Conducting polypyrrole–polyimide composite films

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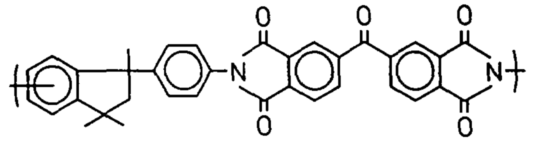
Novel polypyrrole–polyimide composite films are reported which combine high electrical conductivity with high thermal stability. The composite films were prepared either by electrochemical polymerization of pyrrole on a polyimide coated electrode (type I films) or by exposing polyimide films containing ferric chloride as an oxidizing agent to pyrrole vapour (type II films). Type I films consist of a sequence of three layers with the polyimide sandwiched between two layers of polypyrrole. The maximum conductivity is about 10 S cm^{-1}. Type II films consist of polyimide containing finely dispersed polypyrrole particles of 10 to 500 nm in diameter. The maximum conductivity is about 5×10^{-4} S cm^{-1}. The composite films are thermally stable up to 350°C.

(Keywords: polypyrrole; polyimide; conducting polymer; composite film; thin film; thermal stability)

INTRODUCTION

New polymeric materials with interesting combinations of physical properties can be prepared by the formation of polymer blends, alloys or composites. Recently electrically conducting polymer composite films have been reported, which combine the electrical conductivity of polypyrrole, for example, with the good mechanical properties of insulating polymers such as polyvinylchloride[1–3], polyvinylalcohol[3–5], polyether–polyester thermoplastic elastomers[6], Nafion[7], brominated polyvinylcarbazole[8], or vinylidene fluoride–trifluoroethylene copolymer[9]. The conducting composite films are prepared either by electrochemical polymerization of pyrrole on an electrode substrate whose surface is coated with an ordinary insulating polymer film[1,2,5–9], or by exposing a polymer film containing an oxidizing agent such as ferric or cupric chloride to pyrrole vapour[3,4]. In every case conducting composite films are obtained whose mechanical properties are considerably improved compared to the brittle polypyrrole. Here we report for the first time on novel polypyrrole–polyimide (PPy–PI) composite films, which combine high electrical conductivity with high temperature stability and good mechanical stability. Our films are based on polyimide 1[10]



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as the insulating matrix polymer, which is readily soluble in numerous organic solvents in the fully imidized state. The composite films were prepared by electrochemical oxidation of pyrrole on a polyimide coated electrode (type I films) or by exposing polyimide films containing ferric chloride as the oxidizing agent to pyrrole vapour (type II films).

EXPERIMENTAL

Materials

Polyimide **1** was prepared from benzophenone tetracarboxylic acid anhydride and 5 (6)-amino-1-(4′-aminophenyl)-1,3,3-trimethylindane. The inherent viscosity was 0.84 dl/g as determined in *N*-methylpyrrolidone at 25°C.

Preparation of PPy–PI composite films

Type I films were prepared using a two electrode arrangement in a single compartment cell. Two platinum electrodes (50 × 20 × 1 mm) were used, one of which was coated with a 1–5 μm thick film of polyimide **1** using ordinary spin casting techniques. The cell contained 0.05 M pyrrole (Fluka purum, redistilled) and 0.1 M tetrabutylammonium (TBA) electrolyte salt (Fluka puriss., for the counterion see *Table 1*) in distilled acetonitrile treated with 1% of water. The two electrodes were placed 4 cm apart and a current density of 1 mA cm^{-2} was applied. The coated electrode was used as the anode. After electrolysis the composite film was washed with acetonitrile and stripped from the substrate.

Type II films were prepared as follows. Films of polyimide **1** (thickness 30–100 μm) were cast from a solution of the polymer (concentration 0.1 g/ml) and anhydrous ferric chloride (Fluka purum p.a.; various concentrations, typically 0.01 g/ml) in chloroform/1,1,2,2-tetrachloroethane (2:1). After solvent evaporation the films were exposed to an argon atmosphere saturated with pyrrole vapour ($T = 20$°C). The films turned gradually dark due to formation of polypyrrole.

The film morphology was investigated by transmission electron microscopy (TEM) (Philips EM 300) and scanning electron microscopy (SEM) (Cambridge Stereoscan S4-10). For TEM observations the films were stained with OsO_4 vapour and embedded in an epoxy matrix. Subsequently, cross-sections were cut using an LKB Ultramicrotome III. For SEM observations a thin layer of gold was evaporated onto the films.

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RESULTS AND DISCUSSIONS

Type I films

Details of the film preparation are described in the Experimental section. After switching on the electrical current the polyimide coated anode turned gradually dark due to formation of polypyrrole. The rate of pyrrole polymerization was dependent on the thickness of the insulating polyimide coating. On thick coatings polypyrrole formation was retarded or even completely prevented. Therefore, composite films of good and reproducible quality were only obtained if the thickness of the polyimide film was precisely controlled and did not exceed 5 μm.

In *Figure 1* the specific electrical conductivity, σ, is plotted as a function of the polypyrrole content of the composite film. The σ values were measured on the film surface by the two-probe technique. The film composition was determined gravimetrically by weighing the coated anode prior and subsequent to electrolysis.

A homogeneous distribution of polypyrrole in the matrix polyimide would lead to the typical behaviour of a filled conducting polymer, which is characterized by a sudden increase in conductivity when a certain filler concentration being usually between 10 and 20% is exceeded. However, type I films already exhibit a fairly high conductivity at very low polypyrrole concentrations (*Figure 1*). We conclude therefore that the initial deposition of polypyrrole mainly occurs at the polyimide–electrode interface and leads to surface, rather than to bulk, conduction of the composite films.

In *Table 1* σ values of type I composite films containing various counterions are listed. The conductivities were measured on both film sides by the four-probe technique. We observed that the σ measurements on the electrode-exposed ('electrode') side were generally better reproducible than on the solution exposed ('surface') side of the composite films, where polypyrrole was inhomogeneously deposited. As shown in *Table 1*, the σ values of the composite films are typically between 0.1 and 10 S cm^{-1}. Lower σ values can be adjusted, if mixtures of pyrrole and *N*-substituted pyrroles are copolymerized[11]. For example, copolymerization of a 1:3 mixture of pyrrole and methyl *N*-pyrrolylacetate leads to a composite film with a σ value of only 1×10^{-4} S cm^{-1}. The temperature dependence of the conductivity is shown by *Figure 2*. The resistivity of the composite film increases by a factor of 15 on cooling from room to liquid nitrogen temperature.

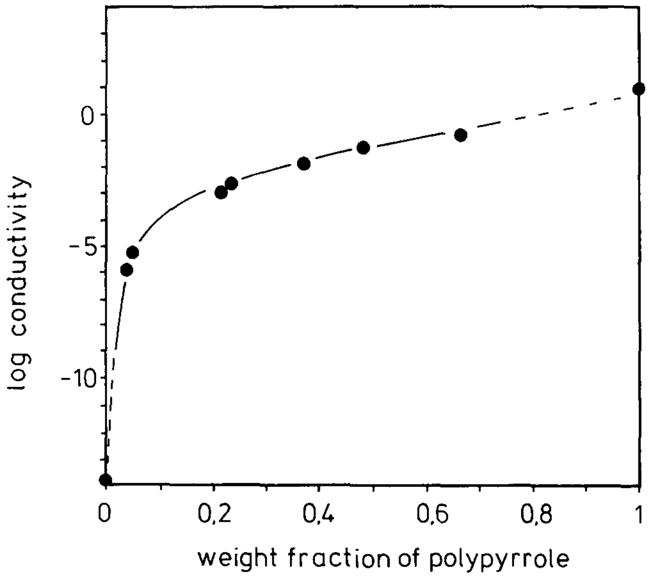

Figure 1 Electrical conductivity as a function of polypyrrole weight fraction

Table 1 Specific electrical conductivity σ of polypyrrole–polyimide composite films (type I films)

Monomer	Electrolyte salt	σ (S cm^{-1})
pyrrole	$TBA^+BF_4^-$	0.5
pyrrole	$TBA^+PF_6^-$	2
pyrrole	$TBA^+ClO_4^-$	14
pyrrole: methyl *N*-pyrrolyl-acetate (1:3)	$TBA^+BF_4^-$	1×10^{-4}

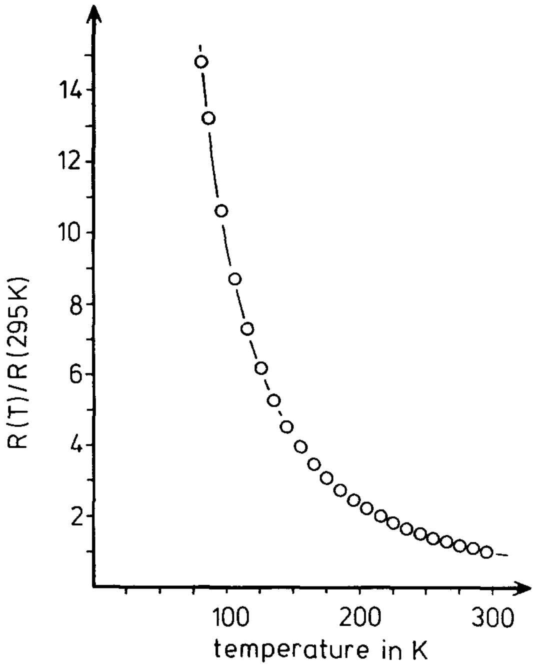

Figure 2 Relative resistivity $R(T)/R(295\,K)$ of PPy–PI type I composite film between 84 K and 295 K

The morphology of the type I composite films was studied by scanning and by transmission electron microscopy. In *Figure 3* scanning electron micrographs of both film sides are shown. The electrode side appears rather smooth, but shows features such as hollows and lines. For example, the latter represent reprints of scratches in the supporting platinum electrode. The surface side of the composite film, however, is very rough. Many irregularly shaped particles can be seen, which adhere to the surface and most probably consist of polypyrrole.

In addition, the cross-section of the composite films was investigated by transmission electron microscopy. In *Figure 4* a typical micrograph is shown. We always observed a layered structure consisting of three different sheets. From a comparison with pure polypyrrole and polyimide films we conclude that the outer layers consist of polypyrrole and the inner layer of polyimide. The formation of the layered structure is a consequence of the poor miscibility of the two polymers. Thus, at the beginning of the electrolysis, polypyrrole is only

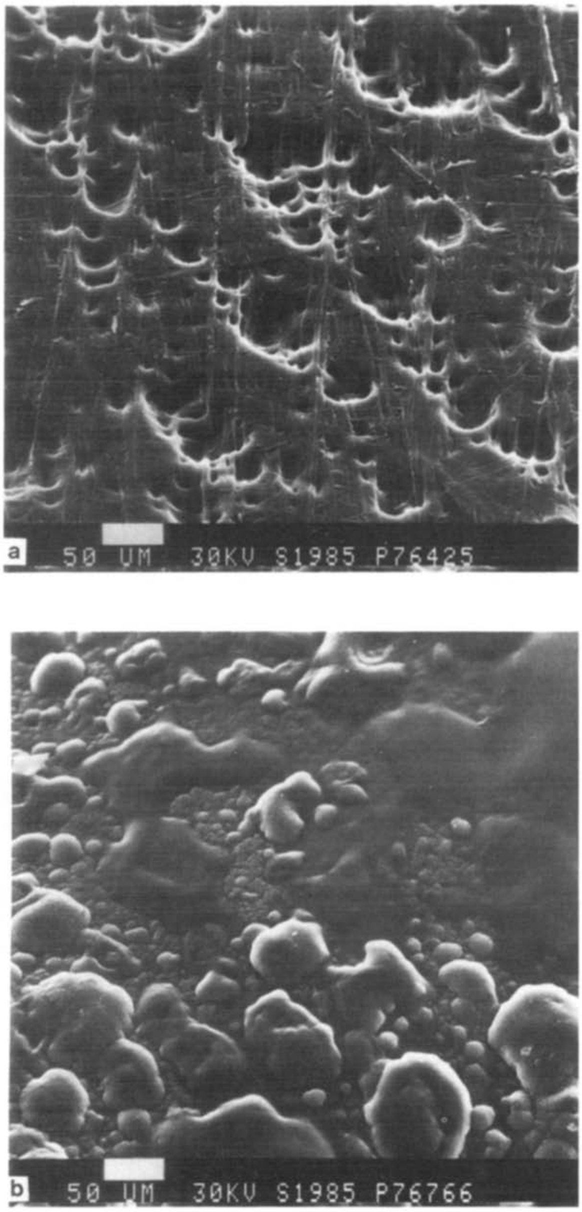

Figure 3 SEM pictures of PPy–PI type I composite film: (a) electrode side; (b) surface side

deposited at the electrode side of the polyimide film forming a continuous layer. Later polypyrrole starts growing through small channels in the polyimide film to the surface side. There irregularly shaped particles are formed as shown in *Figure 3b*, which eventually grow together and form the other polypyrrole layer observed in the micrographs.

Type I composite films are highly flexible and exhibit a good thermal stability. Their mechanical properties are comparable to those of pure polyimide **1**. Conventional polypyrrole composite films lose their stability at the melting point or glass transition of the matrix polymer, which usually occurs at temperatures below 500 K. Differential scanning calorimetry of the PPy–PI composite films, however, does not indicate any transition in the entire temperature range between 220 and 620 K, although the pure polyimide **1** exhibits a glass transition at about 600 K. A thermogravimetric analysis carried out in air indicates weight losses of 10 and 30% at temperatures of 645 and 835 K, respectively.

Type II films

The polymerization of pyrrole using ferric chloride as an oxidizing agent represents an alternative method for preparation of conducting polypyrrole[12]. Spectroscopic and morphological studies of polypyrrole–polyvinylalcohol composite films have recently been described in the literature[13].

Following the procedures described in the Experimental section we succeeded in the preparation of novel PPy–PI composite films which were considerably different in their properties from the type I films. A main advantage of these films is that they can be prepared in different thicknesses up to the millimetre range and exhibit excellent mechanical stability similar to the pure polyimide films. In order to optimize the conductivity, the concentration of ferric chloride in the polyimide and the exposure time of the films to an argon atmosphere saturated with pyrrole vapour were systematically varied.

In *Table 2* the σ values of type II composite films are listed. As shown by the data, the conductivity depends on both the concentration of the oxidizing agent and the period of pyrrole vapour treatment. A maximum value of 5×10^{-4} S cm^{-1} has been reached, when the polyimide

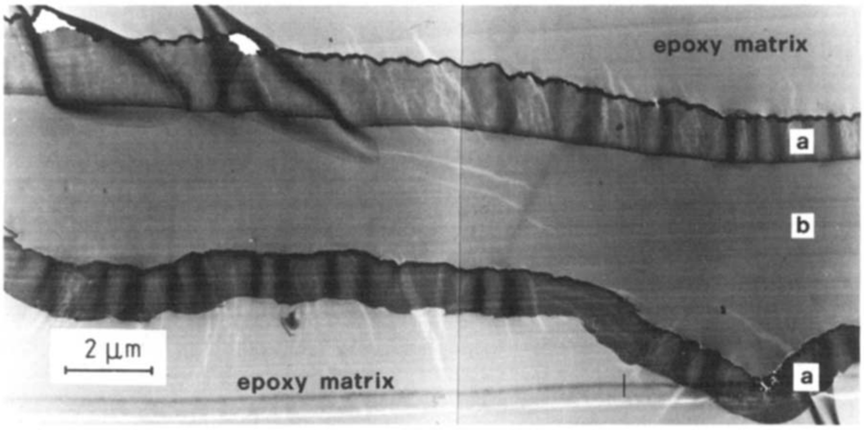

Figure 4 TEM picture of a cross-section of a PPy–PI type I composite film embedded in an epoxy matrix. The film consists of three layers. The outer layers (layers a) are polypyrrole and the inner layer (layer b) is polyimide. The additional thin black layer on the film surface is due to excess OsO_4

Table 2 Specific electrical conductivity σ of polypyrrole–polyimide composite films (type II films)

$FeCl_3$ concentration in polyimide (wt%)	Polymerization time (h)	σ ($S\,cm^{-1}$)
7.4	16	1.5×10^{-4}
10.7	16	6.4×10^{-4}
13.8	16	4.1×10^{-4}
7.4	0.5	2.5×10^{-7}
7.4	1	1.6×10^{-6}
7.4	2	6.2×10^{-6}
7.4	4	3.2×10^{-5}
7.4	9	9.6×10^{-5}
7.4	16	1.5×10^{-4}
7.4	23	4.5×10^{-4}

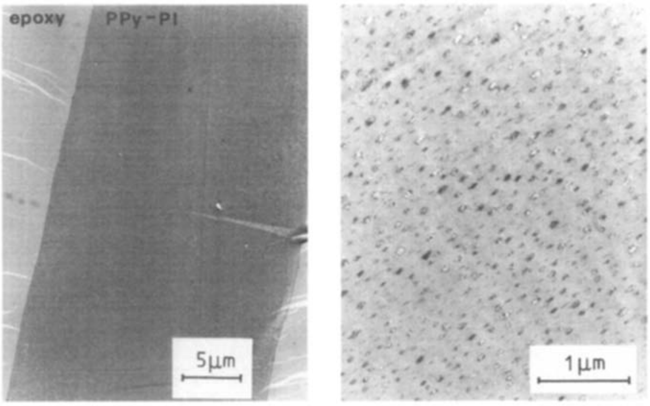

Figure 5 TEM pictures of a cross-section of a PPy–PI type II composite film embedded in an epoxy matrix. Two different magnifications are shown. The film exhibits a two phase structure, the small particles being polypyrrole and the matrix being polyimide

film contained 10 wt% of ferric chloride and was exposed to pyrrole vapour for about 12 h. Neither a higher ferric chloride concentration nor a longer exposure time had an essential effect on the σ value.

The morphology of the type II composite films was investigated by transmission electron microscopy. From the cross-section shown in *Figure 5* a two-phase structure is clearly indicated. Irregularly shaped particles with diameters between 10 and 100 nm consisting most probably of polypyrrole are embedded in the polyimide matrix.

The relatively low σ values of the type II composite films can be explained by the fact that the chemically prepared polypyrrole is always found to be less conducting than the electrochemically prepared polymer. In addition, the low conductivity originates from the two-phase structure, which causes relatively poor contacts between the individual polypyrrole particles.

A differential calorimetric study of the type II composite films does not indicate any phase transition up to 620 K. A thermogravimetric study of a film exposed to pyrrole vapour for about 12 h indicates a weight loss of about 10% at 600 K.

CONCLUSION

We describe two different methods for the preparation of novel polypyrrole–polyimide composite films. These films combine the electrical conductivity of polypyrrole with the thermal stability of polyimides. Clearly the choice of the matrix polyimide is crucial for the preparation of the composite films. Conventional polyimides are insoluble after imidization and therefore do not swell enough in organic solvents in order to allow the pyrrole monomer to penetrate the film and to become polymerized within the film or at its electrode side. The polyimide **1**, however, is excellently suited for this purpose. Films can be easily cast due to the solubility in various organic solvents even in the fully imidized state. Moreover, **1** is swellable in a number of electrolyte solvents and pyrrole is able to penetrate the polymer either in the dissolved or in the gaseous state. It is clear that other polyimides might also be suited for this purpose provided that they are soluble or swellable in organic solvents.

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