### Synthesis of new hybrid material based on copolymer and Pd-nanoparticles.

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# ABSTRACT

In this work, the synthesis of new hybrid material based on a poly (buthyl acrylate -co-vinyl formamide) copolymer using the emulsion polymerization and doped with Pd, is discussed. The copolymer structure was confirmed by FT-IR. Afterwards, Pd nanocrystals previously synthesized, resulting on a spherical shape of ~ 5 nm, as measured by High-resolution transmission electron microscopy (HR-TEM), were deposited on the structure of the organic material. The films were analyzed using AFM and Scanning electron microscopy (SEM), giving rise to a hybrid material that could be applied in areas such as nanolithography, catalysis, and sensors.

## INTRODUCTION

Organic-inorganic composites appear as a creative alternative for obtaining new materials with specific features and properties. This is related to their structure, which leads to multifunctional materials. The design of chemical structures, the interface over control organic-inorganic materials play an important role, since it will determine its potential application in different areas such as catalysis, [1] magnetic, [2] optical [3] and sensors. [4]

## EXPERIMENTAL PROCEDURE

Nanoparticles were prepared separately, using an acrylamide sol-gel technique [5]. The palladium was produced according to a previous report. [6]

The poly butyl acrylate-co-poly vinylformamide (PABut-co-PVFA) synthesis was carried out by the emulsion copolymerization technique [7]. The chemical reactants used were n-

Butyl acrylate Aldrich, 99%) monomers, vinylformamide (VFA Aldrich, 99%), which were distilled under reduced pressure with sodium lauryl ether sulfate (SLES, Aldrich, 98%) as surfactants and Octylphenol Ethoxylate (Triton X-305) (Dow 70%), potassium persulfate (KPS) the initiator, and distilled water.

The reaction was carried out in a 500-ml three-necked flask equipped with a condenser. The Table I summarizes a series of synthesized copolymers with different compositions. The surfactant and the monomers were placed in the flask under stirring in an argon atmosphere at 80°C. Then, the potassium persulfate (KPS) was added into the reactor. The reaction took place for 5 h.

| Copolymer  | Butyl    | Vinylformamide | SLES   | Triton X- | KPS    | Distilled |
|------------|----------|----------------|--------|-----------|--------|-----------|
| proportion | acrylate | (g)            | (g)    | 305 (g)   | (g)    | $H_2O(g)$ |
|            | (g)      |                |        |           |        |           |
| 70-30      | 26.03    | 6.187          | 0.5370 | 1.009     | 0.1074 | 126.12    |
| 50-50      | 14.47    | 8.025          | 0.34   | 1.40      | 0.07   | 126.30    |
| 90-10      | 30.34    | 1.8690         | 0.6445 | 1.009     | 0.1074 | 126.20    |

Table I. Synthesized copolymer composition

Copolymer films were deposited over an aluminum cylinder-shaped substrate. The film growth was performed employing the evaporation technique at room temperature (~45 °C) with the assistance of a lab stove to streamline the process of formation of films. The thickness control was carried out by simple calculation, considering the geometry and weight of the substrate. This method allows getting an average film thickness of 20 nm. On the other hand, previously, Pd particles were synthesized by the sol-gel method with the aim of getting a suspension of Pd particles and anhydrous benzyl alcohol (Aldrich 99%) with a Pd concentration of  $[2x10^{-3} \text{ M}]$ . After applying an ultrasonic treatment to the suspension around 30 minutes, this was dispersed, by an airbrush, over the copolymer to dope them. Once this process was completed, the doped films were heated to ~ 45 °C for five years to guarantee the dissolvent evaporation.

## **RESULTS AND DISCUSSION**

The synthesized copolymer structure was confirmed by FT-IR. Figure 1 shows the FT-IR spectrum of the copolymer corresponding to composition 50-50 of PABut-co-PVFA. The spectrum exhibits the stretching signal related to amine N-H at 3280 cm<sup>-1</sup>, as well as that corresponding to stretching bands of aliphatic chain of copolymer (2965-2930 cm<sup>-1</sup>), while at 1728 cm<sup>-1</sup>, the C=O group contribution, corresponding to butyl acrylate carbonyl. On the other hand, at 1671cm<sup>-1</sup>, the contribution of the nearest carbonyl to amide stretching is observed. Finally, the signals obtained for the bands, from 1552 a 765 cm<sup>-1</sup> represent the C-H of the aliphatic chain and several contributions of C-N due to the amide.



Figura 1. FT-IR Analysis for synthesized copolymers by emulsion.

The particles synthesized obtained by the sol-gel method, using acrylamide and the microwave method [6], were of a spherical shape with an average nano-size around 5 nm. The Figure 2 displays a micrograph of the material produced. The size distribution was determined from the HRTEM micrographs, while the size distribution histograms were calculated using the software named "Image J" (Image Processing and Analysis in Java). This program considers the scale at which the micrograph was taken, and then it measures individually the particle diameters. In this work, the diameters of at least 80 particles were measured, including the statistical error.



Figure 2. HR-TEM analysis for the Pd-nano-particles and particle size distribution.

The XRD technique was applied to material films showing and ensuring the presence of pure Pd phase in the films. The Figure 3 displays the XRD patterns from hybrid material films, indicating the Pd characteristic lines localized in  $2\theta$ = 40°, 46° y 68°(PDF file 88-2355).



Figure 3. XRD Analysis of the hybrid material films (Copolymer – Pd)

The results for the morphology obtained by the SEM study are illustrated by Figure 4. The Figure 4a corresponds to the undoped material looking like a smooth morphology, while Figure 4b represents the hybrid material with the 70-30 (PABut-co-PVFA +Pd) proportion that shows Pd particles forming clusters on the surface. Finally Figure 4c exhibits the hybrid material in the 50-50 proportion, containing the greatest Pd dispersion in the copolymer.



Figure 4. SEM micrographs of (a) the undoped copolymer film, (b) the PABut-co-PVFA 70-30 + Pd hybrid material, and (c) PABut-co-PVFA 50-50 + Pd.

The hybrid material synthesized may be applied as a sensor and membrane, due to its amphiphilicity property combined with its capacity of absorption and desorption of  $H_2$ , provided by the palladium. It is important to indicate that the Pd particles are on the surface and not in the material, allowing them to participate together with the copolymer (copolymer + Pd). L. Bronstein et al. [8] used the block copolymer, polybutadiene-*b*-poly (ethylene oxide)s (PB-*b*-PEO), as a template to grow Pd and Pt nanoparticles, preparing them separately, as us, and then incorporating them into the polymer, creating the hybrid. The polymer was removed by calcination, finding that the results are affected by chain lengths and functional groups present, because the metallic particles are anchored, slowing its growth. In contrast to Bronstein's work, in this work, it was observed that the particles tend to accommodate along the segmentations formed naturally by the copolymer film growth. Moreover, our films do not contain any stabilizer agent and they naturally form clusters, allowing them to be applied as sensors.

#### CONCLUSIONS

In the present study, the hybrid (PABut-co-PVFA –Pd nanoparticles) was synthesized with varying copolymer ratios. Morphology, particle size and chemical structure of the Pd nanoparticles and copolymer were estimated by FT-IR, HR-TEM, SEM, DRX techniques, respectively. The HR-TEM results show that the Pd average particle size is around 5nm. Meanwhile the SEM analysis showed that the Pd nanoparticles formed agglomerates in the grain boundaries created by the copolymer film, exhibiting the greatest Pd nanoparticles dispersion on the surface of the copolymer with the 50-50 ratio.

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