Composite films of nylon-6/polypyrrole: thermal behaviour, mechanical properties and electrical conduction

D. S. Kelkar*
Department of Physics, Institute of Science, Bombay-32, India

and N. V. Bhat
Department of Physics, University Department of Chemical Technology, Bombay-19, India

The thermal stability, mechanical properties and electrical conduction of nylon-6/polypyrrole composite films are reported, where nylon-6 films were predoped with various concentrations (0.5, 1.25, 2.5, 5 and 12.5% w/w) of copper chloride. The thermal behaviour of the composite films was studied using differential thermal analysis. The mechanical properties, namely the elongation at break and breaking strength, were measured. The results show that there is an improvement in the mechanical properties of the composite films for the nylon-6 film doped with up to 2.5% of copper chloride. The thermal stability of the composite films, however, does not show any improvement. The melting point and the degradation temperature both reduce as the concentration of copper chloride in nylon-6 is increased. The electrical conductivity (σ) of these films was measured in vacuum as a function of temperature. The plots of log (σ) versus temperature (T) show that the conduction mechanism is quite complicated.

(Keywords: composite film; polypyrrole; nylon-6; doped film; differential thermal analysis; tensile strength; electrical conductivity)

INTRODUCTION

In the last few years there has been increasing interest in the electrical conduction of polymers. Most of the work in this area has concentrated on two main classes of polymers: polyacetylene and its derivatives[1] and polyheterocyclic cations[2,3]. The interest in polyacetylenes stems from their good mechanical properties which are associated with high electrical conductivity (σ) when doped with iodine ($\sigma \simeq 10^3 \, \Omega^{-1} \, cm^{-1}$)[4]. Mechanical and electrical properties of oriented polyacetylene films have also been studied[5,6]. On the other hand, polyheterocyclic cations such as polypyrrole exhibit good electrical conductivity ($\sigma \simeq 100 \, \Omega^{-1} \, cm^{-1}$) when doped, associated with high stability in ambient conditions[7]. Electrical conductivity of undoped polypyrrole is lower[8], although its mechanical properties are good. When doped, the electrical conduction in polypyrrole increases to a large extent; however, this takes place at the cost of its mechanical properties. Structure–property relationships in conductive polymers, particularly polypyrrole, have been reported[9]. The influence of counterion on the physical properties of polypyrrole has also been studied[10].

The drawbacks of these doped polymers are: for polyacetylene, its poor stability at ambient conditions[11]; and for polypyrrole, its poor mechanical properties as indicated by its low elongation at break and its brittleness[7]. These properties severely restrict the technological application of these two classes of polymers. However, such an application is possible by synthesizing a composite film of two polymers. One of the two polymers should have good mechanical properties and the other should have good electrical conducting properties. It has been reported that the electrochemical polymerization of pyrrole on a platinum electrode covered with a film of poly(vinyl chloride) produces a dark brown, ductile and flexible composite film with an electrical conductivity comparable to polypyrrole and mechanical properties very similar to poly(vinyl chloride)[12]. Conducting composites of polyacetylene/polypyrrole have been reported[13]. Polypyrrole conductive composites can also be prepared by coprecipitation[14]. The effect of a surface active pyrrole on the conductivity of polypyrrole composites has also been studied[15].

A highly conducting composite of polypyrrole/poly(vinyl alcohol) has been reported[16], as have transparent and conducting composites of polypyrrole prepared by vapour phase polymerization[17]. Connections between geometric and electronic structure of electrically conducting polymers have been established[18]. Thermal effects in iron chloride-doped poly(3-alkylthiophene) and its blends have been reported by Salaneck and co-workers[19,20]. The use of polypyrrole/polyanion composite as an anode in a polymer battery[21] and composite films of Nafion/polyaniline, Nafion/poly(3-methylthiophene) have also been studied[22]. Electrical conductivity of doped polypyrrole has been reported by Mohammadi et al.[23]. Based on experimental data, Kaiser[24] has suggested models which will provide quantitative accounts of transport properties of metallic polymers. Recent progress in conducting polymers and opportunities for

---

their technological applications have been reviewed by Heeger et al.[25].

Electrochemical synthesis has been used to produce several interesting polypyrrole/plastic composites[12,26] with improved mechanical properties of electroactive material. A procedure for obtaining polypyrrole film and polypyrrole/plastic composite chemically has also been reported[27], where the monomer was polymerized at an interface. The chemical method of polymerization had the advantage of obtaining highly conducting polymer film, having a large area, and using low cost reagents for a short reaction time. Free-standing polypyrrole film and polypyrrole/plastic composites were prepared at room temperature by contact between pyrrole and aqueous $FeCl_3$ solution.

The possibility of obtaining polypyrrole/plastic composite film chemically, led us to prepare nylon-6/polypyrrole composite film. It was observed that the surface conductivity was very high for the side of nylon-6 film on which polypyrrole was deposited; however, on the other side of the nylon film the surface conductivity was low. When the bulk conductivity of the composite film was measured by holding the sample in a sandwich configuration, the conductivity was again low. In order to increase the bulk conductivity of the composite film, the nylon-6 film was predoped with various concentrations (0.5, 1.25, 2.5, 5 and 12.5%) of $CuCl_2$. Pristine and doped films of nylon-6 were used to form composites with polypyrrole. The present work reports the thermal stability and mechanical properties of such composite films. The mode and mechanism of conduction of these composite films over a temperature range from room temperature to 100°C is also reported.

EXPERIMENTAL

Materials

Nylon-6 beads (M/s Nirlon Synthetic Fibres & Chemicals, Bombay, India) were dissolved in formic acid (4% w/v). The solution was stirred well for 4 h and then spread evenly on a plane glass plate which was heated at 70°C for about 30 min. During this time the solvent evaporated and the film could be peeled off. This served as the control nylon-6 film.

$CuCl_2$-doped films of nylon-6 were obtained by adding a measured weight of $CuCl_2$ in the required ratio to the solution of nylon-6 in formic acid. The films containing various concentrations of $CuCl_2$ (0.5, 1.25, 2.5, 5 and 12.5% w/w) were then cast as described above.

Pristine as well as $CuCl_2$-doped films of nylon-6 were used to prepare composite films with polypyrrole according to the method of Bocchi et al.[27]. A brief description of the method is as follows. An aqueous solution (10%) of $FeCl_3$ was prepared and nylon-6 film was floated on the surface of the solution. Diluted pyrrole solution (1 ml, 10% in benzene) was spread over the nylon-6 film. The film was left undisturbed for about 6 h during which pyrrole permeated through the nylon-6 film. A polypyrrole film was thus deposited on the surface of the nylon-6 film in contact with $FeCl_3$ aqueous solution. The film was washed with distilled water and then with acetone. Similar composite films were prepared using various $CuCl_2$-doped films of nylon-6. The films are designated as shown in Table 1. The thickness of the films was about 30 μm.

Measurements

X-Ray diffraction analysis. The X-ray diffraction (XRD) patterns of the composite films were recorded using a Philips X-ray generator (PW 1729) and automatic X-ray diffractometer unit (PW 1710). Nickel-filtered copper $K\alpha_1$ radiation was incident on the sample, which was scanned at $1°$ min^{-1} in reflection over a range of 2θ from 5 to 35°.

Differential thermal analysis. The measurements of heat capacity were carried out using a simultaneous thermal analyser (Stanton Redcroft, STA 780). The instrument is designed to give simultaneous thermogravimetric analysis (t.g.a.) records (i.e. weight *versus* time or temperature) and differential thermal analysis (d.t.a.) curves. Alumina was used as the reference material and all the d.t.a. measurements were made with dry nitrogen gas continuously flowing through the furnace. The heating rate was 10°C min^{-1} and the full scale was adjusted to correspond to 10 mV. A known weight of experimental sample ($\sim$ 10–15 mg) was used to fill the crucible. T.g.a. measurements were directly plotted from the data of sample mass (measured by a microbalance attached to the unit) *versus* the temperature of the sample. The d.t.a. curves, obtained as plots of the temperature difference between the sample and reference sample (Δt) *versus* the temperature of sample (t), were recorded on a strip chart recorder.

Tensile strength measurement. The tensile strength and elongation for different composite films were measured using an Instron tensile tester. A film of width 2 mm was gripped between two jaws of the instrument such that the specimen length was about 2 cm and the breaks in the film occurred along the machine direction. The head speed was 50 mm min^{-1}. The average breaking load and the elongation were obtained as the average of at least six measurements.

Electrical conductivity. Thin films of aluminium (10 mm × 10 mm) were deposited on both sides of the composite films by vacuum deposition. The sample to be studied was sandwiched between two aluminium electrodes and was introduced into a specially designed cryostat, the temperature of which could be changed or maintained constant. A vacuum of about 0.13 Pa was maintained in the cryostat. The d.c. voltage was applied using a regulated power supply across the electrodes and the current flowing through the sample was measured using a digital multimeter connected in series with the sample. The voltage was varied from 0 to $\sim$ 30 V and the temperature was varied from room temperature to 100°C in steps of 10°C. At each temperature, current and voltage values were recorded. The conductivity (σ) was calculated for an applied voltage of 5 V at each temperature.

Table 1 Designation of the samples

Sample	Designation
Pure nylon-6	N
Composite of nylon-6 + polypyrrole (PPY)	NP
Composite of 0.5% $CuCl_2$-doped nylon-6 + PPY	NCP1
Composite of 1.25% $CuCl_2$-doped nylon-6 + PPY	NCP2
Composite of 2.5% $CuCl_2$-doped nylon-6 + PPY	NCP3
Composite of 5% $CuCl_2$-doped nylon-6 + PPY	NCP4
Composite of 12.5% $CuCl_2$-doped nylon-6 + PPY	NCP5

Table 2 Crystallinity index for composite films of nylon-6/polypyrrole

Sample	Crystallinity index
NP	0.62
NCP3	0.54
NCP4	0.44
NCP5	0.40

Table 3 Values of melting point, percentage weight loss at melting point and degradation temperature for composite films of nylon-6/polypyrrole

Sample	Melting point T_m (°C)	Percentage weight loss at melting point (%)	Degradation temperature (°C)
N	215	–	395
NP	211	1.5	380
NCP1	210	8	346
NCP2	210	10	341
NCP3	210	7.5	366
NCP4	209	5	375
NCP5	205	3	380

RESULTS AND DISCUSSION

X-Ray diffraction analysis

XRD scans for sample NP show only two peaks appearing at $2\theta = 20$ and 24°, corresponding to the α phase in nylon-6 film. As the concentration of $CuCl_2$ in nylon-6 increases, a third peak at $2\theta = 22°$ appears for samples NCP3, NCP4 and NCP5. Similar results were observed for the nylon-6 films doped with $CuCl_2$ and have been reported, elsewhere[28]. The crystallinity index for the composite films is given in *Table 2*. The calculations of crystallinity index for the composite films of $CuCl_2$-doped nylon-6/polypyrrole show a trend similar to the $CuCl_2$-doped nylon-6 film[28], namely a reduction in the crystallinity index with increase in $CuCl_2$ concentration. This shows that the structure of $CuCl_2$-doped nylon-6 films does not change subsequent to pyrrole doping.

Thermal analysis

From the d.t.a. curves, the melting points of pure nylon-6 and composites of undoped as well as doped films of nylon-6 were determined and are given in *Table 3*.

It is observed that the melting point of the undoped nylon-6/polypyrrole composite is slightly lower than that of pure nylon-6. As the amount of dopant in nylon-6 is increased, the melting point decreases slightly, reaching a minimum for the NCP5 film. These results indicate that during polymerization of pyrrole it is likely that part of the pyrrole is polymerized within the nylon-6 matrix. This is possible because it has been reported[28] that the added $CuCl_2$ salt remains uncomplexed in the nylon-6 matrix for higher concentrations, and $CuCl_2$ itself can polymerize pyrrole[27]. Thus pyrrole also gets polymerized within nylon-6 and may weaken the intermolecular interaction, therefore the melting point decreases. The presence of polypyrrole in the nylon-6 matrix, however, is not reflected in the XRD scans. This may be because the chemically polymerized pyrrole does not have any definite crystal structure. The XRD scan of chemically polymerized polypyrrole exhibits a halo, showing its amorphous structure. Thus, even though polypyrrole is present in the nylon-6 matrix, the XRD scan shows the crystal structure of nylon-6 only.

From t.g.a., which was carried out simultaneously with d.t.a., it is observed that the percentage weight loss for the sample at its melting point reduces (*Table 3*). The temperature at which fast degradation occurs was also observed, and from *Table 3* it is seen that the degradation temperature reduces as a result of doping and is minimum for sample NCP2.

Mechanical properties

The values of the tensile strength and elongation at break for the composite films obtained using the Instron tester are given in *Table 4*. It is seen that the breaking strength increases by almost 100% as the percentage of $CuCl_2$ in nylon-6 is increased up to 2.5%. However, when the percentage of $CuCl_2$ is increased to 5%, the breaking strength suddenly decreases. This decrease continues up to 12.5% $CuCl_2$ doping, for which the breaking strength is almost the same as that for the control nylon-6 sample. It is also seen from the table that the elongation at break decreases continuously with increase in percentage of $CuCl_2$. These results show that the composite films formed with nylon-6 film are homogeneous up to 2.5% $CuCl_2$ doping and there is considerable improvement in the mechanical properties. For higher concentration of $CuCl_2$, as reported previously[28], part of the added salt remains uncomplexed and collects somewhere within the nylon-6 matrix. During the polymerization of pyrrole, this salt may be polymerizing a part of the added pyrrole inside the nylon-6 film. Since it is likely that the uncomplexed salt collects in the amorphous portion of nylon-6, the polymerized pyrrole may also be collected in the same portion, thus forming an inhomogeneous composite film. The breaking strength, as well as elongation at break for such films, therefore shows a decrease.

Electrical properties

The dependence of electrical conductivity, σ, on the temperature has been determined in the case of a few heterocyclic conducting polymers such as polypyrrole[29], polyselenophene and poly(phenylene oxide)-pyrrole co-polymer[30]. The variation of σ as a function of temperature has been shown to obey the following relations.

$$\sigma = A\exp(-E_a/KT^{-1/3}) \qquad (1)$$

or

$$\sigma = A\exp(-E_a/KT^{-1/4}) \qquad (2)$$

where E_a is the activation energy of conduction, T is the temperature (K), A is a constant for a given material and K is Boltzmann's constant. The fact that σ varies as $T^{-1/4}$ or $T^{-1/3}$ implies the presence of a variable-range hopping

Table 4 Values of breaking strength and percentage elongation for composite films of nylon-6/polypyrrole

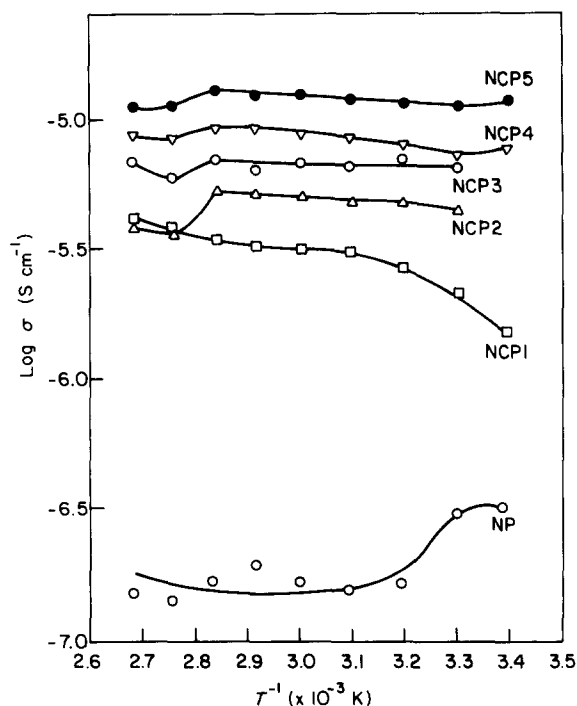| Sample	Breaking strength ($\times 10^4 \, g\,cm^{-2}$)	Elongation (%)
N	35.83	10.29
NP	35.83	8.82
NCP1	53	6.98
NCP2	63.75	5.73
NCP3	76.75	5.88
NCP4	40.44	5.3
NCP5	35.63	4.56

Figure 1 Plot of $\log \sigma$ versus $1/T$ for composite films

mechanism for bipolarons operating between different chains in these types of materials.

In the present work, the surface of the nylon-6 film on which polypyrrole is deposited becomes conducting and follows a variable-range hopping mechanisms of conduction (as for polypyrrole)[29]. The other surface (undoped or doped nylon-6) is non-conducting and like a semiconductor follows the Arrhenius law[31].

Graphs were plotted of $\log \sigma$ versus $T^{-1/4}$ and $T^{-1/3}$ for each film. However, it was observed that $\log \sigma$ does not vary with these functions of temperature and therefore these plots are not reproduced here.

Graphs of $\log \sigma$ versus T^{-1} were plotted for the films and are depicted in *Figure 1*. From these plots it is clear that there is a significant increase in conductivity for the composite films of doped nylon-6 as compared to the undoped film. It is also seen that the conductivity increases as the concentration of $CuCl_2$ dopant in nylon-6 is increased. This indicates that the dopant is helping pyrrole to be polymerized within the nylon-6 matrix.

Figure 1 also shows that the variation of conductivity with temperature does not follow the Arrhenius law. As stated above, neither does conductivity follow $T^{-1/4}$ or $T^{-1/3}$ laws. Thus the mechanism of conduction for the composite films seems to be complicated, since it is the net effect of two different types of mechanism. From the plots (*Figure 1*) it is seen that for sample NP, conductivity σ varies with temperature in a haphazard manner. The variation of σ with temperature is progressively smoother for samples NCP1, NCP2, NCP3, NCP4 and NCP5; for NCP5, $\log \sigma$ changes only marginally with temperature and the plot is almost a straight line parallel to the temperature axis. For all the samples it is found that $\log \sigma$ suddenly decreases at around 80°C, and increases again beyond 80°C; however, this effect is less pronounced for samples NCP4 and NCP5. The reason for this may be that since nylon-6 films in these two samples are doped with a high concentration of $CuCl_2$, not all of which forms a complex with nylon-6, the polymerization of pyrrole might be taking place at the sites where

uncomplexed salt is situated in nylon-6 film. The pyrrole polymerized at these sites provides links of polypyrrole across the nylon-6 film. The semiconducting nature of nylon-6 therefore has less effect on the entire conduction mechanism.

CONCLUSION

These investigations reveal that there is an improvement in the mechanical properties of some of the composite films. The electrical conductivity increases with the concentration of dopant. However, contrary to expectations, the thermal stability of nylon + $CuCl_2$ + polypyrrole composites is reduced. However, in view of the great improvement in electrical conduction and mechanical properties, this slight loss in thermal stability is not a deterrent for the innovative technological application of such composite films.

REFERENCES

1   Shirakawa, H., Louis, E. J., MacDiarmid, A. G., Chiang, C. K. and Heeger, A. J. *J. Chem. Soc., Chem. Commun.* 1977, 578
2   Diaz, A. F. *Chem. Ser.* 1981, **17**, 145
3   Tourillan, G. and Garnier, F. *J. Electroanal. Chem.* 1982, **135**, 173
4   Chiang, C. K., Fincher, C. R., Park, Y. W., Heeger, A. J., Shirakawa, H., Louis, E. J., Gau, S. C. and MacDiarmid, A. G. *Phys. Rev. Lett.* 1977, **39**, 1098
5   Cao, Y., Smith, P. and Heeger, A. J. *Polymer* 1991, **32**, 1210
6   Cao, Y., Smith, P. and Heeger, A. J., *Synth. Met.* 1991, **41**(1–2), 181
7   Diaz, A. F. and Kanazawa, K. K. *J. Chem. Soc., Chem. Commun.* 1979, 635
8   Salmon, M., Kanazawa, K. K., Diaz, A. F. and Krounbi, M. J. *J. Polym. Sci., Polym. Lett. Edn* 1982, **20**, 187
9   Bloor, D., Monkmann, A. P., Stevens, G. C., Cheung, K. M. and Pugh, S. *Mol. Cryst. Liq. Cryst.* 1990, **187**, 231
10 Cheung, K. M., Bloor, D. and Stevens, G. C. *J. Mater. Sci.* 1990, **25**(9), 3814
11 Deits, W., Cukor, P., Rubner, M. and Jopson, H. *Synth. Met.* 1982, **4**(3), 199
12 Paoli Marco, A. D., Waltman, R. J., Diaz, A. F. and Bargon, J. *J. Chem. Soc., Chem. Commun.* 1984, 1015
13 Ahlgren, G. and Krische, B. *J. Chem. Soc., Chem. Commun.* 1984, 946
14 Ruckenstein, E. and Chen, J. H. *Polymer* 1991, **32**, 1230
15 Ruckenstein, E. and Chen, J. H. *J. Appl. Polym. Sci.* 1991, **43**, 1209
16 Ojio, T. and Miyata, S. *Polym. J.* 1986, **8**, 95
17 Ojio, T. and Miyata, S. *Nippon Kagaku Kaishi* 1986, **3**, 348
18 Salaneck, W. R. and Lundstroem, I. *Phys. Ser. T.* 1989, **25**, 9
19 Nilson, J. O., Guttafsson, G., Inganaes, O, Uudal, K., Salaneck, W. R., Osterholm, J. E. and Laakso, J. *Synth. Met.* 1989, **28**(1–2), C445
20 Oesterholm, J. E., Laakso, J., Nyholm, P., Isotalo, H., Stubb, H., Inganaes, O. and Salaneck, W. R. *Synth. Met.*, 1989, **28**(1–2), C435
21 Takeo, S., Akira, O., Tomokazu, I. and Kenichi, H. *J. Chem. Soc., Chem. Commun.* 1987, 327
22 Bidan, G. and Ehui, B. *J. Chem. Soc., Chem. Commun.* 1989, 1568
23 Mohammadi, A., Hasan, M. A., Liedberg, B., Lundstroem, I. and Salaneck, W. R. *Synth. Met.* 1986, **14**(3), 189
24 Kaiser, A. B. *Synth. Met.* 1991, **43**(1–2), 3329
25 Heeger, A. J., Smith, P., Fizazi, A., Moulton, J., Pakbaz, K. and Rughooputh, S. *Synth. Met.* 1991, **41**(3), 1027
26 Niwa, O. and Tamamura, T. *J. Chem. Soc., Chem. Commun.* 1984, 817
27 Boochi, V. and Gardini, G. P. *J. Chem. Soc., Chem. Commun.* 1986, 148
28 Kelkar, D. S. and Bhat, N. V. *J. Appl. Polym. Sci.* 1991, **43**, 191
29 Kaneto, K., Yoshino, K. and Inuishi, Y. *Solid State Commun.* 1984, **161**, 51
30 Kumar, N., Malhotra, B. D. and Chandra, S. *J. Polym. Sci., Polym. Lett. Edn* 1985, **23**, 57
31 Bhat, N. V. and Kelkar, D. S. *J. Phys. D., Appl. Phys.* 1990, **23**, 899