PREPARATION AND TESTING OF HYDRO INSULATING SILICONE SEALING WITH ADDITION OF THERMOCHROMIC DYE DEA-CUCL4

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https://doi.org/10.37904/nanocon.2022.4591

Abstract

Nanoparticles of thermochromic complex pigment bis- (diethylammonium) tetrachloridocuprate (II) with chemical formula $[NH_2(C_2H_5)_2]_2CuCl_4$ (abbreviated DEA-$CuCl_4$) was prepared by crystallization and subsequent grinding in a cryo-mill. Nanoparticles were incorporated into a flexible hydro insulating transparent silicone matrix. The surface properties, especially surface hydrophobicity and elasticity of the resulting composite, as well as color indication of thermal changes and resistance to mold were tested.

Keywords: DEA-$CuCl_4$, bis-(diethylammonium) tetrachloridocuprate (II), thermochromic dye, antifungal, silicone

1. INTRODUCTION

Smart functional dyes are the new trend in many application fields such as textile industry, medicine, automotive, robotics, biotechnology etc. Reversible color changes characterizing a chromism can occur depending on physical or chemical stimulations, but thermochromism is the most studied of all chromisms.

In this study, we focused on the incorporation of nanoparticles of the inorganic thermochromic pigment bis-(diethylammonium) tetrachlorocuprate (II) into a silicone matrix to create a smart multifunctional composite material which combines the waterproofing and water-repellent properties of silicone [1] with the thermochromic effect of the inorganic dye DEA-$CuCl_4$. Exterior and interior applications of silicone sealants often expose this material to conditions ideal for biofilm growth on their surfaces: biofilm is created by bacteria and fungi which thrive in moisture and heat in the areas difficult to clean. For this reason, these materials (called "sanitary silicones") are often treated with a biocide with the purpose to block the growth of biofilm on their surface. Although the antibiotic properties of the DEA-$CuCl_4$ dye have not been described yet, it could give the composite the ability to resist bacterial biofilm and mold growth. The DEA-$CuCl_4$ dye contains copper (II) thermochrome and many studies have already demonstrated the antifungal and antibacterial effects of various copper compounds in both nanoparticle and solution form [2-6].

1.1. DEA-$CuCl_4$

Bis-(diethylammonium) tetrachloridocuprate (II) with chemical formula $[NH_2(C_2H_5)_2]_2CuCl_4$ (abbreviated DEA-$CuCl_4$) is an inorganic complex crystalline dye that exhibits discontinuous thermochromism. Its bright green colour changes rapidly to yellow at temperatures above approximately 55 °C. This colour change corresponds to a change in the coordination geometry of the tetrachlorocuprate anion (which is the chromophore of the compound) from a deformed square plane to a deformed tetrahedron [7,8]. Diethylammonium cations form hydrogen bridges via N-H···Cl interactions with tetrachlorohydrate anions, leading to the formation of a two-dimensional planar hydrogen bridge network [9]. Although the cause of the colour changes is the aforementioned change in the geometry of the tetrachlorocuprate anion, in fact, the weakening of the hydrogen bonds and the stretching of the ethyl chains of the organic component (diethylammonium cations) due to increasing temperature are the driving forces behind this change [10]. Although the process is reversible, it has recently been found that the dynamic phase transition process is not perfectly reversible - the green-to-yellow transition is driven primarily by the weakening of hydrogen bonds, whereas during the yellow-to-green transition, the reconstitution of hydrogen bonds falls behind the rearrangement of alkyl chains [11].

1.2. Silicone

Silicone rubber is an inorganic – organic elastomer. Chemically it is a polysiloxane that consist of an inorganic silicon-oxygen backbone chain with two organic groups (mostly methyls) attached to each silicon center. Properties include low chemical reactivity, low toxicity, high biocompatibility, heat resistance in the temperature range -100 to 300 °C and water repellency. It is used e.g., as insulation, sealing, coating and specialty products in construction, electronics, food, medical and cosmetic surgery, automotive, etc. One component condensation acetoxy curing silicones are used most often. These silicones cure with the presence of atmospheric moisture and generally have a very fast cure time (within 24 hours). Unfortunately, although these silicones adhere very well to most materials, the acetic acid could be corrosive to metals [12].

2. EXPERIMENTAL PART

2.1. Chemicals and materials

Diethylammonium hydrochloride (Sigma Aldrich), copper (II) chloride dihydrate (Sigma Aldrich), transparent acetoxy silicone (Den Braven), transparent sanitary acetoxy silicone (Monton), rice agar in Petri dishes (Viamar International).

2.2. Synthesis of DEA-CuCl4

Bis-(diethylammonium) tetrachloridocuprate (II) was prepared in the laboratory from aqueous solutions of diethylammonium hydrochloride and copper (II) chloride dihydrate, compounds were mixed in stoichiometric proportions according to equation (1). The resulting solution was left in a wide glass dish for several days at room temperature when crystallization occurred. After a few days, the entire bottom of the glass dish was covered with a continuous layer of light green crystalline dye. This crystalline pigment was subsequently cooled to -5 °C and then ground in a laboratory cryo-mill (Retsch) using a zirconium oxide grinding jar and balls. Two 30-second cycles of impact ball milling with a frequency of 20 Hz in dry grinding mode allowed the preparation of DEA-CuCl4 pigment nanoparticles with a size of 236 ± 44 nm (95% confidence interval).

$$2[(C_2H_5)_2NH_2]Cl + CuCl_2 \cdot 2H_2O \rightarrow 2[(C_2H_5)_2NH_2]_2CuCl_4 + 2H_2O \tag{1}$$

2.3. Preparation of silicone/DEA-$CuCl_4$ composite

Three samples with a diameter of 3.5 cm and a thickness of about 0.5 cm were prepared based on a transparent neutral silicone paste with 0.02 wt.% (sample A) and 0.2 wt.% (sample B) of crushed DEA-$CuCl_4$ nanoparticles. The reference sample (sample 0) contained only silicone without the addition of DEA-$CuCl_4$ nanoparticles. The samples containing DEA-$CuCl_4$ were thoroughly homogenized, and all samples were left at room temperature for 4 days to dry. After drying, these samples were measured and tested for: hardness measurement, color reversal of the composite, surface hydrophobicity (measurement of the contact angle of the water droplet), and testing for resistance to mold (*Penicillium* spp.) growth.

2.4. Shore hardness measurement

Silicone rubber is often applied as a sealing compound that retains a certain degree of elasticity even after curing (drying). It was investigated whether the addition of DEA-$CuCl_4$ nanoparticles to silicone rubber in amounts up to 0.2 wt.% would significantly affect its hardness. For this purpose, a Shore durometer measurement according to [ASTM D2240] is standardly performed. Especially for the measurement of flexible rubbers, thermoplastic elastomers and semi-rigid plastics, the Shore A method is suitable. In this measurement, a hardened steel rod of 1.4 mm diameter with 35° truncated cone of 0.79 mm diameter is pressed into the material, spring force approximately 8.05 N. The Shore A hardness scale 0 - 100 measures the hardness of flexible rubbers that range from very soft and flexible to hard with almost no flexibility at all. Each specimen was measured 10 times and the results averaged.

2.5. Thermochromic properties measurement

Measurement of the reversible thermochromic properties of the formed composite was performed. For this purpose, the composite was repeatedly heated and cooled, and the thermal changes were recorded using a Fluke thermal imaging camera. An RGB-2000 color analyzer (10 bits) with 45° geometry was used to record the color changes.

2.6. Surface hydrophobicity measurement

The hydrophobicity of silicone surfaces is well known, which is why silicone rubbers are often used as waterproofing seals. Investigation was focused on the addition of DEA-$CuCl_4$ nanoparticles significantly affects this hydrophobicity. To this end, the contact angle of the water droplet with the surface of the samples was measured using a USB 2.0 VGA Video Device and evaluated with the See System for surface energy measurement software (version 6.3) using the Li-Neumann model. The result was obtained from 10 measurements of each sample.

2.7. Fungal growth resistance testing

The antifungal activity test of the composite was arranged as a classic disc diffusion antimicrobial assay. The samples were tested in contact with spores of *Penicillium* spp. The surface of rice agar in petri dishes was inoculated with 1 ml of fungal spore suspension, which was obtained by simply rinsing the fungus growing on organic waste. A sample of the composite was loosely placed on the surface and the sample was left in the dark at room temperature for 48 hours. The growth of CFUs in the vicinity of the test samples was monitored and the average width of the following rings was measured: a clearing ring (denoted as "halo zone" in **Table 1)** where the number of CFUs grown was reduced, and a completely clear ring around the samples (denoted as "zone of clearing" in **Table 1**) where the growth of CFUs of bacteria or mold was completely suppressed. For comparison, an additional sample X was made of so-called sanitary silicone sealant, which is a commercial silicone rubber that contains a fungicide to inhibit mold growth and is intended for use e.g., in bathrooms.

3. RESULTS AND DISCUSSION

The results of the tests performed on samples 0, A and B are summarized in **Table 1**. As regards the hardness of the samples, the Shore A values were around 20, which corresponds to values of relatively soft and flexible rubber. The confidence intervals of pure silicone and sample A overlap, indicating that the low content of dye nanoparticles (here 0.02 wt. %) practically does not affect the hardness and flexibility of silicone. However, the confidence interval values of sample B are slightly higher, and it can be concluded that the hardness of the composite increases slightly with higher content of dye nanoparticles in the silicone matrix. As for surface hydrophobicity, the contact angle of the water droplet with the surface of the composites exceeded 90° for all samples, which is the limit at which the material can be described as hydrophobic. However, the confidence intervals of the water droplet contact angles overlap for all three samples, therefore it can be concluded that the addition of DEA-$CuCl_4$ dye nanoparticles to the silicone did not significantly affect the surface hydrophobicity even at a dye content of 0.2 wt.%.

During heating and cooling of the composite, the color changes of samples B were recorded using RGB coordinates (**Figure 1**). A significant change in the RGB-coordinates values in the region around 55 °C corresponds to the phase transition of DEA-$CuCl_4$ and the color change of the composite.

Table 1 An overview of the test results of samples 0, A and B

Sample	Shore A	Contact angle of water	Phase transition temperature	Halo zone (zone of clearing)
0	20.7 ± 0.6	93.0° ± 7.5°	-	0
A	19.0 ± 1.3	94.5° ± 5.5°	55 °C	8-12 mm (2 mm)
B	22.5 ± 0.5	93.5° ± 4.5°	55 °C	8-12 mm (2 mm)

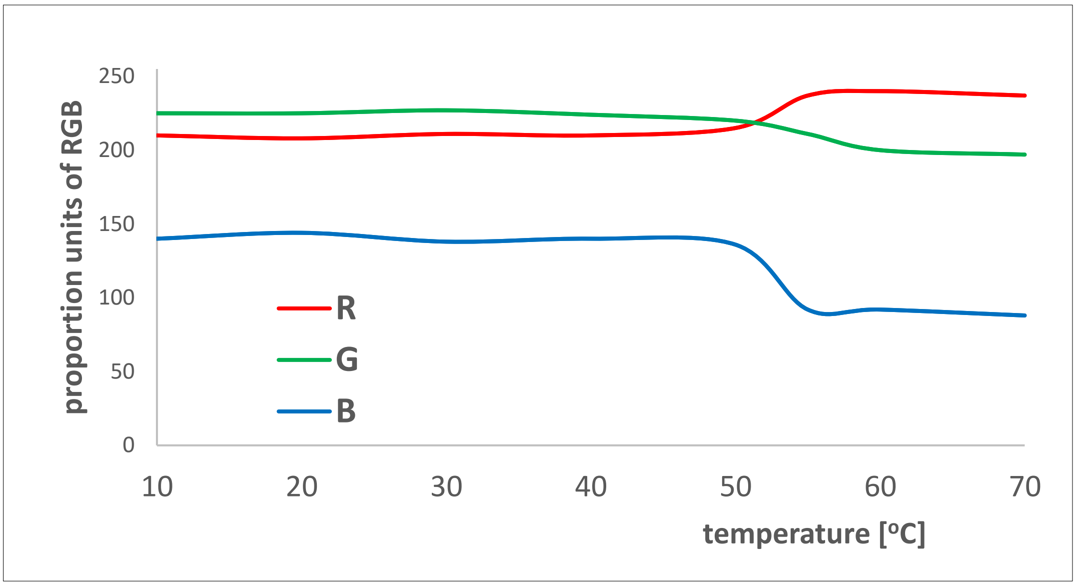

Figure 1 Changes in RGB values of the composite in the temperature range 10 to 70 °C

Figure 2 Sample 0 on rice agar inoculated by *Penicillium*

Figure 3 Sample B on rice agar inoculated by *Penicillium*

Figure 4 Sample X on rice agar inoculated by *Penicillium*

When the samples were contacted with rice agar inoculated with *Penicillium* spp. spores, a distinct clearing (halo zone) of 8-12 mm width occurred in samples A, B and X within 48 hours, with a completely clear ring of approximately 2 mm width (zone of clearing) in the immediate vicinity of the samples. No clearing was observed for sample 0. Interestingly, the inhibition zones were approximately the same in samples A and B regardless of the DEA-$CuCl_4$ concentration (**Figures 2 – 4**). A similar width of inhibition zones was observed in sample X. This suggests that the DEA-$CuCl_4$ content of 0.02 wt.% is already sufficient to inhibit fungal growth and that the diffusion of the dye, like the diffusion of the fungicide from the silicone matrix into the surroundings, is limited. The test results support our expectation of the DEA-$CuCl_4$ dye antifungal effects due to its cuprate (II) chromophore content and it can replace fungicides that are standardly added to so-called sanitary silicones. It is also necessary to draw attention to the issue of instability of this system. We observed that the samples changed color and decreased thermochromism over several days. DEA-$CuCl_4$ is sensitive to corrosive environments, acids and atmospheric oxygen or the presence of base metals due to its copper cation content. The use of so-called neutral silicones, which are one-component oxime or alkoxy silicones intended for contact with copper and zinc, did not solve this issue either, because the dye in contact with these systems immediately lost its thermochromic properties. This issue could be solved, for example, by protective encapsulation of dye particles, which is beyond the scope of this study.

4. CONCLUSION

We created a silicone composite with the addition of 0.02 and 0.2 wt.% of the thermochromic dye DEA-$CuCl_4$ in the form of nanoparticles with a size of approximately 236 ± 44 nm. While the dye content of 0.2 wt.% slightly increased the hardness of the silicone rubber, the surface hydrophobicity of the composite did not change. The thermochromic properties of the dye were maintained even after repeated heating-cooling cycles in the temperature range 10 to 80 °C with a temperature phase transition around 55 °C. It was demonstrated that the presence of the DEA-$CuCl_4$ pigment nanoparticles can replace the addition of a fungicide, which is added to commercial silicone hydro insulating sealing for wet applications and that the composite inhibited growth of *Penicillium*. Hydrophobic surface, waterproofing properties, color indication of thermal transition in 55 °C and resistance to mold growth could make this composite an ideal insulating material for indoor and outdoor applications in warm and humid areas with large temperature ranges (e.g., sauna, spa, tropical areas). However, the issue of dye degradation still needs to be improved as copper is reduced in contact with the external environment and the dye loses its thermochromic properties over time.

ACKNOWLEDGEMENTS

This work was supported by Iceland, Liechtenstein and Norway through the EEA Grants and the Technology Agency of the Czech Republic within the framework of project "inherently Flexible Aerogels for energy effiCient structurES (i-FACES)" (Grant number TO01000311).

REFERENCES

[1] CHANG, J.W., GORUR, R.S. Surface recovery of silicone rubber used for HV outdoor insulation. In: *IEEE Transactions on Dielectrics and Electrical Insulation*. 1994, vol. 1, no. 6, pp. 1039-1046.

[2] KŘÍŽOVÁ, H., ROTKOVÁ, J. Green Synthesis of Copper-Based Nanostructures Using Tannic Acid and Testing of Their Antibacterial Properties. In: *Nanocon* - 6th International Conference on Nanomaterials. Brno: Tanger, 2014, pp. 621-626.

[3] CIOFFI, N., TORSI, L., DITARANTO, N., TANTILLO, G., GHIBELLI, L., SABBATINI, L., ...TRAVERSA, E. Copper nanoparticle/polymer composites with antifungal and bacteriostatic properties. *Chemistry of Materials*. 2005, vol. 17, no. 21, pp. 5255-5262.

[4] DANG, J., ZHANG, Y., DU, Z., ZHANG, H., LIU, J. Antibacterial properties of PES/CuCl2 three-bore hollow fiber UF membrane. *Water Science and Technology*. 2012, vol. 66, no. 4, pp. 799-803.

[5] CHATTERJEE, A.K., CHAKRABORTY, R., BASU, T. Mechanism of antibacterial activity of copper nanoparticles. *Nanotechnology*. 2014, vol. 25, no. 13, 135101.

[6] CHALANDAR, H.E., GHORBANI, H.R., ATTAR, H., ALAVI, S.A. Antifungal effect of copper and copper oxide nanoparticles against Penicillium on orange fruit. *Biosciences Biotechnology Research Asia*. 2017, vol. 14, no. 1, pp. 279-284.

[7] CHOI, S., LARRABEE, J.A. Thermochromic tetrachlorocuprate (II): an advanced integrated laboratory experiment. *Journal of Chemical Education*. 1989, vol. 66, no. 9, p. 774.

[8] KAPUSTYANYK, V.B., KORCHAK, Y.M. Thermochromic phase transition in [NH2 (C2H5) 2] 2CuCl4 Crystals. *Journal of Applied Spectroscopy*. 2000, vol. 67, no. 6, pp. 1045-1049.

[9] ALDRICH, E.P., BUSSEY, K.A., CONNELL, J.R., REINHART, E.F., OSHIN, K.D., MERCADO, B.Q., OLIVER, A.G. Crystal structure of the thermochromic bis (diethylammonium) tetrachloridocuprate (II) complex. *Acta Crystallographica Section E: Crystallographic Communications.* 2016, vol. 72, no. 1, pp. 40-43.

[10] KELLEY, A., NALLA, S., BOND, M.R. The square-planar to flattened-tetrahedral CuX42−(X= Cl, Br) structural phase transition in 1, 2, 6-trimethylpyridinium salts. *Acta Crystallographica Section B: Structural Science, Crystal Engineering and Materials*. 2015, vol. 71, no. 1, pp. 48-60.

[11] XIE, D., XU, J., CHENG, H., WANG, N., ZHOU, Q. The role played by amine and ethyl group in the reversible thermochromic process of [(C2H5) 2NH2] 2CuCl4 probing by FTIR and 2D-COS analysis. *Journal of Molecular Structure*. 2018, vol. 1161, pp. 267-272.

[12] DE BUYL, F. Silicone sealants and structural adhesives*. International Journal of Adhesion and Adhesives*. 2001, vol. 21, no. 5, pp. 411-422.