Attractive mechanical properties of a lightweight highly sensitive bi layer thermistor: polycarbonate/organic molecular conductor

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Abstract. The paper covers some of the basic mechanical characteristics of a recently developed bi layer thermistor: polycarbonate/(001) oriented layer of organic molecular conductor \( \alpha'-(\text{BEDT-TTF})_2I_xBr_{3-x} \), were BEDT - TTF=bis(ethylenedithio)tetrathiafulvalen. The nano and macro mechanical properties have been studied in order to use this flexible, low cost thermistor in sensing applications by proper way. The nano-mechanical properties of the temperature sensitive semiconducting layer of \( \alpha'-(\text{BEDT-TTF})_2I_xBr_{3-x} \) were tested using nanoindentation method. The value of Young’s modulus in direction being perpendicular to the layer plan was found as \( 9.0 \pm 1.4 \text{ GPa} \). The macro mechanical properties of the thermistor were studied using a 5848 MicroTester. The tensile tests showed that basic mechanical characteristics of the thermistor are close to those of polycarbonate films. This indicates a good mechanical strength of the developed sensor. Therefore, the thermistor can be used in technologies that need to be instrumented with highly robustness lightweight low cost temperature sensors. The paper also reports synthetic details on fabricating temperature sensing e-textile. As the temperature control is becoming more and more important in biomedical technologies like healthcare monitoring, this work strongly contributes on the ongoing research on engineering sensitive conducting materials for biomedical applications.

1. Introduction

Temperature is one of the crucial parameters to be measured in numerous modern technologies. Healthcare, environment and food control, biomedical applications call for low cost, lightweight flexible thermistors for precise and accurate temperature measurements [1-4]. For example, temperature is the most important factor in controlling rate at which food go bad: cod will remain edible for up to 15 days at 0°C, whereas it may be unfit to eat after only six days at 5°C. [5] There is also a particular interest in integrating lightweight conductive sensing materials in human wearable interfaces such as fabrics, since wearable electronics could offer personalized healthcare, security and comfort [1-4]. These fabrics are able to sense and react to environmental conditions.

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Recently, we have suggested a novel approach to engineering lightweight flexible sensors that consists in covering polymeric films with organic molecular conductors \((\text{BEDT-TTF})_2X\), were BEDT-TTF=bis(ethylenedithio)tetrathiafulvalen (figure 1) and \(X\) is trihalide ion \([6-9]\). These conductors are charge transfer salts with a 1/2 filled conducting band; they have very deformable layered crystal structures with strong electron–phonon coupling; due to this they demonstrate unique electronic properties that may be exploited in numerous sensing applications \([10-12]\).

In this context, we have developed a bi layer (BL) thermistor: polycarbonate/polycrystalline \((001)\) oriented \(\alpha’-(\text{BEDT-TTF})_2I_xBr_{3-x}\) molecular conductor (hereafter it will be as polycarbonate/\(\alpha’-(\text{BEDT-TTF})_2I_xBr_{3-x}\) \([13, 14]\) that can be successfully used as a highly temperature sensing component in e-textiles \([15, 16]\). Such textiles are capable of controlling very small temperature changes with accuracy of 0.005 degree. This is significantly better than that reported for the commonly used thermistors: the accuracy of a Pt-1000 detector is 0.01 degree \([17]\). Here it is necessary to recall that some of nonelectronic properties of polycarbonate/\(\alpha’-(\text{BEDT-TTF})_2I_xBr_{3-x}\) are also equally important for its applications in sensing electronics. In this context the study of the basic mechanical characteristics of both components of the developed bi layer thermistor are very important since the similarity of the elastic properties of layered components is one of the key requirements for engineering highly robust electronic layered systems. The above conclusion motivated us to study nano and micro mechanical properties of the developed BL thermistor: polycarbonate/\(\alpha’-(\text{BEDT-TTF})_2I_xBr_{3-x}\).

Here we report the Young’s moduli of the thin \((001)\) oriented layer of \(\alpha’-(\text{BEDT-TTF})_2I_xBr_{3-x}\) molecular conductor measured using a nanoindentation method, as well as basic mechanical characteristics \([\text{Young’s Modulus (E), Yield Strain (}\varepsilon_{\text{yield}}, \text{and Tensile Yield Strength (TYS)}]\) of the developed BL thermistor; these characteristics were determined from stress-strain dependences measured using a 5848 MicroTester. The paper also presents a new approach to the preparation of a temperature sensing e-textile in which the polycarbonate/\(\alpha’-(\text{BEDT-TTF})_2I_xBr_{3-x}\) thermistor was embedded as an active component.

2. Experimental

2.1. Preparation and characterization of the flexible lightweight BL thermistor: polycarbonate/\(\alpha’-(\text{BEDT-TTF})_2I_xBr_{3-x}\)

In line with a reported synthetic procedure \([13, 18]\) the BL thermistor was fabricated as follows: first, a 25 \(\mu\text{m}\) thick polycarbonate (PC) film that contains a 2 wt. % of BEDT-TTF was prepared. To do this, the film was cast on a glass support at 130 °C from a 1,2-dichlorobenzene solution of polycarbonate and BEDT-TTF. Second, to cover the film with the \((001)\) oriented layer of \(\alpha’-(\text{BEDT-TTF})_2I_xBr_{3-x}\), we exposed the film surface to the vapors of a dichloromethane solution of IBr. The surface of the film easily swells under this treatment that facilitates the migration of BEDT-TTF molecules from the bulk of the film to the swollen film surface where they are oxidized by IBr. This redox process induces the rapid nucleation of the \((\text{BEDT-TTF})_2I_xBr_{3-x}\) conductor with a consequent formation of the conductive polycrystalline covering layer \([18]\). The resulting surface-modified film was fully characterized using Scanning Electron Microscopy (SEM), Atomic Force Microscopy (AFM) and X-ray diffraction techniques; its \(R(T)\) dependence in the range of the human body temperatures was also studied.
SEM topographic images (figure 2) shows that the covering layer of the polycarbonate/α’-(BEDT-TTF)$_2$I$_x$Br$_{3-x}$ thermister consists of submicro plate-like oriented crystallites whose crystal planes are parallel to the film plan.

![Figure 2. SEM image of the conductive covering layer based on (BEDT-TTF)$_2$I$_x$Br$_{3-x}$](image)

The powder X ray diffraction data indicate the presence of only (001) reflections of the α’-(BEDT-TTF)$_2$I$_x$Br$_{3-x}$ conductor suggesting that the covering layer is dominantly formed from (001)-oriented α’-(BEDT-TTF)$_2$I$_x$Br$_{3-x}$ crystallites that is consistent with reported data [13, 18].

Direct current resistance measurements reveal that in the human body temperature range the change of the electrical sheet resistance of BL film is 250-300 Ω per degree. Therefore, the BL film, as it was reported in [15], is capable of controlling very small temperature changes.

2.2. Nanomechanical testing

Mechanical measurements were performed by means of the Force Spectroscopy mode, which consists on using the AFM probe as a nanoindenter. The force (F) value necessary to provoke a plastic deformation was experimentally assessed and topographically detected as a hole in the sample surface (permanent deformation). Then, F value for the mechanical measurements was set to be 70% of this plastic-onset F value to ensure that all reported mechanical measurements are fully inside the elastic deformation region. In all cases F value of 250 nN was chosen. In order to obtain results as representative as possible, one force curve was performed in each sample location so as to ensure that previous mechanical tests did not change the local mechanical response of the sample and a minimum of 200 individual experiments were performed for the sample. In order to extract the E value from the extension force curve, Hertz model considering a spherical indenter of radius R was applied [19, 20].

2.3. Macromechanical testing of the BL thermistor: polycarbonate/α’-(BEDT-TTF)$_2$I$_x$Br$_{3-x}$

Mechanical properties of the thermistor were studied using a 5848 MicroTester, equipped with a 1 kg load cell (Instron). Film strips in dimension of ca. 28x2 mm$^2$ and free from physical imperfections, were held between two clamps positioned at a distance of ca. 18 mm. During measurement, the strips were pulled by the top clamp with velocity being equal to 2.0 µm/s. The force and elongation were monitored up to the film samples were broken. Measurements were run in two replicates of the BL thermistor: polycarbonate/α’-(BEDT-TTF)$_2$I$_x$Br$_{3-x}$.

3. Results and discussion

Taking into account that mechanical properties of both components of the developed BL thermistor: polycarbonate/α’-(BEDT-TTF)$_2$I$_x$Br$_{3-x}$ are very important for its applications in sensing
electronics we studied them using two different approaches. We use a nanoindentation method to
determine Young’s moduli of the (001) oriented layer of α’-(BEDT-TTF)2I_xBr_{3-x} because it is known
as the most realistic mechanical testing technique to determine the elastic modulus for thin layers. [20-
23]

Another approach - tensile testing – was used to determine the basic mechanical characteristics of
the BL thermistor. The 25 µm thick sample of the BL thermistor of was prepared as it was early
reported [18]. The sample was morphologically and structurally characterized as it is described in the
Experimental part (paragraph 2.1); X-ray powder diffraction data and resistance temperature
dependence of the sample fully consistent with those reported for the BL film: polycarbonate/α’-
(BEDT-TTF)2I_xBr_{3-x} [13, 18 ]. For comparison a 25 µm thick polycarbonate film was additionally
prepared using the same casting parameters. This uncovered polycarbonate film was studied as a
reference sample.

2.1. Nano mechanical properties of the (001) oriented layer of α’-(BEDT-TTF)2I_xBr_{3-x}
The mechanical properties of the conductive sensitive α’-(BEDT-TTF)2I_xBr_{3-x}-based layer were
studied using the nanoindentation method. At the arrangement of the BL-based thermistor under AFM
testing (figure 3), the AFM probe – nanoindenter - was applied perpendicular to thermistor’s
conductive sensing layer.

As figure 4 shows, the X-ray powder pattern of thermistor’s sensing layer demonstrates the (00l)
reflections of the α’-(BEDT-TTF)2I_xBr_{3-x} crystal phase; this is in agreement with previously reported
data.[18] At this orientation, the molecular conducting ab planes of the α’-crystallites are parallel to
the plane of the BL-based thermistor. Therefore, the nanoindentation study permitted us to measure
Young’s moduli in a direction being perpendicular to the crystallographic ab plan (E_{ab}) of the α’-
(BEDT-TTF)2I_xBr_{3-x} crystallites. For definiteness sake, nanoindentation was also done on a
polycarbonate film that was prepared using a drop casting technique, parameters of which - solvent,
concentration, temperature, support - were the same as in the case of the BL film polycarbonate/α’-
(BEDT-TTF)2I_xBr_{3-x} casting.

2.1. Nano mechanical properties of the (001) oriented layer of α’-(BEDT-TTF)2I_xBr_{3-x}

Figure 3. Schematic representation of BL-based thermistor for mechanical
testing using the nanoindentation method
The values of Young’s modulus were extracted from the force-displacement curves measured during nanoindentation; AFM probe contact points are shown in figure 5. From dispersion of Young’s moduli and its Gaussian fit (figure 6) the value of $E_{\perp}$ of $\alpha’$-(BEDT-TTF)$_2$I$_x$Br$_{3-x}$ crystallites was estimated to be $9.0 \pm 1.4$ GPa.

The value of $E_{\perp}$ of the polycarbonate film sample was found as $0.8 \pm 0.2$ GPa. Although the value of $E_{\perp}$ of $\alpha’$-(BEDT-TTF)$_2$I$_x$Br$_{3-x}$ crystallites is an order of magnitude higher than the elastic modulus of polycarbonate film, it is an order of magnitude less than that reported for the thin metallic films, for example, a gold film (78 GPa) deposited over a POLY2 layer [23]. Therefore, the robustness of the BL thermistor: polycarbonate/$\alpha’$-(BEDT-TTF)$_2$I$_x$Br$_{3-x}$ significantly surpasses the same mechanical characteristics of plastics metalized with gold and other conventional metals that commonly used in flexible electronics.
3.2. Mechanical properties of the BL film: polycarbonate/α’-(BEDT-TTF)$_2$I$_x$Br$_{3-x}$

To provide an overview of the mechanical and some of electromechanical properties of the developed thermistor, its response to unidirectional stress was studied. For this purpose tensile testing in the elastic range was coupled with direct resistance measurements. For reference, the prepared 25 µm thick polycarbonate film was tested. Results on tensile tests are presented in figure 7 and summarized in Table 1.

![Figure 7. Full stress-strain curves for the BL polycarbonate/α’-(BEDT-TTF)$_2$I$_x$Br$_{3-x}$ thermistor (curve 1) and polycarbonate film reference (curve 2); I-Yield point, II-fracture point, III- plastic deformations, IV- ultimate tensile stress (UTS).](image)

Table 1. Tensile and electromechanical data for the BL thermistor and polycarbonate film.

| sample             | $E$ (GPa) | $\varepsilon_{Yield}$ (%) | Yield Stress (N/m$^2 \times 10^7$) | $\varepsilon_{Yield}$ (%) | Yield Stress (N/m$^2 \times 10^7$) | UTS (N/m$^2 \times 10^7$) |
|--------------------|-----------|---------------------------|-------------------------------------|---------------------------|-------------------------------------|--------------------------|
| BL thermistor      | 1.99±0.2  | 1.18                      | 2.3                                 | 1.18                      | 4.50                                |                          |
| Polycarbonate film | 2.05±0.2  | 1.24                      | 2.5                                 | -                         | 4.65                                |                          |

As data presented in figure 7 and table 1 show, the covering of a polycarbonate film with the (001) oriented α’-(BEDT-TTF)$_2$I$_x$Br$_{3-x}$ layer slightly decreases the basic mechanical characteristics of polycarbonate film. So, the values of $E$, Elastic Limit ($\varepsilon_{Yield}$) and Yield Stress decrease by $\pm 3\%$, $\pm 5\%$, and $\pm 8\%$, respectively. The ultimate tensile stress (UTS) value also decreases by $3\%$. From the stress-strain curves presented in figure 7, only one difference stands out: the significantly wide plastic region for the developed BL thermistor. Thus, the thermistor plastic behavior is observed in the range of relative strain from 1.18 to 5.4%, while the reference polycarbonate film demonstrates the plastic region between 1.24 and 3.6% of relative strain. Therefore, the BL thermistor undergoes larger plastic deformations without cracking compared with the uncovered polycarbonate film that was prepared under similar casting parameters. In spite of the above mentioned differences, the measured basic mechanical characteristics of the BL thermistor are very close to those of the reference polycarbonate film. This imparts a good robustness to BL film: polycarbonate/α’-(BEDT-TTF)$_2$I$_x$Br$_{3-x}$ and makes possible the integration of the developed thermistor in different devices as an active component.

As figure 8 shows, the electrical resistance of the thermistor, which was simultaneously measured at tensile testing, deviates from linear proportionality at the elastic limit point of the polycarbonate/α’-(BEDT-TTF)$_2$I$_x$Br$_{3-x}$ bilayer. Here it should be noted that such coincidence was not observed for the recently reported highly piezo-resistive BL film: polycarbonate/β$_{II}$-(BEDT-TTF)$_2$I$_x$, the resistance of
which deviates from linear proportionality versus strain at $\epsilon=0.65\%$, while Yield point of this BL film was observed at $\epsilon_{\text{Yield}}=1.2\%$ [8, 24]. By analogy with the elastic limit point (Yield point), we have suggested to term the point at which the resistance of BL films: polycarbonate/(BEDT-TTF-based molecular conductor deviates from linearity versus strain as the resistance proportional limit ($R_{\text{yield}}$). [24] As it was shown [8, 24], the nonlinearity above $R_{\text{yield}}$ is associated with small numerous nanocracks formed perpendicularly to an elongation direction. Relying on such data, one may conclude that the point of the resistance proportional limit of the BL thermistor corresponds to the elastic limit point of the (001) oriented $\alpha'-(\text{BEDT-TTF})_2\text{I}_x\text{Br}_{3-x}$ layer. At the end of this paragraph, an important conclusion have to be made: the (001) oriented $\alpha'-(\text{BEDT-TTF})_2\text{I}_x\text{Br}_{3-x}$ layer, formed on the surface of a polycarbonate film significantly surpass similar layers of the $\alpha_-, \beta_{\text{H-}} (\text{BEDT-TTF})_2\text{I}_3$ organic molecular metals in elasticity. The significant enhancement of the resistance proportional limit of BL thermistor makes it very usable and expands the scope of sensing devices to which the developed thermistor might be adopted.

![Figure 8. Resistance-strain (plot 1) and stress–strain (plot 2) curves for the BL thermistor polycarbonate/$\alpha'-(\text{BEDT-TTF})_2\text{I}_x\text{Br}_{3-x}$; the data were simultaneously collected at room temperature.](image)

4. Conclusions

For the first time the anisotropy of elastic properties of the $\alpha'-(\text{BEDT-TTF})_2\text{I}_x\text{Br}_{3-x}$ molecular conductor was studied: the measured values of Young’s moduli in the direction perpendicular to its molecular conducting $ab$ plan ($\approx 9$ GPa) and along the plan ($\approx 2$ GPa) indicate that the crystal structure of this molecular conductor is a highly anisotropic mechanical system.

The measured values of Young’s moduli reveal that the thin conductive $\alpha'-(\text{BEDT-TTF})_2\text{I}_x\text{Br}_{3-x}$-based layer is significantly softer than thin layers of conventional metals deposited on plastic substrates; this permits one to fabricate durable conductive sensing multilayer structures for their applications in sensing technologies.

It was shown that the (001) oriented $\alpha'-(\text{BEDT-TTF})_2\text{I}_x\text{Br}_{3-x}$ layer, formed on the surface of a polycarbonate film, significantly surpass similar layers of the $\alpha_-, \beta_{\text{H-}} (\text{BEDT-TTF})_2\text{I}_3$ organic molecular metals in both elasticity and plasticity. The significant enhancement of the resistance
proportional limit of the BL thermistor: polycarbonate/α’-(BEDT-TTF)$_2$I$_3$Br$_3$x makes it very usable and expands the scope of sensing devices to which the developed thermistor might be adopted.

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