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# Nickel- and copper-coated carbon fibre reinforced tin–lead alloy composites

C. T. HO
*Department of Mechanical Engineering, National Yun-Lin Polytechnic Institute of Technology, Yun-Lin, Taiwan*

Nickel and copper were deposited over brominated, surface treated, and pristine P-100 carbon fibres using cementation and electroplating techniques. The fibres were brominated by bromine vapour for 48 h and then desorbed at 200 °C in air for 12 h. The anodic oxidation treatment of the fibres involved electrochemical etching in a dilute sodium hydroxide electrolyte for 3 min. Electroplated coated fibres showed better tensile properties than cementation coated fibres. In addition, nickel coating exhibited better bonding with the carbon fibres compared to copper coating. The effect of bromination and surface treatment was improved adhesion between coating and fibres. Nickel- and copper-coated fibres, which were brominated, anodically oxidized, and pristine, reinforced tin–lead alloy composites were fabricated by squeeze casting. The composites containing coated treated carbon fibres had higher tensile and shear strength than the ones containing coated pristine carbon fibres. Moreover, the composite with coated brominated carbon fibres had better tensile strength and shear strength than the surface treatment. The results also showed the composites containing nickel-coated fibres had higher tensile and shear strength than the ones containing copper-coated fibres.

## 1. Introduction

The white metal, Babbit, or bearing metal, based on lead or tin, has excellent frictional properties. It also possesses a number of other important properties such as embeddability, conformability, and corrosion resistance. However, bearing metals are mechanically weak. Tin–lead alloys are most commonly used for solders and bearings. Solder preforms are used to join various parts of electronic packages. Because the thermal expansion coefficient of a solder is in general much higher than that of the substrate, the solder joint often suffers from poor resistance to thermal fatigue. Thus, there is a need for a solder with a low thermal expansion. If tin–lead alloys can be made stronger, they can also carry greater loads and hence offer the possibility of reduction in overall bearing size for a given application.

Composite materials can be tailored to exhibit a chosen thermal expansion coefficient, as the filler species and the filler volume fraction can be wisely chosen. For a low thermal expansion composite, the filler must have a low thermal expansion coefficient. Moreover, the filler is preferably a good electrical conductor because the soldered joint may serve as an electrical connection as well as a mechanical one. It is also preferably a good thermal conductor for heat dissipation from the electronic package. In addition, the filler should have good mechanical properties in order to strengthen the tin–lead alloy.

One of the suggested means of strengthening bearing materials involves the incorporation of carbon fibres, thus using the fibres as a reinforcing agent and possibly also as a lubricating agent by virtue of their graphic nature.

Carbon fibres also have near zero thermal expansion coefficient. Furthermore, carbon fibres are widely available in a continuous form, which makes them more effective for lowering the thermal expansion coefficient of the composite, and which prevents the fibre distribution from becoming non-uniform after remelting and solidification [1].

Carbon fibre-reinforced tin–lead alloys had been previously fabricated by liquid metal infiltration [1, 2] and by investment casting for a fundamental process study [3, 4]. It is well known that carbon fibres are not wetted by liquid lead or tin. In order to produce good wetting and to prevent chemical reaction between the carbon fibres and the metal matrix during the synthesis of the composites, fibres were often coated with refractory or metal materials [4–7]. In the works mentioned above [1–4], the carbon fibres were electroplated with copper or nickel in order to ensure good wetting of the fibres by the alloy, but the weak bonding between the fibres and coating causes the stripping of coating material by the flow of liquid metal and it would also decrease the efficiency of reinforcement. Amorphous carbon has been used to coat the carbon fibres in order to improve the bonding between the $SiO_2$ coating and the carbon fibres [8]. Acetic acid treatment of carbon fibres or better coating techniques have also been tried to improve the bonding between the metal coating and the carbon fibres [9].

It has been clearly shown that fibre treatments lead to an increase in specific surface area. The increased roughness in the fibre may contribute significantly to the increase in fibre-matrix adhesion after these treatments. The surface of the fibre consisted of exposed edges of graphite planes as well as graphite basal planes. The edge carbon atoms of a graphite plane have high-energy $sp^2$ hybridized bonds, which are known to be important in resin-based composites [10]. It has been suggested that these complexes also bond with the metal matrix [11].

Surface treatments on carbon fibres would pit some of the highly convoluted planes and thus expose the reactive edges that would not otherwise have been exposed. Consequently, the number of reactive surface sites should increase. The increase in reactivity between the matrix and the fibre may contribute to the increase in fibre-matrix adhesion in addition to the surface roughness after surface treatment.

Brominated and other surface-treated carbon fibres have been used to improve the mechanical strength of polymer and metal matrix composites [12–15] by enhancing the adhesion between the fibre and the matrix. The effect of surface treatment on carbon fibres was comprehensively reviewed in [10, 16, 17]. Although the bromination of the carbon fibres has shown the same effect, of increasing the interface shear strength and tensile strength of the composites through surface treatment, the mechanical properties of the fibres were not affected by bromination [13].

In this paper, the morphology and the tensile fracture mode of the copper- and nickel-coated pristine, brominated, and surface-treated carbon fibres are compared. The tensile strengths of coated fibres are determined. The coated fibre reinforced tin–lead alloy was investigated.

## 2. Experimental procedure

Pitch-based carbon fibres (Amoco's Thornel P-100) were used in the present investigation. The surface treatment of fibres involved anodically etching in 0.1 mol $l^{-1}$ concentrated sodium hydroxide electrolyte for 3 min. Other fibres were brominated by bromine vapour for 48 h and then desorbed at 200 °C in air for 12 h. For copper coating or nickel coating by the cementation method, $CuSO_4$ or $NiSO_4$ solution was used with Mg as the displacing agent [18]. Using an electroplating technique, copper was coated from a $CuSO_4$ bath for 12 min at 8 V and 10 A current level and nickel was coated from a $NiSO_4$ bath under the same conditions as copper [19]. The alloy used contained 60 wt % Sn and 40 wt % Pb. The solidus of this alloy is 183 °C; the liquidus is about 192 °C.

Fibres of each type were attached individually to a card stock "picture frame" with epoxy cement, and then the samples were tested for their tensile strength and tensile ductility using an Instron tensile tester.

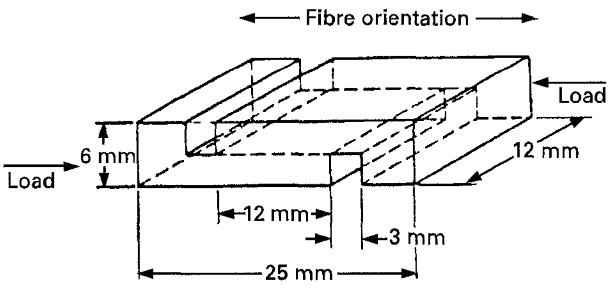

*Figure 1* Specimen geometry for composite shear strength tests.

The carbon fibre reinforced tin–lead alloy was prepared by squeeze casting, using a mould cavity of 6 cm in length and 1.3 cm in width. After placing carbon fibres of 4 cm in length unidirectionally along the length of the mould cavity, the temperature of mould was raised to 150 °C. Then liquid solder heated to 300 °C was poured into the mould which was maintained at 150 °C, and pressure ranging from 30 to 50 MPa was immediately applied through a piston at the top of the mould. The pressure was maintained for 10 min while the mould was allowed to cool to near room temperature.

Dog-bone samples with a gauge length of 25 mm and a cross-sectional area of 48 mm$^2$ were machined from the squeeze-cast sample. The tensile tests were performed on these samples using a hydraulic material testing system (MTS). The strain was measured by a strain gauge. All the composites contained 15 vol % fibres.

Rectangular double-notched samples, as shown in Fig. 1, were machined from each of the castings and then tested in compression so as to evaluate the composite's shear strength, which is defined as the load divided by the projected area, 144 mm$^2$. The sample geometry was similar to that recommended by ASTM D3846-79 [20] for the shear testing of polymer composites.

The morphology and fracture surface of coated fibres were examined by scanning electron microscopy (SEM), and the composites were examined by optical microscopy and electron spectroscopy for chemical analysis (ESCA) after polishing.

## 3. Results and discussion

### 3.1. Nickel- and copper-coated carbon fibres

The SEM photographs for the surface of the coated pristine and brominated fibres by cementation or electroplating method are shown in Figs 2 and 3. The metal coatings covered well the entire surface of the fibre in both Cu and Ni cases. The major portion of the fibres has a coating thickness between 0.5 to 1.1 µm for copper and 0.6 to 0.9 µm for nickel from either technique. Dendritic type growth was observed at higher coating thicknesses ( > 1.0 µm for copper, > 0.8 µm for nickel) for both pristine and treated fibres (Fig. 3a). Fig. 4 showed that cracks were found when the coating thickness of nickel is higher than 1.0 µm for both treated fibres (brominated and anodic oxidation), but were not found in coated pristine fibres. Cracks were also observed in the copper coating when the copper coating thickness was higher than 1.2 µm for both treated fibres, but were not found in coated pristine fibres. This indicates bromination and surface treatment induce better adhesion between the coating and

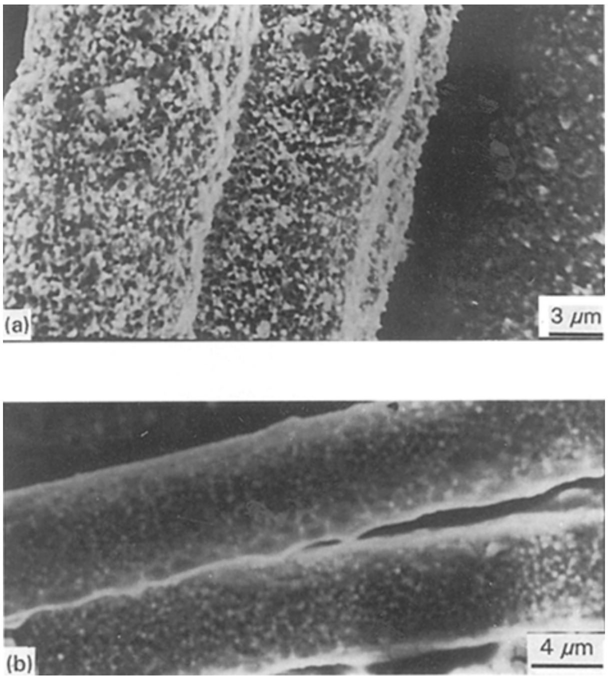

*Figure 2* (a) Copper-coated pristine carbon fibres produced by the cementation method. (b) Copper-coated carbon fibres with bromination produced by the electroplating method.

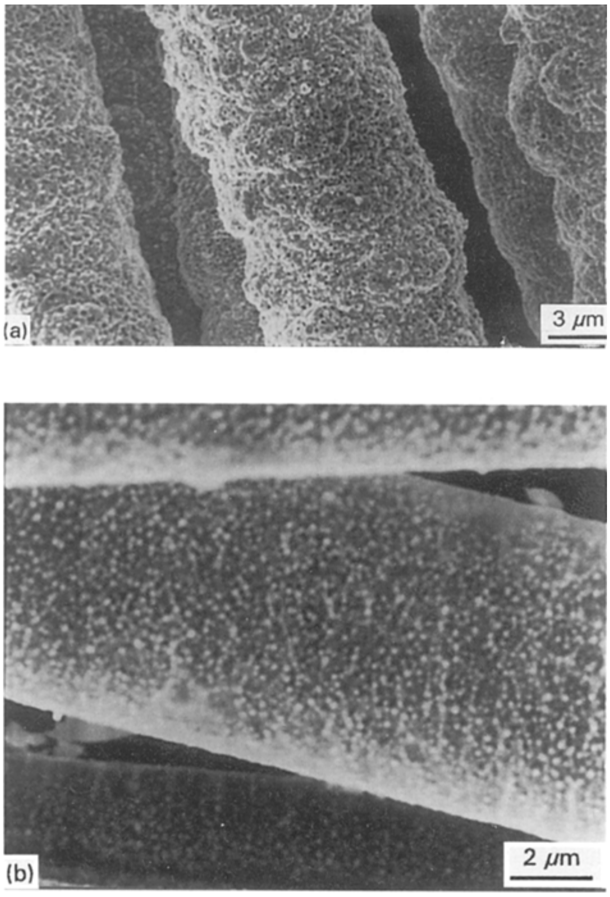

*Figure 3* (a) Nickel-coated pristine carbon fibres produced by the cementation method. (b) Nickel-coated carbon fibres with bromination produced by the electroplating method.

the fibres. This also demonstrates that the nickel coating has stronger bonding with the carbon fibres compared to the copper coating.

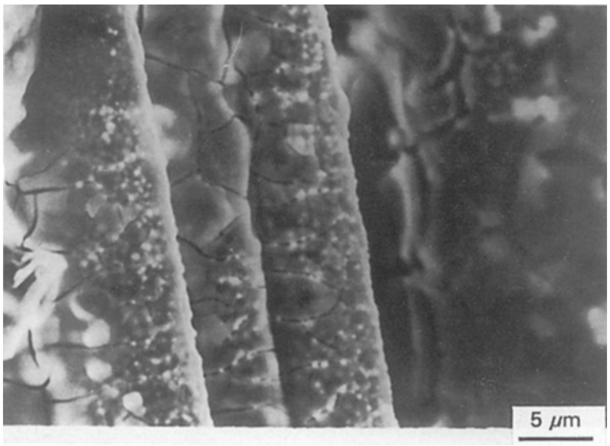

*Figure 4* Cracking of the nickel coating with coating thickness > 1.0 μm for brominated fibres.

TABLE I Fibre properties under different treatment conditions

| Condition | UTS (MPa) | Failure strain (%) |
|---|---|---|
| (a) *Copper coating* | | |
| 1. Pristine (P) | 2400 | 0.3 |
| 2. Anodic oxidation (A) | 2100 ± 120 | 0.25 ± 0.03 |
| 3. Bromination (B) | 2300 ± 80 | 0.32 ± 0.03 |
| 4. Coating P by cementation process | 1500 ± 340 | 0.22 ± 0.03 |
| 5. Coating A by cementation process | 1700 ± 310 | 0.24 ± 0.04 |
| 6. Coating B by cementation process | 1900 ± 280 | 0.27 ± 0.05 |
| 7. Coating P by electroplating process | 1930 ± 246 | 0.26 ± 0.05 |
| 8. Coating A by electroplating process | 1950 ± 235 | 0.27 ± 0.04 |
| 9. Coating B by electroplating process | 2250 ± 220 | 0.27 ± 0.04 |
| (b) *Nickel coating* | | |
| 10. Coating P by cementation process | 1510 ± 196 | 0.18 ± 0.03 |
| 11. Coating A by cementation process | 1780 ± 151 | 0.23 ± 0.06 |
| 12. Coating B by cementation process | 1890 ± 142 | 0.25 ± 0.04 |
| 13. Coating P by electroplating process | 1941 ± 151 | 0.22 ± 0.05 |
| 14. Coating A by electroplating process | 1980 ± 110 | 0.23 ± 0.05 |
| 15. Coating B by electroplating process | 2220 ± 85 | 0.24 ± 0.03 |

The tensile strength and elongation of the fibres under different conditions are listed in Table I. All data were the average of at least five tests. The bromination did not reduce the mechanical properties [13], but the anodic oxidation did reduce the strength by about 10%.

Coated pristine fibres produced by the cementation process had the lowest tensile strength of 1.5 GPa and 0.22% failure strain for the copper coating process, but brominated carbon fibres coated by the electroplating technique gave the highest tensile properties of 2.25 GPa and 0.27% elongation. In the case of nickel-coated pristine fibres, the cementation process also

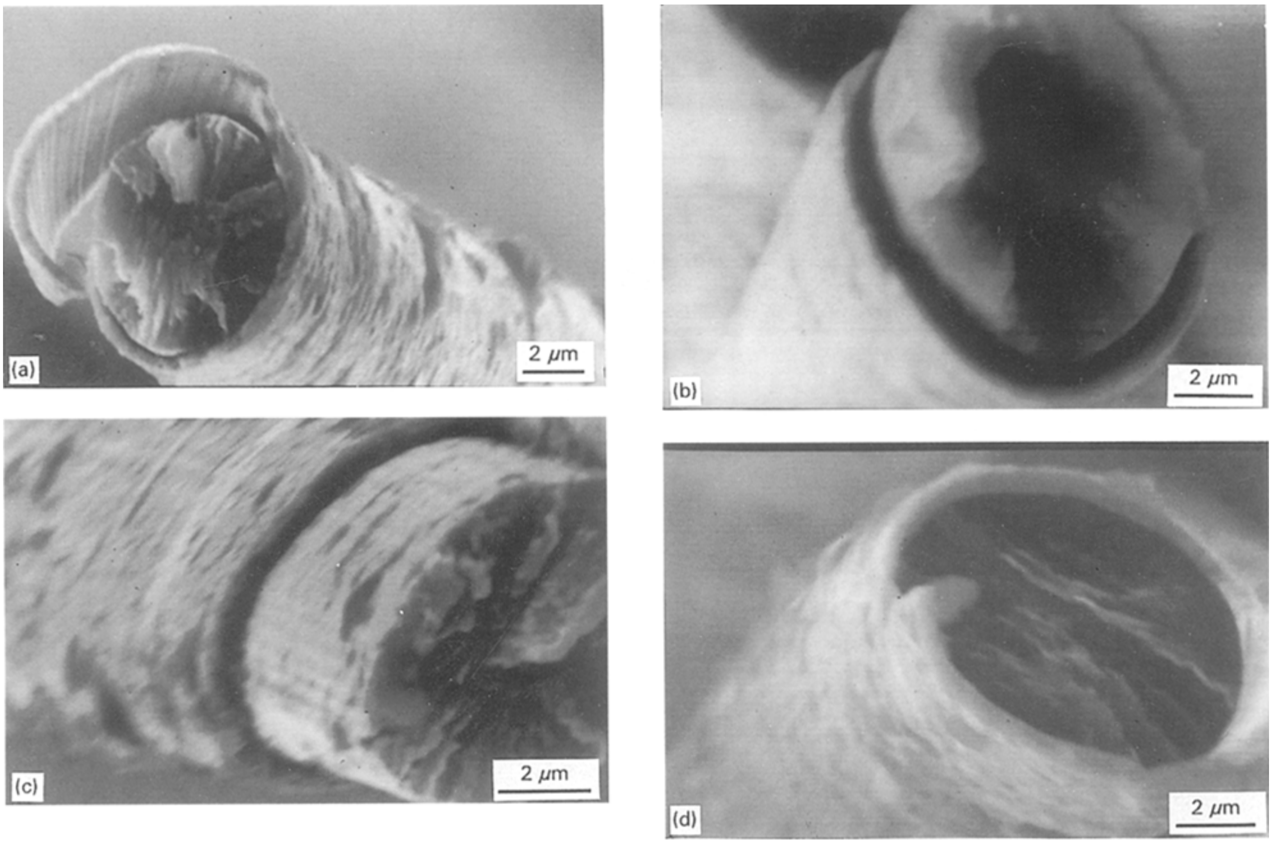

*Figure 5* (a) Tensile fracture surface of a copper-coated pristine fibre produced by the electroplating method. (b) Tensile fracture surface of a copper-coated brominated fibre produced by the electroplating method. (c) Tensile fracture surface of a nickel-coated pristine fibre produced by the electroplating method. (d) Tensile fracture surface of a nickel-coated fibre with bromination produced by the electroplating method.

had the lowest tensile strength of 1.41 GPa and 0.21% strain, while brominated carbon fibres coated by the electroplating technique gave the best tensile properties of 2.22 GPa and 0.24% tensile strain. In both the nickel and the copper coating, the electroplating process gave a better coating and better tensile properties that are nearer to those of pristine fibre.

The fracture surface of copper-coated pristine fibres exhibited a ductile fracture in both coating techniques (Fig. 5a), but the copper-coated treated fibres exhibited a moderate brittle fracture surface that showed debonding of the coating from the fibre (Fig. 5b). Pristine fibres nickel-coated by both techniques showed similar fracture morphology to that observed in the case of the copper-coated treated fibres (Fig. 5c). The fracture surface of nickel-coated fibres that are either brominated or surface treated exhibited brittle type fracture (Fig. 5d).

The lower strength in the cementation coating process may be due to the coating spread not being smooth and uniform (Figs 2 and 3), as in the electroplating process [21]. The scatter range of the tensile property results and the fractured surface of the coated fibres may suggest that the Ni coating has stronger adhesion to the fibres than the copper coating.

## 3.2. Composites

Fig. 6a shows one region of the composite containing copper-coated pristine fibres. In some regions, it was found that they consist of bare carbon fibres and partially copper clad carbon fibres (Fig. 6a). The stripping of the coating metal resulted in fibres almost debonding completely from the matrix. The copper that was swept away reacted with the matrix to form the ternary equivalents of phases $Cu_3Sn$ and $Cu_6Sn_5$ that were identified by ESCA analysis. These precipitates were found around the fibre (Fig. 6a, dark area). The composites containing the coated fibres with bromination or surface treatment did not show such phenomena, and only a small amount of copper was swept away to form the ternary phase (Fig. 6b). Similar observations were also made in the composites containing nickel-coated fibres, but the swept-away nickel reacted with the matrix forming the compound $Ni_3Sn_4$ instead.

Table II shows results for the tensile and shear tests performed on these composites, along with the calculated values for the rule of mixtures. All data were the average of at least five tests. The composites containing coated fibres with bromination or surface treatment led consistently to an increase in the average tensile strength and to an increase in the composite shear strength.

The shear fracture surface of the composite containing nickel-coated fibres with a surface treatment is shown in Fig. 7. The majority of the fractures had occurred by decohesion between the coating and the fibres. Similar observations were also made in other composites. This indicated that the adhesion between

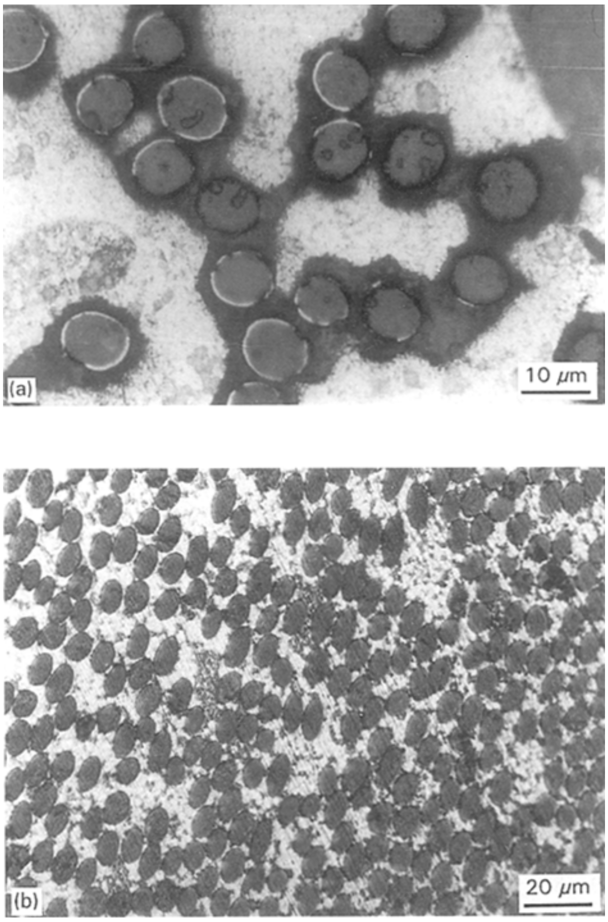

*Figure 6* (a) One region of the composite containing coated pristine fibres produced by the electroplating method. (b) The composite containing coated brominated fibres produced by the electroplating method.

TABLE II Mechanical properties of composites with different fibres as reinforcement

| Condition[a] | UTS (MPa) and Strength (MPa) (in parentheses) | Composite shear |
|---|---|---|
| 7 | 180 ± 30<br>(347)[b] | 77 ± 9 |
| 8 | 200 ± 22<br>(350)[b] | 86 ± 9 |
| 9 | 240 ± 15<br>(395)[b] | 91 ± 11 |
| 13 | 202 ± 24<br>(349)[b] | 88 ± 14 |
| 14 | 229 ± 21<br>(354)[b] | 99 ± 11 |
| 15 | 260 ± 19<br>(390)[b] | 107 ± 12 |

[a] The number indicates the fibre's conditions as marked in Table I.
[b] Rule of mixture values.

coating and fibre may contribute significantly to the interface shear strength (ISS). Therefore, the increase in shear strength of the composites with metal-coated treated fibres must arise from an increase in ISS resulting from better fibre-coating adhesion, since the composite shear strength is a combination of matrix shear strength and ISS.

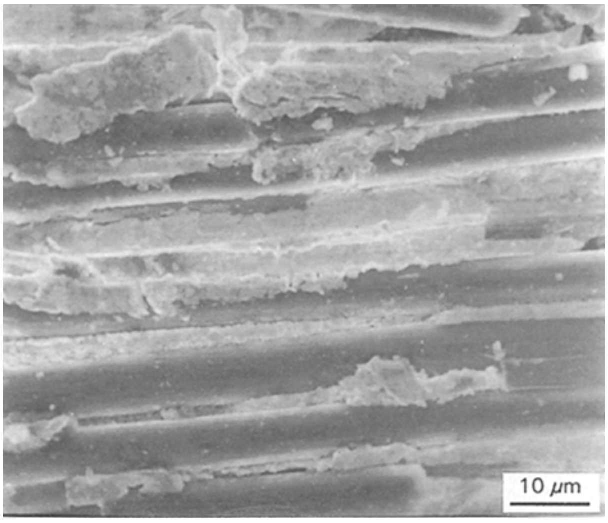

*Figure 7* Shear fracture surface of the composites containing nickel-coated fibres with bromination produced by the electroplating method.

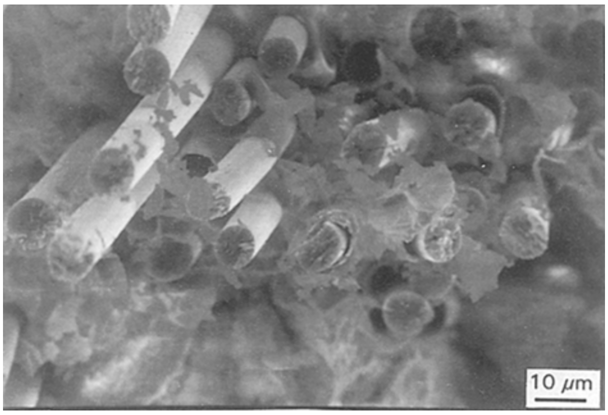

*Figure 8* Tensile fracture surface of the composite containing nickel-coated pristine fibres produced by the electroplating method.

The typical area of the tensile fracture surface of the composites containing nickel-coated pristine fibres, shown in Fig. 8, consisted of two distinct regions, bare carbon fibre pullout and a flat fracture surface. Similar fracture types were also observed in other composites with coated treated fibres, but the degree of bare fibre pullout was less than that of composites with coated pristine fibres. The tensile properties of composites containing coated fibres that were brominated or surface treated were approximately up to 65% of the rule of mixture values, with strengths higher than those with untreated fibres. This is consistent with the improved bonding between metal coating and fibre due to the bromination and surface treatment. The composite containing coated fibres, produced by bromination with electroplating, had better tensile strength than the others. This may be due to the mechanical properties of the fibres only being effected a little by the bromination [13]. The composites prepared with nickel-coated fibres had higher tensile and shear strength than the ones prepared with copper-coated fibres. This may be due to the nickel coating having better adhesion to the fibres than the copper coating, as has been discussed in Section 3.1.

## 4. Conclusion

Tin–lead alloy composites were successfully made by squeeze casting for copper- and nickel-coated carbon fibres that were either brominated or surface-treated as well as untreated. The fibres coated by the electroplating method had better tensile properties than the fibres coated by the cementation method. Additionally, the Ni coating has exhibited stronger bonding to the carbon fibres than the Cu coating.

The coated fibres increase the tensile modulus and tensile strength of the alloy. However, the coated fibres with bromination and surface treatment are preferred because they result in composites with higher tensile and shear strength. This effect of bromination and surface treatment is associated with the fact that bromination and surface treatment improved the adhesion between the fibres and the metal coating. Furthermore, the composite containing coated carbon fibres with bromination showed the best performance in the tensile and shear tests. In addition, the composites with nickel-coated fibres had better tensile and shear strength than the ones with copper-coated fibres.

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