Electroless Copper Plating on PVC Composites As Affected by Organic Acids

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Electroless copper plating on polyvinyl chloride (PVC) is influenced by organic acid treatment of a calcium carbonate filler. Acids used include stearic, methacrylic and poly-methacrylic. They are added to increase the compatibility of calcium carbonate ($CaCO_3$) with PVC. The mixtures of PVC with treated $CaC0_3$ are called PVC composites. This paper describes the pre-treatment cycles and the electroless copper plating process on PVC composites. Percent coverage of the copper deposit, the coating thickness and morphology were also investigated.

Plating on plastics has found wide application in many branches of industry. Electroless copper is preferred for its superior electrical conductivity, uniform coverage and tendency to be stress- free.[1]

PVC cannot be roughed by acid treatment alone. The adhesion between smooth PVC and metal is poor, consequently PVC has so far failed to play an important role in the surface finishing industry. A number of efforts to metallize PVC have been reported.[2,3] This problem was solved by mixing PVC with *a* $CaC0_3$ filler treated with organic acids to increase the compatibility of $CaC0_3$ with PVC. Mixtures of PVC with treated $CaCO_3$ were named PVC composites. The treated filler was then extracted by etching from the surface of PVC composites, producing cavities which enable mechanical bonding between metal and PVC. The compatibility of $CaCO_3$ with PVC is very important for obtaining a single homogeneous phase because, during the processing conditions of PVC sheet preparation (high temperature and pressure), it yields areas rich in $CaCO_3$ and other areas that are poor. To increase the compatibility of $CaCO_3$ with PVC, the surface of $CaCO_3$ must be treated with some organic acid (e.g., stearic, methacrylic and polYmethacrylic). The effect of these organic acids upon the properties of electroless copper deposits on PVC composites is the scope of this study. The properties studied comprised coverage, thickness and morphology.

Table 1
Composition of Sensitization, Activation and Electroless Copper Solutions

Operation	Chemicals	Concentration	Temp. “C	Time min.
Sensitization	$SnCl_2$	2 g/L		
	HCl	40 mL/L	30	5
Activation	$PdCl_2$	1 g/L		
	HCl	5 mL/L	30	5
Electroless copper	$CuSO_4{\cdot}5H_2O$	13 g/L		
	$KNaC_4H_4O_6{\cdot}4H_2O$	66 g/L		
	HCHO (37% with 12.5% methanol)	38 mL/L		
	NaOH	20 g/L	30	6(

Experimental Procedure

The sequence of steps for electroless copper plating on PVC is outlined in Appendix 1.

Treatment of $CaC0_3$ Surfaces

Six samples were investigated; some based on different conditions of $CaCO_3$ treatments:

Sample 1: $CaC0_3$ without acid treatment.
Sample 2: $CaCO_3$ treated with stearic acid (hand-blended with PVC).
Sample 3: $CaC0_3$ treated with polymethacrylic acid.
Sample 4: $CaCO_3$ treated with methacrylic acid.
Sample 5: $CaCO_3$ treated with stearic acid.
Sample 6: PVC only.

The treatment of $CaC0_3$ surfaces with acids was carried out as follows:

1 g $CaC0_3$ (5 µm avg. particle size) was mixed with 10 mL Of treating acid solution, using the adsorption process (i.e., adsorption of stearic and methacrylic from cyclohexane, and adsorption of polymethacrylic from ethanol to get well-defined monolayer surface coverage of the acid molecules on $CaCO_3$ surfaces.

Preparation of PVC Samples (PVC Composites)

Preparation of PVC samples for electroless copper plating (except Sample 2, in which $CaCO_3$ was blended with PVC by hand) was carried out by mixing (by weight) 100 parts of PVC powder with 30 parts of treated or untreated $CaCO_3$. This mixture was blended in a rotatable homogenizer for seven min. The blends were molded in a 110 x 50 mm steel mold, using 1100 g at 170 °C for four min, then allowed to cool, then divided into samples of 35 x 15 mm. These samples were treated with a mixture of dimethyl formamide and cyclohexanone at 60 °C for five min to remove PVC molecules from the surface to help adhesion of $CaCO_3$ particles.

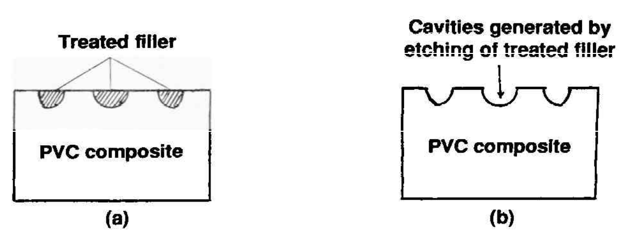


Fig. 1—Schematic diagram of the substrate surface: (a) before treatment; (b) after treatment.

Plating Sequence of Test Samples

The test samples were degreased in an alkaline cleaner containing 15 g/L NaOH, 25 g/L $CaCO_3$, and 20 g/L Na_3PO_4 at 70 “C for 10 min. Then the samples were etched in a mixed acid solution containing 15 wt percent CrO_3 and 35 wt percent H_2SO_4 at 70 “C for five rein, to remove the treated $CaCO_3$ filler from the surface of the PVC composite and to obtain a rough surface (Fig. 1). The etched samples were neutralized with five percent NaOH at room temperature for 3 rein, then subjected to sensitization, activation and electroless copper plating, as shown in Table 1. The samples were rinsed with distilled water after each step.

Scanning electron microscopy (SEM) was used to determine the morphology as well as the degree of coverage. The thickness of the plated copper was measured using an optical microscope. The properties of PVC and the organic acids used in treating the $CaCO_3$ filler are given in Appendix 2.

Results and Discussion

The effect of properties of PVC composites upon electroless copper plating are tabulated in Table 2, while Appendix 2 shows some properties of PVC and the acids used in treatment.

Percent Coverage

The variation of percent coverage of the different samples is given in Table 2. Figure 2 illustrates an unplated sample, showing irregular, small cavities on the surface, which were not sufficient to make good mechanical bonding between the substrate and the metallic deposit. The number and size distribution of the cavities affect the adhesion of the copper deposit, causing, in this case, zero coverage after plating. The irregularity of the cavities was attributed to the maximum sediment volume of $CaC0_3$ in organic media (1.7 cm^3/g), where increasing the sediment volume decreases the homogeneity. The percent coverage of Sample 2 was 95. This can be explained by the reducing action of stearic acid, in which released hydrogen atoms increased reduction of the metal ions in the solution to metal atoms for deposition.

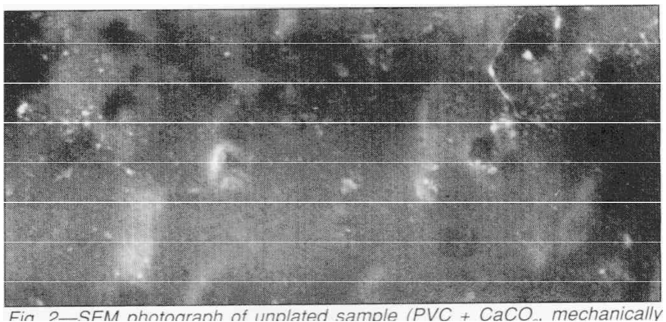


Fig. 2—SEM photograph of unplated sample (PVC + $CaCO_3$, mechanically blended. 1000X.

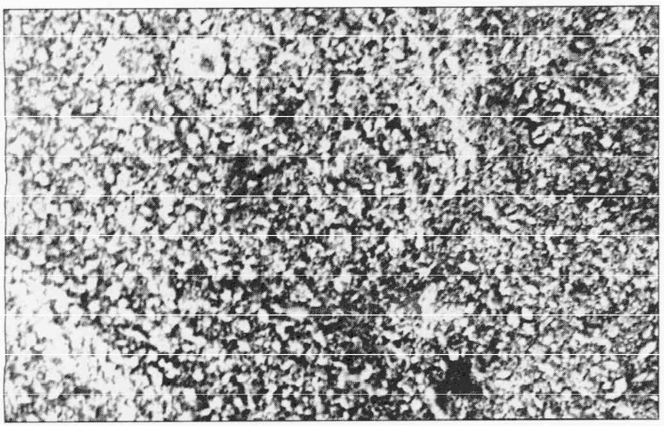


Fig. 3—SEM photograph of electroless copper deposit on PVC composite ($CaCO_3$ treated with stearic acid and hand-blended) 2000X.

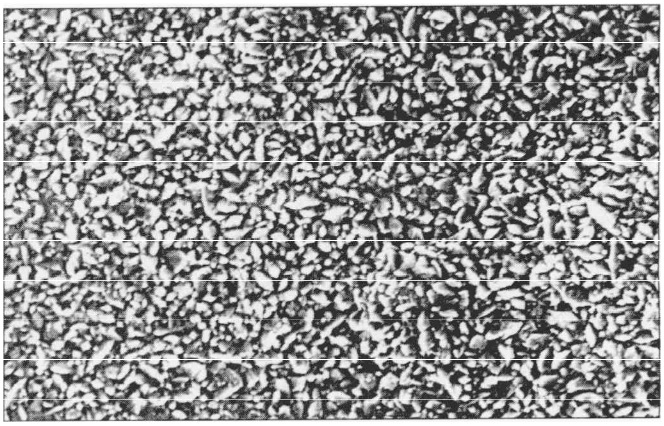


Fig. 4—SEM photograph of electroless copper deposit on PVC composite ($CaCO_3$ treated with methacrylic acid, mechanically blended). 2000X.

Table 2
Effect of PVC Composites on Electroless Copper Plating

Sample No.	PVC composites	Conductivity before plating ohm-cm	sediment volume cm^3/g	Coverage percent	Thickness µm
1	PVC + $CaCO_3$ (mechanically blended)	19.2×10^{11}	1.7	**0**	**0**
2	PVC + $CaCO_3$ **treated with stearic acid (hand-blended)**	410×10^{11}	0.7	95	3
3	PVC + $CaCO_3$ treated with polymethacrylic acid (mechanically blended)	41×10^{11}	1	0	0
4	PVC + $CaCO_3$ treated with methacrylic acid (mechanically blended)	317×10^{11}	0.5	80	4
5	PVC + $CaCO_3$ treated with stearic acid (mechanically blended)	633×10^{11}	0.4	100	4
6	Pure PVC	2.4×10^{11}	.	—	—

Appendix 1
Process of Electroless Copper Plating on PVC* Treatment of CaC0$_3$ with PVC

Mixing of PVC with organic acids treated $CaCO_3$ (PVC composites)

Molding

Decreasing

Etching

Neutralization

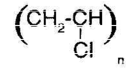
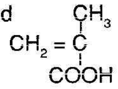
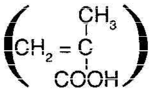
Sensitization

Activation

Electroless copper plating

*A distilled water rinse was used after each step

Appendix 2
PVC and Properties of Treating Acids

Material	Chemical structures	Properties	Molecular weight	Number of repeating units (n)
PVC	 $(CH_2\text{-}CH(Cl))_n$ $(C_2H_3Cl)_n$	Oxidizing agent	62 x 1.9x10^6	1.9 x 10^6
Treating acids:				
1. Stearic acid	$CH_3(CH_2)_{16}\cdot COOH$ $C_{18}H_{36}O_2$	Reducing agent	284	1
2 Methacrylic acid	 $CH_2=C(CH_3)COOH$ $C_4H_6O_2$	Reducing agent	86	1
3. Poly-methacrylic acid	 $(CH_2=C(CH_3)COOH)_n$ $(C_4H_6O_2)_n$	Reducing agent	86 x 12.7x10^4	12.7 x 10^4

Despite the action of polymethacrylic acid in Sample 3 as a reducing agent, no coverage was obtained. This can be a result of its high molecular weight (86 x 12.7 x 104). Its number of repeating units (n = 12.7 x 10^4) is very great, in which oxygen atoms increased more than necessary during the reaction and inhibited the copper deposition.

The percent coverage of Sample 4 was 80. It had less coverage than Sample 2 because of fewer available hydrogen atoms (six) for reduction of metal ions compared to 36 for stearic acid.

Maximum coverage of 100 percent was obtained with Sample 5. This could be because of the reducing effect of the stearic acid and the high homogeneity of the treated filler, as a result of mechanical mixing with PVC, which leads to low sediment volume.

The percent coverage of Sample 6 was zero. This result indicated that PVC cannot be roughened by acid etching alone and that PVC in this circumstance acts as an oxidizing agent—the oxidized chlorine atoms released during the reaction inhibit copper deposition.

Thickness

Table 2 shows the variation of deposit thickness with different PVC composites and their conductivity values before plating. The thickness varied from zero to four µm, corresponding to the reduction or oxidizing effect of each acid added (Appendix 2) to modify the $CaCO_3$ surface, and to the conductivity of the sample surface. This suggests that PVC mixed with $CaCO_3$ and treated with stearic and methacrylic acids provided anchoring sites for nucleation, growth and, as a result, good adhesion strength. This phenomenon can be explained by the high conductivity values of $CaCO_3$ surfaces treated with the aforementioned acids, leading to an easier autocatalytic reaction and, therefore, good coverage and a good rate of deposition.

Deposit Morphology

Figure 3 (Sample 2) shows coarse, rough, heterogeneous copper grains with irregular shapes as a result of hand-mixing of treated $CaCO_3$ with PVC, which gives a relatively high sediment volume (0.7 cm^3/g), as in Table 2. This led to less homogeneity and irregular distribution of the treated $CaCO_3$ in the tested substrate.

In Fig. 4 (Sample 4), the surface of the deposit is homogeneous, with great roughness. The copper grains are overlapped with sticky shapes as a result of less sediment volume (Table 2) (i.e., more homogeneous because of less reduction by methacrylic acid; therefore the copper grains are coarser than those of Sample 2).

The SEM photograph of Fig. 5 (Sample 5) reveals a deposit of greater homogeneity, dense and smooth. The copper grains are round, with regular shapes. This can be attributed to mechanical mixing of the treated $CaCO_3$ with PVC and minimum sediment volume (0.4 g/cm^3), per Table 2.

This observation is consistent with the results reported in Refs. 4 and 5 for the change in the sediment volume of $CaCO_3$ in the organic media. The decrease of sediment volume here means an increase in homogeneity of the treated CaC0$_3$ in the media and, consequently, increased homogeneity of copper grains in the deposit.

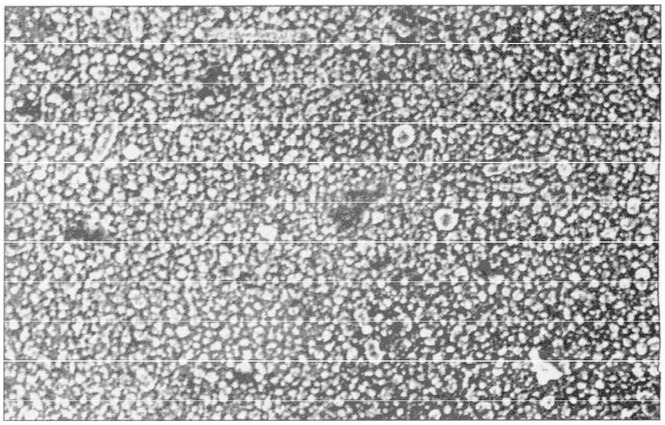


Fig. 5—SEM photograph of electroless copper deposit on PVC composite ($CaCO_3$ treated with stearic acid, mechanically blended). 1000X.

Conclusions

To increase the compatibility of $CaCO_3$ with PVC, the surface of the $CaCO_3$ must be treated with some organic acid (e.g., stearic, methacrylic and polymethacrylic acids). Adhesion of a metal deposit on PVC composites was enabled by creating cavities, which were produced by proper etching and by extraction of organic-acids-treated $CaCO_3$ filler.

Percent coverage, thickness and deposit morphology of copper were influenced by the action of the treating acids on the $CaCO_3$ surfaces, by the molecular weight of the acids, especially the number of repeated monomers, and by the conductivity values of the test samples before plating.

The optimum copper deposit of 100 percent coverage, four µm thick, with greater homogeneity and regular fine microstructure, was achieved with Sample 5.

References

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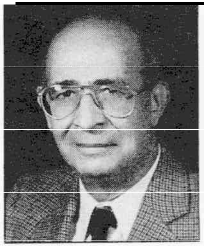

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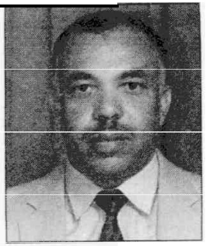

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