

Conductivity of Layer and Matrix Polyaniline–Silver–Copper Composites by Plasma

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ABSTRACT: This work presents a study on the formation of polymer–metal composites by means of plasma, combining silver and copper alloys with semiconducting polymer films. The objective is to improve the electric conductivity of polyanilines by forming layer and matrix composites. In this way, it is possible to increase the superficial and/or volumetric conductivity of the polymers. Electronic variables as the electronic density and energy along the reactor and their influence on the chemical composition, deposition rate, and

the morphology of plasma polymer–metal composites are taken into consideration in the course of this study, as the shower of the most energetic particles in the plasma can produce multiple bonds between the metals and the polymers. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 1031–1036, 2004

Key words: plasma polymerization; conducting polymers; metal–polymer complexes

INTRODUCTION

Both polymers and metals are materials with a wide variety of applications. Each one can be combined with other metals or polymers to construct alloys and copolymers with enhanced properties when compared to those of the initial materials. However, polymers and metals cannot be easily combined in such a way that the resulting material benefits necessarily from the characteristic properties of their components.

One of several interesting properties of the combination of polymers and metals is an enhanced electric conductivity. In polymers, this and other properties have been the object of diverse studies about how their behavior is modified by the presence of different doping elements.^{1–6} When metallic elements are added to polymers, the electric conductivity of the group can result in the overlapping of the individual conductivities. Metals have conductivities in the order of 10^8 S/m, while polymers lie usually in the order of insulators: 10^{-16} S/m.

Among other techniques, polymer–metal composites can be formed by means of electric glow dis-

charges as alternated thin layers of the two materials. However, the layers would have to be chemically linked at the interface to have one properly sole material. These composites would be anisotropic with different behavior to the transport of the electric charges, high conductivity on the metallic layers, and an almost insulator conductivity on the polymer layers. Another factor that can be added to the transport of charges in the composites is to combine a different polymer in each layer, for example, alternating semiconductor and insulator polymers. In this way, there are greater possibilities to design layered polymer–metal composites with the right conductivity for each application.

Other polymer–metal composites can consist of metal clusters dispersed throughout polymer matrices. If the metals are homogeneously distributed, the conductivity of these composites can be isotropic. These materials would have high volumetric conductivity, although they would not reach those values obtained on the metallic surfaces of the layered composites with low metal content. However, if the metal content is carefully increased, the conductivity can rapidly increase.

Conductivity in metals decrease with temperature, yet, the opposite occurs in nonconducting polymers. Having the two components in one material, the changes in conductivity with temperature overlap so that the composite can be designed to behave with

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temperature as it is needed, increasing, decreasing, or keeping constant. Therefore, between certain limits, the behavior of the electric conductivity can be controlled by changing the metal content in the composite.

From the point of view of the applications, if a high volumetric conductivity is required, it will be necessary to form composites with metal dispersed in polymer matrixes; however, if only a high superficial conductivity is needed, alternated thin layers of polymers and metals would be sufficient. However, combinations of both techniques, preparing one layer with simultaneous polymerization and metallic ablation followed by layers of metals, would give a volumetric conductivity sharply increased in the entire material.

Thus, this study deals with the electric conductivity of composites made by plasma with polyaniline and silver-copper alloys. It is divided in three sections: synthesis of polyaniline doped with iodine (PAn/I), formation of metallic layers of Ag-Cu on PAn/I (PAn/I-Ag-Cu), and synthesis of polymeric matrices with metal particles dispersed in the structure by polymerization and metallic ablation (PAn-Ag-Cu) simultaneously. As the conductivity would be very low in plasma PAn without dopants; in the first case, iodine atoms are added to the polyaniline structure to increase the electric conductivity in the material; in the other cases, the metal phase can be considered to be responsible for the increase of the conductivity.

EXPERIMENTAL

The reactor employed for the synthesis is a vacuum chamber composed essentially by a glass tube with stainless steel flanges at both ends, where a pair of electrodes, connected to a direct current (DC) or radiofrequency (rf) power supply, can be inserted. The reactor contains two negative and two positive electrodes. To study the energy and density of electrons inside, the reactor was divided in three zones: behind the negative electrode (Zone 1), between the positive and negative electrodes (Zone 2), and behind the positive electrode (Zone 3). The reactor volume is around 1000 cm³ (see Fig. 1).

The plasma variables were gauged with a Langmuir single electrical probe, and the resulting calculations were conducted after the algorithm described by D. J. Ball.⁷ The plasma variables were recorded at DC power levels that varied from 15, 25, 35, and 50 W. The potentials were established between 680–1235 V with currents between 21–47 mA at 3×10^{-1} mBar.

Metallic layers were formed by atoms released from the electrodes by DC resistive glow discharges. The cathode was a 3.5-cm diameter made of a 90% silver and 10% copper alloy. The voltage for the metallic ablation was set from 900 V to 1200 V DC and pressure around $(3-4) \times 10^{-1}$ mBar with a 5 mm separation

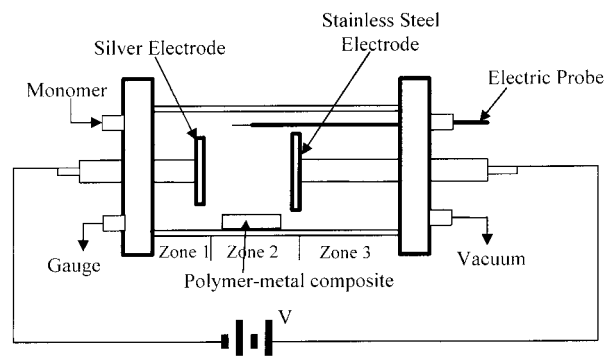


Figure 1 Diagram of the reactor used in the polymer-metal composite synthesis.

using air as a carrier gas. The ablation process took between 45 and 120 min.

For the purpose of plasma polymerization, the materials were synthesized by DC and rf resistive glow discharges in the same reactor and similar electric configuration as those used in ref. 8. Two flat stainless steel electrodes, 6.5 cm diameter, were used. The polymers were formed on the reactor walls and on the electrodes. The total synthesis time varied from 60 to 300 min.

Simultaneous polymerization of aniline and metal ablation was used to synthesize composites where clusters of metals were dispersed in polymer matrices. The polymer-metal composites were synthesized in two processes, namely, simultaneous polymerization and metallic ablation and metallic layer deposition. The final composites have metallic particles dispersed in the polymer and thin metallic layers on the surface.

All the polymers were separated from the reactor surfaces, swelling them with distilled water and acetone. The analysis of the polymers was carried out by means of scanning electron microscopy (SEM) with a Philips XL30 scanning electron microscope. The volumetric conductivity was calculated by measuring the resistance of the polymers, perpendicular to the plane of the layers, in a two-probe capacitive arrangement (see Fig. 2). The electric conductivity of PAn/Ag-Cu and PAn/I-Ag-Cu was compared to that of plasma PAn/I films at a temperature range between 30 and 100 C. The study was based on the intrinsic electronic conductivity of the material. This condition was achieved after most of the humidity and solvents were removed from the polymer.

RESULTS AND DISCUSSION

Plasma conditions

In preparing polymer-metal composites, the control of the plasma characteristics is very important, as high electron energies lead the organic molecules to destruction, and yet, low energies do not allow the ab-

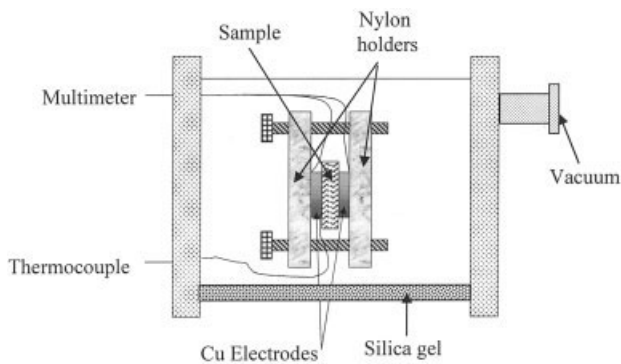


Figure 2 Cell to measure the resistance of the polymers.

lation of the metal particles to occur. In particular, the density and energy of the discharges need to be carefully controlled in order to achieve good polymeric materials.

The Langmuir probe used in this work was activated during the DC glow discharges of the metal ablation, but not during the polymerization reactions. A detailed description of the analysis of the plasma variables during the polymerization reactions in rf glow discharges can be found in refs. 9 and 10. Figures 3 and 4 correspond to the electronic density and energy, respectively, along the reactor at different power levels.

The electronic densities were established between 1×10^{15} and $5 \times 10^{15} \text{ m}^{-3}$. The maximum densities were located around the center of the reactor (Zone 2), and they decrease at both sides of the reactor, namely Zones 1 and 3. The electronic density increases in accordance with the applied power. The electronic energies varied from 3 to 9 eV. The maximum energy was located between the positive electrodes (Zone 3) for almost all the power regimes. This can be associ-

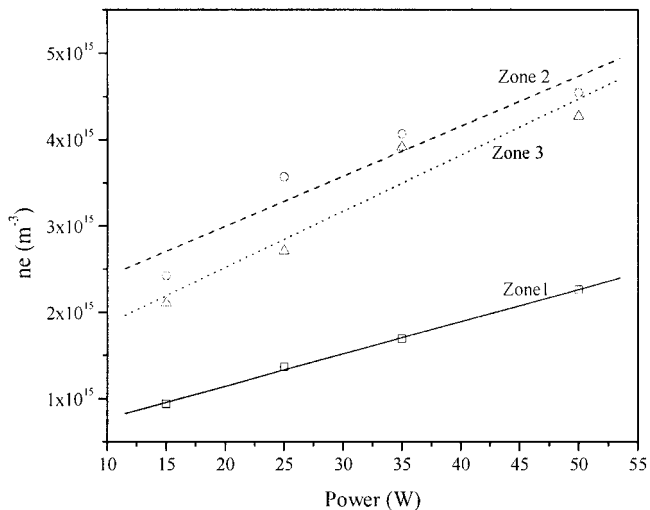


Figure 3 Electronic density in the plasma.

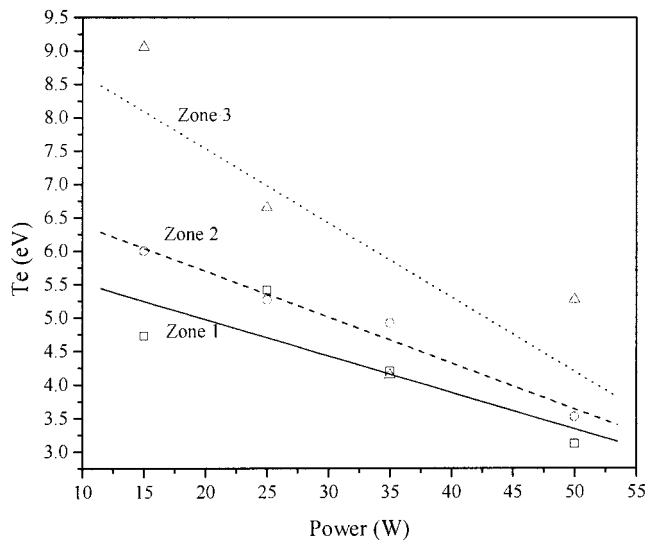


Figure 4 Electronic energy in the plasma.

ated to the electrical attraction of electrons to the positive flange. The quantitative behavior of the curves suggests pressure fluctuations.¹¹

Thickness and morphology of the layers

A layer of Ag-Cu deposited by plasma ablation is presented in Figure 5. Note the melted appearance of the Ag-Cu layer surface, as the surface of silver is comparatively soft. If a polymerization reaction occurs at the same time of the ablation, some of the metal particles can be physically trapped among the polymer chains so that two or more phases dispersed among them can be formed. Other metallic atoms present are excited in the process, and can be chemically linked to the polymers producing organometallic macromolecules.

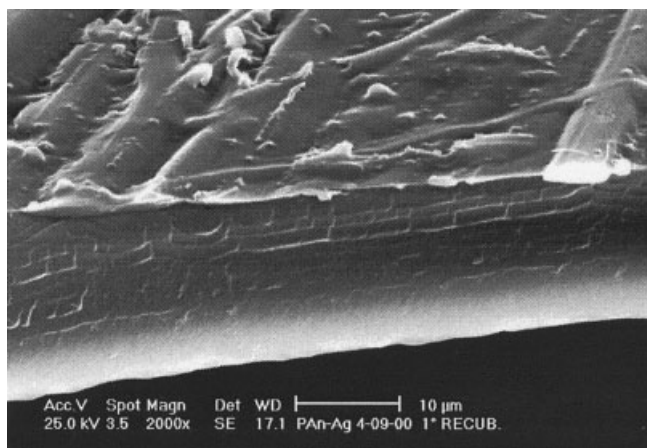


Figure 5 Layer of Ag-Cu formed by plasma ablation.

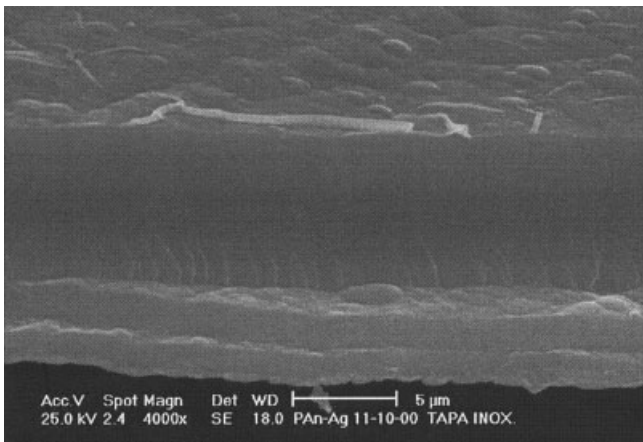


Figure 6 Layered PAN-Ag-Cu composite made by one layer of PAN and two layers of Ag-Cu.

Layered composites

Figure 6 shows a micrograph of a PAN-Ag-Cu composite made by three layers. The first one was made with PAN synthesized for 90 min, and has approximately a $7.5 \mu\text{m}$ thickness. The others were formed with Ag-Cu in two steps of 60 min DC discharges each with approximately a $1.8 \mu\text{m}$ thickness. The growing of the PAN layer was 83 nm/min and the Ag-Cu layers were 30 nm/min . The growing rate of the polymer phase was almost three times that of the metal phase. The layers grew one over the other joined in between without hollow sections in the interface.

Figure 7 shows a micrograph of a PAN-Ag-Cu composite synthesized by simultaneous polymerization and metallic ablation for 45 min. The thickness is around $0.5 \mu\text{m}$, with a growing rate of 11 nm/min . The polymers formed in rf glow discharges grew at a higher rate than those formed in dc glow discharges. In this case, the film is formed by only one solid phase composed by polymers and metals.

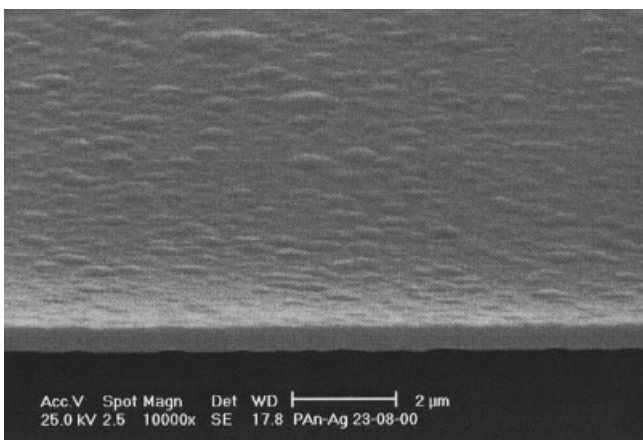


Figure 7 PAN-Ag-Cu composite film with simultaneous polymerization and ablation.

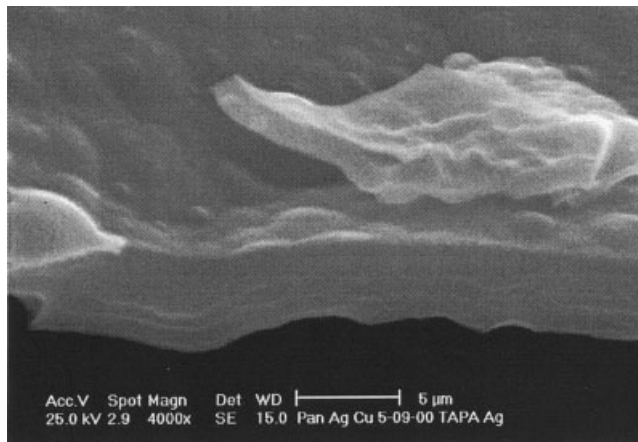


Figure 8 PAN-Ag-Cu composite made by layers: 180 min PAN, 60 min Ag-Cu, 180 min PAN, 60 min Ag-Cu.

Figure 8 shows a micrograph of a PAN-Ag-Cu composite made by alternated layers of 180 min of PAN, 60 min of Ag-Cu, 180 min of PAN, and 60 min of Ag-Cu. The thickness of the first layer, from bottom to top, is around 500 nm , having grown at approximately 8 nm/min ; the second one is about 800 nm , at a rate of 4.5 nm/min ; the third one has approximately 600 nm at 10 nm/min ; and the last layer is around $3 \mu\text{m}$, with a growing rate of 50 nm/min .

Figure 9 shows a micrograph of a composite made by one 180-min layer of simultaneous polymerization ablation of PAN-Ag-Cu and another layer with 60 min of Ag-Cu ablation. The thickness of the PAN-Ag-Cu layer is approximately $5 \mu\text{m}$, with a growing rate of 28 nm/min , while the Ag-Cu layer is approximately $1 \mu\text{m}$ with a 17 nm/min rate.

Electric conductivity

Anisotropic materials present conductivities that depend on the orientation of the measuring direction.

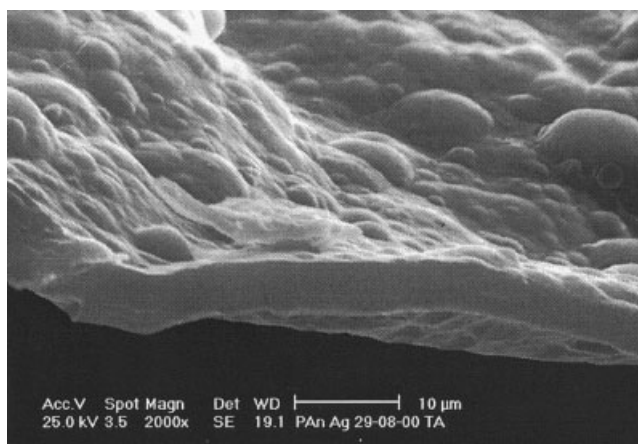


Figure 9 Composite made by one layer of 180 min of PAN-Ag-Cu simultaneous polymerization-ablation and another layer with 60 min of Ag-Cu ablation.

The conductivity perpendicular to the plane of the layers is complex, because the charges have to travel through all the strata, and the total resistance will behave as a series of individual resistances. Consequently, the total resistance is highly sensitive to the layer structure with the maximum resistance.

Composites with dispersed polymers and metals can be considered as isotropic materials, and do not have a preferential direction for the transport of charges from a macroscopic point of view. However, inside the material, the charges travel as a function of the concentration of the more conductive component, and when one of latter reaches a critical concentration, the conductivity increases rapidly. The layered composites do not exhibit such behavior.

Solvents, moisture, and other chemical reagents modify the movement of the electric charges adding ions to the system and allowing the polymeric chains to move to new positions among them, so that the conductivity increases or decreases depending on the new order of the structure. Without solvents or moisture, the conductivity can be considered as intrinsic, mainly due to the movement of electrons inside the structure of the material.

Earlier conductivity measurements of plasma-polymerized PAN/I films reported conductivity variations as a function of the atmospheric humidity with values up to 10^{-2} S/m.¹² The electric conductivity of the polymer–metal material was studied at temperatures between 30 and 100°C. The humidity effect was overcome in this study by applying one or two heating–cooling cycles to the samples before measuring its conductivity. The combined polymer–metal intrinsic conductivity was compared to that of plasma PAN/I films to observe the effects of the metal in the material.

The measurement of volumetric conductivities of PAN/I, PAN/I–Ag–Cu, and PAN/Ag–Cu, as films, were obtained from their electric resistance using a parallel device with two Cu electrodes in which the layers of the polymer–metal samples, synthesized in different energetic regions of the reactor, were placed. In this way, the volumetric conductivity measurements can be considered as the average for each synthesis.

Another way to measure the volumetric conductivity of this polymer–metal material has been grinding the polymers. The resulting powder contains particles of bounded polymer and metals mixed in the entire sample. Such group of particles can behave also as polymer matrices interpenetrated with metallic elements, and can be also considered as the average for each synthesis. The same scheme for measuring the resistance of the films was used in the powder samples.

The conductivity of PAN/I films increases with temperature displaying a typical semiconductor behavior. The conductivity fluctuated one and a half

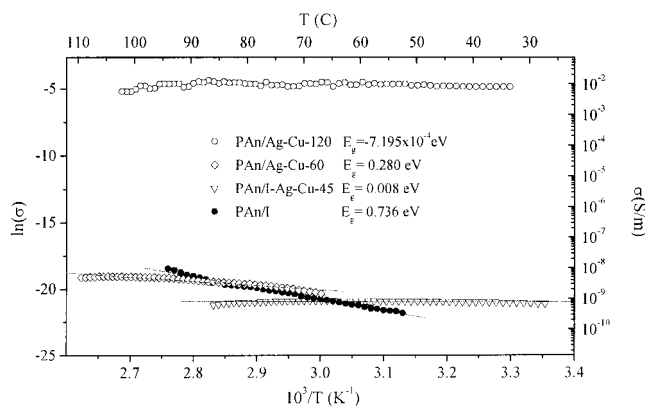


Figure 10 Arrhenius behavior of PAN/Ag–Cu, PAN/I–Ag–Cu, and PAN/I conductivity.

orders of magnitude in the measured temperature interval. This type of polymer presented a typical Arrhenius behavior expressed in eq. (1), with $E_g = 0.736$ eV (see Fig. 10).

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

Layered PAN/Ag–Cu exhibits the typical conductivity of PAN on one face and the usual metallic conductivity on the other face. The average conductivity is 7×10^{-10} S/m: the same value as that of PAN without metals. The insulating nature of the polymer dominates in the whole composite.

The electric conductivity of PAN/Ag–Cu-120, PAN/Ag–Cu-60, PAN/I–Ag–Cu-45, and that of PAN/I films, as powder and without humidity, is shown in Figure 10. The numbers immediately after the composite symbols indicate the time, in minutes, for the metallic ablation for each sample. The electric conductivity of PAN/I–Ag–Cu-45 is almost the same as that of PAN/I, around 10^{-9} S/m. However, their behavior differs because the electric conductivity changes its slope with temperature. As the slope is related to the energy of activation necessary for the charge carriers to jump from the valence to the conduction bands, higher negative slopes indicate that the electrons require more energy to jump from one band to another. On the other hand, when the slope turns smaller, negatively, the electrons take a lower energy to do the same action. When the slope is approximately zero, the activation energy is also approximately zero and both bands are very closely located. When the slope is positive, both bands are overlapped and the conductivity decreases with temperature. Thus, the energy of activation is an indicator of the energetic position of the valence and the conduction bands in the material.

The activation energy in PAN/I–Ag–Cu-45 was calculated to be 0.008 eV. This polymer–metal material does not behave as a conductor, neither as an insulator

nor as a semiconductor. The conductivity is almost constant, irrespective of temperature. The ablation time of the Ag–Cu alloy was not enough to significantly change the conductivity, but just to modify its dependence on the temperature.

PAn/Ag–Cu-60 reaches approximately the electric conductivity of PAn/I with a slope that indicates lower activation energy. The metals altered the energy of activation and the level of conductivity. PAn without iodine and metals present conductivity in the order of 10^{-10} S/m and the Ag–Cu alloy increased the conductivity in two orders of magnitude in the polymer.

PAn/Ag–Cu-120 increases the conductivity in around six orders of magnitude, reaching 10^{-2} S/m, with approximately the same tendency as PAn/Ag–Cu-45. The slope of PAn/Ag–Cu-120 was positive, that is, the calculated activation energy was negative: $E_g = -7.195 \times 10^{-4}$ eV with respect to the others. The increase of temperature in that material resulted in a slight reduction of conductivity. The behavior is more metallic than semiconductor-like, due to the long time of the metallic ablation.

CONCLUSIONS

Polymer–metal composites were synthesized by plasma leading to the increase of the electric conductivity of the material. The energy of electrons varied from 3 to 9 eV, which is slightly higher than most of the bonding energy of the organic compounds (3–6 eV). Under the described plasma conditions it is possible to elaborate very thin silver–copper alloy films by plasma, at approximately 1.27 nm/min on polyaniline films. The superficial electric conductivity of these materials can be highly enhanced in this way.

It was found the typical metallic conductivity on the coated face of the polymer with just a few layers of metal on the polymer. A big difference was not observed in the volumetric conductivity of the polymers, as films, before and after being covered with the metallic layer. Between 50 and 95°C, the conductivity of PAn/I films ranked from 3.3×10^{-10} to 9.6×10^{-9} S/m. However, the volumetric conductivity of polya-

niline as powder, with 120 min of Ag–Cu plasma ablation, increased around six orders of magnitude with respect to iodine-doped polyaniline, reaching up to 10^{-2} S/m in the range from 30 to 100°C. The conductivity of the polymer–metal films changed the semi-insulator behavior with temperature to semi-metal behavior thanks to the addition of the Ag–Cu alloy.

One important observed characteristic of the semiconductor polymer–metal composites is their activation energy, which reduces around 10^3 times in PAn/Ag–Cu composites with respect to the polymers as a function of the metallic extent in the material. It was observed that the activation energy of the composed material diminishes as the time of the metallic ablation increases, improving the volumetric electric conductivity. This effect also depends on the intrinsic electric properties of the polymers and the metals.

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