

**THE ROLE OF HYDROSTATIC PRESSURE ON
THE D.C. CONDUCTIVITY OF FRESH AND
THERMALLY AGED
POLYPYRROLE-POLYANILINE CONDUCTIVE
BLENDS**

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Abstract. In the present work we investigate the effect of hydrostatic pressure on the electrical conductivity of polypyrrole-polyaniline conductive (protonated) blends of various compositions. Results are presented for thermally aged blends, as well. The modification of the conductivity on pressure is more pronounced in the fresh samples than in the de-doped ones. The phenomenon is discussed within the frame of the granular metal. The percentage variation of the conductivity upon pressure variation for the polypyrrole rich blends is not influenced from the aging process. This feature suggests that these blends could possibly be used as pressure sensors, which are insensitive to the thermal aging.

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1. Introduction

A serious disadvantage of the conductive polymers is the degradation of their electrical conductivity caused by a thermal treatment. The polyaniline and the polypyrrole are exceptionally stable under environmental conditions. In the present work, we study the effect of the hydrostatic pressure on the d.c. electrical conductivity of non aged and thermally aged polypyrrole-polyaniline blends. The scope is to investigate the role of the hydrostatic pressure on the percentage variation of the conductivity as a function of the polypyrrole-polyaniline composition of fresh and thermally treated blends. Both polymers have an inhomogeneous structure of the granular metal type and the thermal degradation of the conductivity is attributed to the reduction of the size of the conducting islands [1, 2]. On the other hand, the thermal degradation of the conductivity occurs by the reduction of the size of protonated "islands" in polyaniline, while a homogeneous reduction of the density of polarons is observed in polypyrrole [1, 2]. This article also reports on the possibility of using these conductive polymer blends as pressure sensors.

2. Discussion

The conductive samples of polypyrrole-polyaniline blends were made from freshly distilled monomers (Merck) under vacuum in the proper ratio polymerized in the presence of FeCl_3 (Merck) as oxidant in HCl acid-water solutions at $\text{pH} = 2.00$ in an ice bath (monomers/oxidant = 1:1 mol/mol) under nitrogen atmosphere. The blends were obtained as black powders, purified by Soxhlet extraction for 36 h [3]. The composition of the samples varied from pure polypyrrole to pure polyaniline with increasing gradually by 10 % of the one constituent against the percentage of the other. Disc shaped specimens 13 mm in diameter and about 1.5 mm thick were then produced by pressing the powder. The thermal aging of the samples was performed at 70°C at ambient atmosphere for about 600 h. The conductivity experiments were performed in a piston-type pressure vessel operating at room temperature up to 0.3 GPa. Details are given in [4].

A typical plot of the logarithm of the conductance G of a virgin sample of 90 wt % polypyrrole as a function of pressure is depicted in Fig. 1. The hysteresis phenomena observed in the low-pressure limit are attributed to the porosity closure on compression. The contribution of the alteration of the porosity is weak and, therefore, the modification of the conductivity results from the change of the intrinsic (bulk) properties of the polymer. In our analyses, the high-pressure data are employed to obtain information for the polymer. The first order pressure derivative of the logarithm of the conductivity against the percentage weight content x of polypyrrole in the different blends is shown in

Fig. 2. $\frac{d \ln \sigma}{dP}$ varies from 0.7 to 1.1 GPa⁻¹ and from 0.4 to 0.9 GPa⁻¹ for the virgin (protonated) and the aged samples, respectively. $\frac{d \ln \sigma}{dP}$ reduces slightly upon x in the virgin samples. A linear fit to the experimental data-points yields:

$$\frac{d}{dx} \left(\frac{d \ln \sigma}{dP} \right) = -(5 \pm 1) \times 10^{-12} \text{ Pa}^{-1}.$$

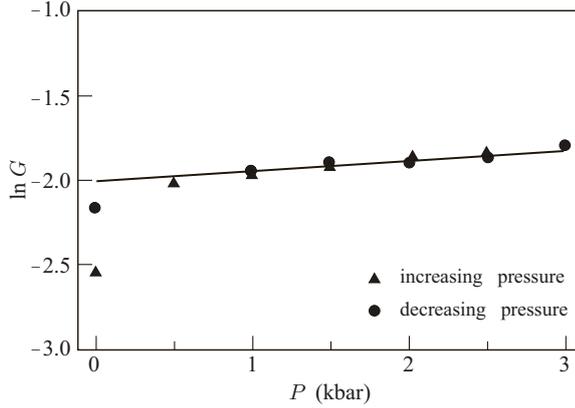


Fig. 1. The logarithm of the conductance G of a virgin sample of 90 wt% polypyrrole as a function of the hydrostatic pressure. The triangles were obtained on pressurization and the circles on pressure release. Error bars are comparable to the size of the data points. The line was fitted to the high-pressure region

From Fig. 2 we see that although in the fresh samples there is a slight decrease of $\frac{d \ln \sigma}{dP}$ with increasing polypyrrole content x , in the aged samples the percentage variation of the conductivity σ under pressure seems to be independent from the particular composition of the blends. The thermal aging is a very complicated process including de-doping by the removal of the HCl, oxidation/hydrolysis/scission and crosslinking of the chains [5]. In the granular metal model where the thermal aging causes the reduction of the conductive islands, pressure is expected to cause relatively a greater effect on the fresh samples in which the distance separating the conductive islands are shorter.

In spite the thermal degradation of σ in conducting polymer, the relative change $\frac{\sigma_0 - \sigma}{\sigma_0}$, where σ_0 is the conductivity of the non-aged samples, reaches a saturation with increasing the time of thermal treatment. The percentage variation of the conductivity upon the pressure variation is not influenced from

the aging process for specimens that are rich in polypyrrole. For $x \approx 100\%$, the percentage variation of the conductivity upon pressure is practically insensitive to the thermal aging. For this reason, the polypyrrole-rich blends are possible candidates as stable pressure sensors.

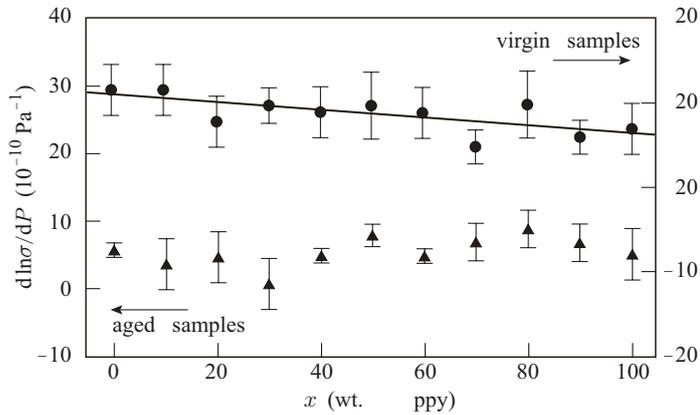


Fig. 2. The percentage variation of the conductivity upon pressure changed as a function of the percentage weight content x in polypyrrole (ppy). The temperature was maintained constant at 295 K

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