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Contributed Paper

Long-term Study of Cu/SiO_2 Microspheres as Antimicrobial Additives in Paints

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ABSTRACT

Cu/SiO_2 microspheres were prepared with the sol-gel process by adding 3-(glycidyloxypropyl)trimethoxysilane (GLYMO), using tetraethoxysilane (TEOS) as a silica precursor. Sol-gel formation with acid catalysts and copper (II) acetate monohydrate was used in combination with a spray dryer, to obtain Cu/SiO_2 microspheres. SEM-EDS showed the surface morphology, the particle size, and the shape of the Cu/SiO_2 microspheres. The long-term effects of Cu/SiO_2 microspheres against microorganisms in paint were determined using the fungus *(P. funiculosum),* Gram-negative bacteria *(E. coli),* and Gram-positive bacteria *(S. aureus)*. The addition of GLYMO increased the stability of antimicrobial properties by lengthening the biocidal effect up to 12 months with 85% inhibition, in comparison with the commercial antimicrobial paint, which showed only 40% inhibition in the same time period.

Keywords: copper, silica microspheres, antimicrobial particles, paint additives, long-term biocides

1. INTRODUCTION

Antimicrobial agents garner interest from the building industry due to their potential benefits for various construction materials such as paint, cement, and concrete. This is because contamination by biofilms is a serious problem that can affect human health and aesthetics. Thus, there is an industrial interest to incorporate safe, durable, and cost-effective antimicrobial substances into paint and cement products to inhibit the growth of biofilms after the products have been applied. Different strategies are used to achieve antimicrobial properties such as the incorporation of antimicrobial agents directly into the paints or cements [1-3] or coating antimicrobial materials onto the finished products [4-6].

Metals such as silver, copper, and gold are often used as an effective antimicrobial agent. This class of antimicrobial materials can have elementary metals in a colloidal form [3, 7-11], metals in some carrier materials such as zeolites [1, 12], or polymer/metal composites [13-15]. Copper and its derivatives have received special attention as antimicrobial agents because the precious metals such as

silver and gold have become significantly more expensive in recent years. Studies have shown that dry copper surfaces were able to kill nearly all contaminated bacteria on the surface in just 2 minutes [16]. In addition, copper has been shown to exhibit antimicrobial properties while being less toxic to the environment, compared to other types of antimicrobial agents such as biocides or toxic coatings [3, 17]. It is believed that the copper element itself does not act as a biocide, but the release of copper ions is responsible for the antimicrobial properties [15-16, 18-19]. The ions can directly damage microbial cell walls and disrupt the structural integrity of cells. Other researchers also suggest that copper ions can cause oxidative damage to the DNA structure of microbes, resulting in deadly mutations [18, 20-21]. The effectiveness of the antimicrobial properties depends on the physicochemical properties of copper and is enhanced by decreasing particle size, which creates a more specific area for interactions. As a result, copper is often used in the form of copper nanoparticles [15].

One issue related to the use of copper nanoparticles is agglomeration, which can result in a decrease of their antimicrobial properties [1]. This problem can be addressed by immobilizing copper nanoparticles on a silica support via the sol-gel process to ensure their stability and durability [1, 12, 22-24]. Tetraethoxysilane (TEOS) is a commonly used silica precursor because it is cheap and environmentally friendly [25-27]. Sol-gel derived silica particles embedded with copper nanoparticles were successfully applied in many antibacterial paint additive applications [1], and have been tested in a hospital environment [5]. However, none of the studies have investigated the long term viability of copper as an antibacterial agent for more than 6 months [28].

Copper nanoparticles that are adsorbed onto a porous silica structure can be released too quickly, which limits the effectiveness of their antimicrobial activity [1]. To achieve prolonged antimicrobial effects, a release of copper ions can be delayed by modifying the silica support with 3-(glycidyloxypropyl) trimethoxysilane (GLYMO), which is an organofunctional silane with an additional branch of glycidyl as a functional group (Figure 1). GLYMO is used to improve the coating adhesion of organic compounds on a metal substrate by serving as a coupling agent between the organic and inorganic materials [6, 26]. GLYMO-doped silica was reported to retain dye particles in the matrices due to its ability to lower the pore size of the silica gel structure, and thus, increase pore density [25]. This creates a smaller porous structure with glycidyl groups to prevent the initial quick release of copper ions seen in previous studies [25].

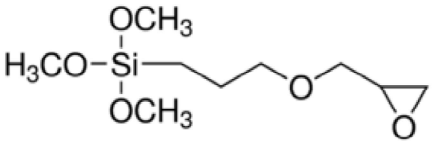

Figure 1. Structure of 3-(glycidyloxypropyl) trimethoxysilane.

This study develops antimicrobial additives for paint by incorporating copper loaded silica particles (Cu/SiO_2 microspheres). The strategy is to enhance the lifetime of the antimicrobial activity by modifying the silica matrix with GLYMO. In previous studies, the antimicrobial ability was reported as the comparison of the number of microorganism (CFU/mL) before and after the incubation with copper nanoparticles [1, 29-30]. However, a comparison with the control group was difficult. One study has

attempted to provide a comparison by instituting a scale to describe the growth of microorganisms on the surfaces using a scale ranging from 0 to 5 [1]. This methodology could be subject to an observer's judgment. As a result, this study presents the antimicrobial activity as percent inhibition, which is defined as the ability to inhibit the growth compared to the control group. This provides a systematic way of quantifying the growth of microorganisms on the surface of the paint samples.

In this study, the Cu/SiO_2 microspheres were synthesized and characterized by Scanning Electron Microscopy (SEM), which included the compositional analysis by Energy Dispersive X-Ray Spectroscopy (EDS). X-Ray Fluorescence, Thermogravimetric analysis (TGA), and Fourier Transform Infrared Spectroscopy (FTIR) were used to identify the composition of the Cu/SiO_2 microspheres. The resulting Cu/SiO_2 microspheres were subsequently mixed with acrylic-based paint for an antimicrobial test with fungus *(Penicillium funiculosum),* gram-negative bacteria *(Escherichia coli),* and gram-positive bacteria *(Staphylococcus aureus)*. The antimicrobial test was repeated after keeping the samples for 6 months and one year to determine the long-term effects of the antimicrobial activities. The results show that the antimicrobial activity is retained after keeping the samples for up to 1 year.

2. MATERIALS AND METHODS

2.1 Materials

Tetraethoxysilane (TEOS, lab grade), 3-(glycidyloxypropyl)trimethoxysilane (GLYMO, lab grade) and nitric acid (HNO_3) were purchased from Merck, Germany. Copper (II) acetate monohydrate (Sigma Aldrich, Singapore) was used as received.

2.2 Synthesis of Cu/SiO_2 Microspheres

Cu/SiO_2 microspheres were synthesized by the hydrolysis and condensation reactions of TEOS, GLYMO, and DI water in an acid catalyst (HNO_3). The total concentration of silica precursors in solution was kept at 0.20 (v/v). The details of the reaction mixture containing TEOS:GLYMO:H_2O and the amount of copper acetate are summarized in Table 1. TEOS, GLYMO, and DI water were mixed in a beaker with a constant speed using a magnetic stirrer. HNO_3 was added to the reaction mixture with continuous stirring. All syntheses were carried out at room temperature (25°C). Initially, the reaction was opalescent, and 1.5 hours after the HNO_3 was added, a clear solution was observed. Thereafter, the solution was continuously stirred for another 3.5 hours. Then, copper acetate was added to the reaction mixture with continuous stirring for another 30 minutes. The final mixture was spray-dried at a temperature of 200°C to obtain Cu/SiO_2 microspheres.

Table 1. Composition of different components used in preparing Cu/SiO_2 microspheres.

Sample No.	Sample Name	TEOS:GLYMO (v:v)	Copper (II) Acetate (w/v)	HNO_3 (v/v)
1	Cu_Si	1:0	0.2%	0.15%
2	Cu_Si_Gly1	1:0.10	1%	0.15%
3	Cu_Si_Gly2	1:0.17	3%	0.15%

2.3 Characterization

Fourier-transform infrared (FTIR) spectra of silica particles were recorded on a Nicolet iS50 with the KBr technique in the transmission mode. The spectra were recorded from 680 to 4000 cm^{-1} with a resolution of 4 cm^{-1} with 64 scans. Thermogravimetric analysis (TGA) was performed with a heating rate of 10 °C/min from 25 to 800 °C under a nitrogen atmosphere, to confirm the amount of the organosilane. The chemical compositions of microspheres were determined by an X-ray Fluorescence Spectrometer (Bruker S8 Tiger, 3 kW). A Field Emissive Scanning Electron Microscope (JEOL JSM 5410 LV) integrated with an Energy Dispersive Spectrometer (Oxford ISIS300) was used to observe the surface morphology of the samples and for the chemical composition analysis.

2.4 Antimicrobial Test

Fungi, gram-positive bacteria and gram-negative bacteria were selected to test for the antimicrobial efficacy of the Cu/SiO_2 microspheres. The acrylic-based paint was modified with different Cu/SiO_2 microspheres and tested with the cultures of a fungus (*Penicillium funiculosum*, *P. funiculosum*), gram-negative bacteria (*Escherichia coli, E. coli)*, and gram-positive bacteria *(Staphylococcus aureus*, *S. aureus*). The procedures were performed under aseptic conditions to prevent contamination. The growth was analyzed by using the image processing program, *ImageJ* (US National Institute of Health) to evaluate the area covered by the microbial growth. The antimicrobial activity was compared to the microbial growth on the control sample and was evaluated in terms of percent inhibition, which is defined in Equation (1):

$$\% \textit{ inhibition} = \left(1 - \frac{\textit{Area covered by the microbes on the sample}}{\textit{Area covered by the microbes on the negative control}}\right) \quad (1)$$

2.4.1 Materials

Whatman filter paper (Grade 1) was used as a support for the paint. Sodium chloride (Qrec, New Zealand), Potato Dextrose Agar (PDA), Eosin Methylene Blue (EMB, HiMedia, India) agar, and mannitol salt agar (Merck, Germany) were used without further purification.

2.4.2 Sample preparation

The sample preparation was modified from Zielecka *et al.* [1]. Acrylic-based paint was prepared by diluting with DI water at a ratio of 1:1 (v:v). The acrylic solution was then mixed with Cu/SiO_2 microspheres at different ratios from 1 to 20 wt.% (see Table 2). The mixture was then applied to the surface of filter papers, which were cut into pieces of 5x5 cm^2. The coated filter papers were air-dried for 24 hours at room temperature. A paper coated with a commercial antimicrobial paint (TOA 213 Water Repellent) was used as a positive control. A paper coated with acrylic-based paint was used as a negative control. The commercial antimicrobial paint (TOA 213) is a silane/siloxane water-based product, which works by repelling water [31]. It does not contain any antimicrobial additives. Most of the available commercial paints that claim to be antifungal and antimold in the market use a similar water repellent strategy.

2.4.3 Microbial preparation

2.4.3.1 Antifungal experiment

The method was modified from ASTM D2574-9700. A sub-culture of *P.funiculosum* was spread on Potato Dextrose Agar (PDA)

to prepare a stock suspension. It was incubated at 30 ± 2°C for at least 3 days, but not more than 7 days. The stock suspension was prepared by diluting *P.funiculosum* with 1% sterile NaCl solution until the fungi suspension contained 0.8 to 1.2 × 10^6 spores/mL as determined with a counting chamber.

The samples, which were coated with different ratios of Cu/SiO_2 microspheres and the commercial antimicrobial paint, were placed on the sterile PDA plates. An auto-pipette was used to drop 25 µL of fungi suspension onto the surface of the samples, and a cell-spreader was used to evenly spread the solution on the surface of the plates. All tests were performed with 5 parallel samples. The plates were incubated at 30 ± 2°C for 4 weeks. At the end of each week, fungi growth was observed and captured by a camera. The *ImageJ* program was used to analyze the growth area.

Table 2. Cu/SiO_2 microspheres content in the coated samples used in antimicrobial experiments.

Sample Name	Wt. % of Cu/SiO2 microspheres in Acrylic-based Paint (w/v)			
Cu_Si	1.0	5.0	10.0	20.0
Cu_Si_Gly1	1.0	5.0	10.0	20.0
Cu_Si_Gly2	1.0	5.0	10.0	20.0

2.4.3.2 Antibacterial experiment

Bacteria inoculum (2 mL) was incubated in 8 mL of Tryptic Soy Broth (TSB) with a tube cap loosely closed at 37 ± 2 °C for 24 hours. The concentration of bacteria was determined by counting colony forming units (CFUs) with a counting chamber. The bacteria stock solution was diluted with a 1% sterile NaCl solution until the concentration of bacteria was approximately 10^6 CFUs/mL.

To evaluate the antibacterial efficacy of Cu/SiO_2 microspheres, different growth media were used. For *E.coli*, Eosin Methylene Blue agar (EMB) agar was used because it is a selective and differential culture medium. *E.coli* growth turns the media greenish/gray metallic color. For *S. Aureus*, mannitol salt agar was used because it is also a differential medium for *S. Aureus*, containing mannitol and the indicator phenol red. It produces yellow colonies with yellow zones, causing the phenol red in the agar to turn yellow.

The samples coated with different amounts of Cu/SiO_2 microspheres were placed on the agar plates. The stock solution (25 µL) was dropped onto the surface of the samples, and a cell-spreader was used to evenly spread the solution on the surface of the plates. All tests were performed with 5 parallel samples, and incubated at 37 ± 2 °C for one week. Bacteria growth was observed on each sample and captured by a camera. The *ImageJ* program was used to analyze the growth area.

2.4.3.3 Long-term antimicrobial study

The coated samples were incubated at 37 ± 2 °C for 6 months and 12 months, and used to test their long-term antimicrobial activities based on the procedure outlined above.

3. RESULTS AND DISCUSSION

3.1 Characterization of Cu/SiO_2 Microspheres

The spectra of Cu/SiO_2 microspheres are showed in Figure 2. All samples show a

strong band at 1100-1080 cm^{-1}, which corresponds to Si-O-Si stretching. This band indicates the formation of the Si-matrix [32]. The broad band around 3600-3200 cm^{-1} corresponds to -OH stretching [33, 34]. However, it is overlapped with Si-OH stretching at ~ 3050 cm^{-1} [35]. The band at ~2850 cm^{-1} corresponds to asymmetrical stretching of the C-H bond in methoxysilane (Si-O-CH_3), which was used to identify the glycidyl group [32]. Both Cu_Si_Gly1 and Cu_Si_Gly2 show a characteristic peak of -Si-O-CH_3 at 2870 cm^{-1} while this peak was not observed in the Cu_Si sample.

The organic content of the Cu/SiO_2 microspheres was analyzed by TGA. The thermogram in Figure 3 shows the sample weight loss at about 25-125°C, which corresponds to a humidity loss. The weight loss from 330 to 700°C corresponds to the degradation of organic compounds, which was used to identify the glycidyl groups. The amount of GLYMO in the final Cu/SiO_2 microparticles is summarized in Table 3.

Table 3. Organic Content of Cu/SiO_2 microspheres determined from TGA.

Sample Name	Organic Content (wt. %)	Theoretical Ratio of TEOS:GLYMO	Experimental Ratio of TEOS:GLYMO
Cu_Si	-	1:0	-
Cu_Si_Gly1	8.39	1:0.10	1:0.12
Cu_Si_Gly2	10.34	1:0.17	1:0.20

SEM images in Figures 4-6 show spheres of silica matrices with a diameter of more than 10 mm. Figure 6 shows that the Cu_Si_Gly2 sample contains copper particles on the silica surface, and the content of copper is denser than on Cu_Si_Gly1 (Figure 5). The copper content was confirmed by EDS, and Figures 4(b)-6(b) show the spectra of characteristic energy dispersive X-ray with the spectral lines of copper. The copper content was determined from the average of 5 data points, and reported in terms of the copper to silica ratio (Cu:Si). The Cu_Si_Gly1 sample has a ratio of 0.18:1, and the Cu_Si_Gly2 sample has a ratio of 0.46:1, while the non-modified Cu/SiO_2 microspheres have a ratio of 0.16:1. Because EDS provides only limited data points, the copper content in GLYMO-modified Cu/SiO_2 microspheres was confirmed by X-Ray Fluorescence (XRF), which is capable of metal analysis from low parts per million (ppm) to 100%, for most of the elements that were present in the samples [36-38]. The results from XRF corroborated the EDS results, and the characteristics of Cu/SiO_2 and GLYMO-modified microspheres are summarized in Table 4. It shows that a sample that contains a higher amount of GLYMO (Cu_Si_Gly2) holds more copper in the sample. In addition, the Brunauer Emmett Teller (BET) analysis showed that the pore volume of the Cu_Si_Gly1 samples was 0.111 cm^3/g, while the pore volume of the Cu_Si_Gly2 samples was 0.017 cm^3/g. This is consistent with an earlier study that reported that GLYMO was effective in shrinking the pore volume [25]. This shrunken pore volume could result in the ability to contain copper ions more effectively in the structure.

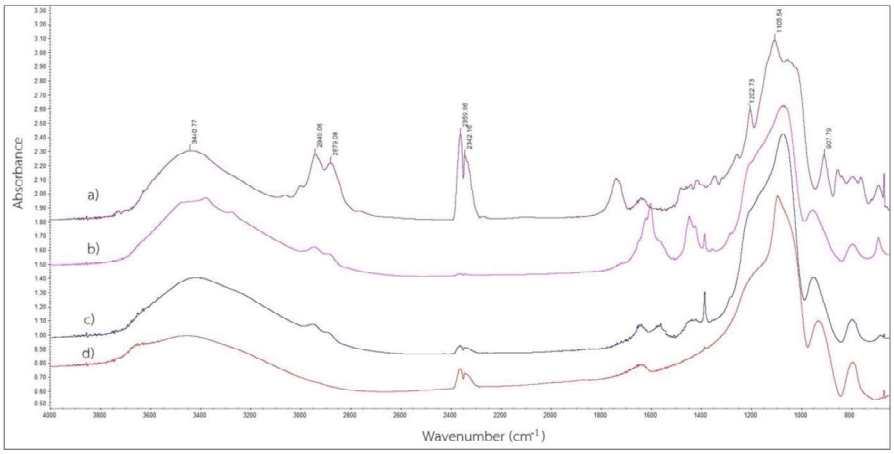

Figure 2. FTIR spectra of (a) Cu_Si sample (b) Cu_Si_Gly1 sample (c) Cu_Si_Gly2 sample and (d) unreacted GLYMO. The composition of all samples is described in Table 1.

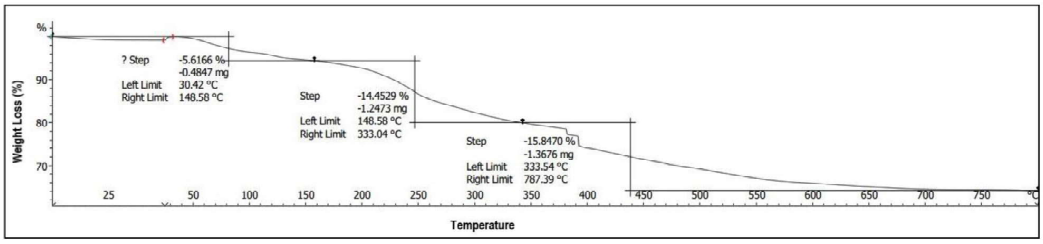

Figure 3. Thermogram of GLYMO modified Cu/SiO_2 microparticles plotted as the sample weight loss, as a function of temperature.

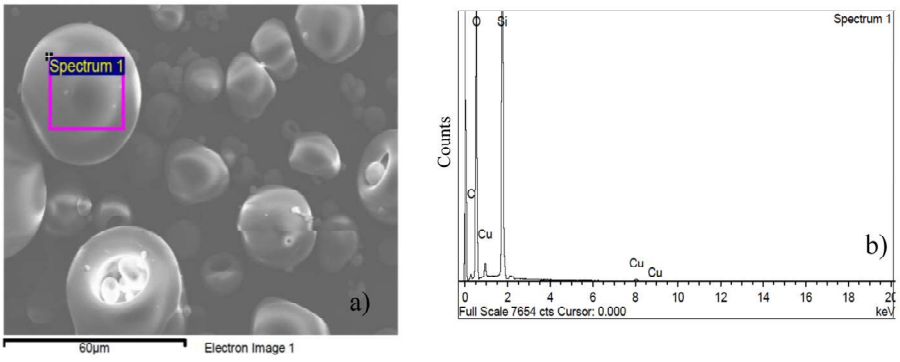

Figure 4. (a) SEM micrograph of sample Cu_Si and (b) EDS spectrum of sample Cu_Si containing copper.

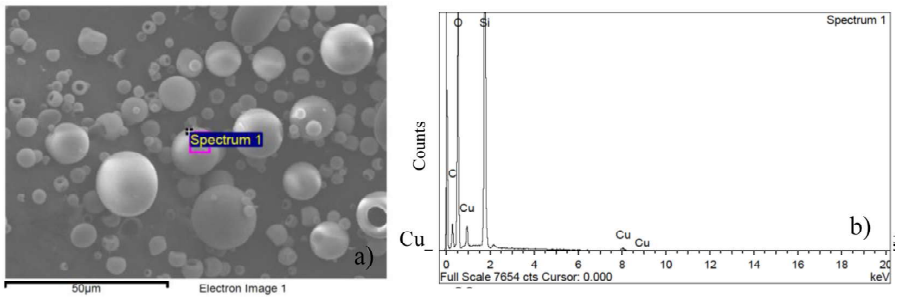

Figure 5. (a) SEM micrograph of sample Cu_Si_Gly1 and (b) EDS spectrum of sample Cu_Si_Gly1 containing copper.

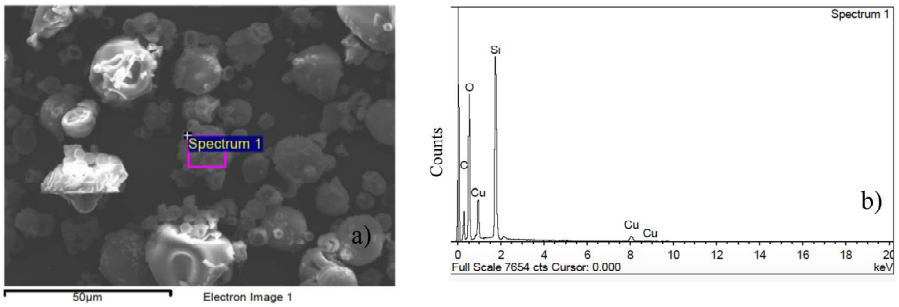

Figure 6. (a) SEM micrograph of sample Cu_Si_Gly2 and (b) EDS spectrum of sample Cu_Si_Gly2 containing copper.

Table 4. Copper content in Cu/SiO_2 microspheres.

Sample No.	Sample Name	Theoretical Ratio of TEOS:GLYMO	Copper Content (w/w)	Ratio of Cu:Si (XRF)	Ratio of Cu:Si (EDS)
1	Cu_Si	1:0	3.51 %	0.08:1	0.16:1
2	Cu_Si_Gly1	1:0.10	6.37 %	0.15:1	0.18:1
3	Cu_Si_Gly2	1:0.17	17.24 %	0.49:1	0.46:1

The particle size distribution of Cu/SiO_2 microspheres is shown in Figure 7. The Cu_Si_Gly1 sample contains particles ranging from 628 to 1,182 nm with a mean particle size of 843 nm and the Polydispersity Index (PI) of 0.63. The Cu_Si_Gly2 sample contains slightly larger particles ranging from 1,352 to 2,494 nm with a mean particle size of 1,651 nm and PI of 0.44. The reduction in polydispersity as GLYMO content increases is consistent with the literature which reported that surface functionalization results in better dispersion [39]. In addition, surface functionalization sometimes results in rougher surfaces, which would induce agglomeration [40]. This can explain why the sample with high GLYMO content (Cu_Si_Gly2) has a larger particle size.

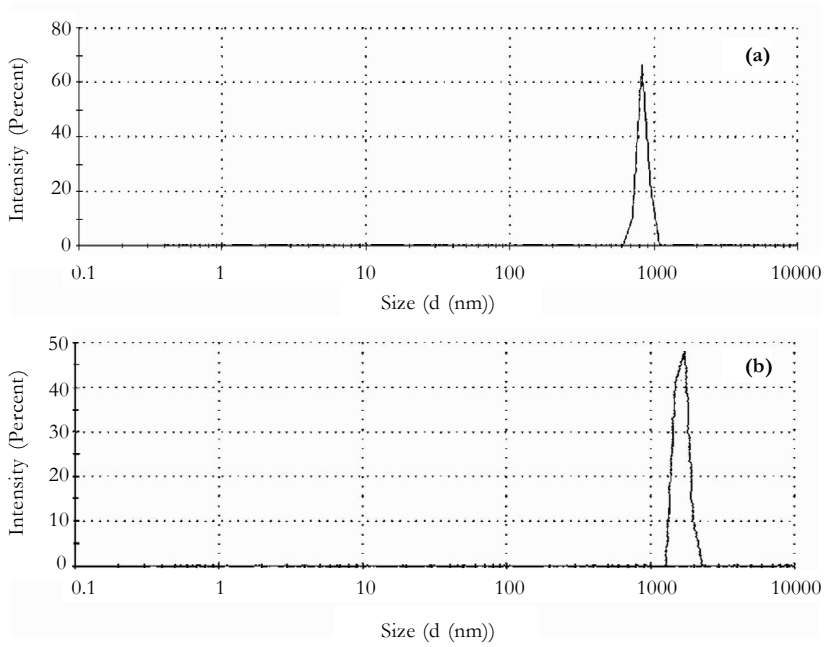

Figure 7. Particle size distribution of Cu/SiO_2 microspheres. (a) Cu_Si_Gly1 (b) Sample Cu_Si_Gly2.

3.2 Antimicrobial Test

3.2.1 Antifungal experiment

The antifungal efficacy of Cu/SiO_2 microspheres was tested throughout the year (immediately after preparation, 6 months and 1 year) and compared to the commercially available antifungal paint. The results show that non-modified Cu/SiO_2 microspheres (Cu_Si sample) exhibit the ability to inhibit *P. funiculosum* growth. As the concentration of Cu/SiO_2 microspheres in the paint increases, the inhibition of fungal growth increases, as seen in Table 5.

Table 5. Percent fungal inhibition for sample Cu_Si as a function of Cu/SiO_2 microspheres concentration.

Cu/SiO_2 microspheres concentration	Cu_Si content (10 wt.%)	Cu_Si content (20 wt.%)	Cu_Si content (30 wt.%)	Commercial antifungal paint (TOA 213)
Week 1	32.75 ± 7.08	51.01 ± 6.79	84.87 ± 6.32	4.96 ± 4.50
Week 2	28.98 ± 7.84	49.96 ± 6.62	75.24 ± 7.93	8.07 ± 4.69
Week 3	18.50 ± 5.55	29.92 ± 11.58	69.16 ± 7.91	8.11 ± 4.60
Week 4	15.67 ± 4.69	29.29 ± 11.58	62.28 ± 9.11	7.85 ± 4.50

All the samples with Cu_Si microspheres in paint below 10 wt.% did not show biocidal activities because the fungal growth covered all the areas of the samples, similar to that of the negative control (acrylic-based paint alone). As a result, they all show 0% inhibition. The result demonstrates that the higher the amount of Cu_Si microspheres added, the higher the percent inhibition, which confirms the assumption that more copper leads to more antimicrobial characteristics. In addition, all concentrations of Cu_Si microspheres

performed better than the commercial antimicrobial paint. Another trend observed in this experiment is a decrease in fungal inhibition with time. For example, for 30 wt.% Cu_Si microspheres, the percent inhibition was reduced to 62% in week 4, from 85% in week 1.

The antifungal efficacy significantly improved with the addition of the organosilane, GLYMO. The results in Figure 8 show that the Cu_Si_Gly2 sample is effective at prohibiting fungal growth at a concentration of 5 wt.% and above. This is consistent with a previous study that suggested the effect of GLYMO was to act as a physical entrapment to lower the pore volume, to prevent the dye from leaching from the silica pores [25]. Nonetheless, the ability to inhibit fungal growth decreased from week 1 to week 4 in all samples.

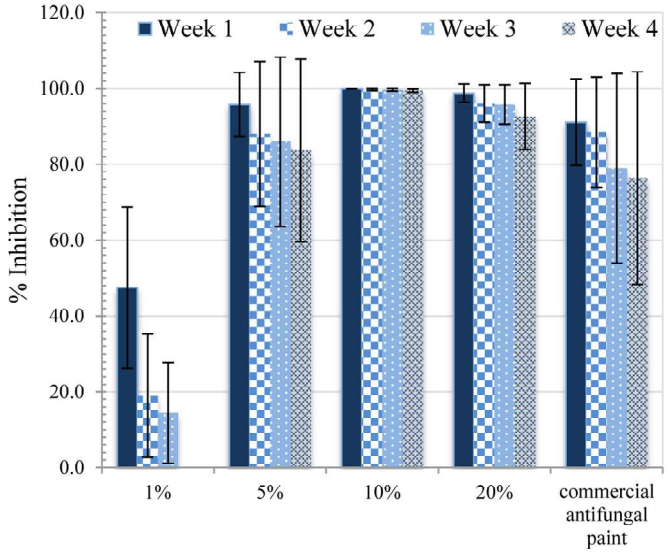

Figure 8. Percent inhibition of Cu_Si_Gly2 sample, plotted as a function of Cu/SiO_2 microsphere content, in comparison with the commercial antifungal paint (performed immediately).

Figure 9 shows a comparison between the two samples modified with GLYMO, Cu_Si_Gly1, and Cu_Si_Gly2. Table 4 shows that the sample with less GLYMO content (Cu_Si_Gly1) had a lower amount of copper loaded into the Cu/SiO_2 microspheres; hence, it was less effective at inhibiting *P. funiculosum* growth, as the percent inhibition of the Cu_Si_Gly1 sample is consistently below that of the Cu_Si_Gly2 sample. The long-term studies of 6 months (Figure 10 (a)) and 1 year (Figure 10(b)) show the better antimicrobial activity of the Cu_Si_Gly2 samples over the commercial antifungal paint at every composition except for 1 wt.%. After 6 months, the samples coated with at least 5 wt.% of Cu_Si_Gly2 were able to inhibit the fungal growth more than 80% over 4 weeks.

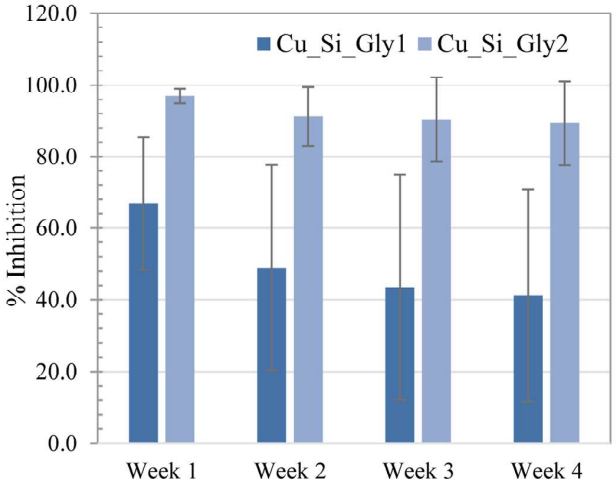

Figure 9. Comparison of Sample Cu_Si_Gly1 and Cu_Si_Gly2 at 5 wt.% of Cu/SiO_2 microspheres in acrylic-based paint.

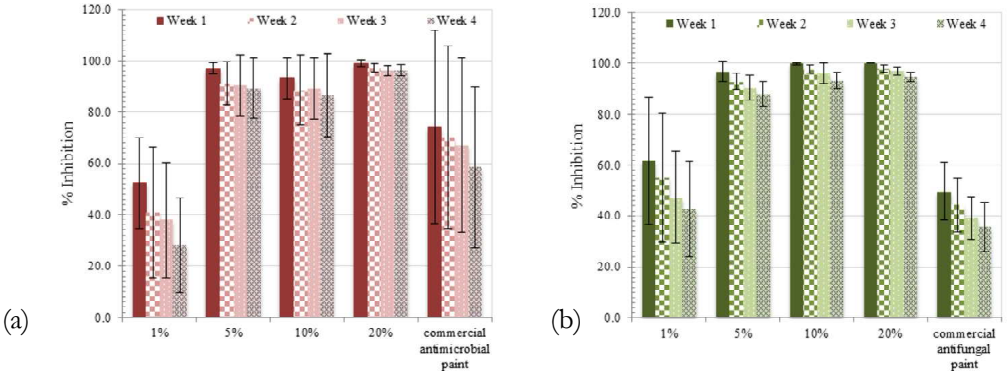

Figure 10. Percent inhibition of Cu_Si_Gly2 sample, plotted as a function of Cu/SiO_2 microsphere content, in comparison with the commercial antifungal paint; (a) performed after 6 months, (b) performed after 12 months.

The antifungal ability of the commercial antimicrobial paint significantly decreases after one year while the modified Cu/SiO_2 microspheres (Cu_Si_Gly2 sample) retained most of their antifungal ability. Figure 10(b) shows that after one year, the sample with 5 wt.% GLYMO-modified Cu/SiO_2 microspheres can inhibit more than 80% of fungal growth while the commercial antimicrobial paint's performance is reduced to 50% inhibition. This result shows that the GLYMO-modified Cu/SiO_2 microspheres can increase the longevity of the biocidal ability. This is possible because of the organosilane (GLYMO), allowing a higher copper loading capacity. However, a higher amount of Cu_Si_Gly2 exhibits a strong blue color, which could lead to color aberration when added to painting. Thus the sample with a Cu/SiO_2 microspheres content of 5 wt.% is preferred.

3.2.2 Antibacterial experiment

For Gram-negative bacteria *(E. coli)*, the

commercial antimicrobial paint (TOA 213) could not completely inhibit bacterial growth. Only 90% inhibition was seen after one week, as some metallic gray colonies were observed. All of the GLYMO-modified Cu/SiO_2 microspheres samples (1 - 5 wt.%), however, could inhibit all bacterial growth with 100% inhibition. It should be noted that the sample that contained only paint still showed some degree of inhibition, which means that the paint, despite not being modified with the antimicrobial agent, is still able to inhibit bacterial growth by itself.

For Gram-positive bacteria (*S. Aureus*), the trend was similar. All samples coated with the acrylic-based paint mixed with the GLYMO-modified Cu/SiO_2 microspheres (1 - 5 wt.%) could completely inhibit the growth throughout one week of incubation, while the papers coated with the commercial antimicrobial paint can only inhibit up to 95% of bacterial growth. A similar trend was seen in the long term antimicrobial study, in which all of the GLYMO-modified Cu/SiO_2 microsphere samples (1 - 5 wt.%) could inhibit 100 percent of the bacterial growth despite keeping the paint samples for one year. This result suggests that the GLYMO-modified Cu/SiO_2 microspheres could be an alternative to provide a sterile environment in household and healthcare facilities. Previous study tried to construct chairs for the waiting room in a hospital by coating them with organic paint mixed with 5 wt.% nanostructured zeolite/copper particles. The study showed the reduction of bacteria colonies compared to the control group but did not show 100 percent inhibition as seen in this study [5].

4. CONCLUSIONS

This study has shown that Cu/SiO_2 microspheres, synthesized by sol-gel and spray drying process, can inhibit microbial growth, and an organosilane (GLYMO) can be used to enhance the copper loading capacity. The amount of copper in the Cu/SiO_2 microspheres increased as the ratio of GLYMO to TEOS (tetraethoxysilane) increased. The copper content in the final product of Cu_Si_Gly2 was confirmed to be higher than that of Cu_Si_Gly1 by EDS and XRF. Cu_Si_Gly2 had better performance in inhibiting microbial growth than Cu_Si_Gly1. In addition, this study showed that incorporating an organosilane, GLYMO into the silica structure can provide durability and maintain copper stability over the long term. These Cu/SiO_2 microspheres exhibited antimicrobial ability over 12 months, and had superior performance over the commercially available antimicrobial paint (TOA 213). After keeping the painted samples for one year, the 5 wt.% GLYMO-modified Cu/SiO_2 microspheres could inhibit more than 80% of fungal growth, while the performance of the commercial antimicrobial paint (TOA 213) dropped to less than 50% inhibition. In addition, these Cu/SiO_2 microspheres could inhibit 100% of bacterial growth for a period of one year.

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