

Article

A Printable Paste Based on a Stable n-Type Poly[Ni-tto] Semiconducting Polymer

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Abstract: Polynickeltetrathiooxalate (poly[Ni-tto]) is an n-type semiconducting polymer having outstanding thermoelectric characteristics and exhibiting high stability under ambient conditions. However, its insolubility limits its use in organic electronics. This work is devoted to the production of a printable paste based on a poly[Ni-tto]/PVDF composite by thoroughly grinding the powder in a ball mill. The resulting paste has high homogeneity and is characterized by rheological properties that are well suited to the printing process. High-precision dispenser printing allows one to apply both narrow lines and films of poly[Ni-tto]-composite with a high degree of smoothness. The resulting films have slightly better thermoelectric properties compared to the original polymer powder. A flexible, fully organic double-leg thermoelectric generator with six thermocouples was printed by dispense printing using the poly[Ni-tto]-composite paste as n-type material and a commercial PEDOT-PSS paste as p-type material. A temperature gradient of 100 K produces a power output of about 20 nW.

Keywords: semiconducting n-type polymer; poly[Ni-tto]; printable paste; surface roughness; dispenser printing; thermoelectric

1. Introduction

The development of the “Internet of things” requires the availability of autonomous (semi-autonomous) power systems that are able to continuously supply different nodes (sensors, transmitters) with electricity. Since the ambient conditions often provide a particular heat source, which ultimately simply dissipates into the surrounding space, thermoelectric generators (TEGs), which convert a temperature difference into an electrical potential difference, are of particular interest. The scope of such devices is not only limited to thermogenerators for sensor nodes. For example, when integrated into clothes, body heat can be harvested for the powering of wearable electronics [1]. Additionally, these materials have great potential for creating flexible temperature sensors [2] that are used in distributed diagnostics, robotics, electronic skins, functional clothing and many other Internet-of-Things (IoT) solutions. One of the basic requirements for such generators is their flexibility, which is necessary for the exact adjustment of the generator and the surface of the heat source.

Although organic TEGs that satisfy this requirement are significantly less effective than inorganic TEGs [3], their thermoelectric characteristics are constantly improving, and their power is already sufficient to power simple low-power devices [4]. The dimensionless figure of merit of thermoelectric materials zT characterises the thermoelectric (TE) performance:

$$zT = \alpha^2 \sigma T / \kappa$$

and is a function of the Seebeck coefficient α , the electrical conductivity σ , the thermal conductivity κ and the absolute temperature T . The low thermal conductivity is the common feature of organic compounds, that is why the power factor ($PF = \alpha^2 \sigma$) is a more usual metric for comparing the performance of organic electronics.

One of the main problems of organic thermoelectricity is the lack of an effective and, most importantly, stable n-type material. P-type materials, and various derivatives of PEDOT, have very high electrical conductivity—up to 4600 S/cm for PEDOT:PSS[5] and 5400 S/cm for other derivatives [6], although the Seebeck coefficient was not measured and is typically in the range of 10 to 39 $\mu\text{V/K}$. This high electrical conductivity has already led to PEDOT's introduction into different applications. The electrical conductivity of most n-type organic semiconductors does not exceed 1 S/cm [7]. Furthermore, this electrical conductivity degrades quickly when interacting with atmospheric oxygen or moisture. Therefore, the development of n-type polymers, which are not only resistant to environmental influences, but also capable of being easily deposited on various flexible substrates, is an urgent task.

Various methods of printing techniques can be used to manufacture TE devices in large quantities: inkjet printing, screen printing, dispenser printing [8]. While inkjet printing is suited for thin films made by a low viscosity ink, screen and dispenser printing are characterized by using a high viscous paste. The advantage of dispenser printing compared to the two others is the ability to print onto non-flat substrates. Though dispenser printing has a slightly lower potential in scalability compared to screen and inkjet printing, it is favourably characterised by the ability to program the printing patterns by CAD (instead of producing a patterned mesh), making it a fast approach for iteration in the development context.

In this study, we examined the possibility of depositing by dispenser printing one of the most promising n-type organic semiconductors—polynickeltetrathiooxalate (poly[Ni-tto])—to a flexible substrate.

The advantages of this material are very good TE characteristics, relatively high stability in air and the ability to form a paste suitable for printing.

2. Materials and Methods

Materials. Chemicals and solvents were purchased from Aldrich (Taufkirchen, Germany) or TCI Europe (Eschborn, Germany) and used as received unless otherwise stated. The polymer poly[Ni-tto] was synthesized and purified as reported in our previous work [6]. After drying, the poly[Ni-tto] powder was maintained at 150 °C under inert gas for 1 h.

Film Fabrication. Polyvinylidene fluoride (PVDF, MW $\approx$ 180,000) was dissolved in dimethyl sulfoxide (DMSO) at 80 °C for 4 h with continuous stirring to form a 20 mg/mL solution. Separately, 6 mL of DMSO were added to 1 g of poly[Ni-tto] powder and stirred for two days. Then the resulting suspension was transferred to a zirconia ball mill vessel, and 24 mL of PVDF/DMSO solution and 40 g of zirconia beads (diameter = 0.5 mm) were added. Ball milling was performed on a Retsch PM100 (Haan, Germany) for two days at 400 rpm without a break. The poly[Ni-tto]: PVDF mass ratio was fixed at 1:0.48.

Characterization techniques. A commercial setup (SRX, Fraunhofer IPM, Freiburg, Germany) was used for the electrical characterization. The setup measures up to 1180 K in air, vacuum or an inert gas atmosphere. All measurements were performed as stated in air or nitrogen. The electrical

conductivity was measured by a four-point probe configuration. The applied current was kept below 10 mA in order to minimize the joule heating effects. Seebeck coefficient measurements were carried out with temperature gradients of 3 K. The sample was placed on two heaters. To set up a temperature gradient, one heater was activated while the other acted as the cold side. The temperature and voltage were measured by two thermocouples. Subsequently, the triggering of the heaters was reversed so that the Seebeck coefficient was measured again. To ensure proper contact, UI curves were tracked and showed linear behaviour. To ensure better electrical and thermal contact of the prepared thin films, carbon foil was applied. No further (sputtered) gold contacts were used whatsoever. The thermocouple distance for measuring the temperature and voltage was set to 3 mm. Each sample was measured 4–6 times; the percentage of error inherent to Seebeck coefficient measurements is not more than 5%.

The characterization of the TEG stripes was performed in a self-made TEG measurement setup (at the Technical University of Dresden) in a vacuum. The cold side was cooled with a Lauda ECO RE 1050 SN (Lauda-Königshofen, Germany) and controlled by a PID controller. For the temperature measurements on the hot and cold side, a Pt100 was used. Hot and cold sides were thermally insulated from each other. The output voltages were measured with a Keithley 2000 multimeter (HTM Reetz GmbH, OH, USA). The load resistances varied between 27 Ω and 9.4 k Ω according to the internal resistance of the TEG at temperatures between 10 and 100 K (with hot and cold sides, respectively, of 30 °C and 20 °C; 40 °C and 20 °C; 60 °C and 20 °C; 80 °C and 20 °C; 80 °C and –20 °C). The best power output is at a load of 964 Ω .

The atomic force microscope (AFM, Bruker Dimension Icon, Karlsruhe, Germany) was operated in tapping mode using silicon-SPM sensors (Budget Sensors, Sofia, Bulgaria) with a spring constant of ca. 40 N/m and a resonance frequency of ca. 300 kHz.

The film thicknesses of the prepared films were measured with a confocal microscope (Leica DCM 3D, Wetzlar, Germany) after the electrical characterization. The thicknesses of the printed films were in the range of 3–5 μm .

3. Results and Discussion

3.1. Polymer Development and Paste Preparation

Polymer development. In this study, a poly[Ni-tto] polymer with good reproducible properties was synthesized according to the procedure described in detail in our previous articles [9,10]. Despite the formal difference between poly[Ni-tto] and the polynickelethenetetra-thiolate (poly[K_x(Ni-ett)]), which has been intensively studied over the past seven years [11–16], they both belong to the same class of coordination polymers and exhibit similar properties. This allows us to perform a comparative characterization and apply the same processing and analysis methods to poly[Ni-tto] as are applied to poly[K_x(Ni-ett)]. For example, since Wolfe and co-authors [17] explain the significant improvement in the thermoelectric characteristics of the polymer composite film after its annealing due to the removal of volatile impurities, we also carried out a heat treatment of the obtained polymer before the paste preparation and after the film deposition. Heat treatment of the polymer powder leads to an improvement in electrical conductivity (Table 1); however, unlike a poly[K_x(Ni-ett)], it does not lead to an improvement in the Seebeck coefficient. Wolfe suggested that a chemical change may be occurring in the poly[K_x(Ni-ett)] powder [17]. Since the value of the Seebeck coefficient of the poly[Ni-tto], both in the sample not subjected to heat treatment and after heat treatment, coincides with the value of the Seebeck coefficient of the post-annealing poly[K_x(Ni-ett)] powder, this serves as additional evidence of the hypothesis that we proposed in the previous article [9]—that tetrathiooxalate is the true monomer for a polymer of this type and does not need any additional chemical converting.

Table 1. Sequential changes in thermoelectrical properties of material.

Material	Conductivity, S/cm	Seebeck Coefficient, $\mu\text{V/K}$	Best Power Factor, $\mu\text{W/mK}^2$
Freshly prepared (after vacuum drying) individual poly[Ni-tto] powder (pressed in pellet)	38–42	−40~−44	7.8
Individual poly[Ni-tto] powder after thermal treatment (pressed in pellet)	56–61	−40~−44	12.1
Freshly prepared (after vacuum drying) polymer composite film	78–90	−18~−20	3.6
Annealed polymer composite film	54–74	−46~−49	15.7

After the ageing of the poly[Ni-tto] powder at 160 °C for 1 h, it was used in the preparation of a printable paste.

Paste preparation. Although poly[Ni-tto] can be considered a kind of organic polymer, it does not possess one of the most important properties of commodity polymers, solubility. Indeed, poly[Ni-tto] cannot be dissolved either in most organic solvents or in water without destroying its chemical structure. Only DMSO and NMF are solvents that are capable of partly dissolving or swelling it. In other words, even after days of mixing, there is an incomplete dispersion, with about 20% of undissolved polymer particles that do not pass through the syringe filter (0.45 μm). Interestingly, the polymer is completely soluble in NMF in the presence of sodium diethyldithiocarbamate. Since this chemical binds heavy metal cations in the form of diethyldithiocarbamates [18], it is often used to remove traces of heavy metals from the medium. In our case, it obviously completely destroys the poly[Ni-tto] structure with the formation of a stronger chelate compound, nickel diethyldithiocarbamate. The preparation of a paste based on poly[K_x(Ni-ett)] powder, which does not require its complete dissolution, is described in several sources [17,19–22]. It was previously shown that DMSO, used as a solvent, and PVDF, as a binder, provide sufficient dispersibility of the polymer and the resulting paste (or ink) is capable to form a film. However, the paste we prepared according to the method described in [22] was not homogeneous enough for dispense printing, since it contained a certain amount of agglomerates, which were essentially nondispersed, sticky polymer particles. This material was used for the preparation of films by drop-casting [22]; however, this method turned out to be unsuitable for dispense or screen printing. To be suitable for those printing techniques, the paste must be homogeneous so it can pass through a needle or mesh with a very small diameter to enable the fabrication of very precise patterns. In order to obtain a more homogeneous paste, we mixed the polymer with DMSO for several days, which led to a visual dissolution of the polymer. It assumed the formation of small poly[Ni-tto] particles upon the dissolution, or at least a swelling of insoluble agglomerates to form a relatively stable dispersion. Further grinding in a ball mill with balls of very small diameter (0.5 mm) for two days (see Section 2) made it possible to obtain a homogeneous paste perfectly suited to dispenser printing (Figure 1).

The ratio of the paste components (poly[Ni-tto]/PVDF/DMSO) allows it to vary its viscosity. As an example, Figure 2 shows the rheological properties of two typical batches of paste, differing in the ratio of components (Table 2). It should, however, be noted that for use in dispenser printing there is no need to obtain a paste with a strictly defined viscosity value. Changing print parameters (e.g., the pressure under which the paste exits the cartridge, dispense gap, print speed, needle diameter) allow us to use both low- and high-viscosity pastes for applying the film of a given geometry.

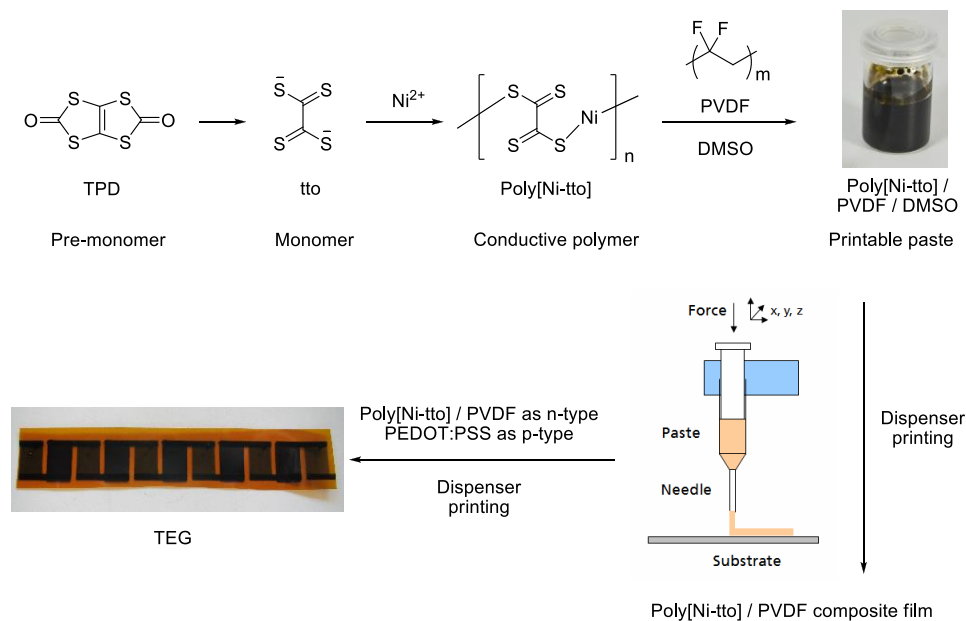


Figure 1. Scheme of the polymer preparation and generator fabrication.

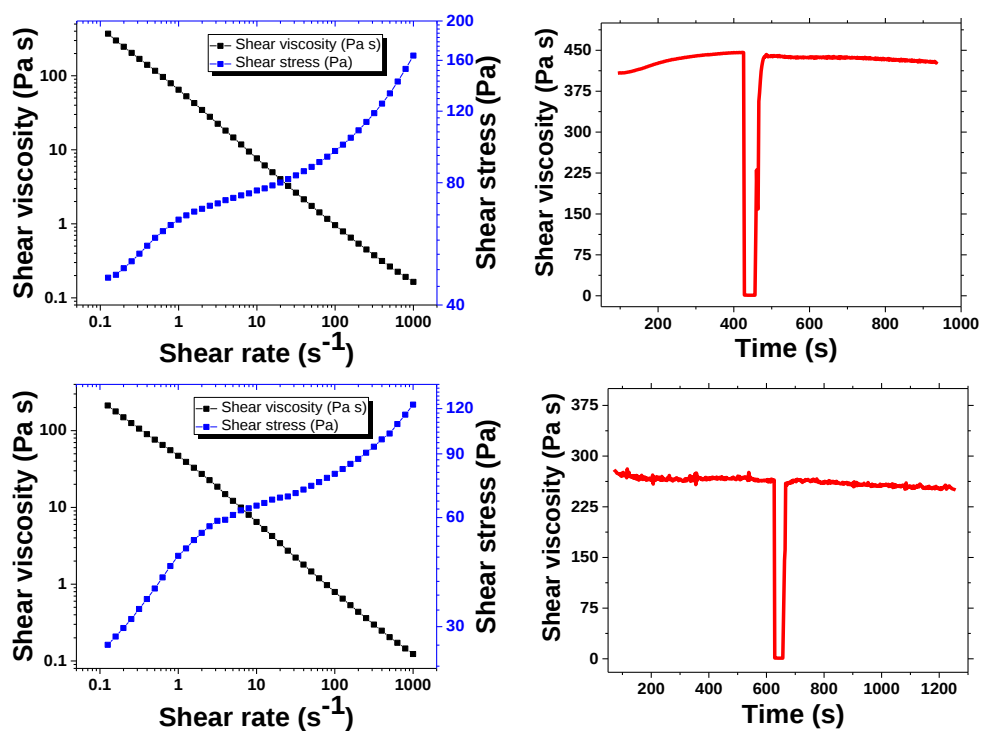


Figure 2. Rheological behaviour of two different pastes: A (top part) and B (bottom part): receiving of the rheological behaviour in the shear rate range of $0.1\text{--}1000\text{ s}^{-1}$ (left side) and investigation of the thixotropic behaviour (right side) of the paste for the shear range 0.1 s^{-1} (10 min)– 100 s^{-1} (30 s)– 0.1 s^{-1} (10 min).

Table 2. Samples of paste with different component ratio.

Blend Component	Active Material (poly[Ni-tto])	Binder (PVDF)	Solvent (DMSO)
Ratio for Paste A	1 g	0.48 g	30 mL
Ratio for Paste B	1 g	0.25 g	25 mL

In order to be suitable for dispenser printing, the rheological properties of the paste must meet certain requirements, including a sufficiently high viscosity of the paste at a low shear rate, a low viscosity of the paste at a high shear rate (Figure 2, left), called shear thinning, and a quick restoration of the high viscosity of the paste after a short-term increase in shear rate (Figure 2, right), which is referred to as thixotropy.

Paste A starts with an initial steady state shear viscosity around 400 Pa·s, while Paste B is at 220 Pa·s (see Figure 2, left). The ratio between solid content and solvent is nearly the same for both pastes: 0.0493 g/mL (Paste A) and 0.0492 g/mL (Paste B). Since the typical viscosity changes are orders of magnitude, the differences in the starting viscosity at 0.1 s^{-1} are very minor. In any case, both pastes show distinct shear thinning behaviour with a shear viscosity of approximately 10 Pa·s at 10 s^{-1} , which is shown to be favourable for dispenser printing.

As can be seen in Figure 2 (thixotropic test), both pastes quickly return to their initial shear viscosity after the simulated printing step. The thixotropy time is 12 s for Paste A and 8 s for Paste B. These properties make them well suited to dispenser printing.

3.2. Deposition: Dispense Printing

The advantage of dispenser printing is that it enables accurate printing of the material to various substrates. In this case, the geometry of the deposited pattern can be very diverse. The rheological properties of the paste we prepared allow us to draw lines with a width of less than 250 μm (Figure 3, right).

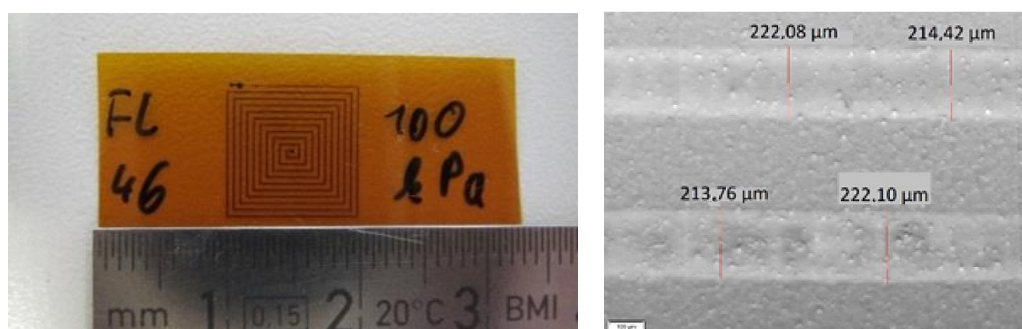


Figure 3. Width of polymer lines applied with dispenser printing.

The paste can be printed on both hard (ceramics, glass, metal) and flexible (Kapton-foil, woven-fabric, fleece) substrates. Depending on the printing parameters, a different amount of paste can be applied, which allows one to control the thickness of the formed film to some extent. Dispenser printing of the paste we made allows for obtaining a film (after drying of the applied paste) with a thickness of 1–20 μm .

After the film has been deposited and dried and until the solvent is completely evaporated, an annealing step was performed. Holding for 1 h in an inert atmosphere at 150°C resulted (obviously due to the removal of volatile impurities) in a significant increase in the material's power factor (Table 1). In general, studying the behaviour of a film upon heating is a complex task, and we will consider it in a separate publication.

3.3. Film Properties

Film morphology. The film-forming properties and thin film morphology of optoelectronic materials are crucial characteristics for their application in devices. As a rule, for the preparation of homogeneous films with controllable thicknesses, a material has to be dissolved, desirably down to a molecular level. Knowing that solubility is an inherent problem of poly[Ni-tto], we expected that the preparation of smooth films would be problematic for this type of material.

To study the film properties, the poly[Ni-tto]/PVDF dispersion was printed onto Kapton substrates and dried at atmospheric pressure at 150 °C for 1 h. Bare Kapton foils possess a moderately smooth surface having a root mean square roughness (rms) of the surface of about 7–10 nm, as deduced by AFM. This roughness is given by randomly located holes and hills with their depth and height in a 10–20 nm range, separated from each other by about 1 μm . Inspection of the Kapton by optical microscopy reveals only a few defects on a sub-mm level, appearing on the reference photo as dark spots. Interestingly, poly[Ni-tto]/PVDF films are even smoother and more homogenous than the underlying Kapton (Figure 4). The deposition of the composite substantially decreased the roughness down to rms = 3–5 nm. As seen from Figure 4c, the size of the features does not exceed 10 nm and their amount on the surface is clearly decreased. Small-area AFM images reveal a fine morphology of the film, which is composed of nanoparticles a few nm in diameter. We suggest that these nanoparticles are primary aggregates present in the solution and are formed upon milling during the preparation of the dispersion. Optical microscopy confirms a more homogeneous appearance of the poly[Ni-tto]/PVDF film compared to the underlying substrate. Such a high quality of the poly[Ni-tto]/PVDF composite film (low roughness, absence of defects) is a remarkable result in relation to the strong propensity of aggregation of the polymer and the high, multi-micron thicknesses of the composite layer. The high film quality looks especially exciting in terms of the preparation method—dispenser printing of a high viscosity paste—which usually does not tend to smoothen the resulting coatings, as do other deposition methods such as spin-coating.

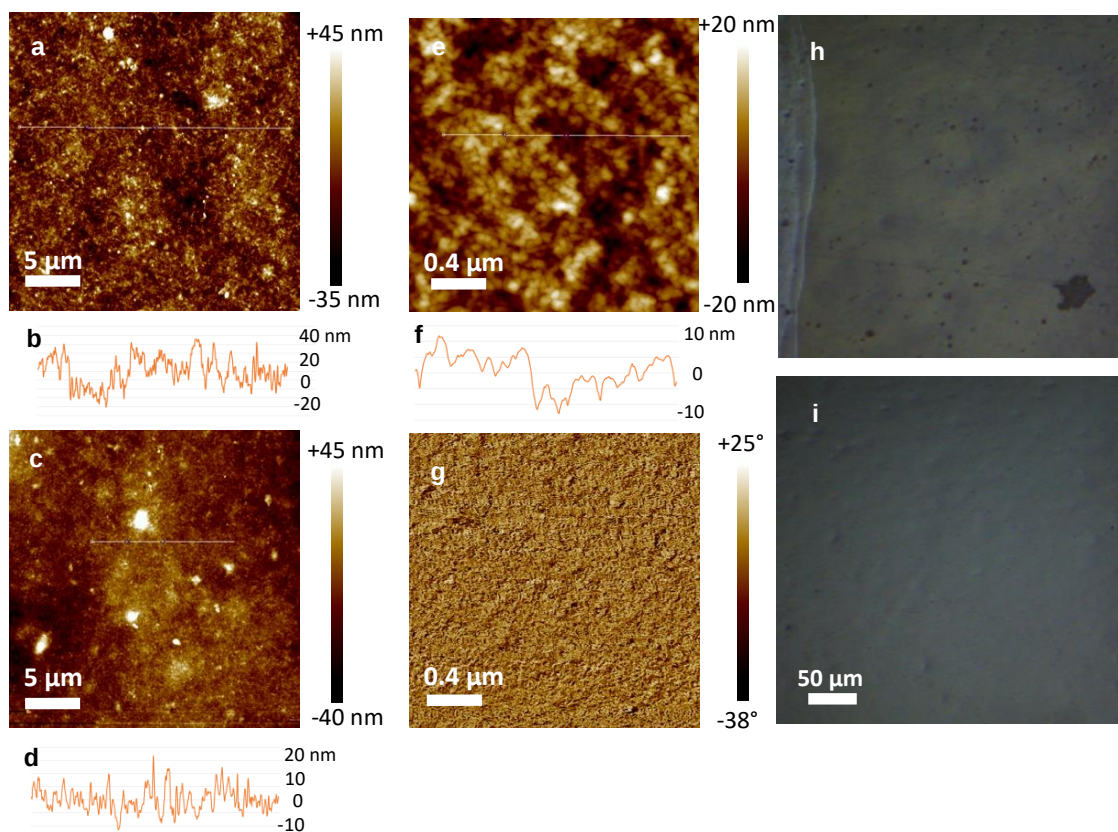


Figure 4. AFM topography (a,c,e) and phase (g) images with corresponding cross-sections roughness measurements (b,d,f) of a bare Kapton substrate (a,b) and poly[Ni-tto]/PVDF films deposited onto the Kapton (c–g); high magnification image (e–g) shows the film structure, which is predominantly composed of uniform 2–5 nm nanoparticles; optical microscopy images of bare Kapton (h) and poly[Ni-tto]/PVDF film (i).

Although all substrates firmly adhered to the film after drying, different substrates have a different ability to peel the film in the presence of DMSO. For example, it is impossible to peel the film from ceramics, Teflon or Kapton without destroying it, while the film can quite easily be separated from a metal surface (Figure 5). Since the integrity of the film is not affected and it has the same thermoelectrical properties as a film that was not removed from the substrate, it can later be used as an individual component in TEG design.

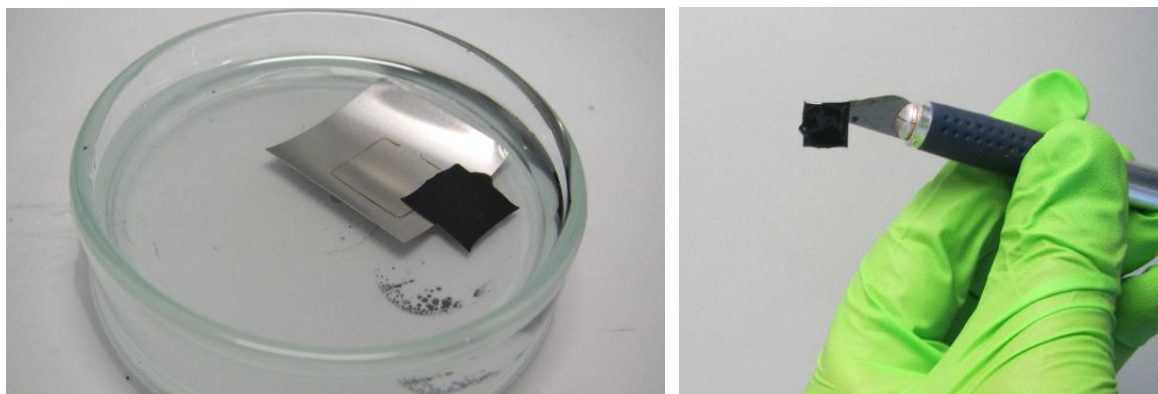


Figure 5. Peeling of the film from a metal surface (left) and the polymer film in a free form, without substrate (right).

Comparing of TE properties of pressed powder and film. In general, the problem of obtaining a printable material with the same electrical properties as a bulk material is well known. So, to print copper or silver by dispenser printing, the metal must be atomized to obtain a powder, from which the paste is then prepared using at least a binder and a solvent. Although thus-prepared material can be printed, the electrical conductivity of the printed film, even after sintering, is significantly lower than the electrical conductivity of the bulk metal [23]. To raise the electrical conductivity of the printed material up to the conductivity level inherent to the source metal (or compressed metal powder), several conditions must be met: i) the majority of the binder must be removed (since it usually functions as an insulator), ii) the material must be heated to the melting point or, at least, to the sintering temperature, to provide the possibility of metal particles forming close contacts with each other.

From this consideration, it is logical to expect a significant deterioration in the thermoelectric properties of the composite polymer film in comparison with the properties of a compressed polymer powder without binder. However, even a freshly deposited paste, after only 10 min of drying (heating to 100 °C to evaporate the solvent) and short drying in a vacuum, shows good thermoelectric characteristics: Seebeck coefficient of $-19 \mu\text{V/K}$; electrical conductivity between 78–90 S/cm (which is even higher than that of compressed powder); and a power factor of $3.6 \mu\text{W/mK}^2$ (Table 1). We explain this by the fact that polymer powder, in contrast to metal powders, is soluble to some extent, although not completely, in DMSO. We suppose that a phase separation of poly[Ni-tto] and PVDF blend components takes place upon drying so that poly[Ni-tto] forms continuous pathways rather than domains encapsulated with PVDF. Accordingly, the Seebeck coefficient is very close to the values of the individual poly[Ni-tto], and the electrical conductivity is slightly better since the expanded polymer chains are in better contact with each other compared to mechanically pressed particles. Further annealing of the film leads to an increase in the power factor up to $15.7 \mu\text{W/mK}^2$. As already mentioned, this phenomenon, and temperature's influence on the polymer in general, will be examined in detail in a separate publication.

It is noteworthy that, unlike individual poly[Ni-tto] [9], the composite film does not show noticeable degradation in its TE properties during two months of storage under ambient conditions.

It should also be noted that poly[Ni-tto] with different counterions was synthesized earlier [24,25] and very recently by Wolfe et al. [26], who obtained poly[Ni-tto] and its composite with PVDF. The authors obtained poly[Ni-tto] with various counterions: Li, Na and K. Nominally, a polymer with K as a counterion should be identical to the polymer we are considering in this paper. However, these compounds have significant differences in terms of the ratio of elements (compare the data from [9] and [26]) and, as a result, different TE properties. The annealed polyK[Ni-tto]/PVDF composite described by Wolfe has an electrical conductivity of about 21 S/cm and a Seebeck coefficient of $\sim 60 \mu\text{V/K}$. Since the insolubility of the polymer limits the methods of its analysis, several reasons for these differences can be suggested: completely different methods for the preparation of tto and, as a result, the synthesis of compounds with different impurities; and different polymerization methods, which should lead to polymers with different chain lengths and polydispersity. This issue should be addressed in the future.

3.4. Thermoelectrical Generator Characterisation

Double-leg TEG strips, with different length and numbers of couples, were printed by using poly[Ni-tto] composite paste as the n-type material and PEDOT:PSS SV3 printing paste (modified with 5% DMSO) as the p-type material.

In order to fit the dimensions of the TEG to the geometry of the characterization test rig, a strip of 95 mm in length was printed, consisting of six couples (Figure 6). Each leg (both n- and p-type) has a rectangular shape with a length of 12 mm and a width of 7 mm. PEDOT:PSS was also used as a contact material: 2-mm-wide stripes were printed to connect the legs in series. As a result, the TEG strips are fully flexible (see Figure 6, right) and can also be used as rigid cross-plane TEGs, when they are coiled up like Scotch tape.

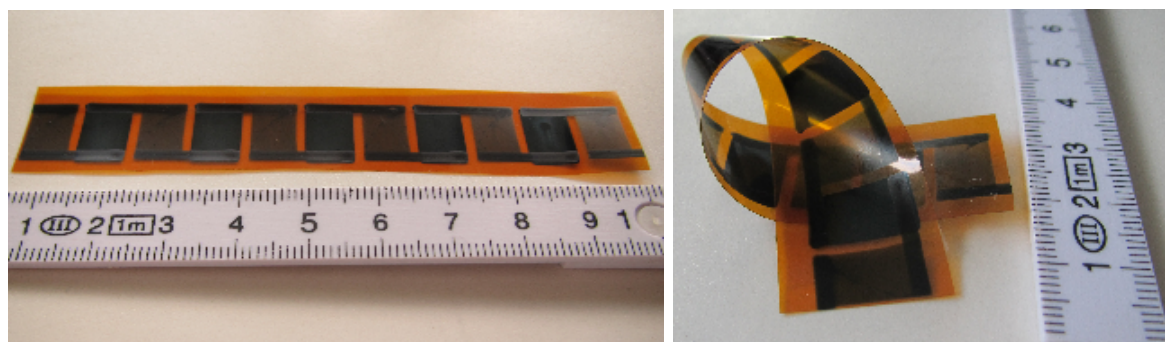


Figure 6. Dispenser printed fully flexible TEG. The performance of the TEG stripe does not change after winding on a cylinder with a diameter of 8 mm.

The TEG stripes were installed into the test rig between the hot and cold side of the heat exchangers and characterized in a vacuum at $\sim 1.0 \cdot 10^{-3}$ mbar to determine the open-circuit voltage and the power output under load. The internal electrical resistance is $\sim 1.0 \text{ k}\Omega$. The TEG was exposed to a temperature gradient between 10 and 100 K with an accuracy of $\pm 0.02 \text{ K}$. The load resistance varied between ~ 27 and $10,000 \Omega$ in 100 steps.

The output voltage in open circuit is shown in Figure 7, left. It is shown that an increase in the ΔT also increases the output voltage. The device shows a thermovoltage up to $\sim 8.5 \text{ mV}$. The thermovoltage shows linear behaviour up to a ΔT of 60 K, but we see a nonlinear increase for 100 K. The cause for that is not clear so far. It might be due to the fact that we decreased the cold side temperature down to -20°C to increase the temperature gradient. The behaviour of poly[Ni-tto] at low temperatures still was not a subject of research, but we will investigate this issue in the near future. The power output for different loads is presented in Figure 7, right. At a given ΔT of 10 K the power output is $\sim 120 \text{ pW}$ and increases to 20 nW (at $\Delta T = 100 \text{ K}$). Due to the high internal resistance of $1 \text{ k}\Omega$ and the low number of thermocouples, the power output is fairly low.

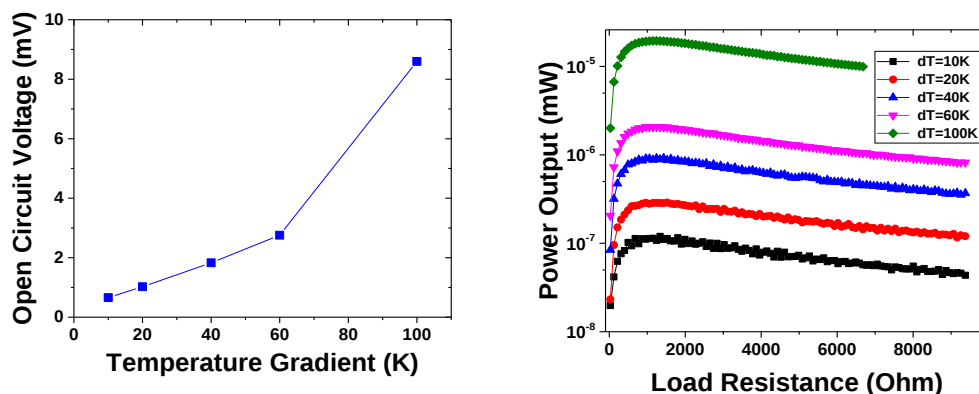


Figure 7. The output voltage in open circuit (left) and the power output for different loads (right).

4. Conclusions

In conclusion, having had the development of a printable paste on the basis of poly[Ni-tto] powder as our overall goal, we also obtained a procedure for polymer composite paste preparation with high homogeneity. Varying the components' ratio allows for preparing pastes with different viscosities, which gives the option of tailoring the rheological properties of the paste to suit different deposition procedures. Smooth films, obtained by high-precision dispenser printing, possess a conductivity in the range of $\sigma = 54\text{--}74\text{ S/cm}$ and a Seebeck coefficient in the range of $\alpha = -46\text{ to }-49\text{ }\mu\text{V/K}$, which are slightly better thermoelectric properties compared to the original polymer powder. The film thickness varies in a rather narrow range from 2 to 10 μm . Future work will be devoted to the development of a procedure for producing thinner films for ultra-small devices and thick layers to make 3D geometry possible. A flexible, fully organic double-leg thermoelectric generator with six thermocouples was printed by dispense printing using the poly[Ni-tto]-composite paste as the n-type material and a commercial PEDOT-PSS paste as the p-type and conductive material. A temperature gradient of 100 K produces a power output of about 20 nW. The main reason for the low output is the high internal resistance of the TEG; solving this problem will pave the way for significant improvements in generator efficiency.

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