Development of Nanocomposites with Antibacterial Effect for Leather and Textile

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Abstract

The aim of this work is to develop new systems of nanocomposites to confer new functions to materials used for seats of public vehicles and public spaces. Specifically, this study focuses on antibacterial effect for leather and technical textile substrates.

The first stage of the research consists of a selection of micro/nanomaterials and active principles: selection and evaluation of nanoparticles, antibacterial and antifungal substances. In the second stage, the process of encapsulation of active principles was studied. The research includes optimization of the encapsulation process by improving the size and stability of the capsules. In addition, the synthesis of a hybrid organic-inorganic polymer acting as a nanomaterial carrier was developed.

To understand the mechanisms of synthesis and action of micro/nanomaterials, characterization techniques have been used: scanning electron microscopy SEM and optical microscopy, analysis and distribution of particle size (DLS, Zetasizer). Regarding the antibacterial and antifungal ability of nanocomposites, we adapted standard ASTM 2180-07 "Test methods for determining the activity or incorporated antimicrobial agent (s) in polymeric or hydrophobic materials."

Different products have been developed and the results obtained allow us to conclude that the synthesized products showed inhibition to the growth of bacteria and fungi on the contact surface.

1. Introduction

The materials involved in the manufacture of seats for public transport and public spaces, specifically leather and 3D technical fabric with hair (tissue-carpet), are subjected to highly extreme conditions of use, safety regulations, demanding physical characteristics, cleaning and maintenance problems (growth of mite, bacteria, low resistance to staining and dirt), and restrictions in content of certain substances. These are constraints that compromise the durability of the said materials[1,2].

Indeed, these materials for upholstery have shortcomings and limitations regarding user functionalities which can hardly be solved by present day technology.

The aim of this work is to develop new systems of micro/nanocomposites to confer new functions to materials used for seats of public vehicles and public spaces (i.e. antibacterial, fire-retardant, auto repair, self-cleaning and thermo control effects). Specifically, in this part of the work we will focus on antibacterial effect for leather and technical textile substrates.

The continuous use by multiple users of public transport seats and seats in public spaces makes the surface of these seats the ideal place for bacteria build-up. On the other hand, if seats are not properly stored during assemblage, excessive humidity in buildings (especially those under construction) facilitates the growth of fungi and bacteria in the leather. The ever growing concern on the part of the user about infections and the thorny issue of adequate protection of materials against fungi call for research into new antibacterial properties and fungicides to ensure protection for upholstery materials.

Nanoencapsulation can be defined as the process by which active substances are coated with materials of different nature, commonly polymeric, with the aim of forming particles of nanometric size. In contrast with conventional processes, nanocapsules have the advantage of protecting and masking the encapsulated substance from unstable or hostile media before its subsequent release, effected in a progressive manner or whenever it is required.

Different techniques can be used in the micro/nanoencapsulation of functional substances, as for example coacervation (i.e., phase separation), interfacial polymeryzation[3], miniemulsion polymerization, polymeric deposition or spray drying. A further technique, liposome formation (spheres formed by a double lipid layer), is based on biological systems of storage, finds large applications in the cosmetic[4] and pharmaceutical industry when used as drug delivery systems[5] and as bioorganic components[6].

With regard to the materials with a bactericide effect, one of the most widely used techniques today in nanotechnology is metallic nanoparticles. One of the approaches consists in including particles with biocidal capacity, as for example silver particles in the coatings. It is not clear though whether the silver particles only work as silver ions acting as a biocidal agent or whether the particles have a biocidal effect. This type of biocidal coating is currently being used for catheters and for surgical instruments, although it is the subject of debate[7].

There are also cosmetic products in the market (e.g., deodorant, and products from the food industry and the textile industry whose advertisements boast the hygienic benefits of using silver nanoparticles[8]. Even some washing machines and refrigerators are coated with silver nanoparticles[9].

One of the most commonly used techniques consists in embedding silver ions in zeolites (i.e., crystalline structures of silicon-aluminum). This produces the release of the ions, in the presence of environmental humidity, for a sustained time and at a controlled rate. The action of silver ions against microorganisms is three-fold: i) block the change of cellular tissues; ii) prevent cells from breathing; and iii) paralyze cell segmentation[10].

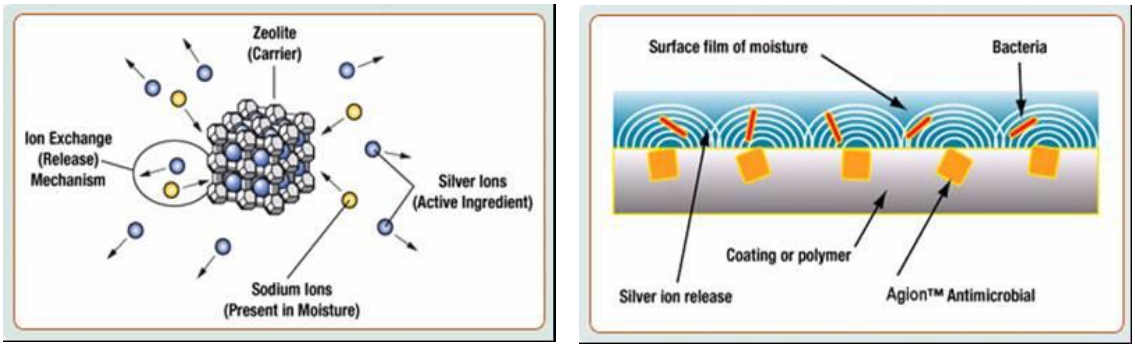

Figure 3. System of random release and distribution of zeolite particles in the coating[10]

There are in the leather sector coating patents containing silver nanoparticles[11] as well as studies focusing on finishing agents with derivatives of nano-SiO_2[12].

Despite the ever-growing applications of metallic nanoparticles and metal oxides in different sectors, the said application is far from being widespread due to difficulties relative to their size the and homogeneous dispersal of the particles, discoloration, limited efficacy, ion instability, and high operation costs.

This study is innovative in that it aims to obtain the antibacterial effect by combining the application of metallic micro/nanoparticles and micro/nanocapsules of antibacterial substances of natural origin.

To this end, the aim is to develop micro/nanocomposites with antibacterial effect by using different types of metallic micro/nanoparticles in combination with organic-inorganic hybrid nanodispersions of crosslinking polyurethane coatings of aqueous base. This will allow a fixation that is highly resistant to abrasion and to any treatment of the leather and the carpet fabric (even the aqueous wash), as well as a long lasting antibacterial effect. The aim is to enhance the effect of inorganic micro/nanomaterials by combining them with the use of various products of natural origin with reliable have a well known bactericidal and fungicidal effects. These products would be microencapsulated and nanoencapsulated using interfacial condensation techniques with self-dispersing polyurethanes-polyureas to prevent the use of products potentially harmful to the environment. Nanoencapsulation allows for the use of fluid materials and even of volatile materials, lengthening the time of its effect.

2. Experimental

The aim of this work is to synthesize a coating with capsules of natural oils of antibacterial effect and/or metallic particles in order to obtain the maximum resistance to abrasion on the one hand, and develop a proper bactericidal and fungicidal capacity on the other that will prevent infections through the materials the seats of public vehicles and public spaces are made of. A further aim is to protect the same materials against the growth of fungi, a common problem with leather, when the conditions of storage are moist and therefore not appropriate.

Three means of syntheses are employed in order to obtain these aims:
1. Encapsulation of oils with bactericidal and fungicidal effect.

2. Synthesis of coated silver particles.
3. Coatings with polymers that incorporate reactives with known antibacterial effect in their structure.

The present work examines the most appropriate technology to obtain hybrid organic-inorganic micro/nanoencapsulated polymers of polyurethane base with crosslinking capacity.

The products obtained have to enable high performance of leather goods and tissue-carpet (including the aqueous wash) as well as a lengthy bactericidal effect. Therefore, the following will be assessed:
-Moistening power and penetration of micro/nanocomposites.
-Affinity for the collagenous structure of leather.
-Antibacterial capacity of micro/nanocomposites.

To understand the mechanisms of synthesis and action of micro/nanomaterials, characterization techniques have been used: scanning electron microscopy SEM and optical microscopy, analysis and distribution of particle size (DLS, Zetasizer). Regarding the antibacterial and antifungal capacity of micro/nanocomposites, we adapted standard ASTM 2180-07 "Test methods for determining the activity or incorporated antimicrobial agent (s) in polymeric or hydrophobic materials."

3. Results

3.1. Encapsulation of natural oils of antibacterial effect

First, 7 tests of synthesis are carried out according to different methods. Table 1 presents a summary of the characteristics of synthesis and the results obtained.

Table 1. Summary of characteristics and results obtained in first seven syntheses

Product	Characteristics	Results
A1	Aliphatic isocyanate + difunctional amine + 2 oils	Lumpy emulsion
A2	Aromatic isocyanate + difunctional amine + stabilizers + 2 oils	Emulsion obtained is not very good
A3	Aliphatic isocyanate + difunctional amine + stabilizers + oils	It is more stable
A4	Aliphatic isocyanate + difunctional amine + stabilizers + 2 oils + more water than A3	Stable emulsion, capsules around 1µm in size
A5	Aliphatic isocyanate + fatty difunctional amine + emulsionants + 2 oils + water	Highly foamy emulsion, capsules between 1-10 µm in size
A6	Aliphatic isocyanate + difunctional amine + stabilizers + 2 oils + water plus dilute	Stable emulsion, capsules between 1-10 µm in size, highly uniform
A7	Aliphatic isocyanate + difunctional amine + stabilizers + 1 oil + water plus dilute	Stable emulsion, capsules between 1-10 µm in size

The capsules obtained with the first 7 syntheses are quite large. Therefore, in order to obtain a particle smaller in size a new product is synthesized changing the type of agitation. In this case, product A8 is synthesized with the following characteristics: aliphatic isocyanate + difunctional amine + stabilizers + 1 oils + water plus dilute + more agitation. The emulsion obtained with this synthesis is stable and with smaller particles. The capsules obtained are shown in figure 1.

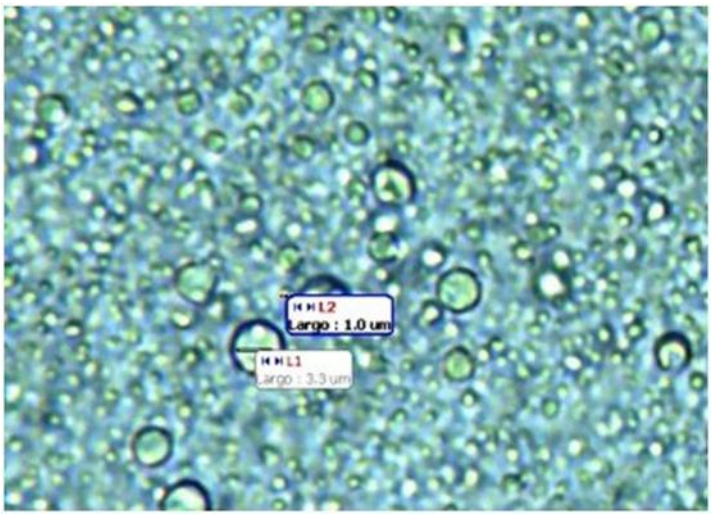

Figure 1. Image of product A8 diluted at 5% obtained under the light microscope (magnification: 400×)

From this point, 3 new products are synthesized (A9-A11) by means of a different method: the amphiphile system. Table 2 shows a summary of the characteristics of synthesis and the results obtained.

Table 2. Summary of characteristics and results obtained with syntheses with amphiphile system

Product	Characteristics	Results
A9	amphiphile system	Good emulsion, small capsules but not well defined
A10	amphiphile system with diferent concentration of polymer	Good emulsion, capsules below 0.5 µm and some 4 µm in size
A11	amphiphile system with greater crosslinking	Good emulsion, capsules of 1 µm and 5 µm, not very spherical

The particles obtained by the amphiphile system are depicted in Figure 2. As can be observed, the capsules obtained are smaller but not properly defined.

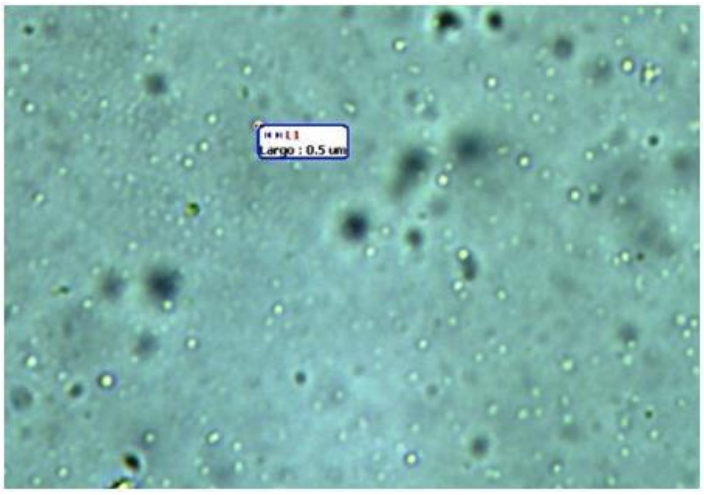

Figure 2. Image of product A9 obtained under the light microscope (magnification: 400×)

Though this means of synthesis, the emulsion obtained by encapsulating only antibacterial oils is not stable enough. Indeed, oil is required to help forming capsules in the interphase. To obtain a more stable emulsion with capsules more homogeneous in size, prior to the emulsion the sample must be below 40% of solids.

3.2. Synthesis of coatings with polymers incorporating reactants with known antibacterial effects in their structure

After the first results obtained, research focuses on the study of now products of lower capsule size. Table 3 shows a summary of the characteristics of synthesis and the results obtained.

Table 3. Summary of the characteristics and results obtained in synthesis of products A12, A13, and A14

Product	Characteristics	Results
A12	Fatty alcohol + anti-dirt	Stable emulsion
A13	Fatty amine + anti-dirt	Stable emulsion
A14	Fatty diamine + anti-dirt	No product is obtained

The products obtained with these syntheses did not conform exactly to the antibacterial requirements for application on leather; therefore this means of synthesis is discarded.

3.3. Synthesis of coatings with silver particles

In this case the aim is to encapsulate the silver ion. As can be seen in figure 3, a mixture of capsules and crystals is obtained.

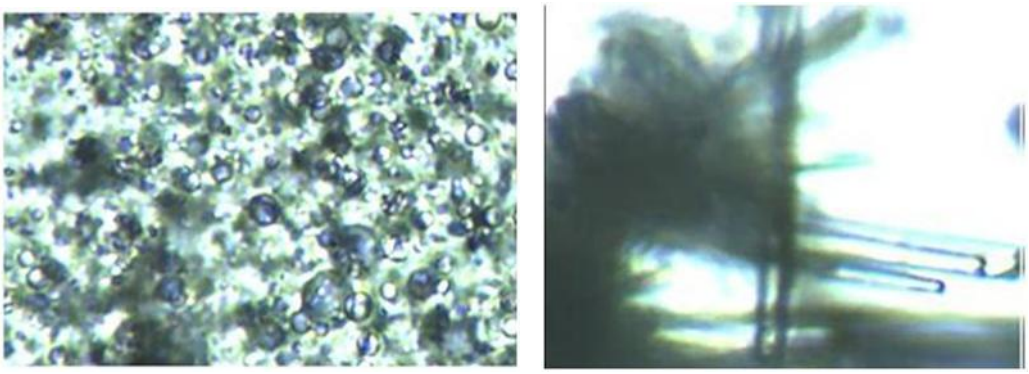

Figure 3. Image of product A15 obtained under the light microscope (magnification: 400×)

Three new products are synthesized from this product by modifying the system of synthesis. Table 4 shows the characteristics of synthesis and the results obtained.

Table 4. Summary of characteristics and results obtained in the synthesis with silver ion

Product	Characteristics	Results
A15	Encapsulated silver ion	Gray emulsion
A16	Encapsulated silver ion	Capsules around 0.6 μm in size
A17	Encapsulated silver ion	Under the light microscope Presence of capsule sis predicted, but it cannot be verified
A18	Encapsulated silver ion	No capsules can be distinguished

According to the results obtained, products A8 and A9 are considered the most appropriate for application to the leather and the tissue-carpet. Since the desirable product has to be highly versatile, a new product resembling A8 is synthesized but with less resistant capsules and more vulnerable to microorganism attack so that, with the mixture, the antibacterial effect can last longer. A8 is the most enduring compound; A22 will only have an effect in the presence of microorganisms; A9 has an immediate effect.

The characteristics of A22 are the same as those of the A8 synthesis but using a different amine. The resulting emulsion is quite thick, with capsules between 1.2 and 0.5 μm.

3.4. Characterization of the selected compounds

A characterization is carrie out by means of SEM microscopy; analysis of distribution of Zetasizer particle size and analysis of morphology are made using the Morphologi G3S. It is an instrument of analysis of morphological parameters of particulate samples consisting of a light microscope combined with an image treatment software that generates statistical distributions of size, length, width, elongation, aspect ratio such as circularity and convexity, from all the particles visualized.

As for nanocompound A8, a morphological analysis of the following situations was made:

- The sample when applied to the surface of MYLAR
- The same sample after having made a lateral movement of friction with a round object with low hardness.

The images correspond to the same zone of capsules of sample A8 before the movement of friction and after the friciton. It can be observed that the movement of friction produces the heating or opening of most of the capsules, since the size increases and the capsules go on to show two concetric layers.

The statistical distributions show that through the frictional movement:

Particle size distribution moves toward higher values. In the two dimensions visualized, the heating of the capsules causes the increase of their size.

- The circularity of the sample increases –the open capsules also show a high circularity.

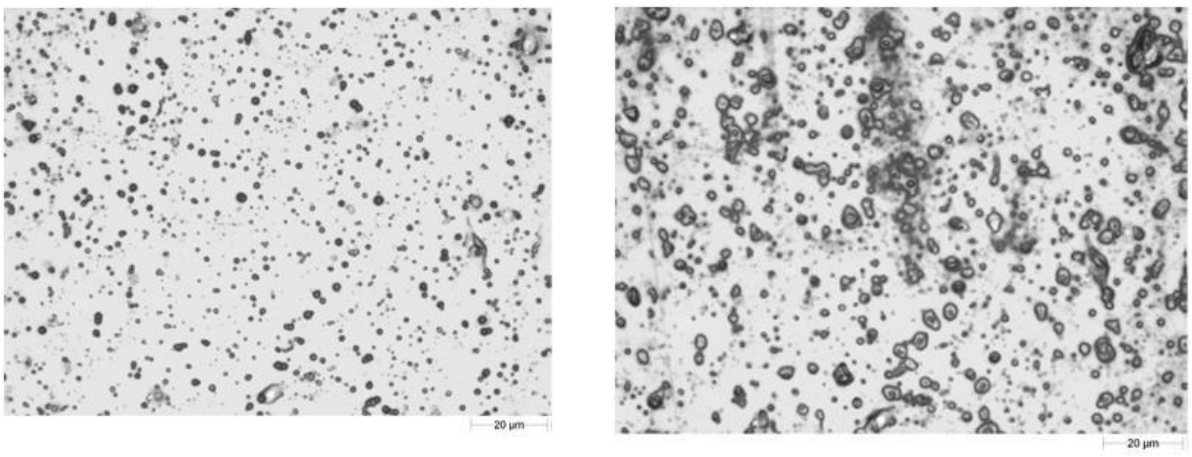

Figure 4. Images obtained with the Morphologi G3 before and after scratching the capsules of product A8

The graph below shows the comparison of diameter distribution of equivalent sphere of product A8 capsules.

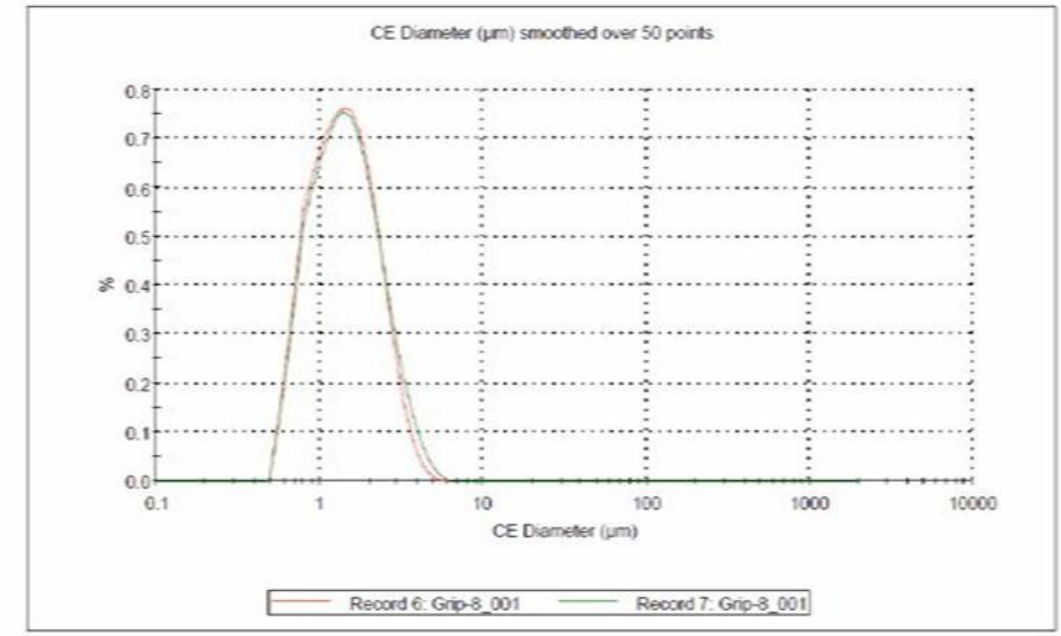

Figure 5. of Diameter distribution in samples subjected to friction. Red line displays sample before friction; green line displays sample after friction.

The graph below shows the comparison of the behavior relating to the maintainance of the original shape of capsules when subjected to friction.

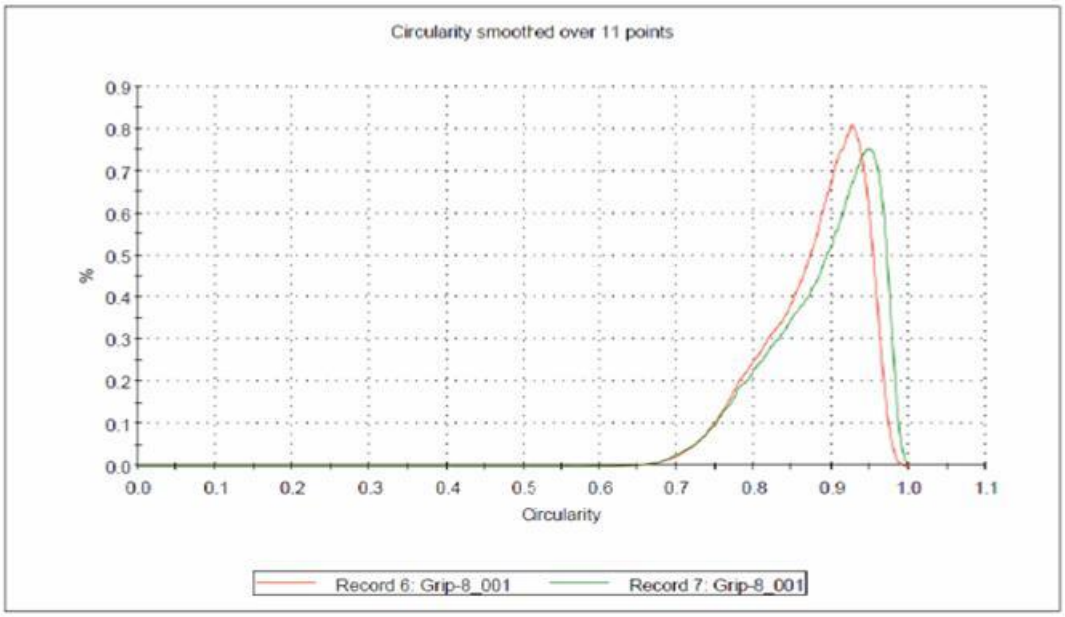

Figure 6. Comparison of circularity distribution (statistics in number of particles). Red line depicts sample before friction; green line depicts sample after friction

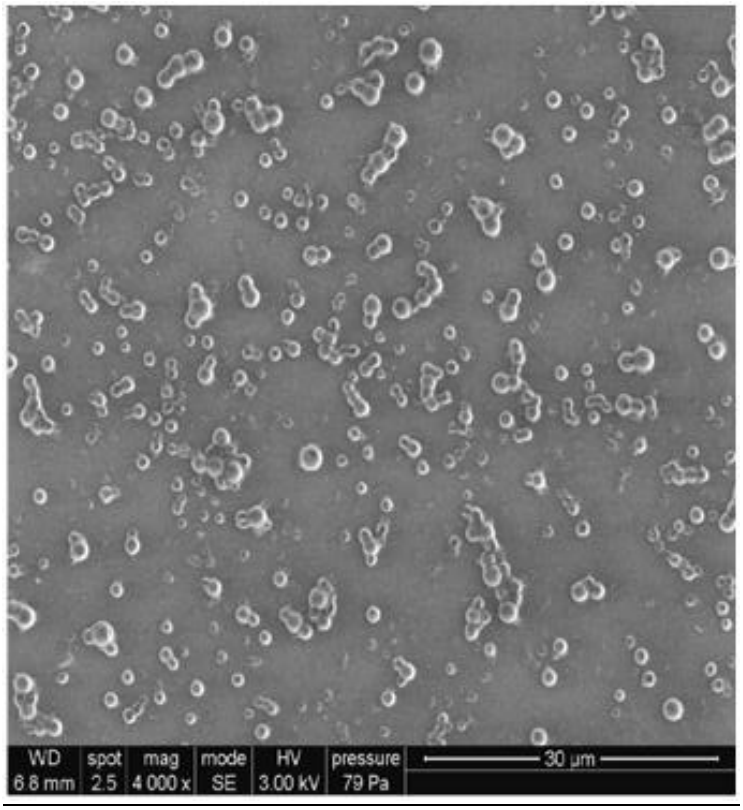

Figure 7. SEM image of product A8 (magnification: 4000×)

To determine capsule size distribution, the Zetasizer instrument is used on the test. The average values obtained are 1451 nm.

Figure 8. Distribution of measurement of product A8 capsules

The results of distribution analysis of A9 capsule size yielded average values of 225 nm.

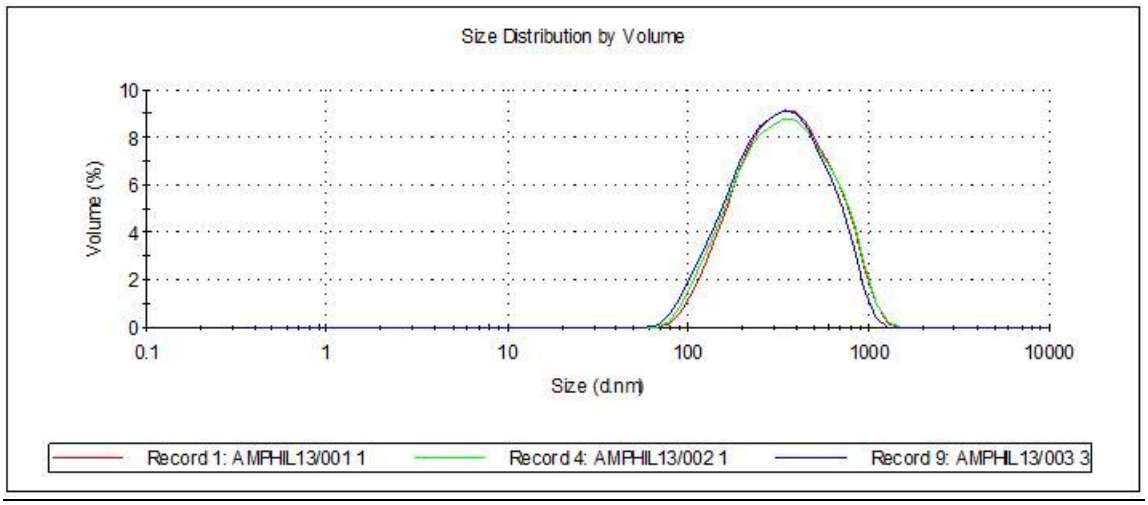

Figure 9. Distribution of product A9 capsules (Zetasizer)

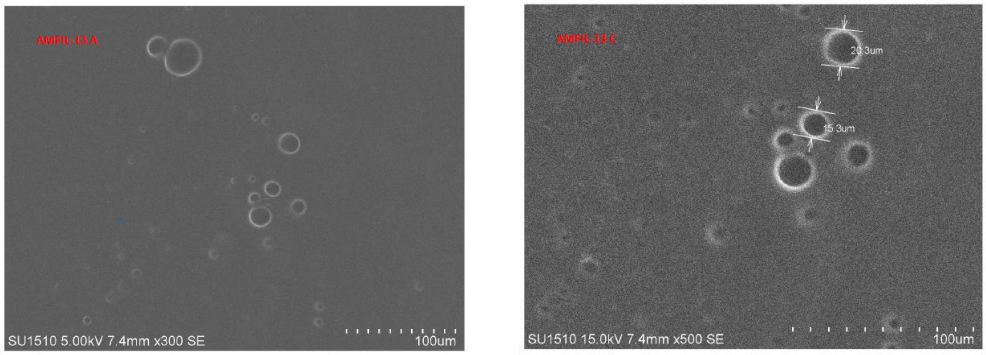

Figure 10. SEM image of product A9 (magnification: 3000×)

The measurement test of particle size distribution using the Zetasizer instrument indicates that the value of capasule size is 1000 nm.

The observation under the SEM microscope shows the product capsules (figure 11).

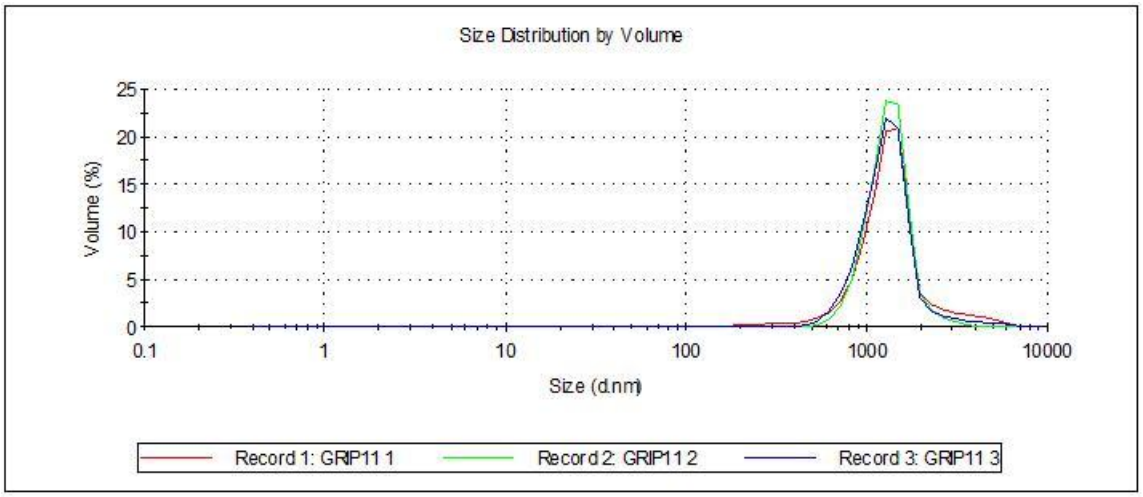

Figure 11. Size distribution of product A22 capsules

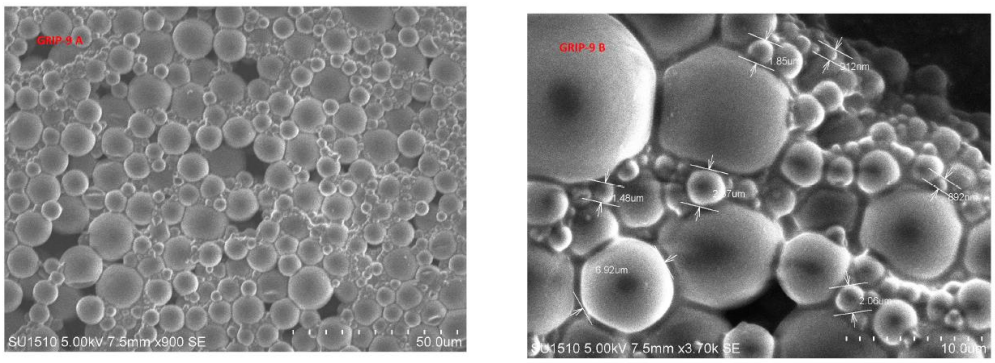

Figure 12. SEM image of product A22 (magnification: 3000×)

3.5. Bactericidal and fungicidal capacity of the selected compounds

The antimicrobial effect of the nanocomponds described in the previous sections is determined by adapting the standard ASTM 2180-07 "Test method for "Determining the activity or incorporated antimicrobial agent (s) in polymeric or hydrophobic on materials".

This method allows for the quantitative determination of antimicrobial effect of incorporated agents or joined to bidimensional surfaces by means of incubation of inoculated Agar (with different mircroorganisms of a known concentration) on the surface of the material (treated with antimicrobial agent), a fact that facilitates contact between surface and microorganisms. Once contact time is completed, the effect on microbial growth is quantified when compared with growth obtained on the control material (without the incorporated agent).

The products are absorbed in a pore matrix (nylon filters of 0.45µm in pore size). This procedure is carried out by means of two techniques: vacuum filtration with negative pressure and filter surface scattering. The filters obtained are used as bidimensional material to carry out the test.

The microorganisms used are the following:

- *Escherichia coli* (Determination of bactericide effect)
- *Aspergillus niger* (Determination of bactericide effect)

Once contact time is completed (incubation time), the medium is resuspended and viable microorganisms of both filters with product and control filters are plate counted.

Next, the results obtained for each of the products are presented in detail.

Table 5. Quantitative determination of antibacterial effect of products A8, A9, and A22

Product	**Microorganism**	**UFC/mL recovered control filter**	**UFC /mL recovered product with filter**	**% antimicrobial effect (reduction of microorganism growth)**
A8	*E.coli*	7.6×10^4	< 30	> 99%
A8	*A.niger*	3.5×10^2	3.5×10^2	< 5%
A8 filtrate; pore size 1 µm	*E.coli*	7.6×10^4	< 30	> 99%
A8 filtrate; pore size 0.45µm	*E.coli*	7.6×10^4	< 30	> 99%
A22	*E.coli*	7.6×10^4	< 30	>99%
A22	*A.niger*	3.5×10^2	10	97%
A22 filtrate	*E.coli*	7.6×10^4	< 30	>99%
A9 filtrate; pore size 0.45µm	*E.coli*	7.6×10^4	$1x10^3$	98%
A9	*E.coli*	7.6×10^4	$5.9x10^4$	22.40%
A9	*A.niger*	3.5×10^2	< 10	>99%
A9 filtrate; pore size 0.45um	*E.coli*	7.6×10^4	< 30	>99%
Mixture (A8+A22+A9)	*E.coli*	7.6×10^4	< 30	>99%
Mixture (A8+A22+A9)	*A.niger*	3.5×10^2	1.8×10^2	49%
Mixture filtrate (A8+A22+A9)	*E.coli*	7.6×10^4	< 30	>99%

The pictures below show the differences in bacterial and fungi growth.

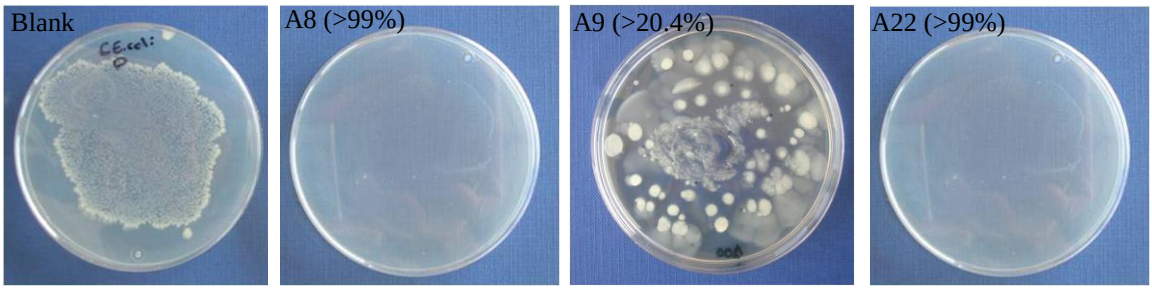

Figure 13. Antimicrobial effect on Echerichia coli

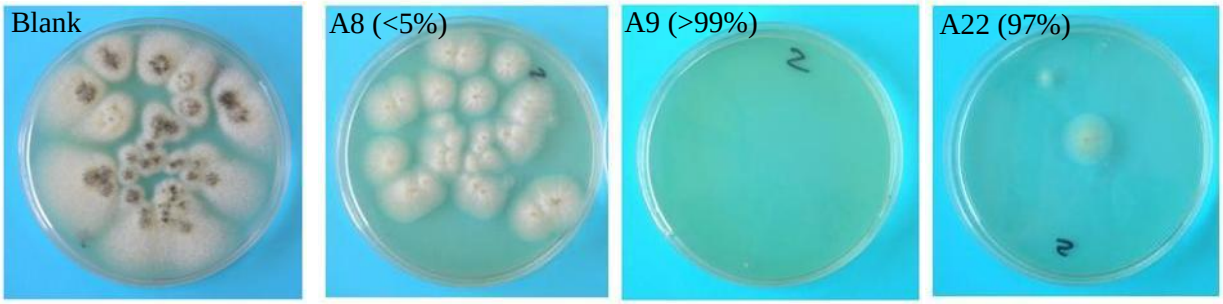

Figure 14. Antimicrobial effect on Aspergillus Niger

We can conclude, from the studies carried out, that the synthesized products have inhibition of bacterial and fungi growth in the surface contact.

To end, table 6 shows the characterstics of the emulsions of syntheiszed products A8, A9, and A22:

Product	Parameter	Result
A8	Solids	5%
	Format	Aqueous dispersion
	Appearance	White
	Polymer content (DIN EN ISO 3251)	3.5±0.1%
	Antibacterial oil content	1.84%
	Capsule size	1 – 10 µm
	pH (DIN 53 785)	7.05
	Density (20ºC) (DIN 51 757)	1.04g/ml

A9	Solids	26%
	Format	Dispersió aquosa
	Appearance	Blanc-grogós
	Polymer content (DIN EN ISO 3251)	15.6%
	Antibacterial oil content	9.61%
	Capsule size	240-250 nm
	Density (20ºC) (DIN 51 757)	1.03± 0.02 g/ml
A22	Solids	64.16%
	Format	Dispersió aquosa
	Appearance	Blanc
	Polymer content (DIN EN ISO 3251)	27.63%
	Antibacterial oil content	6.87%
	Capsule size	1 - 5 µm

And finally, we can observe the results obtained when working with the mix of A8, A9 and A22.

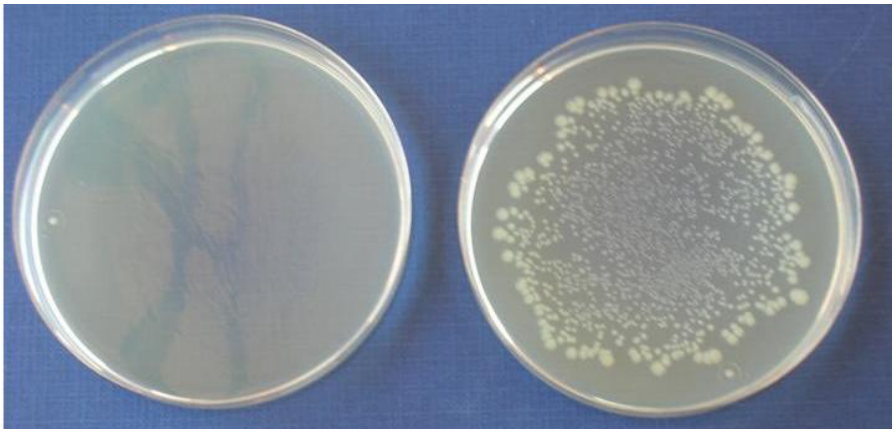

Figure 15. Blank sample showing growth and antimicrobial effect (>95%) of mix on Echerichia coli

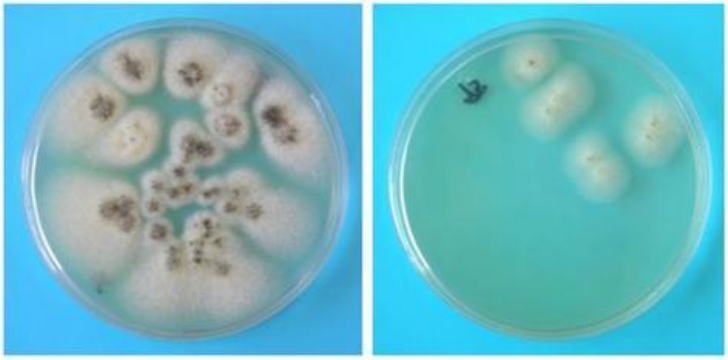

Figure 16. Blank sample showing growth and antimicrobial effect (49%) of mix on Aspergillus niger

4. Conclusions

The characterization of the nanocomposites obtained with the instruments (SEM, particle size analysis and DSC) provided us a greater understanding of how nanomaterials act. This is important for the optimization of the developed products and for the design of a methodology that is more appropriate for the application to the leather substrate and tissue-carpet in subsequent activities of the project.

The most suitable products for application to the substrates is a mixture of different types of capsules with walls with different time behavior relative to the stability and mixture of capsules with different active principles (mixture of 3 different types of encapsulations of antibacterial oil).

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6. Aknowledgments

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