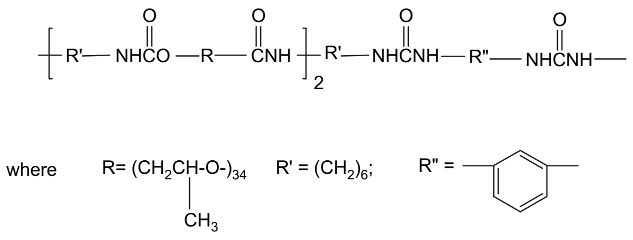

Fig. 1. Chemical structure of PU elastomer used in this study.

Three sets of PU/PANI–HCl film samples were prepared. The first set included one-side surface-modified samples prepared by the technique similar to the one used earlier for the preparation of PET/PANI and PVDF/PANI films [12,16]. Prior to surface modification, parent PU films with the thickness approximately 300 μm were washed with hexane and then dried to a constant weight. This procedure was followed by immersing the samples into aniline for a time of 0.5–3 s to swell the parent PU film up to 7–15.3 wt.%. Swelled samples were then placed between two filter papers in order to remove free aniline from the sample surface. Further these samples were fixed in a special cell [16], which allowed a contact of their one side with the oxidizing 0.1 M $(NH_4)_2S_2O_8$ and 1 M HCl water solution for 30 min. After polymerization, aniline residues and by-products were extracted with *n*-hexane in Soxhlet apparatus for 5 h followed by dynamic vacuum drying to achieve the constant weight. This procedure resulted in three-layer PU/PANI–HCl composite films with pronounced surface conductivity. The first layer consisted of pure PANI doped with HCl, which appeared due to oxidation of aniline that escaped from the bulk of the swelled PU film onto its surface. The second layer consisted of PANI–HCl, which was formed inside a thin subsurface layer of the PU matrix. It was cohesively connected with the third layer being a pure PU layer constituting the majority of the film thickness.

The second set of the samples included two-side surface-modified film samples prepared similarly to the first set of samples except that both sides of the PU film (being previously swelled with aniline) were exposed to the oxidant solution. The oxidation step was realized through a simple immersion of this PU film into the vessel with the above-mentioned oxidizing solution. Obtained film samples were then treated in Soxhlet apparatus similarly to the first set of samples. Finally, these treatments resulted in five layer composites including two PANI–HCl-containing layers at each side as described above with the pure PU layer sandwiched in-between them.

The third set included film samples containing PANI–HCl homogeneously distributed in the PU matrix volume. PANI–HCl for these samples was synthesized in accordance with the known procedure [17]. PU/PANI–HCl volume-modified composite films were made through mixing of PANI–HCl dispersed in dimethylformamide with a solution of PU dissolved in the same solvent at necessary weight ratio (10% of PANI–HCl) followed by casting of the obtained mixtures on PVC substrate and drying in air and then in vacuum at $\sim 10^{-5}$ Torr for at least 24 h.

The cross-sections of three types of studied films, one-side, double-side and volume-modified, were observed under optical microscope and captured images were used to measure the thickness of PANI–HCl-containing layers by using an optical diffraction grating as a scale standard.

In order to measure electrical characteristics of studied PU/PANI–HCl composites, a pair of electrodes were deposited on the sample surface by thermal evaporation of silver in a vacuum chamber by employing a 250 μm diameter wire as a shadow mask [12]. After deposition of the Ag electrodes the wire mask was removed leaving a 200 μm gap between the deposited electrodes. The thickness of the electrodes was at least 100 nm. Such prepared samples were mounted onto a mechanical deformation device where special clamps simultaneously served both to hold the sample for application of the external tensile deformation and as electrodes to insure ohmic contact with the deposited silver electrodes on the sample surface. The degree of deformation was controlled by rotation of a micrometer screw. Relative elongation was calculated during the deformation process from the clamps' distance using calipers. *I–V* characteristics of the samples were measured *in situ* at various stages of their deformation using a Keithley multimeter model 2400 operated from a PC with Labview software.

3. Results and discussion

Fig. 2 shows the images for each type of PU/PANI–HCl composite films captured with an optical microscope. The thickness of the green PANI–HCl-containing layers for surface-modified samples was found to be in the range of 12–18 μm for one-side and 18–30 μm (on each side) for double-side, which constitute around 10–20% of the total thickness of PU/PANI–HCl composite film sample, showing very weak dependence on aniline concentration during synthesis.

The modified PANI–HCl-containing layer is not completely uniform in its cross-section, which is due to the formation of two dissimilar PANI–HCl-containing layers (see samples' description in Section 2 and Fig. 2). Specifically, washing of the sample surface with ethanol revealed that the very top of the layer is most likely consisted of pure PANI–HCl, which is not cohesively tightly attached to PU substrate. This fact gives evidence of a heterogeneous nature of the composite. Formation of such dissimilar PANI–HCl-containing layers in the final composite implies two different polymerization processes taking place in the system. Firstly, polymerization of aniline escaped onto the surface of the swelled PU film from its bulk, and secondly polymerization of aniline that remained inside a thin subsurface layer of the PU film. As a result, the skin of the composite film consists of two electrically coupled conducting PANI–HCl-containing layers, which have different morphology and give probably different input into electrical and mechanical behaviors of the composite. The upper layer of pure PANI–HCl should have properties similar to the bulk PANI–HCl material, while the underlying composite layer of PU/PANI–HCl should possess the properties controlled by those of the individual components as well as by the preparation procedure. Indeed, during formation of PU/PANI–HCl composites aniline penetrates into porous (and generally free volume network) of PU under swelling procedure. This insures formation of a conductive PANI–HCl network in the subsurface layer of PU matrix during polymerization. Distribution of pores in a polymer has been proved to be a fractal system in many publications [18,19]. Possible interaction between functional groups of PU matrix and aniline, for example formation of hydrogen bonds of type NH···O=C or N–H···O–C between specific groups of

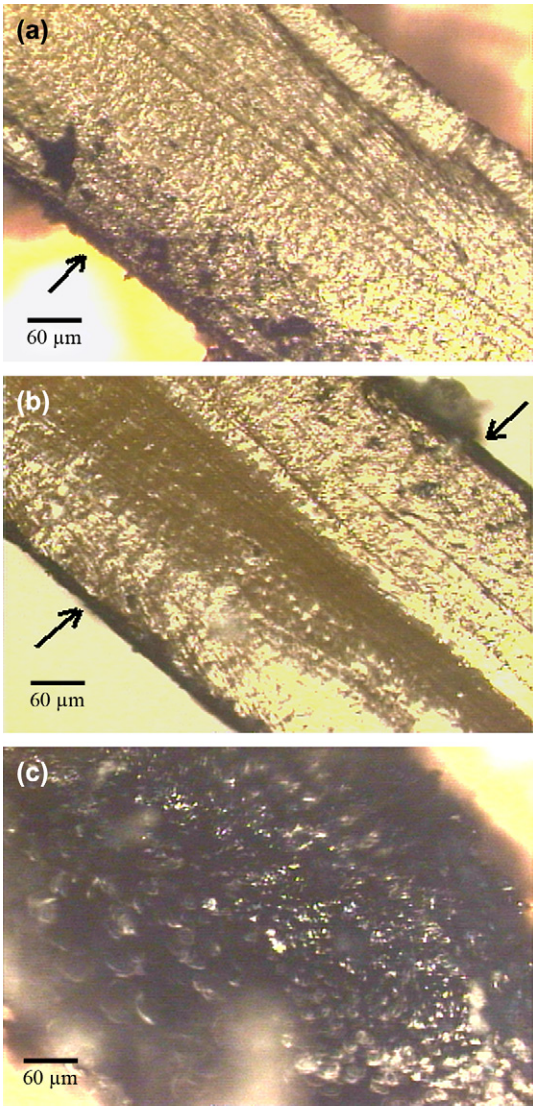

Fig. 2. Optical microscopic images of cross-sections for (a) one-side, (b) double-side and (c) volume-modified PU/PANI–HCl composite films (arrows indicate the surface-modified side with PANI–HCl).

neighboring molecules [20], may bring, in addition, orientation of PANI molecules and their conductive clusters. Therefore the final architecture of the percolation network will be determined by two factors: (i) distribution of the free volume in PU matrix and (ii) specific interactions between the components. Virtually, polymerization of aniline into PANI makes visualization of the fractal network previously constituted with the free volume of the PU matrix.

PU/PANI–HCl composite films were tested for their *I*–*V* characteristics at different levels of relative elongation. Typical *I*–*V* characteristics and the changes resulting from mechanical stress and elongation are illustrated in Fig. 3. It can be seen that the electrical current that is passing through the polymer composite is decreasing as the strain increases. Naturally, the effect should be due to dimensional changes of a formed PANI conductive network during deformation of the composite sample. However, the strong difference in the electrical behavior is observed between the surface and bulk PANI-modified PU samples (Fig. 3). Specifically, the former demonstrates nonlinear *I*–*V* characteristics, whereas the latter shows typical ohmic linear dependence and lower current response despite similar PANI loading. Similar peculiarity of *I*–*V* characteristics has been previously observed in the case of PVDF/PANI–HCl surface and bulk-modified composites [12]. One can speculate therefore that the observed nonlinearity can be associated with two factors: (1) specific conductivity mechanism in the PANI-enriched surface layer of the composite [12], and (2) the difference in the percolation network structure between the surface-modified and the bulk-modified PU/PANI–HCl composites.

Mechanical deformation of the PU/PANI–HCl composite leads to deformation and disruption of the percolation network. This deformation is either partial or complete interruption of network depending on the stress applied. Fig. 4a shows

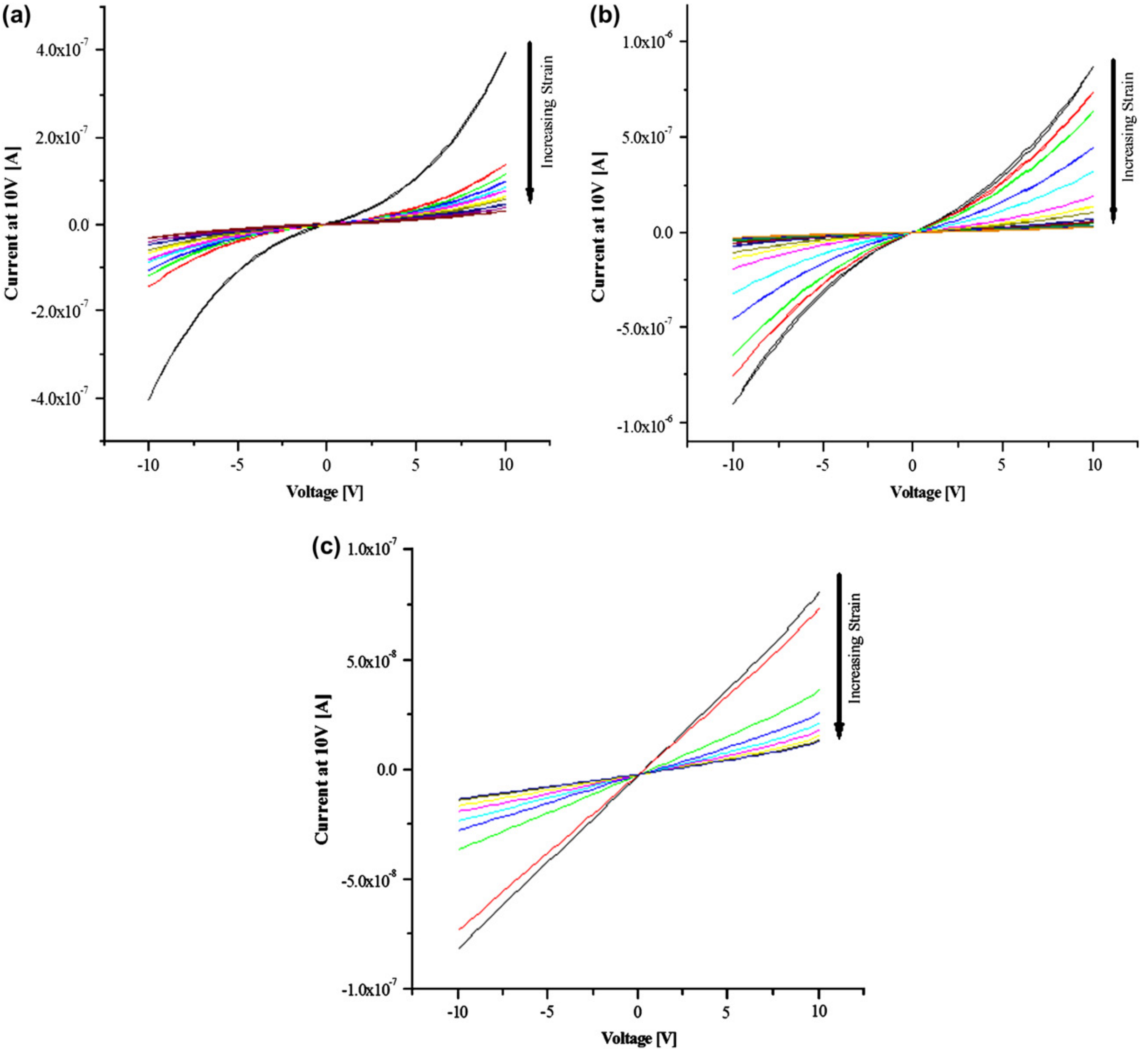

Fig. 3. The changes of *I*–*V* curves characteristic for (a) one-side (7% aniline), (b) double-side surface-modified (4.5% aniline) and (c) volume-modified (10% PANI–HCl) PU film with increasing strain.

the deformation of PU/PANI–HCl network under increasing strain in longitudinal direction (one-side modified sample with 15.3% aniline concentration during polymerization is used as an example). For simplification, only current measured at 10 V was considered here when constructing and studying the relationship of current and relative elongation. In the first step, samples were submitted to gradually increasing mechanical stress up to relative elongation of 25–30%, after which the mechanical stress was released (unload 1). In order to determine the time needed for maximum conductivity recovery after applied stress, *I*–*V* characteristics were measured every minute and it was found that in about 8–10 min after unload the conductivity reaches the maximum of recoverable electrical conductivity (Fig. 4b). In the second step, the samples were put under relative elongation exceeding 50% and only then the stress was released. As can be seen from Fig. 4 the conductive network deforms rather gradually and deformation is reversible to some extent depending on the applied stress. In addition, there is a portion of unrecoverable elongation, which is due to mechanical properties and relaxation of deformation for parent PU films used in the study. It has been reported [21] that almost complete recovery (up to 98%) can be reached in pure polyurethane. However, the presence of the conductive filler reduces the recovery rate down to 70% when the load is above the percolation threshold.

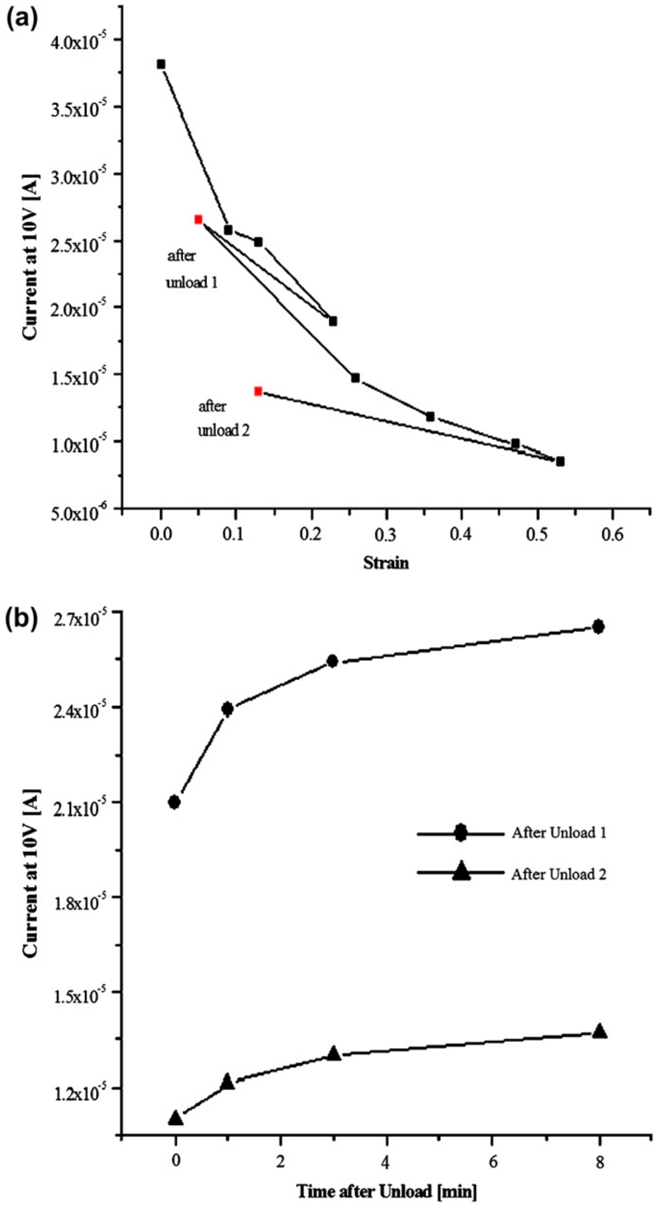

Fig. 4. Illustration of deformation and recovery for PU/PANI–HCl one-side modified sample (15.3% aniline); (a) conductivity change during deformation of conductive network with unload and (b) conductivity relaxation after deformation of the composite (unload 1 = after applied strain of 0.25–0.3, unload 2 = after strain > 0.5).

Fig. 5 presents the relationship between electrical current measured at 10 V and relative elongation as it was measured for the three types of studied PU/PANI–HCl composite films during increasing elongation. One should expect a decrease of electrical conductivity of a composite sample due to increasing average distance between clusters (particles) of the conductive filler (PANI–HCl) and interruption of electrical contacts between them under elastic deformation of the elastomer matrix, which is equivalent to a decrease of an effective concentration of the filler particles. In other words conductivity versus mechanical strain behavior should be similar but reciprocal to conductivity versus concentration of the conductive filler behavior. The latter case represents a well-known percolation problem, i.e., the system is switching from insulating to conducting behavior at some critical concentration x_c known as a percolation threshold and electrical conductivity σ increases as a power law function of the composition, x above this limit: $\sigma \sim (x - x_c)^\alpha$. Fig. 5 shows that conductivity of all types of composite samples under study is indeed decreasing with the mechanical deformation following some nonlinear law. Therefore, the experimental data for $I(\varepsilon)$ were analyzed using nonlinear fitting functions available in Microcal Origin 6.0. We applied a power law function in the form of: $y = a \times x^b$ with a being a constant characteristic of the tested material, x the applied strain and b experimentally measured exponent of electrical current versus deformation dependence.

Generally, electrical current, which can be passed through a conductor under application of a certain external voltage, is proportional to the cross-sectional area of the conductor and reversely proportional to its length. In the assumption of the conductor material to be a continuous homogeneous medium (i.e., with a uniform isotropic density distribution), its tensile deformation with a strain $\varepsilon_\parallel$ in the direction of the applied deformation (longitudinal direction) will cause linear reduction of its dimensions in transverse direction $\varepsilon_\perp$ in accordance to Poisson's ratio ($\nu = -\varepsilon_\perp/\varepsilon_\parallel$). Elastomers are traditionally considered as incompressible materials with $\nu \approx 0.5$ and therefore the sample's volume remains constant during deformation, which can be described mathematically as $\lambda_\parallel \lambda_\perp \lambda_\perp = 1$ (where $\lambda_\parallel$ and $\lambda_\perp$ are sample elongation in longitudinal and transverse directions correspondingly and $\lambda = \varepsilon + 1$). Under tensile deformation the length of the elastomer sample is increasing linearly with strain $\sim\varepsilon$, while its cross-sectional area is decreasing as ε^{-2} (please note that here and later in the text the index $\parallel$ will be omitted and we will be talking

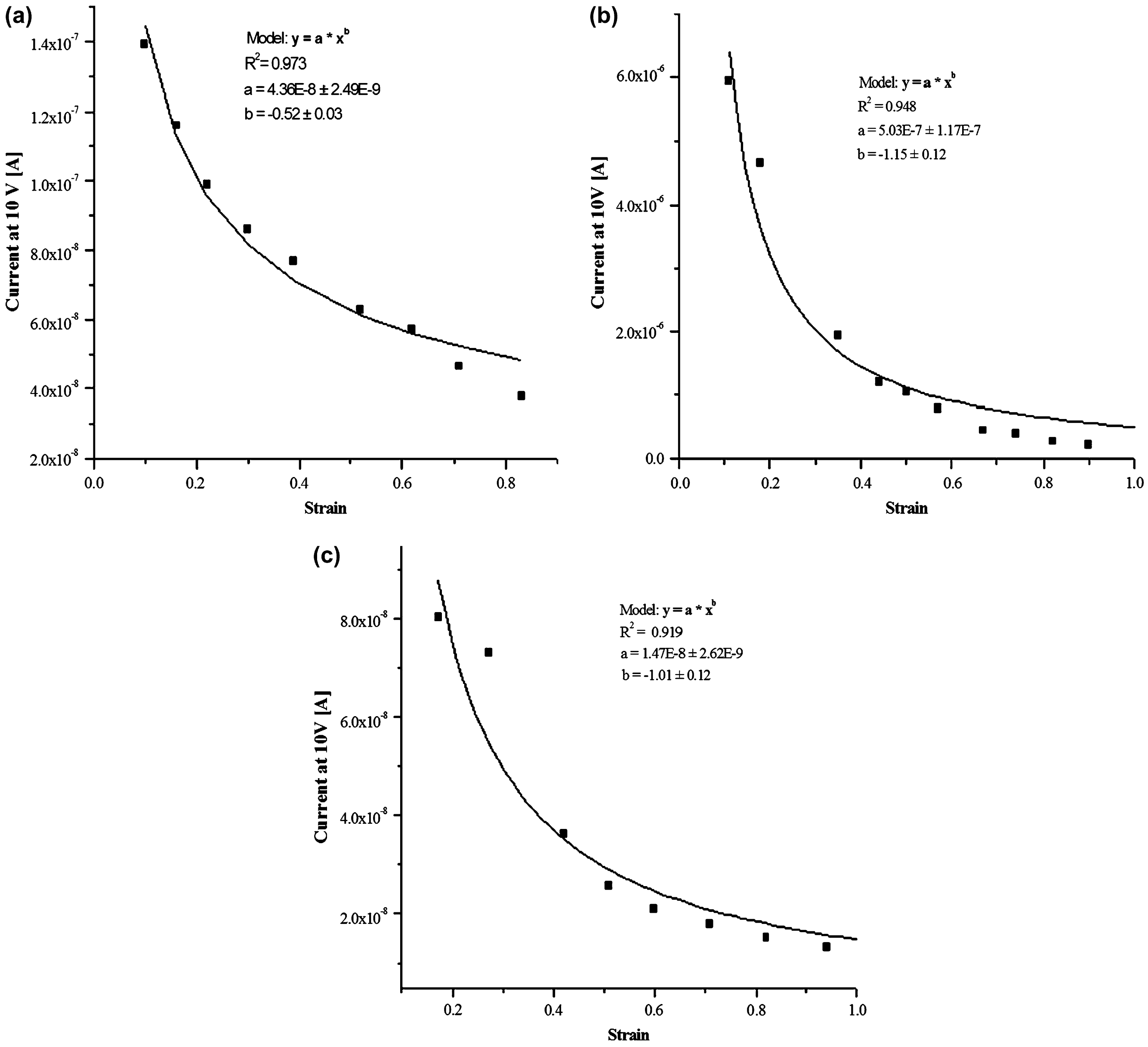

Fig. 5. The relationship between electrical current measured at 10 V and strain for three types of studied PU/PANI–HCl composite films; (a) one-side modification (7% aniline), (b) double-side modification (4.5% aniline), (c) volume-modified (10% PANI–HCl).

about experimentally measured longitudinal strain or elongation). The net effect of such tensile elongation is reduction of current $\sim\varepsilon^{-3}$ for a three-dimensional (3D) continuous conducting film. Similar consideration of a 2D sample (conductive coating on top of insulating polymer substrate) brings ε^{-2} reduction of current due to tensile deformation of the sample. The situation is, however, more complex for fractal percolation network samples, which may be considered as composites with conductive particles randomly distributed within insulating matrix. Increasing the conductive particles concentration promotes the formation of clusters, which act as conductive passes through the otherwise insulating film. Below the percolation threshold conductivity of such composite sample is very low. Above the percolation threshold so-called infinite cluster is formed and conductivity increases by many orders of magnitude [22]. Near but above the percolation threshold the probability of creation of a cluster of a certain size is described with power law dependence versus concentration of conductive particles (concentration of the conductive filler). In the latter case current has to be proportional to a probability of creation of a "critical cluster" fractal spanning through the sample which in turn is proportional to conducting component concentration $\sim x^{\alpha}$.

In our case the infinite cluster is created in a composite sample from the beginning just due to modification of PU with PANI–HCl and high enough concentration of the latter. Deformation of the composite sample can be considered as a process opposite to formation of a percolation network under increase of conductive filler concentration (just above the percolation threshold). One can therefore expect $\varepsilon^{-\alpha}$ power law dependence of the conductivity on strain during mechanical deformation.

The system under study is expected to be a fractal due to a polymer nature of the PU matrix and peculiarities of chemical synthesis of the conductive composites [18,22]. Therefore, one should anticipate an electrical response, which is a combination of dimension-driven variation of the current (geometrical consideration) and concentration-driven (fractal-type) contribution from interruption of the conductive network during deformation. Both factors depend on the dimensionality of the imbedding (Euclidian) space: 2D (surface-modified) or 3D (volume-modified) samples in our case. The influence of deformation is similar to that of the concentration of the conductive particles just acting in the opposite direction (i.e., while increase of the concentration enhances the electrical conductivity, increase of uniaxial tensile deformation would decrease it). The net dependence of the current (I) passing through the fractal network conductor on the applied tensile strain is then described as:

$$I \sim \varepsilon^{-d}\varepsilon^{D_\mathrm{f}} \sim \varepsilon^{b}$$

where d, D_f, and b are dimensionality of the imbedding space, fractal dimension of the network and experimentally measured exponent of electrical current versus deformation dependence ($b = D_\mathrm{f} - d$), respectively. Theoretical predictions show that the exponent α is an indicator of a degree of interaction between the components of the composite and dimensionality of the "imbedding space" (Euclidian space) and can be related to the fractal dimension of the material, D_f:

$$\alpha = d - D_\mathrm{f} \quad \text{and therefore } \alpha = -b$$

For instance 3D network formed by non-interacting clusters of particles is characterized with $D_\mathrm{f} = 1.78$ while strongly interacting particles (chemically interacting clusters) are characterized with $D_\mathrm{f} = 2.04$ [23]. Such exponents can be predicted both with renormalization analysis of the fractal networks and with computer simulations of the fractal systems [20].

Table 1 summarizes theoretical predictions for exponent α and fractal dimension D_f based on different models [22] and compares them with our experimental results for PU/PANI–HCl composites. One-side surface-modified samples and volume-modified samples are two extreme cases in our set of samples and obviously should be described with theoretical models of different dimensionality of the percolation network: two-dimensional (2D) one for the former and three-dimensional (3D) one for the latter.

As can be seen from Table 1 our results for one-side modified samples are in good correspondence with the Brownian model in assumption of 2D network. Volume-modified samples are in concurrence with a Chemical model for 3D network, which considers strong interactions between clusters. A more complex case corresponds to double-side modified samples. Comparison with theoretical predictions derived for different strength of interaction between clusters and different dimensionality of the network allows concluding that this intermediate case shows similarity to the Brownian 3D network model (i.e., volume-distributed clusters with no or weak interactions between them). The observed small discrepancy in theoretical and experimental exponents (Table 1) can be attributed to a non-equilibrium character of the percolation network deformation. Electrical conductivity is not completely recoverable under loading–unloading cycles (Fig. 4), which is probably due to micro-heterogeneity of PU/PANI–HCl composite. Specifically, deformation of the PU matrix interrupts the percolation network formed by inclusion phase of PANI–HCl. This means that some places previously occupied by PANI–HCl clusters become micro-pores ("free volume places") and may be filled with polymer segments or PANI–HCl clusters during mechanical unloading. The probability of their complete healing (i.e., penetration of the same PANI–HCl clusters (or its segments) back into previously occupied places) is negligible considering very small content of the PANI phase in the composite. Moreover, intermolecular interactions will promote diffusion of flexible and chemically similar chain segments of the elastomer matrix rather than reversion of dissimilar and hard fragments of PANI–HCl into these vacant "free volume places" of the PU matrix.

Deformation of the percolation network can be seen under optical microscope. Fig. 6 shows variation of the morphology under tensile deformation for a one-side modified PU/PANI (7% aniline) sample as an example. PANI has a rich green color and appears darker on the images in comparison to optically transparent PU elastomer. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.) Pristine sample is almost featureless due to homogeneous distribution of PANI on the surface of PU elastomer. Deformation of the sample causes enhancement of the optical contrast due to interruption of the conductive layer with insulating PU micro-regions. The latter appear

Table 1
Theoretical and experimental scaling exponents and fractal dimensions of the system depending on the dimensionality of embedding space, d or type of PU matrix modification with PANI

Theoretical predictions [21]			Experimental results		
Version of theoretical model	α	D_f	Type of modification	$-b$	D_f
2D (Brownian model ∼ no interactions)	0.56	1.44	One-side	0.52 ± 0.05	1.48 ± 0.05 ($d = 2$)
2D (Chemical Model ∼ strong interactions)	0.45	1.55	Double-side	1.15 ± 0.12	0.85 ± 0.12 ($d = 2$)
3D (Brownian Model ∼ no interactions)	1.22	1.78			1.85 ± 0.12 ($d = 3$)
3D (Chemical Model ∼ strong interactions)	0.96	2.04	Volume	1.01 ± 0.12	1.99 ± 0.12 ($d = 3$)

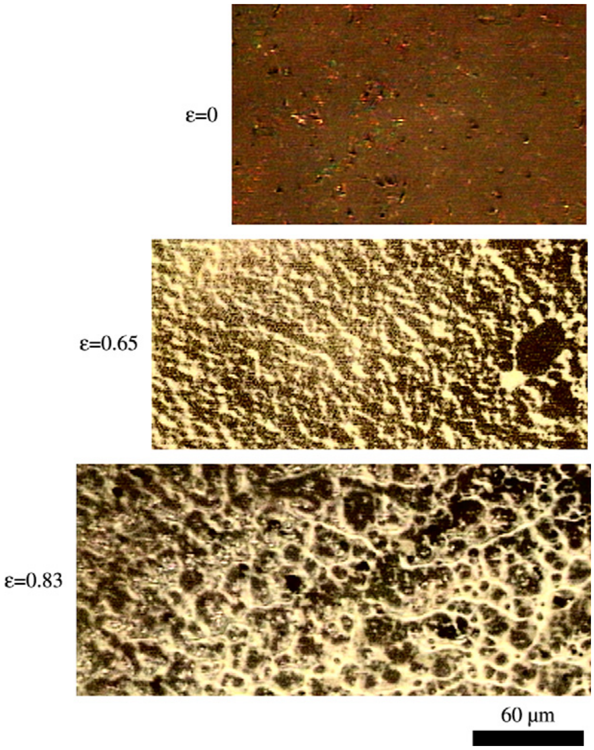

Fig. 6. Top view optical microscopic images of one-side modified PU/PANI–HCl (7% aniline) sample under mechanical deformation (the corresponding strain shown for each picture). Undeformed sample (top) looks dark and featureless giving evidence of uniform surface modification of PU elastomer matrix (optically transparent) with a non-transparent PANI layer. Deformation causes interruption of the conductive PANI network (middle and bottom images) and drastic enhancement of the contrast. The middle image corresponds to ~10 times reduction of electrical conductivity in comparison to a pristine sample, while the bottom image corresponds to its practically complete interruption.

bright on the images due to optical transparency of the PU elastomer. At $\varepsilon = 0.65$ PANI regions are still inter-connected and the sample looks electrically percolated, however, its electrical conductivity is about 10 times lower in comparison to the pristine sample. Further deformation ($\varepsilon = 0.83$) leads to interruption of the conductive paths (dark regions of PANI appear to be not connected to each other). Simultaneously, electrical conductivity of the sample falls to less than 1% of its original value.

Interestingly, PU/PANI–HCl surface-modified composites exhibit nonlinear current–voltage characteristics similar to ones previously reported for PVDF/PANI system [12]. In both systems the effect is observed only for the case of surface modification and reflects an anisotropic electrical response of the matrix to the external electrical field. Both PVDF and PU belong to ferroelectric polymer materials [22]. Application of the external electrical field causes electrical polarization of the surface of the host polymer film, which opposes the external field and therefore ''slows down'' the electrical charge carriers in the PANI layer. The situation is different for volume-modified sample where due to isotropic distribution of the conductive filler within the matrix such polarization is acting symmetrically in all directions.

4. Conclusions

Electrical properties of the PU/PANI–HCl film composites strongly depend on their preparation method. Specifically, the chemical polymerization of aniline in the PU film matrix resulted in the formation of the surface-modified composites with the nonlinear electrical behavior. Unlike this, simple solution mixing of the PU and PANI–HCl followed by casting allowed formation of the volume-modified film composites exhibiting smaller conductivity and linear current–voltage characteristics. Due to combination of highly elastic mechanical properties of the elastomer matrix and considerable conductivity level the developed composite material appeared to be attractive for sensing mechanical stresses. This was demonstrated by changes of electrical behavior and conductivity of tested composites under external mechanical stress (elongation). The observed decrease in conductivity was interpreted in terms of deformation of a fractal percolation network formed in the system during its preparation. Conductive paths are gradually disrupted during increasing mechanical elongation due to increasing the distance between clusters of the conductive component (PANI) and ultimately complete destruction of the conductive network. In traditional consideration, increase of conductive component content gives a higher probability of contact between small conductive clusters and ultimately formation of an infinite cluster necessary for conduction (percolation). In our case, mechanical extension of electrically conductive composite (which is initially a conductive network system above the percolation threshold) results in larger distances between conductive component clusters and thus decreases the electrical conductivity. The fractal network disruption is shown to depend strongly on dimensionality of the network and the strength of interaction between building components of composite.

We believe that the observed variation of the electrical properties of the developed PU/PANI–HCl composites with the deformation may be used for construction of amperometric stress sensors or electrically driven micro-actuators. Furthermore, the discovered nonlinearity of electrical properties of the surface-modified (asymmetric) PU/PANI–HCl samples together with well-known chemical versatility of polyurethanes opens their additional applications in all-plastic electronics or active elements of gas or bio-sensors [23].

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