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Properties of Metal-Chlorides Intercalated Graphite Fibres

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Abstract: The effect of different factors on useful properties of pitch-based graphite fibres intercalated with metal chlorides is investigated. Fibrous intercalation compounds were prepared with acceptor intercalants such as $MnCl_2$ and $CuCl_2$. The lowest resistivity value (10.6 $\mu\Omega$cm) was obtained for $MnCl_2$-intercalated P-120 graphite fibres. The intercalation was found to influence the fibre mechanical properties significantly. A decrease in tensile strength and Young's modulus during intercalation was observed for all examined fibres. The stability of intercalated fibres in different environments (air, argon, epoxy matrix) was studied. The influence of current flow on resistance changes is shown. © 1997 Elsevier Science Limited and Techna S.r.l.

1 INTRODUCTION

Carbon and graphite fibres are being used in increasing quantities by the aerospace industry because of their high strength, high elastic modulus and low density. By chemically modifying these fibres, their range of application can be extended further, e.g. as catalysts, ion-exchanges, sorbents and, above all, as constituents of composite in various high-tech materials.[1-3] The range of properties of graphite fibres with a high structural ordering can be extended by intercalation, i.e. the incorporation of elements other than carbon to produce graphite intercalation compounds.[4,5] Because of intercalation, the electrical properties-to-weight ratio of carbon fibres is a promising factor for further utilization of these materials as light and strong current carriers for electrical power transmission.[6,7] One of the important problems to resolve in the technology of intercalated carbon fibres is their chemical and physical instability after intercalation. It is known that the intercalation process results in structural changes and often degradation of the properties that the fibres originally possessed.[8-10] The loss in Young's modulus and tensile strength depends on the intercalation advance. Such a tendency is observed for all types of fibres, type of intercalants and method of preparation.[11] However, the mechanical properties are important for the use of carbon fibres in composite materials technology. Considerable progress has been made in the last few years in determining techniques, intercalation conditions and intercalation compounds, but the problem of a compromise between the mechanical properties of intercalated carbon fibres and their electric conductivity is still open.[12,13] The other problem concerns the properties retention of carbon fibres after intercalation with the time. Because graphite intercalated with donor compounds is definitively unstable in air, we have specially studied the possibility of using acceptor compounds for intercalation in pitch-based graphite fibres.

This study was conducted to determine the influence of intercalation of graphite fibres with metal chlorides ($MnCl_2$, $CuCl_2$) on their electrical conductivity and mechanical properties. The stability in air and in epoxy matrix of the intercalated fibres typically used in the fabrication of composites was examined.

2 EXPERIMENTAL

Three types of carbon fibres from mesophase were used as host material: P-75, P-100 and P-120. Before intercalation, the fibres were heated at 400°C in a nitrogen atmosphere in order to remove the surface sizing. Commercial $CuCl_2$ and $MnCl_2$ powders were dried by heating to 200°C for several hours and then placed in the reaction tube.

The intercalation process was carried out by heating the fibres and anhydrous chlorides between 400 and 500°C in a chlorine atmosphere. The intercalation conditions are described elsewhere.[8] Conductivity and diameter changes were controlled by selecting the optimum reaction temperature and reaction time. The characterization of pristine and intercalated carbon fibres was performed using X-ray diffraction. Interlayer spacing (d_{002}), coherence length (L_c) and stage number were determined. The resistivity of an individual filament was measured by means of a four-point probe. The diameter of the fibre was measured by Lanametr optical microscopy. The mechanical properties of individual fibres were determined using a Zwick-1435 testing machine according to the ASTM procedure. The environmental stability of intercalated fibres was studied under laboratory conditions, a humidity-free atmosphere, in argon and by direct exposure of the fibres to water vapour. A portion of the samples was used to manufacture the intercalated graphite fibres' reinforced resin epoxy composites. The composites were fabricated by immersing a tow of intercalated fibres with resin epoxy. The two uncoated ends of the fibres' tow were attached to silver wire with silver paint and then coated with resin. This allowed the variation in resistance of the composites to be measured, as a function of time. The current density tests on single filaments up to 200 A mm^{-2} were made using a d.c. power supply.

3 RESULTS

Table 1 summarizes the properties of the pristine fibres used for intercalation. The resistivities and other parameters of all types of fibres directly after intercalation with $CuCl_2$ and $MnCl_2$ are shown in Tables 2 and 3.

The samples were prepared under optimum conditions to obtain the lowest resistivities possible. These results confirm a general relationship between the electrical properties of pristine carbon fibres and their ability to intercalate, namely a better structural ordering of fibres gives a higher electrical conductivity. The lowest resistivity value has been obtained for $MnCl_2$ intercalated P-120 graphite fibres. A decrease of resistivity in this case was almost 20 times as compared to pristine fibres.

X-ray diffraction patterns showed the mixture-staged stage-2 and -3 for P-100 and P-120 fibres, whereas higher stages for P-75 fibres were achieved. In all samples after intercalation, the non-intercalated graphite phase was also found. As indicated in Tables 2 and 3, because of intercalation, the mechanical properties decrease. An average

Table 1. Structural parameters and properties of pristine fibres

Fibre	d_{002} (A)	L_c (A)	Diameter (μm)	Resistivity ($\mu\Omega$cm)	σ_r (GPa)	E (GPa)
P-75	3.41	156	9.9±0.6	580±78	2.1	540
P-100	3.37	202	9.7±0.7	260±32	2.4	690
P-120	3.36	232	9.8±0.7	212±17	2.7	752

Table 2. Properties of $CuCl_2$ intercalated fibres

Fibre	Diameter (μm)	Resistivity ($\mu\Omega$cm)	σ_r (GPa)	σ_c* (GPa)	E (GPa)
P-75	12.1±1.9	78.1±29.3	1.73±0.21	1.4	347±27
P-100	12.4±2.1	26.3±8.9	1.34±0.17	1.47	386±34
P-120	12.3±1.8	12.3±3.2	1.6±0.23	1.56	590±67

*σ_c=tensile strength of graphite fibres calculated from the diameter increase caused by intercalation effect.

Table 3. Properties of $MnCl_2$ intercalated fibres

Fibre	Diameter (μm)	Resistivity ($\mu\Omega$cm)	σ_r (GPa)	σ_c* (GPa)	E (GPa)
P-75	11.8±1.7	59.9±6.3	1.43±0.23	1.47	312±29
P-100	12.1±1.3	31.1±13.7	1.54±0.13	1.54	337±39
P-120	12.4±1.4	10.6±2.8	1.3±0.13	1.56	578±78

*σ_c=tensile strength of graphite fibres calculated from the diameter increase caused by intercalation effect.

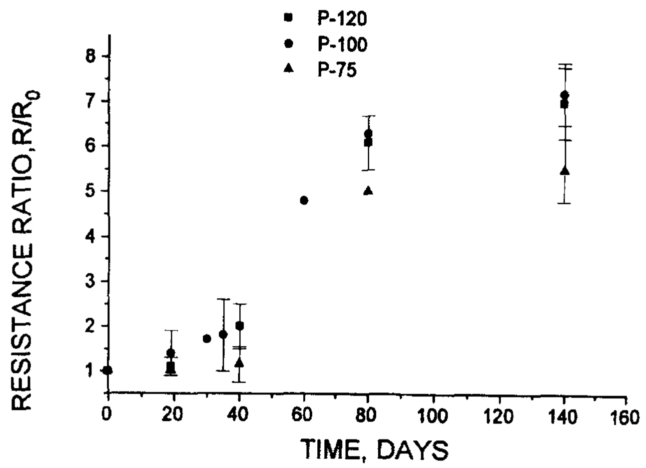

Fig. 1. Stability test of different $MnCl_2$ intercalated graphite fibres in air at 25°C.

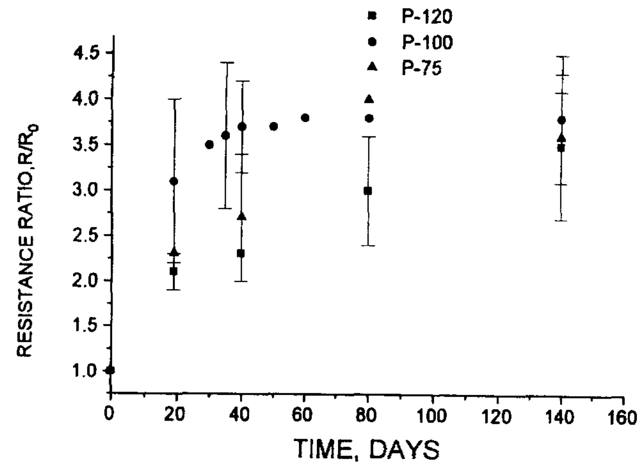

Fig. 3. Stability test of different composites—$MnCl_2$ intercalated graphite fibres/resin epoxy.

decrease of tensile strength is about 30% for $CuCl_2$ intercalated carbon fibres and about 40% for $MnCl_2$ intercalated graphite fibres. A decrease in strength may be considered as a consequence of the combined effect of structural dilatation (diameter increase) and the generation of defects during intercalation. Taking into account the dilatation effect alone, the calculated tensile strength (σ_c) after intercalation shows good accordance with the experimentally determined value for intercalated graphite fibres (Tables 2 and 3). It indicates a stronger influence of an increase in fibre diameter than the defects forming during intercalation. This effect, resulting from a swelling of fibres, confirms the earlier work showing that intercalation has little influence on the mechanical properties of basal carbon layers.[9,13] The changes of electrical resistance of intercalated carbon fibres versus time in air at 25°C are shown in Figs 1 and 2. The relationships indicate that the $MnCl_2$ intercalated carbon fibres are not stable. The changes of electrical properties of the fibres are considerable after about 20 days of exposure in air. This effect is probably due to the humidity in air. The rate of resistance changes is greater for P-100 graphite fibres. This may be attributed to the radial orientation of fibre texture. By contrast, copper chloride intercalated fibres are air-stable for at least 200 days. The electrical resistivity of these fibres fluctuated temporarily, resulting in a slight growth. It was found that after 960 days of exposure to the air, the increase in resistivity was about 20%.

The variations of resistance ratio of graphite fibres intercalated with $MnCl_2$ and $CuCl_2$ and introduced to resin epoxy matrix as a function of time are shown in Figs 3 and 4, respectively. The changes of resistance for $MnCl_2$ intercalated fibres are similar to that observed for the samples in air. In contrast, the electrical properties of $CuCl_2$ intercalated carbon fibres covered with resin epoxy are practically unchanged.

The considerable increase of resistance observed for $MnCl_2$ intercalated carbon fibres exposed to air or in organic matrix may be caused by the reaction of $MnCl_2$ with oxygen-containing groups from moisture or organic matrix which leads to the formation of manganous hydroxide or other neutral

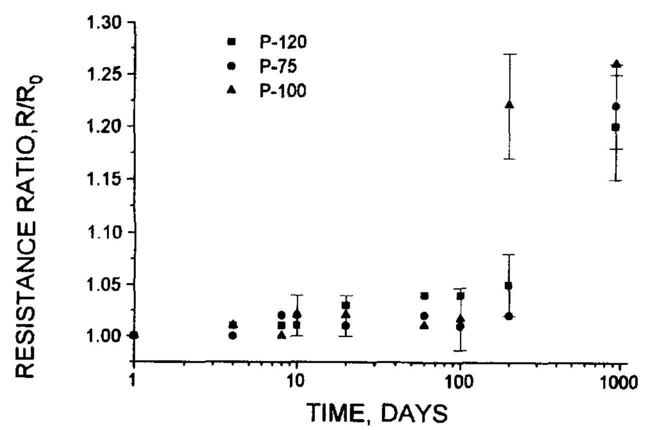

Fig. 2. Stability test of different $CuCl_2$ intercalated graphite fibres in air at 25°C.

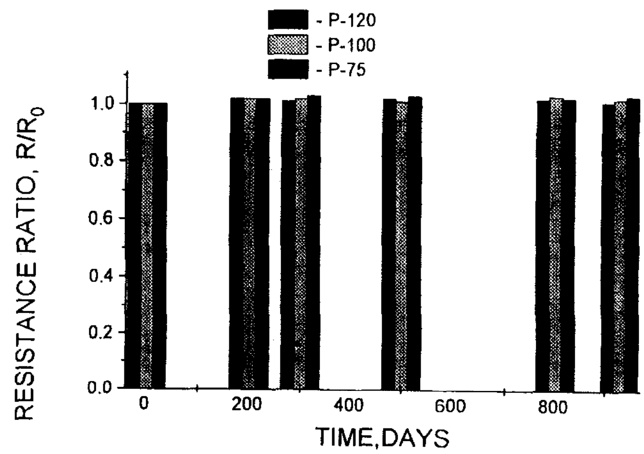

Fig. 4. Stability test of composite—$CuCl_2$ intercalated graphite fibres/resin epoxy.

Table 4. Properties of graphite fibres intercalated with metal-chlorides

Types of fibre	Average resistivity of the pristine fibre ($\mu\Omega$cm)	Resistance ratio (R/R_0) after 7 h exposure to 100% humidity at 60°C	Resistance ratio (R/R_0) after 7 h exposure to 100% humidity at 70°C
P-75-$MnCl_2$	72	2.5	7.2
P-100-$MnCl_2$	34	3.4	8.4
P-120-$MnCl_2$	13	2.5	8.1
P-75-$CuCl_2$	87	1.15	1.7
P-100-$CuCl_2$	35	1.8	2.2
P-120-$CuCl_2$	18	1.1	1.9

compounds. According to Sugura *et al.*,[14] deintercalation of metal-chloride intercalated graphite takes place in the presence of OH^- anions. The anions cause hydrolysis of metal-chloride, resulting in the formation of metal-hydroxides. The degree of decomposition is influenced by the type of metal-chloride and the type of environment. A strong influence of humidity on the deintercalation process of the examined compounds was confirmed in the high-humidity test. The high-humidity stability data show that these compounds are highly instable to attack from water vapour (Table 4). The environmental stability of these compounds is quite low, and the changes of resistivity are not reversible (i.e. drying does not yield the original values after intercalation). For P-75 and P-100 fibres intercalated with manganous chloride, the samples exposed to 100% humidity at 70°C, after 7 h reached almost their pristine resistivity. However, the stability test in an argon atmosphere and in humidity-free ambient conditions showed that both $CuCl_2$ and $MnCl_2$ intercalated carbon fibres retain their electrical properties. As a final experiment, the resistance change of P-120 intercalated with two intercalants during current flow was registered. Typical relationships of the current flow on resistance of the individual intercalated fibre are shown in Fig. 5. These curves represent the metallic-like behaviour at a higher current density (above 200 A mm^{-2}) due to Joule's effect. The presented relations are reversible. From these curves, the value of direct current flow for long-term test was determined. The variation of the resistances ratio (measured value to initial resistance) of intercalated fibres versus time under direct current flow (200 A mm^{-2}) in air is shown in Fig. 6. Surprisingly, the resistance variation is less under electric current for $MnCl_2$ than for $CuCl_2$.

4 SUMMARY

Three types of pitch-based graphite fibres were intercalated with metal chlorides. The intercalation of these fibres resulted in an improvement of electrical conductivity, the best being 10.6 $\mu\Omega$cm for $MnCl_2$ intercalated P-120 fibres. However, the mechanical properties of the fibres after intercalation were 30–40% lower, on average, than pristine graphite fibres. This degradation of mechanical properties is caused mainly by dilatation of the graphite matrix during intercalation. The stability test indicates that copper chloride intercalation graphite fibres introduced to the organic matrix retain their electrical properties even after 960 days. However, the humidity stability of all intercalated fibres is very low and depends on the temperature and water concentration. The ambient stability tests showed that copper chloride intercalated graphite

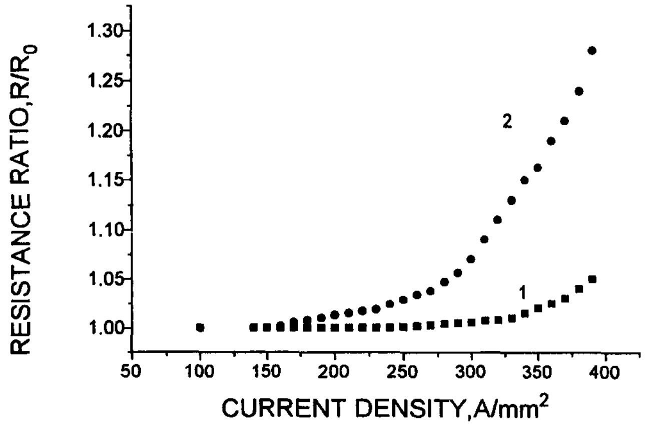

Fig. 5. Effect of direct current flow on resistance ratio of P-120 intercalated fibres in air. 1: P-120-$MnCl_2$. 2: P-120-$CuCl_2$.

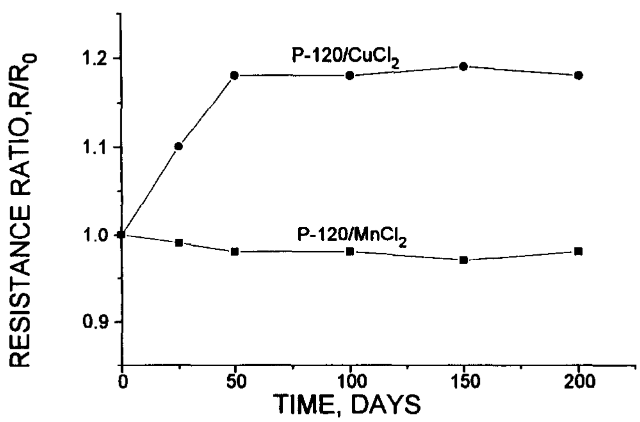

Fig. 6. Stability test of P-120 intercalated fibres under direct current flow (200 A mm^{-2}) in air.

fibres are more stable as compared to manganous chloride intercalants. The likely reason for the instabilities of the intercalated fibres examined is their decomposition in the presence of oxygen-containing chemical groups. A current density as high as 200 A mm^{-2} was maintained for several months in air for $MnCl_2$ intercalant, whereas for $CuCl_2$ intercalated fibres, the resistance ratio increased about 20% after 50 days and then remained unchanged.

REFERENCES

1. ERMOLENKO, I. N., LYUBLINER, I. & GULKO, N. V., *Chemically Modified Carbon Fibers and Their Applications*. VCH Verlagsgesellschaft, D-6940 Weinhein, 1989, pp. 271–298.
2. ISMAIL, I. M. K., *Carbon*, **25**(5) (1987) 653.
3. ENDO, M., OKADA, Y. & NAKAMURA, H., *Synthetic Metals*, **34** (1989) 739.
4. DAVIS, G. P., ENDO, M. & VOGEL, F. L., *15th Biennial Conference on Carbon*, 1981, p. 363.
5. KALNIN, I. L. & GOLDBERG, H. A., *Synthetic Metals*, **3** (1981) 159.
6. MURDAY, J. S. & DOMINGUEZ, D. D., *Synthetic Metals*, **9** (1984) 397.
7. YAMAGUCHI, Y., SHIOYA, J., MIZOGUCHI, A., UEBA, Y., MATSUBARA, H. & MURAKAMI, S., *Sumito Elec. Tech. Rev.*, **26** (1987) 203.
8. TOUZAIN, PH., BAGGA, G. R. & BŁAŻEWICZ, S., *Synthetic Metals*, **18** (1987) 565.
9. FISCHBACH, D. B. & ARNOLD, M. G., *Synthetic Metals*, **34** (1989) 733.
10. LUSKI, S., SELIG, H., DAVIDOV, D. & RETTORI, C., *Synthetic Metals*, **34** (1989) 725.
11. BŁAŻEWICZ, S. & TOUZAIN, Ph., *Carbon '92*, Essen, 1992.
12. HO, C. T. & CHUNG, D. D., *Carbon*, **28**(4) (1990) 521.
13. HERINCKX, C., PERRET, R. & RULAND, W., *Carbon*, **10** (1972) 711.
14. SUGIURA, T., ILJIMA, T., SATO, M. & FUJIMOTO, K., *Synthetic Metals*, **23** (1988) 449.