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Effects of surface and volume modification of poly(vinylidene fluoride) by polyaniline on the structure and electrical properties of their composites

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Abstract

The structure and electrical properties of polyaniline (PANI) modified poly(vinylidene fluoride) (PVDF) films have been studied depending on the type of modification (surface or volume) and the type of dopant (HCl or dodecylbenzenesulfonic acid). The structure was studied with differential scanning calorimetry, atomic force microscopy and Raman spectroscopy (including the surface enhanced mode—SERS) techniques. Surface modification of PVDF with PANI creates a two-dimensional (2D) conductive network on the surface of PVDF films with the thickness of approximately 8 μm. The network is characterized with non-linear current voltage (*I*–*V*) characteristics and enhanced conductivity at elevated temperatures (up to 160 °C), which is opposite to volume modified samples behaviour. Conductivity of the composite films varies in the range of 10^{-8} to 10^{-3} S/cm depending on the preparation conditions. The observed non-linear conductivity is explained by formation of the surface conductive network of PANI alternated with β-crystalline PVDF microdomains.

Keywords: PVDF–PANI composites; Structure; Non-linear electrical properties

1. Introduction

Considerable interest in intrinsically conducting polymers (ICP) is due to their unique set of electrical, electrochemical and optical properties, with high prospects for practical applications in various electronic devices [1,2]. However, problems such as low stability of physical properties, poor processability and relatively high cost of ICP need to be solved before a large scale practical application is possible. There are several approaches to solve these problems which are based either on optimizing the ICP to a special state for its possible application [3] or formation of blends or composites with other organic or inorganic polymers. In the latter case, the necessary complementary properties like mechanical, chemical, and long term stability can be achieved without a compromise on the electrical characteristics [4,5].

Among the known conductive polymers, probably, polyaniline (PANI) has the best quality to cost ratio in combination with reasonable time stability and processability. Composites of PANI with other common polymers possess much higher mechanical characteristics and chemical stability in comparison to pure PANI [6]. Moreover, some other properties such as optical transparency and electrical conductivity can be simultaneously improved with such blending [6,7]. Furthermore, a synergistic enhancement of useful properties and development of new physical characteristics not typical for the initial components can be expected in some cases as a result of specific interactions between the components. For example, Kaiser et al. [7] reported a higher conductivity of PANI–poly(methyl methacrylate) composites as compared with pure PANI, which was ascribed to the reduction of the height of energy barriers near conductive particles of PANI under the assumption that conductivity is mainly due to hopping charges in such composites. On doping PANI macrochains possess positive electrical charges, which should be taken into account in composites with other dielectric polymers to produce considerable local mechanical stresses, local electrical fields and variation of the dielectric characteristics. This effect was found in PANI–poly(ethylene terephthalate) (PET) composites formed via polymerization of aniline in a thin surface layer of PET matrix [8]. While the surface of undoped (i.e. uncharged) form of this composite and that of a pristine PET are relatively flat, doping brings a remarkable enhancement of the surface roughness as measured from atomic force microscopy (AFM)

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images. The surface roughness of the composite films was also found to be sensitive to the size of the dopant. The films with $HClO_4$ (bigger dopant size) had higher roughness compared to the films doped with HCl. These changes also effected the dielectric relaxation spectra of the composites [8].

Polarization of PANI molecules in electrical field (electrical poling) also can have a considerable influence on the properties of composites involving PANI with other dielectric polymers. Radhakrishnan and Kar, indeed, observed enhancement of piezo-sensitive conductivity of poly(vinylidene fluoride) (PVDF) when PANI was doped with HCl up to 15 wt% followed by electrical poling procedure [9]. It is interesting to note that an inorganic dopant, HCl, caused much higher enhancement of piezo-sensitivity in comparison to dodecylbenzenesulfonic acid (DBSA) a plasticizing organic dopant. This effect is most probably due to the fact that PANI–HCl is incompatible with PVDF and, therefore, forms small conductive particles distributed in the PVDF matrix. Mechanical and electrical contact between these particles is improved by compression producing low contact resistivity [9]. On contrary, PANI–DBSA system is more compatible with PVDF that produces molecular level (or at least nanometer level) distribution of the components with formation of a homogeneous composite film [6,9]. This structural organization by definition makes more efficient electrical contact between PANI and DBSA clusters. The same effect leads to a reduction of the percolation threshold of the PANI–DBSA/PVDF composite. As a result of such behavior the compression has no influence on electrical conductivity of such composites [9]. Considering arguments given by Radhakrishnan and Kar [9] to explain the concentration and piezo-electric dependence of the PANI–HCl/-PVDF resistivity a linear current-voltage (*I–V*) characteristics should be expected. This has been actually revealed by experimental observations when no electrical poling was applied [9]. The appearance of a hysteresis on *I–V* loading-unloading curves and their weak non-linear character after electrical poling gives an evidence of the importance of space charge limited conduction (SCLC) for the system under study [9]. Despite the weakness of the observed non-linearity of electrical current, the effect highlights the most critical factors responsible for its appearance (such as the nature and concentration of the doping agent, application of macroscopical electrical poling, etc.) [9]. Such a consideration in conjunction with a remarkable variability in physical properties of PANI (which depend on the conditions of composite formation and environment [6–8]) provides routes for an enhancement effects and practical application in electrical devices. With these prospects in mind we aimed to study a possibility of non-linear electrical characteristics on demand in PVDF–PANI composites. The main strategy applied in our paper considers a special case of surface modification (used earlier for the PANI–PET [8,10]) of PVDF films instead of the known volume modification [9]. The advantages of the approach in creation of nanocomposites with special electrical properties (non-linear *I–V* characteristics) suitable for microelectronics and sensor applications will be addressed.

2. Experimental

2.1. Sample preparation

Six PVDF–PANI samples with different type of doping and modification of PVDF have been studied (Table 1). Pure PVDF film (~100 μm thickness) was also prepared by compression molding of PVDF Kynar 1000 powder (Atofina) at 200 °C and was used for comparison. PVDF–PANI-1 surface modified sample was prepared as described earlier [10], by swelling extruded commercial Kynar PVDF film (Atofina) in aniline up

Table 1
General description of samples under investigation

Sample	Type of modification	Conditions of film preparation	Dopant	Initial aniline concentration in polymerization systems (wt%)	Expected undoped PANI loading (wt%)
PVDF pure	–	Compression molding PVDF Kynar 1000 powder at 200 °C	–	–	–
PVDF–PANI-1	Surface	Aniline polymerization inside surface layer of the extruded commercial PVDF film (Kynar)	HCl	4.3	~1.7–2.1[a]
PVDF–PANI-2	Volume	Aniline-DBSA salt polymerization in Kynar 1000 latex medium followed by separation of PVDF/PANI–DBSA powder and its compression molding at 200 °C	DBSA	1.8	1.6
PVDF–PANI-3	Surface	Similar to PVDF–PANI-1 but the parent PVDF film was prepared by compression molding PVDF Kynar 1000 powder at 200 °C	HCl	3.38	~1.4–1.7[a]
PVDF–PANI-4	Surface	Similar to PVDF–PANI-3 but the compression molding at 175 °C	HCl	3.67	~1.5–1.8[a]
PVDF–PANI-5	Volume	By re-doping of PVDF/PANI–DBSA powder to PVDF/PANI–HCl and its compression molding at 200 °C	HCl	2.1	1.9
PVDF–PANI-6	Surface	Similar to PVDF–PANI-3 but dopant HCl was replaced by redoping procedure with DBSA	DBSA	3.63	~1.5–1.8[a]

For some additional details see sample preparation part.

[a] A rough estimation based on the assumption of 40–50% yield of aniline polymerization within the thin subsurface layer of the PVDF matrix films.

to 4.3 wt% loading followed by contact of its one side with the oxidant chlorine water solution for 35 min. Then extraction of the aniline residues and by-products was carried out using *n*-hexane in Soxlet apparatus for 5 h followed by dynamic vacuum drying. This procedure allowed obtaining a new transparent two layer PVDF/PANI–HCl composite films with pronounced surface conductivity. The first layer of these materials consisted of PANI doped with HCl, which was distributed inside a thin surface/subsurface layer of the PVDF matrix. It is cohesively connected with a second virtually PANI-free PVDF layer constituting the majority of the film thickness (the matrix).

The PVDF–PANI-2 film with volume modification was prepared by completely different technology. According to [11], aniline was polymerized in a medium of PVDF Kynar 1000 latex in a presence of dodecylbenzenesulfonic acid (DBSA). The final PVDF/PANI–DBSA composite powder was compression molded at 200 °C, which resulted in PVDF–PANI-2 composite film containing PANI doped with DBSA.

The PVDF/PANI–DBSA composite powder was also used as the starting material to prepare the PVDF/PANI–HCl powder composite. For this the former one was undoped by known procedure in 5 wt% NH_3 water solution for 20 h followed by a new doping in 0.2 M HCl water solution for 20 h followed by separation and drying procedures. The prepared PVDF/PANI–HCl powder was compression molded at 200 °C. The resulting PVDF–PANI-5 composite film was volume modified by PANI doped with HCl. This film was prepared for comparison with other surface modified samples also doped with HCl and for evaluation of the effect of the dopant size and nature on the PVDF–PANI composite properties.

The next set of the surface modified samples (PVDF–PANI-3 and PVDF–PANI-4) was prepared from PVDF films compression molded from the Kynar 1000 (Atofina) powder at 200 and 175 °C correspondingly. Following this the PVDF films were treated similar to that of the above PVDF–PANI-1 film, but with aniline loading of 3.38 and 3.67 wt% correspondingly. Therefore, these three surface modified samples were similar except for the pristine PVDF film preparation and the amount of PANI loading.

Finally, PVDF–PANI-6 surface modified sample (doped by DBSA) was prepared similar to PVDF–PANI-3 but with aniline loading to 3.63 wt%. After the preparation of PVDF–PANI–HCl film HCl was removed by dedoping in 5 wt% NH_3 water solution for 24 h. This was followed by a new doping in 1 M DBSA water solution for 10 days at 40 °C until a constant value of conductivity was achieved. This procedure was followed by separation and drying procedures.

The thickness of the modified surface layer was measured in a special experiment for PVDF–PANI-1 and PVDF–PANI-4 samples. For this purpose the composite films were embedded into epoxy glue, then cut with a sharp knife and produced cross-sections were studied under optical microscope (2000× magnification). The modified region with a deep-green color could be easily recognized in comparison to the colorless PVDF matrix. The thickness of the PVDF modified with PANI was measured to be 6 ± 2 μm in case of PVDF–PANI-1 and 8 ± 2 μm in case of PVDF–PANI-4.

2.2. *Differential scanning calorimetry*

The equipment used in this case was MT-differential scanning calorimeter (DSC). The scan conditions were as follows. The first heating cycle was a ramp up by 20 °C/min to 200 °C, then ramp down to 30 °C again at 20 °C/min. The second heating cycle was a ramp up by 20 °C/min to 200 °C, then ramp down to 30 °C again at 20 °C/min. Crystallinity was calculated using the melting peaks. The formula used for this was:

$$\text{Crystallinity} = \frac{\text{area under melting peak}}{\Delta H_\mathrm{f} \text{ of PVDF}}$$

where ΔH_f is the enthalpy of melting.

2.3. *Raman spectroscopy*

The Raman spectra of the samples were obtained by Solution 633 (Detection Limit Inc.) spectrometer. The excitation source was a He–Ne laser with a wavelength of 632.8 nm (1.96 eV). Surface enhanced Raman spectroscopy (SERS) [12], which is a special technique of Raman Spectroscopy, provides greatly enhanced Raman signal from Raman-active analyte that has been adsorbed onto specially prepared metal surfaces. In our experiments silver was thermally evaporated in a controlled way on to the polymer film in vacuum so that the silver did not form a complete film but was deposited as islands on the surface. The silver evaporated samples were used to obtain the Raman spectrum.

2.4. *Conductivity measurements*

For in-plane *I*–*V* measurements a pair of silver electrodes was formed using shadow mask technique. The electrodes were deposited by thermally evaporating silver in a vacuum chamber and by using 250 μm diameter wire as a mask. Silver wire was used as the electrode material to be deposited onto the samples. After the deposition was completed, the wire mask was removed and the gap was measured to be 200 μm. For across the thickness conductivity measurements, special masks were made so that a selected area on the sample surface would be exposed to the silver deposition. This was repeated for both sides of the sample so that the area of electrode overlap could be easily measured. The Keithley 2400 multimeter operated from PC equipped with a virtual instrument developed in Labview™ language was used to measure electrical characteristics of both in-plane and across the thickness conductivity. The thicknesses of the samples were measured by two independent techniques. Firstly, the difference in the *Z* position of the AFM probe when in contact with the film and the substrate on which the film was attached, secondly, with the help of a Vernier calipers. Electrical conductivity measurements were also performed at elevated temperatures using digitally controlled oven. The readings were taken at 20 °C temperature increments, between 30 and 160 °C. The samples were placed in an oven to expose them to the incremental temperature changes, and *I–V* response was collected in the same manner as described above.

2.5. Atomic force microscopy

The samples were studied with atomic force microscopy (AFM) technique using an Autoprobe CP (Thermo Microscopes Inc.) machine in contact and non-contact modes scanning. The scans were performed on various locations on the samples and were done at different scan sizes. The most informative scale for AFM study was found to be 2 μm×2 μm and 5 μm×5 μm for the majority of samples. These scans were performed on both the modified and unmodified side of the samples. In the case of PVDF pure, and PVDF–PANI-2, these samples were only scanned on one side as the volume modification and the pure compressed samples were expected to have similar surface morphology. To see quantitatively if there was a difference between the two sides scanned, the root mean square (RMS) roughness values were calculated using the AFM images. All roughness measurements were done for the same scan size of 5 μm×5 μm.

3. Experimental results

3.1. DSC crystallinity

These measurements were mainly made to see the effect of modification by PANI on the crystallinity of the samples. From the results seen in Table 2, there does not seem to be significant change to the crystallinity of any of the samples. Both the surface and the volume-modified samples are not significantly different from the pure PVDF one. The only exception to this is the PVDF–PANI-1, which showed the highest crystallinity of 52.7% probably due to the fact that its parent PVDF film was produced by extrusion. The only other information that may be deduced from the data is that the volume modified sample PVDF–PANI-2 had the overall lowest crystallinity possibly due to the presence of plasticizing dopant DBSA, which is able to effect formation of crystalline regions in the composite under compression molding conditions. Melting transition temperature varies in the range of 166–169 °C. As reported before [12] the melting transition of PVDF depends strongly on the type of PVDF crystalline phase. β-phase, which is more common for melt proessed PVDF, is characterized with higher T_m (177 °C) in comparison to α-PVDF ($T_m = 171$ °C) [12].

In our case the crystalline nature is additionally masked with deposition of PANI and its doping with low molecular mass compounds. Both species may act as plasticizers efficiently depressing T_m of PVDF. However, we can conclude that α-phase is more probable state of PVDF judging on the observed value for the pure PVDF sample ($T_m = 168$ °C).

Table 2
DSC crystallinity of PVDF-based composite samples

Sample	Average crystallinity (%)
PVDF pure	45.3
PVDF–PANI-1	52.7
PVDF–PANI-2	43.9
PVDF–PANI-3	47.2
PVDF–PANI-4	46.3

3.2. Raman spectroscopy

Raman spectroscopy studies were done to prove the presence and the structural state of the polymer components at the composites surface depending on the preparation conditions. The spectra were first obtained for 'as is' samples. These spectra were characterized with two weak peaks at 607 and 823 cm^{-1}. Therefore, surface enhanced Raman spectroscopy technique [13] was employed to enhance the intensity of the peaks observed. To realize this an ultra-thin layer of silver was deposited on the surface of the samples.

Fig. 1(a) shows a comparison of a fingerprint region of the Raman spectrum recorded for PVDF–PANI-1 with those recorded for pure PANI. The spectrum shows the presence of both the parent polymer (PVDF) and the modification (PANI). The set of peaks representative of PANI, can be seen in spectrum obtained from composite also at ∼810 and 1441 cm^{-1}. Fig. 1(b) shows position of characteristic PVDF Raman bands, which allow distinguishing between different PVDF crystalline modifications [14]. It is interesting to note that these bands at 800–840 cm^{-1} look differently for the different samples despite the superposition of the PANI and PVDF bands. Specifically, pure PVDF sample is characterized with a strong peak at 800 cm^{-1} (α-phase) and much smaller peak at 830 cm^{-1} (β-phase). Naturally, PANI masks these

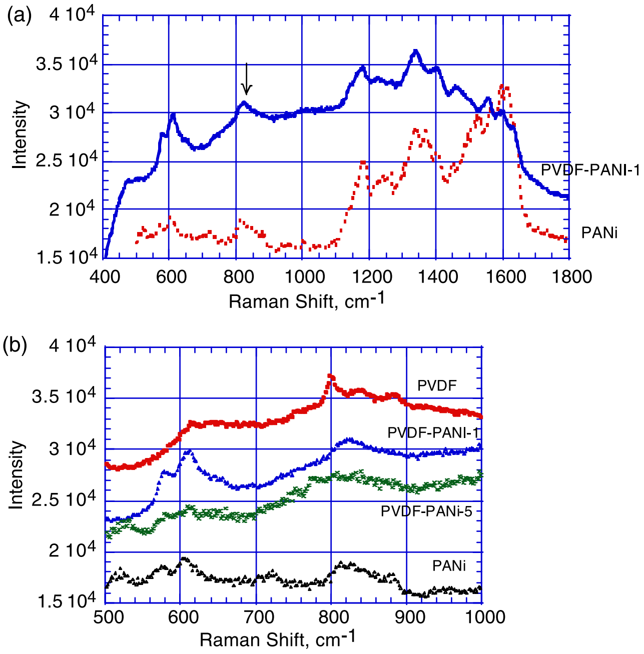

Fig. 1. (a) Raman spectra of PVDF–PANI-1 compared to those of pure PANI. An arrow shows the position of a characteristic band of PVDF, which can be used for identification of the type of crystalline phase in it; (b) crystalline phase sensitive Raman band of PVDF near 800 cm^{-1} for different PVDF–PANI composites under study.

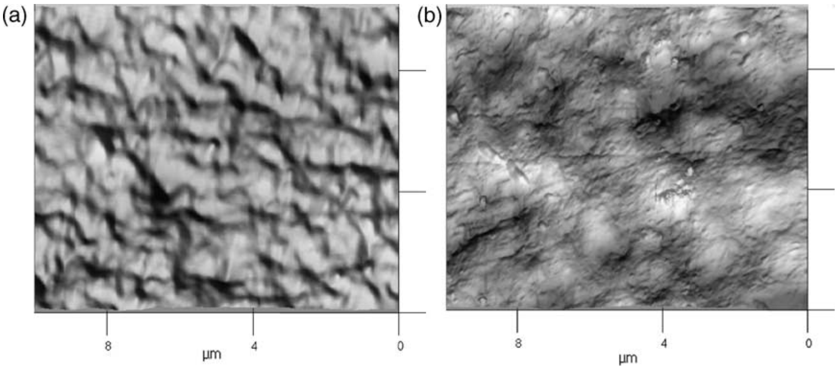

Fig. 2. AFM images of sample PVDF–PANI-1: unmodified PVDF surface (left) and surface modified with PANI (right). Reduction of the PVDF surface roughness as a result of its modification with PANI can be clearly seen.

phase bands but in this case a small difference can be observed. Specifically, for PVDF–PANI-5 (volume modified sample) the peak of α-phase (800 cm^{-1}) appears to be decreased to the level of the β-phase peak (830 cm^{-1}). Furthermore, in the case of PVDF–PANI-1 (surface-modified sample) the band of α-phase obviously disappeared and only the superposition of peak corresponding to β-phase with the PANI band is observed. It should be specified at this point that SERS method applied in this case is highly sensitive to the surface structure (∼100 nm) and not sensitive to the bulk material below the surface. Therefore, one can speculate that both PANI and PVDF are present within a very thin 'skin' layer on the surface of the composites and that surface modification changes the type of PVDF crystalline modification from mainly α-phase (typical for the bulk material) to the β-phase.

3.3. AFM and roughness

Atomic force microscopy scans were performed on the samples both in contact and non-contact mode. One of the objectives was to observe the surface morphology difference between the volume and the surface modified (extruded commercial and compression molded films) samples. Fig. 2 shows comparison of a pristine and PANI modified side of PVDF–PANI-1 sample. Relatively rough crystalline like morphology of unmodified surface is characterized with domains of an average size of ∼200–400 nm. Modification of the surface with PANI 'masks' this original roughness and brings a new morphology with finer domains (less than 100 nm in size), which often appear as chains or 2D network of lines. As one can see from Table 3, the PVDF–PANI-1 sample made by surface modification of the extruded commercial film (being a matrix), displays the least roughness on the both sides as compared with the other samples and decrease of the surface roughness after formation of PANI at the surface and inside subsurface layer of the matrix. Similar difference between modified and unmodified sides is observed for the compression-molded sample PVDF–PANI-4. However, the roughness of the compression-molded samples (both the control one and PVDF–PANI-2) is much higher probably due to technological reasons. This is quantitatively seen in Table 3 where the roughness for pure PVDF, being in the range of 20–40 nm depends on the type of modification, is higher (38 nm) for the volume-modified PVDF–PANI-2 and drops to ∼10 nm for the modified side of the surface modified samples. Moreover, practically in all cases modification of PVDF with PANI effectively reduces the surface roughness of the samples (Table 3). This is true to a lesser extent in the volume-modified samples. However, the difference is much more noticeable when both the modified and unmodified sides PVDF–PANI-4 are analysed (Table 3).

Fig. 3 displays influence of two basic types of modification (volume or surface one) on the morphology of PVDF samples. Generally surface-modified samples are characterized with smaller roughness in comparison to volume-modified analogs. In both cases development of more porous structure is observed. But the surface modification is characterized with generally finer morphological features. Also, as can be seen from Fig. 3(b) surface modification produces some network-like morphology on the surface.

Overall, the AFM and the roughness measurements show that the PANI plays a critical role in changing the surface morphology of the surface modified samples. We can deduce that the surface modification of the samples by PANI results in formation of the PANI deposits in the crevices or pits of PVDF, thus smoothing out the sample surface and reducing the roughness. At the same time, the appearance of this separate phase of PANI does not exclude the PANI formation in a thin subsurface layer of the PVDF matrix, as it was observed in PET matrix [8,10] earlier.

Naturally, there is no difference in roughness between both sides of the volume modified sample PVDF–PANI-2 obtained

Table 3
Roughness of PVDF-based films (AFM data)

Sample	Roughness (5 μm×5 μm)	
	Unmodified side (nm)	Modified side (nm)
PVDF pure	24	
PVDF–PANI-1	23	13
PVDF–PANI-2		38
PVDF–PANI-3	21	9.4
PVDF–PANI-4	31	10
PVDF–PANI-5		9.3
PVDF–PANI-6	11	10.5

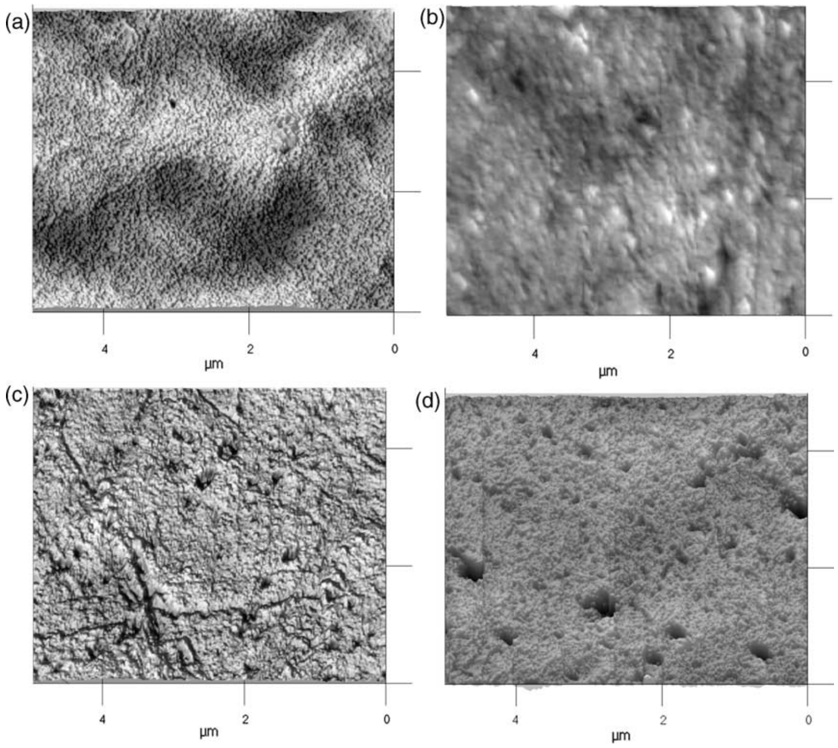

Fig. 3. AFM images of pure PVDF (a), PVDF–PANI-3 (b), PVDF–PANI-4 (c) and PVDF–PANI-5 (d).

after compression molding of the previously prepared PVDF/PANI–DBSA powder (discussed in Section 2). In this case, unlike the surface modification, the roughness is determined mainly by the compression molding conditions and plasticity of the PVDF–PANI-2 composite material. The latter parameter causes slightly less roughness of this sample compared to the pure PVDF film sample (Table 3) due to the presence of plasticizing dopant DBSA.

3.4. *I–V* characteristics and conductivity

There were basically two kinds of *I–V* curves obtained for the samples under investigation for in-plane conductivity measurements. One was a linear current response to the applied voltage, and the other one was a non-linear response (Fig. 4). Specifically, pure PVDF and volume-modified samples (PVDF–PANI-2 and PVDF–PANI-5) are the only samples that displayed linear *I–V* characteristics. Unlike this, all surface modified samples exhibited a non-linear *I–V* response that displayed a pronounced difference in conductivity behavior. In these samples PANI was localized inside the surface and subsurface layer as compared to the volume distributed PANI. The difference in *I–V* characteristics stems probably from different conditions and distributions of PANI in the thin surface layers of both kinds of the samples. In volume-modified samples the conductive component (PANI) is relatively uniformly distributed through the whole thickness of the sample. In case of surface conductivity measurements, current can flow mainly through the top layer limiting the role of volume-distributed PANI in their conductivity behavior (PVDF–PANI-2 and PVDF–PANI-5, compare Tables 4 and 5). This allows assumption that volume-distributed PANI is playing very little role in the conductivity of either of these

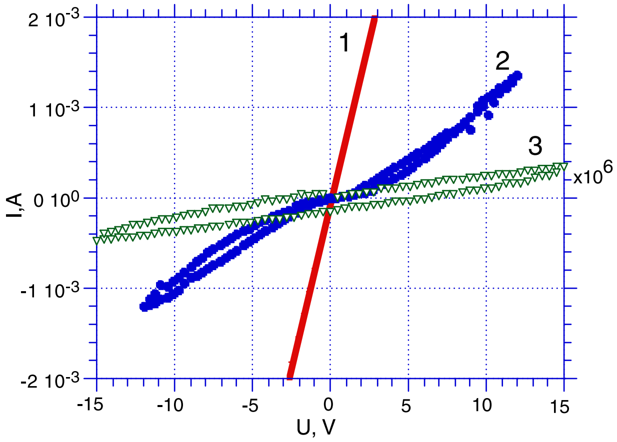

Fig. 4. *I–V* curves of volume modified sample PVDF–PANI-2 (1), surface modified sample PVDF–PANI-3 (2) and unmodified PVDF sample (3). Actual current is multiplied by factor 10^6 in the latter case. Non-linear character of the curves appears in case of the surface modification only.

Table 4
In plane conductivity of PVDF-based composite samples

Sample name	Conductivity (S/cm)
PVDF pure	4.4×10^{-9}
PVDF–PANI-1	2.35×10^{-3}
PVDF–PANI-2	5.9×10^{-3}
PVDF–PANI-3	6.0×10^{-3}
PVDF–PANI-4	1.8×10^{-3}
PVDF–PANI-5	3.7×10^{-8}
PVDF–PANI-6	1.0×10^{-6}

Table 5
Through thickness conductivity of volume-modified samples

Sample name	Conductivity (S/cm)
PVDF pure	10^{-12}
PVDF–PANI-2	1.3×10^{-4}
PVDF–PANI-3	10^{-6}
PVDF–PANI-5	10^{-10}

samples, and the linearity of their *I–V* curves (Fig. 4) is determined by the PANI distribution in their surface layers. In turn, the non-linear course of *I–V* curves of the surface modified samples containing conductive PANI component only within 6–8 μm thickness layer testifies the PANI distribution and may be its condition caused the maximized PANI effect in this case.

Important features of electrical behaviour of volume modified and surface modified samples can be also confirmed with conductivity measurements (Tables 4 and 5). Specifically, significant variation in electrical characteristics observed cannot be explained with a variation of their PANI content alone but is strongly effected by technology of preparation and the nature of dopant. For example, volume modified PVDF–PANI-2 sample has five orders of magnitude higher in-plane conductivity than volume-modified PVDF–PANI-5 while the content of PANI is almost equal for both materials. In case of the samples prepared by compression molding of PANI–PVDF powders at 200 °C (Table 1, PVDF–PANI-5), a volatile inorganic dopant (HCl) can be only partially removed during the film formation. Unlike this, a large organic dopant DBSA remains in the PVDF–PANI-2 sample. This difference can strongly affect both the degree of PANI doping and the quality of the percolation network being formed in the final composite film [6].

For all surface modified samples prepared under similar polymerization conditions (Table 1) one should expect close yields of PANI. With an assumption of ∼40–50% of the PANI yield within the surface (modified) layer the total PANI based content per sample can be estimated as ∼1.4–2 wt%, which is close to the corresponding value of the volume modified samples (Table 1). For the samples PVDF–PANI-1, 3 and 4 doped with inorganic dopant HCl, this results in good in-plane conductivity of the order of 10^{-3} S/cm. However, in case of PVDF–PANI-3 sample the conductivity is about three times higher as compared to PVDF–PANI-1 and 4. This testifies some advantage of PVDF–PANI-3 preparation conditions (compression molding of PVDF film at 200 °C).

The redoping procedure and replacing small inorganic dopant HCl from such sample as PVDF–PANI-3 by large organic dopant DBSA to produce PVDF–PANI-6 results in dropping conductivity by three orders of magnitude (Table 4). This case demonstrates a problem in the diffusion limited redoping of PANI within the solid matrix by large size dopant DBSA that explains much lower conductivity of PVDF–PANI-6 sample. Naturally, the replacment of relatively small HCl molecules by much larger DBSA ones in the solid matrix cannot be very efficient.

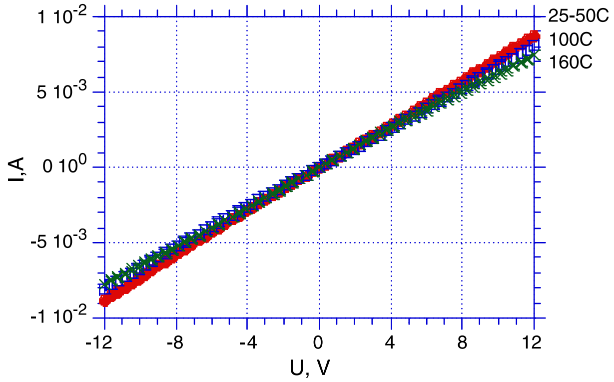

Fig. 5. Change of *I–V* characteristics with increasing temperature for the volume modified sample PVDF–PANI-2 (temperature is shown to the right from appropriate curve). Conductivity of the volume modified sample slightly decreased as the temperature was increased from 30 to 160 °C.

In-plane conductivity levels match with non-linearity of *I–V* responses of the surface modified samples. Specifically, the highest non-linearity is in case of PVDF–PANI-3 and the lowest one is in case of PVDF–PANI-6 sample.

The observed in-plane conductivity values are mirrored when conductivities are measured across the sample thickness (Table 5). In this setup, the current is forced through the entire thickness of the sample. Here, only the volume-modified sample PVDF–PANI-2 (dopant DBSA) shows high enough conductivity values. The pure PVDF, PVDF–PANI-5 (dopant HCl) and the surface modified sample PVDF–PANI-3 conductivities are much smaller. The presence of PANI coating on one side of the film still makes some contribution to the overall conductivity. For the PVDF–PANI-3 sample across the film thickness conductivity is many fold higher (10^{-6} S/cm) than that observed for the pure PVDF sample (10^{-12} S/cm) (Table 4). This value corresponds to a series connection of two resistors (one for PVDF–PANI 2D network and one for pure PVDF underneath). The same consideration naturally explains the value of across the film thickness conductivity for all surface modified composites, which is in-between the values for pure PVDF 10^{-12} S/cm and volume modified PVDF 1.3×10^{-4} S/cm.

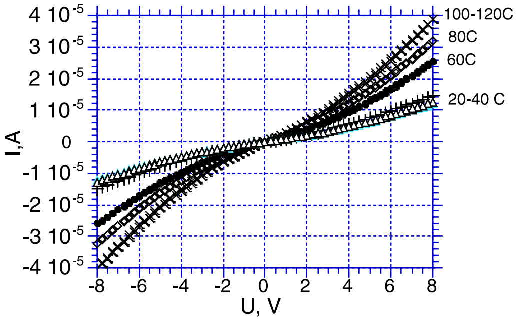

Fig. 6. Change of *I–V* characteristics with increasing temperature for surface modified sample PVDF–PANI-3. Conductivity increased as the temperature was increased still remaining essentially non-linear in the whole range of temperature variation.

3.5. I–V measurements at elevated temperatures

Studying the *I–V* characteristics of both volume and surface modified samples at elevated temperature showed different behaviour. Fig. 5 shows the results obtained for a volume modified sample PVDF–PANI-2. Here the conductivity decreased slightly as the temperature was ramped up from 30 to 160 °C. The opposite case was observed for the surface modified sample PVDF–PANI-3. As shown in Fig. 6, the non-linear behaviour was still there at elevated temperatures, but the conductivity of the sample is seen to increase. Both these tests were done for in-plane conductivity mode.

4. Discussion

As follows from DSC and Raman spectroscopy analysis the surface and volume modified samples differ strongly by the type of PVDF crystalline phase in the surface layer. This suggested both a critical role of PVDF crystalline morphology in the observed variation of electrical conductivity of the surface modified samples and the transformation of the α crystalline form of PVDF to the β crystalline form under the effect of surface-modification of PVDF with PANI. In fact, we met here probably not typical way of the structural evolution in PVDF matrix (compare, e.g. with [13,15]) being the result of its swelling in aniline and of the followed hot extraction procedure in hexane.

The situation is different for the volume-modified samples where the sample surface is represented with both α- and β-phases. The surface of these samples is also enriched with a polar β-phase but to a less extent in comparison to the bulk material. The latter is represented mainly with α-phase. As a consequence, comparison of both the modifications testifies that the surface-modification technique causes a specific structural morphology within the surface layer of the samples PVDF–PANI-1, -3 and -4, namely PANI clusters distributed mainly among β crystallites of PVDF.

Simultaneous consideration of Raman and surface enhanced Raman spectra (SERS) of the surface modified samples gives evidence that PVDF is highly diluted with PANI on the surface. Perhaps, one may expect a nanometer-level ‘skin’ layer coating of PANI on top of PVDF, which in accordance to AFM and SERS data results in clear differences both among and inside the groups of the samples prepared at different conditions. This variation of the surface morphology and the roughness can be clearly seen (Figs. 2 and 3, Table 3): (1) between the control sample, volume-modified sample and surface-modified sample obtained by compression molding at the same temperature 200 °C; (2) between extruded and compression molded surface modified samples both from modified and unmodified sides; (3) between surface modified samples obtained via compression molding at 200 and 175 °C; (4) between samples with a different type of dopant in couples of the volume type modification (PVDF–PANI-2 and 5) or the surface modification (PVDF–PANI-4 and 6).

The quantitative morphological differences are strikingly supplemented with a qualitative difference in the electrical behavior of the volume and surface-modified samples, which is manifested by non-linear *I–V* characteristics of the latter (Fig. 4). Moreover, this effect is drastically enhanced at elevated temperatures, at which the increased conductivity and current relaxation experiments (which will be reported in a separate publication) testified to some ionic conductivity contribution and simultaneously showed the dependence of the latter on the type of modification and doping (Figs. 5 and 6). Nevertheless, comparison of the conductivity of volume modified samples and surface modified samples of the same doping type, conditions of doping and the matrix film formation gives evidence that the type of PVDF modification (2D or 3D) rather than other factors plays the most crucial role in the non-linear behavior observed.

Non-linear *I–V* behavior is observed only for the surface modified samples. In order to explain such unusual phenomenon one has to take into account the following considerations: (a) PVDF is a crystalline polymer with a non-linear polarization behavior (ferroelectric and piezoelectric) at room temperature which depends on α- and β-phases ratio; (b) PVDF also possesses certain ionic conductivity at least at elevated temperatures (at ambient temperature PVDF the main contribution to the conductivity comes from electronic conductivity which is very low $\sim 10^{-12}$–10^{-13} S/cm); (c) finally, pyroelectricity can be observed in this interesting polymer at elevated temperatures [13].

It is natural to suggest that polarization properties of PVDF itself and polarization effects within the subsurface layer of the composites at least partially are responsible for unusual

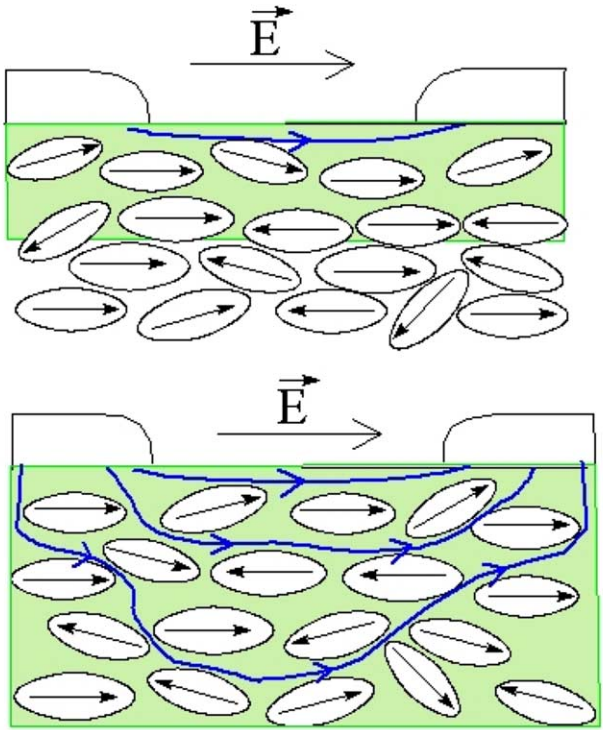

Fig. 7. Percolation of electrical current and polarization of PVDF micro-domains in case of surface modification with PANI and formation of 2D conductive network (top) and volume modification with PANI and formation of 3D conductive network (bottom).

non-linear *I–V* curves. This important contribution from the matrix is confirmed by the fact that no such effect was observed for other dielectric polymers (PS, PET, Nylon [15]).

However, one should not underestimate the role of PANI in the non-linear conductive behavior of the surface modified PVDF–PANI composites. Such composites were prepared by chemical polymerization of aniline placed within the free volume of the PVDF amorphous phase. This results in formation of conductive percolation network of HCl doped PANI distributed among crystallites of the surface layer (thickness ~ 6–8 μm) of the composite film. Therefore, the architecture of conductive PANI network should be dictated by distribution of the free volume in the initial PVDF film.

Based on these considerations, we suggest a model shown in Fig. 7, which may assist understanding the peculiarity of the surface modified PVDF–PANI composites in comparison to the volume modified ones. The surface modified samples are characterized with a 2D network of conducting PANI paths incorporated into the micro-domain structure of PVDF matrix. This network can be clearly seen on the surface of some of the samples (for instance Fig. 3(c)). Under influence of an external electrical field these domains of PVDF are polarized (aligned in the direction of the applied external field). This effect in turn leads to development of a local electrical field, which promotes (accelerates) carriers flow through conductive channels of PANI. The orientation ability of PVDF domains on the surface is less hindered in comparison to the bulk as it is less restricted by neighboring domains. The situation is different for 3D network formed in volume-modified samples. Rotational polarization of ferroelectric domains is restricted and the influence of the surface local field is negligible. At elevated temperatures a simultaneous increase of ionic current contribution and higher mobility and easiness of domain's reorientation leads to enhancement of electrical conductivity. The effect is smaller for PANI doped with DBSA. Here the size of dopant molecules plays the most critical role decreasing significantly the carrier mobility in case of PVDF–PANI-6 in comparison to other surface-modified samples.

5. Conclusions

The whole set of our results demonstrates correlation between the structure (especially surface structure) and electrical characteristics of PVDF–PANI composites. Surface modification of PVDF with PANI creates a 2D conductive network on the surface of PVDF films with the thickness of approximately 8 μm. The network is characterized with non-linear current-voltage characteristics and increased conductivity at elevated temperatures, which is opposite to volume modified samples. Raman spectroscopy revealed surface polymorphism of PVDF and shift to a polar β-phase under influence of PANI preparation process while the overall crystallinity of the matrix remains unchanged (DSC data). Interaction between PANI conductive network and polarized micro-domains of PVDF within ultrathin surface-modified layer and formed by the latter local electrical field may be the major factors controlling the non-linear electrical behavior of the system.

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