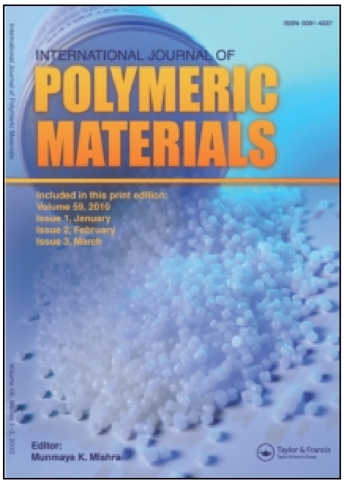

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

PLASMA FORMATION OF POLYMER-METAL COMPOSITES

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To cite this Article Palacios, J. C. , Olayo, M. G. , Cruz, G. J. , Morales, J. and Olayo, R.(2002) 'PLASMA FORMATION OF POLYMER-METAL COMPOSITES', International Journal of Polymeric Materials, 51: 6, 529 — 536
To link to this Article: DOI: 10.1080/00914030209696298
URL: http://dx.doi.org/10.1080/00914030209696298

International Journal of Polymeric Materials, 51:529–536, 2002

0091-4037/02 $12.00 + .00
DOI: 10.1080/00914030290046101

PLASMA FORMATION OF POLYMER-METAL COMPOSITES

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Looking for improving the electric conductivity of polymers, films consisting of polyaniline with particles and layers of silver and copper have been prepared by glow discharge plasma. The material obtained in this way had metallic particles dispersed within the polymer structure and thin metallic layers on the surface. The ionic and electronic rain in the plasma produces good inter-particle contacts between the metal and the polymer that increases the electric conductivity of the material. The polymer-metal composites were characterized by transmission electronic microscopy, energy-dispersive X-ray microanalysis, X-ray diffraction and thermal gravimetric analysis. The electric conductivity was measured between 20–60 C.

Keywords: plasma, polymerization, composites, polyaniline, silver, copper

1. INTRODUCTION

By means of a plasma, it is possible to carry out the synthesis and the processing of materials with innovating results. An example of this possibility is the formation of very thin films of polymers [1–5] and metallic layers on different surfaces including the surfaces of both these materials. Although in both cases the materials are very different, the techniques are similar. Thus, the plasma techniques can be used to form complex materials

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Received 27 December 2000; in final form 31 December 2000.

The authors want to thank to Leticia Carapia for her help in the SEM analysis, to Thelma Falcon for the X-ray diffraction analysis and to Juan Bonifacio for the thermal gravimetric analysis. We also thank to CONACyT for the partial support of this work.

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with the characteristic properties of every component, giving the possibility to produce combinations of materials so distinct as polymer and metals.

A simple conducting metal-polymer composite can consist of metal powder dispersed throughout a polymer matrix. The drawback of this system is that the metallic particles remain isolated from each other. The conductivity is not improved for the entire composite, unless the metal particles are present in very high concentration [6, 7]. High metal concentrations, however, tend to destroy some of the desirable mechanical properties of polymers.

Another way to improve the electric conductivity of this kind of composites, using a small quantity of the conductive component, is controlling the quality of the inter-particle contacts; for example constructing particles with polymer and metals bonded together without having both components as separated particles. This task can be done, in the case of polymer and metal composites, by laser or plasma ablation. Metals can be easily deposited on many surfaces by these techniques; however, polymers cannot be deposited so easily because the high temperatures reached in the process may rapidly degrade the polymer. On other hand, the process by plasma works differently because, polymers do not evaporate from one surface to be condensed on another, most polymers need to be chemically constructed, step by step from the monomers, on the surface of interest.

Looking for improving the electric conductivity of polymers, polymer-metal composites, have been formed and reported in many works summarized in [7]. Thin polyaniline films with silver and copper particles dispersed in their structure were synthesized by plasma with very thin metallic layers on the polymer surface. The interaction of the surface with the plasma particles produces a good inter-particle contact between layers. Thus, the volumetric electric conductivity of the entire composite can be improved.

2. EXPERIMENTAL

The polymer-metal composites were synthesized by plasma in two steps, simultaneous polymerization with metal ablation and metallic layer deposition. The films of polyaniline were synthesized by glow discharges with a resistive coupling technique [1, 2]. The reactor was constructed with a glass tube of 9 cm diameter and 20 cm long with two stainless steel flanges at the sides, see Figure 1. The aniline was introduced to the reactor in vapor phase with a polymerization time of 165 min.

For polyaniline films with silver (PAn/Ag), two silver-copper alloy electrodes, of 3.5 cm diameter, were used. The composition of these electrodes was 89.9% Ag and 10.1% Cu. Inside the reactor, the electrodes were placed with a separation of 0.5 cm. The plasma was generated at a pressure of 4×10^{-1} mBar and 1200 V dc. The films were formed in the region

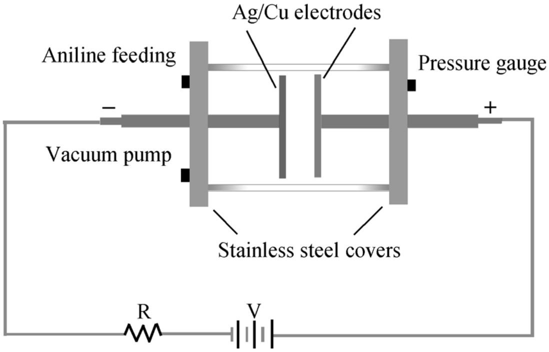

FIGURE 1 Set-up of the reactor used in the plasma polymerization and in the formation of metallic layers.

between the negative flange and the anode. The length of this region was around 7 cm. PAn/Ag films were obtained from 7 to 16 μm thickness.

Polyaniline with copper films (PAn/Cu) were synthesized with the same experimental arrangement, but instead the silver electrodes, two copper electrodes of 6.5 cm diameter were used. The plasma was generated under the same conditions than those of PAn/Ag. The thickness of PAn/Cu films was between 6 and 13 μm.

The metallic layers were formed at a pressure of 1.3×10^{-1} mBar and 1400 V dc in both cases (PAn/Ag, PAn/Cu). Without aniline feeding, the same reactor and the same experimental arrangement than in the PAn films process were used. The metal deposition time was 180 min in each case.

For the characterization of the composed material, scanning electron microscopy, energy-dispersive X-ray microanalysis, X-ray diffraction and thermal gravimetric analysis were used. The electric volumetric conductivity of the composite, from 20 to 60 C, was measured in a capacitive arrangement.

3. RESULTS AND DISCUSSION

3.1. Morphology and Elemental Analysis

The morphology was studied with a Philips XL30 scanning electron microscope coupled with an EDAX EDS probe for elemental analysis. The micrograph of PAn/Cu film showed in Figure 2 presents the typical rough morphology of plasma-synthesized polymers. However, PAn/Ag films have smoother and less rough regions than PAn films without metallic layers. This effect can be associated to the metal presence in the material.

During the polymerization, the continuous impact of the ions and electrons on the electrodes remove metal particles that are trapped in the structure of the polymers. Figure 3 present a micrograph of PAn/Ag using

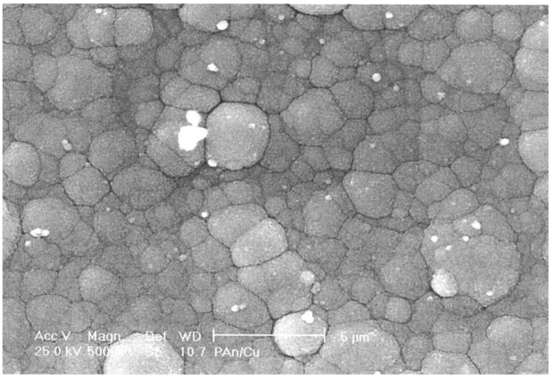

FIGURE 2 PAn/Cu morphology.

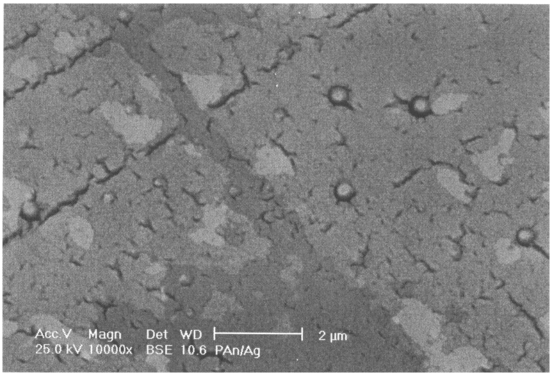

FIGURE 3 PAn/Ag back scattering micrograph. Metal dispersed particles are observed, 10000x.

the back scattering technique. Spherical metal particles with diameters from a few nanometers to some microns appeared in the micrographs. The metal particles appear isolated from each other. Amorphous metallic-polymer "islands" irregularly distributed, with bigger dimensions can be also observed. The metallic layers deposited on the polymer surface were very thin. They have a good adhesion with the polymer layers and do not separate neither by heating nor by means of organic solvents. High metal quantity was deposited near to the electrodes.

Thermal decomposition of the composite was carried out with the purpose of estimating the rate of the metal deposit under the previously described conditions. Table 1 shows the superficial elemental analysis of films with high metal content.

TABLE 1 Superficial elemental analysis of PAn/Ag and PAn/Cu

	Mass (%)	
Element	*PAn/Ag*	*PAn/Cu*
C	42.38	13.38
O	1.85	8.57
N	11.87	5.98
Ag	39.89	–
Cu	2.97	70.86
Fe	1.04	1.21
Total	100%	100%

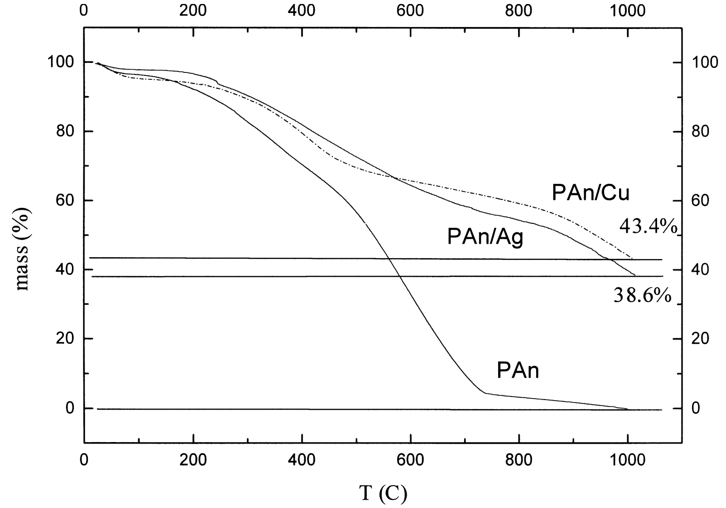

FIGURE 4 Thermal decomposition of PAn, PAn/Ag, and PAn/Cu films.

Figure 4 presents the thermal decomposition of PAn, PAn/Ag and PAn/Cu. The PAn decomposition curve was completed near 1000 C. The curves of PAn/Cu and PAn/Ag do not show the same behavior than that of PAn, and around 1050 C had an uncompleted decomposition. This difference may be associated to the remaining metal quantity in the sample. Thus, the maximum mass proportion of the Ag-Cu alloy in the entire sample was approximately 38.6% and the proportion of Cu was around 43.4%.

The PAn deposition rate was calculated as 63.6 nm/min. The thickness of the metallic layers was around 785 nm for Ag and 885 nm for Cu. The average deposition rate for Ag and Cu was approximately 4.4 nm/min and 4.9 nm/min respectively, see Table 2.

TABLE 2 Estimation total content of metal, thickness, and deposition rate of PAn/Ag and PAn/Cu films

Composite	*Maximum mass of metal* (%)	*Estimated thickness of metal layer* (*nm*)	*Metal deposition rate* (*nm*/*min*)
PAn/Ag	38.6	785	4.4
PAn/Cu	43.4	885	4.9

3.2. Crystallinity

With the purpose to observe the crystalline extent of the resulting material, X-ray diffraction of the composites was obtained. The analysis was made with a Siemens D5000 diffractometer. Figure 5 presents the diffractograms of PAn, PAn/Ag and PAn/Cu samples. The crystallynity was calculated as reported by Kakudo [8]. The vertical lines represent the diffraction angles of Ag and Cu respectively, given an fcc arrangement. Crystallinity was observed in the composite samples, reaching 11.8% for PAn/Ag samples. The increment in the crystallinity is due to the dispersed particles and to the metallic layers deposited on the polymer surface. However, because the particles are isolated from each other, the main contribution to electric conductivity improvement can be due to the metallic deposit.

3.3. Electric Conductivity

The coated faces of metal present high electric conductivity. However, although the polymer has metallic particles inside its structure, the electric

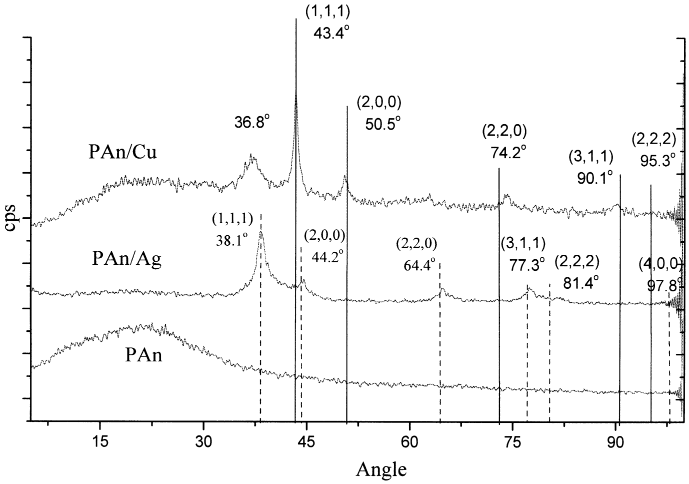

FIGURE 5 Diffractograms of PAn/Ag and PAn/Cu. The vertical lines represent the silver and copper diffraction with a face centered cubic arrangement.

conductivity of the material, as films, did not improve visibly. The conductivity was also calculated measuring the electric resistance of the material in powder form using a capacitive device. The powder showed elevated electric conductivity because in this form, the quality of the inter-particle contacts improves. The electric conductivity of this material showed a great dependence on humidity. Heating-cooling cycles were carried out to release humidity from the composites.

The electric conductivity with temperature of PAn/Ag and PAn/Cu is shown in Figure 6 assuming an Arrhenius behavior [1, 3, 9], as in Eq. (1)

$$\sigma = \sigma_0 e^{(E_g/kT)} \tag{1}$$

Little variations are observed in the conductivity up to 50 C, which remains almost constant. From Figure 6, PAn/Ag and PAn/Cu had $\sigma_0 = 0.019\,\mathrm{S/m}$, $E_g = -0.026\,\mathrm{eV}$, and $\sigma_0 = 0.015\,\mathrm{S/m}$, $E_g = -4.63 \times 10^{-3}\,\mathrm{eV}$, respectively. The negative energy of activation corresponds to a metallic behavior, more than a semiconductor behavior.

The hypothetical maximum conductivity and the activation energy in the second heating cycles are summarized in the Table 3.

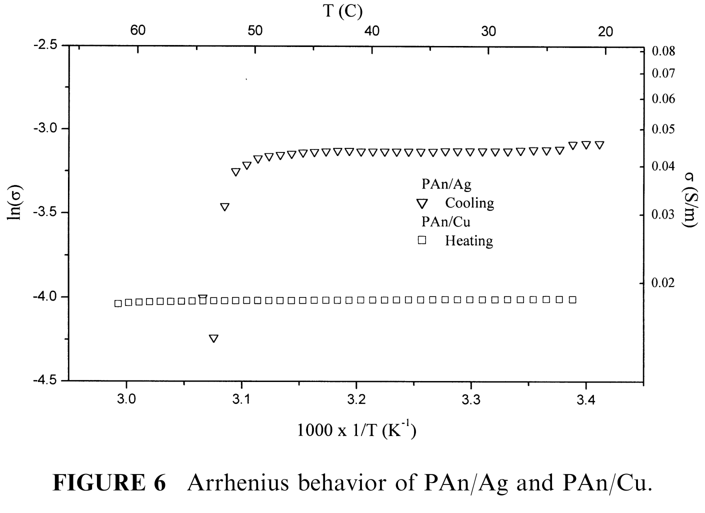

FIGURE 6 Arrhenius behavior of PAn/Ag and PAn/Cu.

TABLE 3 Energy of activation and maximum hypothetical conductivity of PAn/Ag and PAn/Cu

Composite (second heating process)	E_g *(eV)*	σ_o *(S/m)*
PAn/Ag	-0.026	0.019
PAn/Cu	-4.63×10^{-3}	0.015

4. CONCLUSIONS

PAn/Ag and PAn/Cu composites were formed by plasma. In the polymerization process, metal particles, randomly dispersed, were introduced in the polymer in formation with several shapes and sizes. Spherical particles with diameters from a few nanometers to some microns were found in the polymers. The deposition rate of both PAn/Ag and PAn/Cu was around 60 nm/min and was similar to other RF-plasma polymers. The average metallic deposition on the composites was different for the copper and the silver-copper alloy, 4.9 and 4.4 nm/min respectively. This difference may be attributed to the different geometry and to the energy necessary to remove metallic particles from the electrodes in each case.

The maximum copper and silver-copper alloy concentrations in the composites were 43.4% and 38.6% mass respectively. With this metal proportion, the composites, as powder, reached conductivities from 2×10^{-2} to 5×10^{-2} S/m. The behavior of the conductivity from 20 to around 60 C was almost constant. The volumetric conductivity in the composites was not improved by the metal inclusion because the metal content was not enough to have good inter-particle contacts. However, the thin metallic layer deposited on the composites did improve the inter-particle contacts and enhanced the charge transport.

REFERENCES

[1] Cruz, G. J., Morales, J., Castillo-Ortega, M. M. and Olayo, R. (1997). *Synthetic Metals*, **88**, 213–218.

[2] Morales, J., Olayo, M. G., Cruz, G. J., Castillo-Ortega, M. M. and Olayo, R. (2000). *Journal of Polymer Science*, *Part B*, *Polymer Physics*, **38**, 3247–3255.

[3] Cruz, G. J., Morales, J. and Olayo, R. (1999). *Thin Solid Films*, **342**, 119–126.

[4] Olayo, M. G., Morales, J., Cruz, G. J., Olayo, R., Ordóñez, E. and Barocio, S. R., *Journal of Polymer Science*, *Part B*, *Polymer Physics*, Vol. 39, Jan., 2001 (to be published).

[5] Gong, X., Dai, L., Mau, A. and Griesser, H. (1998). *Journal of Polymer Science*, **36**, 633–643.

[6] Blythe, A. R., "*Electrical properties of polymers*". Cambridge University Press, 1980, pp. 123–139.

[7] D'Agostino, R., "*Plasma deposition*, *treatment*, *and etching of polymers*". Academic Press, San Diego, 1990, pp. 269–317.

[8] Kakudo, M. and Kasai, N. (1972). "*X-ray diffraction by polymers*". Kodansha, Japan, pp. 359–362.

[9] Shi, F. (1996). *Surface and Coatings Technology*, **82**, 1–15.