Polymer Materials for the Heat Recovery

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Abstract. Many of the processes in the industry, agriculture and microscale systems are associated with the waste heat generation, which often may be a menace or lower the efficiency of the processes. The thermoelectric cooling is becoming increasingly popular and gives the possibility to convert waste heat into electricity. The current thermoelectric cooling solutions are based on alloy materials. However, the new technologies pay attention to the environment burden, moreover the regulations of the production and recycling are becoming more and more restrictive. Conducting polymers are thermoelectrically active at low temperatures, cheap and environmentally safe. In this paper authors discuss the possibility of the application of conducting polymers for the heat recovery. Due to the operating temperature range and different nature of the waste heat sources, polymers might be an interesting solution and a complement for alloy-based thermoelectric materials. The character and nature of the formation of waste heat sources and conventional technologies of its recovery are also described in this paper. Moreover the advantages of thermoelectric cooling with the use of polymers are presented and two materials based on polyaniline are proposed.

1. Introduction
The energy conversion and technological processes in the industry, agriculture, motorization, domestic appliances, as well as microsystems are associated with the heat generation. In some of the cases the heat generation may be unsafe and may reduce the efficiency of the main process or negatively influence the operating conditions of machines or electronic equipment. Regardless of the phenomenon scale, the cooling is needed in most of the cases. The cooling methods based on the use of fans, radiators or refrigerating cycles are not always feasible, because of the freons toxicity, progressive miniaturization, specialization and complexity of the devices. The thermoelectric cooling, which also gives the possibility to convert the waste heat into the electricity, is becoming increasingly common.

2. The thermoelectric phenomena and parameters
In the conductors and semiconductors, the interdependent processes of electric charge and heat transport can occur. This means that the thermal process generates the charge transport, or vice versa, the flow of the electric current causes the thermal effect. These phenomena may occur in one conductive material or at the interface between two different materials. The thermoelectric Seebeck
effect considered in this paper consist in the heat conversion into the electricity and it can be described mathematically by the eq. (1) [1, 2].

\[ U_S = \alpha \cdot (T_1 - T_2) \]  

(1)

where \( U_S \) [V] – generated voltage, \( \alpha \) [V/K] - Seebeck coefficient, \( T_1 - T_2 \) [K] - temperature gradient.

Seebeck phenomenon can be applied in the energy storage devices and electrical generators.

The efficiency of the heat transfer and the energy conversion in the thermoelectric materials and devices can be estimated with the dimensionless thermoelectric figure of merit \( ZT \) (2).

\[ ZT = \frac{\alpha^2 \sigma T}{\lambda} = \frac{\alpha^2 T}{\rho \lambda} \]  

(2)

where \( \alpha \) [V/K] - Seebeck coefficient , \( \sigma \) [S/m] - electrical conductivity, \( \rho \) [Ω∙m] - electric resistivity (inverse of conductivity), \( \lambda \) [W/m∙K] - thermal conductivity, \( T \) [K] - absolute temperature [3, 4]. Also, the value of the figure of merit \( Z \) with the dimension \([K^{-1}] \) is popular in the literature and it is commonly used for the material efficiency estimations. For the practical application the thermoelectric materials with a \( ZT \) approx. 3 are needed. Such value is comparable to the efficiency of mechanical cooling and would allow to use the thermoelectric materials in a larger scale [1].

3. The alloy thermoelectric materials

The development of thermoelectric generators and coolers is observed since the 2nd half of the twentieth century. Currently, the most common thermoelectric materials are the modified semiconductors e.g. bismuth telluride \( \text{Bi}_2\text{Te}_3 \), bismuth antimonide \( \text{BiSb} \) or multicomponent alloys, which are produced in the high - temperature metallurgical processes. The value of \( ZT \) for this materials is ca. 1 i.e. in case of \( \text{Bi}_2\text{Te}_3/\text{Bi}_2\text{Se}_3 \) (25 mol%) \( ZT = 0.6 \) and in case of \( \text{Bi}_2\text{Te}_3/\text{Sb}_2\text{Te}_3 \) (75 mol%) \( ZT = 0.9 \) [1]. Fleurial et al [6] summarized the common alloy materials and shown that the most of these materials have the best thermoelectric efficiency at temperatures above 400 K.

Table 1. The properties of chosen semiconductors and metals [5, 6]

| Material    | \( \sigma \) [1/Ω∙cm] | \( \alpha \) [µV/K] | \( \alpha^2 \sigma \) [W/mK²] | \( \lambda \) [W/mK] | \( Z \) [K^{-1}] |
|-------------|----------------------|---------------------|-------------------------------|---------------------|---------------|
| \( \text{Bi}_2\text{Te}_3 \) | 1000                 | 200                 | 4,0\cdot10^{-3}               | 1,6                 | 3,0\cdot10^{-3} |
| \( \text{PbTe} \)        | 450                  | 20                  | 2,6\cdot10^{-3}               | 2,0                 | 1,2\cdot10^{-3} |
| \( \text{SiGe p-type} \) | 758                  | 144                 | 1,6\cdot10^{-3}               | 4,8                 | 3,3\cdot10^{-4} |
| \( \text{SiGe n-type} \) | 990                  | -136                | 1,8\cdot10^{-3}               | 4,45                | 4,1\cdot10^{-4} |
| \( \text{Cu} \)          | 580000               | 1,83                | 1,9\cdot10^{-4}               | 398                 | 4,8\cdot10^{-7} |
| \( \text{Ni} \)          | 138889               | -19,5               | 5,3\cdot10^{-3}               | 90,5                | 5,9\cdot10^{-5} |
| \( \text{Ti} \)          | 23810                | 9,1                 | 2,0\cdot10^{-4}               | 21,9                | 9,1\cdot10^{-6} |

The electrical conductivity (\( \sigma \)), the Seebeck coefficient (\( \alpha \)), the thermoelectric power factor (\( \alpha^2 \sigma \)), the thermal conductivity coefficient (\( \lambda \)) and the thermoelectric figure of merit (\( Z \)) for chosen metals and semiconductors are presented in Table 1. Metals have highest values of the electrical conductivity. However, the \( ZT \) (\( Z \)) of these materials are even 3-4 orders lower than in the case of the alloy materials. Semiconductors are characterized by much higher values of Seebeck coefficient, which affects the value of \( Z \) in a second power (eq. 2). Their thermal conductivity is significantly lower than in the case of metals. Such parameters, despite the high electrical conductivity, causes that the thermoelectric figure of merit \( Z \) for metals is in the range \( 10^6 - 10^5 \) [K^{-1}]. Raw semiconducting alloys are characterized by the values of the thermoelectric figure of merit \( Z \) from the range of \( 10^5 - 10^3 \) and the suitable modification can improve it.
4. The polymer thermoelectric materials
The technologies of the 21st century pay attention to the environment burden and the regulations in this field are becoming more and more restrictive. The recovery and reuse of raw materials are also nowadays very important. Alloy inorganic materials burden the environment through the life cycle of the ore, refining processes and scrap materials. The synthesis and molding processes are high energy consuming thus, the costs of the products are high, but the recovery and recycling of waste are negligible. Environmentally friendly technology should eliminate or at least limit the use of heavy metals and reduce the energy consumption of the production processes.

Conductive polymers can be a good complement to the classic alloy materials, reducing the environmental burden due to their chemical composition, lower manufacturing and processing costs and the recycling ability. Polymers are lightweight, can be formed in variety of shapes [5, 8, 9] and are thermoelectrically active at the ambient temperature. It is still a relatively new group of materials so even a slight change in their properties may become a breakthrough in the field of the waste heat conversion, removal and recovery [10]. The modified conductive polymers may have the value of the thermoelectric power factor (\(\alpha/\sigma\)) from 10\(^{-8}\) up to 10\(^{-3}\) W/mK\(^2\) and Seebeck coefficient from several to hundreds µV/K. These properties are listed in Table 2 for the selected materials. In the case of these materials the properties are comparable to the alloy materials. The maximum value of the conductivity of polyacethylene reaches 10\(^6\) S/cm, which is comparable to metals. Lower values are observed for other polymers [11]. This shows how the different modification methods effect the polymer and how important is the choice of the modifier.

| Table 2. The properties of the selected conductive polymers [5, 7, 12, 13] |
|---------------------------------------------------------------|
| Polymer                  | Modifier | \(\sigma\) \([Ω\cdot cm]^{-1}\) | \(\alpha\) [µV/K] | \(\alpha^2\sigma\) [W/mK\(^2\)] |
|--------------------------|----------|---------------------------------|-----------------|-------------------------------|
| Polyacethylene (PAC)     | -        | 6405                            | 20,6            | 2,7\(\times\)10\(^4\)       |
|                          | I*       | 60000                           | 15              | 1,3\(\times\)10\(^5\)       |
| Polyaniline (PANI)       | -        | 18                              | 3               | 1,6\(\times\)10\(^6\)       |
|                          | CSA*     | 200                             | 10              | 2,0\(\times\)10\(^6\)       |
| Polypyrrole (PPY)        | -        | 26                              | 5               | 6,5\(\times\)10\(^6\)       |
|                          | PANI     | 15                              | 7               | 7,4\(\times\)10\(^6\)       |

*I – iodine
**CSA – camphor sulfonic acid

5. Experimental
Polyaniline was chosen by the authors because of its properties typical for polymers i.e. good heat resistance, environmental and chemical stability. PANI can be compounded with other materials common in the industry (e.g. metals, glass, plastics) in the form of composites and layer systems. The main problem in the practical application is improving its thermoelectric efficiency. The modification with the use of the protonic acids or conducting additives is referred to be the solution to improve the thermoelectric efficiency [14].

The authors obtained products based on polyniline with the parameters shown in Table 3. Both materials were obtained by chemical oxidative method at a temperature of 0-5 °C. The synthesis method was comprehensively described in [15]. The PANI-HCl material is the polyaniline protonated with hydrochloric acid, the PANI-HCl-Ag is its composite filled with 20% wt. of silver. The raw materials: aniline 95% (Chempur), hydrochloric acid 35 – 37% (Chempur) and silver nanopowder <100 nm 99,5% (Sigma Aldrich) were used as purchased.
The measurement of Seebeck voltage, which determines the Seebeck coefficient $\alpha$ in accordance with equation (1) was carried out with a temperature gradient of 300 - 453 K using a digital multimeter HP34401A. The degradation temperature $DT$ was determined by thermal analysis performed on TGA/DSC1 Mettler Toledo. Thermal conductivity $\lambda$ was measured by Poensgen method and the resistivity $\rho_v$ using Keithley 6517. The value of the thermoelectric figure of merit $ZT$ at 453 K was determined according to equation (2). The materials should be applied at temperatures below 550 K. Their efficiency $ZT$ is similar to that of the unmodified alloys, and the Seebeck coefficient is significantly greater.

| Material         | $\rho_v$ [Ω·cm] | $\lambda$ [W/mK] | $\alpha$ [µV/K] | $ZT$          | $DT$ [K] |
|------------------|-----------------|------------------|-----------------|--------------|---------|
| PANI-HCl         | 19,57           | 0,18             | 2193,55         | 6,19$\cdot$10$^{-2}$ | 573     |
| PANI-HCl-Ag20    | 16,43           | 0,22             | 3290,32         | 1,36$\cdot$10$^{-1}$ | 598     |

6. The low-temperature waste heat sources and the standard methods of the waste heat recovery

The low-temperature waste heat sources may have different physical form and geometry, as well as chemical nature and corrosivity. The thermal and power output characteristics of such heat sources may also be various, thus waste heat can be generated at the different temperature levels and different thermal power. The waste heat is generated in almost all of the energy conversion processes, especially in the following branches of the industry and households [16]:

- **power engineering** (exhaust gases 250 - 1200°C, coolants 40 - 150°C, solid and liquid waste 40 - 200°C, hot surfaces 40 - 400°C, waste steam 150 - 350°C),
- **chemical industry** (gases 100 - 600°C, liquids 40 - 200°C, hot surfaces 40 - 300°C),
- **food industry** (liquids 40 - 100°C, cooling air 50 - 100°C, hot surfaces 40 - 400°C),
- **metallurgy** (exhaust gas 250 - 1200°C, process gases 300 - 1400°C, coolants 40 - 150°C, solid and liquid waste 40 - 200°C, hot surfaces 40 - 700°C),
- **motorization** (exhaust gases 500 - 1100°C, coolants 40 - 100°C, hot surfaces 40 - 500°C),
- **households** (flue gases 150 - 300°C, liquids 40 - 90°C).

The main available technologies for waste heat recovery from such sources are external combustion engines [16], and steam power plants (e.g. Kalina and Organic Rankine Cycle). The detailed description of these systems, with principle of their operation was comprehensively described in [16] and [17]. The main disadvantages of these systems is limited and relatively low efficiency and high investment costs. Thermoelectric material can be used for direct waste heat recovery from the heat source without the necessity of applying the expensive and low efficient heat engines. Thus, the thermoelectric materials are very interesting and perspective for the waste heat recovery when compared with the currently used technologies.

7. Summary and conclusions

In this paper the comparison of the different thermoelectric materials possible for application in the waste heat recovery and cooling of devices was presented. In particular the alloy-based and the polymer thermoelectric materials were analysed. Moreover the results of the experimental analyses of the specially designed thermoelectric polymers were here presented. The results of the comparison and experimental works proves the following conclusions:
• The composites based on polyaniline can be a complement for alloy materials at lower temperatures,
• The thermoelectric parameters of thermoelectric polymers are promising,
• These materials may be formed in variety of shapes (coatings, bulk products) and compounded with other materials (glass, plastics, metals), what is the advantage in comparison with the currently used waste heat recovery technologies.
• The discussed examples of the waste heat sources show the proper conditions (temperature range and gradient) for the application of the materials based on polyaniline.

8. References
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