BIOCIDAL ACRYLIC LATEXES PREPARED BY MINIEMULSION POLYMERIZATION FOR WOOD COATING APPLICATIONS

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Summary

Miniemulsion polymerization was used to synthesize biocidal latexes so that they can be employed in water-based wood coatings formulations. Silver nanoparticles functionalized with different ligands of varying nature and length were incorporated in acrylic polymer particles. Depending on the synthesis used, silver nanoparticles obtained have a size ranging from 6 nm to 13 nm. Dynamic light scattering analysis shows that regardless of the type of silver nanoparticles, the size of the polymer particles does not vary significantly and that the resulting latexes have a mondisperse size distribution. Latex stability and resistance to three fungi strains; *E. nigrum*, *P. funiculosum* and *A. niger* were investigated. The acrylic latexes containing silver nanoparticles synthesized in this study are stable in time and show antifungal activity against *E. nigrum*, *P. funiculosum* et *A. niger* at low silver concentration (0.1% m/m).

1. Introduction

Fungal growth is a serious problem for outdoor wooden structures and sidings. Fungal attack modifies the mechanical and aesthetic properties of wood, thus reducing its performance. This slows the growth in market share of external wood products at the expense of alternative materials such as fibercement and vinyl (Freedonia Group, 2014). Moreover, fungal growth on outdoor wooden structures and sidings has an economic impact on the market; in the state of California alone, it is estimated that building decay costs 364$ million annually (Morrell, 2012).

Growing consumer awareness of health and environment issues, combined with new regulations for architectural coatings and energy efficient building codes, stimulates the emergence of new products and technologies. The utilization of exterior thermal insulation composite systems (ETICS) or Exterior Insulation and Finish Systems (EIFS) as a high energy saving building technology promotes condensation which, in turn, increases susceptibility to fungal attack (Wangler *et al*., 2012). Coupled with the utilization of waterborne coatings, which require greater quantities of biocides (Künniger *et al*., 2014), durable, antifungal coatings with high performance are in great demand to protect wood and increase its service lifetime. However, organic biocides are more expensive than their predecessor; chromated copper arsenate (CCA) (33-55$/kg versus 3$/kg for CCA) (Green III and Schultz, 2003). Organic biocides can also deteriorate over

time with ultraviolet radiation and thus lose their effectiveness. The replacement of organic biocides with nanomaterials is one of the avenues considered by the paint industry (Kaiser, Diener and Wick, 2013).

The antibacterial power of silver and its salts has been known for a long time (Rai, Yadav and Gade, 2009; Russell and Hugo, 1994). However, the arrival of nanotechnology has allowed the development of new applications by enabling access to new chemical and physical properties of metals, mainly due to the increase of the surface/volume ratio. We are witnessing a renewed interest for silver and silver-containing materials, driven, among others, by the medical field, where more and more bacteria are showing resistance to common antibiotics. Several studies have been conducted on the antibacterial activity of silver nanoparticles. These studies demonstrated the antibacterial action of silver nanoparticles against more than 12 types of bacteria including *Escherichia coli* and *Staphylococcus aureus* (Kim *et al*., 2007). In addition to having excellent antibacterial activity for both Gram-positive and Gram-negative bacteria (Panacek *et al*. 2006), these nanoparticles are also effective against fungi, viruses and algae (Marambio-Jones and Hoek, 2010). However, the mechanism for this activity is not fully understood and several contradictory studies are found in the literature. Morones and co-workers (Morones *et al*., 2005) demonstrated that silver nanoparticles attach to the cell membrane and penetrate within the cell, thus modifying its membrane and DNA. Other studies demonstrated that silver nanoparticles cause cell death by oxidative damage but not because of a modfication in DNA (Hwang *et al*., 2008). Silver ions (Ag^+) are also assumed to have a role in the antibacterial power. Ag^+ ions should react with protein thiol groups, resulting in their inactivation (Feng *et al*., 2000). On the other hand, proteomic analyzes carried out by Lok *et al*. (Lok *et al*., 2006) established that silver nanoparticles and silver ions appear to have the same mechanism of action.

When compared to organic biocides, silver presents numerous advantages, such as stability at high temperature, resistance to degradation, being odorless and having low volatility. For all the reasons outlined above, silver nanoparticles are considered by the paint industry as a good alternative to conventional organic biocides (Kaiser, Diener and Wick, 2013). Currently, some indoor and outdoor paints containing silver nanoparticles exist, but they still represent a niche market (Künniger *et al*. 2014). Moreover, one of the main concerns of using these nanomaterials is the possibility of leaching and long-term effects on humans and the environment. Leaching of nanoparticles reduces the coating properties and may result in silver accumulation in soils and water. Although it has been shown that nanoparticles can be fixed effectively to the coating matrix and the risks of leaching into surrounding water and soils is low (Gladis *et al*., 2010), other studies have shown that leaching of nanoparticles remains problematic. Kaegi *et al*. (Kaegi *et al*., 2010) report that 30% of the total amount of silver nanoparticles applied in an outdoor façade was released after one year and of this number, more than 80% of the total amount was released during the first two months of the study. It is assumed that the encapsulation of nanoparticles in polymer particles could decrease leaching. Miniemulsion polymerization has already been used to encapsulate organic pigments (Steiert and

Landfester, 2007) and inorganic nanoparticles (Costoyas, Ramos and Forcada, 2009; Erdem *et al*., 2000). This polymerization technique has been used over the traditional emulsion polymerization to encapsulate inorganic particles into polymer particles as it offers a better control of the structure, morphology and size of the nanocomposites spheres (Hu, Chen and Wu, 2011). In this work, the antifungal activity and stability of latexes containing functionalized silver nanoparticles, prepared by miniemulsion polymerization, is investigated.

2. Methodology

2.1 Silver nanoparticles synthesis

2.1.1 Particles functionalized with oleylamine ligand

This synthesis, based on the work of Cheng *et al.* (Chen *et al*., 2007), allows for the preparation of silver nanoparticles of 10 to 15 nm in size, stabilized with oleylamine. In a three-neck round-bottom flask, 0.455g of silver nitrate ($AgNO_3$) is dissolve in 3 mL of oleylamine and 60 mL of paraffin. The solution is mechanically stirred, under nitrogen, for 20 minutes at room temperature. The three-neck round-bottom flask is then placed in a thermostated paraffin bath and heated under reflux. The temperature is gradually increased at the rate of 4°C/min until a temperature of 180°C is reached. This temperature is maintained for 2 hours in order to reduce the silver present in the medium. The temperature is then decreased to 150°C and maintained for 6 hours. When the solution has returned to room temperature, 20 mL of chloroform and 60 mL of acetone are added. The solution is then centrifuged at 15 000 rpm for 15 minutes. After centrifugation, the supernatant is removed and the silver nanoparticles are redispersed in a minimum of chloroform. Acetone is then added and the suspension is centrifuged at a speed of 5000 rpm for 5 minutes. This last washing step is repeated twice.

2.1.2 Particles functionalized with thiol ligands

Silver nanoparticles functionalized with thiol ligands (octanethiol and butanethiol) are obtained by a modification of the method published by Kang *et al*. (Kang and Kim, 1998). In an Erlenmeyer, 0.1533g of silver nitrate is dissolved in 30 mL of ethanol. To this solution, 0.1 mL of ligand (octanethiol or butanethiol) is added drop wise. In a beaker, a saturated solution of $NaBH_4$ is prepared in 60 mL of ethanol. The saturated solution is added drop wise to the silver nitrate solution over a period of 2 hours, under vigorous stirring. Finally, the solution is placed in a freezer for 4 hours at -18°C. The supernatant is aspirated and the nanoparticles are redispersed in a minimum of chloroform.

2.2 Latex synthesis

The latexes are prepared by miniemulsion polymerization. Firstly, monomers and the hydrophobic agent (hexadecane) are mixed together in a beaker. In a second beaker, surfactant (SDS) and sodium bicarbonate ($NaHCO_3$) are dissolved in nanopure water. The organic phase is added to the aqueous phase and the resulting solution is stirred mechanically for 1 hour. The mixture is sonicated using an ultrasonic probe. The miniemulsion is then transferred to a three-neck round bottom flask and purged under nitrogen for 20 minutes. The initiator (KPS) is added and the system is heated under reflux for 4 hours at 70°C. The quantities of each component used to obtain a latex with a solid content of 15% are provided in Table 1.

Table 1 List of the reactants and quantities used to obtain a latex with a solid content of 15% weight by miniemulsion polymerization

Products	Quantity (g)	Concentration
Methyl methacrylate (MMA)	3,795	
Butyl acrylate (BuA)	3,697	15% wt.
Acrylic acid (AA)	0,075	
Potassium persulfate ($K_2S_2O_8$)	0,150	2% wt.[b]
Hexadecane	0,100	1% wt. [b]
Sodium dodecyl sulfate(SDS)	0,450	40 mM[a]
Sodium bicarbonate ($NaHCO_3$)	0,004	0,5 mM[a]

[a] with respect to the aqueous phase

[b] with respect to monomers

For the synthesis of latexes containing silver nanoparticles, the same procedure is followed except that the functionalized silver nanoparticles are added to the initial monomer mixture so that the mass of the nanoparticles corresponds to 0.1% of the solid mass of the latex.

2.3 Characterization methods

2.3.1 Transmission electronic microscopy (TEM)

A transmission electronic microscope was used to determine the size of the silver nanoparticles. The JEOL JEM-1230 microscope was operated at an acceleration voltage of 80kV. One drop of latex was deposited on a TEM grid and dried at room temperature before being analyzed.

2.3.2 Dynamic light scattering

The size and size distribution of the polymer particles in suspension were determined with a Zetasizer Nano ZS from Malvern. This apparatus is based on the principle of dynamic light scattering which correlates particle size to Brownian motion. This technique provides the average size distribution of the particles (z-average) and the polydispersity index (PDI). A polydispersity index of 1 means that the sample in question has a broad size distribution, whereas values under 0.05 indicate quasi-monodispersity and are rarely obtained, except for standard latexes.

2.3.3 Fungi resistance tests

The method used to evaluate the fungi resistance of the synthesized latexes is based on the ASTM Standard D5590-00 (2005b) «*Standard Test Method for Determining the Resistance of Paint Films and Related Coatings for Fungal Defacement by Accelerated Four-Week Agar Plate Assay*». This standard allows the evaluation of a latexes resistance to fungal growth in an accelerated manner. For these tests, four fungi strains were used; *Aspergillus niger*, *Penicillium funiculosum*, *Aureobasidium pullulans* and *Epicoccum nigrum*, at a concentration of 1.2 x10^6 spores/mL. In order to reduce the number of samples, the *Aspergillus niger* solution and *the Penicillium funiculosum* solution were mixed. The spore suspensions were prepared by adding 10 mL of sterile distilled water to a petri dish containing the fungus strain. The fungus was then gently lifted off the agar gel and the solution was stirred and filtered. The collected filtrate constitutes the spore solution. The concentration of spores is determined by optical microscopy and if necessary, the solution is diluted with sterile distilled water.

The substrate used is filter paper (Glass fiber, grade 391, 4.2 cm) cut in squares of 1 inch x 1 inch and presterilized. Once dry, filter papers are impregnated with each latex and placed on an enriched agar 2 % malt extract. A few drops of the different spore solutions are deposited on the filter papers. Each filter paper should be covered with the same amount of spore solution. Petri dishes are sealed and incubated at 28°C and a relative humidity of 85-90%, for 4 weeks. Each week, a visual assessment of the petri dishes is made according to the grading scale provided by the standard. This scale is shown in Table 2.

Table 2 Rating of the observed growth according to the standard ASTM D5590-00

Observed growth	Rating
None	0
Traces	1
Light growth (10-30%)	2
Moderate growth (30-60%)	3
Heavy growth (60% et plus)	4

3. Results and Discussion

3.1 Silver nanoparticle characterization

The size and distribution of the silver nanoparticles was evaluated from transmission electron microscopy (TEM) images. The TEM image of the silver nanoparticles functionalized with oleylalmine is presented in Figure 3. The size distribution of this population is also shown, and indicates an average diameter of 13 nm.

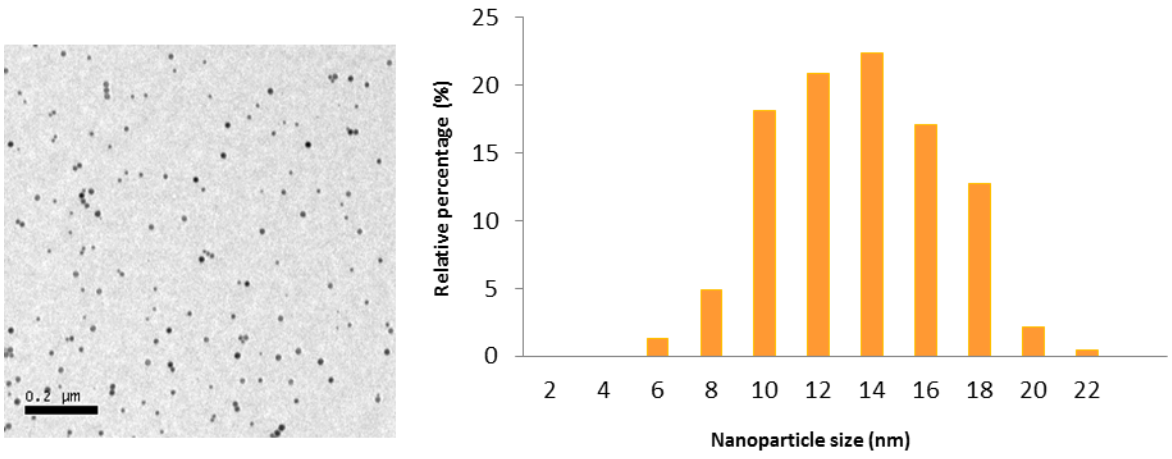


Figure 3 TEM image of the silver nanoparticles functionalized with oleylamine and corresponding size distribution of the population.

The size distributions of silver nanoparticles functionalized with different thiol ligands are illustrated in Figures 4 and 5. Silver nanoparticles with an average size of 6 nm are obtained with octanethiol ligands.

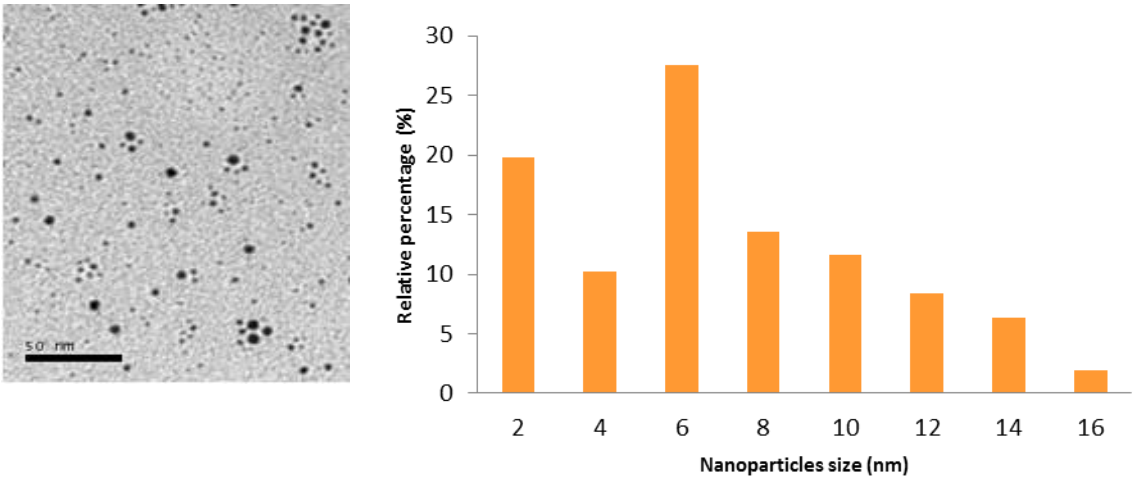


Figure 4 TEM image of the silver nanoparticles functionalized with octanethiol and corresponding size distribution of the population.

In the case of the synthesis with the butanethiol ligand, the nanoparticles obtained are polydisperse. The average size of the nanoparticles is 6 nm, but large aggregates of 100 nm are also present. This can be explained by the relatively short hydrocoarbon chain of butanethiol which reduces the stabilization of silver nanoparticles.

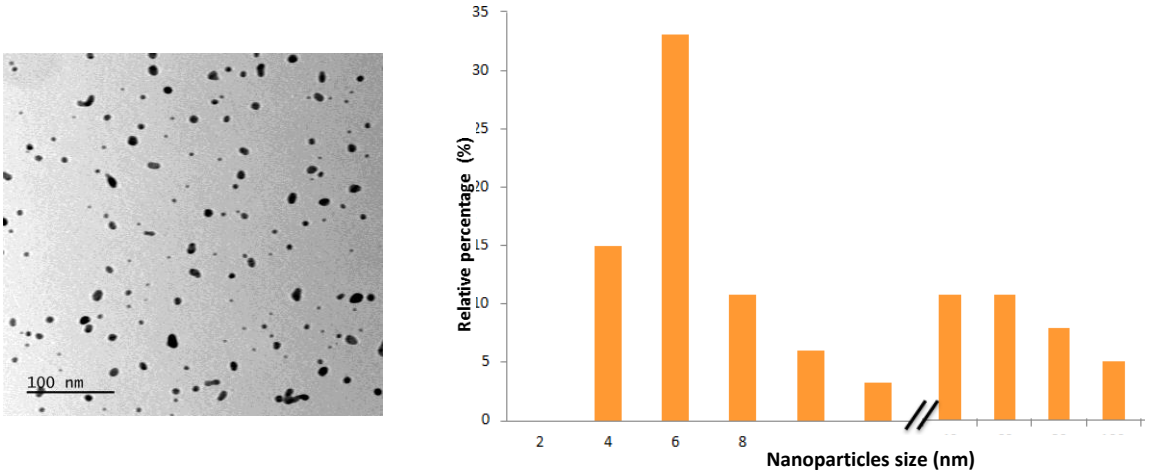
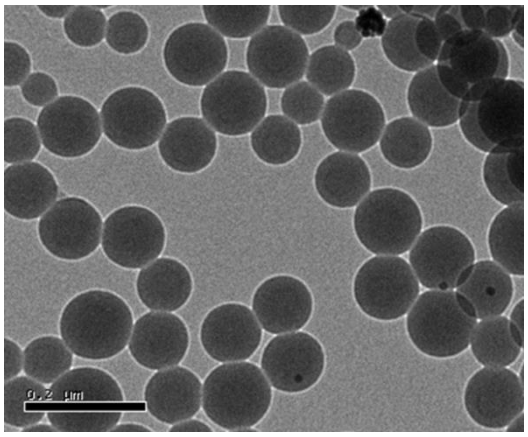


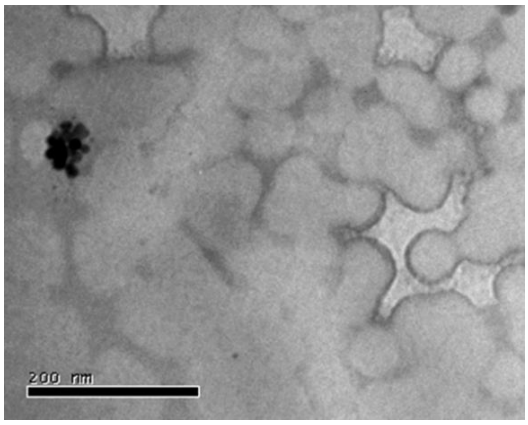
Figure 5 TEM image of silver nanoparticles functionalized with butanethiol ligands and corresponding size distribution of the population.

3.2 Assessment of the incorporation of silver nanoparticles in the polymer particles

One objective of this work is to determine if the silver nanoparticles are incorporated into the polymer particles. To do this, TEM images were acquired. However, as the glass transition temperature (T_g) of the latexes is about 15°C, the heat generated by the microscope beam fuses the polymer particles. Thus it was not possible to draw conclusions regarding the incorporation of the nanoparticles within the polymer particles. The monomer formulation was thus modified to allow for TEM analysis; specifically, the amount of methyl methacrylate was increased in order to raise the T_g of the latexes. Figure 6 presents TEM images of two latexes; one synthesized with styrene monomers (a) and the other with acrylate monomers (5,255 g of MMA / 2,232g of BuA / 0,075 g of AA) (b). Styrene monomers was used as comparitif since metallic nanoparticles were successfully encapsulate within (Desbiens, 2012) and the T_g is high. For comparison, the latex (a) has a T_g of about 95°C whereas the modified latex (b), has a T_g of about 37°C.



a) TEM image of a polystyrene latex containing silver nanoparticles stabilized with oleylamine ligands (T_g ~95°C)



b) TEM image of a MMA/BuA/AA latex with silver nanoparticles stabilized with oleylamine ligands (Tg ~37°C)

Figure 6 TEM images of latexes with different T_g and different monomer composition.

From these TEM images, the size of the polymer particles can be estimated at 50 nm. However, it is impossible to determine the exact position of the silver nanoparticles in the polymer particles; within the polymer particles or on the surface. Another observation is that the distribution of silver nanoparticles in the polymer particles is uneven. Indeed, the silver nanoparticles tend to cluster within a single particle. This phenomenon was also observed in previous work (Desbiens, 2012).

3.3 Dynamic light scattering analysis

The sizes of the polymer particles for various latexes containing 0.01% (m/m) of silver nanoparticles were determined by dynamic light scattering. The results are shown in Table 4.

Table 3 Polymer particle size and the polydispersity index obtained with a ZetaSizer Nano ZS as a function of the silver nanoparticles added.

Formulations	Size (nm)	PDI
Without nanoparticles (Base)	50,4 ± 0,4	0,04
Oleylamine (O)	51,2 ± 0,6	0,07
Butanethiol (C_4)	47,7 ± 0,2	0,06
1-octanethiol (C_8)	50,2 ± 0,6	0,08

The first conclusion to be drawn from this table is that regardless of the type of silver nanoparticles used, the size of the polymer particles does not vary significantly. Another observation is that all of the polydispersity indices presented are smaller or equal to 0.08. A PDI smaller than 0.08 indicates a relatively monodisperse latex. The lowest polydispersity index is obtained for the latex without nanoparticles. A polydispersity index smaller than 0.05 is characteristic of a monodisperse latex. Finally, the sizes obtained by DLS are close to those observed by transmission electron microscopy.

3.4 Fungi resistance test

The different latexes tested are shown in Table 5 and six replicas of each were made. The control (filter paper without latex) is required to ensure that no contamination is present in the samples.

Table 5 Latexes tested and their identification codes

Code	Samples
Control	Filter paper without latex
Base	Latex without silver nanoparticles
C_4	Latex with Np stabilized with 1-butanethiol
C_8	Latex with Np stabilized with 1-octanethiol
O	Latex with Np stabilized with oleylamine

Figure 7 presents pictures taken after 1 week and 4 weeks of testing for samples inoculated with strains of *P. funiculosum* and *A.niger*.

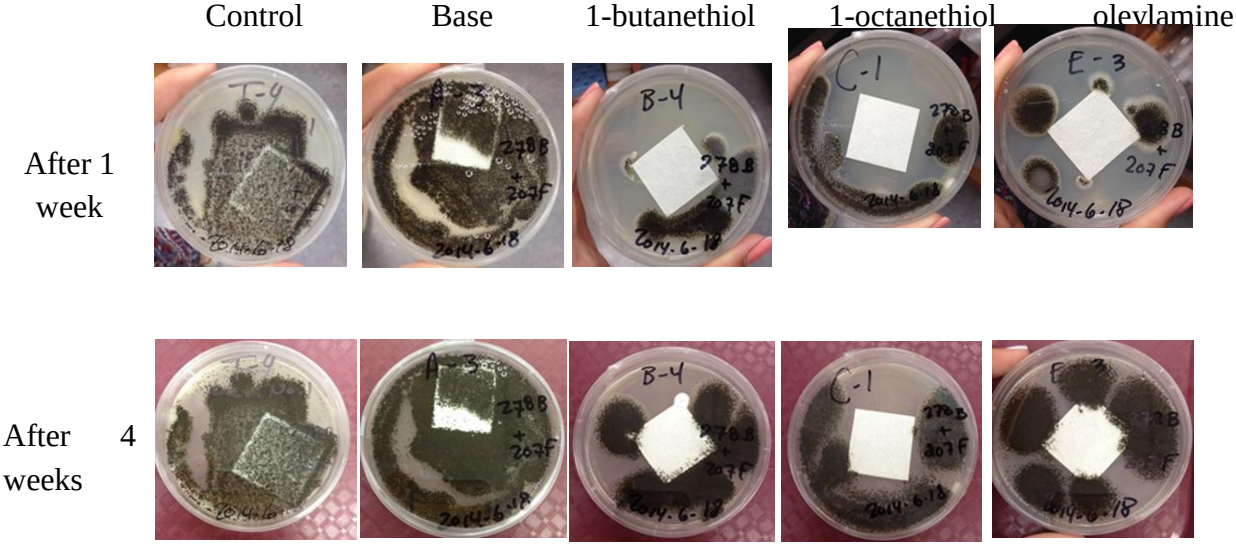


Figure 7 Pictures of fungal growth observed for each sample after 1 and 4 weeks for the strains of *P. funiculosum* and *A. Niger.*

After only one week, 100% of the surface of the control sample filter paper is covered with fungal growth. For the latex without silver particles ("base"), 80% of the surface is covered. Strikingly, after one week, no growth is observed on the filter papers treated with latexes containing nanoparticles. After 4 weeks, the fungal growth increases on all samples, but it remains very low (less than 10%) on the samples treated with the latex containing silver nanoparticles. This visual assessment is plotted in Figure 8 to facilitate the interpretation of the results.

For the *P. funiculosum* and *A. niger* strains, Figure 8 illustrates that the latex containing nanoparticles stabilized with 1-butanethiol, with a radius of 6 nm, has a higher antifungal activity than latexes with larger silver nanoparticles stabilized with ligands with longer alkyl chains. It is therefore possible that for the strains mentioned above, the size and nature of the ligand influence the antifungal activity. However, further studies are required for definitive conclusions.

Figure 9 shows pictures taken after 1 week and 4 weeks of tests for the samples inoculated with the strain of *E. nigrum.*

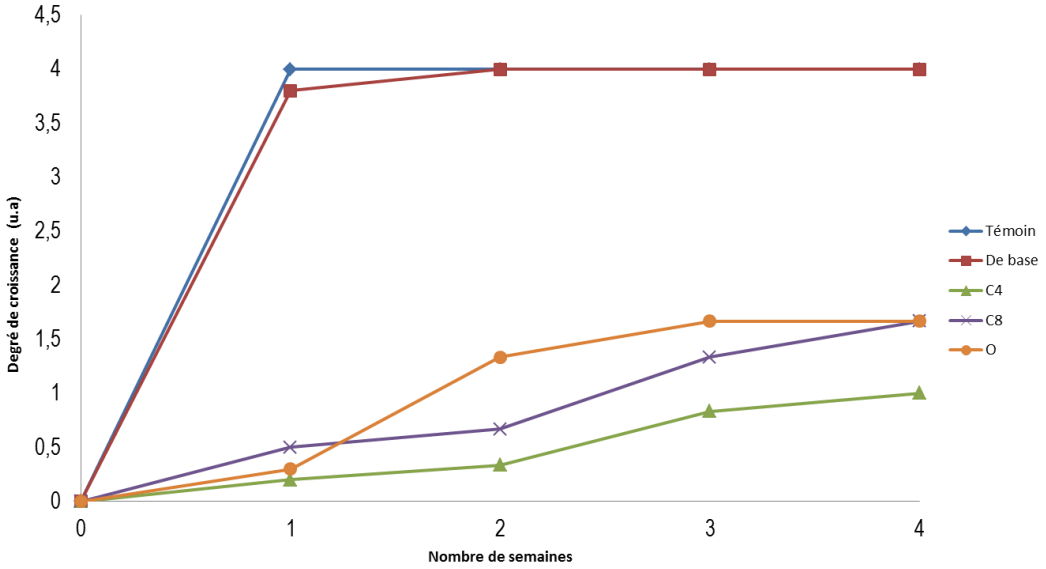


Figure 8 Degree of growth for strains of *P. funiculosum* and *A. niger* as a function of the number of weeks for latexes with and without silver nanoparticles

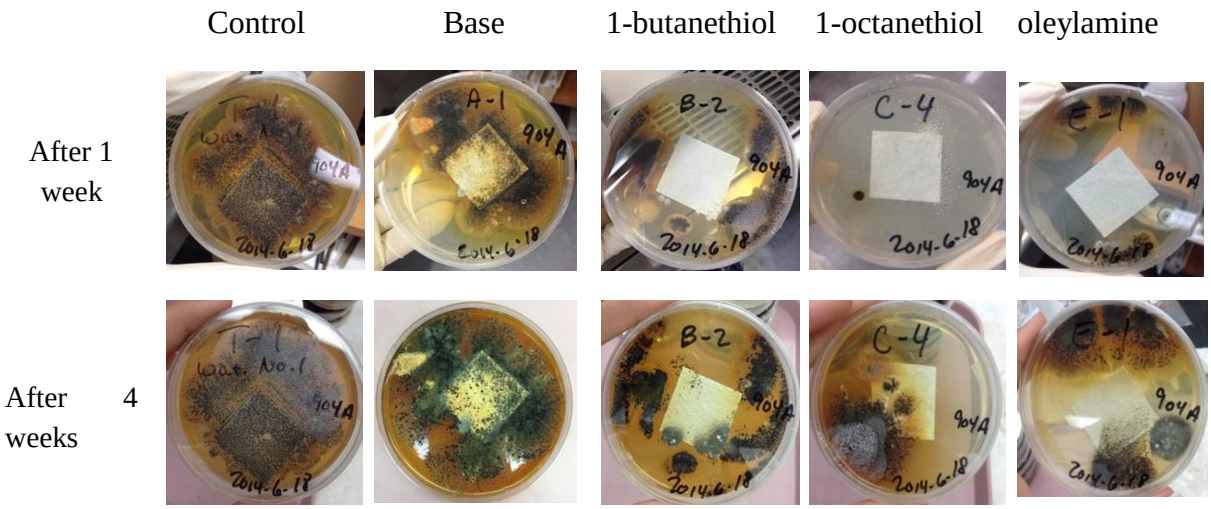


Figure 9 Pictures of fungal growth observed for each sample after 1 and 4 weeks for the strains of *E. nigrum*.

For samples inoculated with *E. nigrum* strain, the observed trends are similar to those treated with *P. funiculosum* and *A. niger* strains. That is to say, after a week the fungus covers 100% of the area for the "control" sample, about 50% of the surface of the "base" sample and no growth is observed for samples treated with latexes containing silver nanoparticles. After 4 weeks, the fungal growth increases on all samples, but remains low (lower than 30%) for the samples treated with the latex containing silver nanoparticles.

Figure 10 presents the graphical representation of the visual assessment for the tests carried out with the *E. nigrum* strain.

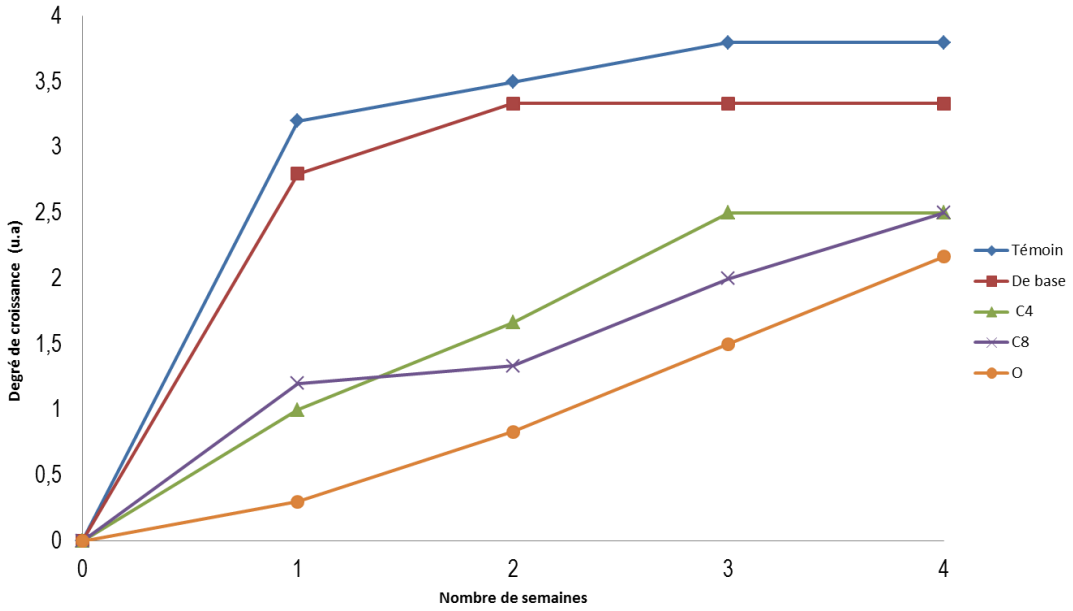


Figure 10 Degree of growth for strains of *E. nigrum* in function of the number of weeks for latexes with and without silver nanoparticles.

Unlike Figure 8, Figure 10 does not suggest the same discrimination of antifungal activity of the latexes as a function of the size of the silver nanoparticles or the length of the ligands.

In light of these results, it is possible to say that the latexes containing silver nanoparticles (0.1% m/m) present significant antifungal activity against the three strains tested. Silver nanoparticles appear more effective against *P. funiculosum* and *A. niger* strains.

4. Conclusions

This work demonstrates that silver nanoparticles functionalized with thiol ligands of different chain lengths (C_4 et C_8) and oleylamine can be stably dispersed in acrylic latexes. Acrylic latexes with silver nanoparticles show antifungal activity against *E. nigrum*, *P. funiculosum* and *A. niger* at low silver concentration (0,1% m/m). For *P. funiculosum* and *A. niger* strains, the size of silver nanoparticle and the length of the ligand used appear to have an effect on the antifungal activity. However, for the E. *nigrum* strain an analgous trend is not observed. Further studies are needed to assess more precisely the influence of the length of the ligands and their nature, and the nanoparticle size on their antifungal activity. The leaching of the encapsulated nanoparticles will also be investigate.

5. Acknowledgements

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6. Literature

Chen, M.; Feng, Y.-G.; Wang, X.; Li, T.-C.; Zhang, J.-Y.; Qian, D.-J. Silver nanoparticles capped by oleylamine: Formation, growth, and self-organization. *Langmuir*. **2007**, 23, 5296-5304.

Costoyas, A.; Ramos, J.; Forcada, J. Encapsulation of silica nanoparticles by miniemulsion polymerization. *Journal of Polymer Science: Part A*. **2009**, 47, 935-948.

Desbiens, J. Synthèse et caractérisation de nanoparticules de polymère dopées d'un complexe luminescent et de nanoparticules d'argent, Thèse de Doctorat, Université Laval, Canada, 2012

Erdem, B.; Sudol, E.D.; Dimonie, V.L.; El-Aasser, M.S. Encapsulation of inorganic particles via miniemulsion polymerization. III. Characterization of encapsulation. *Journal of Polymer Science: Part A*. **2000**, 38, 4441-4450.

Feng, Q. L., Wu, J., Chen, G. Q., Cui, F. Z., Kim, T. N. and Kim, J. O. A mechanistic study of the antibacterial effect of silver ions on *Escherichia coli* and *Staphylococcus aureus*. *J. Biomed. Mater. Res.* **2000**, 52, 662–668.

Freedonia Group, US Siding Market report, 2014, New-York, USA

Gladis, F.; Eggert, A.; Karsten, U.; Schumann, R. Prevention of biofilm growth on man-made surfaces: evaluation of antialgal activity of two biocides and photocatalytic nanoparticles. *Biofouling: The Journal of Bioadhesion and Biofilm Research*. **2010**, 26, 89-101

Green III, F.; Schultz, T.P.; New environmentally-benign concepts in wood protection: The combination of organic biocides and non-biocidal additives. In *Wood deterioration and preservation: Advances in our changing world*, American Chemical Society Series. Oxford University Press. Goodell, B., Nicholas, D., Schultz, T., 2003, 378-389.

Hwang, E.; Lee, J.; Chae, Y.; Kim, Y.; Kim, B.; Sang, B.; Gu, M. Analysis of the toxic mode of action of silver nanoparticles using stress-specific bioluminescent bacteria. *Small*. **2008**, 4, 746-750.

Hu, J.; Chen, M.; Wu, L. Organic-inorganic nanocomposites synthesized via miniemulsion polymerization. *Polym. Chem.* **2011**, 2, 760-772.

Kaegi, R.; Sinnet, B.; Zuleeg, S., Hagendorfer, H.; Mueller, E.; Vonbank, R.; Boller, M.; Burkhardt. Release of silver nanoparticles from outdoor facades. *Environmental Pollution*. **2010**, 158, 2900-2905.

Kaiser, J.P.; Diener, L.; Wick, P. Nanoparticles in paints: A new strategy to protect façades and surfaces ?. *Journal of Physics: Conference Series.* **2013,** 429, 012036**.**

Kang, S.Y.; Kim, K. Comparative study of dodecanthiol-derivatized silver nanoparticles prepared in one-phase and two-phase systems. *Langmuir*. **1998**, 14, 226-230.

Kim, J.S.; Kuk, E.; Yu, K.N.; Kim, J-H.; Park, S.J.; Lee, H.J.; Park, Y.H.; Hwang, C-Y.; Kim, Y-K.; Lee, Y-S.; Jeong, D.H.; Cho, M-H. Antimicrobial effects of silver nanoparticles. *Nanomedecine: Nanotechnology, Biology, and Medicine*. **2007**, 3, 95-101

Künniger, T.; Gerecke, A.C.; Ulrich, A.; Huch, A.; Vonbank, R.; Heeb, M.; Wichser, A.; Haag, R.; Kunz, P.; Faller, M. Release and environmental impact of silver nanoparticles and conventional organic biocides from coated wooden façades. *Environmental Pollution*, **2014**, 184, 464-471

Lok, C.-H.; Ho, C.-M.; Chen, R.; He, Q.-Y.; Yu, W.-Y.; Sun, H.; Tam, P.K.-H.; Chiu, J.-F.; Che, C.-M. Proteomic analysis of the mode of antibacterial action of silver nanoparticles. *J. Proteome Res*. **2006**, 5, 916-924.

Marambio-Jones, C.; Hoek, E.M.V. A review of the antibacterial effects of silver nanomaterials and potential implications for human health and the environment. *J. Nanopart. Res*. **2010**, 12, 1531-1551.

Morones, J.B.; Elechiguerra, J.L.; Camacho, A.; Holt, K.; Kouri, J.B.; Ramirez, J.T.; Yacaman, M.J. The bactericidal effect of silver nanoparticles, *Nanotechnology*. **2005**, 16, 2346-2353.

Morrell, J.J. Protection of wood-based materials. In *Handbook of Environmental Degradation of Materials,* Second Edition, Elsevier Inc., Oxford, UK, 2012; pp 407-439.

Panacek A, Kvitek L, Prucek R, Kolar M, Vecerova R, Pizurova N, et al. Silver colloid nanoparticles: synthesis, characterization, and their antibacterial activity. *Journal of Physical Chemistry: Part B*. **2006,** 110, 16248–53

Rai, M.; Yadav, A.; Gade, A. Silver nanoparticles as a new generation of antimicrobials. *Biotechnology Advances*. **2009**, 27, 76-83.

Russell, A.D.; Hugo, W.B. Antimicrobial activity and action of silver. *Prog.Med.Chem*. **1994**, 31, 351-370.

Steiert, N. and K. Landfester, Encapsulation of organic pigment particles wia miniemulsion polymerization. *Macromol. Mater. Eng*. **2007**, 292, 1111-1125

Vlad-Cristea, M.S., Revêtements nanocomposites anti-UV pour le bois à usage extérieur, Thèse de Doctorat, Université Laval, Canada, 2011

Wang, L.; He, X.; Wilkie, C.A. The utility of nanocomposites in fire retardancy. *Materials*. **2010**, 3, 4580-4606.

Wangler, T.P.; Zuleeg, S.; Vonbanl, R.; Bester, K.; Boller, M.; Carmeliet, J.; Burkhardt, M. Laboratory scale studies of biocide leaching from façade coatings. *Building and Environment*. **2012**, 54, 168-173