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Ultrasound-assisted electroless deposition of copper onto and into microporous membranes for electromagnetic shielding

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Ultrasonication reduces the plating time for electroless deposition of copper onto microporous membranes. Ultrasonication also helps eliminate the need for pretreatment or chemical etching of the membranes. Electroless plated materials have high enough bulk conductivities (up to 0.82 S cm^{-1}) to give electromagnetic shielding efficiencies of 55 ± 5 dB in the frequency range 10 kHz to 1 GHz.

(Keywords: ultrasound; membranes; electromagnetic shielding)

Introduction

The versatility of ultrasound in materials science is now accepted[1-3]. The effect of ultrasound on polymer synthesis[4], electroplating[1-3], electrosynthesis[5] and electropolymerization[6] have been exploited to good effect. However, no report exists on the effects of ultrasound on the electroless plating of metals and inherently conducting polymers (ICPs). Electroless plating of copper, nickel, silver and cobalt is used extensively in electronics and decorative applications[7-10]. Electroless deposition of ICPs into the pores of microporous membranes by a 'suction' method has been described[11]. This method involves a monomer passing through a membrane by suction followed by oxidative polymerization of the occluded monomer. This impregnation has now been established with enhanced efficiency by ultrasonication. Microporous membranes are used as 'separators' in batteries, in sensors and in other applications such as water purification and breathable garments. These are generally hydrophobic and need surfactants to improve their wetting characteristics. Electroless plating of metals is usually carried out from aqueous solution, therefore surfactants are normally added. This has an undesirable effect on the conductivity of the deposits. Further, most plastics need some form of pretreatment or etching to ensure good adhesion with the metal deposit. The pretreatment or etching not only affects the polymer base but also has a deleterious effect on the pore and surface structure. This paper describes the use of ultrasound, which eliminates the need for pretreatment or etching in the electroless plating of copper onto and into microporous membranes of polyethylene (PE), polyurethane (PU) and non-woven poly(ethylene terephthalate) (PET). The ultrasonication also results in as much as a three-fold reduction in electroless plating time.

Experimental

Microporous PE (40 μm, from Scimat Ltd, Swindon, UK), carbon-loaded microporous polyester-modified PU (2.3 mm, from Porvair plc, Norwich, UK) and non-woven PET (115 μm, from Geca BV, The Netherlands) were employed in the study.

In a typical experiment, the microporous material was cut into a circular disc of diameter 24 cm. This was placed on a Buchner funnel and a $PdCl_2$ solution (0.01% in 1 M HCl) was sucked through the membrane using a vacuum pump. A 15 cm × 11 cm sample was cut from the centre of the disc and immersed in a 2 l beaker containing 1.25 l of copper electroless plating solution at 40°C. The copper electroless plating solution consisted of copper(II) sulfate (0.15 M), potassium sodium tartrate (0.66 M), sodium hydroxide (2.07 M) and formaldehyde (25 ml, 38%). The beaker was placed in an ultrasonic bath (50 cm × 40 cm × 30 cm) operating at a frequency of 20 kHz at an input power density of 40 W cm^{-2}. On occasion, an ultrasonic bath operating at 20 kHz but at an input power density of 80 W cm^{-2} was also used. The ultrasonication was continued for various predetermined lengths of time. The copper-coated materials were washed thoroughly with water and dried in a vacuum oven at 80°C for 24 h. An electroless coating of nickel was then applied, using dimethylaminoborane as the reductant. The nickel electroless plating solution consisted of nickel(II) chloride (0.23 M), citric acid (0.28 M) and dimethylaminoborane (0.84 M); the pH was 7 (adjusted with NH_3(aq.)) and the temperature was 70°C.

Results and discussion

Table 1 summarizes the results obtained on electroless deposition of copper. No pretreatment or etching of the membrane was used except the necessary activation with palladium chloride. With the microporous PE, only a patchy deposit of copper was obtained even after 60 min of reaction, during which the solution was stirred mechanically. No conductivity measurement was possible because of the incoherent nature of the deposit. On ultrasonication for a period of 30 min, with 30 min of stirring, although only a patchy deposit was obtained conductivity measurement was possible. After 60 min of ultrasonication, the surface was completely covered with copper deposit (3 ± 1 μm) on both sides, giving a surface conductivity of 10^{-1} S (four-probe method) and a bulk conductivity of 3.0 S cm^{-1} (sandwich cell method). If the sample is isotropic, then a volume conductivity of 25 S cm^{-1} is expected from the four-probe surface

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Table 1 Results of electroless deposition of copper at 40 W cm^{-2} and 20 kHz

Material	Total reaction time (min)	Ultrasonication time (min)	Conductivity	
			Surface (S)	Bulk (S cm^{-1})
Microporous PE	60	0	patchy deposit	
	60	30	patchy deposit	
			10^{-3}	–
	60	60	10^{-1}	3.0[a]
Carbon-loaded non-woven PET	90	0	10^{-1}[b]	4×10^{-2}[b]
	30	10	2×10^{-1}	8.0
	30	30	1.1	9.0[a]
Carbon-loaded polyester-modified PU (2300 μm)	60	0	patchy and particulate deposit	
			1×10^{-6}	5×10^{-4}[c]
	60	15	some deposit, but not uniform	
			1×10^{-4}	
	60	30	good uniform deposit	
			2.0	0.75[d]
	60	40	2.1	0.82
	60	60	deposit started to peel off	

[a] Thickness of copper deposit 3 ± 1 μm per side
[b] Starting material had a surface conductivity of 1×10^{-3} S and bulk conductivity of 2×10^{-2} S cm^{-1}
[c] Starting material had a surface conductivity of 1×10^{-6} S and bulk conductivity of 5×10^{-4} S cm^{-1}
[d] Copper content 9 ± 2% (m/m), thickness of copper deposit 6 ± 1 μm per side

conductivity measurements. Clearly, the material is anisotropic, which was expected in view of the nature of the pore structure. It is clear that copper has not only been plated onto the surface but has also impregnated the microporous membrane. An experiment carried out with microporous PE membrane 100 μm thick did not result in full impregnation of the membrane. Although this can be attributed to the thickness effect, it was possible to impregnate a PU membrane 2.30 mm thick, as described later. It was also noted that copper deposit produced on a microporous matrix in this manner was so reactive to atmospheric oxygen that it had to be transferred to a vacuum oven within 15 min of production, or else a further coating of nickel was necessary to prevent oxidation. The high reactivity may be attributed to the nature of the deposit, quite apart from the freshness of copper produced in this manner. The copper deposits on non-woven materials were stable for at least 9 months.

The carbon-loaded non-woven PET was readily coated with copper even without the assistance of ultrasound. However, the use of ultrasonication shortened the plating time (i.e. increased the rate of deposition), improved conductivity of the deposit 10-fold and improved impregation 225-fold (in the bulk conductivity).

The carbon-loaded microporous PU (2.3 mm thick) had an initial surface conductivity of 1×10^{-6} S and bulk conductivity of 5×10^{-4} S cm^{-1}. Normal plating conditions produced patchy, particulate and non-adherent coatings. Ultrasonication for 15 min produced some deposit, but it was still non-adherent. After 30 min of ultrasonication, good uniform deposits were obtained with surface conductivities as high as 2.0 S and bulk conductivity of 0.75 S cm^{-1}. Further ultrasonication for up to 40 min improved the coating and conductivity. Continued ultrasonication (60 min) resulted in pitting of the coating, which started to peel off. The electroless plating of copper on PU has now been repeated over 100 times with good reproducibility of the conductivity results. Again, copper impregnated the membrane.

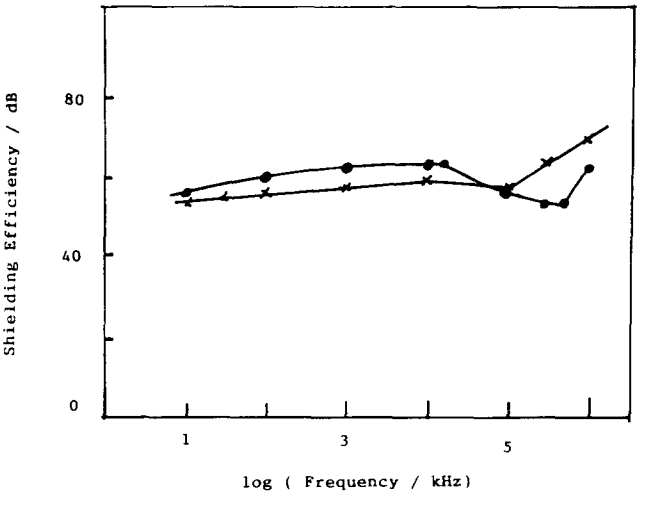

Figure 1 Shielding efficiency *versus* frequency for 80% (m/m) Ag/silicone (●) and nickel/copper-plated polyurethane (×)

Optical microscopy revealed the existence of isolated copper crystallites (1–2 μm) within the matrix of the membrane. It appears that a small number of isolated crystallites are sufficient to produce good transverse (bulk) conductivity. The copper deposited on PU matrix was found to be extremely sensitive to air (forming black copper oxide), and a layer of nickel (5 ± 1 μm) was deposited on it to protect it from aerial oxidation. The Ni/Cu/PU so obtained can be used as a conducting gasket against electromagnetic interference because of its compliant nature.

Figure 1 compares the electromagnetic shielding efficiency of Ni/Cu/PU and 80% (m/m) silver-loaded silicone measured according to ASTM D 4395/89 from 10 kHz to 1 GHz at an input power of 20 mW. It is obvious from *Figure 1* that the shielding efficiency of Ni/Cu/PU (total metal content $16 \pm 2\%$ (m/m) is comparable to that of the silver-loaded system. This not only gives about a seven-fold reduction in weight but also offers a low-cost alternative.

In conclusion, it has been shown that ultrasonication provides an enhanced rate of electroless deposition of copper, and improved adhesion of the metal to the surface of the membrane. Ultrasonication is thus useful in the production of highly conducting three-dimensional matrices at a low loading level of the conductive filler. Impregnated conductive materials are useful in electromagnetic interference shielding. It would be interesting to see the effect of ultrasonication on the electroless plating of Ni, Ag, Co, Au, etc. The effect of ultrasonication on the direct electropolymerization of ICPs into microporous membranes will be described elsewhere.

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