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Copper coating on coir fibres

C. PAVITHRAN, K. GOPAKUMAR, S. V. PRASAD, P. K. ROHATGI
Regional Research Laboratory (CSIR), Trivandrum-695019, India

Conditions for obtaining continuous coatings of copper (thickness range 1.5 to 5 μm) on coir fibres have been reported. Activation of the surface of coir fibres was achieved by treating the surface of the fibres with NaOH–HCHO/ammoniacal $AgNO_3$ solution. Copper was deposited on the activated surface of coir fibres from Fehling–formaldehyde solution. The effects of variation in formaldehyde and sodium hydroxide concentrations and pressures inside the coating vessel on deposition rates were determined. The minimum concentrations of NaOH and HCHO required for maintaining a maximum rate of deposition of copper from a solution contaning $10\,g\,l^{-1}$ copper sulphate were found to be $6.6\,g\,l^{-1}$ and 2.5 to $3.5\,g\,l^{-1}$, respectively. Optical and scanning electron microscope studies show that relatively more uniform and non-porous copper coatings were obtained when deposition was carried out under reduced pressures. A 5 μm thick copper coating on coir fibre prevents the propagation of flame as was shown by flammability tests. Copper coating on coir fibre decreases its electrical resistivity from $2.55 \times 10^6\,\Omega$cm to $4.68 \times 10^{-3}\,\Omega$cm with 1.5 μm thick coating and $3.76 \times 10^{-5}\,\Omega$cm with 5 μm thick coating. Reinforcement of polyester with copper-coated coir fibre leads to an increase of about 25% in tensile strength and flexural strength as compared to polyester reinforced with plain coir fibre.

1. Introduction

Coir fibre comes from coconut palm and is available in very large quantities, of the order of 5 million tons year^{-1}, world-wide. Coir consists of cellulose fibres with hemicellulose and lignin as the bonding material for the fibres. The coir fibre is therefore in a sense a fibrous composite material (Fig. 1a).

Natural fibres have been one of the cheap and renewable resources of materials and they are receiving increasing attention as reinforcements in polymeric materials in composites due to the shortage of non-renewable resources [1, 2]. However, low and variable strength, poor resistance to weathering and lack of wettability with various polymeric matrix materials make natural fibres less desirable compared to synthetic fibres as reinforcements. To overcome some of these drawbacks we have explored the possibility of coating the coir fibres with metals, specifically copper.

As a result of metal coatings, the fibres can also become electrically and thermally conductive, and the polymer composites made out of these fibres can find uses in electromagnetic interference (EMI) shielding, electrical heating and discharging static electricity like metal–polymer composites [3–5].

In this paper we report optimum conditions for coating coir fibre with copper using an electroless technique. Flammability, mechanical and electrical properties of coated fibres are compared with those of uncoated fibres. Mechanical and electrical properties of polyester composites containing both uncoated and copper-coated fibres are also reported.

2. Experimental procedure

Retted coir fibres supplied by a local manufacturing unit were graded and trimmed according to thickness and uniformity. The length of the trimmed fibres varied from 7 to 15 cm. The thickness of the fibres selected for coating was in the range 0.15 to 0.30 mm. The fibres were thoroughly washed with water to remove dirt and salt adhering to the surface.

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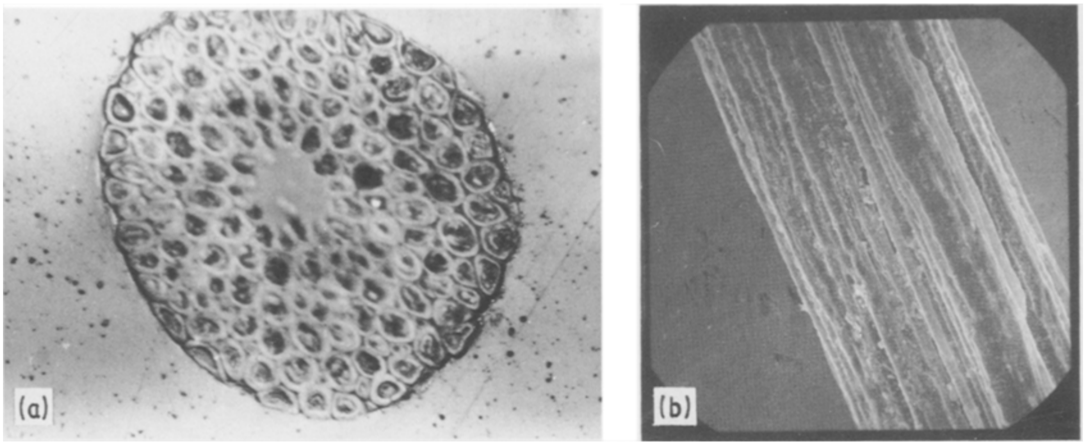


Figure 1 (a) Photomicrograph of cross-section of coir fibre (X 370) showing individual fibrils, (b) scanning electron micrograph of coir fibre (X 215).

2.1. Coating of coir fibres with copper

Coating of fibres with copper involved two steps: (a) activation of the fibre surface by treating the fibre with NaOH–HCHO/ammoniacal silver nitrate solution, and (b) deposition of copper from Fehling–formaldehyde solution.

5 g batches of fibres were soaked in 200 ml 1% NaOH solution for 2 to 3 min and rinsed with distilled water. These fibres were then treated with 300 ml 0.025% ammoniacal silver nitrate solution. The adsorbed silver ammonium complex was reduced to silver by treating the fibres with an aqueous solution of 1% NaOH and 1% HCHO for 1 min. The process was repeated until a pale brown stain was obtained on the surface of the fibre.

Activated fibres (0.5 g) were quickly transferred to 300 ml Fehling–formaldehyde solution containing 1% copper sulphate pentahydrate and 2.5% potassium sodium tartrate and stirred with a glass rod at 60 rpm. Care was taken to ensure that the stirrer did not touch the sides of the container. Concentrations of NaOH and HCHO in the reducing bath were varied from 6.6 to $10\,\mathrm{g\,l^{-1}}$ and 2.5 to $10\,\mathrm{g\,l^{-1}}$, respectively. Fibres were removed at predetermined intervals and washed with water to remove the alkali adhering to the fibre surface. The coated fibres were dried in vacuum after washing with methanol. The process was repeated under reduced pressure of 10^{-1} Torr.

2.2. Investigation of coating

The coatings were dissolved in 1 : 1 nitric acid and the amount of copper deposited on the fibre surface was estimated gravimetrically using 1% 3,5-dimethyl-1-nitroguanyl pyrazole in ethanol as precipitating agent [6] and volumetrically using standard thiosulphate solution [7]. The nature of the coating was studied using optical and scanning electron microscopy.

2.3. Physical properties

Specimens for flammability tests were prepared by winding a bundle of fibres (100 mm long) weighing 75 mg with a cotton thread, coated with PF resin. The specimens were held at 45° to the horizontal and one of the bundles was introduced into a vertical luminous flame of about 35 mm height. The flame was removed after 12 sec and the rate of flame propagation in the fibre bundles was recorded.

2.4. Evaluation of copper-coated coir as a reinforcement in plastic

Coir fibres in the as-received condition and coated with 1.5 μm thick copper (Grade I) under reduced pressures, were used for making composites with polyester (HSR 8131 isophthalic polyester) as matrix material. Fibres 100 mm long were aligned unidirectionally by stretching the fibres in a mould of dimensions 100 mm x 15 mm and a predetermined quantity of polyester resin mixed with 2% MEK peroxide as initiator and 2% cobalt naphthanate as catalyst was poured into the mould. A slight pressure was applied to keep the fibres in position. Chopped fibre–polyester composites were prepared by mixing fibres of length 20 mm with the resin and were then moulded as described above. Samples were post-cured at 80°C for 24 h. The volume fraction of fibres in the composite was calculated from the weight fraction of fibre in the composite and the measured densities of fibres and polyester.

Mechanical properties of composites were measured using an Instron testing machine. Flexural properties were measured on a three-point bend jig at a cross-head speed of $1\,\mathrm{mm\,min^{-1}}$ employing a span-to-depth ratio of 16 conforming to ASTM D790. Dumb-bell shaped test specimen pieces were machined from rectangular samples for tensile testing. Measurements were made on six samples at each composition and the average value was taken.

The ends of composite specimens used for electrical conductivity measurements were first polished and coated with a conducting layer of silver paint. The specimens were then pressed between two thin copper foils, as shown in Fig. 2a and the electrical resistivities along three directions, shown in Fig. 2b, were measured using a Kelvin bridge. The resistivities of polyester, uncoated coir fibres and composites containing uncoated fibres were measured using a megaohmmeter.

3. Results and discussion

A considerable amount of work has been reported in the literature on the deposition of copper from Fehling–formaldehyde solutions on plastic surfaces activated by a noble metal such as Pt, Pd, Au or Ag [8–10]. In the present investigation, Ag is relatively less expensive compared to other noble metals. A metal complex such as diamine Ag(I) may become co-ordinated to the hydroxyl groups at the surface of the fibre [11] and get reduced to metallic Ag in NaOH–HCHO solution. Since the deposition of Ag occurs through the reduction of Ag ions adsorbed on the fibre surface, a uniform and thin layer of Ag is likely to occur in the presently employed method unlike the possible irregular deposition of Ag by putting the fibres in a reducing bath containing Ag ions.

It has been reported in the literature that the deposition of copper from Fehling–formaldehyde solution proceeds according to Lukes equation [8]:

$$\begin{aligned}\mathrm{Cu^{2+}} + 4\mathrm{OH^-} + 2\mathrm{HCHO} &\rightarrow \mathrm{Cu^0}\\ &+ 2\mathrm{HCOO^-} + 2\mathrm{H_2O}.\end{aligned}$$

However, unlike plastics, lignocellulosic materials like coir can undergo degradation under alkaline conditions. Therefore, the concentrations of the ingredients should be optimized to arrive at a sufficiently rapid rate of coating at minimum pH levels.

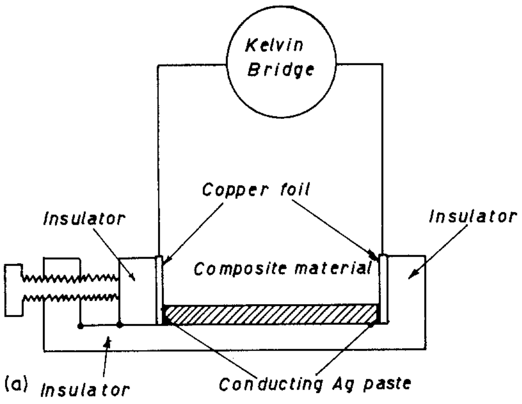
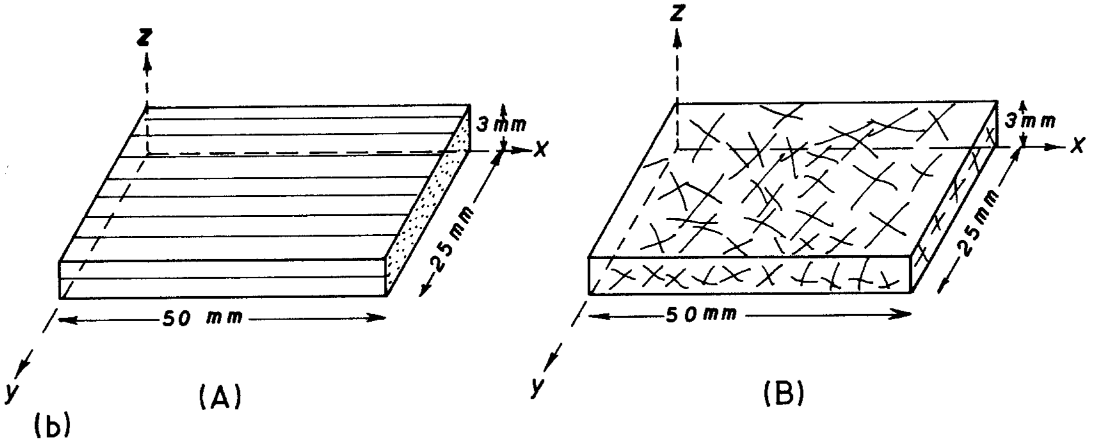


Figure 2 Schematic illustration of the device used to measure electrical resistivity of copper coated fibre–polyester composites. (b) Specimens for measuring electrical resistivities (A) Unidirectionally-alligned fibres. (B) Randomly orientated fibres.



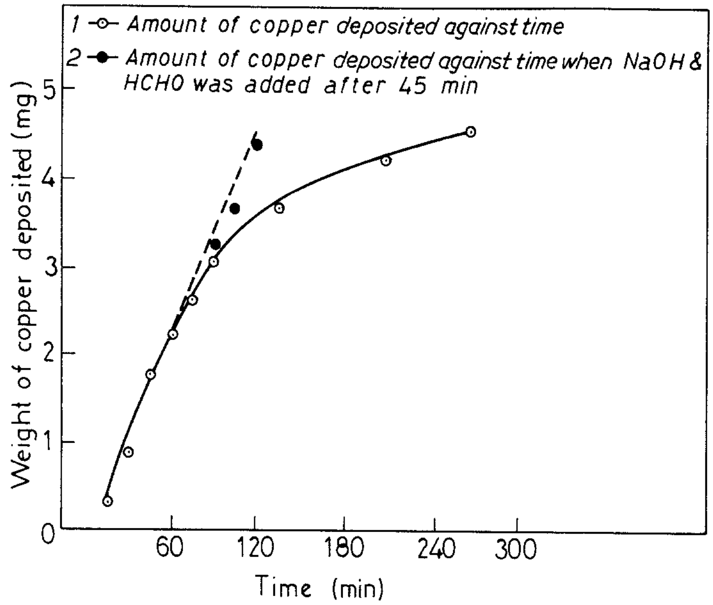


Figure 3 Progress of deposition of copper on 3.7 mg (length ~ 10 cm) fibres as a function of time.

3.1. Effect of variation in concentration of NaOH and HCHO in Fehing–formaldehyde solution on deposition of copper

The amounts of copper deposited on 3.7 mg coir fibre (~ 10 cm) after 4.5 h treatment in Fehling–formaldehyde were taken for comparison. When the concentration of NaOH was below 6.6 g l^{-1}, deposition of copper did not occur in measureable amounts. The same was found to be true with HCHO at concentrations below 2.5 g l^{-1}. When the NAOH and HCHO concentrations were 6.6 and 2.5 to 3.5 g l^{-1}, respectively, the amount of copper deposited was 4.5 mg. Any change in concentration of NaOH above 6.6 g l^{-1} resulted in an increase in the amount of copper deposition reaching a maximum of 5.5 mg at 10 g l^{-1}. Variation in concentration of HCHO between 2.5 and 5 g l^{-1} did not have an measurable effect on deposition. However, at a higher concentration of HCHO a decrease in deposition (3.2 mg for HCHO concentration of 10 g l^{-1}) was observed. In view of the above observations, and taking into consideration the ease of degradation of fibre at high pH, the concentrations of NaOH and HCHO were fixed at 6.6 and 2.5 to 3.5 g l^{-1}, respectively, for further studies.

3.2. Deposition of copper on fibres with time

It can be seen from Fig. 3 that the amount of copper deposited on the fibre increases linearly with time up to 60 min. After this the plot of the amount deposited against time deviates from linearity indicating a drop in the rate of reaction after 60 min. By the addition of the required amount of NaOH, HCHO and $CuSO_4$ after a 60 min interval to attain the initial concentration, it was found that the amount deposited on the fibre continued to increase linearly (Fig. 3). This indicates that the reaction rate drops after a 60 min interval due to the possible depletion of constituents other than potasium sodium tartrate, and the reaction rate can be kept constant by replenishing the various constituents in the bath. A slightly higher value (2 to 3%) of deposition was observed when the deposition was carried out under reduced pressure. However, the amount deposited against time at reduced pressures showed trends similar to that deposited at atmospheric pressure.

3.3. Optical and SEM studies

The thicknesses of coatings as observed in the optical micrographs of transverse sections are in the range 1.5–5.0 μm (Fig. 4). When the coatings are very thin (below 1.5 μm) they are generally discontinuous, and only after a 30 min coating period, when the percentage of copper is around 15%, do the coatings become continuous (Fig. 4c). Similar phenomenon of initial discontinuous deposits of copper have been observed when attempts have been made to deposit copper on carbon fibres [12] and graphite [13] to produce

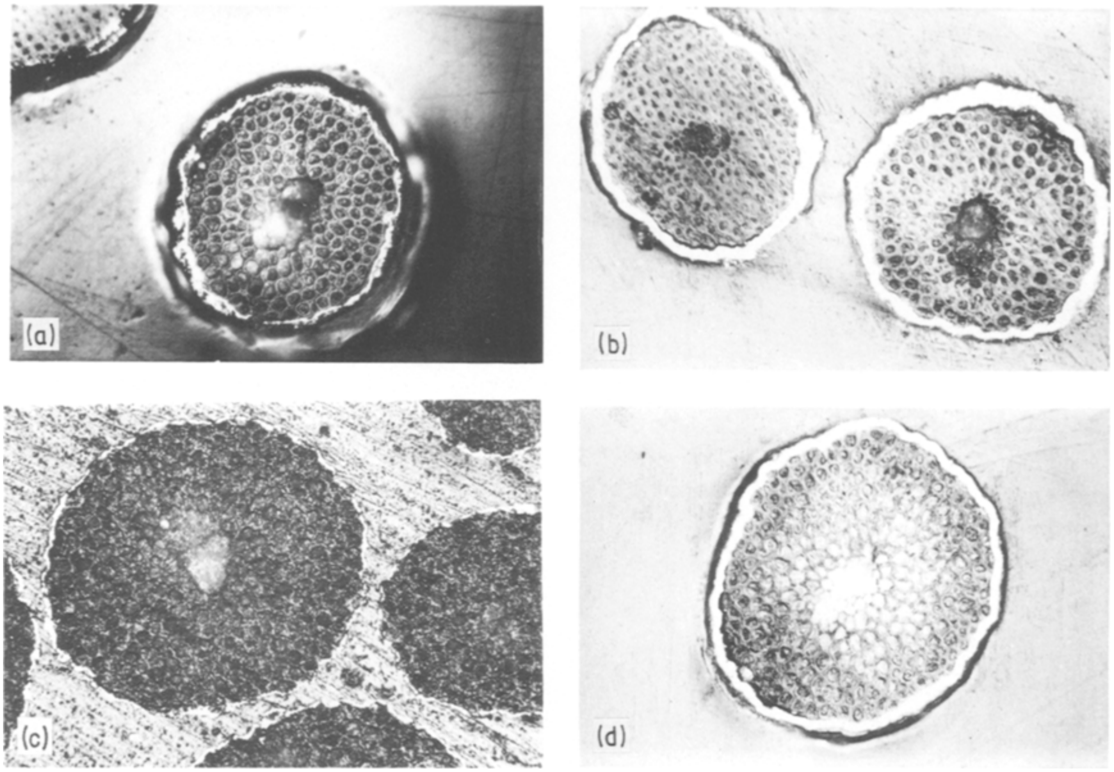


Figure 4 Photomicrograph of cross-section of the copper-coated coir fibre. Deposition of copper on fibre carried out for: (a) 40 min (20% copper) at atmospheric pressure (X 315); (b) 120 min (55% copper) at atmospheric pressure (X 315); (c) 30 min (15% copper) under reduced pressure (X 360); (d) 120 min (55% copper) under reduced pressure (X 315).

copper-coated graphite particles or fibres [14–16] for subsequent incorporation in composites. When the coating was carried out under reduced pressure, a relatively more uniform deposition was observed (Fig. 6a). A possible explanation for this could be as follows. Hydrogen molecules evolved during the reaction might be adhering to the fibre before leaving the surface after gaining a critical size by the addition of more hydrogen molecules. Therefore, futher deposition of copper atoms will be hindered at these sites making the coatings non-uniform and porous (Figs 4a and 5). In this case, continuity of coatings was found to occur only when the amount of copper was above 20%. By lowering the pressure inside the vessel below atmospheric pressure, hydrogen molecules leave the bath without adhering to the fibre. Therefore, coatings were found to be relatively more uniform and less porous (Fig. 6) even with less amounts of copper deposited (15%) as seen in Figs 4c and 6.

Calculations of the thickness, t, of the copper coating were made with respect to the amount of copper deposited using the following equation:

$$t = \frac{m}{2\pi l r d}, \qquad (1)$$

where m is the mass of copper deposited (mg), l is the length of fibre (100 mm) r is the radius of cross-section (0.1 mm), and d is the density of copper (8.93 g cm^{-3}).

Fig. 7 shows that theoretically calculated values of coating thickness are slightly higher than the measured values from the optical micrographs of transverse sections. Apparently the actual surface areas of the fibres are considerably higher (due to the non-uniformity of diameter and surface irregularity of the fibres) than the values calculated for perfectly smooth and uniform fibres used in our calculations. This, in fact, more than compensates for the porosity in the deposits leading to lower measured values.

4. Physical properties

Flammability tests on fibre bundles have shown that the propagation of flame was approximately at the same rate (100 mm in 40 sec) in raw fibres

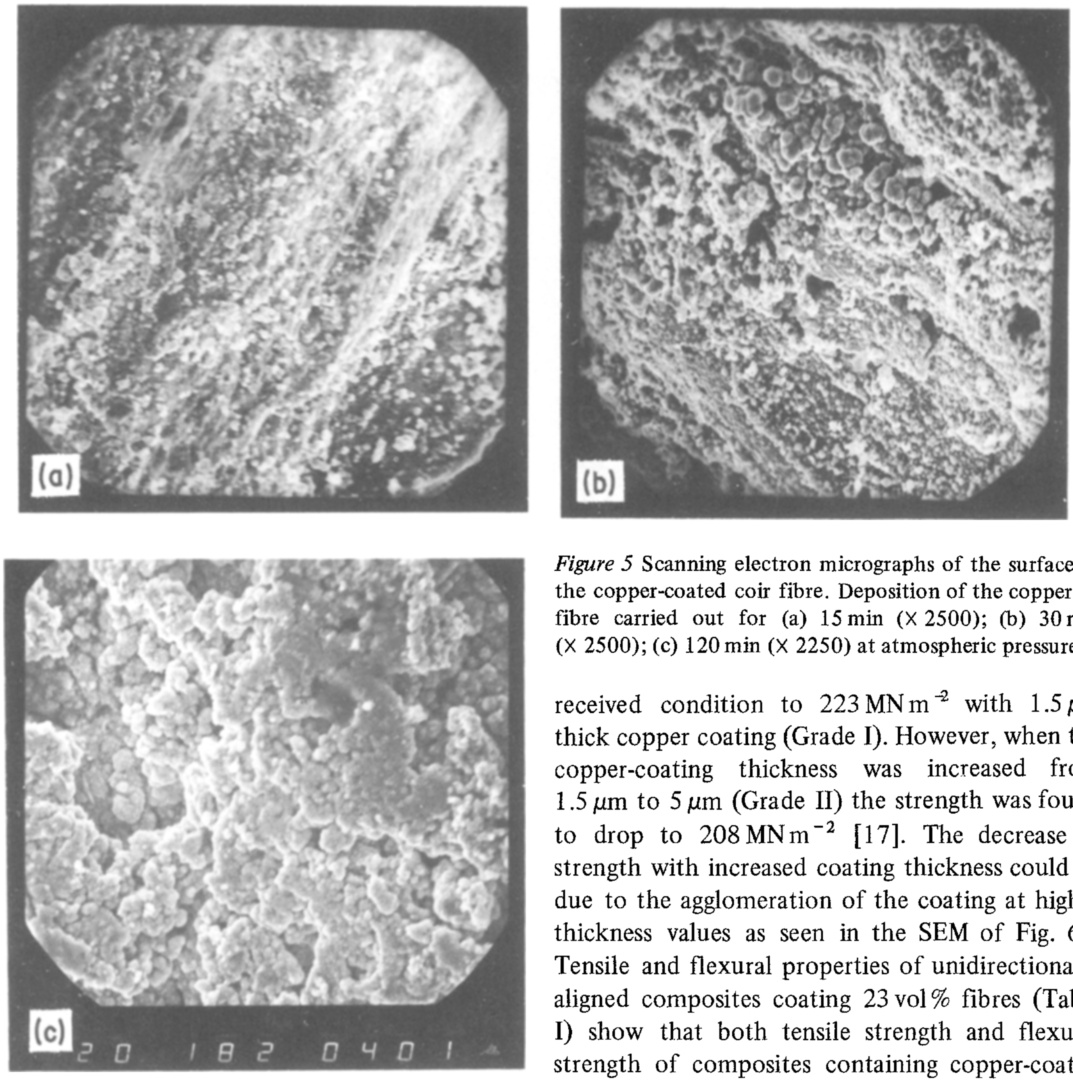


Figure 5 Scanning electron micrographs of the surface of the copper-coated coir fibre. Deposition of the copper on fibre carried out for (a) 15 min (X 2500); (b) 30 min (X 2500); (c) 120 min (X 2250) at atmospheric pressure.

as well as in coir fibres coated with 1.5 μm thick copper (Grade I). However, unlike in raw fibres, no after-glow was observed in Grade I copper-coated fibres. As a contrast, when the thickness of copper coating was increased to 5 μm (Grade II) and tested under identical conditions, neither flame propagation nor after-glow were observed. The copper coating was found to conduct part of the heat of the flame away from the fibre surface. This appeared to be one of the reasons for the reduced flammability. From these preliminary investigations, it appears that a minimum thickness of copper coating is required above which copper-coated fibres become flame retardant.

5. Mechanical and electrical properties

Ultimate tensile strength (UTS) of coir fibre was found to increase from 169 MN m^{-2} in the as-received condition to 223 MN m^{-2} with 1.5 μm thick copper coating (Grade I). However, when the copper-coating thickness was increased from 1.5 μm to 5 μm (Grade II) the strength was found to drop to 208 MN m^{-2} [17]. The decrease in strength with increased coating thickness could be due to the agglomeration of the coating at higher thickness values as seen in the SEM of Fig. 6b. Tensile and flexural properties of unidirectionally aligned composites coating 23 vol% fibres (Table I) show that both tensile strength and flexural strength of composites containing copper-coated fibres (Grade I) are about 25% higher than those of composites containing raw fibres. It can be seen from Table I that there is no significant difference in the properties of composites containing raw fibres, and the base polyester, whereas the com-

TABLE I Mechanical properties of unidirectional coir fibre–polyester composites

Material	Flexural strength (MN m^{-2})	Tensile strength (MN m^{-2})
Polyester	52.2	49.6
As-received coir fibre–polyester composite V.F. = 0.23	56.2	45.9
Copper-coated coir fibre–polyester composite V.F. = 0.23	69.8	56.9

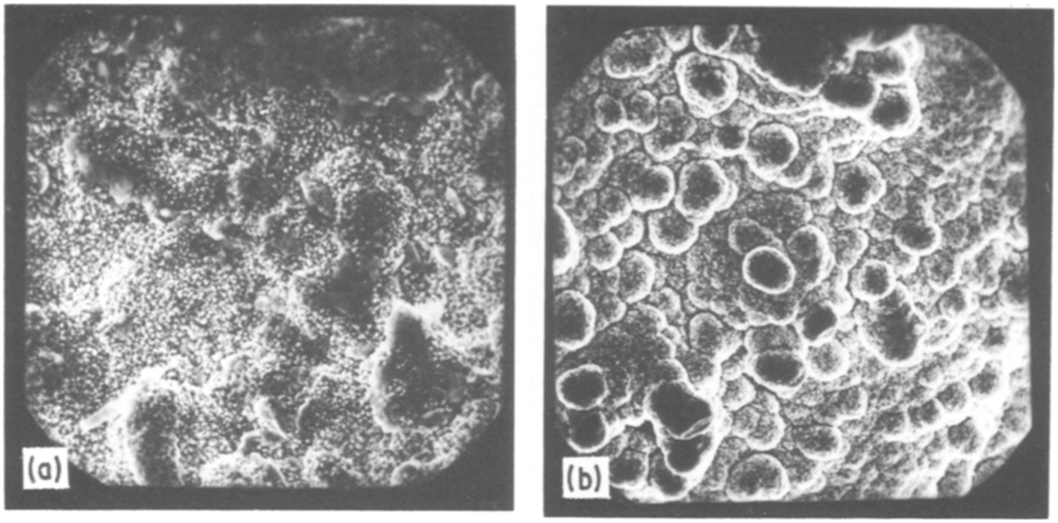


Figure 6 Scanning electron microgrphs of the surface of the copper-coated coir fibre. Deposition of copper on fibre carried out for (a) 30 min (X 2500) and (b) 120 min (X 2500) under reduced pressure.

posites containing copper-coated fibres show an increase of 15% in tensile strength and 34% in flexural strength over that of polyester. This shows that copper coating can change the coir fibres from fillers to reinforcements when composited with polyester.

Electrical resistivity measurements have shown that the resistivity of coir fibre decreases from $2.55 \times 10^6\,\Omega$cm in the as-received condition to 4.68×10^{-3} and $3.76 \times 10^{-5}\,\Omega$cm with 1.5 and 5 μm thick copper coatings, respectively. For a polyester composite containing 23 vol% unidirectionally-aligned copper-coated fibres (Grade I) the minimum resistivity was $9.93 \times 10^{-3}\,\Omega$cm along the length of the fibres and the maximum resistivity was $17.16\,\Omega$cm across the thickness. These values are much lower than the resistivity of polyester ($1.35 \times 10^{11}\,\Omega$cm) and polyester/uncoated coir fibre composites ($1.23 \times 10^{10}\,\Omega$cm). The resistivity values of composites containing a lower volume fraction of randomly orientated chopped copper-coated fibres having an aspect ratio of 100 also fall below $100\,\Omega$cm (Table II), which are well below the values required for EMI shielding and discharging of static electricity [2].

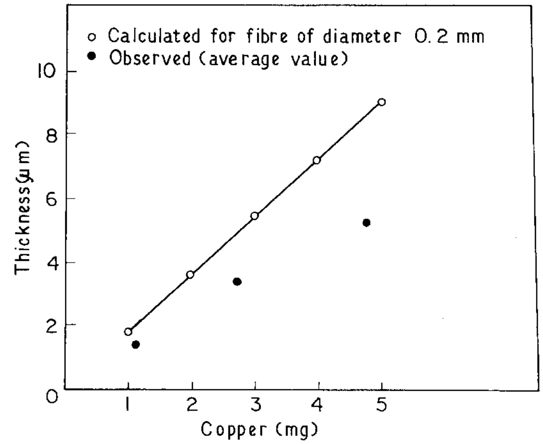


Figure 7 Thickness of coating as a function of the amount of copper deposited.

6. Conclusions

(1) Copper ions reduced to metallic copper from Fehling–formaldehyde solution can be deposited on coir fibre surfaces, (activated by treating with NaOH–HCHO/ammonical $AgNO_3$ solution) in the form of coatings 1.5 to 5 μm thick.

TABLE II Electrical resistivities of copper-coated fibres and polyester composites

Material	Resistivity (Ωcm)		
	ρ_x	ρ_y	ρ_z
Polyester	1.35×10^{11}	—	—
Coir fibre–polyester composite (V.F. = 0.23)	1.23×10^{10}	—	—
Grade I copper-coated coir polyester composite unidirectionally alligned (V.F. = 0.23)	9.93×10^{-2}	15.22	17.16
Grade I copper-coated coir–polyester composite chopped fibres with aspect ratio of 100. Random orientation	1.77	2.21	63.13

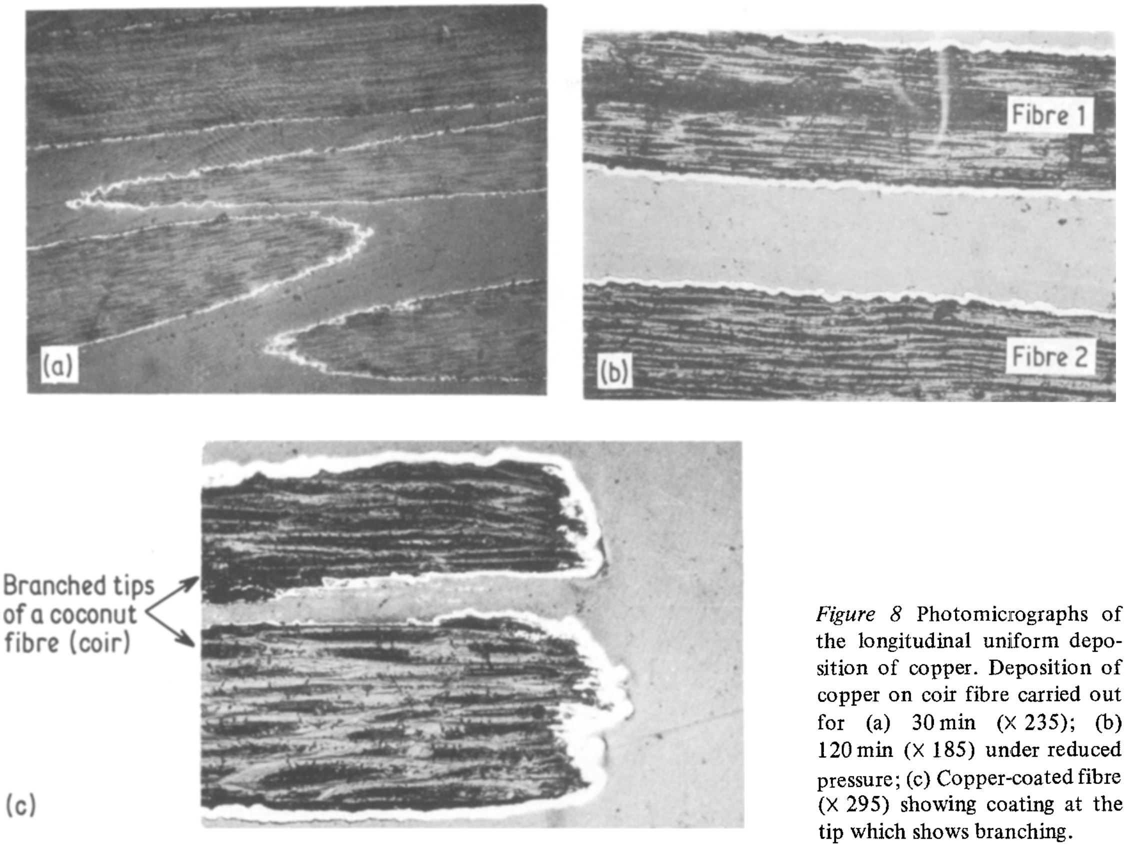


Figure 8 Photomicrographs of the longitudinal uniform deposition of copper. Deposition of copper on coir fibre carried out for (a) 30 min (× 235); (b) 120 min (× 185) under reduced pressure; (c) Copper-coated fibre (× 295) showing coating at the tip which shows branching.

(2) Concentrations of sodium hydroxide and formaldehyde in Fehling–formaldehyde solution should be 6.6 and 2.5 to 3.5 $\mathrm{g\,l^{-1}}$, respectively, to maintain the deposition rate in the range of 3 to 4 $\mathrm{mg\,min^{-1}}$ (when the concentration of copper sulphate is 10 $\mathrm{g\,l^{-1}}$).

(3) The copper coating becomes more uniform, less porous and requires less copper for the coatings to become continuous, when coatings are done under reduced pressure compared to the case when coatings are done under atmospheric pressure.

(4) Coir fibres become flame retardant when they are coated with copper more than 5 μm thick.

(5) Composites containing copper-coated coir fibres have shown considerable increase in tensile and flexural strengths over their counterparts containing the same amounts of uncoated coir fibres.

(6) With the incorporation of copper-coated coir fibres in polyester matrix, it is possible to make conducting composites having a resistivity below 100 Ωcm, which may be suitable for EMI applications.

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