Charge Carrier Transport in Heterogeneous Conducting Polymer Materials

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Summary: The similarities of conductivity mechanisms of composites and nanocomposites and doped conjugated polymers that are also characteristic of specific heterogeneity are discussed. It is shown that the formulae developed to account for internal heterogeneity of conductive polymers can be applied also for polymer composites in spite of low overall content of the conductive phase. For fully organic nanocomposites (reticulate doped polymers) showing metal-like conductivity and a crossover temperature effective contribution of metallic phase is estimated. Examples of different properties of nanoparticles forming conducting networks as compared with the bulk crystals are discussed.

Introduction

Preparing polymer composites is now the most effective method of getting speciality materials. Depending on the technique of composite preparation and on the kind of materials used one can distinguish several main groups of heterogeneous electrically conductive polymer composites and nanocomposites: (i) non-conductive polymers or polymer blends filled with inorganic conductors, (ii) conducting colloid composites, blends of processable conducting polymers and inert matrices and (iii) reticulate doped polymers (RDP) consisting of crystalline networks of low molecular weight organic metals penetrating inert polymer matrices. In the nineties an important progress has been made in obtaining electrically conductive fully organic or hybrid heterogeneous polymeric materials and in understanding the structure-property relationship.

Although the number of new conductive polymeric composites is quickly growing but the mechanism of conductivity in such heterogeneous systems is not fully understood. Most of the usually considered models are not quite adequate because they do not sufficiently take into account the complex morphology of such systems. There are two basic dependences that should be described by the theory: conductivity dependence on the volume fraction of the conducting phase as well as on the temperature and frequency.

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The first one is the domain of percolation theories while the two other should take into account the mechanism of charge transport on nanoscopic and molecular level.

In principle the percolation theory using calculations and computer simulations can predict quantitatively the appearance of the percolation threshold and the dependence of conductivity on volume fraction of conducting elements but for real systems they often give only qualitative agreement. The main reason of important discrepancies is that in the case of best composites developed (high conductivity combined with low percolation threshold) two assumptions of the percolation theories are not strictly fulfilled (i) distribution of conducting particles is not statistical and (ii) conductivity of the particles is not the same as that of the bulk material in particular it can depend on the particle size and on the preparation technique.

The aim of this discussion is to point out that there is a similarity in conductivity mechanisms of polymer (fully organic) composites and nanocomposites and doped conjugated polymers that are also characteristic of specific heterogeneity.

Charge transport in model conjugated polymers

Conducting and semiconducting polymers have been since two decades the object of interest of many research groups including physicists, chemists and material engineers. The news that Alan Heeger, Alan MacDiarmid and Hideki Shirakawa won in 2000 the Nobel price was therefore no surprise as their discovery [1] opened up a broad field of research and possible applications.

Pure, undoped conjugated polymers are insulators or at most semiconductors and high conductivity is obtained upon doping with low molecular weight electron donors or acceptors. It should be noted that such doping differs from doping in semiconductors. The ratio of dopant molecules to monomer is typically several percent or more i.e. by orders of magnitude greater than in inorganic semiconductors. Another important difference is quasi-one-dimensional character of polymer chains which makes the charge transport highly anisotropic. Very important is also structural and morphological inhomogeneity inherently related with macromolecular systems, contrasting with good quality single crystal structure of most inorganic semiconductor devices.

Polymers are characteristic of very small size of crystalline regions (5-50 nm). Ordered crystallites are interconnected by disordered, amorphous regions. However many concepts familiar from classical conductors such as metal-to-insulator transition in disordered materials, hopping or tunnelling of charge carriers appear also to be applicable to conducting polymers. Thus it is reasonable to assume that structural inhomogeneity plays an important role also in the conduction mechanism in conducting polymers and composites. In all cases the macroscopic conductivity is limited by disordered regions. It is therefore important to point out that in the case the composites involving organic conductors, particularly polymers, formation of conducting networks within inert polymer matrices might not increase significantly the volume fraction of disordered regions in the conductive phase. Also the electrical properties of such regions are not expected to differ significantly from that of pure organic conductor. Consequently the conduction mechanism in the composite can be the same.

The model conductive polymer polyacetylene (PA) was not widely used to produce composite materials because of its poor stability in air. It is however instructive to discuss the influence of non-homogeneity on charge transport mechanism also in this case because of many detailed data available. In spite of high value of its conductivity, approaching these of medium conducting metals, the temperature dependence of PA conductivity is semiconductor-like. It was over 20 years after discovery of its high conductivity [1] that first PA samples showing metal-like temperature dependence down to helium temperatures were obtained [2]. For the well conducting samples of PA, polyaniline (PAni) and its composites and low molecular weight (lmw) organic metals composites the conductivity is metallic above the crossover temperature and falls down (but remains high) as the temperature decreases down to liquid helium temperatures.

Heterogeneous nature of conduction was pointed out soon after synthesis of Shirakawa PA when its fibrillar morpholgy was discovered. In a simplest form the fibre would consist of highly ordered and highly conducting regions showing metal-like temperature dependence of conductivity and disordered regions in which e.g. variable range hopping (VRH) conduction mechanism would operate. Such morphology justifies the so called heterogeneous models proposed for highly conductive polyacetylene and recently extensively discussed by Kaiser [3] in which higher and lower conductivity sections are connected in series (in some cases also in parallel). Quality of the polymer (the chain length and the concentration of chemical defects) as well as preparation conditions determin its morphology and it can be accounted for taking appropriate weighting factors and different mechanism of charge transport in imperfect regions. For instance in the case of extended metallic regions separated by narrow imperfect barriers fluctuation-assisted tunnelling mechanism is assumed for the barriers and the temperature dependence of resistivity is described by the formula:

$$\rho_{(\mathrm{T})} = f_1 \rho_{\mathrm{m}} \exp\left(\frac{-T_m}{T}\right) + f_2 \rho_\tau \exp\left(\frac{T_t}{T + T_s}\right) \tag{1}$$

where f_1 and f_2 denote appropriate weighting factors, while T_m , T_t and T_s denote characteristic temperatures and ρ_m, ρ_τ preexponential factors of the respective processes. For smaller metallic regions and bigger disordered parts charging limited tunnelling or variable range hopping are more appropriate and the appropriate formula becomes:

$$\rho_{(\mathrm{T})} = f_1 \rho_{\mathrm{m}} \exp\left(\frac{-T_m}{T}\right) + f_2 \rho_\tau \exp\left[\left(\frac{T_o}{T}\right)\right]^\gamma \tag{2}$$

where T_0 is a constant depending e.g. for VRH on the wavefunction decay and the density of localised states at the Fermi level. The exponent γ depends on the dimensionality of charge transport for 3D it is 1/4 and for 1D case (conducting polymers) it is 1/2.

According to these equations the overall resistivity may show a crossover temperature at which the temperature coefficient changes sign. It is due to the fact that metal-like resistivity increases with increasing temperature while hopping and tunelling processes lead to a decrease of the resistivity when T increases. An important difference between the two formulas is that according to Eq.2 the conductivity falls down to zero in the low-temperature limit (resistivity becomes infinitely high) while in Eq.1 the low-temperature limit of resistivity is determined by T_t/T_s ratio.

The contribution of metallic regions in both formulae is represented by the first term. which describes resistivity in quasi-1D systems proportional to the number of thermally excited phonons according to Kivelson and Heeger [4]. The value of T_m for PA is usually taken after [4] to be 1400 K [2,3,5] while for PAni Kaiser at al. used 1000 K [3] or even 2000 K [6]. Such dependence however gives unrealistically low resistivities at temperatures below 100 K. It is because it takes into account the electron-phonon scattering only, neglecting electron scattering on impurities and lattice imperfections which lead to temperature independent residual resistivity ρ_o . In real systems this contribution is quite high. Especially it should not be neglected in polymer crystals as their perfection is generally much lower as compared with lmw crystals even in a nanoscopic scale (particularly in PA where crystalline structure is formed during synthesis, eventually drawn and doped). It is well seen in the best conducting organic metals (also lmw ones e.g. [7] for which conductivity at low temperatures remains constant or (e.g in the case of the best PA [2]) even linearly decreases. This effect can not be accounted for by the series model. Including ρ_o term is also not sufficient to account for the temperature dependence in all the temperature range but it gives much better approximation as shown in [2] (c.f. squares and their fit in fig.1).

If conductivity is fitted in a linear scale (as presented in e.g. [4-6]) the low temperature data have small effect on the fitting result, especially in the case of less conductive samples. Slightly better fit can not be taken as a strong argument in favour of choosing a given mechanism. More realistic seems therefore assuming that the temperature dependence of conductivity in including residual resistivity term:

$$\rho_{(T)} = f_1\left[\rho_o + \rho_m \exp\left(\frac{-T_m}{T}\right)\right] + f_2\rho_t \exp\left(\frac{T_t}{T + T_s}\right) \tag{3}$$

Examples of such fitting are presented in fig.1 for selected well conducting samples.

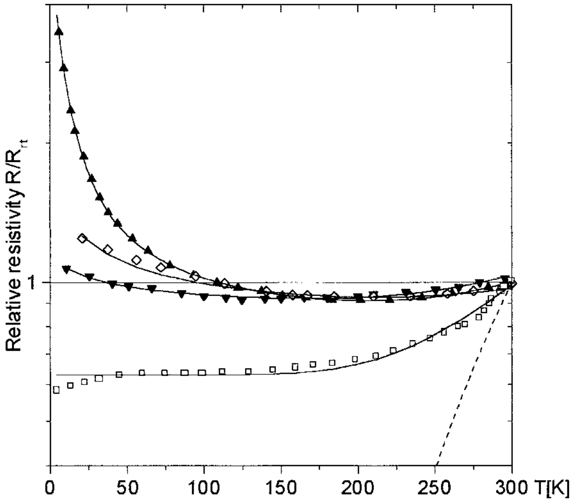

Fig.1 Selected data for PA and PAni samples fitted using Eq.3. PA data of Tsukamoto [8] (diamonds) are fitted using the parameters obtained for Park PA [2] (squares). For fitting PAni (full symbols) data of Holland [9] (down triangles) and Fedorko [10] (up triangles) similar parameters Tm, ρ_m and ρ_o for metallic regions were used. Solid lines show fitting results. Broken line represents the normalised phonon contribution to Park's data fit (without ρ_o term).

For the samples of lower resistivity (PA, PAni and other polymers) the second formula describes quite well the experimental results. The conductivity rapidly falls down and tends to zero as the temperature decreases so the parameters of the hopping term can be more precisely determined if resistivity (not conductivity) is fitted (unless fitting of the log σ is made to give similar weight to all results.

Charge transport in conductive polymer composites

In good conductive polymer composites the volume fraction of the conductive filler may be as low (0.1 - 1wt.%). Comparing these values with the fraction of metallic regions in PA or PAni. (ca.50%) it seems at the first sight that the situation is completely different and the discussed models are inappropriate. However one must keep in mind that the distribution of conductive particles in such composites is deliberately made non-random. The preparation conditions and the properties of filler itself are adjusted so to obtain "agglomeration" of particles to from conducting paths. Therefore most of the inert matrix does not contribute to charge transport and the only elements that limit the conductivity are contacts between particles or microcrystals within the conducting paths. Considering quasi 1D conductivity along the path one should consider concentration of conducting particles and their volume fraction within a 'tube' or 'wire' approximating conducting path. Such effective volume fraction can be by orders of magnitude higher and easily exceed 50%. or even approach unity for fibres, whiskers and other elements of high aspect ratio.

Overall weight fraction of the conducting phase is of course an important technical parameter but it is of little use for understanding the mechanism of charge transport in the composite, because the submicroscopic network morphology is by far more important. Of course this fact is recognised and the existence of a percolation threshold is well known and percolation theories relating conductivity of the system near the percolation threshold are compared with experiment by many researchers. In the systems in which conductive element distribution is close to random it works pretty well. For the systems with specific network morphology, far from statistical distribution, the percolation threshold is usually used only as a phenomenological parameter and fitting conductivity data to percolation theories leads to values of parameters different from theoretical predictions. Conductive network topology is difficult to determine precisely (because of its 3D character) and it is even more difficult to describe by a mathematical model. In some cases fractal theory was successfully used but generally the problem is difficult and remains unsolved.

We want to point out that beside of the topological considerations dealing with the network morphology there is a problem of the mechanism of charge transfer within the network. It is difficult to elucidate quantitatively because of the lack of data on the nanoscopic internal structure of the network. However one can get some insight into its properties studying temperature and frequency dependence of conductivity in a broad temperature range [3,14]. For understanding of charge transport the models developed for intrinsically conductive polymers taking into account their structural inhomogeneity can be very helpful. An indication that at least in some cases they can be directly applicable is the fact that in those composites involving organic conductors for which detailed data are available experimental results show similar dependences and can be well fitted using these models.

Conductivity of polyaniline protonated with camphor sulphonic acid (CSA) and other counter ions can reach very high values (400 S/cm). For the optimum counterion concentrations it shows metallic properties and the crossover temperature around 200-250 K e.g. [10,11] (see full symbols in Fig.1). Depending on the dopant concentration such temperature dependence of conductivity can be fitted using Eq.1, Eq.2 [3,5,6] or Eq.3. It is processible and can be blended with different polymers [6,12,13]. Conductivity of such blends can be high also at low loadings ca.1% showing metal-like character at higher temperatures and the crossover temperature [3,5,6]. It can be best fitted using Eq.2. because the conductivity tends to zero in the low temperature limit. It indicates that virtually the same transport mechanisms operate in bulk material (conductive polymer) and in conducting paths in the composite [3,5,6,14].

Also in the case of other fully organic composites - reticulate doped polymers such approach is applicable. It has been shown that even at the organic metal concentration is of the order of 1 vol% conductive network is continuous at the microscopic scale (as evidenced by frequency dependence of conductivity). Moreover detailed analysis of the results of ESR experiments show that defect distribution within conductive network is non-homogeneous i.e. there are elements of nearly perfect structure and metallic properties and elements of high defect concentration and semiconducting properties [15]. There is therefore a close structural analogy to the situation in e.g. polyacetylene except that only the structure of the conductive network is taken into account. In some such systems metal-like temperature dependences and crossover temperatures are observed [7,14,16,17] similarly as in the case of conjugated polymers.

In such systems resistivity of the metallic term should be taken in a form suitable for quasi-2D organic conductors i.e.

$$\rho_o = \rho_o + aT + bT^2 \tag{4}$$

where the linear term (absent in quasi-1D conductors like TTF-TCNQ) is believed to be a consequence of two-dimensional electronic band structure in ET salts [18] (see also below). Fig.2 presents the results of fitting the data from [16] for organic polymer nanocomposites with bis(ethylenedioxy)-tetrathiafulvalene (BEDO-TTF) salts (2 wt.%) using the series heterogeneous model with the metallic conductivity term described by Eq.4 i.e.

$$\rho_{(T)} = f_1\left(\rho_o + aT + bT^2\right) + f_2\rho_\tau \exp\left(\frac{T_t}{T + T_s}\right) \tag{5}$$

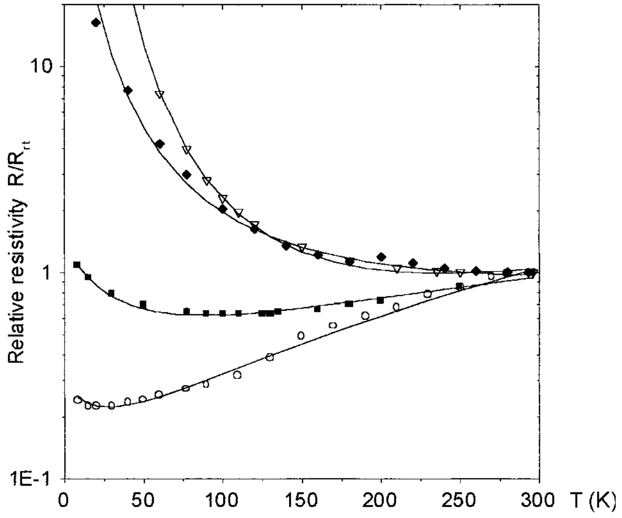

Fig.2 Fitting of the temperature dependence of resistivity for polycarbonate/BEDO-TTF salts nanocomposites prepared at different conditions (see [17] for details). Experimental data from [17], fitting using Eq.5 . Closed symbols Br salt open symbols I salt. Parameters obtained from fitting of single crystals data were used for metallic component in Eq.5.

Like in the case of conducting polymers the coefficients ρ_o, a and b used for iodine and bromine salts were determined by fitting the experimental data for single crystals of BEDO-$TTF_{2.4}I_3$ and BEDO-$TTF_2Br(H_2O)_3$ respectively [7]. Parameters of the tunneling term depend on the properties of the barriers between metallic crystals so they must be different for samples, prepared under different conditions. Well conductive samples show higher T_t up to 250 K while T_s changes are smaller (20-50 K). Lower T_s values are obtained for less conductive samples. It reflects decreasing importance of the elastic, temperature independent tunnelling as the resistivity increases. One can see that also in this case the series heterogeneous model can reproduce the temperature dependence of the conductivity of these nanocomposites quite well in spite of the problems with the properties of the conductive phase discussed below.

Importance of the preparation conditions for the properties of organic conductive phase in nanocomposites.

It is well known that the properties of nanoscopic particles of inorganic materials show different properties than these of the bulk material. The most interesting effects are due to quantum confinement. The size of particles in conductive composites seldom approach this range (1-3 nm). Therefore the assumption that the properties of the elements of the conducting network are the same (or worse) as that of corresponding perfect and imperfect bulk material regions seems reasonable and it is usually fulfilled. It implies that the conductivity of the composite is lower then estimated on the basis of conductivity of bulk conductive phase and its volume fraction which is justified because of generally higher resistivity of contacts between particles which follows in a first approximation simply from geometrical considerations[19].

However in some cases the reverse effect is observed – conductivity of the composite is higher than that of the pure conductive phase (at least below some temperature). This effect was observed for two TCNQ salts in RDP [20,21] and also for PAni/PVC and PAni/PMMA blends [5,6,22]. In the case of RDP the content of the conductive phase was as low as 1-2%. In the PAni blends it was 20-40%. Such phenomenon is observed only in fully organic composites. It can be explained taking into account that of the phase separation and conductive phase formation (and crystallisation) takes place from solution during composite solidification under specific conditions. In the case of lmw conducting phase unusually high conductivity was attributed to different crystal structure while in the case of PAni to reduction of the barriers surrounding PAni particles due to the presence of the 'inert' polymer matrix.

In the case of nanocomposites with BEDO-TTF salts (and with other salts too) their structure and chemical composition and consequently conducting properties strongly depend on preparation conditions. It is not surprising that the crystals obtained under not optimised conditoions show semiconductive or even insulating properties. However also the samples showing the same crystalline structure (as proved by X-ray studies) show different temperature dependence of conductivity (and conductivity differing by an order of magnitude). In Fig 3. we show the data for $(BEDO\text{-}TTF)_{2.4}I_3$ single crystals taken from [7] and [23] and the data for three nanocomposites in which the structure of conducting phase is the same [16]. It can be seen that the temperature dependence is significantly different in these three cases. Fitting to Eq.4 reveals that the contribution of different terms changes significantly. For the data of [7] the linear term dominates at higher temperatures and ρ_o becomes significant below 10 K and dominant below 5 K (it can not be well seen in this scale).

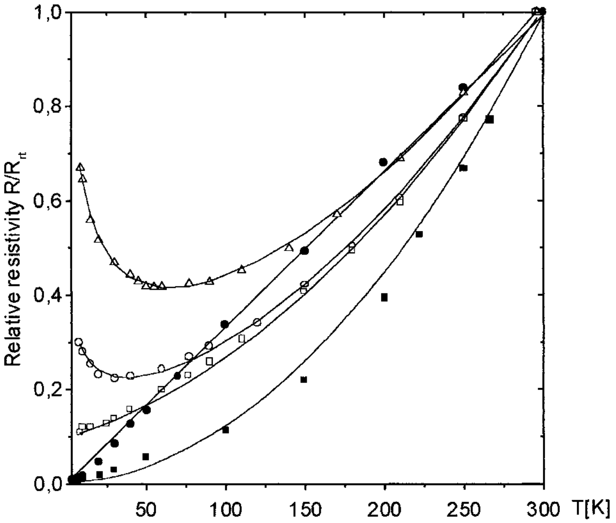

Fig.3 Fitting of the temperature dependence of resistivity for single crystals of $(BEDO\text{-}TTF)_{2.4}I_3$ (data from [23] - full squares) and [7] - full circles, fitting using Eq.4) and for some well conductive polycarbonate/ $(BEDO\text{-}TTF)_{2.4}I_3$ nanocomposites obtained in a different way (experimental data from [17], fitting using Eq.5). The parameters obtained from fitting of metallic nanocomoposite (open squares) were used for the metallic component in the samples showing crossover temperatures.

For the crystal of [23] the quadratic term in Eq.3 dominates in practically all the temperature range (down to 3K). The best reticulate doped nanocomposite shows intermediate behaviour with all three terms in Eq.4 being important. It should be noted that ρ_o is relatively much bigger in this case reflecting higher concentration of defects as compared with the single crystal very slowly grown by electrocrystallisation method. These samples do not show semiconductor-like temperature dependence down to the lowest temperatures which proves very high quality and continuity of the nanocrystalline layer in the composite. However for worse composites as shown in figs 2 and 3 the crossover temperatures are observed and in this case the series model (Eq.5) allows good fitting of the data. The observed phenomena discussed in this section show big importance of preparation conditions for the intrinsic properties of the conducting phase in the case of fully organic composites and nanocomposites.

Conclusion

We show that the models of conduction mechanism in heterogeneous materials developed and verified for bulk conducting polymers such as PA or PAni can be helpful in understanding microscopic electrical properties of conducting networks in polymer composites and nanocomposites regardless of the problems with understanding network topology. Conductivity of nominally the same material can differ by orders of magnitude depending on its nanostructure (crystallite size, perfection and degree of crystallinity). Therefore above the percolation threshold these microscopic properties of the conducting phase can have much stronger influence on the composite properties than the conducting network topology.

In view of some oversimplification of the commonly used series heterogeneous model we argue that more realistic results for composites and nanocomposites are obtained using the parameters determined for best conducting samples of the "filler". Dominant role of the perfection of the structure of the conducting phase on the nanoscopic level should be taken into account in developing better conductive polymer composites and nanocomposites.

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