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# Temperature- and Humidity-Related Degradation of Conducting Polyaniline Films

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**Summary:** The time dependence of dc conductivity of conducting polyaniline films was measured in relation to temperature and relative humidity of the environment. Optical and structural properties of the samples were checked using Fourier transform infrared (FTIR) spectroscopy.

**Keywords:** ageing; conducting polymers; humidity; polyaniline; temperature

## Introduction

Polyaniline (PANI) has been reported as a material having one of the best environmental stabilities among conducting polymers[1,2]. However, this is true mainly for its non-conducting form, emeraldine base, while the more interesting conducting form, protonated emeraldine salt, is much less stable. The decay of the electrical conductivity with time under environmental conditions is an undesirable phenomenon, which sets fundamental restrictions to possible technical applications, and, so far, it has not been satisfactorily solved. The variations of conductivity of PANI can be related to both intrinsic and external factors. The former are related to polymer structure through the perfection of quinoid and benzenoid unit repetition, the chain ordering, and the dopant selection. The latter are linked to the conditions of the ageing tests through the effect of the atmosphere and temperature. The decline of the conductivity of protonated PANI appears as a result of combination of these factors, which can interact through different mechanisms (loss of conjugation, chain degradation, deprotonation, oxidation, and crosslinking)[3]. Therefore, a simplification becomes crucial. In this work, our interest is reduced to the effect of the two most common factors, temperature and humidity, on ageing of direct-

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current conductivity (dc) of PANI.HCl films. An attempt to describe the observed behaviour as a sum of two parallel processes is presented.

## Experimental

**Preparation of samples.** PANI hydrochloride was prepared by the oxidation of aniline hydrochloride (0.20 M) with ammonium peroxodisulfate (0.25 M) in dilute hydrochloric acid[4]. The films were polymerized in situ on substrates immersed in the reaction mixture. Disc-shaped glass supports, 13 mm in diameter, with deposited gold electrodes, were used for dc measurement, while doubleside-polished crystalline silicon substrates were coated for FTIR spectroscopy study.

**Properties.** The average conductivity of the films polymerized on glass supports was of the order 10 S $cm^{-1}$. The average film thickness was assumed to be 130 nm, which was determined by Stejskal et al.[4] from the correlation between interferometric and absorption measurements.

**Equipment.** *The dc conductivity* ($\sigma$) was measured by the four-point van der Pauw method[5]. The sample holder was placed in a humidity chamber Heraeus-Vötsch VLK 07/35 operating in temperature range from +5 °C to +90 °C and at relative humidity (RH) from 30 % to 90 %. *Thickness* of several samples was checked on a Surfometer SF200 (Planer Products Ltd.) or Taly Step (Taylor Hobson Taly Step Surface Profiler S/N) and the values obtained were in good agreement with the previous result[4]. *Infrared measurements* were performed on a Nicolet Impact 400 FTIR spectrometer. The transmission spectra in the range 400 – 4000 $cm^{-1}$ with 2 $cm^{-1}$ spectral resolution were obtained on films deposited on silicon substrates.

**Regime.** Samples are put into a chamber to following conditions:

1. start-up conditions (25 °C, 50 % RH) - for 2 h
2. at 25 °C the RH is set to 30 %, 45 %, 60 %, 70 %, 75 %, or 90 % - for 17 h
3. RH is held at the same value, the temperature is elevated to 90 °C. - for 85 h

## Results and Discussion

**Time variations of dc conductivity at constant increased temperature and various relative humidities.** Dc conductivity was measured as a function of time at increased temperature, relative humidity was set to 30 – 90 % according to the regime described above. In this work, the data of the 90 °C series are presented. Time dependence of conductivity of PANI.HCl films aged at 90 °C at four humidities is shown in Figure 1 (the time scale begins just after the temperature 90 °C was stabilized; see Regime/step 3 above). The shape of curves depends remarkably on RH. Initially, a simple decrease in conductivity with time, $\sigma(t)$, is a response to the previous temperature increase. Subsequently, the shape of $\sigma(t)$ strongly depends on RH. It reaches a constant value for lower RH (30 % < RH < 60 %), while for higher RH (70 % < RH < 90 %) it is growing.

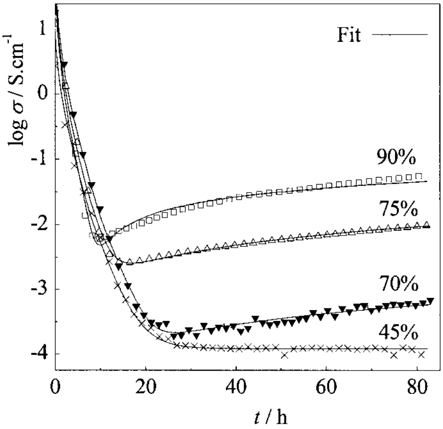

Figure 1. Time dependence of dc conductivity, $\sigma$, of PANI.HCl at 90 °C and various relative humidity; the fit (4) to experimental curves $\sigma = \sigma_D \exp[-(t/t_D)^{1/2}] - \sigma_R \exp(-t/t_R) + \sigma_\infty$

There are three possible reasons for the initial steep decrease in conductivity mentioned in literature most often[6–9]. These are: (1) loss of moisture, as most of the ageing experiments have been carried out in ambient atmosphere and only the effect of elevated temperature was followed, (2) oxidation due to diffusion of oxygen, (3) deprotonation. As to the morphology, PANI may be considered as a heterogeneous structure consisting of conducting grains (polaronic clusters) embedded in insulating, less ordered regions[10]. In this case the decrease in conductivity can be correlated with a decrease in grain size[7,11,12].

Long-term evolution of $\sigma$ was studied[7] for another conducting polymer, polypyrrole, which shows similar properties to PANI in many respects. Polypyrrole pellets or coatings on various substrates were annealed at elevated temperature in ambient atmosphere. For $t > 40$ h, the fitting of $\sigma_1(t)$ according to stretched exponential of the ageing time $t$ was successful

$$\sigma_1(t) = \sigma_D \exp[-(t/t_D)^{1/2}] \tag{1}$$

where $\sigma_D$ is an initial dc conductivity value and $t_D$ is the characteristic time of the degradation process. (1) gave satisfactory results from the very beginning of the ageing process and the $t_D$ parameter was used to characterize the stability of the materials under study[7,11,12].

The use of Eq. (1) to our samples brings good results for ageing at low RH, while the subsequent increase in conductivity at higher RH requires introduction of another term, closely related to the presence of water in the material, which would act against the conductivity loss. If we assume that the measured changes of conductivity are attributed to development of the conducting grain size, we can refer to the "variable-size conducting-island" model proposed by Kahol[8]. It is based on the concept that the absorbed water increases the effective size of conducting grains. Assuming in the first approximation that degradation and recovery processes develop independently, we can treat the total conductivity $\sigma(t)$ of a film as a sum of the final conductivity $\sigma_\infty$ of the aged film at time tending to infinity and two time-dependent terms

$$\sigma(t) = \sigma_1(t) + \sigma_2(t) + \sigma_\infty \tag{2}$$

where $\sigma_2(t)$ is the dc conductivity associated with the recovery process occurring under given conditions.

For establishing the recovery component $\sigma_2(t)$, let us consider the processes that are likely to occur. There is the diffusion of water molecules to the interior of the sample. Rannou[3] and Travers[13] estimated the diffusion coefficient $D \sim 10^{-9}$–$10^{-10}$ cm$^2$ s$^{-1}$ for their samples. Taking into account the average thickness of our samples (~100 nm) and that range for $D$, we can say that our films reach the equilibrium with environment within seconds, which is negligible compared with ageing times of $5\times10^5$ s. Having been absorbed in the polymer, the water molecules enhance (probably through the gradually increasing grain size[8]) the electric charge transfer. Let us assume for the recovery component

$$\sigma_2(t) = -\sigma_R \exp(-t/t_R) \tag{3}$$

where $\sigma_R$ and $t_R$ are characteristic parameters of the recovery process. According to Eqs. (1), (3) and the initial assumption (2), the final conductivity can be expressed as

$$\sigma(t) = \sigma_D \exp[-(t/t_D)^{1/2}] - \sigma_R \exp(-t/t_R) + \sigma_\infty \tag{4}$$

The fit of Eq.(4) to experimental curves is shown in Figure 1. The data from long-term ageing were analysed according to the classic model Eq. (1) and the model with the recovery process given by Eq. (3). For low RH, the fit parameters calculated according to both models give close values, while at RH > 60 % the fit (1) is not satisfactory. Following figures illustrate the dependence of the mean fit parameters on RH. Figure 2 offers information about the parameters related to the degradation process. The time $t_D$ is interpreted as a main measure of the resistance to ageing. It is not very sensitive to RH; it is of the order of $10^2$ s for each of the tested samples.

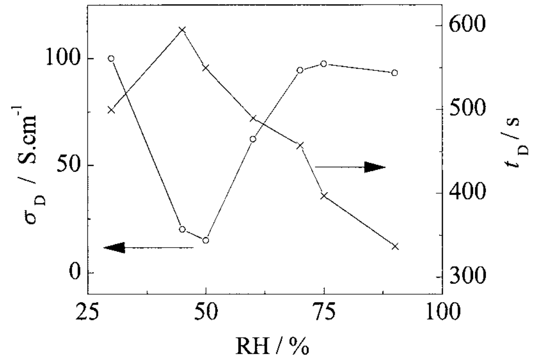

Figure 2. Dependence of the fit parameters $\sigma_D$ and $t_D$ on RH

However, while the stability at both low and high RH decreases, it reaches the maximum at RH 45 %. This may follow from the fact that the samples, which were prepared in air, are close to equilibrium conditions at RH ca. 45 %. The conductivity $\sigma_D$ is associated with the volume fraction of the polymer that can be degraded while ageing. It shows the minimum at RH 50 %, where, according to $t_D$, the highest stability can be expected. The RH dependence of parameters $t_R$ and $\sigma_R$ on RH, related to the conductivity recovery process, is shown in Figure 3. Similarly to the degradation, $t_R$ is a measure of the recovery process and $\sigma_R$ relates to the conductivity of the volume fraction that is able, at given RH, to react with the absorbed water, which results in an increase in conductivity. Obviously, the decreasing $t_R$ parameter and increasing $\sigma_R$ reflect a direct correlation with the fact, that the recovery process is induced by the presence of water.

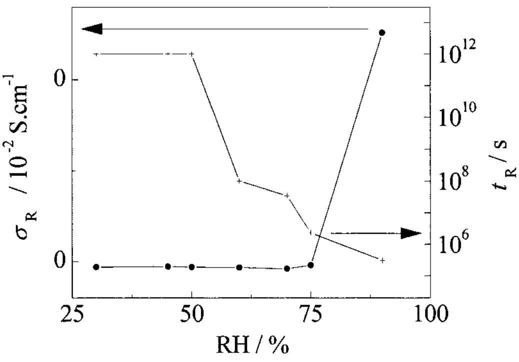

Figure 3. Dependence of the fit parameters $\sigma_R$ and $t_R$ on RH

**FTIR spectroscopic study.** Films were annealed in the humidity chamber together with those tested for dc conductivity. Infrared spectra were measured after the ageing (Regime/step 3) was finished. The FTIR spectrum of PANI.HCl film (curve 1) is shown in Figure 4.

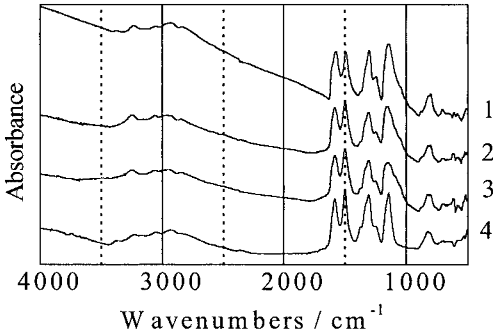

Figure 4. The FTIR spectra of PANI hydrochloride film

The spectra of samples annealed for 85 h at 90 °C and two values of RH are shown in the same figure (curve 2 – 30 %, curve 3 – 90 %). The spectrum of sample annealed at 120 °C for 30 min under ambient conditions (curve 4) is presented for comparison. The most significant feature of the annealed films is the disappearance of a broad band at wavenumbers higher than 2000 cm$^{-1}$, which is characteristic of the conducting form of PANI. It is more pronounced for the film annealed for 30 min at 120 °C. It is in good correlation with the decrease in conductivity of the samples, thus confirming the deprotonation of PANI.HCl film. Comparing the spectrum of the fresh film with the spectra of the annealed samples, we observe many changes which indicate deprotonation. The main peaks observed at 1578 $cm^{-1}$ and 1495 $cm^{-1}$ in the PANI.HCl film are blue-shifted to 1584 $cm^{-1}$ and 1502 $cm^{-1}$ in the spectra of films annealed at 90 °C for 85 h and exposed to different humidities (curves 3 and 4). The absorption band at 1308 $cm^{-1}$, the band observed at about 1240 $cm^{-1}$, characteristic of the conducting protonated form, and the 1140 $cm^{-1}$ band decreased in the spectra of films annealed at 90 °C and RH 90 % for 85 h (curve 3) and annealed at 120 °C under ambient conditions (curve 4). This confirms that deprotonation increases with humidity and temperature.

## Conclusion

Analysis of the time dependence of dc conductivity with respect to the two processes involved in ageing at elevated temperature and at various relative humidities has been presented. The recovery observed in dc conductivity is probably associated with the presence of water in the film. It is more pronounced for films annealed at higher relative humidity. Both the degradation and recovery processes are compatible with the concept of heterogeneous metallic structure[10] and can be correlated with changes in the conducting grain size[7,8,11]. Further analysis of the parameters obtained from fitting is envisaged. FTIR study brings evidence of deprotonation of the films related to the conditions of ageing. The degree of deprotonation increases with increasing both temperature and humidity. The structures in the presence of water are more pronounced in the samples annealed at higher RH. No evidence of the oxidation process expected in the paper by Sixou et al.[7] is apparent.

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