

SOLUBLE ANILINE THIN FILMS POLYMERIZED BY PULSED PLASMA

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Introduction

In continuous plasma polymerization syntheses (CPP), the available energy to carry out the different chemical reactions can reach more than 8 eV. This relatively high energy usually causes crosslinking and/or branching in the polymers, which reduces the electrical properties in the material. One of the alternatives to reduce these problems is to pulse the discharges to allow the system to recombine the free radicals and ions between the pulses. Therefore, controlling the internal pressure of the reactor and the plasma duty cycle (PDC) (time on / time on + time off), the polymerization chemistry can be partially controlled. Thus, the polymers obtained by pulsed plasma polymerization (PPP) can be more linear and hypothetically could have better electrical properties. Polymers obtained by PPP have been studied before, using aromatic monomers in many cases [1-3], all of them are insoluble.

Experimental

In Fig. 1 the reactor for PPP syntheses is shown. The experimental conditions were: pressure of $2\text{--}8 \times 10^{-2}$ Torr, power of 10 W. Thin films of polyaniline (PAn) were synthesized at different PDCs 0.5, 0.28 and 0.34, all with a total synthesis time of one hour.

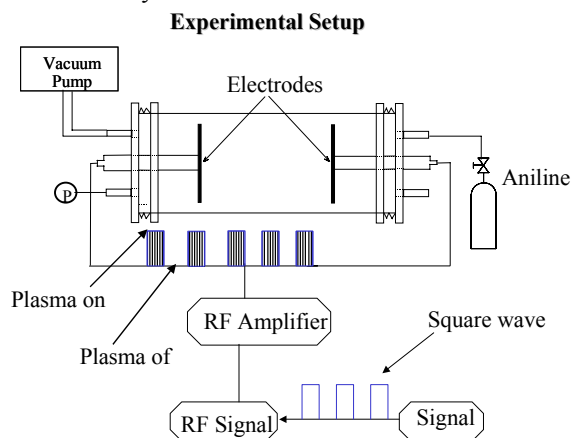


Fig. 1. Experimental setup by pulsed plasma polymerization

Two different material types were obtained. The first one, with PDC of 0.5 and time on of 1 s, was powder of polyaniline, soluble in acetone and THF. The second ones, with PDCs of 0.28 and 0.34, with time on of 10 s, were a thin films of insoluble polyaniline. The polymers

were characterized with FT-IR, TGA, SEM and elemental analysis. The electrical conductivity was calculated measuring the electrical resistance of the material in a type capacitor arrangement.

Results

FT-IR Analysis

Fig. 2 shows the FT-IR spectra of both, pulsed and continuous plasma PAn thin films. The pulsed PAn shows most of the characteristic peaks of the continuous PAn. The peak at 3556 cm^{-1} corresponds to the amine groups -NH_2 , N-H, is confirmed by the additional peak in 1641 cm^{-1} . Centered in 2933 cm^{-1} , the aliphatic vibration C-H is found. In 2863 is located the symmetrical tension vibration C-H. In 2211 is located the vibration of the nitriles bonds, $\text{N}\equiv\text{C}$. In 1641 cm^{-1} is found the imines vibration $\text{C}=\text{N}$ -aromatic and of the amines -NH_2 . In 1453 is located the methyl vibration, with the asymmetrical deformation of the C-H. In 751 , 695 and 669 cm^{-1} are the *ortho*, *meta* and *para* disubstitutions of the benzene rings, respectively.

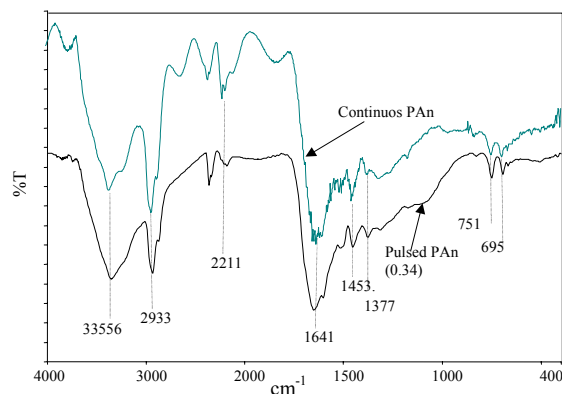


Fig. 2. Comparison between continuous and pulsed PAn.

NMR Spectrum

Fig. 3 shows the NMR spectrum of pulsed PAn at plasma duty cycle of 0.5. The spectrum indicates that the aromatic ring is suffering multiple fragmentations as the signals for CH_2 and CH_3 indicate (between 1 and 3 ppm). However, there is clear signal for the aromatic rings, around 7 ppm, this signal is wide so it shows that there is crosslinking in the polymer.

TGA Analysis

The thermal decomposition of PAn at different plasma duty cycles is shown in Fig. 4. In the temperature interval of 25 to 120 °C, the samples lose between 0 and 5 % of mass. This loss is associated with the evaporation of humidity and solvents. The sample 0.28 presents a proportional thermal decomposition without large changes in the mass lost; this is the typical behavior of linear polymers. The sample 0.5 presents two falls of mass, the first begins in approximately 120 °C and ends in 450 °C. This fall is more pronounced than in the sample 0.28, however this sample was dissolved in acetone and THF, which suggests a linear structure. After 450 °C begins the second fall of mass with similar tendency up to 800 °C. At 800 °C, the samples preserve between 20 and 30 % of their initial mass.

The PAn/I sample (5/10), doped with iodine, shows the typical fall of the iodine atoms between 120 and 450 °C, after this fall a moderated loss of mass is observed.

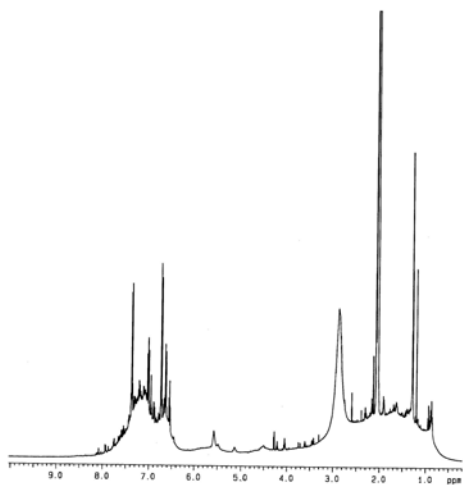


Fig. 3. RMN spectrum of pulsed PAn.

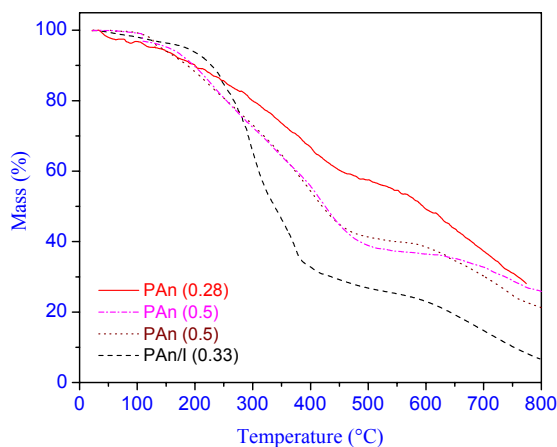


Fig. 4. Thermogravimetric Analysis of Pulsed PAn.

Electrical Conductivity

In Fig. 5, the electrical conductivity of different iodine doped polymers synthesized by plasma is shown. The pulsed polyaniline has larger electrical conductivity for relative humidity (RH) below 80%. Above this value, the conductivities are similar. The less crosslinked structure of the pulsed polyaniline chains could permit a more effective transportation of the electrical charges.

Morphological Analysis

Fig. 6 presents a micrograph of pulsed PAn formed on one of the electrodes in the reactor. It shows a three-dimensional lattice growing in a random way with voids of different sizes making a porous film. This effect can not be appreciated in the polymers synthesized by continuous plasma synthesis. These holes give to the pulsed PAn the possibility of applying it as membranes for gas separation.

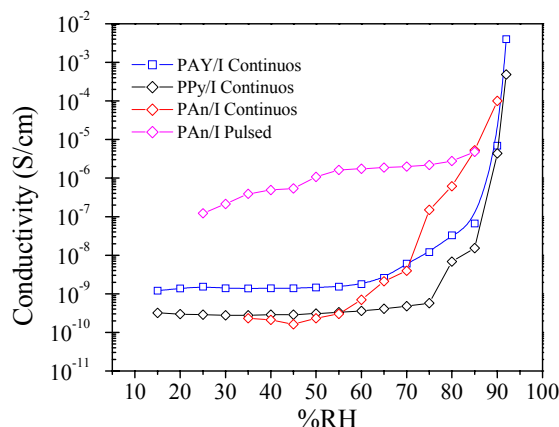


Fig. 5. Electrical Conductivity at different RH

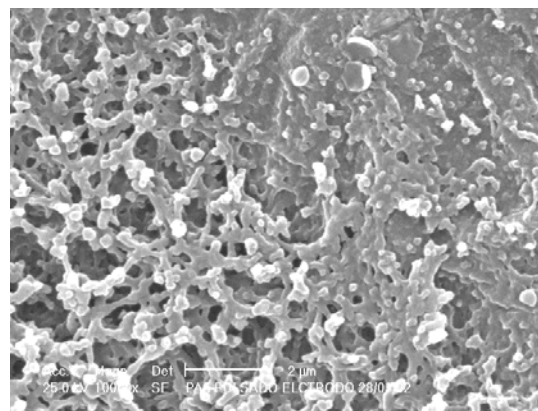


Fig. 6. Microphotograph of pulsed PAn

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