

# Hybrid Silica Nanoparticles for formaldehyde-scavenging in high performance resins

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**Abstract:** Urea-formaldehyde resins (UFR) have seen an increased growth in usage ever since their discovery and subsequent industrial production in the first half of the XX century. Nowadays, their use as strong adhesives has made these resins an important part in the production of wood composites. These adhesives show great competitive advantages, both economically and in performance. However, a big drawback in utilizing UFR is the emission of residual formaldehyde after the curing process. Formaldehyde has been classified by the International Agency for Research on Cancer (IARC) as a carcinogen, with other symptoms, such as skin and eye irritation, at higher concentrations of exposure. One solution to avoid formaldehyde emissions is the use of scavenger materials. Silica nanoparticles (SNP) are a great option for formaldehyde scavenger nanomaterials due to their remarkable versatility of functionalization, high surface area and control over size and structure. The purpose of this work was to develop SNP scavengers, synthesized using the Stöber method, containing amine groups that react with free formaldehyde, capturing it and therefore reducing its emission. For the implementation of a smart system, two types of SNP were synthesized: one with a core of silica functionalized with amine groups (SNP1); the other, with an added silica shell without the amine groups, to act as a barrier to formaldehyde capture before the curing process (SNP2). The nanoparticles have diameters of  $(5.9 \pm 0.4) \times 10^2$  nm for SNP1 and  $(7.3 \pm 1) \times 10^2$  nm for SNP2. The system shows successful scavenging capabilities of the synthesized nanoparticles, decreasing the value of formaldehyde emissions from 0.53 ppm (control test) to 0.11 ppm using SNP1 and 0.22 ppm using SNP2, with SNP2 increasing scavenging activity by 50% after exposure to a heat treatment in the same conditions as the ones for UFR curing.

**Keywords:** hybrid nanoparticles, Stöber process, formaldehyde, scavenging, urea-formaldehyde resins.

## 1. Introduction

Since their inception in the early decades of the XX century, synthetic polymers have seen widespread use, becoming an indispensable commodity today, due to their versatility in application and relative cheap production. Their origin can be traced to Leo H. Baekland who, in 1907, successfully developed a method of producing moldable phenolic resins, with immediate household applications such as in radio and telephones [1]. Their chemical properties also turned them into cheaper alternatives to natural resins. In summary, the industry of synthetic polymers last century was both groundbreaking and profitable, with development ongoing in the XXI century [2].

More recently, instead of the traditional phenol-formaldehyde formulations, urea-formaldehyde resins (UFR) have seen increased usage. It is estimated that 1 million metric tons of UF resins are produced annually [3], with the majority being used in the production of adhesives for bonding wood composites, wood laminates,

particleboards, and plywood. Their importance comes from their high reactivity, performance and low cost [4].

UF resins are produced by reacting urea and formaldehyde. In a first step, the two reactants form a mixture of mono, di and trimethylolureas. The next step is a water condensation reaction continuing the polymerization. The last step is a final condensation with release of formaldehyde (Figure 1) [5].

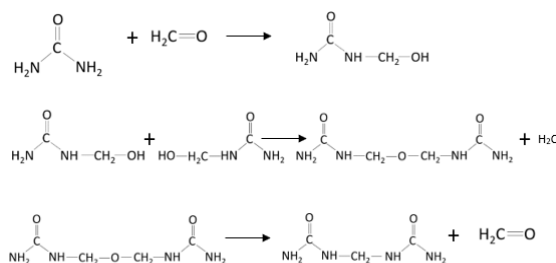


Figure 1 UF Resin polymerization reaction. The first step is a methylolation, followed by condensation in acidic conditions, resulting in the release of formaldehyde.

Lastly, the cure process occurs, hardening the material, at high temperature, around 120°C in acidic conditions. The hardening of the UFR results from the crosslinking between chains formed previously [6]. After the curing process, any remaining volatile reagent, namely formaldehyde, is released to the environment.

Formaldehyde, one of the main chemicals used in the production of UFR, has been classified as a human carcinogen, therefore posing a great risk to human health on prolonged (chronic) exposure. Also, reports of acute exposure also have led to irritation in various body parts, such as eyes, nose, throat and skin. Therefore, it is important to ensure a safe environment when working with this dangerous chemical. Reported case studies have shown that exposure to formaldehyde can happen not only to workers related to areas referred before (chemical, particle board production and furniture workers), but to office, laboratory workers and even firefighters and mortuary employees [7]. The range of exposure can be varied, from around 0.05 ppm up to 2-3 ppm, across various developed and developing countries. Therefore, the importance of developing methods for detection and subsequent lowering of the emission values. Moreover, of all the common consumer products that have shown to emit formaldehyde over time, UF wood products have the highest emission rate, therefore getting more attention [8-9].

Different techniques have been proposed and implemented to analyze formaldehyde emissions from particle boards and wood-related products. These procedures are standardized so that results between different laboratories can be compared (Table 1) [10].

*Table 1 Most common methods for measuring formaldehyde emissions and respective norm.*

Method	Norm	Country
Chamber	EN 717-1 [11]	EU
	JIS A 1901 [12]	Japan
	ISO/CD 12460 [13]	International
Gas analysis	EN 717-2 [17]	EU
Flask	EN 717-3 [18]	EU
Desiccator	JIS A 1460 [19]	Japan
	JAS 233 [20]	Japan
Perforator	EN 120 [21]	EU

For photometric determination, the most common method is the acetyl acetone method. Emitted formaldehyde absorbed in water reacts with acetyl acetone, producing a colored derivative, diacetyldihydrolutidine (DDL), that can be measured in solution by UV/Vis spectroscopy (absorption maximum of DDL is at 412 nm) [14-15]. Alternatively, DDL concentration can be determined through fluorimetric spectroscopy, measuring at an emission wavelength of 410 nm and excitation wavelength of 510 nm [16].

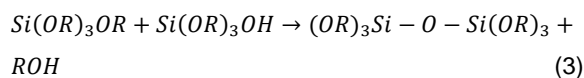
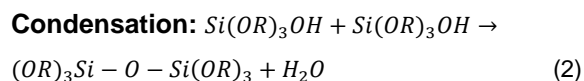
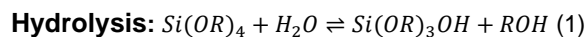
In Europe, the emission limit (E1) for the chamber method is 0.12 mg m<sup>-3</sup> or 8 mg/100 g for the perforator method. In the US the emission limit can range from 0.08 to 0.21 depending on the product tested. In Japan, for the F\*\*\* grade, the limit is 0.5 mg/L and the highest grade, F\*\*\*\* is even lower, at 0.3 mg/L. The importance of enforcing these values comes from the health issues associated with formaldehyde exposure.

To reduce formaldehyde emissions in particle board and wood-based composite materials made with UF resins, one proposed solution is the use of scavengers. These are additives that react with free formaldehyde to reduce its emission after the resin's curing process, without compromising the resin's properties. Depending on the type of scavenger, it can be added post-treatment, or post-curing, or added directed in the mixing process [22]. Focusing on scavengers that capture formaldehyde through chemical bonding, a wide array of different approaches can be taken, from bio-based scavengers to nano-scavengers. While urea has shown to be a good formaldehyde scavenger, especially when combined with ammonium chloride, inorganic additives also show favorable results, namely sodium metabisulfite and ammonium bisulfite when added to wood-based composites made with UF resin [23]. As the most convenient way is to incorporate the scavenger into the UF resin, nano-scavengers are strong candidates compared to the previously mentioned types. Their small sizes, high specific surface area and easy incorporation in UF resin formulations make them prime materials for use in both academic and industrial areas. Also, the incorporation of these nanoparticles can reinforce or otherwise affect several properties of the UF resins, such as curing, flame retardancy and, most important, formaldehyde emissions. The most common nano-scavengers used as particle board additives are aluminum oxide (Al<sub>2</sub>O<sub>3</sub>) nanoparticles and silica nanoparticles [24].

When added to UF resins, alumina nanoparticles have been shown to work efficiently as a sorbent for capturing free formaldehyde, reducing its emission on the final product [25]. Other properties can also be affected by alumina nanoparticles incorporation, such as lowering the curing temperature when increasing the wt% of added nanoparticles [26]. Kumar et al also claimed that the Al<sub>2</sub>O<sub>3</sub> nanoparticles' surface can act as a catalyst, accelerating the UF resin's curing step due to hydroxyl groups' presence. Al<sub>2</sub>O<sub>3</sub> nanoparticles can also change physical properties, such as increasing the thermal conductivity [27]. Other properties have also been observed to change after the addition of alumina nanoparticles. For example, viscosity increases with higher percentages of added nanoparticles, also altering the UF resin behavior [28].

With a wide variety of favorable properties such as chemical and thermal stability and versatile configurations, silica nanoparticles (SNP) are prime candidates as added scavengers to UF resins.

The Stöber process [29], proposed in 1968, is a sol-gel method of producing monodispersed silica nanoparticles, with sizes ranging from 50 nm to 2000 nm. It is a two-step process, starting with hydrolysis of the silica precursors and subsequent condensation, in the presence of ammonia as a catalyst.



Further hydrolysis and condensation lead to crosslinking between chains, creating a three-dimensional structure. In this case, the structures are monodispersed silica spheres. To capture free formaldehyde, the SNPs can be functionalized, i. e., by using silica precursors containing certain groups that when present on the surface of the nanoparticles react with formaldehyde. In this specific case, silica precursors containing amine groups are a great option for the intended application, as NH<sub>2</sub> reacts with formaldehyde through the Mannich mechanism [30-31].

Since the scavenger activity shows better results when mixed directly with the resin, it is not convenient to have the amine groups react prematurely with formaldehyde before the resin's curing process, as it is one of the reagents necessary for the resin's formation. Therefore, the implementation of a smart system solves the problem by restricting the activity of the amine groups until certain conditions are met. Since the curing process is the process happens at high temperature and pressure, these two parameters can be used as triggers for the system.

Another type of silica material is the mesoporous silica, developed by Mobil Oil Corporation. This type of structure, initially called MCM-41, consists in a porous structure, with cylindrical-shaped pores arranged in a hexagonal distribution [32]. To adapt it to nanoparticles, such structure is achieved via the use of a surfactant that works as a template. In this case, cetyltrimethylammonium bromide (CTAB) is used for two reasons: First, it forms cylindrical micelles; Second, as a cationic surfactant it can direct the silicate source to condense around the template. The next steps, hydrolysis and condensation are similar to the ones mentioned above for the Stöber method [33]. Lastly, the template is removed, either by solvent extraction [34] or by a series of thermal treatments [35].

The objective of this work was to develop amine functionalized silica nanoparticles for formaldehyde scavenging. A smart system where the amine groups react with free formaldehyde only after the curing process, the SNPs had two distinct regions: a functionalized core with the amine groups, and a more hydrophobic shell built without the amine groups. As SiO<sub>2</sub> is not expected to react with Fa, the shell was expected to work as a barrier, shielding the free formaldehyde from the core (Figure 2)

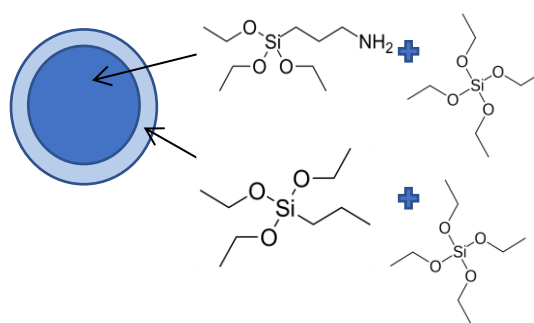


Figure 2 Model of the proposed SNPs' structure (left) and its respective monomers (right). Regions of the model not at scale.

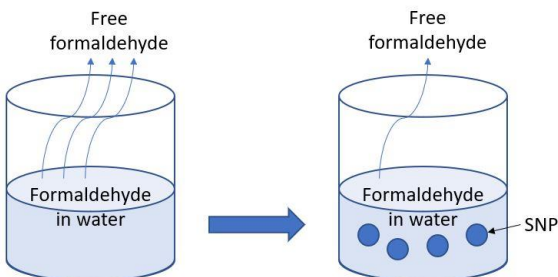


Figure 3 Schematic of the scavenging test: SNP dispersed in a solution of known formaldehyde concentration

Scavenging tests were conducted with a method like the desiccator method. formaldehyde was measured inside a desiccator, a flask containing a solution of known formaldehyde concentration and synthesized SNPs was used and airborne formaldehyde concentration was monitored inside the desiccator (Figure 3). Results were compared between a control test, without SNPs, and using two types of SNPs: one with functionalized amine groups on the surface (SNP1), and another containing the hydrophobic shell (SNP2) as to compare the shell's efficiency in stopping the scavenging of free formaldehyde during the hot press cure of the UF resins.

## 2. Experimental Section

### 2.1 Materials

For the silica nanoparticles, Tetraethyl Orthosilicate (TEOS, Sigma-Aldrich, 98%), 3-Aminopropyltriethoxysilane (APTES, Sigma-Aldrich, 99%), Triethoxy(propyl)silane (TCI, >98%), Ammonium hydroxide (NH<sub>4</sub>OH, Sigma-Aldrich, 27%) absolute Methanol (MeOH, Sigma-Aldrich), Formaldehyde solution (Sigma-Aldrich, ≥36.0% in H<sub>2</sub>O) and absolute Ethanol (EtOH, Riedel-de-Haën) were used. Deionized water was obtained from a Millipore system Milli-Q ≥18 MΩcm (with a Millipak membrane filter 0.22 μm). For Rroton Nuclear Magnetic Resonance, 1,3,5-Trioxane (Fluka, 99%) was used as the internal standard, Sodium Hydroxide (NaOH, Panreac) to destroy the silica and Deuterium Oxide (D<sub>2</sub>O, CIL, 99.9%) as the solvent.

### 2.2 Synthesis of SNPs

Silica Nanoparticles (SNP) were synthesized by the Stöber process in a two-fold method. In a polypropylene flask (250 mL), 80g of MeOH/H<sub>2</sub>O

(50% w/w) were poured and 228 μL of NH<sub>4</sub>OH 27% were added. Then, 133 μL TEOS and 38,6 μL APTES were added and left stirring overnight (400 RPM, ~20h). The obtained particles were washed and centrifuged and left drying at 60°C for at least 24h, coded SNP1. The same procedure was replicated in another propylene flask (same volume), but after stirring overnight, a “shot” of 114 μL NH<sub>4</sub>OH 27%, 45 μL TEOS and 135 μL Triethoxy(propyl)silane was added left stirring again overnight. The second obtained particles, containing an amine-functionalized core and a shell with no amine groups, was coded SNP2.

### 2.3 Formaldehyde Scavenging

Formaldehyde scavenging was performed using the desiccator method. A control experiment was performed with a 15mL flask containing 10mL of a formaldehyde solution 7.2 PPM. The formaldometer and the flask were put inside the desiccator and closed (Figure 4), isolating the system. The sensor measured the concentration of formaldehyde in the air inside the desiccator. 10mL samples of air were taken by the sensor's internal pump every 5 minutes and formaldehyde concentration determined for 1 hour.

On a separate experiment, 0.8 mg SNPs were added to another 15mL flask also containing 10mL of a formaldehyde solution 7.2 PPM and left stirring overnight. The same procedure was implemented for each type of nanoparticle.



Figure 4 Photograph of the laboratory configuration for the scavenging experiment.

### 3. Results

The strategy was to synthesize two types of silica nanoparticles, which then were used as scavengers.: SNP1, with exposed amine groups, and SNP2, containing a silica shell that covers the NH<sub>2</sub>. The two particles were then subjected to scavenging tests, where in each system the formaldehyde emission was determined and compared. Lastly the final objective was to subject SNP2 to temperature and pressure conditions similar to the ones present during the curing process of UF resins and performed a final scavenging test.

#### 3.1 SNPs synthesis and characterization

Two types of SNPs were synthesized through the Stöber method: SNP1 and SNP2. As per the method used, the particles obtained were rigid spheres, with sphericity very close to 1 (they are practically perfect spheres) and diameters of  $(5.9 \pm 0.4) \times 10^2$  nm for SNP1 and  $(7.3 \pm 1) \times 10^2$  nm for SNP2 (Figure 5). average diameter and sphericity were determined by TEM imaging, sampling 100 nanoparticles for SNP1 and SNP2.

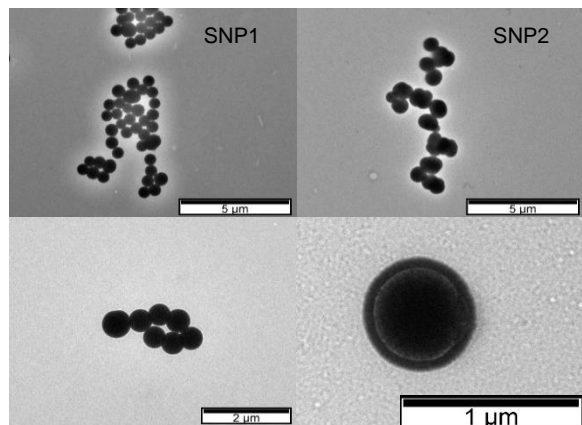


Figure 5 SNP1 (left) and SNP2 (right). Determined size diameter:  $582 \pm 38$  nm and  $729 \pm 100$  nm respectively.

SNP1 and SNP2 diameters were measured using ImageJ software [36].

The size distribution histograms of SNP1 and SNP2 is shown in Figure 6.

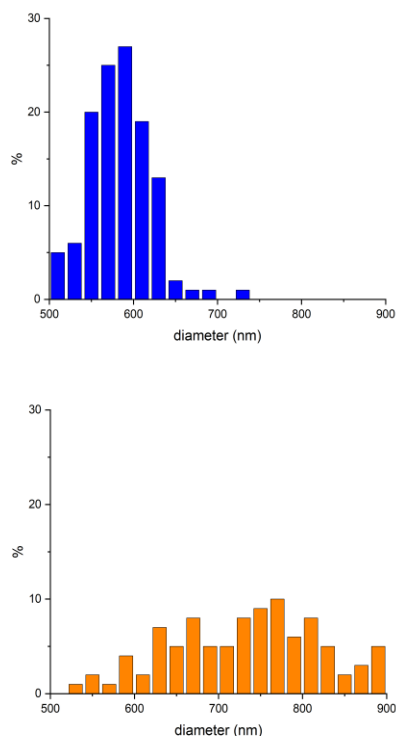


Figure 6 Histograms of SNP1 (blue) and SNP2 (orange).

While SNP1 show a narrower distribution, with a peak between 580 and 600 nm, SNP2 have a broader distribution, with no clear peak. Determination of the hydrodynamic diameter by DLS show distribution curves with an average value, in number, of  $981 \pm 36$  nm for SNP1 and  $640 \pm 196$  nm for SNP2 (Figures 7 and 8). The values showed a lower average diameter for SNP2 compared to the values obtained for SNP1. One explanation to the discrepancy observed comes from the SNPs' tendency to flocculate. This way, the equipment would detect the aggregates rather than the individual particles, which can be seen happening over time as the results for the same sample start to shift, with a wider range of values and a higher average diameter (Figure 9). Moreover, SNP1 show more aggregation than SNP2. The former were functionalized with amine groups, not present on the surface of the latter, which have propyl groups. The results in intensity presented in Figures 7 and 8 are the primary result obtained from DLS measurements. It is based upon the intensity of light that is scattered by particles. The results in number are derived from the intensity distribution using Mie theory [37].

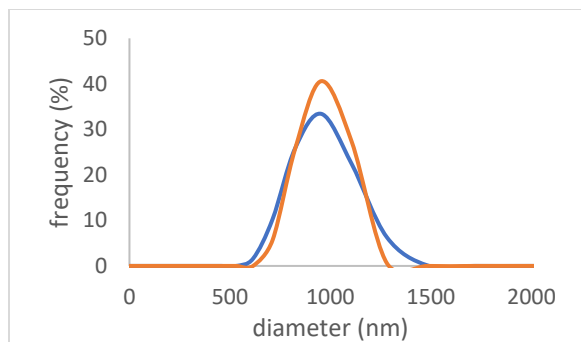


Figure 7 Hydrodynamic diameter distribution for SNP1 in number (blue) and intensity (orange).

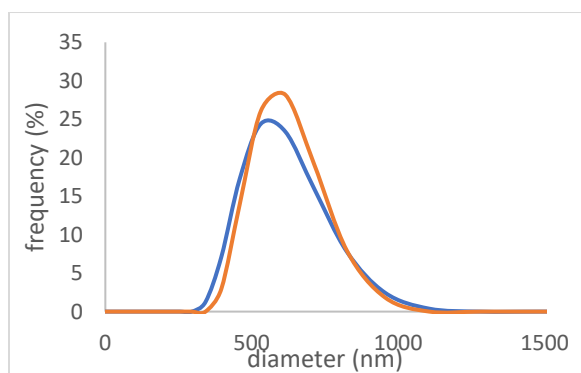


Figure 8 Hydrodynamic diameter distribution for SNP2 in number (blue) and intensity (orange)

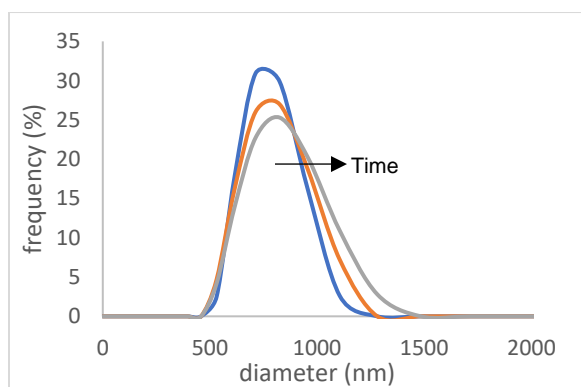


Figure 9 Size distribution for diameter for SNP1 over time (intensity). First measurement in blue, followed by the second measurement in orange and last measurement in grey. Time between measurements was 3 minutes, to a total of 6 minutes elapsed between the first and the last measurements.

The hybrid SNPs synthesized had 3.5 mmol/g of amine groups, obtained by  $^1\text{H}$  NMR analysis, for both SNP1 and SNP2.

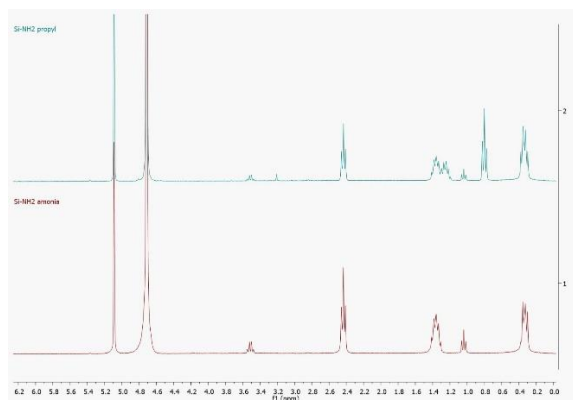


Figura 10  $^1\text{H}$  NMR spectra for SNP1 (red) and SNP2 (blue)

### 3.2 Surface charge measurement

One key difference between SNP1 and SNP2 is the type of functionalized groups present on the surface of each. While SNP1 have amine groups, these are absent on SNP2's surface. Instead, SNP2 surface contains propyl groups. Depending on the medium's pH, surface ionization occurs, in the amine groups in SNP1 and in the propyl groups in SNP2. When a net charge develops at the surface, the distribution of ions around them is affected, resulting in a double layer, with counter ions closest to the particles' surface. Movement of the particles leads to movement of ions within the double layer, while ions beyond that boundary remain in the dispersant. The potential at this boundary is called the zeta potential (ZP). Therefore, by measuring the zeta potential for SNP1 and SNP2 at a wide range of pH values, from highly acidic (pH 3) to low basic (pH 8), a transition from positive ZP to negative values, the isoelectric point, would be expected at different points, for each surface. The experimental results obtained show a clear distinction between the two structures, as the isoelectric point of SNP1 (pH 7.5) is close to the theoretical value for  $\text{NH}_2$ , and the one obtained for SNP2 (pH 3.6) is within the range expected for only  $\text{SiO}_2$  structures, in fact confirming the shell formation (Figure 11) [38].

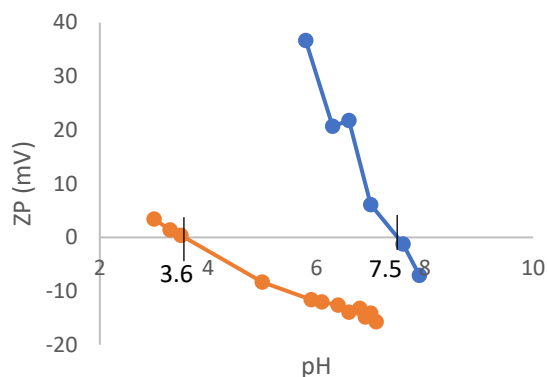


Figure 101 Zeta potential measurements for each type of NP, blue for SNP1 and orange for SNP2, at different pH values and respective experimental isoelectric points, pH 7.5 for SNP1 and 3.6 for SNP2.

### 3.3 Temperature annealing of SNP2

SNP2 were subjected to a heat treatment in conditions that mimic the ones employed in the curing process of UFR. The purpose was to have a comparison in emissions before and after the curing process, as the intended purpose for this proof-of-concept was to scavenge formaldehyde only after curing the resin. Therefore, SNP2 were suspended in water and heated to 106°C inside an autoclave for 1 hour (SNP3). After cooling, TEM images were obtained of SNP3 (Figure 12).

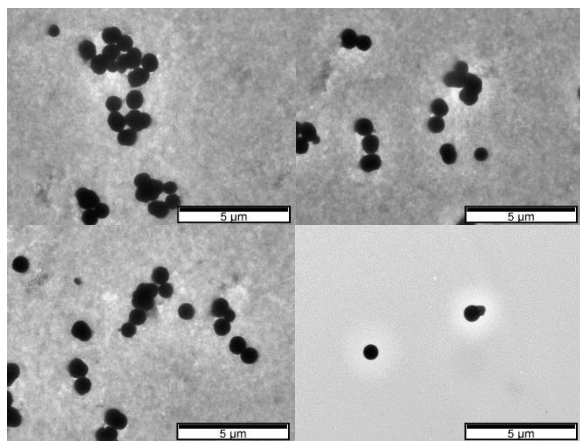


Figure 112 TEM imaging of SNP3, obtained after subjecting SNP2 to heat conditions analogous to the resin's cure conditions

### 3.4 Formaldehyde scavenging

Formaldehyde scavenging tests were conducted by measuring formaldehyde emissions from a prepared solution, of known formaldehyde concentration, inside a desiccator. Concentration

values in the air inside the desiccator were measured in 5-minute intervals and plotted against time (Figure 13). All particle types were tested in a molar ratio of 1:1 and 2:1 between amine groups present on the SNPs and formaldehyde in solution. The hybrid SNPs synthesized had 3.5 mmol/g of amine groups, obtained by <sup>1</sup>H NMR analysis.

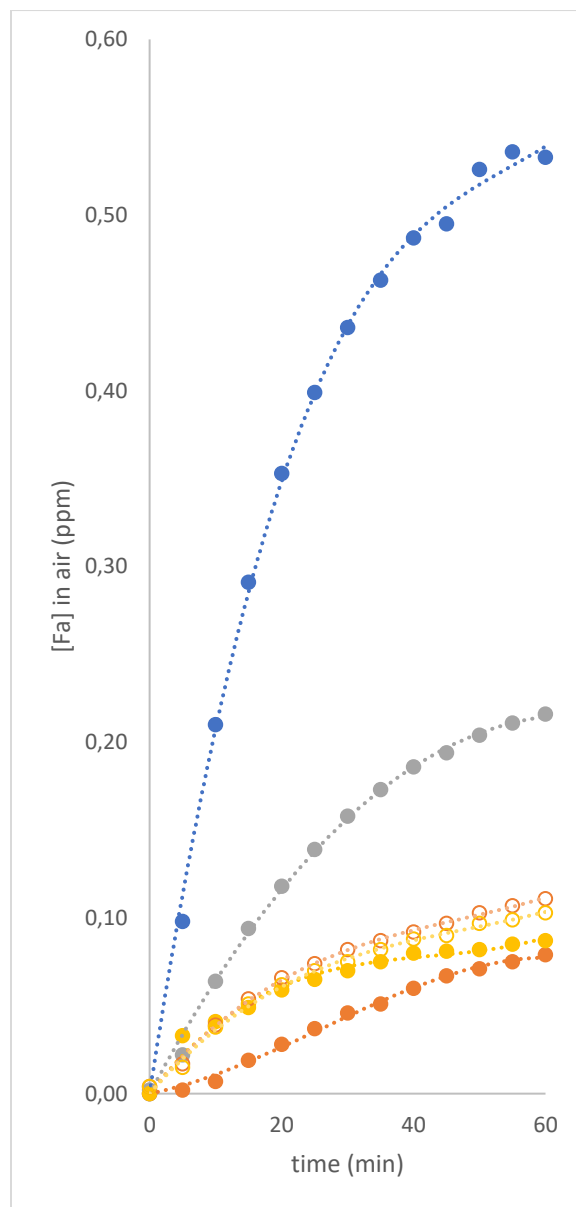


Figure 123 Formaldehyde concentration measured inside the desiccator (in ppm) for both molar ratios (amine groups:formaldehyde). Molar ratio 1:1: control/no nanoparticles (filled blue ●), SNP1 (filled orange ●), SNP2 (filled grey ●) and SNP3 (filled yellow ●); Molar ratio 2:1: SNP1 (open orange ○), and SNP3 (open yellow ○)

Correlation curves obtained for each experiment:

Control (filled blue):  $c = 2 \times 10^{-6}t^3 - 4 \times 10^{-4}t^2 + 2.46 \times 10^{-2}t, R^2 = 0.9985$

Molar ratio 1:1.

SNP1 (filled orange):  $c = -5 \times 10^{-7}t^3 + 4 \times 10^{-5}t^2 + 7 \times 10^{-4}t, R^2 = 0.9962$ .

SNP2 (filled gray):  $c = 1 \times 10^{-7}t^3 - 6 \times 10^{-5}t^2 + 7.1 \times 10^{-3}t, R^2 = 0.9975$ .

SNP3 (filled yellow):  $c = 8 \times 10^{-7}t^3 - 1 \times 10^{-4}t^2 + 4.8 \times 10^{-3}t, R^2 = 0.9817$ .

Molar ratio 2:1.

SNP1 (open orange):  $c = 6 \times 10^{-7}t^3 - 8 \times 10^{-5}t^2 + 4.6 \times 10^{-3}t, R^2 = 0.9973$ .

SNP3 (open yellow):  $c = 5 \times 10^{-7}t^3 - 7 \times 10^{-5}t^2 + 4.3 \times 10^{-3}t, R^2 = 0.9957$ .

For SNP1, formaldehyde concentration after 1 hour stabilized around 0.11 ppm, lower than the value obtained for SNP2 (approximately 0.22 ppm). The difference between these values was expected as the shell worked as a deterrent to formaldehyde scavenging by blocking the available amine groups for formaldehyde to react with. Moreover, comparing with the control experiment, both values are below the one obtained in the control experiment (approximately 0.53 ppm). Meaning that, using SNP1, formaldehyde emissions decreased to only 20% of value obtained in the control experiment, while using SNP2 reduced to 40% the value of the control group. Also, SNP2's scavenging power increased after activation, reducing emissions to half after heat treatment. Temperature was also monitored throughout the experiment since the equipment is calibrated for the temperature of the experiment and is very sensitive to high fluctuations,  $\Delta T > 1^\circ\text{C}$  (Figure 14).

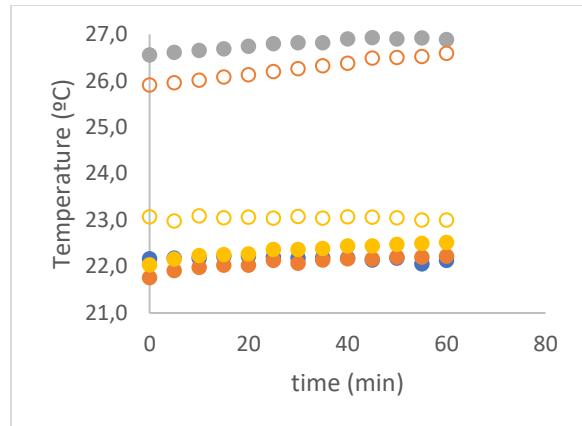


Figure 134 Temperature results for each experiment Molar ratio 1:1: control/no nanoparticles (filled blue ●), SNP1 (filled orange ●), SNP2 (filled grey ●) and SNP3 (filled yellow ●); Molar ratio 2:1: SNP1 (open orange ○), and SNP3 (open yellow ○)

For the second set of experiments, molar ratio 2:1, the emission value stabilized at 0.08 ppm, or 15% of the control value, when using SNP1, even lower than before, expected as the number of nanoparticles was increased. For SNP3, the value obtained was 0.08 ppm, the same value as SNP1, showing that after heat treatment, the presence of the shell no longer acts as a deterrent to the scavenging activity.

In both cases, the presence of SNPs showed a significant reduction of free formaldehyde emissions inside the desiccator, compared to the control experiment. Temperature variations registered in each experiment was also negligible, with the highest  $\Delta T$  less than  $1^\circ\text{C}$ . Moreover, SNP3 show results very similar to SNP1 in both molar ratios, meaning that, after being subjected to temperatures similar to the resin's hot press conditions, ( $106^\circ\text{C}$  for 1 hour), the particles' results are comparable to the ones that have amine groups exposed, although no visual difference could be observed through TEM imaging.

Lastly, the weight percentage (wt%), in mass, of nanoparticles present in the test solutions was 0.008% and 0.016% for molar ratios 1:1 and 2:1 respectively. International emission limits vary depending on the product, its application, and the country, but the most common limit used, and one of the lowest, is  $0.12\text{ mg/m}^3$ , or 0.1 ppm [39-40].



The SNPs synthesized and used in this work lowered test samples' emissions from 0.53 ppm to 0.1 and even below, at 0.08, with very low wt%. Although testing directly with wood composites would give a more accurate result as to the behavior of the synthesized particles, they have shown promising results, reducing emissions to safer levels with very little SNPs added to the product.

#### 4. Conclusion

In this work, a formaldehyde scavenger for use in high performance resins was prepared. For testing purposes, two types of hybrid silica nanoparticles were synthesized: Ones containing functionalized with amine groups on the surface (SNP1) and others, similar with the former, but with an added shell functionalized with propyl groups (SNP2). Scavenging tests were made with both and compared with the control experiment. In the control experiment, the system registered a formaldehyde emission of 0.53 ppm, for a formaldehyde solution with concentration 7.2 ppm, a stable value obtained after 1 hour had elapsed since the start of the experiment. For the same system, adding SNP1 reduced emissions to 0.11 ppm, only 20% of the value obtained in the control. Using SNP2 the registered emissions reduced to 0.22 ppm or 40% of the control experiment's value. Lastly, SNP2 were subjected to a heat treatment with temperature conditions similar to the ones observed in the hot press curing process of UFR, 106°C for one hour. This step was to verify if SNP2 would activate, increasing their scavenging activity. Such was verified, as SNP2's new emission value dropped from 0.22 ppm to 0.10 ppm, almost identical to the value obtained for SNP1, which lack the silica shell. The same procedure was performed two distinct conditions: molar ratio of 1:1 and 2:1 for amine groups and formaldehyde present in solution, which for 10 mL of a formaldehyde solution 7.2 ppm correspond to 0.8 mg and 1.6 mg of silica nanoparticles, or 0.008% and 0.016% in weight, respectively. All values discussed above were from the first set of tests, with molar ratio 1:1. For the second set, ratio 2:1, SNP1's emissions stabilized at 0.08 ppm, the same value for SNP2 after heat treatment. Since international regulations set formaldehyde emissions to levels no higher than 0.21 ppm, with 0.1 ppm being the

benchmark for the highest concentration before compromising a person's safety, the system purposed in this work, as a proof-of-concept could achieve such targets with little amounts of added nanoparticles to UFR.

In conclusion, the system showed that the synthesized silica nanoparticles were capable of successfully scavenge free formaldehyde in solution. Also, the synthesized silica shell worked as intended, reducing the particles scavenging activity only before the heat treatment. However, the hybrid SNPs were still able to scavenge a significant portion of formaldehyde, which was not ideal, as formaldehyde is required for the resin's curing process.

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