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Application of percolation concepts to electrical conductivity of polyaniline–inorganic salt composites

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The dependence of the resistivity of protonated polyaniline–inorganic salt composites with the volume fraction of electrically conducting component was analyzed on the basis of percolation theory. A short analysis and a discussion of basic treatment in the evaluation of percolation parameters are included. Microscopical observations showed a non-uniform distribution of polyaniline particles in the composites. The composites of polyaniline sulfate with ammonium sulfate and potassium bromide have a low percolation threshold (<3 vol.% conducting component). This has been explained as a property of the segregated structure of the composites, which is formed because of a large difference in the particle sizes. Basic quantitative characteristics of the morphological structure have been obtained using the percolation model, as proposed by Ewen and Robertson, to explain the properties of thick film resistors.

Introduction

Polyaniline (PANI) is one of the frequently studied electrically conducting polymers.[1,2] The preparation of composite materials of PANI is one of the ways used to tune its electrical, mechanical and utility properties for specific purposes. PANI composites are most commonly prepared by polymerization of aniline in the presence of a suitable polymer substrate, *viz.* latex particles,[3,4] films[5–9] or fibers.[10,11] Polyaniline dispersions[12–16] yield submicrometre PANI particles embedded in the matrix of an insulating polymer after precipitation and drying.[17,18] The composites studied in the present work were prepared by hydraulic pressing of PANI–inorganic salt blends at 700 MPa.

Studies of PANI–inorganic salt composites have been initiated in the search for materials for measurements of the temperature dependence of PANI conductivity. Typically inorganic salts are stable even at elevated temperatures whereas organic compounds decompose or, as in case of polymers, undergo various transitions.

Polyaniline composites usually have common percolation behaviour. The threshold PANI volume fraction is typically in the range 8–10 vol.% for materials prepared from dispersions.[17] In particle mixtures, however, much lower percolation threshold values (<1 vol.% PANI) have been reported.[3,19–21] Phase separation can be also introduced by orientation of the conducting particles in an electric field[22,23] prior to the formation of a composite.

Simple models[24,25] and numerical simulations of resistor networks[26,27] have confirmed that the resistivity ρ of a percolating system depends on the concentration (volume fraction) v of conducting sites (at least in range $0 \leqslant v - v_c \leqslant 0.2$) as a power law

$$\rho = \rho_0 (v - v_c)^{-t} \qquad (1)$$

where v_c is the critical volume fraction (percolation threshold), the lowest conducting component concentration at which the system behaves as a (poor) conductor. The critical exponent t describes the rate of resistivity change developed upon change of the conducting component concentration v. The factor ρ_0 is a measure of the conducting phase resistivity and takes into account any contact resistance between particles.

The critical volume fraction v_c and the exponent t are used to classify the structure of percolating systems; they are sensitive to various factors one of the most important being the relative size of conducting and insulating particles.

Let us consider a system composed of a disordered mixture of conducting (metallic) spheres of radius R_M and insulating (or missing) spheres of radius R_I, such that $R_M \approx R_I$. If the space between the spheres is regarded as part of the insulating phase, then the volume fraction v, which is occupied by conducting phase, is

$$v = pf \qquad (2)$$

where f is the packing fraction, and the percolation probability p denotes the number fraction of conducting spheres from all spheres. It has been shown[27] that the relation (Scher and Zallen criterion)

$$v_c = p_c f \cong 0.154 \qquad (3)$$

where p_c is the critical percolation probability, holds in 3D arrangements with various packing fractions f. Using the same assumption, the critical exponent t is believed to have an invariant value of close to 1.9.[28] In the case $R_M \gg R_I$, the conducting particles are embedded in an insulating matrix formed by fine particles filling the spaces in between. Such a system exhibits percolation only in the trivial limit of random close packing equal approximately to 64% of the total volume.[29] Real composites usually can conduct without geometrical contacts between particles since charge carriers can tunnel through thin barriers in polymers filled with metal particles.[30] In mixtures fulfilling the condition $R_M \ll R_I$, metal particles fill non-spherical voids between the insulating particles (segregated structure). Extensive analysis of this type of system[31] shows that the critical concentration of metal may be reduced from 35 to 6% by a change of the ratio R_I/R_M from 1 to 16. If the conducting component can be considered rather as a continuum, then the ratio $R_I/R_M \to \infty$ and consequently $v_c \to 0$.[3,17,32,33]

Numerous modifications of percolation theory have been developed.[32,34,35] In order to fit the observed ρ–v curves of thick film resistors having segregated structure, Ewen and Robertson[34] suggested a more sophisticated percolation model. They assumed that percolation inside the voids between large insulating particles is controlled by eqn. (1). Using eqn. (2), they expressed the percolation probability p related to the interstitial region (the volume fraction occupied by the voids is $1-f_g$, where f_g is the packing fraction for the large non-conducting particles) by means of the volume fraction v related to the system as a whole

$$p = \frac{v}{f_m(1-f_g)} \tag{4}$$

where f_m is the packing fraction for the conducting particles inside the voids. However, conducting particles are often not distributed homogeneously in the interstitial region, *e.g.* in our present experiment in which, owing to electrostatic forces, small PANI particles cover the surface of large salt particles even before they are pressed together. As a result, percolation can be achieved far below the value p_c, which is considered to be the percolation threshold when the particles are distributed homogeneously. In other words, the conducting network spans only a small part of the interstitial region. In the described model,[34] the simple transform formula

$$p' = (p^n + p_c{}^n)^{1/n} \tag{5}$$

ensures that the percolation probability p' (related to the region spanned by the network) is always not below the threshold p_c for each value of the percolation probability p (related to the whole interstitial volume). The parameter n relates to how well the conducting particles fill the interstitial space. The analogue to eqn. (1) is then

$$\rho = \rho_0{}^* \left\{ \left[\left(\frac{v}{f_m(1-f_g)} \right)^n + p_c{}^n \right]^{1/n} - p_c \right\}^{-t} \tag{6}$$

The factor $\rho_0{}^*$ is also a measure of the conducting phase resistivity, but cannot be compared directly with ρ_0, because the structure of eqn. (6) differs from that of eqn. (1).

Evaluation of percolation parameters

In principle, a non-linear fitting method should be used to evaluate the unknown parameters v_c, t and ρ_0, in eqn. (1) from experimental pairs $[v_i, \rho_i]$. On the other hand, a convenient method is to perform the linear regression to a set of data plots with non-linear axes.

Linear regression with non-linear axes

The power law given by eqn. (1) will give straight lines when using log–log scales.[36] Plots of $\log \rho$ *vs.* $\log(v-v_x)$ can be constructed with the parameter v_x being varied and the linear regression yielding the correlation coefficient closest to unity was searched for. In this case the v_x value gives an estimate of v_c. The unknown parameters t and ρ_0 are then obtained from

$$\log \rho = \log \rho_0 - t \, \log(v - v_c) \tag{7}$$

It is necessary to exclude the pairs $[v_i, \rho_i]$ for $v_i \leqslant v_x$ from the regression, because the condition $v_i > v_x$ must be fulfilled to evaluate $\log(v-v_x)$. This reduces the data set and usually distorts the results—the correlation coefficient then may reach several local maxima even at v_x far from the critical region. A more suitable method is to plot $\rho^{1/t}$ *vs.* v for a varying parameter t and the plot with the maximum correlation coefficient gives the best estimate of the exponent t. The unknown parameters v_c and ρ_0 can be obtained from the regression line[17,30]

$$\rho^{-1/t} = \rho_0{}^{-1/t}(v - v_c) \tag{8}$$

This type of linearization reduces the influence of fluctuations of the parameters near the percolation threshold.

Non-linear regression

In order to find the unknown parameters in eqn. (6), a non-linear fitting method has to be used. Besides others, the Levenberg–Marquardt method can be found in the literature.[37] A suitable curve equation for the regression will be analogous to eqn. (8). While we do not often know the packing fraction f_m of (irregular) conducting particles, if we suppose that the Scher and Zallen criterion is valid inside the voids between large insulating particles, a well defined quantity will be the product in eqn. (3). When we modify eqn. (6) according to these assumptions, we obtain an equation with three unknown fitting parameters: the packing fraction f_g for insulating particles, the exponent n and the multiplication factor $\rho_0^{*-1/1.9}/f_m$

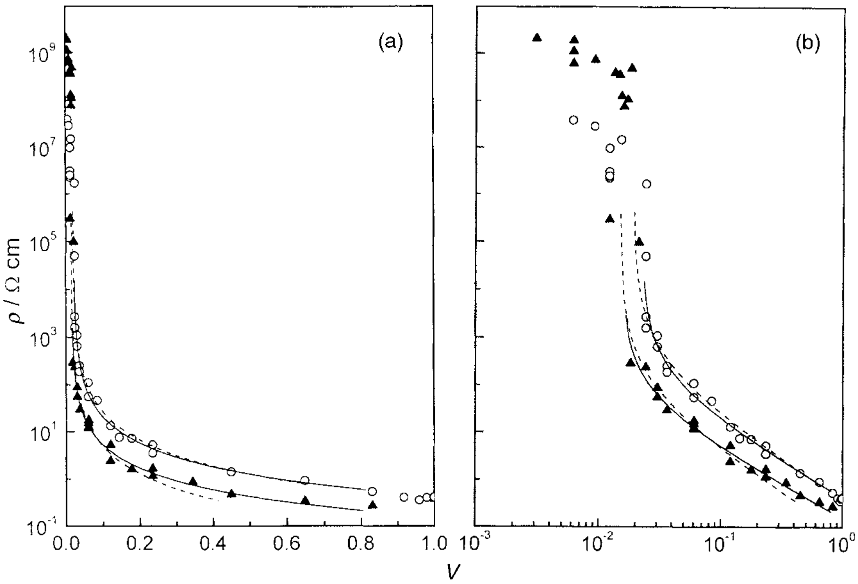

Fig. 1 Semilogarithmic (a) and double logarithmic (b) plots of the dependence of the resistivity ρ on the volume fraction v of polyaniline sulfate in composites with ammonium sulfate and potassium bromide. Points represent the experimental values [(○) PANI–ammonium sulfate, (▲) PANI–potassium bromide] measured at room temperature. Full lines are regression curves given by eqn. (1) and dashed lines are fitted curves described by eqn. (6).

$$\rho^{-1/1.9} = \frac{{\rho_0}^{*-1/1.9}}{f_{\mathrm{m}}} \left\{ \left[\left(\frac{v}{1-f_{\mathrm{g}}} \right)^n + (f_{\mathrm{m}} p_{\mathrm{c}})^n \right]^{1/n} - f_{\mathrm{m}} p_{\mathrm{c}} \right\} \quad (9)$$

where the critical exponent estimate $t = 1.9$[28] is used.

Experimental

Samples

Polyaniline was prepared using the standard procedure,[38] which ensures the purity that is usual for polymeric materials of this type. Aniline sulfate (28.4 g, 0.1 mol) was dissolved in 800 ml of water and ammonium peroxodisulfate (45.6 g, 0.2 mol) in 200 ml of water. Both solutions were cooled to 0 °C and mixed together to start the polymerization. The mixture became light blue, then dark blue, and finally a dark green precipitate formed within 1 h. Next day the precipitate was collected on a filtration funnel, washed repeatedly with dilute (0.1 M) sulfuric acid and then several times with acetone. Polyaniline (emeraldine sulfate) was dried at 60 °C *in vacuo*. The typical size of PANI particles was about 1 μm.

Ammonium sulfate and potassium bromide were of analytical grade purity and were dried *in vacuo* over phosphorus pentaoxide for several days. The typical size of the salt particles was about 50 μm. Polyaniline sulfate and the inorganic salt were mechanically blended with a pestle in an agate mortar for 15 min in various proportions. The blend (250 mg) was pressed in a manual hydraulic press at 700 MPa into a pellet of 13 mm diameter.

The composite structure near the percolation threshold was studied from micrographs of the surface of the pellets at low PANI concentrations (see Fig. 2) and results were similar for both salts. The insulating light areas (typical size *ca.* 5 to 40 μm) contain salt particles shattered during the pressing process. Dark polyaniline particles together with small salt fragments form the percolation channels in between. The channels are *ca.* 1 to 5 μm thick and occupy a volume fraction of 0.2 ± 0.1 (standard deviation). While the relative particle sizes are not well defined, it is clear that the PANI particles are considerably smaller than the insulating regions and that segregation is present. The packing fraction for the large salt particles (f_{g}) must be $\geq 0.8 \pm 0.1$ (standard deviation); the equality holds if the conducting channels occupy just voids between the large salt particles.

Electrical conductivity

The electrical conductivities of the samples were measured at room temperature using either the two-point method with a Keithley 6517 electrometer or the four-point van der Pauw method.[39] The two-point method was used when the sample resistance exceeded the kΩ range. The experimental setup for four-point measurement included a Keithley 238 current source, a Keithley 706 scanner equipped with a matrix card and a Solartron-Schlumberger 7081 voltmeter.

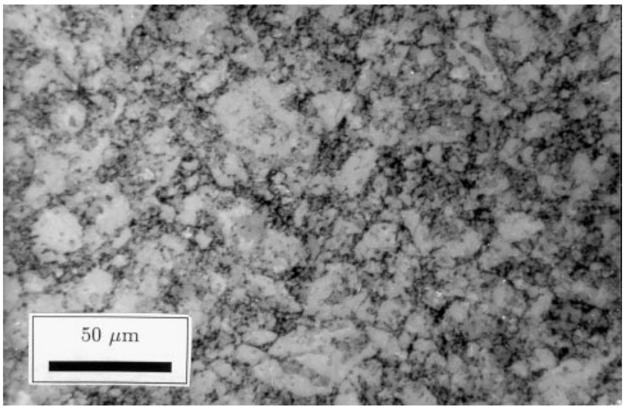

Fig. 2 Surface of an ammonium sulfate pellet contaning 5 wt.% PANI sulfate observed by optical microscopy.

Results and discussion

The electrical resistivity of protonated PANI is typically of the order of 10^{-1} to 10^{0} Ω cm while the resistivity of the composite is inversely proportional to the PANI content (Fig. 1) according to eqn. (1). It can be seen from the double logarithmic plots that the experimental points for volume fractions v below 0.015 do not conform to power law (1). Such values were excluded from the evaluation. The values of the unknown parameters ρ_0, v_{c} and t were determined by procedures based on a least-squares fit using eqn. (1) converted to the forms of eqn. (7) and (8). A combination of both the described methods was used and the results are listed in Tables 1 and 2, respectively. Despite certain limitations, the results demonstrate that the treatment based on the simple log–log plot [eqn. (7)] gives values that are in good agreement with those of the more correct method based on eqn. (8). Moreover, eqn. (7) gives an opportunity to estimate the statistical deviation of the exponent t.

The critical exponent t obtained for both the composites is below the theoretical value of 1.9, typical of 3D models.[28] Results on composites containing PANI in the literature, usually do not include the critical exponents. The only published value for the composite PANI–ammonium sulfate

Table 1 Results of the least-squares fit based on eqn. (7) for the critical exponent t, the multiplication factor ρ_0 and the critical volume fraction v_{c} of conducting component for composites of polyaniline sulfate with inorganic salts at room temperature. Standard deviations of t and ρ_0 calculated from the optimal fit as well as estimated f_{g} values for further evaluation are also listed

	PANI–potassium bromide	PANI–ammonium sulfate	Eqn.
t	1.39 ± 0.14	1.48 ± 0.15	(7)
ρ_0/Ω cm	0.15 ± 0.28	0.42 ± 0.37	(7)
v_{c}	0.021	0.025	(7)
f_{g}	0.86	0.84	(10)

Table 2 Results of the least-squares fit based on eqn. (8) for the critical exponent t, the multiplication factor ρ_0 and the critical volume fraction v_{c} of conducting component for composites of polyaniline sulfate with inorganic salts at room temperature. Standard deviations of ρ_0 and v_{c} calculated from the optimal fit as well as estimated f_{g} values for further evaluation are also listed

	PANI–potassium bromide	PANI–ammonium sulfate	Eqn.
t	1.43	1.53	(8)
ρ_0/Ω cm	0.15 ± 0.01	0.41 ± 0.01	(8)
v_{c}	0.016 ± 0.006	0.023 ± 0.005	(8)
f_{g}	0.90	0.85	(10)

Table 3 Results of the Levenberg–Marquardt fit based on eqn. (9) for the multiplication factor $\rho_0{}^*f_m^{1.9}$ the packing fraction f_g and the exponent n for composites of polyaniline sulfate with inorganic salts at room temperature. Standard deviations of the factors $\rho_0{}^*f_m^{1.9}$ and f_g calculated from the fit are also listed

	PANI–potassium bromide	PANI–ammonium sulfate	Eqn.
$\rho_0{}^*f_m^{1.9}/\Omega$ cm	7.0 ± 4.0	12.4 ± 6.7	(9)
f_g	0.91 ± 0.03	0.89 ± 0.03	(9)
n	228	136	(9)

presented by us[17] was slightly lower and because it was only a preliminary result obtained on a subset of the present data, it was characterized by a rather higher standard deviation.

The low percolation threshold value observed for PANI with both inorganic salts is in accord with the observation that the composite structure is segregated. Therefore eqn. (9) was also applied to our experimental data. This was performed in two steps. (i) We used the value v_c determined from eqn. (1) to estimate the value of the parameter f_g while the exponent n was eliminated from eqn. (9) using the assumption $p' \cong p$ for p sufficiently far above p_c. The critical volume fraction v_c and the Scher and Zallen criterion value [eqn. (3)] was then related to the packing fraction f_g

$$f_g \cong 1 - \frac{v_c}{f_m p_c} = 1 - \frac{v_c}{0.154} \qquad (10)$$

The estimates for f_g (listed in Tables 1 and 2) do not contradict the microscopical observations described above. (ii) The estimates for f_g were then used as initial values for the non-linear fitting procedure based on eqn. (9).

Table 3 lists the results of Levenberg–Marquardt fitting. The concentration dependence of the resistivity of both the PANI–inorganic salt composites exhibits a classic steep rise when the conducting fraction decreases to a percolation threshold (Fig. 1). It is known[34] that in such cases the exponent n reaches high values. The main importance of eqn. (9) then consists in rescaling the critical concentration by a factor $1-f_g$. For high exponent n values, the shape of the curve depends only very weakly on the exponent n. Therefore the statistical deviations of the exponent n are very large and have no physical meaning. The fits accord with the experimental data (Fig. 1) and give the packing fractions f_g, which are in good agreement with the values obtained from optical observations.

Conclusions

It has been demonstrated that the behaviour of PANI–inorganic salt composites can be described using the segregated system model proposed originally by Ewen and Robertson[34] to explain the properties of thick film resistors. After fitting the model equation to the experimental data, the packing fraction for insulated particles was obtained. This quantitative characteristic of the morphological structure is in good agreement with microscopical observations.

It has been shown that the electrically conducting PANI is distributed non-uniformly in the composites. The percolation process is concentrated to a small part (only *ca.* 10%) of the total occupied space. Such a morphology is responsible for the low critical concentration (<3 vol.% conducting component).

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