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Electrically conducting high-strength aramid composite fibres prepared by vapour-phase polymerization of pyrrole

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Electrically conducting aramid/polypyrrole (PPy) composite fibres were prepared by vapour-phase polymerization of pyrrole using $FeCl_3 \cdot 6H_2O$ as an oxidant. Conducting stability and mechanical properties were investigated and the change of electrical resistance due to the applied strain and its recovery were analysed. Composite fibres showed a good thermal stability in conductivity within a range of 170 °C. The mechanical properties of conducting composite fibres were affected slightly by polymerization of pyrrole, and could maintain good mechanical properties of the original aramid fibre. The modulus increased slightly with polymerization of pyrrole, and tenacity decreased only slightly. The electrical resistance of the composite fibres initially increased slowly with increasing elongation, but increased sharply near breaking point. The residual electrical resistance appeared on removal of the applied strain. This indicates the possibility of the application of conducting aramid/PPy composite fibres as an intelligent material.

1. Introduction

Electrically conducting polymers have attracted much attention, not only from the viewpoint of scientific interest, but also from the practical viewpoint for potential applications such as EMI shielding, conductive coating, rechargeable batteries, and antistatic agents. Among the electrically conducting polymers, the synthesis and electrical properties of polypyrrole (PPy) have been studied in particular because of its high conductivity, good stability in ambient conditions, and film-forming property on an electrode surface [1–5]. However, the brittleness of PPy has limited practical use as a conducting polymer [6]. PPy based composite may offer an effective means for overcoming the disadvantages in mechanical property without adversely affecting the nature of PPy conductivity, whereas many of the most interesting conducting polymers are not processable by conventional methods because of their intractable property. Various methods are available for the production of conducting PPy composites: electrochemical polymerization of pyrrole in some insulating or conducting polymer matrix [7–9], *in situ* electropolymerization in plastic matrices [10], preparation of conducting composite fibres in electrochemical flow cells [11, 12], chemical polymerization of pyrrole in solutions [13–16], and block or graft polymerization of the conducting polymer with the insulating polymer [17].

Interest is growing in some novel techniques for the preparation of electrical conducting composite fibres using high-modulus and high-strength fibres such as aramid fibre [18–21] or gel-spun ultra-high molecular weight polyethylene fibre [10, 22, 23] as carrier polymers. Some techniques are available for preparing high-strength conducting fibres, for example, a solution processing method for conducting hybrid fibre, deposition of conducting polymer on to a fibre carrier by vapour phase polymerization of the monomer, a self-compositing process involving the dry-jet spinning method, and chemical polymerization of the monomer within the fibre structure [18]. Vapour-phase polymerization is expected to be one of the most convenient methods, because it is relatively simple and easy to control the conductivity whilst maintaining high strength of carrier fibre. Very recently, the continuous vapour-phase polymerization of pyrrole has also been reported [24].

It has been of recent interest in our laboratory to prepare high-performance conducting fibres for application as an intelligent material [25–27], which can play a role of sensing and predicting the failure of structured materials. Prediction of failure of structural materials can be carried out by analysing the change of residual electrical resistance in a conducting composite fibre when repeated strains are applied and recovered. On the other hand, the intelligent material system using conducting polymers has been demonstrated in some examples, such as release of drugs or other chemically active compounds using electrical stimuli [28, 29], or transducers as intelligent gas sensors [30].

In this study, conducting aramid/PPy composite fibres were prepared by vapour-phase polymerization of pyrrole in the presence of $FeCl_3 \cdot 6H_2O$. Their

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conducting and mechanical properties, and the possibility of application as an intelligent material, were investigated.

2. Experimental procedure

The fibres used were aramid fibres (commercial Kevlar 49, Du Pont), and prior to use, they were washed with acetone and distilled water, and dried. $FeCl_3 \cdot 6H_2O$ was used as an oxidizing agent and the fibres were immersed in $FeCl_3 \cdot 6H_2O$ solutions at different concentration (3%–40% wt/wt). After swelling and drying, the fibres were exposed to pyrrole/H_2O vapour in a vaccum desiccator at 0 or 20 °C for 24 h, unless otherwise noted. Then pyrrole vapour was diffused into the fibres and reacted to form PPy/aramid composite fibres. After polymerization, the fibres were dried at 40 °C for 24 h.

The electrical conductivity was measured using the standard four-probe technique. Scanning electron micrographs were taken on a Streoscan 430 (Leica Co.). The temperature dependence of conductivity was obtained by measuring the conductivity of a sample during heating at a rate of 10 °C min^{-1} in an oven. Thermo-gravimetric analysis was carried out with a thermogravimetric analyser 951 (Du Pont Instruments). Tensile strength, modulus, and breaking strain were obtained using an Instron tensile tester at an elongation speed of 1 in min^{-1} and with fibres 10 cm long. The change in electrical resistance in conducting composite fibres was recorded continuously as a function of time during a constant elongation and the recovery at a speed of 10 mm min^{-1} by an Instron tensile tester. Fig. 1 shows a schematic diagram of the equipment for measuring the change of electrical resistance of a sample.

3. Results and discussion

As the PPy started to grow on aramid fibres with a polymerization of exposed pyrrole vapour, the initial yellow colour of aramid fibres gradually became brown, and finally black, depending on the concentration of $FeCl_3 \cdot 6H_2O$ aqueous solution, polymerization time and polymerization temperature. The surface photographs of aramid/PPy fibres are shown in Fig. 2.

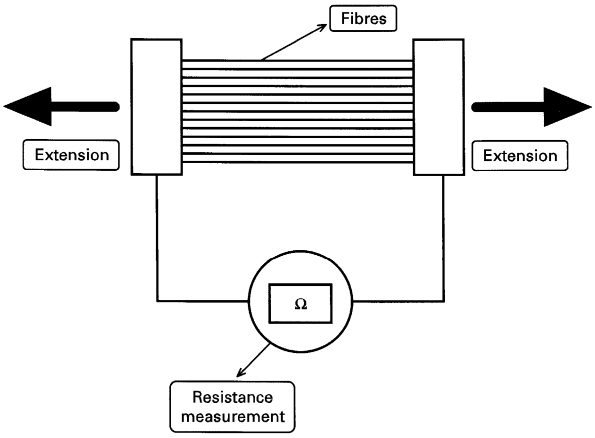

Figure 1 Schematic diagram of the apparatus for measuring the change in electrical resistance during the elongation of fibres.

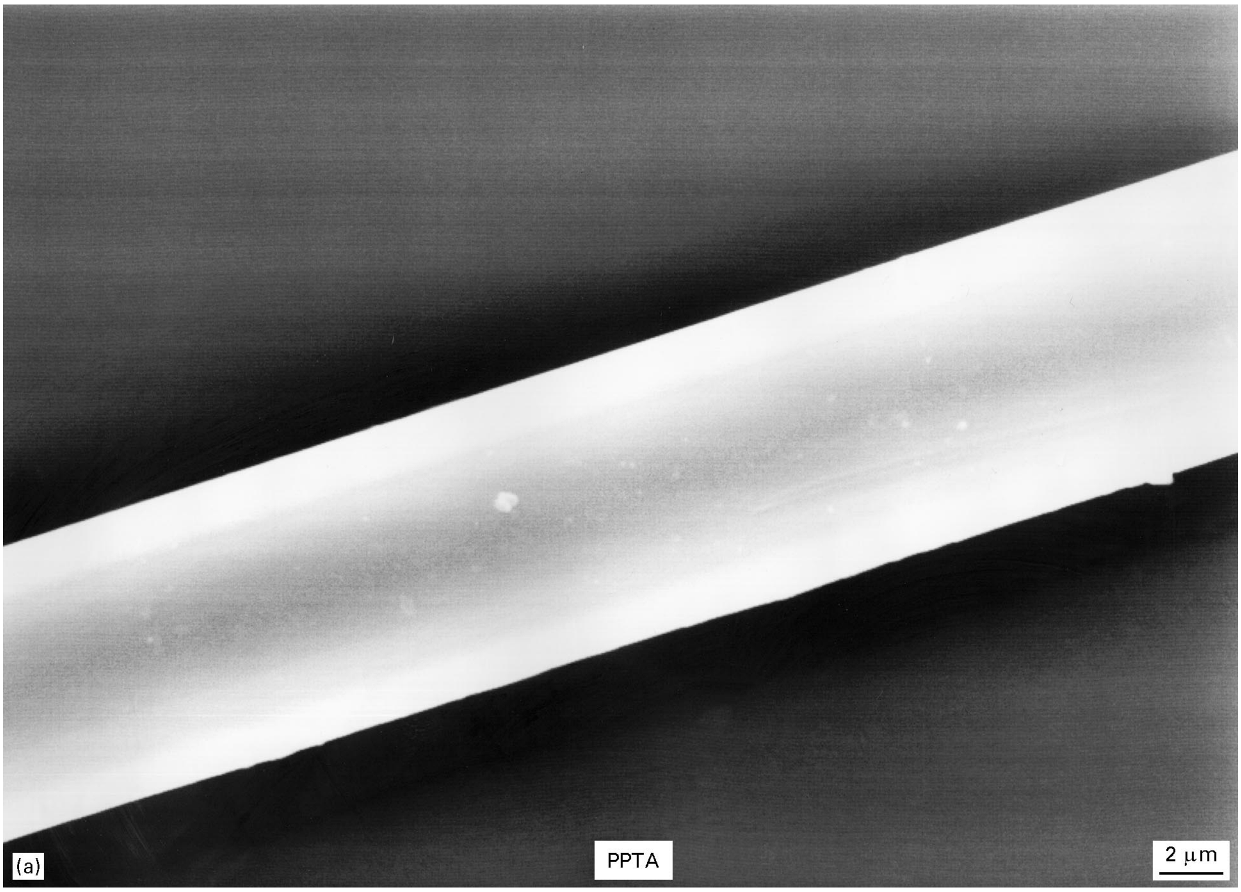

Figure 2 Scanning electron micrographs of aramid/PPy composite fibres: (a) original kevlar fibre, (b) 20% $FeCl_3$.

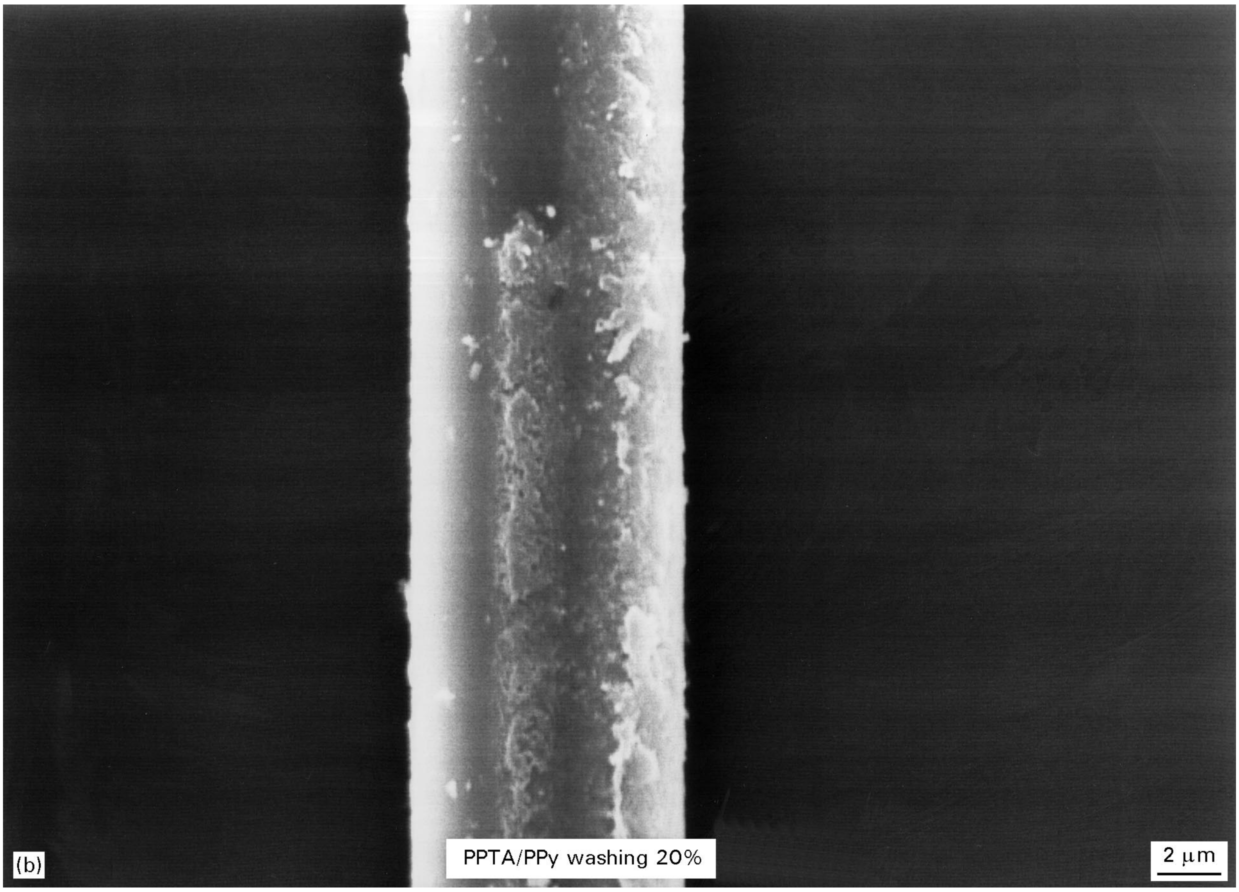

Figure 2 (*Contd*).

Their SEM images indicate that after polymerization of pyrrole, the surface of the aramid fibre is covered with a relatively smooth and microporous PPy layer between the filaments of nonconductive materials, as well as on the outside surface of the filaments. It was regarded that PPy had diffused into the interior as well as on the surface of the aramid fibres as the reaction of pyrrole occurred [18]. As a result, aramid/PPy composite fibres could be successfully obtained by vapour phase polymerization of pyrrole.

Fig. 3 shows the effect of concentration of $FeCl_3 \cdot 6H_2O$ aqueous solution on the conductivity of aramid/PPy composite fibres prepared with polymerization of pyrrole for 24 h. The conductivity of $\sim 1.3 \times 10^{-3}$ S cm^{-1} was obtained in the case of polymerization of pyrrole at 20 °C, which was three times or more higher compared with that at 0 °C, although it was lower than other published results [24]. The dependence of polymerization temperature on the conductivity is ascribed to the difference in diffusion of pyrrole at each temperature, resulting in the difference in surface morphology of PPy [3]. Conductivity increases largely with increasing concentration of $FeCl_3$ at low concentration. However, it does not increase further above about 15% $FeCl_3$ concentration, and reaches an equilibrium value. The conductivity is also affected by polymerization time, as shown in Fig. 4. At an initial stage of polymerization of pyrrole, conductivity increases very steeply with time due to the deposition of PPy. However after about 10 h polymerization, the conductivity no longer increases. This is ascribed to the presence of PPy already formed in the outer surface of the aramid fibre interrupting the diffusion of pyrrole into the interior of the fibre. In particular, at later stages of polymerization when the concentration of $FeCl_3$ is high, it is more difficult for pyrrole vapour to diffuse into the interior of the composite fibre.

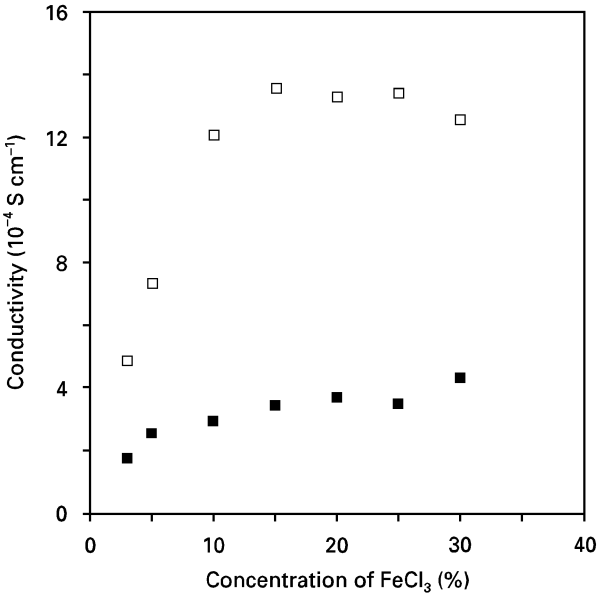

Figure 3 Conductivity of aramid/PPy composite fibres prepared at (■) 0 °C and (□) 20 °C versus the concentration of $FeCl_3$.

The ageing in the conductivity of the sample exposed to ambient conditions was investigated by measuring the change of conductivity as a function of decay time, as shown in Fig. 5. The conductivity decreases with

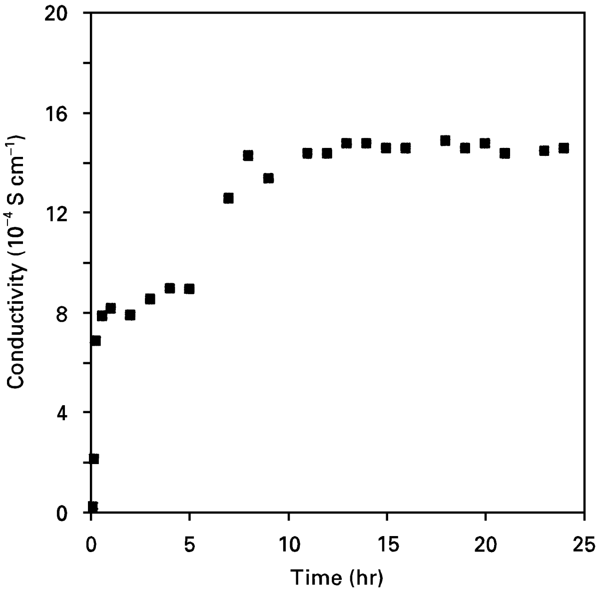

Figure 4 Conductivity versus polymerization time in a composite fibre prepared at a concentration of 30% $FeCl_3$.

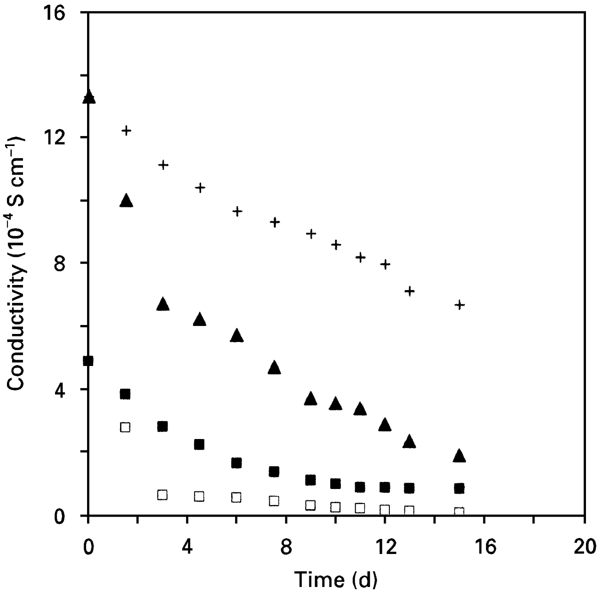

Figure 5 The conductivity change versus decay time in composite fibres prepared at concentrations of 3% at (■) 20 °C, (□) 50 °C, and 20% $FeCl_3$ at (+) 20 °C, (▲) 50 °C.

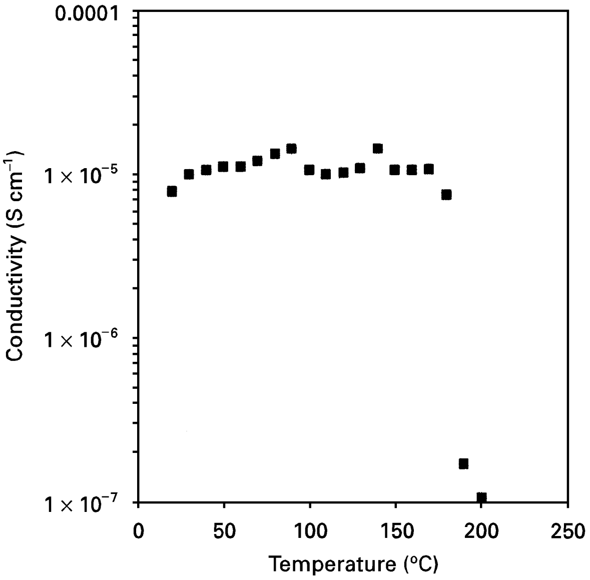

Figure 6 Temperature dependence of conductivity of composite fibres prepared at a concentration of 30% $FeCl_3$.

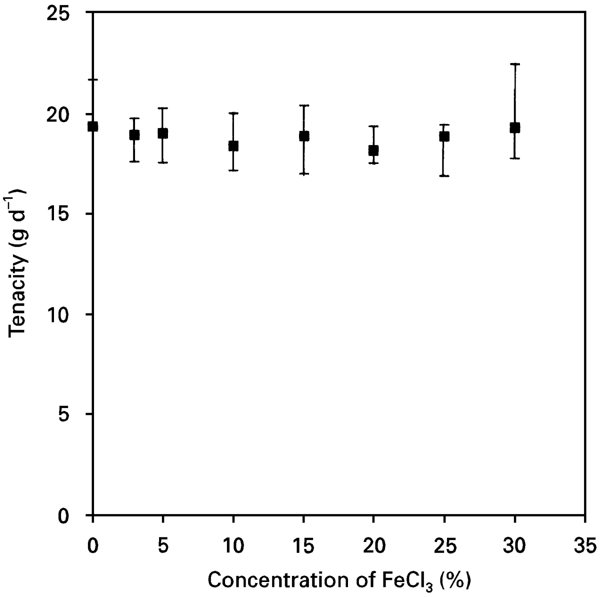

Figure 7 Tenacity of aramid/PPy composite fibres versus the concentration of $FeCl_3$.

increase in decay time, which is thought to be due to oxygen attack of the conjugated double bonds [32]. The decreasing rate in the conductivity versus decay time curve is more dependent on the exposure temperature rather than the concentration of $FeCl_3$. The decreasing rate of the conductivity of a sample at the same concentration of $FeCl_3$ becomes larger as the exposure temperature increases. Fig. 6 shows the thermal stability of conductivity, which indicates that the conductivity never decreases significantly within 170 °C but falls very sharply near 180 °C. The large decrease in conductivity near 180 °C is thought to be due to the dissociation of the dopant anion such as Cl^- [32]. On the other hand, TGA curves, as in Fig. 10, show large weight loss at about 600 °C, which is due to thermal degradation of the aramid fibre. Up to 600 °C, a weight loss of only several per cent appears with the increasing concentration of $FeCl_3$. PPy is known to be relatively stable over long periods of time under ambient conditions. For example, its conductivity decreases by an order of magnitude in a year, and only 4% and 77% weight losses in PPy appear when heated up to 250 and 600 °C, respectively, in a nitrogen atmosphere [33]. Consequently, results from Figs 5, 6 and 10, suggest that the electrical conduction of aramid/PPy composite fibres is considerably stable up to about 170 °C.

Figs 7–9 show the results of stress–strain mechanical test measurements of conducting aramid/PPy composite fibres. The stress–strain relation of conducting composite fibres had a good linearity with no yield stress, as in the original aramid fibre. Conducting composite fibres almost retained the good mechanical

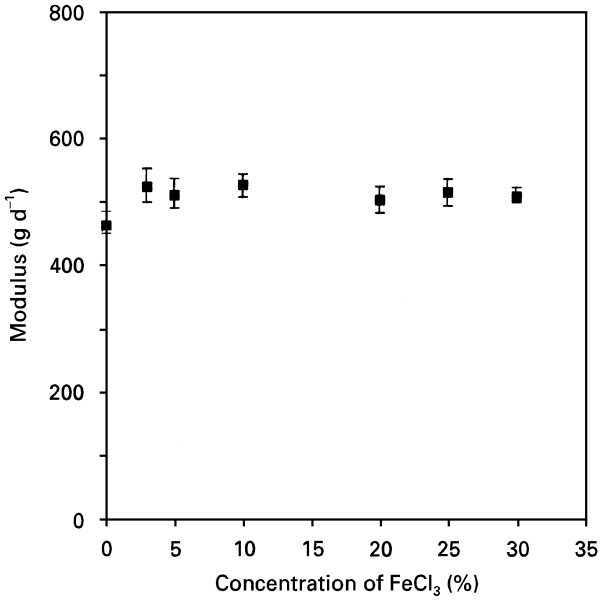

Figure 8 Modulus of aramid/PPy composite fibres versus the concentration of FeCl$_3$.

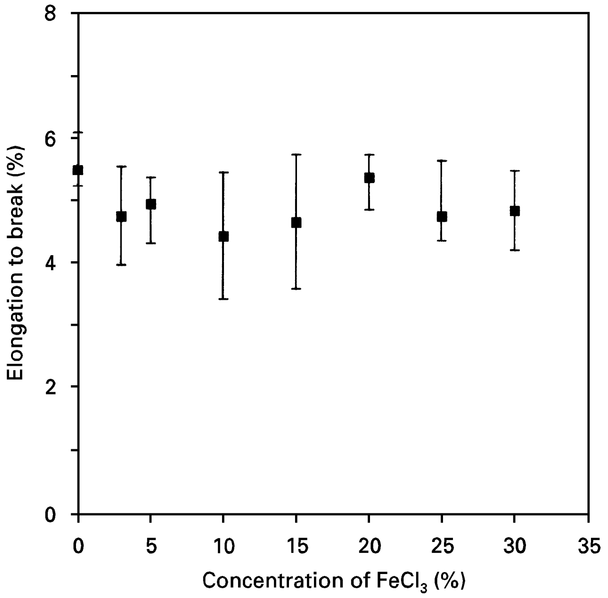

Figure 9 Elongation to break of aramid/PPy composite fibres versus the concentration of FeCl$_3$.

properties of aramid fibres, even after polymerization of pyrrole. Interestingly, the modulus of conducting composite fibres increased slightly with increasing concentration of FeCl$_3$ and tenacity tended to decrease only slightly, whereas elongation to beak decreased to some extent. The reinforcement effect due to the incorporation of stiff PPy molecules in composites seems to give a rise to the increase in modulus, but the tenacity is likely to decrease slightly by partial destruction of the crystalline region of the aramid fibre on polymerization. Consequently, the high-strength conducting fibres could be obtained without a large degradation in mechanical properties. This indicates that the vapour-phase polymerization method is a promising one for obtaining high-strength conducting composites, compared with other polymerization methods.

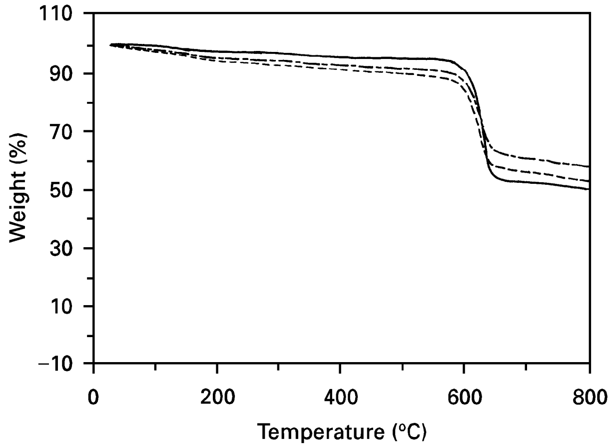

Figure 10 TGA curves of composite fibres at different concentrations of FeCl$_3$: (——) 0%, (– · –) 10%, (– – –) 20%.

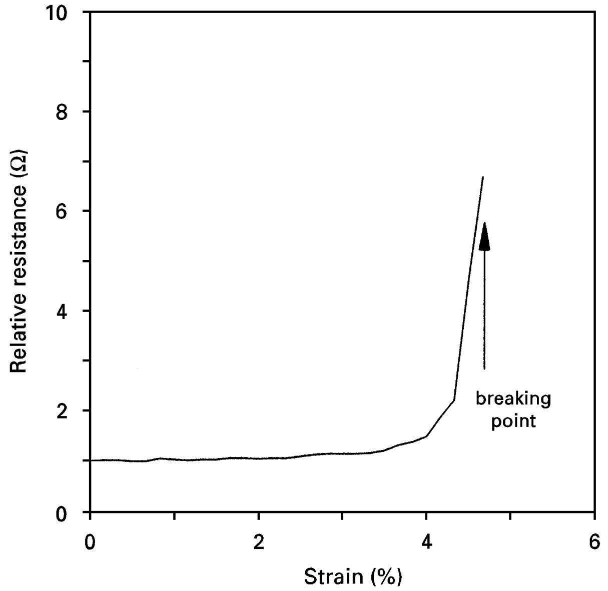

Figure 11 Electrical resistance change versus strain of aramid/PPy composite fibres prepared at a concentration of 10% FeCl$_3$.

Fig. 11 represents a plot of the change in electrical resistance versus the applied strain of the conducting composite fibre. The breaking strain of aramid fibre does not usually exceed a maximum of 5%. The electrical resistance of the sample initially increases slightly with increasing strain, but begins to increase rapidly beyond a certain critical strain. On being further strained, the electrical resistance of the sample increases very sharply. On removal of the applied strain, the electrical resistance decreases irreversibly, and leaves a residual electrical resistance. The residual resistance is dependent on the magnitude of the previously applied strain. Fig. 12 shows the change of electrical resistance when loading and recovery of strain are repeated. Then the residual resistance is determined by the previous strain history. Using this fact, we can notice the extent of strain applied to the sample previously. Therefore, the failure of a sample can be predicted in advance by measuring the residual electrical resistance. This indicates the possibility of application of conducting aramid/PPy composite fibres as an

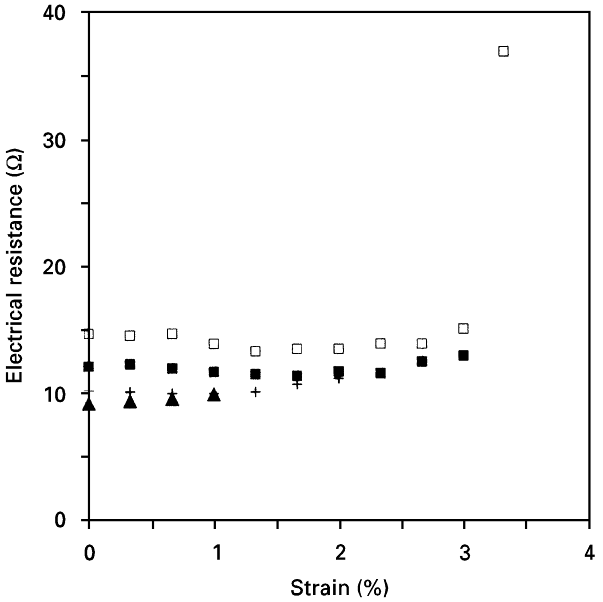

Figure 12 Electrical resistance change due to the repeated loading and recovery of strain in the composite fibres prepared at a concentration of 25% of $FeCl_3$: (▲) first strain; (+) second strain after recovery of first strain; (■) third strain after recovery of second strain; (□) fourth strain after recovery of third strain).

intelligent material in predicting the failure of structured materials.

4. Conclusion

From the preparation of aramid/PPy composite fibres by vapour phase polymerization of pyrrole using $FeCl_3$ as an oxidant, the following conclusions were derived. Aramid/PPy composite fibres with a conductivity of the order of 10^{-3} $S\,cm^{-1}$ were obtained, and good mechanical properties of aramid fibres could be maintained even after polymerization of pyrrole. The composite fibres showed the good thermal stability of conductivity up to 170 °C. The residual electrical resistance appeared on the removal of the applied strain. This indicates the possibility for the application of conducting aramid/PPy composite fibres as an intelligent material.

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