

Abstract

Polyamide microcapsules and method to produce the same

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The invention relates to polyamide microcapsules prepared by means of activated anionic polymerization of lactams in a hydrocarbon solution containing organic or inorganic payloads in their cores and with porous polyamide shells. The capsules possess spherical or spheroid forms with average diameters in the range of 5-500 microns including payloads whose amount could vary from 0.05 to 50-60% of their weight which payload can include metals, metal oxides, carbon allotropes and/or their functionalized derivatives, clays, or any other polymeric or low molecular compounds that do not inhibit the polymerization process, being either soluble or insoluble in the reaction media. The microcapsules of the present invention can be used as obtained or can be transformed into molded parts of advanced thermoplastic composites comprising polyamide matrices reinforced by homogeneously distributed organic or inorganic reinforcements.

DESCRIPTION

Polyamide microcapsules and method to produce the same

Field of the Invention

The present invention relates to encapsulation of solid materials in polymeric capsules and discloses new polyamide microcapsules, their preparation and some of their possible applications as advanced thermoplastic composite materials.

The present invention relates to polyamide microcapsules with organic or inorganic payload, the method to produce the same and possible applications. More specifically, the invention relates to porous polyamide microcapsules with organic or inorganic payloads in their core. This invention may be used in pharmaceuticals industry, food industry, in rapid prototyping and selective laser sintering, as well as in new composite materials, among others.

Background of the Invention

According to the prior art, there exist two basic methods to produce pulverulent polyamides in the form of microcapsules. Empty porous polyamide particles can be made by activated anionic ring-opening polymerization (AAROP) of lactams in hydrocarbon solvents. Thus, patent publications **US Pat. 3705871** and **DE Pat. 1964533** disclose a process for the production of polyamide 12 (PA12) in pulverulent form by AAROP of the corresponding lactam in aromatic hydrocarbons catalyzed by a two-component catalytic system: basic alkali hydride initiator and an imide activator compound, the latter being produced in-situ or prior to AAROP and added to the reaction media. Finely divided PA12 powders are obtained in good yields and without concurrent formation of agglomerates larger than

1000 microns, the grain size being dependent on the AAROP conditions. These patent publications teach also about the possibility to perform AAROP in the presence of certain amounts of additionally introduced polyamide powders. Notably, these powders are added to the reaction mixture after the introduction of the initiator. This publication does not discuss AAROP in the presence of other appropriate organic or inorganic finely divided fillers, which limits the fields of application of this invention.

US Pat. Appl. 2010/0098880 A1 (Arkema Inc.) explores the production and use of shell-core polyamide micron-sized particles prepared by AAROP of lauryllactam, of caprolactam or of a mixture thereof in a hydrocarbon solvent, in the presence of seeds (i.e., powder particles) of other polyamides from the group of PA6, PA11, PA12, PA6/12, PA6,6, PA8 and PA4. Notably, apart from the two-component catalytic system that comprises a basic initiator (typically alkali hydride) and a specific activator, the AAROP according to this document requires the presence of at least one N,N'-alkylene bisimide. The shell-core particles obtained in such a way are with controlled difference between the temperatures of melting and crystallization and are especially useful in rapid prototyping by selective laser sintering. This document does not consider the production or applications of polyamide microparticles obtained by AAROP that comprise seeds of other inorganic materials' powders and, therefore, suffers of the same limitations indicated in the aforementioned patents.

A second group of methods, according to the prior art, useful to microencapsulate solid payloads in polyamide microcapsules is related to controlled precipitation of polyamide solutions. **US Pat. 4334056** (Hüls AG) discloses the production of powdered polyamide (i.e., empty microcapsules) with grain size no bigger than 100 microns by precipitation of alcohol solutions of hydrolytic PA12, PA6 or their mixtures

carried out in the 100-130°C range in autoclaves. Furthermore, **EP 1964875 B1** teaches that precipitation of phenol solutions of polyamides by alcohol/aqueous solutions can produce polyamide spherical porous particles with diameters up to 0.5 microns. They can be loaded subsequently with metal oxides by means of physical mixing of the respective powders and washing out the excess oxide particles. Reportedly, this procedure deposits the oxide particles on the surface or into the pores of the polyamide particles and not in their nuclei.

The abovementioned processes describing the present state-of-the art in the field of polyamide powders still fail to be fully satisfactory because of the following reasons. First, all solution precipitation based methods are costly because they require the use of very large amounts of harmful or even toxic solvents whose complete deactivation and/or recuperation is difficult if not impossible. Second, the final powders must be carefully purified so as to be completely free of any toxic solvent traces. The methods of the prior art including AAROP in a hydrocarbon solvent have the big advantage of using cheap lactam monomers as raw materials, to be rapid and to produce small amounts of wastes. However, the known patents in this field do not contemplate microencapsulation of substantial amounts of inorganic or organic payloads but only seeding with other polyamide microparticles. A possible reason for this could be that the known patents of the prior art employ as initiators only alkali hydride compounds that are extremely sensitive to moisture or any acidic substances, or other metals brought into the reaction media that could block the formation of the AAROP initiating anions and therefore inhibit or completely stop the polymerization process that forms the microcapsules.

Summary of the invention

The technical term "microcapsules", as understood in this invention, describes spherical or spheroid aggregates with diameters between 0.005-0.5 mm. They possess at least one solid core that comprises the payload, covered by at least one polyamide shell being continuous but porous at micrometer length scale. Capsules with two or more different cores, as well as such with multi-shell structure can be produced by adequately changing the preparation conditions. Empty mono-shell polyamide microcapsules are named "particles". In all of the discussed cases, the final microcapsules have the aspect of very fine powder with variable color.

The present invention comprises polyamide microcapsules obtainable by means of AAROP - activated anionic ring-opening polymerization - of lactams in hydrocarbon solution whereby the organic or inorganic payload is concentrated in the core of the microcapsule and the polyamide shell(s) comprise pores with average diameters typically in the 10-500 nm range, preferably 20-100 nm. The present invention also relates to the preparation of polyamide microcapsules which are able to accommodate payloads of up to 60% of metals, metal oxides, carbon allotropes and/or their functionalized derivatives, clays, or any other polymeric or low molecular compound that does not inhibit the polymerization process, being either soluble or insoluble in the reaction media.

The preparation process disclosed in the present invention makes use of anionic polymerization of lactams carried out in hydrocarbon solvents in the presence of the respective payload, in which as anionic polymerization initiators instead of the alkali hydrides of the prior art, organo-aluminum lactamate compounds are used, the latter being a source of more stable anions thus preventing inhibition or complete inactivation of the microcapsule forming process.

The microcapsules of this invention charged with various types and amounts of payloads can be directly transformed into molded parts by means of conventional melt processing techniques obtaining in such a way thermoplastic composites that comprise a thermoplastic polyamide matrix reinforced by finely dispersed inorganic or organic reinforcements with sizes are in the nano- or micrometer length scale. Alternatively, the microcapsules of the present invention can be used directly in their pulverulent form.

Brief explanation of the drawings

Figure 1 shows a scanning electron microscopy general view of microcapsules obtained in Example 1 that contain payload of organically treated aluminum-silicate clay.

Figure 2 is a transmission electron microscopy image of the same microcapsules showing the distribution of the inorganic aluminum-silicate particulate filler.

Figure 3 visualizes the porosity of the microcapsules of Example 1.

Figure 4: Images 1-18 represent SEM micrographs of Au-coated PA6 microcapsules with payloads indicated. Images 19-24 represent SEM micrographs after cryogenic fracture of composite films (initial size 50x50x2 mm) obtained by compression molding of the respective microcapsules in a hot press at 230°C and pressure of ca. 5 MPa.

Preferred embodiments of the invention

In the invention, the polyamide microcapsules obtained represent porous aggregates including various fused polyamide spheres, these aggregates having typical average diameters of 5-500 μm (Figure 1). The organic or inorganic payload is dispersed within the capsule (Figure 2) as differently shaped and sized particles depending on the size of the payload powder used and its solubility in the reaction media. The shell of the microcapsules is highly porous (Figure 3), the pores size and form depending on the AAROP conditions (mostly temperature, boiling point of the hydrocarbon solvent, and time of addition of the catalytic system), as well as of the payload type.

In one embodiment the polyamide microcapsules comprising a polymerizable lactam that forms their shell can be 2-pyrrolidone, ϵ -caprolactam, ω -lauryl lactam, or their mixtures. Alternatively, microcapsules with two or more shells as well as with copolymeric shells can be produced. This will permit tailoring of the physical and chemical properties of both microcapsules and of the products thereof obtained via a molding process.

In one embodiment the polyamide microcapsules are characterized in that the payload they comprise can be selected from the group of the phyllosilicates, advantageously from the group of smectites, more advantageously montmorillonite, hectorite, saponite or their mixtures, being soluble or insoluble in the reaction media, for example Nanomer® of Nanocor, Cloisite® of Southern Clay Products, Dellite® of Laviosa Chimica Mineraria etc.

In one embodiment the polyamide microcapsules are characterized in that the payload they comprise can be metal particles, advantageously Au, Ag, Cu, Al, Mg, Zn, Fe or other appropriate metal powders with grain sizes in the micron

length scale, or mixtures thereof, which do not block the anionic polymerization process.

In one embodiment the polyamide microcapsules are characterized in that the payloads they comprise in their cores are ZnO, Sb₂O₃, FeO, Fe₂O₃, Fe₃O₄, TiO₂, or other appropriately pulverized metal oxides (pigments) that do not block the anionic polymerization process.

In one embodiment the polyamide microcapsules are characterized in that the payload they comprise in their core can be carbon allotrope particles, e.g., carbon black, multi- or single-wall carbon nanotubes, carbon nanofibers, graphite, graphene, fullerenes or their functionalized derivatives, being soluble or insoluble in the reaction media.

In one embodiment the polyamide microcapsules are characterized in that the payload they comprise can be of other polyamide particles, e.g., of poly(tetrafluoroethylene), poly(vinylidene fluoride), polyethylene, polypropylene, polylactide or other pulverized synthetic or natural polymer, being soluble or insoluble in the reaction mixture.

Other aspect of the present invention disclosed a shell-core polyamide microcapsule described as a waste waters, mineral water or aqueous solutions purifier, by absorbing the contaminants through their porous shell followed by separation of the microcapsules by filtration.

The relationship payload/monomer(s) introduced into the reaction mixture expressed in weight percentage is between 0.001% and 60%, preferably between 0.005% and 45%, more preferably between 0.01-30% and advantageously between 0.05-20%. Microcapsules with combinations of organic-inorganic, particulate-layered, layered-fibrous payloads or other opportune combinations are possible.

The invention likewise provides a process for the preparation of polyamide porous microcapsules with various payloads by anionic polymerization in solution, the reaction

media comprising: an appropriate solvent, a lactam monomer or a mixture of various such monomers, an initiator, an activator and the respective amounts and types of organic or inorganic powdered payload.

The solvent used dissolves the monomer but not the microcapsules and can or cannot dissolve the payload. The solvent is a hydrocarbon or mixture of various hydrocarbons whose boiling range is between 80-170°C, preferably between 120-160°C. Non-limiting examples of suitable solvents may be benzene, toluene, xylenes, decalin, teralin, or mixtures thereof, among others.

The initiator used in this invention is selected from the group of alkali metals, their hydrides or alkoxides (fast initiators), or, advantageously, from the group of less active organo-aluminum caprolactamates. As identified in the present invention, the use of fast initiators together with small amounts of hydrophobic payloads resulted in the formation of particles aggregates larger than 150 µm or even polyamide lumps, whereas high concentration of hydrophilic loads in the reaction media such as metals or metal oxides resulted in low yields of powdered polymer or almost total inhibition of the polymerization process.

The activator used has the role to stimulate the propagation step of the AAROP process. A number of compounds suitable as AAROP activators are given in **US Pat. Appl. 2010/0098880 A1**. The activator compound may be optionally formed in situ, for example by reaction of alkyl isocyanates with the lactam monomer which produces the activating N-acyl lactam derivatives.

The present invention also relates to the use of the polyamide microcapsules in various areas, namely pharmaceuticals industry, food industry more precisely wine making, in rapid prototyping and selective laser sintering, as well as in new composite materials, among others. The inventors have

established that by means of a processing technique involving melting of the polyamide shell, e.g., compression or injection molding, extrusion, rotational molding, selective laser sintering, pultrusion, prepreg consolidation, they are converted into finished articles of homo- or copolymeric polyamide composites comprising property modifying fillers dispersed at micron or nanometer length scale.

In one embodiment polyamide microcapsules with clay payload were transformed by compression molding into exfoliated clay/polyamide thermoplastic hybrid composites with improved mechanical properties (i.e., higher Young's moduli and maximum tensile stresses) as compared to neat polyamide samples prepared under the same conditions from commercial hydrolytic polyamides of the same type.

In one embodiment polyamide microcapsules with carbon allotrope payload (i.e., carbon black, carbon nanotubes, graphite, carbon nanofibers or C₆₀ fullerenes) were transformed by compression molding into thermoplastic composites with good mechanical properties and enhanced electro- and thermoconductivity suitable for use as static charge dissipating or even semiconducting materials.

In one embodiment polyamide microcapsules with metal or metal oxide payloads were transformed by compression molding into thermoplastic composites with good mechanical properties, enhanced electro- and thermoconductivity also suitable for use as static charge dissipating materials or in energy accumulating devices. Microcapsules comprising pure Fe or Fe-oxide payloads display pronounced magnetic properties which upon molding are transferred to the molded parts produced thereof that are responsive to magnetic fields.

In one embodiment polyamide microcapsules with or without payloads were compression molded in the presence of textile structures made of glass or carbon fibers or, advantageously, of fiber-forming polymers thereby producing polyamide laminate

composites with tailored properties including enhanced stiffness and tensile strength, higher electro- and thermoconductivities. In case PA6 or PA66 textile structures are employed, one-polymer or all-polyamide laminate composites are obtained capable of full recycling by reprocessing.

The present invention is not, in any way, restricted to the embodiments described herein and a person of ordinary skills in the area can provide many possibilities to modifications thereof without departing from the general idea of the invention, as defined in the claims.

The embodiments, and preferred embodiments, and more preferred embodiments, described above are obviously combinable. The claims define further preferred embodiments of the present invention.

Examples

The following non-limiting examples demonstrate the preparation of various microcapsules types, their properties (Table 1) as well as their transformation into thermoplastic composite materials (Table 2). The sizes of the microcapsules are observed by electron and light microscopy methods. Data about their roundness, area and size distributions are obtained by computerized analysis of panoramic light microscopy images in a manner well known by art using a specialized software package. The mechanical properties of composites prepared by compression molding of microcapsules are determined in tension in accordance to DIN 53504-S3. The volume resistivity of molded composites is obtained by measuring the characteristic I-V curves at room temperature using a Keithley 6487 picoammeter/voltage source. The solution viscosity of both microcapsules and thermoplastic composites thereof is calculated based on the specific viscosity measured

at 20°C on concentrated sulfuric acid solutions with standard concentration of 0.2 g/dL. The viscosity-average molecular mass is calculated on the basis of solution viscosity in a manner well known by art.

Example 1 - PA6 microcapsules with clay payload

In a typical synthesis, 56.5 g ϵ -caprolactam (ECL) and 2 wt% of the clay are dissolved in 120 mL of the solvent while stirring under nitrogen atmosphere and refluxing the reaction mixture for 10-15 min to eliminate any traces of water by azeotropic distillation. After setting the temperature of the resultant clear solution at 110°C, 3 mol % of the initiator sodium dicaprolactamato-bis-(2-methoxyethoxy)-aluminate (DL) and 1.5 mol % of the activator Bruggolen C20 of Brueggerman Chemicals (an adduct of hexamethylene di-isocyanate and ECL) are added at once. The polymerization process was carried out for 2h at 120°C at a constant stirring rate of 350 revolutions per min. The white polymer powder was separated from the reaction mixture by hot vacuum filtration, washed with methanol and dried for 120 min in a vacuum oven at 120°C. The yield of microcapsules is 36 g i.e., 64% in respect to the ECL monomer. The morphology of the resulting microcapsules is presented in the SEM micrographs in Figures 1-3.

To the hot filtrate containing ca. 35% oligomers 3 mol% of DL and 1.5 mol % of C20 are added and the solution AAROP was carried out at 120°C for another 2h rendering additionally 12 g of powdered PA6 which, combined with the yield of the previous stage, reached 48 g or 85%. This process can be performed until total exhaustion of the oligomer solution.

Example 2 - PA12 microcapsules with clay payload

The procedures of Example 1 are repeated except that instead of ϵ -caprolactam 98.5 g ω -lauryl lactam is used to get a total amount of 80 g of PA12 microcapsules loaded with Cloisite

clay, i.e., 81%. The basic characteristics of the clay-loaded PA12 microcapsules are given in Table 1.

Example 3 - PA6 microcapsules with Cu payload

The procedures of Example 1 are repeated except that instead of clay 3 wt% of copper powder with grain size 14-25 μm is added to the reaction media. The AAROP rendered in this case a total yield of 75% of Cu-loaded microcapsules whose characteristics are given in Table 1.

Example 4 - PA6 microcapsules with Al payload

The procedures of Example 1 are repeated except that instead of clay 3 wt% of Al powder with grain size $<45 \mu\text{m}$ is added to the reaction media. The AAROP rendered in this case a total yield of 78% of Al-loaded microcapsules (Table 1).

Example 5 - PA6 microcapsules with Zn payload

The procedures of Example 1 are repeated except that instead of clay 3 wt% of Zn powder with grain size $<10 \mu\text{m}$ is added to the reaction media. The AAROP rendered in this case a total yield of 80% of Zn-loaded microcapsules (Table 1).

Example 6 - PA6 microcapsules with Mg payload

The procedures of Example 1 are repeated except that instead of clay 3 wt% of Mg powder with grain size $< 35 \mu\text{m}$ is added to the reaction media. The AAROP rendered in this case a total yield of 80% of Mg-loaded microcapsules (Table 1).

Example 7 - PA6 microcapsules with Fe payload

The procedures of Example 1 are repeated except that instead of clay 3 wt% of soft carbonyl Fe powder with average grain size of 3 μm are added to the reaction media. The AAROP rendered in this case a total yield of 76% of Fe-loaded microcapsules whose characteristics are given in Table 1.

These microcapsules display well-expressed paramagnetic properties.

Example 8 - PA6 microcapsules with Fe₃O₄ payload

The procedures of Example 1 are repeated except that instead of clay 3 wt% of finely grinded magnetite Fe₃O₄ (grain size 50-100 nm) is added to the reaction media. The AAROP rendered in this case a total yield of 82% of Fe-loaded microcapsules whose characteristics are given in Table 1. These microcapsules display well-expressed paramagnetic properties.

Example 9 - PA6 microcapsules with carbon nanotube payload

The procedures of Example 1 are repeated except that instead of clay 2 wt% of multi-walled carbon nanotubes (MWCNT) is added to the reaction media. The AAROP rendered in this case a total yield of 73% of MWCNT-loaded microcapsules whose characteristics are given in Table 1.

Example 10 - PA6 microcapsules with graphite payload

The procedures of Example 1 are repeated except that instead of clay 5 wt% of finely ground graphite (grain size <50 μm). The AAROP rendered in this case a total yield of 81% of graphite-loaded microcapsules (Table 1).

Example 11 - PA6 microcapsules with poly(tetrafluoroethylene)

The procedures of Example 1 are repeated except that instead of clay 5 wt% of poly(tetrafluoroethylene) (PTFE) with particle size of <10 μm. The AAROP rendered in this case a total yield of 79% of PTFE-loaded microcapsules (Table 1).

Table 1 Characteristics of microcapsules obtained in Examples 1 - 11

Shell material	Payload type and content, wt. % *	Yield of AAROP, wt. %**	Viscosimetric molecular weight M_v , kDa	Average equivalent diameter, μm	Roundness ($R_{\text{max}}/R_{\text{min}}$)
PA6	Cloisite, 3	85	29.5	10-15	1.2-1.3
PA12	Cloisite, 3	81	25.8	10-20	1.2-1.3
PA6	Cu, 3	75	30.2	80-100	1.4-1.6
PA6	Al, 3	78	33.0	100-125	1.3-1.8
PA6	Zn, 3	80	32.4	90-100	1.5-1.8
PA6	Mg, 3	80	29.1	80-110	1.3-1.5
PA6	Fe, 3	76	28.6	55-80	1.2-1.3
PA6	Fe ₃ O ₄	82	38.7	20-25	1.2-1.3
PA6	MWCNT, 2	73	35.0	35-50	2.0-2.2
PA6	Graphite, 5	81	36.2	50-60	1.3-1.5
PA6	PTFE, 5	79	27.5	10-15	1.2-1.3

* In respect to lactam monomer

** After two consecutive polymerizations as explained in Example 1.

From the results in Table 1 it is understood that the microcapsules of Examples 1-11 are obtained in yields ranging from 75-85 wt% in respect to the monomer used and with molecular weights between 25,800 - 38,700 Da which is comparable or even higher than the molecular weight of commercial hydrolytic PA6 granulated material with $M_v = 36,000$ Da. The microcapsules size and form depends on the size and form of the payload particles involved in the AAROP process, as well as on the catalytic system and polymerization conditions.

Example 12 - Thermoplastic composites from clay-loaded microcapsules

A portion of the clay-loaded microcapsules prepared according to Example 1 are compression molded at 230°C and 5 MPa pressure to plates with dimension of 80 x 80 x 1 mm, from which standard dog-bone tests samples are cut. Subsequently, these are strained to failure at 23°C and 60% relative humidity at a rate of 50 mm/min. The results of the mechanical tests along with some other properties of the thermoplastic composites resulting from these microcapsules are presented in Table 2.

Example 13 - Thermoplastic composites from copper-loaded microcapsules

A portion of the Cu-loaded microcapsules prepared according to Example 3 are compression molded as indicated in Example 12. The properties of the thermoplastic composites resulting from these microcapsules are presented in Table 2.

Example 14 - Thermoplastic composites from Fe-loaded microcapsules

A portion of the Fe-loaded microcapsules prepared according to Example 7 are compression molded as indicated in Example 12. The properties of the thermoplastic composites resulting from these microcapsules are presented in Table 2. Notably, the composite materials of this example possess well-expressed paramagnetic properties combined with strongly reduced volume resistivity.

Example 15 - Thermoplastic composites from graphite-loaded microcapsules

A portion of the graphite-loaded microcapsules prepared according to Example 10 are compression molded as indicated in Example 12. The properties of the thermoplastic composites resulting from these microcapsules are presented in Table 2.

Example 16 - Thermoplastic composites from Sb₂O₃-loaded microcapsules

Sb₂O₃-loaded microcapsules are prepared according to Example 1 except that 0.5 wt% of Sb₂O₃ with grain size <250 nm is used that are subsequently compression molded as indicated in Example 12. The properties of the thermoplastic composites resulting from these microcapsules are presented in Table 2.

Example 17 - Thermoplastic laminate composites from clay-loaded microcapsules

A portion of the clay-loaded microcapsules prepared according to Example 1 are compression molded between glass-fiber textile structures (aerial density of 200g/m²) at 230°C and pressure of 3-8 MPa adjusting the weight fraction of textile fiber to 55-60%. Laminate plates with dimension of 80×80×2 mm are obtained and mechanically tested as in Example 12. The results of the mechanical tests along with some other properties of the thermoplastic composites resulting from these microcapsules are presented in Table 2.

Table 2 Characteristics of thermoplastic composites obtained in Examples 12 - 15

Composite type (matrix material/ reinforcement, in wt%)	Viscosimetric molecular weight M_v , kDa	Strength at break, MPa	Young's modulus, GPa	Volume resistivity, $\Omega.m$
Commercial hydrolytic PA6	36.0	51.2	1.2	1.7×10^{12}
PA6/Cloisite, 1	30.0	85.0	2.4	1.2×10^{12}
PA6/Cu, 3	32.2	72.5	2.1	0.8×10^5
PA6/Fe, 3	29.0	92.5	3.8	8.7×10^5
PA6/Graphite, 3	35.4	76.8	2.2	9.1×10^4
PA6/Sb ₂ O ₃ , 0.5	51.2	89.5	3.6	4.1×10^{12}
PA6/glass fiber textile, 55	-	114.2	4.8	2.0×10^{12}

From the results in Table 2 it is understood that the thermoplastic composite materials obtained via microcapsules display strength and Young's modulus values being significantly superior to those of the commercial hydrolytic PA6 sample. Composites produced from microcapsules with conductive payloads display volume resistivity of up to eight orders of magnitude lower than neat PA6. Notably, the Sb₂O₃ included as payload in the microcapsules promotes additional polymerization during the molding process resulting in sensitive increase of the samples' molecular weight, strength and stiffness. Laminate composites produced from empty microcapsules in the presence of textile structures display very high tensile strength complemented by high modulus values.

Cited References

This patent application cites several references compiled mostly for the reader's convenience and as illustration of the present state of the art.

US Pat. 3705871, 1972 - Biensan et al., Process for obtaining of polylactam powders.

DE Pat. 1964533, 1968 - Biensan et al., Verfahren zur Herstellung von Pulverförmigen Polyamid.

US Pat. Appl. 2010/0098880, 2010 - Senff H., Core-shell polyamide powder.

US Pat. 4334056, 1982 - Feldman et al., Method for polytropically precipitating polyamide powder.

EP 1964875 B1, 2008 - Tatsuya et al., Powder composed of inorganic-loaded polyamide porous particles.

Guimarães, 3rd of June of 2014

Claims:

1. A powdered material comprising shell-core microcapsules obtainable by anionic ring-opening polymerization of lactam, wherein the core contains finely dispersed organic or inorganic fillers, said core covered by one or more shells of polyamide homo- or copolymer, in particular wherein said lactam is selected from a list of: 2-pyrrolidone, ϵ -caprolactam, ω -lauryl lactam, or their mixtures.
2. Shell-core polyamide microcapsules, wherein the shell is obtainable by anionic ring-opening polymerization of a polymerizable lactam selected from a list consisting of: 2-pyrrolidone, ϵ -caprolactam, ω -lauryl lactam, or their mixtures.
3. The microcapsules according to claims 1-2, wherein the core comprises finely dispersed micron- or nanometer sized particles selected from a list consisting of: polymers, metals, metal oxides or salts, mineral or organic pigments or dyes, carbon allotropes, synthetic or natural clays or mixtures thereof.
4. The microcapsules according to claims 1-3, wherein the core metal particles are selected from a list of: Au, Ag, Cu, Al, Mg, Zn, Fe in quantities from 0.5 to 50 wt%.
5. The microcapsules according to claims 1-4, wherein the core metal oxide particles are selected from a list consisting of: ZnO, Sb₂O₃, FeO, Fe₂O₃, Fe₃O₄, TiO₂, or pigments suitable for the anionic polymerization process, preferably in quantities from 0.05 to 30%.

6. The microcapsules according to claims 1-5 wherein the core carbon allotrope particles are selected from a list of: carbon black, multi- or single-wall carbon nanotubes, carbon nanofibers, graphite, graphene, fullerenes or their functionalized derivatives, preferably in quantities from 0.05 to 40 wt%.
7. The microcapsules according to claims 1-6, wherein the core further contains pristine or organically treated synthetic or natural phyllosilicate, titanosilicate or other suitable pulverized mineral fillers, preferably in quantities from 0.5 to 20 wt%.
8. The microcapsules according to claims 1-7, wherein the core polymer particles are selected from a list of: of polyamide 12, polyamide 6, poly(tetrafluoroethylene), poly(vinylidene fluoride), polyethylene, polypropylene, polylactide or other synthetic or natural polymer, preferably in quantities from 0.05 to 50 wt%.
9. The microcapsules according to any one of the previous claim wherein the diameter is between 10 - 500 nm, preferably 20-100 nm; depending on the payload grain sizes.
10. The microcapsules according to any one of the previous claim, for use in medicine or as a medicament.
11. The microcapsules according to claims 1-10, for use in treatment of diseases that need as systems for time-controlled delivery of the substances enclosed in their core, in particular cancer, namely breast cancer, lung cancer.

12. A method to obtain a shell-core polyamide microcapsules describe in claims 1-11 comprising the polymerization of lactams by anionic ring-opening in the presence of a suitable solvent, wherein the core contains finely dispersed organic or inorganic fillers covered by one or more shells of polyamide homo- or copolymer and the shell comprises a polymerizable lactam selected from a list consisting of: 2-pyrrolidone, ϵ -caprolactam, ω -lauryl lactam, or their mixtures.
13. The method according to any one of the claims 12, wherein the solvent for the lactam polymerization is selected from the group of benzene, toluene, xylenes, decalin, teralin, mixtures thereof or any hydrocarbon suitable to dissolve the lactam monomer above 60°C but unable to dissolve the respective polyamide microcapsules.
14. The method according to any one of the claims 11-13, wherein the anionic ring-opening polymerization step further comprises one or more initiators, provided that at least one initiator is an organo-aluminum stabilized anion.
15. The method according to any one of the claims 11-14, wherein the anionic ring-opening polymerization step further comprises an activator compound.
16. The method according to any one of the claims claims 11-15 further comprising the melting of the polyamide shell by one of the following methods: compression or injection molding, extrusion, rotational molding, selective laser sintering, pultrusion, prepreg consolidation.

17. Use of a shell-core polyamide microcapsule described in any one of the claims 1-10 as a waste waters, mineral water or aqueous solutions purifier.

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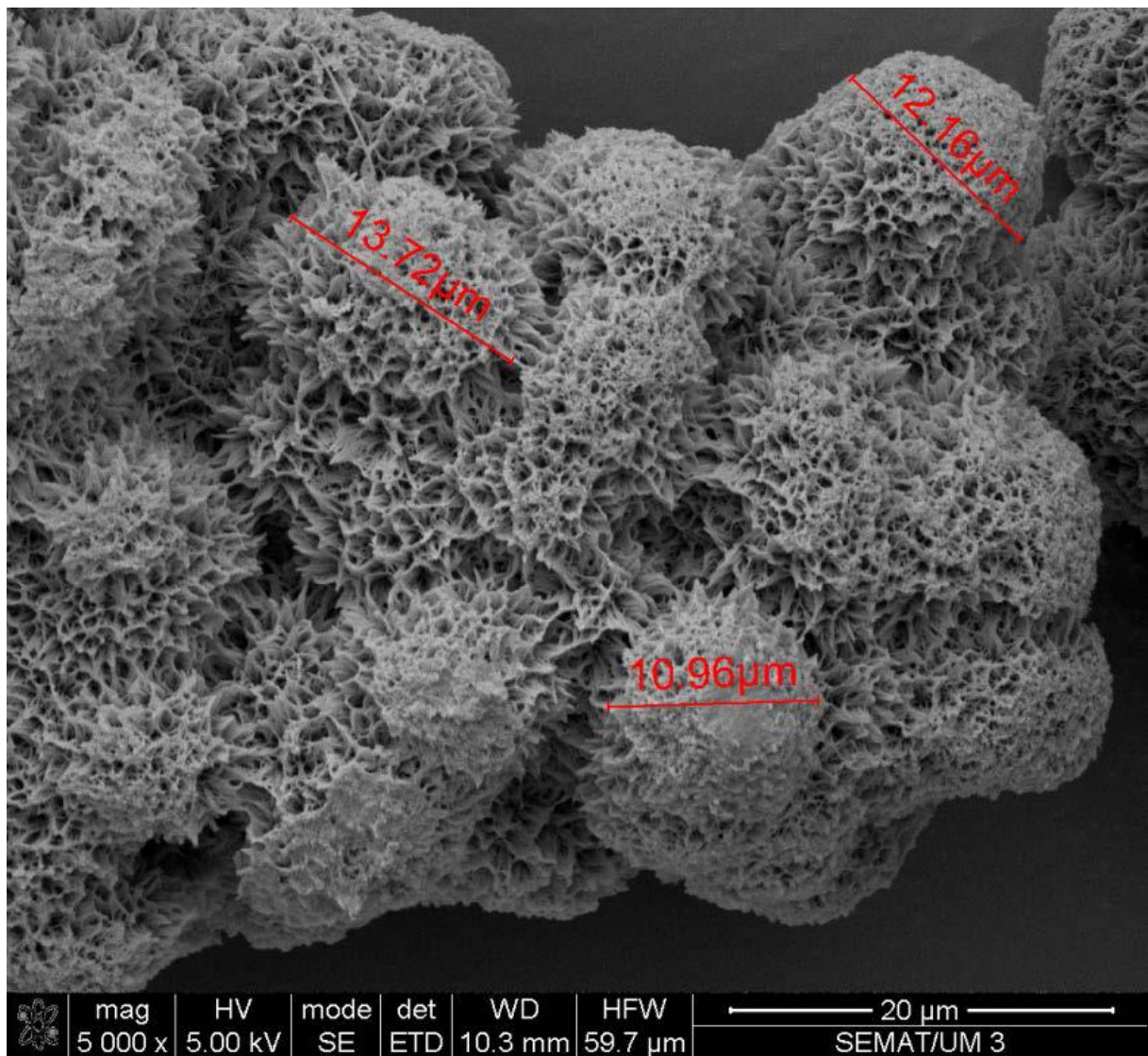


Figure 1

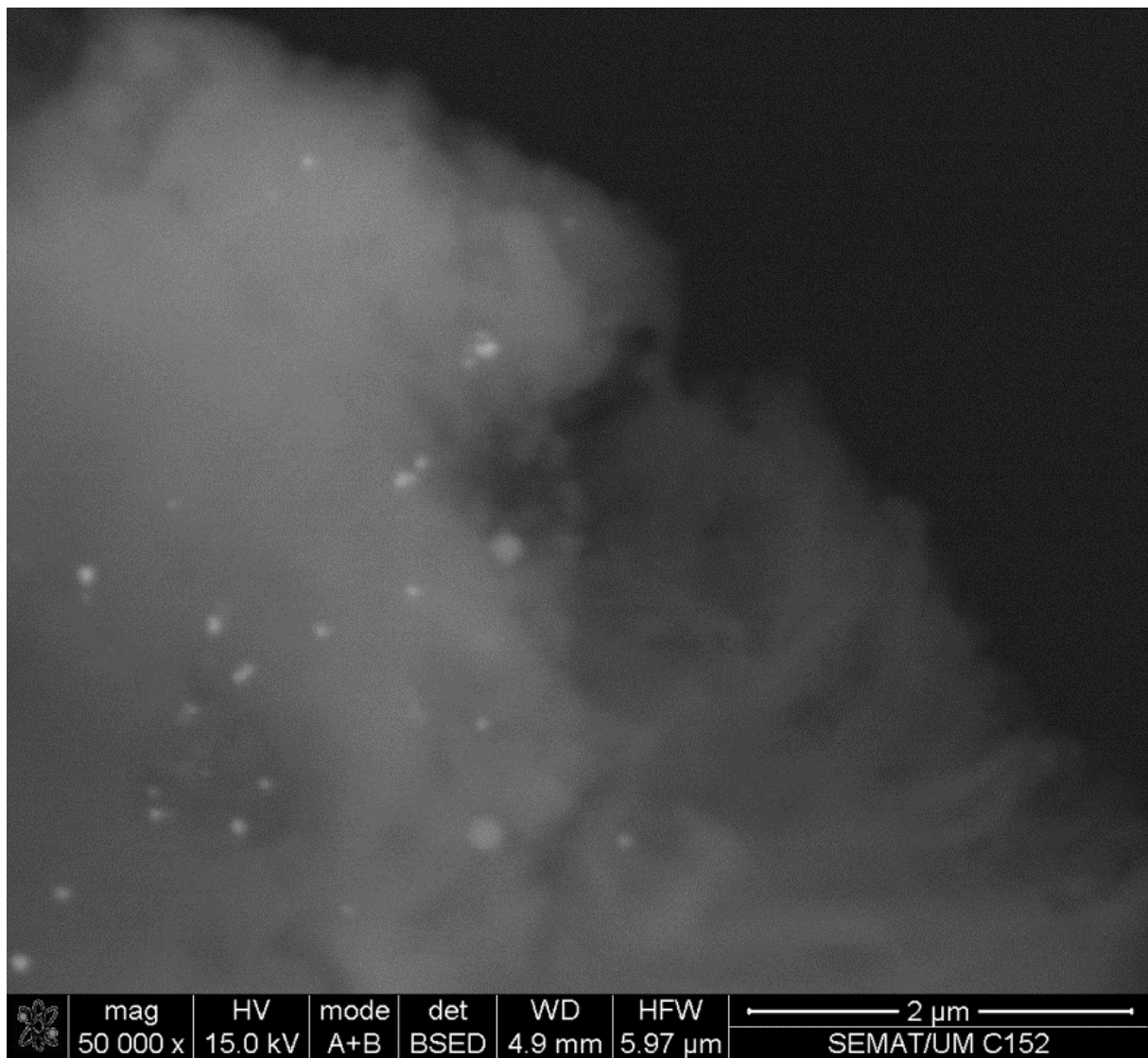


Figure 2

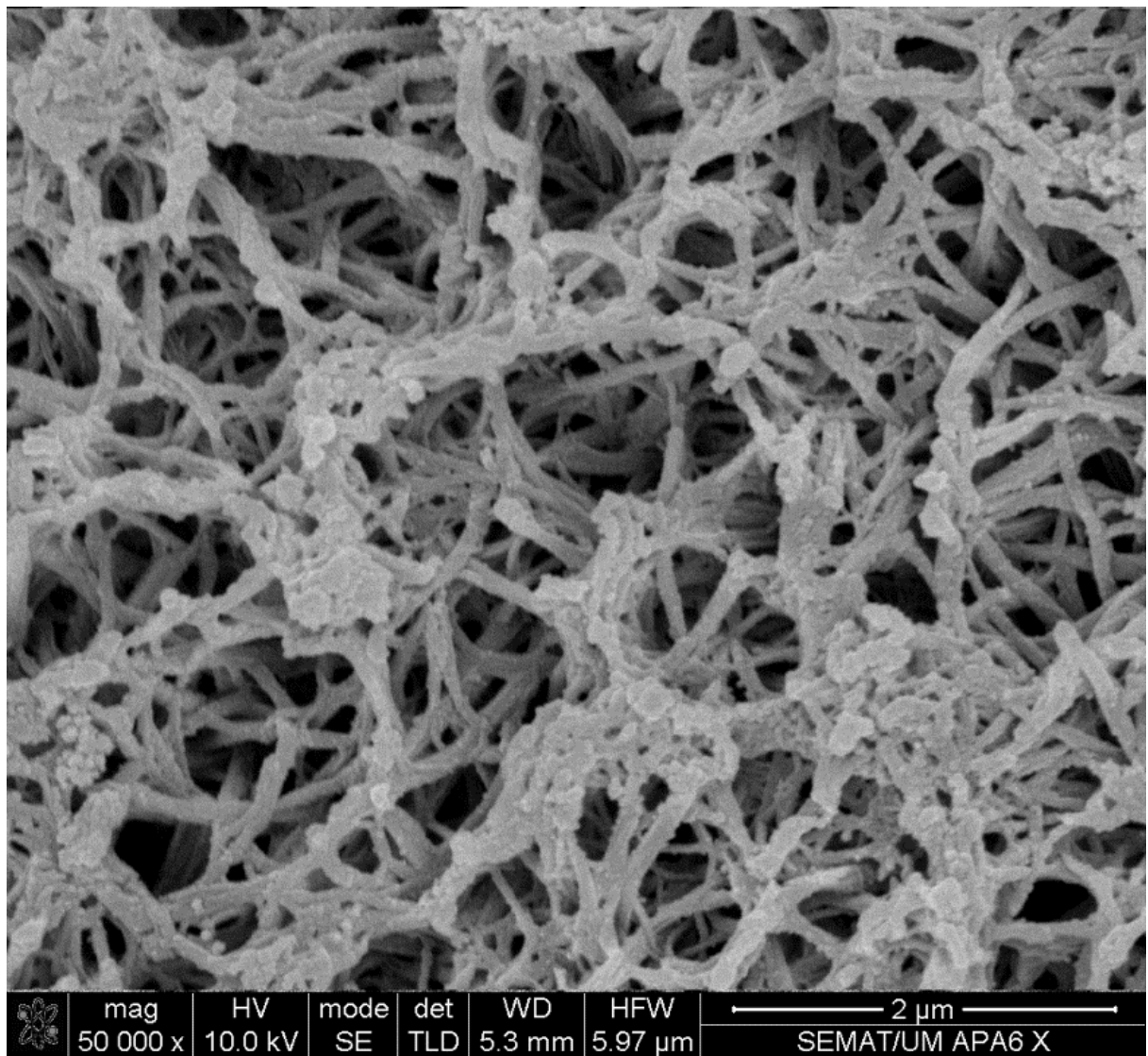
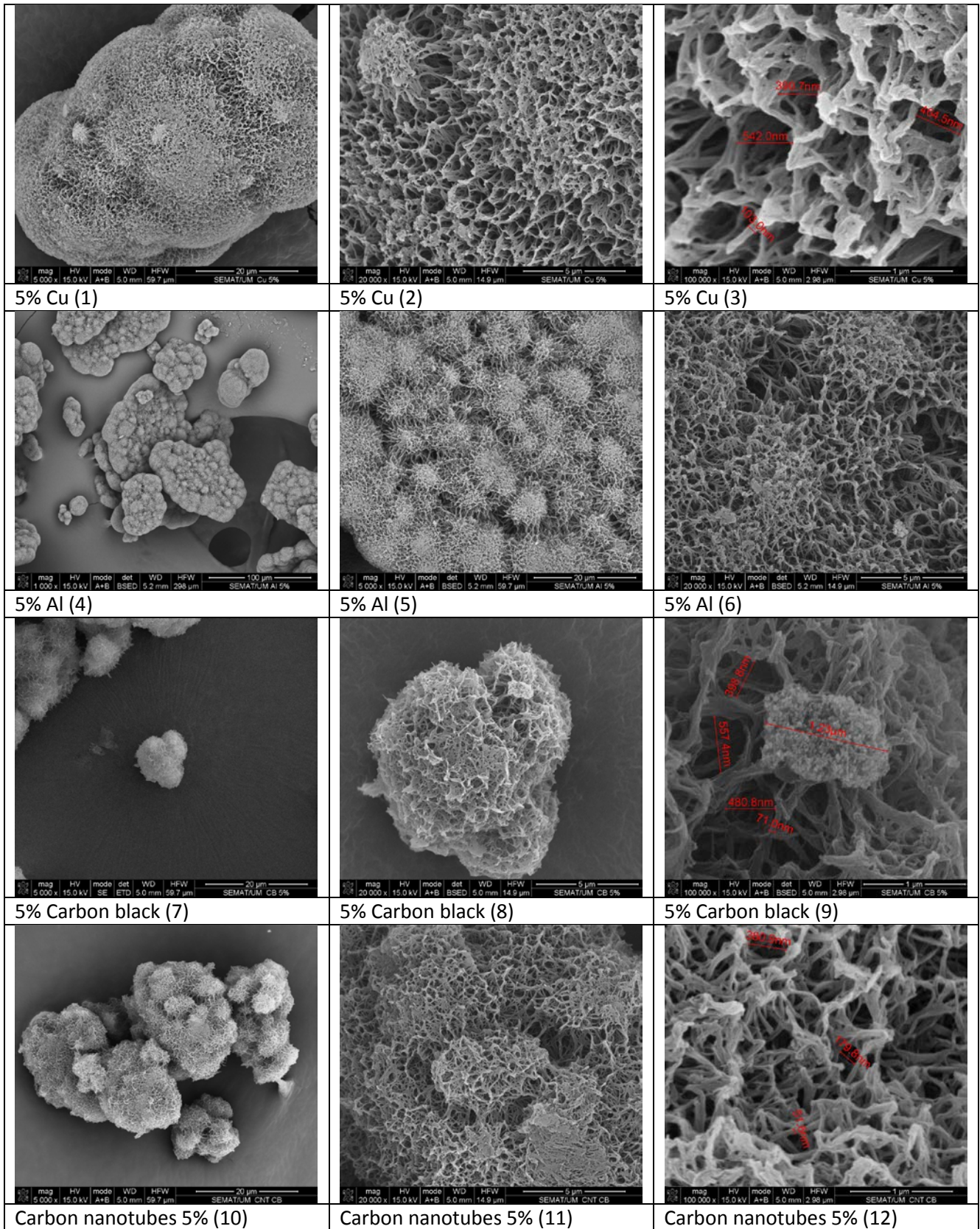


Figure 3



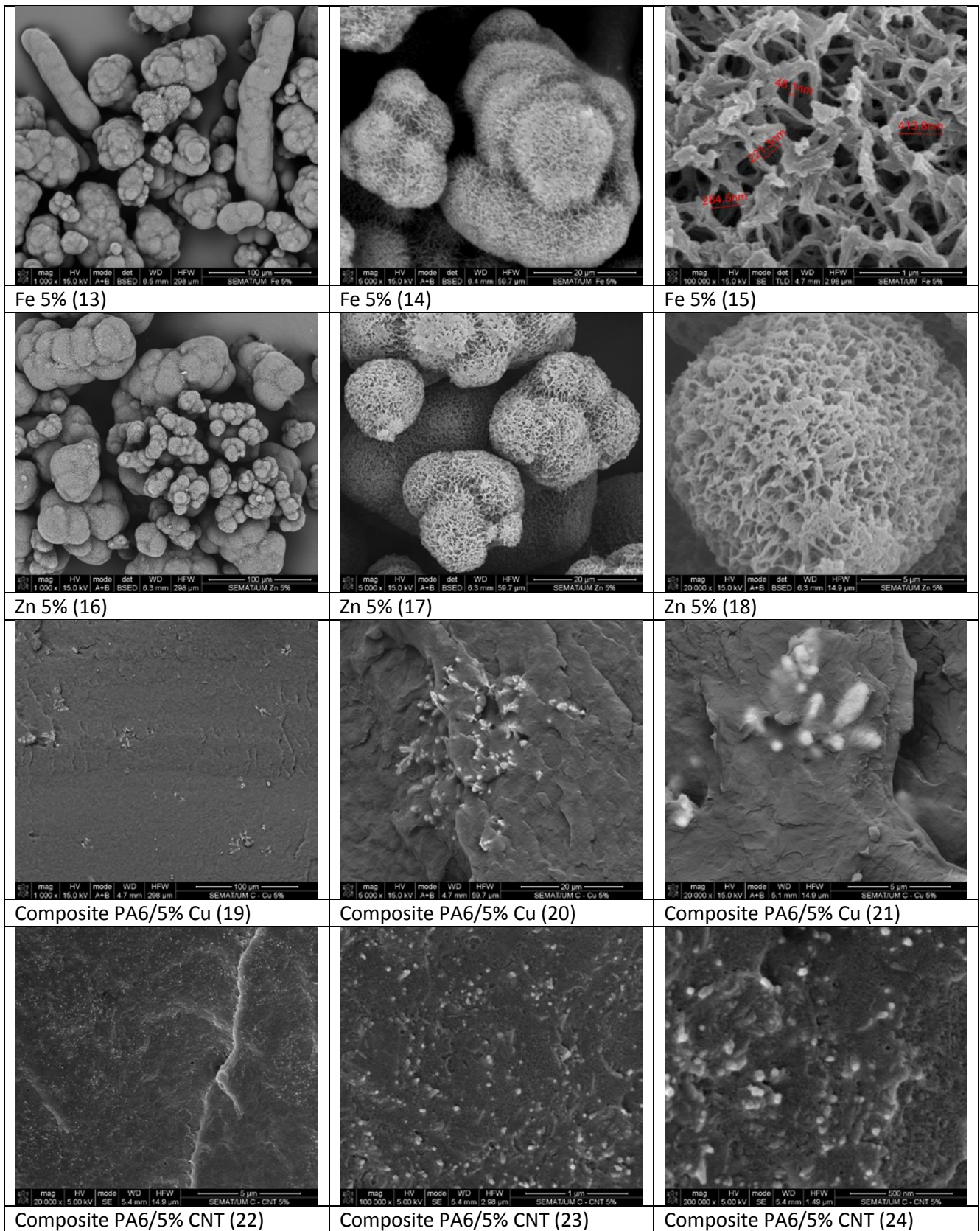


Figure 4