#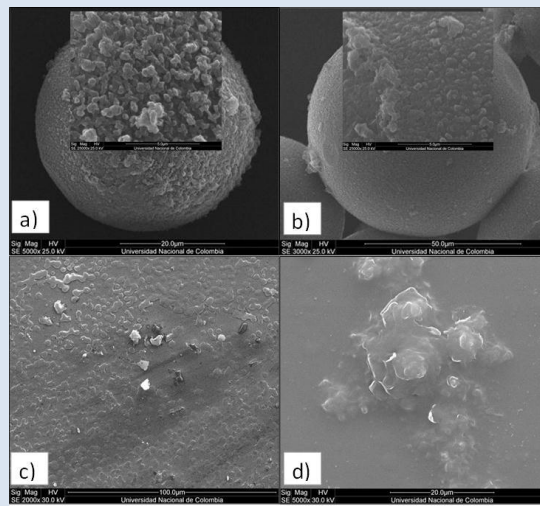 SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF SULFONATED STYRENE DIVINYLBENZENE COPOLYMERS AS STABILIZERS FOR METALLIC NANOPARTICLES

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ABSTRACT

Nanostructured metallic materials can have an industrial potential because these materials have chemical and physical properties different from those of the same materials in bulk. Therefore, sulfonated styrene-divinylbenzene copolymers were synthetized, and the porosity, solubility and degree of sulfonation were measured for the selection of the polymeric matrix. Polymer/metal nanocomposites of bismuth and tin were obtained via ultrasonic radiation in a medium of dimethylformamide using a nonionic surface agent stabilizer. Differential scanning calorimetry (DSC) was used for identification of the reaction products. Long term stability of tin and bismuth-tin metal/copolymer solutions may indicate that nanometric metal particles were obtained.

Keywords: metallic nanoparticles, polymer, nanocomposites, Tin, Bismuth

SÍNTESIS Y CARACTERIZACIÓN ESTRUCTURAL DE COPOLIMEROS SULFONADOS ESTIRENO-DIVINILBENCENO COMO ESTABILIZADORES DE NANOPARTÍCULAS METÁLICAS

RESUMEN

Materiales metálicos nanoestructurados pueden tener un potencial industrial debido a que estos materiales tienen propiedades químicas y físicas diferentes de las de los mismos materiales por bloque. Por lo tanto, copolímeros de estireno-divinilbenceno sulfonados se sintetizaron, y la porosidad, la solubilidad y el grado de sulfonación se midieron para la selección de la matriz polimérica. Nanocompuestos de polímero / metal de bismuto y estaño se obtuvieron a través de la radiación ultrasónica en un medio de dimetilformamida utilizando un estabilizador del agente tensioactivo no iónico. La calorimetría diferencial de barrido (DSC) se utilizó para la identificación de los productos de reacción. La estabilidad a largo plazo de las soluciones de estaño y bismuto y estaño metal / de copolímero puede indicar que se obtuvieron partículas metálicas nanométricas.

Palabras Claves: nanopartículas metálicas, nanocomposites, Estaño, Bismuto

1. INTRODUCTION

Metal/Polymer composite materials exhibit properties intermediate between their components. The polymeric matrix provides qualities such as processability, solubility or thermal stability, while metal provides electronic, magnetic, or catalytic properties [1], [2].

Metalic nanoparticles (MNPs) may be considered as being in an intermediate situation between bulk metals and the atoms that compose them. Due to their small size, they exhibit properties (electric, magnetic, optical and catalytic) different from the macroscopic metal and the isolated atoms. However these properties may be transient. This means that inestability is possible for this kind of particle, so the stabilization of MNPs is needed for the following reasons: to avoid an uncontroled growth of the particles, to avoid coagulation, to control the growth rate and the final size. And to allows solubility of the partciles in different sovents [1], [3], [4].

Different means have been empolyed for the synthesis of nanoparticles in a polymer matrix, almost all based on reactions *in situ*, where the particles are generated from the metallic precursor in the precence of the polymeric material, which sometimes acts as a nanoreactor [2]–[4]. The variuos procedures employed for the metal reduction are: chemical, thermal, photochemical, and electrochemical reduction. The material can be pulverized or melted on a substrate for subsequent applications.

The stabilization mechanism of nanoparticles can be classified into electrostatic, steric, and a combination of the two. The first is based on the separation of electric charges due to the formation of an electrical double layer around the particles, while the second is based on geometric and spatial repulsion due to the large size of the adsorbed molecules on the nanoparticle surface [5].

The production of charges on the metallic surface may occur due to the presence of ionogenic groups or the adsorption of ionic surfactants. Unfortunately, this mechanism is not sufficient in practice because of the high concentration of electrolyte usually employed. An alternative is the use of nonionic surfactants or polymeric surfactants such as polyvinyl pyrrolidone, polyaniline or polyethylene oxides [6], [7] as well as ionic liquids, although the latter exhibit strong coordination, which is good for applications in physics, such as quantum dots but not for catalysis or sensors, where access to the metallic surface is required [5].

Wang *et al*. [6] and other researchers [8]–[10] have used different copolymers or derivatives as a stabilizer for producing mono disperse bismuth nanoparticles (NPs) and bismuth compounds using various techniques such as micro emulsion, chemical reduction and high temperature reactions.

Moreover, Sang *et al.* [11] produced tin nanoparticles from sulfate and ethylexanoate precursors employing polyvinylpirrolidone as a polymer stabilizer, and Jiang et al. [12] produced tin nanoparticles from tin acetate as a precursor in the presence of surface agents, with an average size of 60 nm that could be reduced to 21 nm when the surfactant/precursor ratio was increased. Ultrasonic radiation also has been employed in nanoparticle synthesis. The chemical effect of ultrasonic waves is due to acoustic cavitation, which consists of the formation, growth, and implosion of liquid bubbles in order to promote chemical reactions. Metallic nanoparticles with sizes between 20 to 100 nm of metals as tin and gold have been obtained by this method [13], [14].

Styrene Divinylbenzene copolymers have been used as matrix for nanoparticles [15]–[17] however its low or none solubility difficult the transformation of composites into films for further applications. In this work partial soluble sulfonated styrene divinylbenzene copolymers were synthetized and used as stabilizer for the stabilization of metal nanoparticles of Sn and Bi.

2. EXPERIMENTAL PROCEDURE

2.1 Polymer synthesis and characterization

Sulfonated styrene-divinylbenzene copolymers were produced in a three-necked flask. As a first step, a copolymer of styrene (Aldrich) and divinylbenzene – DVB (Merck) was produced by suspension polymerization with toluene (Merck) as a solvent, benzoil peroxide (Merck) as an initiator, and polyvinyl alcohol (Aldrich PM 30000-50000) as a colloid protector. Quantities, temperatures, and reaction time were previously calculated based on the model proposed by O. Okay [18], and are shown in Table 1. The sulfonation of dry polymer beads was carried out with concentrated sulfuric acid 98%

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(Merck) as in [19] and with Oleum (Merck) for 90 and 180 min at 353 K. Parameters for the sulfonation process are shown in Table 2. The copolymers obtained are named P_nS_m (with n=1-5 and m=1-4).

Table 1. Parameters for copolymer synthesis at 353 K.

Pol (Pn)	Reactive mix/water	Reactive mix composition			Initiator %w	Time (h)
		Styrene % vol	DVB% vol	Tol % vol		
P1	0.20	47.0	3.0	50	0.42	4
P2	0.10	70.0	5.0	25	0.42	4
P3	0.10	65.0	10.0	25	0.42	4
P4	0.10	67.0	3.0	30	1.30	3
P5	0.10	74.5	0.5	25	0.50	4

Table 2. Sulfonation parameters at 353 K.

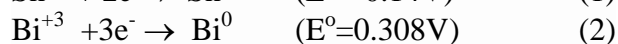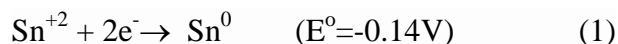| Process (Sm)	Sulfonation agent	Time (min)
S1	Concentrated H_2SO_4	180
S2	Concentrated H_2SO_4	90
S3	Oleum	180
S4	Oleum	90

Copolymer characterization was as follows: The porosity of selected copolymers was measured through nitrogen adsorption at 77K in a Quantachrome Autosorb system. The morphology of the beads and films was observed via SEM microscopy in a FEI QUANTA 2000. The products were analyzed via differential scanning calorimetry (DSC) performed on a TA Instruments equipment model TA2910. These materials were previously dried at 388K, and the test was performed in an aluminum cap with a nitrogen flow of 50 mL/min and heating rate of 10 K/min. The content of the -SO_3H group was measured by titration of washed copolymer beads, with NaOH 0.015N, and the solubility in different solvents was determined gravimetrically by measuring the increase in weight of a glass substrate after evaporation of a known quantity of solution.

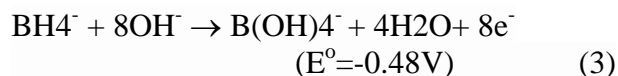## 2.2 Metal nanocomposite synthesis

Only two selected copolymers were used as a nanocomposite matrix, also Nafion resin was used for comparison. Three different solutions were prepared: i) copolymer solutions in dimethylformamide –DMF (Aldrich) were mixed with a nonionic surface agent stabilizer – polyethylene glycol dodecyl ether 70% - Brij 35 (Fisher); ii) Solutions of precursors salts (only bismuth, only tin and bismuth/tin chlorides, Aldrich/Merck) dissolved in DMF were prepared. iii) Sodium borohydride (Merck) in DMF solution freshly prepared was used as reducing agent. 2mL of copolymer-nonionic surfactant solution was mixed with 1 mL of metal precursor solution and submerged in an ice-water bath. Cup horn sonicator Branson 250 was employed for ultrasonic radiation. 20% amplitude (44W) and 10 min of the sonication program were predetermined. When sonication started, 0.5 mL of reducing solution was quickly added. The composition in the final reactive mix was: nonionic surfactant 7 mM, total metal content 2 mM, and reducing agent 10 mM. Half reactions involved are given by equations 1-3:

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Reduction:

$$Sn^{+2} + 2e^- \rightarrow Sn^0 \quad (E^o=-0.14V) \quad (1)$$
$$Bi^{+3} + 3e^- \rightarrow Bi^0 \quad (E^o=0.308V) \quad (2)$$

Oxidation:

$$BH4^- + 8OH^- \rightarrow B(OH)4^- + 4H2O + 8e^-$$
$$(E^o=-0.48V) \quad (3)$$

3. RESULTS AND DISCUSSION

3.1 Polymer characterization

Isotherms of adsorption in nitrogen are shown in Figure 1a. Beads of sulfonated and non -sulfonated copolymers exhibited a type V isotherm, which implies little interaction between adsorbent and adsorbate, while the film of sulfonated copolymer exhibited an isotherm type IV, which indicates the presence of mesopores. Surface area was calculated using the Dollimore Heal method (DH) for desorption isotherm, and low surface area was obtained for all copolymers analyzed compared with sulfonated-styrene-divinil-bencene beads used as ion exchange resins [19]: 26.3, 2.97, and 1.22 m^2/g were the results for films of P2S2, beads of P2S2 and beads of non sulfonated P2, respectively. However the sulfonated copolymers exhibited a mesoporous structure with pore size between 20 and 200 nm, as can be seen in Figure 1b. These pore sizes can serve in our case as compartments for metal nanoparticles in subsequent applications.

The morphology of the copolymers in the beads and films was examined via SEM technique and shown in Fig 2. As can be seen for copolymer P3, a less dense structure was obtained (Fig 2a) compared with the sulfonated one for P3S3 (Fig 2b). This behavior was observed for all the copolymers, and could be due to the additional crosslinking caused by --SO$_3$H groups in the polymer structure. The crosslinking can also cause a smaller pore size in the polymer, as observed in the adsorption test. This can help to control the size and access to metal nanoparticles for further applications.

Powders of copolymers were analyzed via DSC for identification of thermal transitions; results are showed in Fig 3. Exothermic peaks can be observed

for non sulfonated copolymers P2-P5 in the range of temperature between 385–400 K (Fig 3a). As can be seen for P5 copolymer in a backward scanning this peaks are no observable so not correspond to a phase change or glass transition, however could be consequence of a non-complete polymerization. All sulfonated copolymers show a similar behavior as the presented in Fig 3b for copolymer P3S4, little change in the slope close to 391 K its observed, also in reverse scan the transformation occurs, it may be due a glass transition. In the table 3 are presented temperatures of glass transition for other sulfonated copolymers, no change were observed at higher temperatures which indicate thermal stability of copolymers.
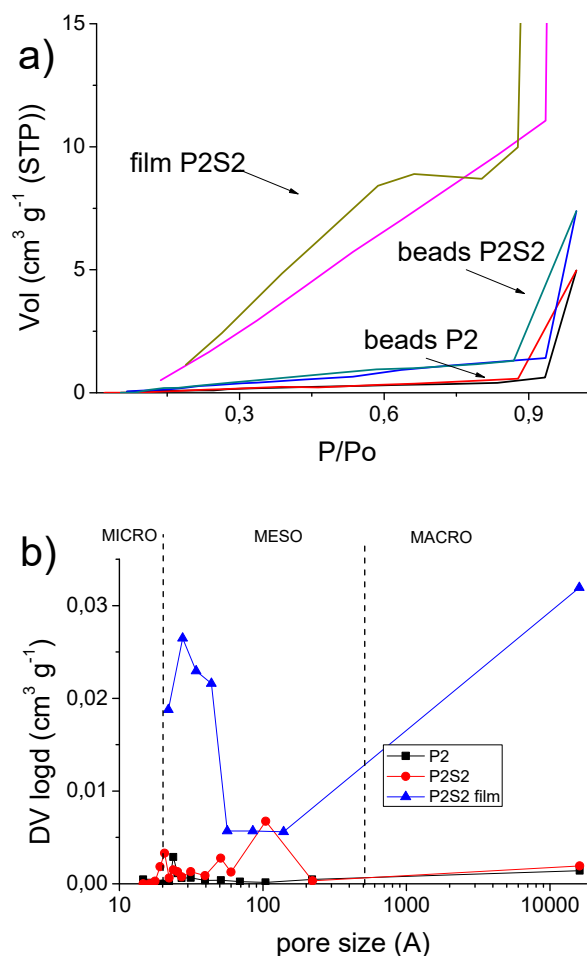

Figure 1. a) Isotherms for nitrogen adsorption at 77K; b) Pore size distribution calculated using the Dollimore Heal method.
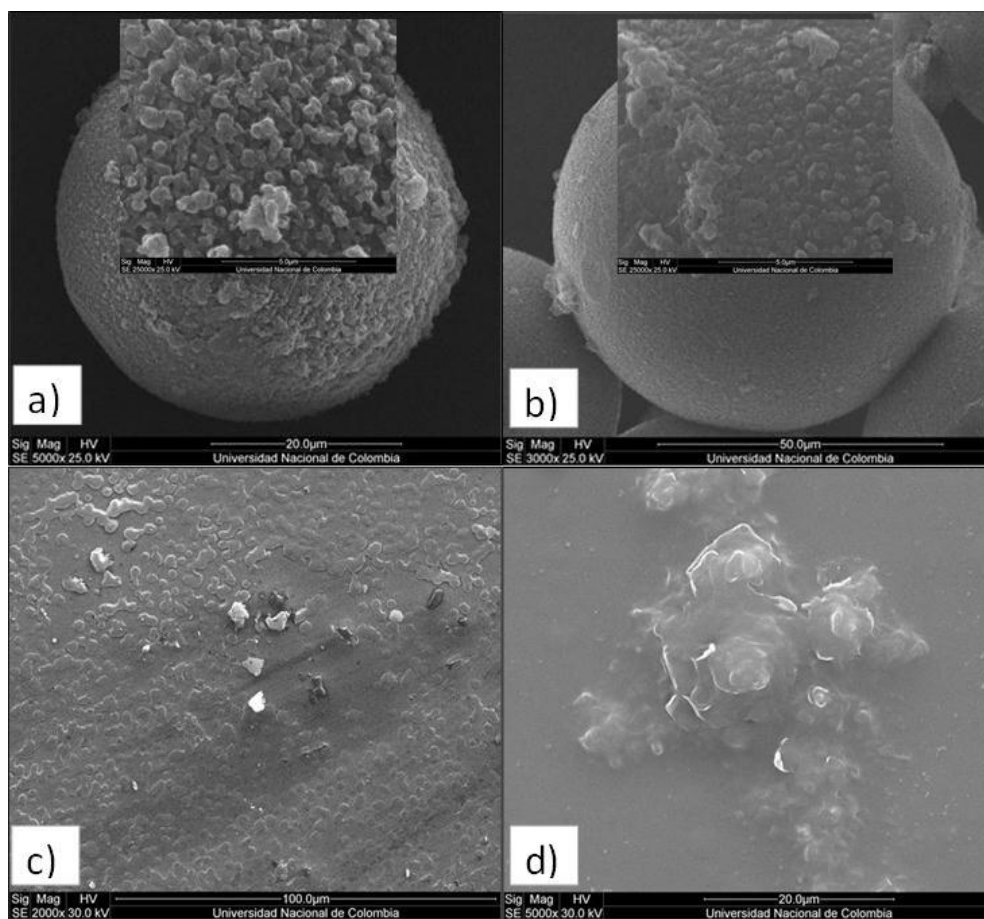
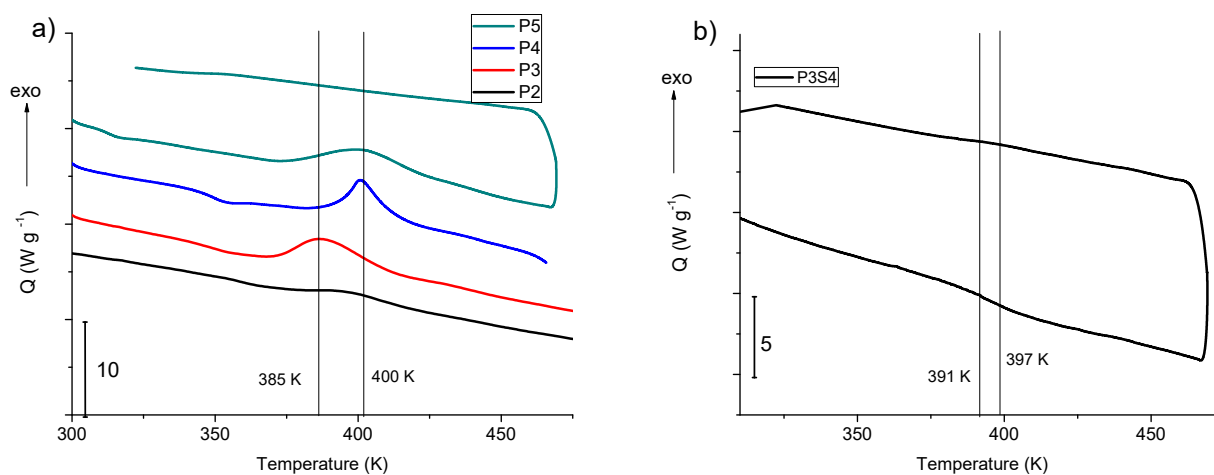**Figure 2.** SEM images of copolymers: a) P3 bead; b) P3S3 bead; c) P4S4 film from DMF; d) P5S4 film from DMF.

Figure 3. DSC for: a) non sulfonated copolymers; b) sulfonated P3S4 copolymer.

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Table 3. Glass transition for sulfonated copolymers.

Polymer	Begin (K)	End (K)	Tg (K)
P2S1	361.9	372.1	366.5
P3S1	372.1	379.5	378.0
P3S4	391.2	397.5	392.4
P4S4	376.0	382.4	381.2
P5S4	357.8	364.9	363.0

Titration of the -SO$_3$H group showed content from 0.08 to 0.1 meq/g for all copolymers, and no significant differences were observed between them. These are low values compared with those presented in [19],[20] and may be caused by poor porosity of the copolymers obtained.

The solubility of the copolymers was measured gravimetrically in toluene (Tol), tetrahidrofurane (THF), and NN-dimethylformamide (DMF). Non sulfonated copolymers exhibited minimum or negligible solubility in polar solvents. However, sulfonated copolymers exhibited partial solubility. Results for the solubility of selected copolymers are shown in Fig. 4. It can be seen that the sulfonated copolymers P4S4 and P5S4 exhibit the greatest solubility in strong polar solvents such as DMF and THF, which also indicates a positive balance between the degree of sulfonation and the crosslinking.

The family of copolymers P3Sm (with higher content of DBV) exhibited lower solubility, due to high crosslinking, while for copolymers P1Sm, P2Sm, and P4Sm which have similar content of DVB, the differences between these can be caused by a lower molecular weight due to higher initiator content in the reactive mix, which can influence greater solubility of P4Sm copolymers (with higher content of initiator).

Films of sulfonated copolymers P4S4 and P5S4 dissolved in DMF were deposited on glass for observation via SEM microscopy. As can be seen in Fig 3c and 3d, there was a difference in morphology between films of P5S4 and P4S4. P5S4 is smoother than P4S4, and this can be due to the different content of DBV.
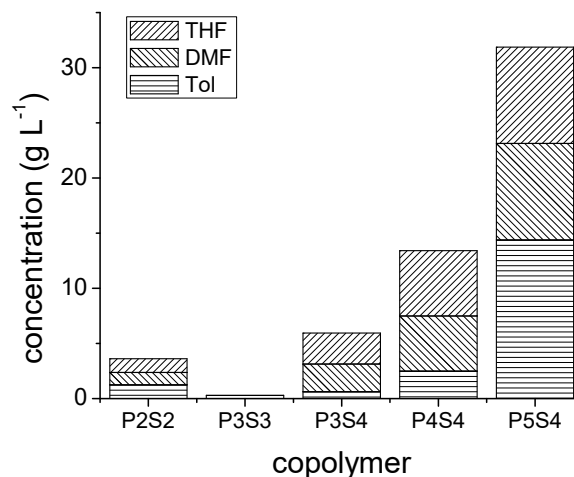

Figure 4. Solubility of selected sulfonated copolymers in: tetrahydrofurane (THF), dimethylformamide (DMF), and toluene (Tol).

Due to the relatively high solubility of copolymers P4S4 and P5S4, only these were selected as matrixes for later nanocomposite production. Henceforth, they will be called simply P4 and P5.

3.2 Nanocomposite characterization

Solutions of all reactants in DMF are translucent, except BiCl$_3$ which exhibited poor solubility in DMF and must be sonicated for good dispersion before reaction. After the addition of the reducer agent, all the solutions change their transparent color to: black for bismuth, dark brown for tin-bismuth, and to amber for tin (see Fig 5).
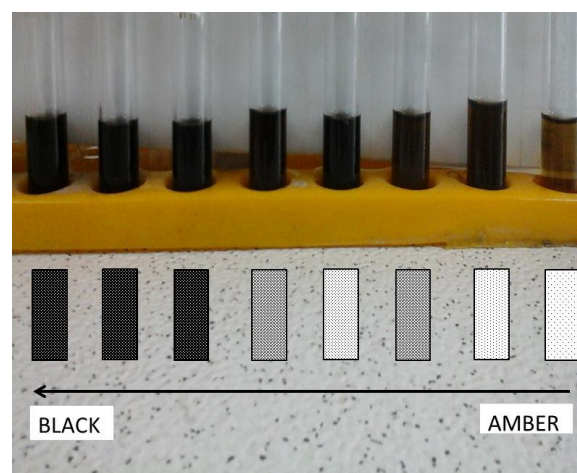

Figure 5. Metal NPs/copolymer solutions in DMF. From left to right: Bi/P5, Bi/P4, Bi/Nafion, BiSn/P5, BiSn/P4, Sn/P5, Sn/P4, and Sn/Nafion

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Nanocomposites obtained with copolymer P4 were always darker than the P5 copolymer solutions, and Nafion solutions were the brightest of all. Bismuth/Nafion NP´s was the most stable of the bismuth solutions prepared. In P4 and P5 copolymers, Bi was unstable and precipitated as a dark powder after a few days, while all tin and bismuth-tin NP´s solutions maintained their color and appearance for many weeks and months. This translucent appearance and no formation of precipitates in the tin and bismuth-tin polymer solutions could be indicative of small size particles stabilized as nanoparticles [21].

Powders of precipitate metals were analyzed via DSC for identification of the materials obtained; results are showed in Fig 6. Melting points of 505.9 K for tin and 544.3 K for bismuth can be seen, which are close to the theoretical values for pure metals (Sn 505 K and Bi 544.3 K). The sharper peak observed for tin could be due to the greater degree of crystallinity. Just one melting point of 505.9 K is observed for tin-bismuth. This could possibly be due to the formation of an alloy with low bismuth content that is soluble in βSn or to the presence of amorphous bismuth.
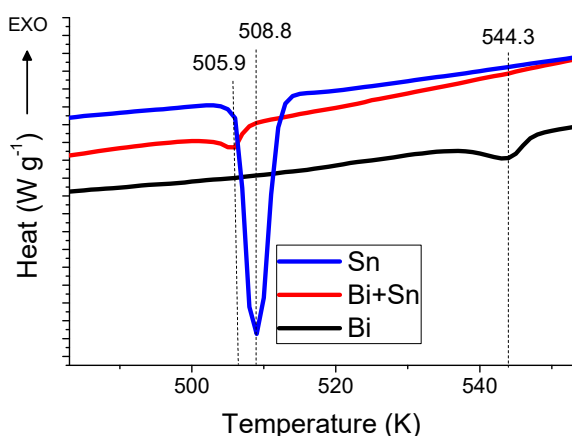

Figure 6. DSC of metal powder precipitates

4. CONCLUSIONS

Styrene-divinylbenzene copolymer was produced and sulfonated in order to form a matrix for a metal-polymer nanocomposite. The copolymers P4S4 and P5S4 sulfonated with oleum for 90 minutes were selected as matrix materials due to their high solubility in dimethylformamide (DMF).

Sulfonated copolymers obtained presented a

mesoporous structure with pore sizes between 20-200 nm, this is suitable for storing metal nanoparticles in the solid state. Polymers with glass transition close to 370K and metal particles with melting point close to the theoretical value were obtained.

Metal/copolymer solutions with Bi, Sn and Bi-Sn particles were synthesized by chemical reduction in a nonionic surfactant – polymer solution as stabilizer (P4S4, P5S4, and Nafion) using DMF as a solvent and ultrasonic irradiation to help maintain a small distribution of particle size. Bi metal solutions were less stable over time than Sn and Bi-Sn solutions. Long time stability of tin and bismuth-tin particles could be indicative that nano metric particles were obtained.

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