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Abstract. Current noise and conductivity in composites of conductive spherical polyaniline particles covered with non-conductive poly(vinyl alcohol) layers dispersed in the same polymer medium were investigated. As the polyaniline particles are fully separated by insulating material, conductive percolation is not possible and electrical conductivity occurs only by thermally assisted charge hopping or possibly tunnelling. An interpretation in terms of quiet conductive paths through the polyaniline particles and noisy conductance through the poly(vinyl alcohol) matrix is given.

1. Introduction

Electrical noise in conductive polymeric materials is a research subject of considerable interest at the present time. Most investigations have concerned composites consisting of non-conductive polymer matrices and conducting fillers such as carbon black [1–7] or metal [8,9] at concentrations near or above the percolation threshold. The present work concerns the results of low-frequency noise and conductivity measurements on poly(vinyl alcohol) (PVAL) containing dispersed particles of a protonated form of polyaniline (PANI) as the conductive component. The system is remarkable for the simple reason that the PANI particles are covered already during polymerization with PVAL shells which after dispersion in the same polymer matrix *a priori* prevent conductive percolation.

Reports on investigations of low-frequency current noise in composites consisting of electrically conducting particles in insulating matrixes at concentrations significantly below the percolation threshold are rare. Mantese and Webb [10] and Mantese and coworkers [11] have reported on blends of platinum in aluminium oxide in which the platinum concentration was only somewhat lower than that corresponding to the percolation threshold. In that concentration region the normalized noise power was essentially independent of the platinum concentration. However, the lowest concentration of platinum was about 33% (volume fill fraction), and on the basis of these data no conclusion can be drawn about the low-concentration (say 1% to say 20% platinum concentration) behaviour of the noise power. On the other hand, Mantese and coworkers provided results of an effective medium theory [11] which indicate that significantly below the percolation threshold the normalized noise power should be nearly constant independent of the concentration of the conducting component. This is compatible with results presented by Rammal and coworkers [12].

The present work concerns a system which provides an insight into the characteristics of $1/f$ noise at concentrations of the conductive component below the percolation threshold. In particular, we find that the normalized noise power increases quickly with increasing PANI content, a result at variance with the results of previous work as described above. Only a qualitative explanation of this result can be given at the present time.

2. Materials

Polyaniline belongs to the group of electrically conductive polymers which are of great interest for practical applications at present. Because of its environmental stability and good mechanical properties, PANI and its blends with some other polymers appear to be very promising materials which may eventually take over some functions of metallic conductors.

An electrically conducting protonated form of PANI can be easily produced by oxidative polymerization of aniline. However, its intractability represents a serious problem in processing, and well defined composites containing PANI are not easy to prepare. The protonated form of PANI is completely soluble only in sulphuric acid [13]. Information on the partial solubility of PANI base in organic solvents is contradictory [13]. Protonation of PANI using suitable organic acids with bulky non-polar groups resulting in soluble complexes has been reported as one possibility which allows preparation of blends with various polymers [14, 15]. Recently aniline has been polymerized in the presence of latex particles [16–18]. These non-conductive particles, which are embedded in the electrically conductive matrix of the protonated PANI, are obtained after drying. Conductive films have also been obtained from a mixture of protonated PANI with acrylate lattices [18]. However, all these blends have irregular structure and allow PANI chains to contact each other directly.

On the other hand, dispersions of spherical PANI particles can be prepared by polymerization of aniline in the presence of a convenient steric stabilizer, typically a water-soluble polymer such as PVAL [19–22]. In this case PANI particles covered by non-conductive PVAL shells arise. When such a dispersion is mixed with a PVAL solution and dried, samples of the non-conductive matrix of PVAL filled uniformly with conductive PANI particles insulated from each other are obtained.

3. Experimental details

3.1. Preparation of dispersions

Steric stabilization allows the preparation of stable dispersions where the PVAL chains attached to PANI cores prevent aggregation of the particles [20–22]. 10 g of 4% aqueous solution of PVAL (type 72000 by Fluka, Switzerland) were mixed with 20 g of 10 M hydrochloric acid and 4 g of aniline (> 99.96%), to which 56 g of distilled water was added [21]. The mixture was cooled to 0–5 °C and 20 g of 20 wt% aqueous solution of ammonium persulphate was introduced. The temperature of the reaction mixture was kept below 5 °C for 2 h. The reaction mixture was dialysed against an excess of water to remove all low-molar-mass components. The concentration of the dispersion particles was evaluated from the mass of the sediment after centrifugation, and particle composition was calculated from nitrogen content obtained by elemental analysis. Dynamic light scattering showed that the uniformity of particles was good [20–22]. Their hydrodynamic diameter including both the contribution of the PANI core and the swollen PVAL shell was 352 nm.

The geometric diameter of the dry particles obtained from scanning electron microscopy was about 200 nm. Based on mass balance and assuming spherical symmetry of the particles, the size of the unswollen PANI cores can be estimated at 92 mm. Thus it can be supposed that in every case the conductive PANI islands are separated by relatively thick non-conductive PVAL shells which prevent direct contact between conductive PANI chains. This is in contrast to the often investigated percolating systems consisting of polymer or other insulating matrices filled with metallic or carbon black particles.

3.2. Preparation of composite films

The known volume of the dialysed PANI dispersion or the dispersion mixed with an appropriate volume of 4 wt% aqueous PVAL solution was deposited on glass ($50\times25\times2$ mm^3) and evaporated. This procedure was repeated several times to get well defined films of a suitable thickness. The electrodes were applied by painting strips of colloidal graphite dispersion 12 mm wide on both sides of the polymer film. The samples were carefully dried over phosphorus pentoxide.

The composition of the films was calculated from the known amount of PANI dispersion and PVAL in cast liquid, while the thickness of the film was determined from the sample geometry. The thickness of the composite layers varied between 13 and 30 μm. The volume fraction of PANI in the four samples used ranged from 0.069 to 0.257. The upper limit of PANI concentration corresponds to the undiluted dispersion. Figure 1 shows the microstructure of the typical composite.
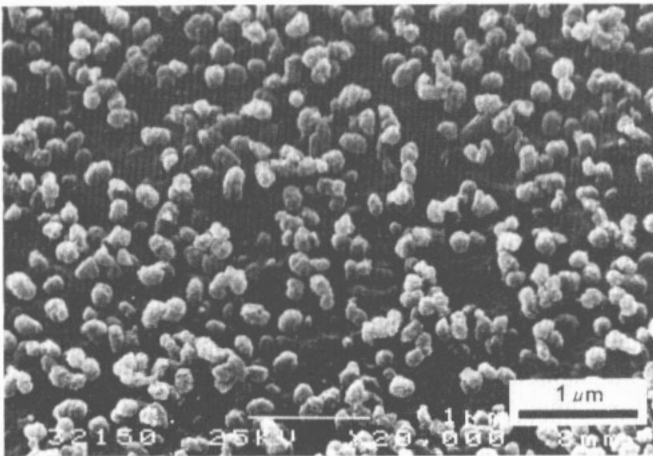

Figure 1. Micrograph of a composite containing 25.7% by volume of PANI.

3.3. Electrical noise and conductivity measurement

The measurement set-up consisted essentially of a voltage source connected to a voltage divider consisting of a 1 MΩ resistance and the sample, across which an impedance divider consisting of a 10 μF capacitor and a 100 MΩ measurement resistor were attached. The wire-wound 1 MΩ resistor, which showed negligible current noise compared to the PANI

samples, prevented the noise signal from being short circuited by the power supply. The sample and the voltage source were placed in a shielded metal box during the measurement.

The electrical noise was measured by means of a low-noise preamplifier followed by a fast Fourier transform analyser (Princeton Applied Research Co., models 113 and 4513) producing frequency spectra of the noise signal on the oscilloscope screen (Tektronix 604 monitor); the spectra were recorded by means of a Phillips x–y recorder. The preamplifier gave a gain of 1000 and the filters cut off the signal under 0.1 Hz and above 300 Hz. The frequency range used was up to 200 Hz.

The conductivity was determined using a conductometer (Radelkis OK-104, Hungary). Some four-probe tests provided the same results as the more convenient two-electrode system. Our experiments have also shown that the same results are obtained when colloidal silver is used instead of colloidal graphite.

4. Results

Figure 2 shows noise spectra for the frequency interval 1–200 Hz. The Nyquist or thermal noise (no applied voltage) is essentially independent of the frequency and much weaker than the current noise, which can be characterized by $S_U \sim U^2/f^\alpha$ where S_U is the noise power, U is the applied voltage and α is the frequency exponent, in the present experiments near 1.2. As the applied voltage was rather low, 0.4 volts, the PANI samples can be considered to be quite noisy. In all the experiments the noise power was found to be closely proportional to the square of the applied voltage.

In figure 3 the dependences of the conductivity and the normalized noise power on the concentration of PANI are shown. The conductivity increases roughly as the PANI concentration cubed while the noise power increases somewhat less quickly, to the power 2.5. As the conductive particles are completely isolated the conductivity values themselves are more than an order of magnitude lower than those reported in composites where PANI was polymerized directly in the presence of latex particles of non-conducting polymer [16, 18]. For all the samples the conductivity increased with temperature between room temperature and the glass transition temperature of the PVAL matrix (77 °C). Figure 4 is an Arrhenius
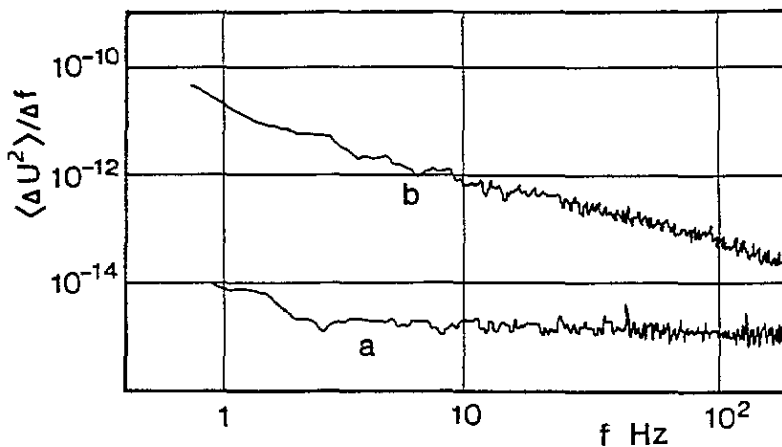
Figure 2. Nyquist noise spectrum (a) and current noise spectrum (b) (applied voltage 0.39 volts) for the sample containing 14.2% by weight of PANI.
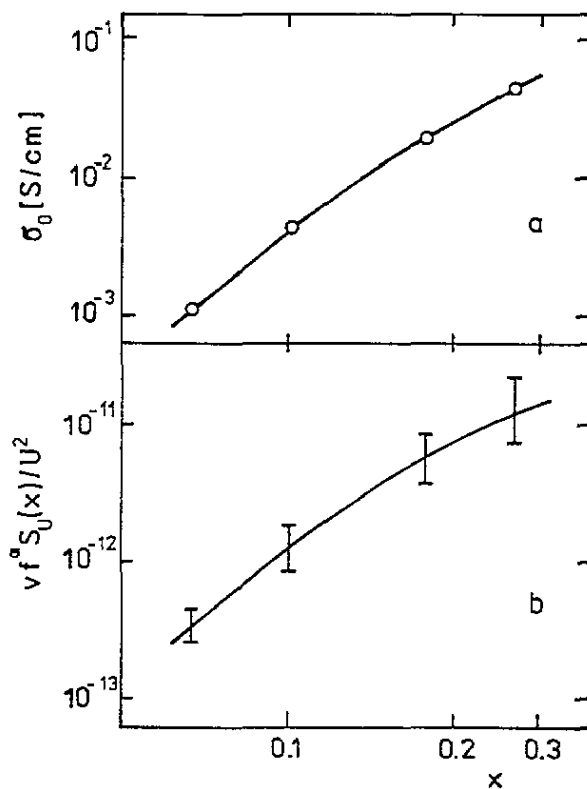
Figure 3. Electrical conductivity (a) and normalized noise power ($vf^{\alpha}S_U(x)/U^2$) (b) against the volume fraction x of PANI at 23 °C (v—volume of the sample).
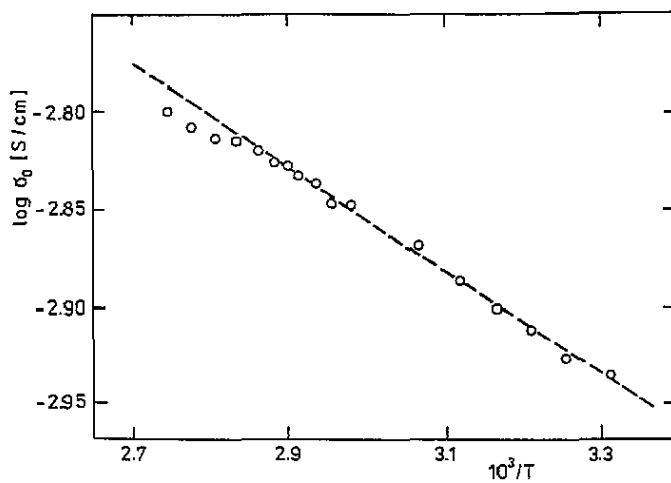

Figure 4. The dependence of electrical conductivity on the inverse temperature for the sample containing 6.9% by volume of PANI.

plot of the conductivity versus the inverse temperature, from which an activation energy of about 5.7 kJ mol^{-1} can be deduced. The implication is that the conductivity is determined by thermally assisted hopping or possibly charge tunnelling between the PANI particles.
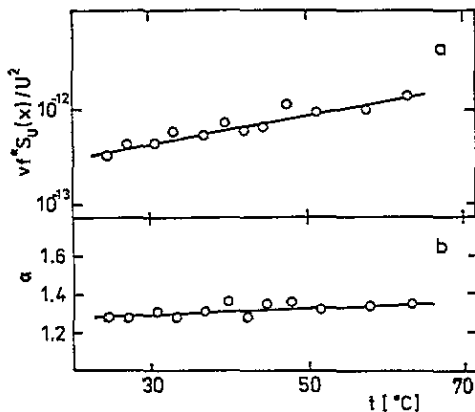

Figure 5. The temperature dependence of the normalized noise power ($vf^{\alpha}S_U(x)/U^2$) (a) and the frequency exponent α (b) for the sample containing 6.9% by volume of PANI.

The temperature dependences of the noise power and the frequency exponent are shown in figure 5. The latter is essentially independent of the temperature, while the noise power itself increases by a factor of four in the temperature interval 25–65 °C.

5. Discussion and conclusions

According to Hooge's semiempirical formula [23, 24] the noise power should be inversely proportional to the conductivity. Such behaviour is usually observed, for instance in granular blends of metal (platinum, platinum–gold) and insulator (aluminium oxide, polytetrafluoroethylene) [9, 10] or carbon black in chloroprene rubber [5] or in wax [25], above the percolation threshold where charge transport along a skeleton of conducting material occurs. In the present case the results in figure 3 clearly show that this is not the case.

The Hooge formula is closely related to the simple statistical result that the average square of the deviation of the number of charge carriers from the average value, $\langle(\Delta N_c)^2\rangle$, is proportional to the average number of charge carriers itself, $\langle N_c\rangle$. This is true under the assumption that the motions of the charge carriers are independent of each other and that deviations from average values can be described by Gaussian statistics. This can hardly be the case here, where most likely large groups of charge carriers hop or tunnel together between PANI islands. In other words, there is significant correlation between the motion of the individual charge carriers, in violation of the independent charge carrier assumption.

Instead of considering the effects of correlations between charge carriers further, we choose to propose a variant of the concept of noisy tunnelling and quiet metallic paths used by Mantese and Webb [10] and by Mantese and coworkers [11]. We note that in general the electrical noisiness of a conducting material decreases with increasing conductivity and with

increasing number of charge carriers. Thus in this case we propose that the quiet paths are through the conductive PANI islands and the noisy conductance is through the PVAL matrix, in analogy with the model used by Mantese and Webb [10] and Mantese and coworkers [11]. However, we do not claim that the normalized electrical noise becomes independent of the conducting component concentration below the percolation threshold because the noise and the conductivity scale similarly with the amount of conducting material [10]. Instead we note that for relatively low PANI content (around 6.9%) the electric current flows through a relatively large proportion of the total volume of the PVAL matrix, probably by means of thermally assisted tunnelling. As the PANI content increases (toward 25.7%) the conduction paths in the PVAL matrix are concentrated to the volumes in the immediate vicinities of the shortest paths between the PANI islands, that is, where the PANI spheres come closest to each other. Thus the volume of the PVAL matrix actually involved in the conduction process decreases as the PANI content increases. At the same time the local electric fields acting on the charge carriers in the PVAL matrix increase since the voltage drop across the sample is spatially distributed between the increasing number of conducting PANI cores with low voltage drops and the PVAL interfaces with correspondingly higher voltage drops. In the end it is expected that the current is carried by an ever decreasing number of charge carriers subjected to ever increasing local electric fields. This would lead to increasing noise powers as the PANI content is increased (but still below the percolation threshold). Of course at sufficiently high PANI concentrations this concentration of current density effect must saturate and the quiet conduction in the PANI cores determine the noise charactertistics of the sample, in agreement with the theory of Mantese and Webb [10] and Mantese and coworkers [11]. We note that our line of argument cannot be extended to very low conducting component concentrations, for instance to PANI concentrations much less than 5%, because there would be no place for the charges to hop or tunnel to. An additional conductivity mechanism would be needed, and its noise generation characteristics are not known.

Acknowledgments

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