

Aspects on the percolation and conduction behavior in polypyrrole-poly (vinyl chloride) composite

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Summary

Polypyrrole-poly(vinyl chloride) composite films are prepared by the modification of the diffusion-oxidative polymerization technique with some treatments. This new technique produces promising flexible and electroactive free standing films. The conductivity profile against the polypyrrole content has a surprising intermediate plateau. This plateau treats the percolation problem and provides an indispensable view on the interfacial phenomenon probably occurs in the binary composite systems. In addition, the temperature dependence of the electrical conductivity is explained in the light of two different hopping mechanisms from which the activation energy and the density of electronic states at the Fermi level are determined, approaching well the values predicted for the semi-conducting materials.

Introduction

During the last decade the development of new conducting polymers such as polypyrrole (PPY), polyacetylene (PA) and polyparaphenylene (PPP)...etc., has been subject of great research effort. Because of its remarkable stability in ambient conditions, polypyrrole is considered one of the most interesting conducting polymers which are indispensable in the fabrication of novel materials usable in technological applications. However, the poor mechanical properties of polypyrrole films prepared by both chemical and electrochemical polymerization render them less practical. Improvements of the mechanical as well as the electrical properties are expected from the synthesis of polymer-polymer composites over metal loaded polymers. Therefore, incorporating conducting polypyrrole fillers within an insulating polymeric matrix underlies a persistently promising aim towards the processability of conducting composites (1-6).

Apart from the mechanical properties of polypyrrole-plastics composites prepared electrochemically, the chemical polymerization of pyrrole appeared to be much cheaper and more useful technique for the preparation of conducting composites possessing both high electrical conductivity and improved mechanical properties. In spite of the low level of conduction resulting from the inhomogeneity of the binary composite system, the composites synthesized by the so-called vapor deposition polymerization (7) or by the diffusion-oxidative polymerization (8) of pyrrole monomer into an insulating polymer shed light on the progress in such class of heterogeneous organic systems.

In this work, free standing films of polypyrrole-poly(vinyl chloride) (PPY-PVC) composite have been prepared based on the oxidative polymerization technique but in a different

manner of treatment (namely, mixing-oxidative polymerization) rather than that introduced elsewhere (8). The percolation problem composite system as well as the temperature dependence of the conductivity are discussed with reference to some simple models.

Results and discussion

The X-ray diffraction experiment showed a broad single peak which was similar for all samples used in this study, indicating amorphous-like structure of the PPY-PVC composite system.

To investigate the morphology and the growth of the conducting polymer (PPY) in the PVC matrix polymer, the transmission electron microscopy has been performed for the samples labeled MO2 and MO5 (see fig. 1a and fig. 1b). From the comparison of the two figures it is evident that the conducting phase represented by the incorporating PPY network through the PVC matrix depends upon the content of pyrrole monomer diffusing within the PVC film during the polymerization procedure. The reason for that might be caused by the swelling of pyrrole to the PVC film. Thereby, a proper creation of pyrrole channels is to be opened leading to the extreme oxidation of pyrrole under the action of the oxidizing agent (FeCl_3).

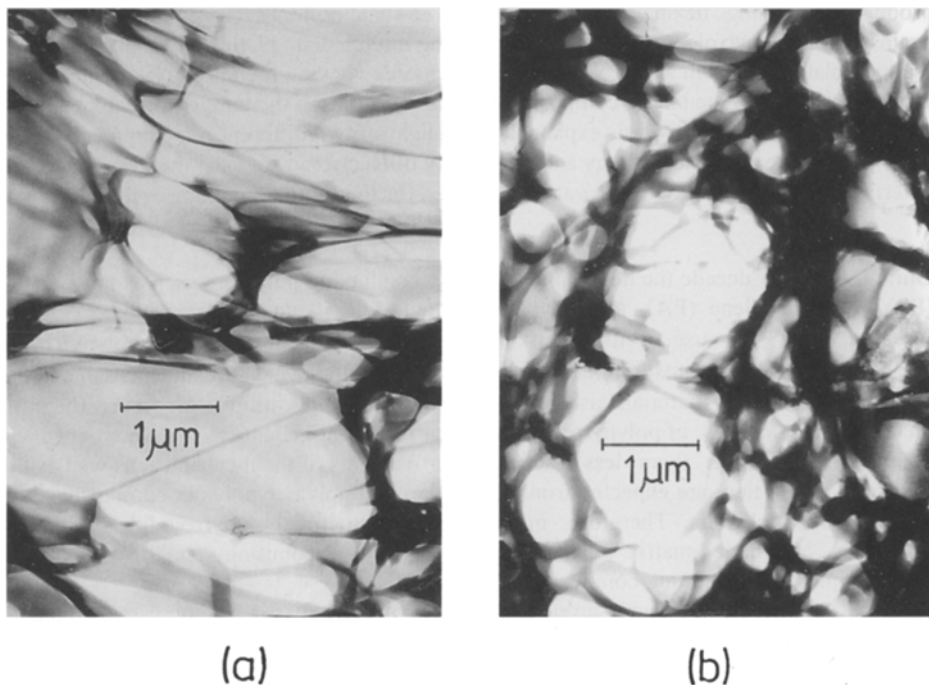


Fig. 1. Transmission electron micrographs of PPY-PVC composite films. (a) Sample MO2 and (b) Sample MO5.

Fig. 2 illustrates the variation of the conductivity with respect to the polymerization time. It is clear obvious that the conductivity is strongly influenced by the time of oxidative polymerization up to about 3 hours after which the dependence goes slowly. This experiment was succeeded for the composites labeled MO3, MO4 and MO5. However, for

the other two composites the conductivity was too low to be measured using polymerization times lower than 6 hours.

In fact, the oxidizing agent (FeCl_3) plays an important role on the doping level of polypyrrole during the oxidative polymerization procedure. This can be manifested as follows: The resultant of the reaction mechanism is an oxidized PY with the dopant FeCl_3 . This dopant ion has well-defined tetrahedral conformation resulting in a strong stability of the PPY phase as well as an enhanced conductivity level with the running time (10,11).

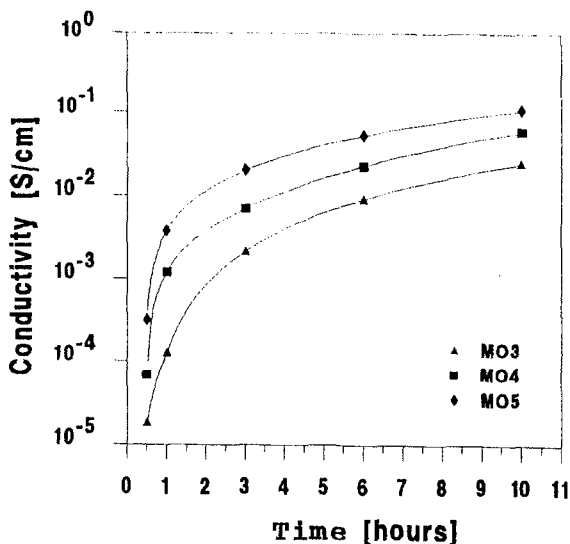


Fig.2. D.C. conductivity as a function of the time of oxidative polymerization. Solid lines are guide lines.

Fig.3 shows the d.c. conductivity for the PPY-PVC films as a function of the volume concentration of polypyrrole content. The conductivity profile surprisingly includes two different regimes of percolation: First, for concentrations, Φ_v , above a critical concentration Φ_{vc} (~15 vol.%) the data satisfy the classical percolation model (12-14). The model correlates the conductivity of real mixtures with the volume fraction of the conductive filler through the equation

$$\sigma = \sigma_0 (\Phi_v - \Phi_{vc})^\mu \quad (2)$$

Where σ_0 is the conductivity of the filler and μ is a quantity depends only on the dimensionality of the system.

The continuous solid line shown in the figure is the theoretical fit given by equation (2). The values of σ_0 , Φ_v and μ were found to be 1.05 S/Cm (pressed pellet of chemically oxidized PPY powder using FeCl_3 as the oxidizing agent), 0.15 and 1.5, respectively. These values are in good agreement with those predicted by the model above in three-dimensions, even with the difference that we are concerned with a continuously propagated PPY clusters within the PVC matrix rather than agglomerating conductive particles in a mixture with the matrix as proposed by the model.

Second, for $\Phi_v < \Phi_{vc}$ we pass through an intermediate plateau which reveals that there should be another threshold existing in the early concentration scale. This plateau sheds a

light to a very important interfacial phenomenon that might happen in the binary composite systems, we call it "coating". The nature of this "coating" probably comes from either a thermodynamic thought of chemical reaction between PPY and PVC phases, creating a new phase with different properties, or rather from some impurities inserted during the polymerization reaction.

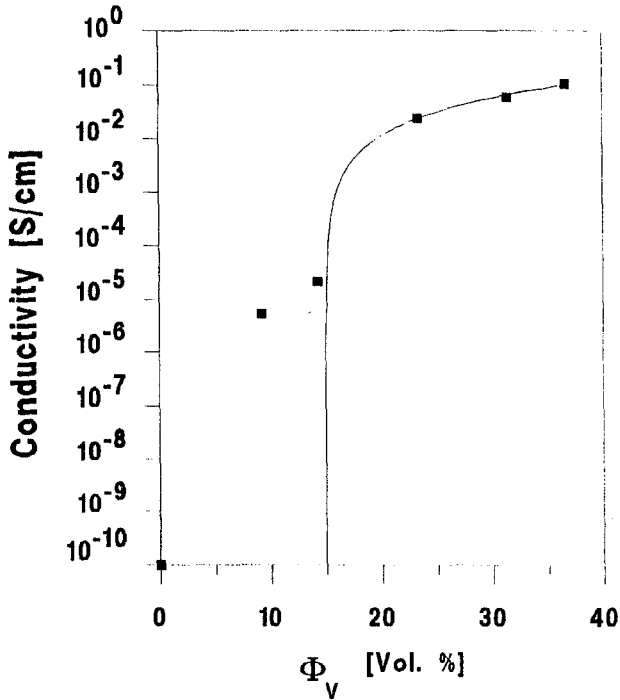


Fig.3. D.C. conductivity as a function of polypyrrole volume concentration. Filled squares are the experimental values. Continuous solid line is the theoretical fit of equation (2) using $\Phi_{vc} = 15$ vol. %.

The percolation in our composite system can be interpreted through the schematic configuration shown in fig.4. In this figure the solid channels refer to the polypyrrole growth inside the PVC matrix whereas the dots refer to the intermediate phase "coating" created during the oxidative polymerization process. One could regard the problem as two-phase percolation formulating in three situations. In the initial state, where the relative pyrrole content is very low, both PPY and "coating" phases grow discontinuously such that the insulating PVC matrix dominantly is responsible for the bulk conductivity as illustrated by the left box. Increasing the pyrrole content enhances the probability of interconnecting "coating" channels in the expense of the PPY ones. Thereafter, at a threshold probability P_1 an incipient infinite cluster of "coating" is formed which affects the conductivity of the whole composite (middle box). Finally, inserting more amount of pyrrole monomer into the reaction gives rise to another threshold P_2 at which the PPY channels percolates (right box). The conductivity in this case is actually determined by the polypyrrole phase. It is worth mentioning that the problem of intermediate plateau has been modeled elsewhere (15).

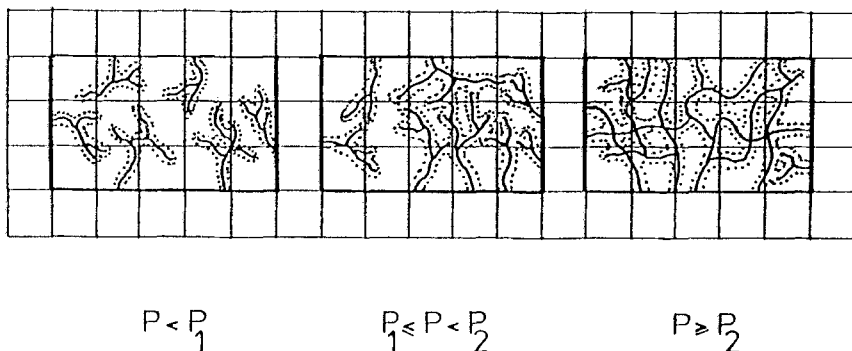


Fig.4. Schematic diagram of the two-phase percolation in PPY-PVC composites, as scaled on a squared lattice. PPY (solid clusters); "coating" (dotted clusters).

Furthermore, our composite system can be treated as a continuum medium due to the continuously growing PPY and "coating" clusters within the PVC matrix. Therefore, one might ask "does the continuum percolation scales with the lattice percolation?". The answer of this question can be guided by the theorem (16) expressing that there should be a transformation between the continuum and discrete (lattice) percolation if the exponents μ (critical exponent of conductivity) and γ (critical exponent of the mean cluster size) are identical for both. Indeed, the data and the calculation in hand confirm the validity of the theorem in our composite only for the percolating PPY clusters, but yet less satisfactory to provide quantitative details about the percolation of the "coating" phase.

Fig.5 illustrates the logarithmic plot of the d.c. conductivity against the reciprocal of the temperature (for the sample MO5). The data represented in that figure fit well the Arrhenius relation,

$$\sigma = \sigma_1 \exp \{ -E_A / K_B T \}, \quad (3)$$

in the temperature range 240-420 K. The conduction mechanism can be attributed to the thermally activated hopping of charge carriers between the localized states near the Fermi level E_F (17,18). Here σ_1 is the pre-exponential factor, E_A the activation energy for hopping and K_B the Boltzmann constant.

The activation energy for the hopping process determined from the least square fit equals 0.04 eV which is in good agreement with the values published for pure polypyrrole (19). This process has been put in analogy with the impurity conduction in heavily doped crystalline semiconductors.

However, below the temperature 240 K the conductivity decay introduced into another mode of calculations, that is the Mott's law of variable range hopping (VRH model) (20) represented by the equation,

$$\sigma = \mathbf{k}_0 T^{-1/2} \exp \{ - (B / T^{1/4}) \} \quad (4)$$

where \mathbf{k}_0 and B are parameters related to α^{-1} (the electronic state localization length), to $N(E_F)$ (the density of states at the Fermi level) and to ν_{ph} (the phonon frequency) by the expressions

$$B = 1.66 \{ \alpha^3 / K_B N(E_F) \}^{1/4} \quad (5)$$

and

$$\mathbf{k}_0 = 1.55 e^3 \nu_{ph} \{ N(E_F) \alpha^{-1} / K_B \} \quad (6)$$

where e is the electronic charge.

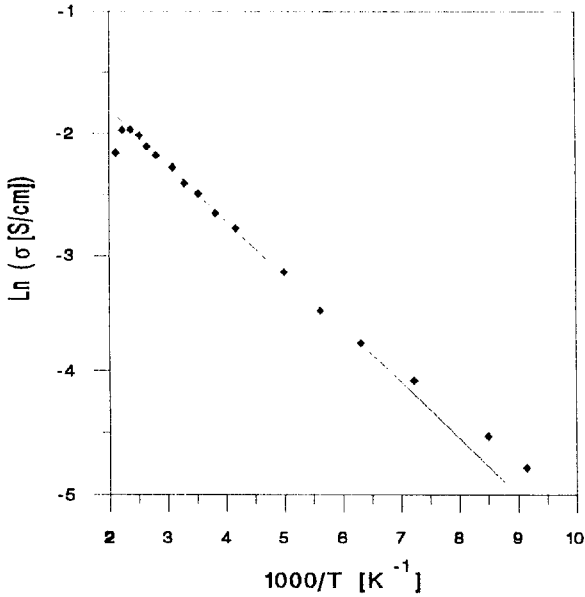


Fig.5. Temperature dependence of D.C conductivity (sample MO5). Solid line is the linear fit to the data.

Fig.6 represents the relation of $\text{Ln } \sigma T^{1/2}$ versus $T^{-1/4}$. From the linear regression analysis of the least square fit of the experimental data, the value of B equals 43.8. Using the value of α^{-1} to be about the pyrrole monomer dimension ($\sim 3 \text{ \AA}$) (21), the density of states at the Fermi level thus equals $\sim 9 \times 10^{20} \text{ cm}^{-3} \text{ eV}^{-1}$. This value is in agreement with that predicted for the semiconductors.

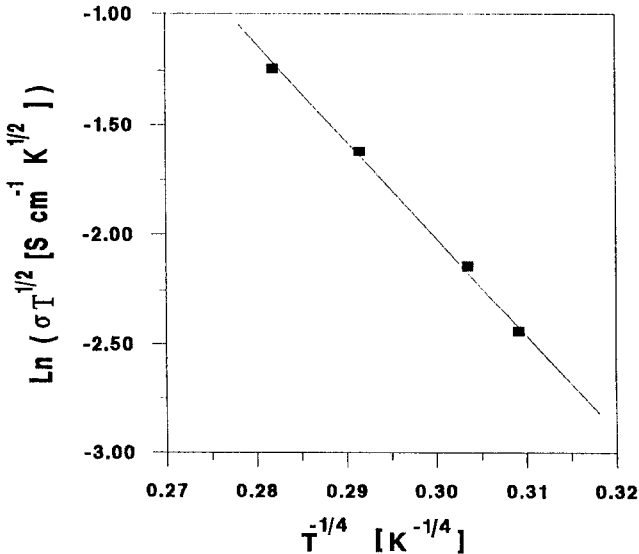


Fig.6. Mott's behavior (VRH model) (sample MO5). Solid line is a linear fit to the data.

Experimental

Materials and PPY-PVC composite film preparation

The materials used in this study are: pyrrole monomer (Aldrich) distilled twice before use and stored darkened in refrigerator, ferric chloride penta hydrate (Fluka) used as received, and high molecular weight poly(vinyl chloride), PVC, (Fluka). The method of preparation of the PPY-PVC composite taking the new name "mixing-oxidative polymerization" proceeds in two successive stages: 1) Purification of pyrrole-containing PVC. In this stage, 500 mg PVC is dissolved in 6 ml tetrahydrofuran, THF. After thorough mixing with a magnetic stirrer a proper amount of pyrrole (300-800 mg) is poured into the solution and stirred at room temperature for about 15 minutes. Then, the solution is casted carefully in a Petri-dish. The purification was processed in a dark place for about 24 hours under environmental conditions such that the evaporation rate of THF is slow enough to avoid devitrification. Then the film is pulled gently and cut into strips (the area of each $\sim 2 \times 4 \text{ cm}^2$). 2) Oxidative polymerization of PVC-incorporated pyrrole. Here, each strip is dipped (the length is vertical) in an aqueous solution of 10 wt.% FeCl_3 (oxidizing agent). After a required polymerization time and for removing any polypyrrole residuals accumulated on the surfaces, the strip is washed in acetone/distilled water mixture, in distilled water and in acetonitrile, respectively. The strip is then taken quickly into evacuated oven operated at 50°C and remained for about 24 hours.

The amount of polypyrrole contained within each composite strip was determined by means of weighting before and after the polymerization procedure. Depending on the amount of pyrrole monomer during the mixing-oxidative polymerization, five samples were obtained, namely: MO1, MO2, MO3, MO4 and MO5, corresponding to 300 mg, 400 mg, 500 mg, 600 mg and 800 mg pyrrole monomer, respectively.

Characterizations

The X-ray diffraction intensity was recorded against the scattering angle (2θ) for the different composite samples using PW 1820 Philips powder diffractometer with $\text{CuK}\alpha$ filter ($\lambda=1.5418 \text{ \AA}$.) and electric supplies of 40 KV and 35 mA.

Transmission electron microscopy (TEM) studies were carried out for the composites MO2 and MO5 using Zeiss EM902 instrument. Ultra thin sections (ca. 200 nm) were prepared in Reichert ultra cut E at temperature of 30°C . Diamond knife was used for this purpose together with a floating liquid consisting of a mixture of H_2O and DMSO. The magnification for micrographs was 18000.

D.C. conductivity measuring method

The d.c. conductivity of the composite samples was measured by the standard linear four-probe method (9): Current I was passed through the outer electrodes and voltage V was measured between the inner electrodes. The conductivity was calculated from the formula

$$\sigma = (1/2\pi) \{ (1/d_1) - (1/d_1 + d_2) - (1/d_2 + d_3) + (1/d_3) \} \quad (1)$$

where d_1 and d_3 are the distances between the outer and inner probes on both sides, each of which equals 7 mm and d_2 is the distance between the inner probes and equals 3 mm. Gold-coated stainless steel spring electrodes were used. For obtaining good contacts, very smooth coatings of silver paste to the touch points were performed.

Conclusion

The new method of mixing-oxidative polymerization gives rise to an electroactive polypyrrole-poly(vinyl chloride) composite system. The intermediate plateau shown by the

relation between the conductivity and the polypyrrole content gives an insight into the interfacial phenomenon "coating" probably occurring in binary systems. This "coating" identifies the compatibility of the constituents entering the polymerization reaction and underlies its entity whether it is some impurities or rather being a kind of thermodynamic chemical reaction between the extreme phases. These varieties probably slower or even precludes the percolation of the conducting phases inside the insulating matrices. The higher conductivity sample (MO5) exhibits temperature dependence of conductivity profiles having semiconductor values of both the activation energy and the density of states at the Fermi level.

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