

## PROPERTIES OF $\text{SbCl}_5$ -DOPED PPP/PPS COMPOSITES\*

### I. ELECTRICAL CONDUCTIVITY STUDY

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#### Abstract

In this set of two papers the electrical and surface mechanical properties for sintered PPP/PPS composites, in a wide range of compositions, are reported. The present paper deals with a conductivity study of these materials. PPP, before and after annealing at 400 °C, was used as a potential conductive component. It is shown that these  $\text{SbCl}_5$ -doped sintered composites undergo a discontinuous transition from non-conductor to conductor at 20% PPP. The surface of the sintered materials and the dopant distribution across the thickness were characterized by scanning electron microscopy and energy dispersive X-ray analysis respectively. Morphological aspects are discussed in the light of conductivity measurements. In addition, the electrical stability after storage of the composites in air and in dry nitrogen atmosphere is examined. Finally, the influence of the annealing behaviour of the PPP component upon the limiting conductivity level is highlighted.

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#### Introduction

The enhancement of electrical conductivity of conjugated polymers by several orders of magnitude upon doping with electron acceptors or donors is a well-established phenomenon [1, 2]. Specifically, the electrical conductivity increase in polyparaphenylene (PPP) doped with antimony pentachloride and chlorosulphonic acid was investigated in our laboratory, *in situ* and after storage, with reference to structural details, using X-ray diffraction and infrared (i.r.) techniques [3, 4]. Besides the problems concerning the instability of conducting polymers in air, it is known that these organic compounds are difficult to process from the melt or from solution, an

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important consideration for their potential applications as materials. Attempts to prepare conductive polymeric materials using thermomechanical processes to obtain modified morphologies have been, nevertheless, recently reported [5, 6]. An alternative possible route to obtain conductive organic materials is to develop blends of conducting polymers with insulating thermoplastic matrices [7 - 10]. In order to improve both the electrical and mechanical properties of doped PPP, poly(*para*-phenylene sulphide (PPS) represents a good candidate as a processable matrix [11]. This is due, first, to its chemical structure, which is similar to PPP, and secondly to its inherent potential conducting capability upon doping [3, 11, 12].

In the present two papers we report electrical conductivity and hardness measurements of doped composites of PPP (conductive polymer) and PPS (matrix) in a wide range of concentrations. The first paper (present) deals with the conductivity behaviour of these composites and examines the electrical stability of these materials through storage in dry nitrogen and in air. The weight uptake, apparent density, scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) analysis were employed to characterize the doping process. The second paper [13] will be concerned with the surface hardening behaviour of these composites upon doping with  $\text{SbCl}_5$ .

## Experimental

Poly-*para*-phenylene was synthesized according to the Kovacic method, [14], *i.e.*, cationic polymerization of benzene using  $\text{CuCl}_2$  as oxidant and  $\text{AlCl}_3$  as catalyst. Some of the PPP powder was annealed at  $\sim 400^\circ\text{C}$  under dynamic high vacuum for 36 h in order to remove the oligomeric component. Both types of PPP, the powder as synthesized (to be called PPP) and the annealed powder (PPPa), have been used as the dispersed phase (micro-additive) to prepare two-phase (composite) conducting materials. Commercial poly-phenylene sulphide (Ryton) in powder form was used as the matrix. Samples of PPP/PPS and PPPa/PPS in a wide range of concentrations were prepared manually by mixing the powders. Platelets 13.0 mm in diameter and  $\sim 600\ \mu\text{m}$  thick were then obtained by sintering the powders at 0.75 GPa for 2 min under rotary vacuum. The apparent density was calculated from the ratio of weight to volume of the sintered undoped samples. Simultaneous doping of both PPP/PPS (A series) and PPPa/PPS (B series) composites was carried out by exposing the samples to the action of vapour pressure of  $\text{SbCl}_5$  under a static rotary pump vacuum. Special attention was given to the location of the samples within the doping cell walls. The doping process was followed through measurement of the *in situ* conductivity of a parallelepipedic sample of PPP attached to the two Pt electrodes within the doping cell.

After doping the samples at room temperature for 21 h, the cell was evacuated for  $\sim 2$  min, removed from the vacuum line and opened within a dry nitrogen atmosphere. After a storage period of more than 3 h, the

electrical conductivity of the samples was measured by the four-point method within the dry inert atmosphere (glove box). The weight of the samples was subsequently measured. Both the electrical conductivity and the weight of the samples were measured throughout their storage time; care was taken to avoid the basal surface contact. An ISI DS/130 scanning electron microscope coupled to a Si/Li detector and a Kevex 8000-II processor was employed for the sample characterization.

## Results and discussion

### Conductivity study of composites

Electrical conductivity data measured first in an inert atmosphere (open symbols) and then in air (solid symbols) are shown in Figs. 1 and 2 for the series A and B respectively. In all cases the concentration dependence of the conductivity has a threshold character defining the transition from non-conductor to conductor near 20% PPP. It is well established that solid mixtures of electrically conductive microadditives (carbon black, metallic particles, molecular charge-transfer complexes) dispersed in a non-conducting matrix undergo similar discontinuous transitions in the vicinity of the percolation threshold [15 - 18]. Below the critical concentration,  $\sigma$  for both series A and B corresponds to the values for doped PPS ( $\sim 10^{-6}$  ohm $^{-1}$  cm $^{-1}$ ). Above the critical transition, the  $\sigma$  level is apparently larger for the B series (PPPa/PPS) than for the A series (PPP/PPS). However, the preferential location of the doping agent within a  $\sim 5$   $\mu$ m surface layer (see next section) imposes a correction of  $\sigma$  for the A samples by a factor of about  $3 \times 10^2$  [19]. After such a correction, the  $\sigma$  values for A samples are slightly

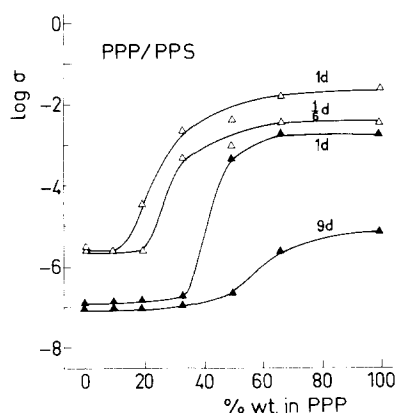


Fig. 1. Plot of  $\log \sigma$  (ohm $^{-1}$  cm $^{-1}$ ) vs. weight percent of PPP for SbCl $_5$ -doped sintered PPP/PPS composites, after different storage times in dry N $_2$  atmosphere (open symbols) and in air (solid symbols).

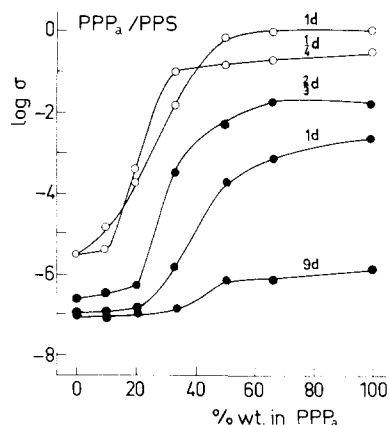


Fig. 2. Plot of  $\log \sigma$  (ohm $^{-1}$  cm $^{-1}$ ) vs. weight percent as in Fig. 1 using annealed PPPa at 400  $^{\circ}$ C as a component in the PPPa/PPS composites.

above the  $\sigma$  values for B samples. Above the critical transition, the  $\sigma$  values for both series after the first few hours (4 - 6 h) of storage in an  $N_2$  atmosphere are  $\sim 10^{-1} \text{ ohm}^{-1} \text{ cm}^{-1}$ . These values still increase by about one order of magnitude after a day of storage in an  $N_2$  atmosphere. After longer storage times, the  $\sigma$  values do not increase any further. Exposure of the composites to air provokes a notable depression in the  $\sigma$  values, which is more pronounced for the B than for the A samples. The final  $\sigma$  level, after nine days in air, is  $\sim 10^{-6} \text{ ohm}^{-1} \text{ cm}^{-1}$  for the (PPPa/PPS) systems and one order of magnitude (three orders after thickness correction) larger for the PPP/PPS materials. In addition, after the first day of exposure to air, a shift of the critical transition towards a concentration of about 33% is observed.

### Morphology and conducting behaviour of composites

In order to examine the conductivity behaviour of these composites in the light of the microstructure and morphology, parallel weight-uptake,  $\Delta W/W$ , apparent density,  $\rho$ , SEM and EDX measurements were carried out. Figure 3 shows the relative weight increase for doped samples after six hours of exposure in an  $N_2$  atmosphere throughout the composition range. It is seen that  $\Delta W/W$  exhibits much larger values for B samples than for A samples. The obtained correlation of weight increase with the apparent density is shown in Fig. 4. The density for B samples varies from  $1.2 \text{ g/cm}^3$  for 10% PPPa (B10) down to  $0.72 \text{ g/cm}^3$  for 100% PPPa (B100). This value is close to the one reported by Froyer *et al.* [20] for PPP annealed at  $400^\circ \text{C}$  for seven days. The density of A samples does not vary substantially throughout the composition range ( $1.2 \pm 0.2 \text{ g/cm}^3$ ). The above results suggest first, that the annealed samples exhibit a weight increase of the dopant that parallels the density deficiency of the material. Secondly, the different behaviour of the A and B samples concerning their weight uptake has no counterpart in the electrical results collected in Figs. 1 and 2.

Scanning electron microscopy illuminates the considerable differences between the microstructure of sintered PPP and PPPa (Fig. 5(a, b)). Sintering

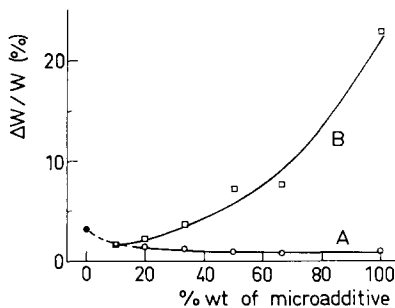


Fig. 3. Relative weight increase measured after  $\sim 6$  h storage in dry  $N_2$  atmosphere for PPP/PPS (curve A) and PPPa/PPS (curve B) sintered composites.

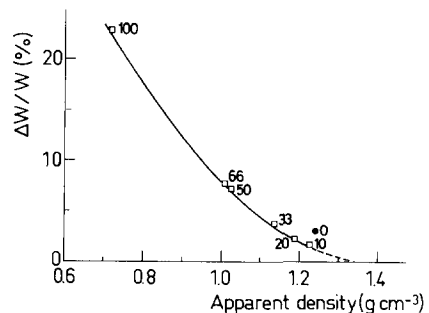
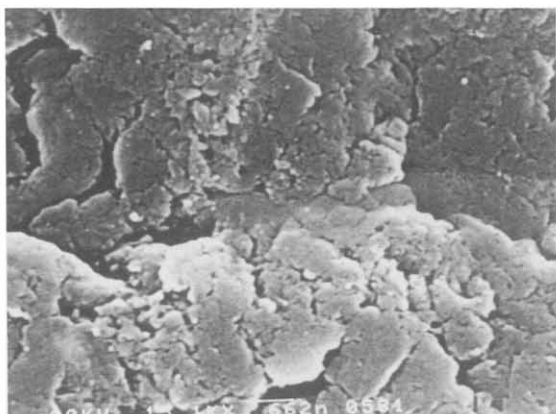


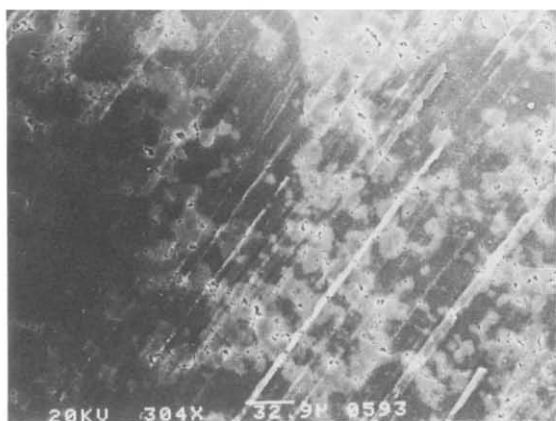
Fig. 4. Correlation of relative weight increase given in Fig. 3 with the apparent density of sintered PPPa/PPS composites.



(a)



(b)



(c)

Fig. 5. Scanning electron micrographs of the surface of sintered samples of: (a) PPP, (b) PPPa, (c) PPP/PPS with 50 wt.% PPP.

involves the densification by coalescence of separated particles to yield a more or less compact mass below the melting point of the material. Essentially, the sintering process must involve an initial interaction between surface molecules of individual particles. Subsequently, there must be some material transfer through the interparticle regions. The original sintered PPP is, indeed, a compact homogeneous material composed of an efficiently compressed assembly of flat globular particles (1 - 2  $\mu\text{m}$ ) (Fig. 5(a)). Sintered PPPa (Fig. 5(b)) exhibits, on the contrary, a rather rough surface consisting of looser particles separated by a great many microvoids of up to 1  $\mu\text{m}$  in size, enhancing the brittleness and lowering the hardness value of the material [13]. The annealing treatment thus seems to modify substantially the surface of the particles, lowering the interaction between surface molecules and consequently reducing the material transfer through the interparticle surface. In any case, the above morphological differences, A samples being more compact and B samples being rather porous, substantiate the  $\Delta W/W$  versus  $\rho$  correlation shown in Fig. 4. Figure 5(c) illustrates the surface of the PPP/PPS (50:50) sintered composite, showing the distinct particle distribution. Darker areas correspond here to the PPP conductive component and brighter ones to the PPS matrix. The apparent homogeneous dispersion of the PPP component within the PPS matrix shown in Fig. 5(c) seems to facilitate the required three-dimensional network structure that rises the  $\sigma$  level to near the value for pure doped PPP. However, the large size of the conductive particles (PPP) ( $\sim 1 - 2 \mu\text{m}$ ) requires a concentration of at least 20 wt.% additive to form the conductive network, *i.e.*, a content of conductive additive 10 - 20 times larger than in the case of other microadditives [15 - 18]. One may suggest that the conductivity in these PPP/PPS composites will depend on the percolation level for the conducting doped PPP particles. Carriers within the composite will consequently be transported above the percolation threshold through the PPP three-dimensional network involving, most probably, a tunnelling mechanism between many adjacent conductive regions. Such a carrier transport mechanism has been shown to occur in other composite systems containing metallic or carbon compound microadditives [17, 21].

EDX line profile analysis of the cross-sections for PPP, PPPa and PPS permits the Sb content across the thickness of these samples to be assessed. The results shown in Fig. 6 confirm the much larger diffusion of the dopant throughout the volume of the sintered PPPa composite. In the cases of sintered PPP and PPS, the doping process is restricted preferentially within the material surface. Hence, while the conductivity mechanism of the PPPa composites is a volume process, the  $\sigma$  behaviour for PPP composites is essentially a surface property.

#### *Electrical stability*

A final relevant aspect concerning the performance of these materials is their electrical behaviour after storage under different atmospheres. Figure 7 shows the variation of conductivity in a log-plot for PPP and PPPa in the

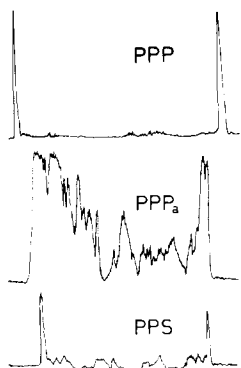


Fig. 6. EDX line profile of  $SbL\alpha$  taken from the cross-section of the sintered single components.

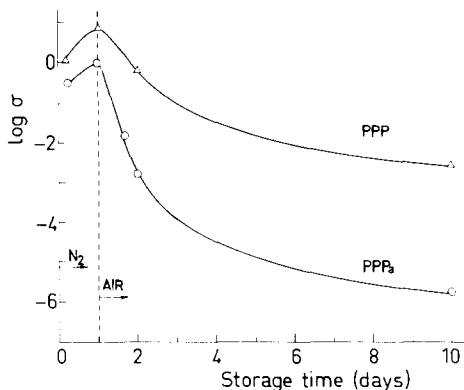


Fig. 7. Variation of  $\log \sigma$  ( $\text{ohm}^{-1} \text{cm}^{-1}$ ) with storage time for the sintered conductive component.

light of a two-stage process: (i) a storage in an inert ( $N_2$ ) atmosphere for one day; (ii) exposure to ambient (air) atmosphere for a further nine days. The behaviour of  $\sigma$  for PPP in a dry  $N_2$  atmosphere within the first days has been verified. However, exposure of the composite to air provokes an exponential decrease in  $\sigma$ , which is more pronounced for the B than for the A samples. The data given for PPP are corrected for the thickness of the doped surface of  $\sim 5 \mu\text{m}$ . This differing rate of decrease for both samples can be correlated to the higher diffusibility to air of B samples. The initial conductivity increase obtained during storage of the material in  $N_2$  (Figs. 1, 2 and 7) can be attributed to a diffusion of the dopant within the samples. According to Fig. 6, diffusion for A samples is essentially a surface effect, while for B samples it is a volume effect. Concurrently, the storage of the composites in  $N_2$  entails a conspicuous weight-loss of the dopant, especially for the B

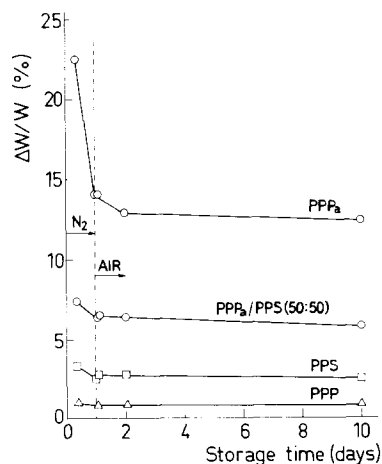


Fig. 8. Relative weight variation of the doped samples as a function of storage time.

samples (Fig. 8). Obviously the latter effect entails the elimination of a substantial volume fraction of ineffective dopant, which does not contribute to the conductivity value.

The main reason for the conductivity-loss of samples exposed to air is the hydrolysis effect suffered by the dopant molecules, presumably reducing the subsequent diffusion of dopant out of the samples. The i.r. spectra from the material surface of doped samples exposed to air show the typical bands of undoped PPP (803, 995, 1475  $\text{cm}^{-1}$ ) and additional new broad bands characteristic for the dopant exposed to air. From the constancy of the ratio of absorbances,  $A_{803}/A_{1475}$ , for undoped and doped spectra, it is inferred that no chemical modification of PPP occurs throughout the doping time used. This result suggests that conductivity enhancement of PPP is probably due to the formation of a charge-transfer complex.

## Conclusions

Doping of sintered PPP/PPS composites has been attempted to develop new light conducting materials. The preparation of sintered PPP/PPS composites, doped with  $\text{SbCl}_5$ -vapour offers, for PPP compositions greater than 20%, compact conducting materials with  $\sigma$  in the range  $10^0 \text{ ohm}^{-1} \text{ cm}^{-1}$  with good electrical stability in dry  $\text{N}_2$  atmosphere. The use of annealed PPP in the sintered composites yields similar conductivity levels, though the material becomes more brittle owing to the large amount of microvoids developed within it. Exposure of both composite types (A and B) to ambient atmosphere reduces the conductivity level by several orders of magnitude.

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