

Resistivity mapping: An example of aged conducting polymer

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Abstract

A simple multi-contact measurement method, which can be used to map the electrical resistivity of small disc-shaped samples of conducting polymer during temperature ageing, was examined for its resolution and accuracy. The method is based on electrical impedance tomography (EIT), which is used especially in medicine to visualise boundaries between areas having different electrical resistivities. In order to eliminate experimental errors, a computer simulation was used for testing. The time series of resistivity maps were recorded during ageing of real polymer samples. The contour maps and their time development are presented graphically and discussed.

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1. Introduction

In present-day polymeric materials science, a lot of attention is paid to stability of key properties of polymers [1]. In the case of conducting polymers, the high electrical conductivity (low resistivity) belongs undoubtedly to the most important properties [2–6]. In order to get valuable information about the time development of electrical resistivity during ageing, the resistivity of tested materials is usually observed *in situ*. It is often measured using four-probe methods, which eliminate voltage drop on current leads. The van der Pauw (VDP) technique [7–9] is frequently used, because it does not need defined sample geometry. The detailed shape and position of contacts are not important, but the sample area must be singly connected. The VDP method can also be modified to measure anisotropic materials [10], but even in this case, the resistivity tensor is assumed to be constant in the whole sample.

Nevertheless, measured samples are often inhomogeneous – the resistivity is a function of position. In such cases,

measurement of the resistivity implicitly includes averaging of the resistivity of each region in the sample. Then the result does not depend only on the particular applied method, but even using the same method, the results can differ for various placements of contacts. A local increase of the resistivity near contacts can cause a decrease of the measured (“average”) value in certain four-probe configurations [11]. This means that “the statistical weight” of various areas differs and can even be negative [12]. The VDP method eliminates regions of negative weighting, but the weighting function value still increases towards the centre of the sample. Effects of resistive inhomogeneities on VDP measurement results were studied together with other error factors (namely the finite contact size and the displacement from the edge of the sample) for various sample shapes [13,14].

Samples provided with contacts at the edge can be measured by electrical impedance tomography (EIT) [15], which gives information about the distribution of the resistivity in the sample. EIT is based on solution of inverse problem to a common task: let us find the distribution of electric field potential $\phi(x, y, z)$ in source-free purely resistive region, when conductivity distribution $\sigma(x, y, z)$ is given. The boundary condition

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$$J_n = \sigma \frac{\partial \phi}{\partial n} \quad (1)$$

specifies the normal component of the electric current density on the surface of the region. Here, $\partial \phi / \partial n$ is the normal derivative of the potential to the surface. The solution of forward problem must satisfy the partial differential equation

$$\sigma \nabla^2 \phi + \nabla \sigma \cdot \nabla \phi = 0. \quad (2)$$

It is usually solved numerically.

To solve the inverse problem, we determine conductivity distribution inside the region from the potential measurements made on its surface for known current density applied to the surface. The back-projection algorithm is one of the very simple single-pass algorithms, which are based on an assumption that the inverse problem is linear [16].

The present article concerns the potential of EIT usage for mapping the resistivity of flat circular polymeric samples. The next sections describe briefly the chemical process of sample preparation and the experimental equipment we use for temperature ageing together with *in situ* resistivity measurement. Further we deal with theoretical restrictions of the method, which follows from the limited number of the contacts on the sample. On the basis of the computer simulation, we have tested the reliability of EIT resistivity maps obtained in our particular configuration. We present the results in graphical form. An independent method used for simultaneously watching the resistance of contacts is described. The development of the resistivity of the polymeric samples during ageing is presented in a form of series of resistivity maps. EIT results are compared to the information we obtained from a couple of independent VDP measurements performed simultaneously on the same sample.

2. Experimental

2.1. Sample preparation

Aniline hydrochloride (0.20 M) was oxidised with ammonium peroxydisulfate (0.25 M) in an aqueous medium at room temperature [17]. PANI precipitate was collected, deprotonated to PANI base in an excess of 1 M ammonium hydroxide, and reprotonated in 1 M aqueous solutions of *p*-toluenesulfonic acid (TSA) or *o*-aminobenzenesulfonic acid (OA; orthonilic acid). The dried samples were compressed into tablets of 13 mm diameter and *ca.* 1 mm thickness with a manual hydraulic press at 700 MPa. The top surface of each sample was provided with eight equally spaced gold electrodes (1 mm in diameter) by vacuum deposition. We denote the electrodes sequentially by numbers 1–8 (Fig. 1).

2.2. Measurement setup

The holder with positions for two simultaneously measured samples was placed in a Heraeus–Vötsch VMT 07/35 thermostatic chamber (operating between -70°C and $+180^\circ\text{C}$ with

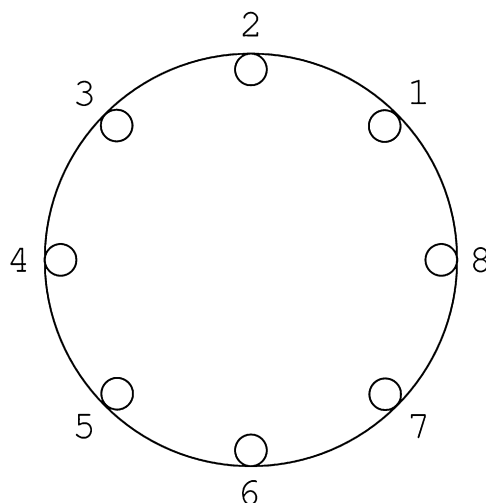


Fig. 1. The figure describes the sample geometry. The top surface of each sample is provided with eight equally spaced gold electrodes (1 mm in diameter).

stability $\pm 1^\circ\text{C}$). The exact temperature of both samples was measured with copper-constantan thermocouples (switched by the 7057A scanner card mentioned below) and a Keithley 195 multimeter before and after each resistivity measurement.

The electrodes on the samples were connected to measurement circuits by probes made from twisted platinum wire. (Combination of platinum wires with golden contacts is sufficiently resistant to aggressive acids which can evaporate during ageing.) Besides the above mentioned chamber and multimeter, the PC controlled experimental equipment for resistivity measurement included a Keithley 238 current source, a Solartron-Schlumberger 7081 voltmeter and a Keithley 706 scanner equipped with four 7164D dry-reed-relay cards and a 7057A thermocouple multiplex card. The connections to devices and probes were configured as a matrix, which enabled the control program to connect the output of current source to any pair of probes and simultaneously read the voltage between probes of another pair. This made possible to alternate VDP and EIT measurements on the same samples.

2.3. van der Pauw procedure

It has already been mentioned that VDP procedure requires four point-like contacts at the edge. Let us denote them sequentially A, B, C and D. We assume that the sample is thin and homogeneous. In order to obtain the resistivity value, several independent measurements are necessary. Initially, applying the current I_{AB} on the contact pair A–B, we measure the voltage difference U_{CD} between contacts C and D. (The current must be sufficiently small to avoid joule heating of the sample.) It is suitable to repeat this measurement for the opposite current $I'_{AB} = -I_{AB}$ to eliminate voltage contributions whose polarity does not depend on current direction (namely contact potentials). Let us denote the resistance $R_{AB,CD} \equiv \frac{1}{2}(U_{CD}/I_{AB} + U'_{CD}/I'_{AB})$. Then we analogously obtain the value $R_{BC,DA}$. The resistivity of the sample can be evaluated from the following equation [7–9]

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