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Dielectric Relaxation Phenomena and Electric Properties of Conductive Composite Polyurethane/Polyaniline Films

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Summary: Composite polyurethane/polyaniline (PU/PANI) films have been chemically prepared by oxidative in-situ polymerization of aniline inside the previously swelled PU film. Swelling kinetic studies have shown that for PU films the swelling degree of aniline is 25 wt.%. The dielectric and electrical properties of the composite films were measured using dielectric relaxation spectroscopy and four-probe method. Dielectric measurements as a function of temperature and frequency revealed the presence of a relaxation process for the composite PU/PANI-HCl film. This relaxation was explained in terms of interfacial polarization due to the double-layered structure of the composite film. The activation energy values found by dielectric and electrical measurements are close and this result confirms the conducting character of the PANI containing layer.

Keywords: composites; conductivity; dielectric relaxation; doping; polyaniline; polyurethane

Introduction

Conducting polymers (PANI, polythiophene, polypyrrole, etc.) are the subject of great scientific interest due to their large potential applications in various fields such as antistatic coatings, electromagnetic screens, anti-corrosive materials and sensors.[1] Among the conducting polymers, PANI has attracted a great attention due to its chemical stability under ambient conditions, [2] high electrical conductivity, [2–4] a rather low cost of a monomer and simple synthesis. However, PANI possesses some disadvantages such as fragility and insolubility in common organic solvents.

It has been proposed that an improved mechanical stability can be achieved by the formation of a composite polymer material based on PANI and traditional polymers: polyethylene terephthalate (PET), polyamide (PA), polyvinylidene fluoride (PVDF), etc. [1] This composite material will, therefore, combine the high conductivity of the conducting polymer and the good mechanical properties of the polymer matrix. Unlike conductive composites obtained with mineral fillers (metal or carbon), which require a high concentration of the filler (~ 30 wt.%) and, consequently, degrade the mechanical properties of the polymer matrix, the percolation threshold for composites based on PANI is very low.[7]

A number of composite systems based on PANI has already been investigated,[1,5–7] but PANI blends with PU have not been completely characterised yet. Besides, PUs are a large class of polymers, displaying all kinds of mechanical behaviour - from hard

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plastics to soft rubbers, including various kinds of foams, coatings, etc.

It was found that the preparation method has a great influence on the final properties of the composite materials.[9,10] Several synthetic methods have been reported. The simplest one is a physical mixture of PANI with the PU matrix in a powder form. In this case the aniline is preliminarily polymerized in the presence of various acids (camphorsulfonic acid, *p*-toluenesulfonic acid, polystyrenesulfonic acid, polyacrylic acid). [3,9,11,12] Amado et al. have obtained composite films with various PANI concentrations ranging from 10 to 20% by using this method.[11] The disadvantage of this method is a weak dispersion of the conducting polymer in the insulating matrix. Also, the mechanical properties of such composite films are poor as high concentration of PANI is necessary for obtaining the conducting films.

The conducting composites can also be obtained by the polymerization of a PU matrix in the presence of PANI.[13,14] Malmonge et al. have obtained composite films with various thickness (varying between 30 and 100 μm) by moulding a mixture of PANI, pre-polymer and polyol on glass slides.[14] A percolation threshold at 5% of PANI is observed due to the formation of an interpenetrating network.

The last method consists in the aniline polymerization in the presence of the polymer matrix. PU films in various forms can be used (for example, PU reticulated with fullerenol,[10] water-based PU latex mixed with poly (N-vinylpyrrolidone),[15] aqueous dispersion of PU prepared from pre-polymers [16]). It was shown with the help of Scanning Electron Microscopy (SEM) measurements that the composite films prepared by this method are characterized by an homogeneous structure, while an inhomogeneous phase segregation of the PANI particles was observed in the case of the films prepared by other methods.[16]

The studies of the electrical properties of the composites have shown that the conductivity value depends on the acid nature,[3,11] on the PANI content[9,11] and on the chemical structure of the matrix.[5,6,12] Also, it was found that the properties of composite films depend on the organization of PANI conducting clusters in the polymer matrix.[5,6,16] On the other hand, the dielectric properties of composite systems based on PANI are still under investigation. Tabellout et al. have investigated the influence of PANI and the doping process on the dielectric properties of PET/PANI and polyamide-6 (PA-6)/PANI composite films.[6,7] Besides, Chwang et al. have shown that the permittivity ε_r of PU/PANI mixture increases with the content of PANI.[16]

Therefore, taking into account all foregoing, the present study reports the electrical and dielectric properties of the composite films obtained by *in-situ* aniline polymerisation in the PU matrix. The influence of the temperature as well as the oxidation state of PANI on the dielectric behaviour of the composite PU/PANI film is of great importance for further development in the fabrication if antistatic coatings.

Experimental Part

Materials

Aniline (p.a., Acros Organics), ammonium persulfate (APS) (98%, Acros Organics), hydrochloric acid (HCl) (37%, Prolabo), n-hexane (Prolabo), NH_4OH aqueous solution (25%, Prolabo) were used without additional purification.

The PU films used for the preparation of the composite films were synthesized in the Unité de Chimie Organique Moléculaire et Macromoléculaire of Université du Maine (France).[17]

Preparation of the PU/PANI Composites

It is a well-known fact that aniline polymerization in a polymer matrix may be achieved only under the matrix film swelling condition in the monomer solution. So, the swelling kinetics of PU film in aniline was investigated in order to determine the time necessary to get the maximum swelling value (Figure 1).

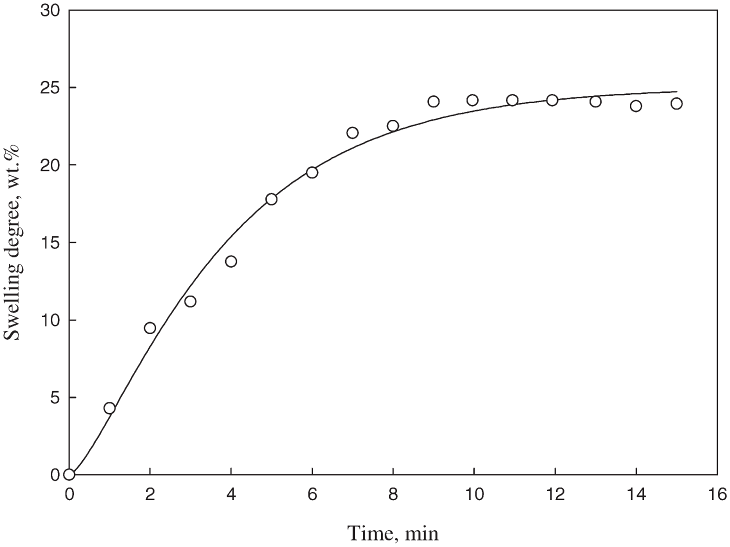

Figure 1.
Swelling kinetic curve of the PU film in aniline.

As one can see from Figure 1, the swelling process of PU film is rather quick in comparison with other polymers [5,8] after 10 min the plateau value of ~ 25 wt % of aniline is reached.

Thus swelled PU films were then subjected to *in-situ* polymerization in the solution of APS (0.1 M) in 1M water solution of HCl (oxidation solution). One-side conductive surface composite films were obtained using a home-built cell. [5] The cell construction prevents the other side of the polymer matrix to be in contact with the oxidation solution. The process of the formation of conducting surface composite films is schematically depicted in Figure 2.:

It is known that during the aniline polymerization the PANI-chain propagation results in the formation of the most conductive PANI form, the emeraldine salt. After the completion of the polymerization process, the green transparent film was taken off from the oxidation solution and placed in a Soxhlet's apparatus for 24 h in order to extract with n-hexane the by products and non-polymerized aniline. In order to study the composite PU/PANI films in the dedoped state, the composite films were treated with the water solution of 5% NH_4OH for 24 h (dedoping process). It should be mentioned that the polymerization process as well as all processes of doping-dedoping were performed at room temperature (25 °C).

The double-layered structure of composite films prepared by this method was confirmed with the help of Raman confocal spectrometry in the case of other polymer matrices, namely PA-6, PA-12, PET: [5,8] the first thin surface layer consists of PANI distributed in the polymer matrix and the second one is pure polymer matrix.

Experimental Techniques

Dielectric relaxation spectroscopy

Dielectric permittivity measurements were performed using a Novocontrol broadband dielectric spectrometer (Novocontrol GmbH, Germany) in a wide frequency (0.1 Hz to 10 MHz) and temperature (153 to 393 K with an accuracy of ± 0.1 K) ranges. The film was placed between two round plate electrodes in order to form plan capacitor geometry.[6] The surfaces containing PANI were facing each other in order to respect the sample symmetry. The

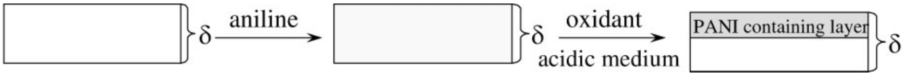

Figure 2.
Schematic presentation of the surface conducting composite film formation via an *in-situ* aniline polymerization (δ - thickness of the PU film).

complex impedance of such capacitor is:

$$\underline{Z} = \frac{1}{j\underline{C}\omega}, \quad (1)$$

where C is the complex capacity; ω is the angular frequency.

The dielectric permittivity of the sample

$$\underline{\varepsilon} = \varepsilon' - j\varepsilon'', \quad (2)$$

is obtained from:

$$\underline{C} = \underline{\varepsilon}\frac{S}{e}, \quad (3)$$

where S and e are the surface and the thickness of the sample, respectively.

The dielectric permittivity (real and imaginary parts) was analyzed according to the empirical Havriliak-Negami (HN) function:[18]

$$\underline{\varepsilon} = \varepsilon_u + \sum_{i=1}^{N} \frac{\Delta\varepsilon_i}{(1 + (i\omega\tau_i)^{\alpha_i})^{\beta_i}}, \quad (4)$$

where τ_i is the relaxation time; ε_u is the dielectric permittivity at very high frequency; $\Delta\varepsilon_i$ is the difference between the low and high frequency of ε'. α_i and β_i are the shape parameters of the relaxation time distribution.

The characteristic relaxation times τ, which were taken at the position of the maximum of dielectric loss for each relaxation process, were fitted according to equation (4). The temperature dependence of these relaxation times were analyzed using an Arrhenius equation (5) and the activation energies of the relaxation processes were obtained.

$$\tau = \tau_0 \exp\left(\frac{E_a}{k_B T}\right), \quad (5)$$

where τ_0 is the relaxation time at a very high temperature; E_a is the activation energy and k_B is the Boltzmann's constant.

Electrical conductivity measurements

The surface electrical conductivity of the PU/PANI composite films was measured using a standard four-probe method as a function of temperature with the help of an Agilent 34970A Data Acquisition Unit. Four copper wires were fixed on the sample conducting surface using conducting silver paint. For the temperature dependence measurements the PU/PANI composite film was placed in a cryostat. The temperature was raised at a rate of 1 °C/min.

Results and Discussion

Dielectric Properties of the Composite Films

Previous studies have shown that the acid doping of PANI strongly modifies the electrical and dielectric properties of the composites.[5,6] These changes induced by doping, result in the appearance of relaxation phenomena, which represent the interaction between the polymer matrix and doped PANI, which contains delocalized electrons. Therefore, the spectral shape may be used as an indicator of the charge transport process through the material.

Figure 3 represents the dielectric loss spectra as a function of frequency for virgin PU, doped and dedoped PU/PANI composite films at T = 183 K. The solid lines are the best fit to the equation (4). The flat dielectric response for the virgin PU indicates that no dipolar reorientation occurs at this temperature. As one can see from Figure 3, the presence of dedoped PANI in the PU matrix does not modify the dielectric spectrum – within the whole range of studied frequencies the value of the dielectric loss ε'' is practically constant. This indicates virtually no charge move-

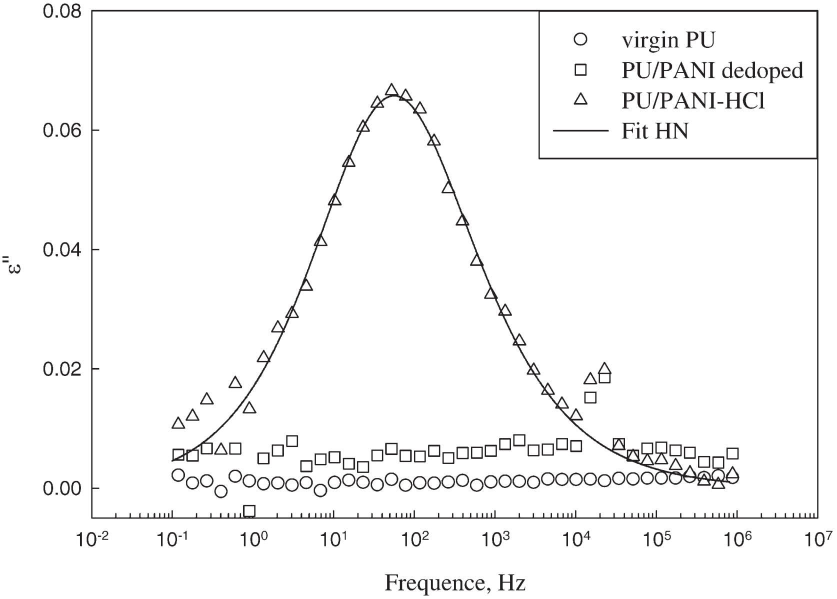

Figure 3.
Dielectric relaxation spectra (dielectric loss ε'') of PU/PANI composite film at 183K. The solid line represents the best fit to equation (4).

ment in the dedoped PU/PANI composite film in this frequency range. However, completely different behaviour is observed for the PU/PANI-HCl composite film (Figure 3). One can observe a well-defined broad relaxation process whose maximum corresponds to the frequency of 100 Hz at 183 K. This relaxation process, characterised by shape parameters $\alpha = 0.6$ and $\beta = 1$, results from interfacial polarization effect [5-7] caused by the accumulation of charge carriers at the particles interfaces. The found value of α is different from 1, which indicates the deviation from ideal Debye relaxation process ($\alpha = \beta = 1$).

As it has been already mentioned in the experimental part, the PU/PANI composite films were prepared by the same method as the PA/PANI composite films, which were previously studied by Resonance Raman spectrometry.[5,8] This technique revealed a double-layered structure of the composite film – the insulating and conductive layers (Figure 2). Therefore, it is most likely that the elaborated by the same technique the PU/PANI composite films will have a similar structure. So, taking this hypothesis into account, we can attribute the relaxation process found in the doped PU/PANI composite film to the interfacial polarization phenomenon taking place between the conducting PANI containing layer and the insulating layer of pure PU.

In order to study in detail the relaxation mechanism in the PU/PANI composite films the dielectric measurements as a function of temperature were performed (Figure 4). As one can see, the broad dielectric loss peak for PU/PANI-HCl composite film is observed at all studied temperatures. It was found that the dielectric strength increased with the increase of temperature. It is known that for relaxations such as α and β, i.e. for relaxations associated with the molecular dynamics in polymers, the dielectric loss decreases with the temperature increase.[18] So, the found behaviour for PU/PANI composite film clearly indicates that found relaxation process is of the interface polarisation type induced by the charge mobility. The relaxation frequency of the interfacial

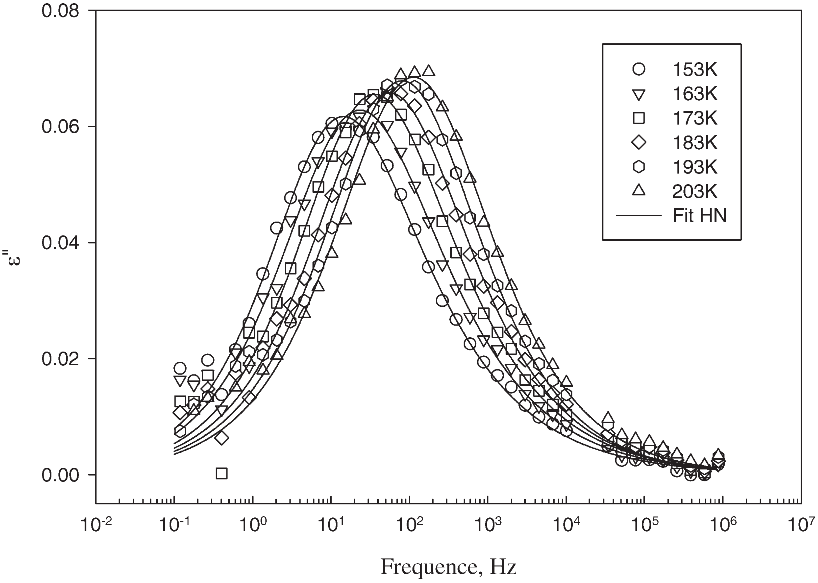

Figure 4.
Frequency dependence of the imaginary part of dielectric permittivity ε'' for the PU/PANI-HCl composite film at different temperatures. Solid lines are the best fit to equation (4).

polarisation process is also found to increase with temperature (Figure 4), i.e. it is a thermally activated process. The appearance of a peak only in the spectrum of the doped film is, hence, due to the extended conjugated structure of doped PANI, which causes delocalisation of the charge.

At higher temperatures (for example at 293 K, Figure 5) an additional relaxation process is observed in low frequency region for PU/PANI composite film as well as for virgin PU film

This relaxation process is attributed to the molecular dynamics induced by dipolar orientation in the PU matrix under an electric field. The relaxation attributed to the doping process is still visible, but it is shifted to the high frequency region (1 kHz) (Figure 5) as compared to the results of Figure 3. In order to emphasize this relaxation process the contribution of the orientation polarization relaxation process was subtracted from the whole spectrum of the PU/PANI-HCl composite film (Figure 6). As one can see from Figure 6 the obtained dielectric spectrum reveals only one relaxation process with maximum at ~1 kHz.

The temperature dependence of the characteristic relaxation times for doped PU/PANI composite film was fitted to equation (5) (see Figure 7). The activation energy is estimated to be 116 meV. Such low value of the activation energy indicates that the found relaxation process originates from the transport mechanism of the charge carriers in the PANI clusters.[5,6]

It should be mentioned that in the case of the surface composite conducting films prepared by the *in-situ* aniline polymerization the difference in the dielectric behavior which depends on the used polymer matrix and, consequently, on its nature can be observed.[5–8,10] One may distinguish at least three additional relaxation processes after doping which can be related to the interfacial polarization relaxation effects. The first relaxation process may arise from the significant difference in conductive properties between the two layers - the PANI containing layer and the pure polymer matrix (the case of PU/PANI composite film) (Figure 2). The second relaxation

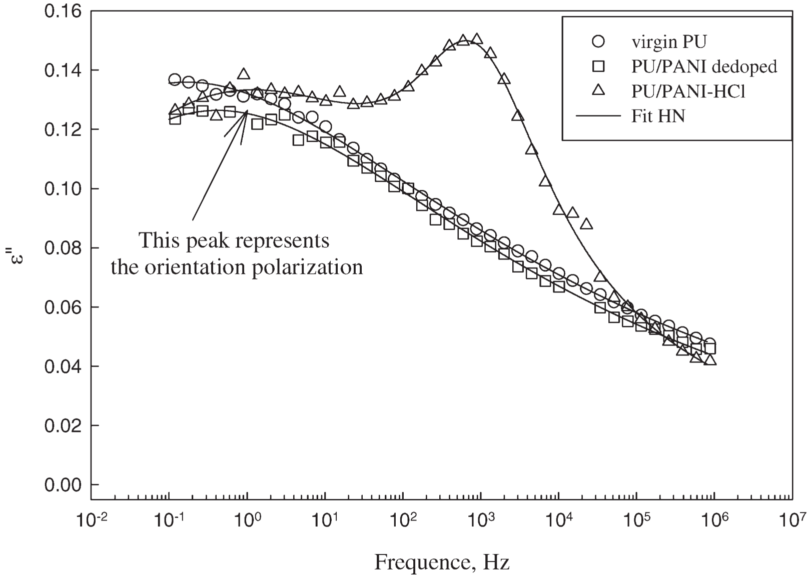

Figure 5.

Dielectric relaxation spectra (dielectric loss ε'') of pure PU and PU/PANI composite films at 293 K. The solid lines represent the best fit to equation (4).

process may be understood if one consider the PANI containing layer which constitutes of conductive PANI clusters surrounded by less or non-conducting medium as it results from AFM electrical images (the case of PET/PANI composite film).[6,7] And the third relaxation process might be connected to the hopping conducting process inside the PANI clusters (the case of PA-6/PANI composite film[5,6]). Thus, the presence as

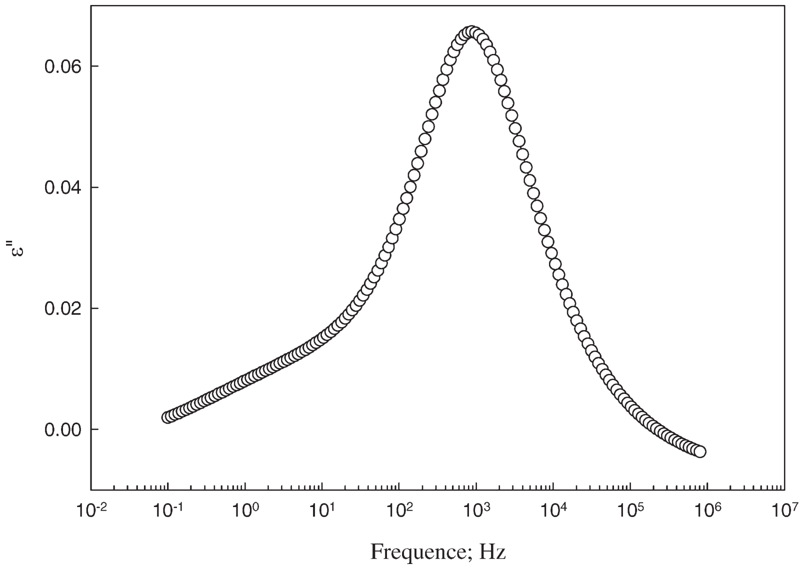

Figure 6.

Dielectric relaxation spectrum of PU/PANI-HCl composite film at 293 K obtained by subtraction of the spectrum of pure PU.

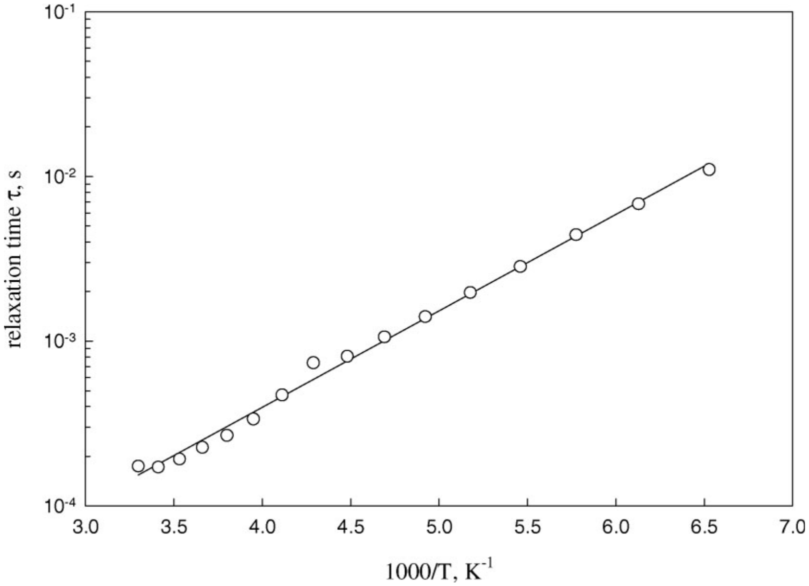

Figure 7.
Arrhenius plot of the characteristic relaxation time for the PU/PANI-HCl composite film. Solid line is the best fit to equation (5).

well as the frequency of these relaxation processes depends strongly on the nature of the polymer matrix.

Therefore, taking all this into account, two explanations can be proposed for the conducting composite films based on PU. The first one is that the thin PANI containing layer obtained in the case of PU/PANI composite film is rather homogeneous. So, in this case there is any pronounced difference between conducting PANI clusters and surrounding non-conducting medium and, as a result, any relaxation process known as the Maxwell-Wagner effect [7] is visible. However, this supposition needs further studies (for example, AFM) that will be done in the future. The second explanation is that in the case of doped PU/PANI composite film the found relaxation peak is an overlap of two relaxation processes. Therefore, the hidden relaxation process could explain the fact that the found relaxation peak is broad and that its shape parameters ($\alpha = 0.6$, $\beta \approx 1$) are different from those of Debye type.

Electrical Properties of the Composite Films

As one can see from the obtained results, the dielectric behaviour of the surface composite films changes after polymerization and doping processes. It is known that the introduction of PANI significantly improves the conductivity of polymer matrix.[1,5,9] Thus, one can suppose that the electrical properties of the composite film will be also modified. The conductivity of the PANI based composite films increases after the doping because of the protonation process, which induces an insulator-to-conductor transition. The surface electrical resistance measurements performed at 293 K using a four-probe method have demonstrated that the resistance value obtained for PU/PANI-HCl composite film (315 kΩ) is 10 times less than for PET/PANI-HCl composite film and 10 times higher than for PA-6/PANI-HCl composite film. [5] The found resistance value clearly shows that the surface PANI containing layer is conductive as the resistance value of pure PU (the other side

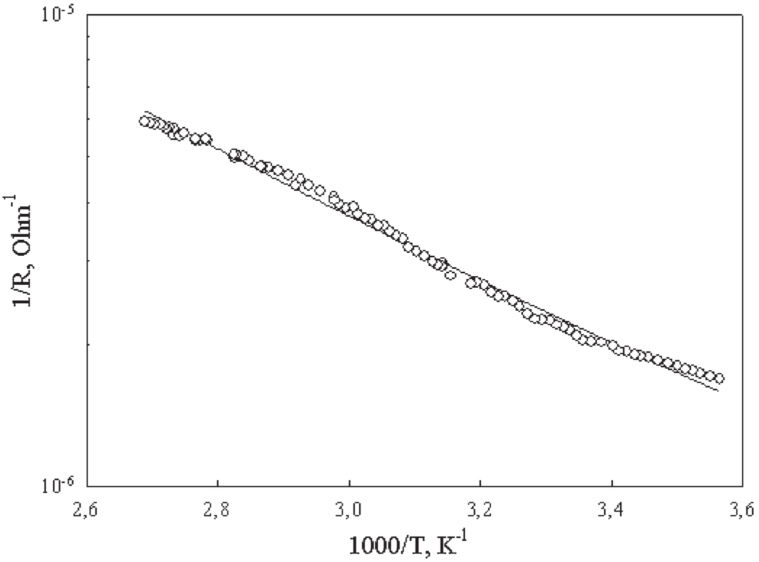

Figure 8.
Arrhenius plot of the electrical resistance of the PU/PANI-HCl composite film.

of the film) is very high (close to $10^{12}\,\Omega$). The less resistance values for PU/PANI composite in comparison with PET/PANI films is attributed to the effective dispersion of PANI particles in PU matrix that favours electronic transport as PANI is a good electrical conductor. The notable improvement of electrical conductivity of synthesized PU/PANI composites results from the formation of the conductive network of PANI within the PU matrix and is also the proof of better homogeneity of the PANI containing layer.

To determine the nature of temperature dependence of electrical conductivity, the surface electrical resistance for PU/PANI-HCl composite film was measured versus temperature (Figure 8). It was found that the obtained dependence followed the Arrhenius equation (equation (5)), indicating the semi-conducting behaviour of the composite film similarly to the other semiconductors. [1,9] The activation energy of the conductivity as derived from the slope of Arrhenius plot (Figure 8) was estimated to be 137 meV, that is close to the value obtained by the dielectric measurements ($E_a = 116$ meV). This result indicates that both processes originate from the same electronic transport mechanism of the charge carriers (electrons) in the conducting PANI clusters.

Conclusion

Conducting PU/PANI composite films have been elaborated by a treatment of PU films swelled in aniline with water solution of APS in HCl. The major advantage of these composite films is their quick swelling kinetics (~ 25 wt.% of aniline in less than 10 min).

The analysis of the dielectric relaxation process observed in the doped PU/PANI composite film reveals a non-Debye behaviour ($\alpha = 0.6$ and $\beta = 1$). The found relaxation process is thermally activated and is characterized by a low activation energy ($E_a = 116$ meV). Such behaviour can be explained as the interfacial polarization effect associated with charge carriers (electrons) in PANI conducting clusters and also by the hidden relaxation process as compared with other composite systems (PET/PANI, PA-6/PANI).

The temperature dependence of the surface electrical resistance of the PU/PANI composite film is well described by the Arrhenius law. The corresponding activation energy ($E_a = 137\,meV$) is close to the value found by dielectric relaxation spectroscopy ($E_a = 116\,meV$). This result proves the conducting nature of the PANI containing layer and the possibility of the PU/PANI composite films using in the antistatic coatings.

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