

RAPID COMMUNICATION

Effect of hydrostatic pressure on the d.c. conductivity of fresh and thermally aged polypyrrole–polyaniline conductive blends

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Received 2 April 2002

Published 16 August 2002

Online at stacks.iop.org/JPhysD/35/L85

Abstract

In this paper 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 due to pressure is more pronounced in the fresh samples than in the aged ones. The phenomenon is discussed within the frame of the granular model. The percentage variation of the conductivity upon pressure change for the polypyrrole rich blends is not influenced by the ageing process. This feature suggests that these blends could possibly be used as pressure sensors, which are insensitive to thermal ageing.

1. Introduction

A serious disadvantage of conductive polymers is the degradation of their electrical conductivity caused by thermal treatment. Polyaniline and polypyrrole are exceptionally stable under environmental conditions. In this paper, we study the effect of hydrostatic pressure on the d.c. electrical conductivity of non-aged and thermally aged polypyrrole–polyaniline blends. The aim is to investigate the role of 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 in size of the conducting islands [1, 2]. On the other hand, what distinguishes the two conductive polymers is that different laws govern the change

of their conductivity versus temperature, suggesting that the distance between conductive grains in polypyrrole is less than in polyaniline, while a homogeneous reduction of the density of polarons is observed in polypyrrole [1, 2]. This paper also reports on the possibility of using these conductive polymer blends as pressure sensors.

2. Results and 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 FeCl₃ (Merck) as oxidant in HCl acid–water solutions at pH = 2.00 in an ice bath (monomers/oxidant = 1 : 1 mol mol⁻¹) 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 gradual increase, by 10%, in the percentage one constituent compared to the other. Disc

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shaped specimens 13 mm in diameter and about 1.5 mm thick were then produced by pressing the powder in an IR press. The thermal ageing 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 figure 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 in the intrinsic (bulk) properties of the polymer. In our analyses, the high-pressure data are employed to obtain information on the polymer. The first order pressure derivative of the logarithm of the conductivity against the percentage weight of content x of polypyrrole in the different blends is shown in figure 2. $d \ln \sigma / dP$ varies from 0.7 to

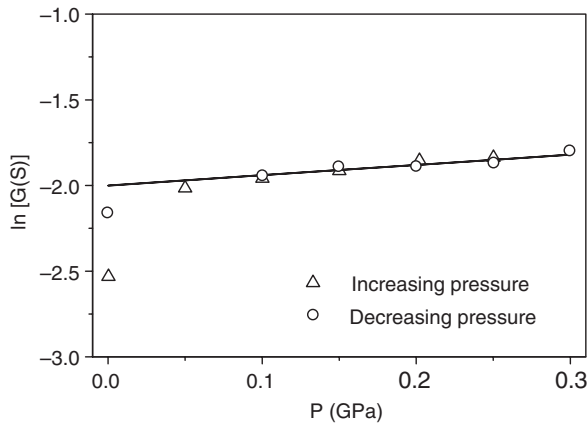


Figure 1. The logarithm of the conductance G of a virgin sample with 90% wt polypyrrole as a function of the hydrostatic pressure. The triangles were obtained at no pressurization and the circles on pressure release. Error bars are comparable to the size of the data-points. The line was fitted to the high-pressure region.

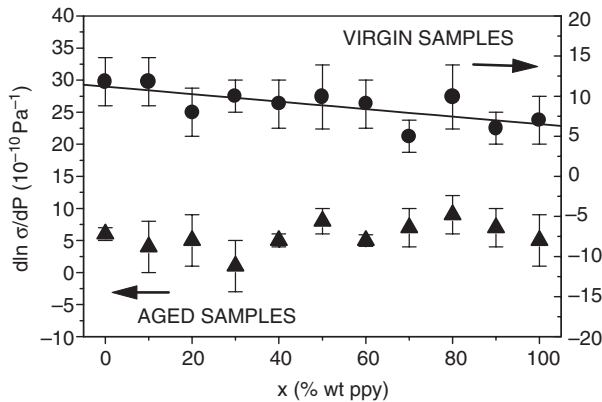


Figure 2. The percentage variation of the conductivity upon pressure change as a function of the percentage weight content x in polypyrrole (ppy). The temperature was maintained constant at 295 K.

1.1 GPa^{-1} and from 0.4 to 0.9 GPa^{-1} for the virgin (protonated) and the aged samples, respectively. $d \ln \sigma / dP$ reduces slightly with x in the virgin samples. A linear fit to the experimental data-points yields

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

From figure 2 we see that although in the fresh samples there is a slight decrease of $d \ln \sigma / dP$ with increasing polypyrrole content x , in the aged samples the percentage variation of the conductivity σ under pressure seems to be independent of the particular composition of the blends. The quantity d labels the departure of the value $d \ln \sigma / dP$ of the virgin samples from the value corresponding to the aged ones ($d \equiv (d \ln \sigma / dP)_{\text{virgin}} - (d \ln \sigma / dP)_{\text{aged}}$). In figure 3, where d is plotted as a function of x , we observe that the variation of d upon pressure variation is not influenced significantly by the ageing process as x tends to 100%. Thermal ageing is a very complicated process including de-doping by the removal of HCl, oxidation/hydrolysis/scission and crosslinking of the chains [5]. In the granular metal model where thermal ageing causes a reduction of the conductive islands, pressure is expected to have a relatively greater effect on the fresh

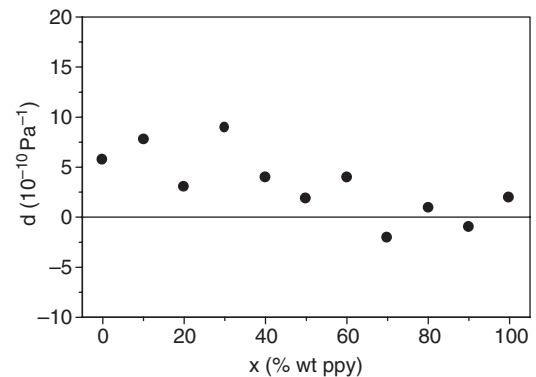


Figure 3. The difference d between the value $d \ln \sigma / dP$ of the virgin samples and the value corresponding to the aged ones as a function of x .

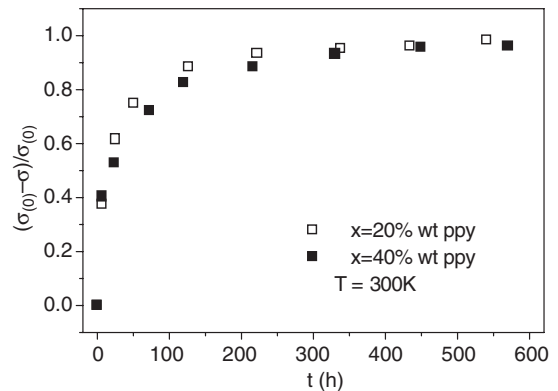


Figure 4. The relative change $(\sigma_0 - \sigma) / \sigma_0$, where σ_0 is the conductivity of the virgin specimen, of two samples, 20% and 40% polypyrrole wt system, with increasing time of thermal treatment.

samples in which the distance between the conductive islands is smaller.

3. Conclusion

Despite the thermal degradation of σ in the conducting polymer, the relative change $(\sigma_0 - \sigma)/\sigma_0$, where σ_0 is the conductivity of the non-aged samples, reaches saturation with increasing time of thermal treatment as shown in figure 4. The percentage variation of the conductivity with pressure variation is not influenced by the ageing process for these specimens that are rich in polypyrrole. For $x \rightarrow 100\%$, the percentage variation of the conductivity with pressure is

practically insensitive to thermal ageing. For this reason, the polypyrrole-rich blends are possible candidates for stable pressure sensors.

References

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