STRENGTH AND ANTIFUNGAL CHARACTERISTICS OF VISCOSE CANVAS WITH ACRYLIC COATING CONTAINING NANOPARTICLES OF ZINC OXIDE AND DOLOMITE

KŘÍŽOVÁ Hana, WIENER Jakub

Technical University of Liberec, Faculty of Textile Engineering, Department of Material Engineering, Liberec, Czech Republic, EU

Abstract

Preserving books for long-term is a challenging task and many methods have been used to prolong their lifespan. In this work, viscose fabric was used as the basis for an acrylic coating with two additives in the form of zinc oxide and dolomite nanoparticles. These two additives were added in order to create a canvas with higher resistance to acidic environments and higher biological resistance against fungi. The canvas has obtained new mechanical properties such as higher strength, and significant elongation changes depending on the amount of dolomite and also without worsening of abrasion. The canvas has been developed and tested specifically for use in libraries and archives in order to increase the lifespan of stored book collections.

Keywords: Zinc oxide, dolomite, nanoparticles, canvas, strength, abrasion

1. INTRODUCTION

Bookbinding canvases are used in library collections and book archives as surface protection of books. They have to meet several requirements such as good strength, resistance to light, humidity, changes of temperature and various aging factors. [1] Water, biological factors (fungi, bacteria, insects etc.) and acidic environment (the acid-generating oxides in the air) form a deadly triad leading to fatal damage of books. [2] The base fabric of canvas is coated with polymer (frequently the various copolymers of acrylic acid). To eliminate the seepage of glue, the reverse side of fabric is laminated with starch or PVA. Other additives in bookbinding adhesive or canvas coating may improve their resistance, prolong lifespan and imbibe new useful properties to the protective surface of books.

Long term effect of the acidic environment is extremely harmful for cellulosic materials like paper, cotton, and viscose. The acid hydrolysis of cellulose leads to rupture of its polymer chains and consequently the strength and durability of books decrease greatly. Calcined dolomite, MgO, CaO, ZnO, $Ca(OH)_2$, $Mg(OH)_2$, $Zn(OH)_2$ and hydrated dolomitic lime (calcium/magnesium hydroxide) are representative alkaline buffers. These chemicals have low water solubility and can react with acids to decrease the acidity of the fluids. In this study, we have used two additives namely dolomite (calcium magnesium carbonate, $CaMg(CO_3)_2$) and zinc oxide (ZnO) in the form of nanoparticles (NPs). Their addition to the acrylic coating was accompanied by thorough mixing to form a homogeneous suspension. These ingredients were expected to provide high resistance of canvas not only to acidic conditions, but also to increase resistance against fungi and bacteria [3]. High surface area of NPs added to the coating was expected to maximize their expected alkaline/buffering effects [4] and fungicide/antibiotic effects [5]). The complementary or synergistic effect of dolomite and zinc oxide in both properties were assumed [3] [6]. NPs were used to ensure particle sizes do not impair the abrasive properties of the surface coating (emery effect).

In this study, the canvases coated with acrylic coating with and without dolomite and/or zinc oxide were prepared. The size and structure of NPs were investigated, and the mechanical properties of canvases were tested depending on the type and concentration of additive. Their antifungal effect was verified using a mixture of four fungi.

2. EXPERIMENTAL PART

2.1. Material and chemicals used

Viscose fabric with area weight of 156 g/m^2 and fabric thickness of 0.25 mm; Acronal S 996 S - aqueous polymer dispersion based on ester of acrylic acid and styrene, viskosity 2 (N·s)/m^2 (BASF SE, GE); granulated natural pink dolomite for agricultural use (Forestina, CZ); suspension No. 208 of zinc oxide NPs with 35 % of ZnO and about 20 % of dispergants (Bochemie, CZ); Petri dishes with rice agar (Biovendor, CZ); water suspension of four fungi with concentration 10^8 CFU/ml: *Penicillium chrysogenum* (CCM F-362), *Aspergillus niger* (CCM 8189*)* and with concentration 10^5 CFU/ml: *Cladosporium sphaerospermum (*CCM F-351)*,* *Chaetomium globosum* (CCM 8156) (Czech Collection of Microorganisms, Masaryk University Brno, CZ).

2.2. Preparation and verification of nanoparticles

Commercial suspension of ZnO NPs was declared as water dispersion of pH 9.1 with NPs total diameter 11 ± 6 nm, hydrodynamic diameter 40 nm and zeta potential -13 mV. Commercial pink dolomite for agricultural use was dosed into cartridges of ball mill with zirconia balls of 1 cm diameter. Ten milling cycles (each of 5 minutes) with cooling intervals was carried out at 800 rpm. The resulting particle size of dolomite was measured using the scanning electron microscope (SEM Vega 3 TESCAN, Brno, CZ). All NPs on the surface of canvas was scanned using the 3D digital multifunction microscope HIROX RH 2000 (MXB 2500REZ lens, diffuse adapter).

2.3. Preparation of canvases with different coating

The experimental canvases viscose fabric with only acrylic coating, viscose fabric with acrylic coating containing 3 wt. % of dolomite NPs, viscose fabric with acrylic coating containing 3 wt. % of ZnO NPs and viscose fabric with acrylic coating containing the mixture of both (1.5 wt. % + 1.5 wt.%) were prepared using a laboratory coating device. All canvases, including the comparative sample of viscose fabric without coating, were coated with 2 layers of coating and were thoroughly condensed at 140 °C for 2 minutes and dried at 100 °C for 15 minutes.

2.4. Measurement of mechanical properties I. (strength, elongation)

The strength and elongation to break of canvases were measured according the standard ISO 1421:2016 [7] using the tensile testing machine TIRA test 2300. Samples of 5 x 30 cm were clamped in the pneumatic jaws with a clamping length of 20 cm. Strength test was carried at a cross-head speed of 100 mm/min at a temperature of 23 °C, each canvas with 10 valid measurements. Measurements of all samples were carried out in machine direction only.

2.5. Measurement of mechanical properties II. (resistance to abrasion)

The abrasion resistance of the canvas coated surface was tested according to the standard ISO 5470-2: 2003 [8] using Martindale Abrasion and pilling tester device (James H. Heal and Co. Ltd. England). Four circular samples with a diameter of 37 mm from each canvas were clamped in holders of Martindale device together with the pad of foam material, each with a down pressure of 12 kPa. Face (coated) side of canvases has been tested with the speed of 1000 revolutions / 15 min. The testing was performed using special Martindale abrasive cloth SM 25 (James Heal, England), ISO 12947-1:1998 [9]. In accordance with the standard [8] the abrading face side of canvases was controlled and visually evaluated according to a standardized scale (grade 0-5) in the following control points: 1600, 3200, 6400, 12800, 25600 and 51200 abrasive revolutions. Testing was stopped at 100 thousand abrasive revolutions.

2.6. Test of antifungal properties

The antifungal properties of canvases were tested according the standard EN 14119:2003 [10]. Three samples of comparative fabric sample, canvas with acrylic coating containing different concentrations of ZnO NPs or dolomite NPs (0 - 10 wt. %), each with area of about 4 cm^2, were placed on agar medium and inoculated with a suspension of four testing fungi. Incubation of the tested samples was conducted for 4 weeks at a temperature of 22 ± 3 °C. After the test, evaluation of antifungal properties was carried out based on visual assessment according to the rating system of standard [10] by determining degree of growth of fungi on the surface of samples (degree 0-5, it means from no microscopically visible growth to very intense growth covering all tested surface).

2.7. Results and discussion

NPs of dolomite obtained via ball mill are shown on **Figure 1**. SEM image of milled dolomite shows that their size ranged from hundreds of nanometers to several micrometers. **Figure 2** shows the surface of the canvas containing both additives in the coating (canvas E) with various inclusions. Their size ranges from nanometers to micrometers.

Table 2 Mechanical properties of viscose fabrics and canvases and summary of additives

Sample	Thickness [mm]	Specific weight [g/m²]	Additive in coating	Concentration of additive [wt. %]	Average strength [N]	Average elongation [%]
A	0.25	156	-	-	441.5	15.7
B	0.30	228	-	-	442.6	14.7
C	0.31	240	dolomite NPs	3	452.3	16.3
D	0.30	228	zinc oxide NPs	3	464.7	15.2
E	0.29	233	dolomite NPs zinc oxide NPs	1.5 1.5	454.1	15.7

Table 2, **Figure 3** and **Figure 4** contain the overview of mechanical properties of all samples detected on tensile testing machine by identifiers: A = comparative sample (viscose fabric without coating), B = viscose fabric with acrylic coating only, C = viscose fabric with 3 wt. % of dolomite NPs in acrylic coating, D = viscose fabric with 3 wt. % of ZnO NPs in acrylic coating and E = viscose fabric with 1.5 wt. % of dolomite and 1.5 wt. % of ZnO NPs in acrylic coating.

The pure acrylic coating (canvas B) penetrates the interfiber spaces and deforms together with the fabric under stress. In comparison to untreated fabric, the strength did not increase (**Figure 3**, B) and elongation even decreased (**Figure 4**, B). This may be due to individual fibers and segments of yarn are fixed and the binder cannot be stretched. Additives in the coating prevent the penetration of an acrylic polymer in interfiber spaces and coating with the additive remains on the surface of the fabric or yarn interspaces. This provides the fabric with coating containing additives (C, D, E) increased strength. The fabric and coating deform independently. It appears that addition of dolomite NPs in the coating leads to the most significant increase to canvas elongation (C), as seen in **Figure 4**. Since the additive prevents the penetration of the acrylic binder into the interior of the yarn, addition of additives to the coating practically does not change elongation of original fabric. The effect is more distinct with presence of larger particles. The larger particles of dolomite block the penetration of coating into the fibers more effectively and the elongation more significantly approaches the original values. As seen in **Figure 3**, most of the confidence intervals of experimental determinated strength to break are overlapping. Statistically, the most significant difference was only between viscose and canvas containing 3 wt. % of ZnO NPs in the coating (A and D). The reason could be the use of aqueous suspension of ZnO NPs, which brings an additional fluid into the coating paste. This fluidity must be eliminated using a thickener to achieve the correct technological viscosity of coating.

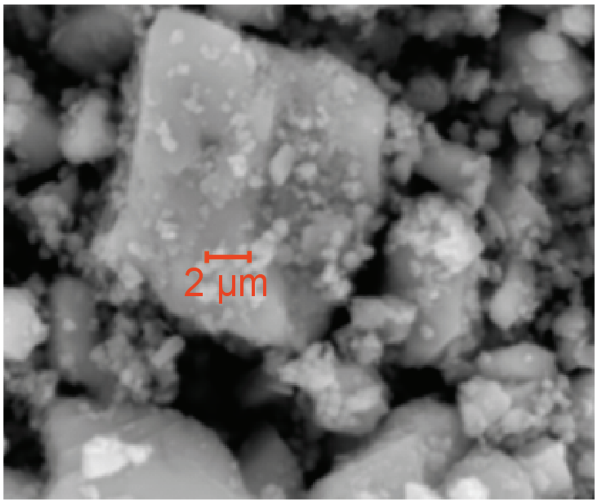


Figure 1 Dolomite (SEM, 3000 x)

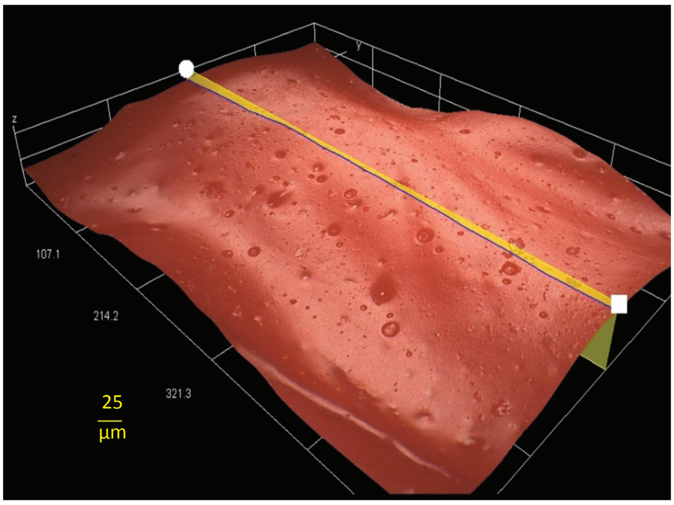


Figure 2 Surface of canvas E (3D microscope, 500x)

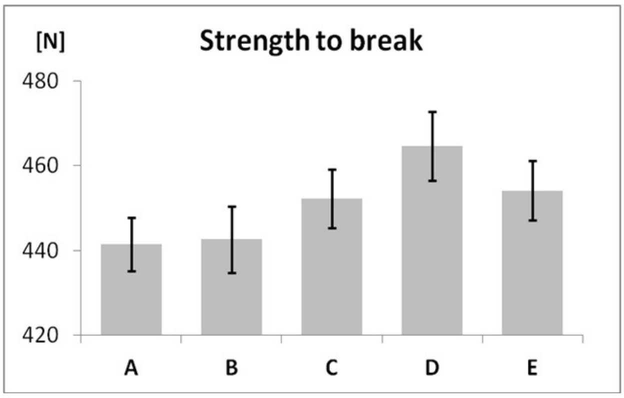


Figure 3 Strength to break of viscose fabrics and canvases

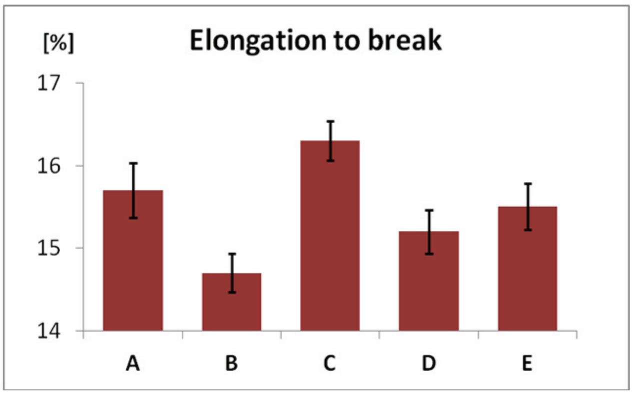
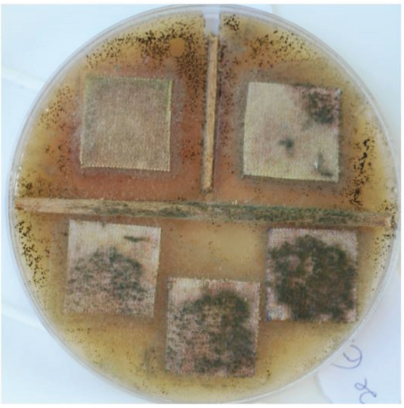
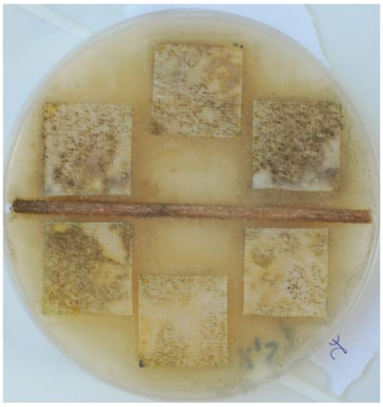


Figure 4 Elongation to break of viscose fabrics and canvases

The basic viscose fabric without coating completely wore out already at 5-8 thousand abrasion revolutions. Most of the samples of coated canvases survived the abrasion up to 100 thousand rpm with only moderate damage and no test sample with the coating was holey or strongly damaged (a change in the gloss as well as moderate disruption of coated layer evaluated by degree 3 according to the standard [8]). Canvas E contained a red pigment added to the coating and special Martindale abrasive cloth began to stain red at 60 - 70 thousand revolutions. It was clear that the first disruption of the surface acrylic layer started at this checkpoint. However, according to the standard, the main terminal checkpoint corresponds to 51200 rpm and at this point the coated surfaces of canvases were only very moderately damaged (degree 2 according the standard [8], i.e. moderate damage with change of gloss, cover coating damaged only slightly). The resistance to abrasion of the canvases B, C, D and E was evaluated as very good.





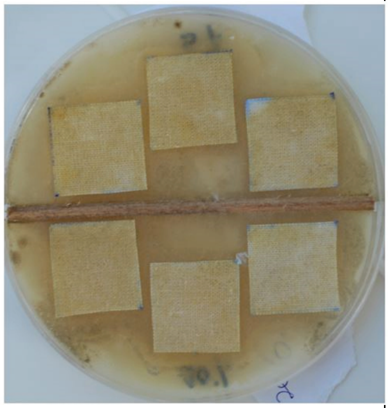
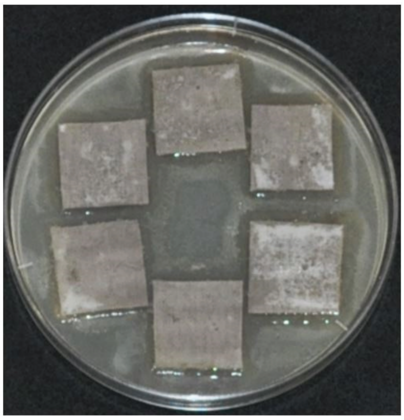


Figure 5
Top left: comparative sample without coating {5}
Top right: canvas with acryle only {3}
Down: canvas with 0.1 wt. % of ZnO NPs in coating {5}

Figure 6
Top: canvas with 1 wt. % of ZnO NPs in coating {3}
Down: canvas with 2.5 wt. % of ZnO NPs in coating {2}

Figure 7
Top: canvas with 5 wt. % of ZnO NPs in coating {0}
Down: canvas with 10 wt. % of ZnO NPs in coating {0}



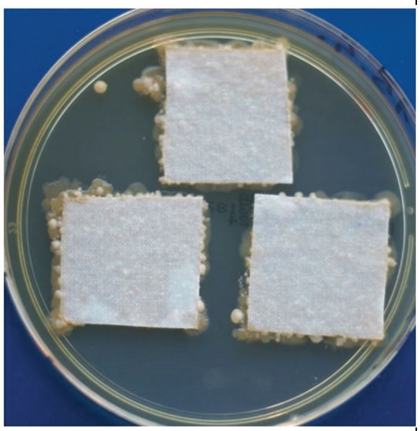


Figure 8
Top: canvas with 0.1 wt. % of dolomite NPs in coating {4}
Down: canvas with 1 wt. % of dolomite NPs in coating {2}

Figure 9
Top: canvas with 2 wt. % of dolomite NPs in coating {0/1}
Down: canvas with 4 wt. % of dolomite NPs in coating {0/1}

Figure 10
Canvas with 1.5 wt. % of dolomite and 1.5 % of ZnO NPs in coating {2/3}

Antifungal assays (**Figures 5-10,** evaluation degrees are in curly brackets) confirmed that the zinc compounds as well as dolomite have some antibiotic and antifungal potential respectively. Increased growth of fungi was observed repeatedly when very low concentration of ZnO NPs was used in suspension (**Figure 5**). It can be explained by the presence of dispersants in the suspension (nitrogen and phosphorus compounds) which act as a mold growth promoter, while the content of ZnO NPs is still very low and ineffective. When antifungal effects of each additive were tested separately, ZnO NPs stopped the growth of fungi on the surface of the canvas reliably at concentration of 5 wt. % (**Figure 7**). Dolomite NPs prevented their growth at concentrations of about 2 wt. % (**Figure 9**). When both additives were used in the coating, each at a concentration of 1.5%, they were sufficient to slightly suppress the growth of fungi on the surface of the coating (**Figure 10**). These samples were unlike the previous ones immersed in the fungi suspension before their cultivation on agar. Consequently, it is evident from **Figure 10** that the molds only slightly grew on the coated surface, but they continued to grow near the samples and below them. This didn´t confirm unambiguously the expected synergistic antifungal effect. Based on the tests, a ZnO NPs concentration of 2.5 % or higher, and a dolomite greater than 2 % by weight of the coating material are recommended for a reliable antifungal effect of the coated canvas.

3. CONCLUSION

The canvas with addition of dolomite and zinc oxide NPs in the coating was prepared to increase its resistance to acidic environments and against the action of fungi. The evaluation of the results didn´t confirm that the addition of both at the concentration of 1.5 wt. % was sufficient. Our recommended concentration for a reliable long-term antifungal effect of coated canvas is more than 2.5 % of ZnO NPs (in the form of a suspension) and more than 2 % of finely milled dolomite from the weight of the wet paste, when the dry matter content of acrylic paste is approximately 45-47 %. The strength was not significantly influenced by addition of both additives. Higher strength was observed when using a thickener in the coating with higher liquid content, when using ZnO NPs in the form of suspension. Increased elongation to break was observed in the canvas with 3 wt. % of dolomite in the coating. Simultaneously, the addition of both compounds to the coating in an amount up to 3% didn´t worsen the resistance to abrasion. Finally, we affirm that the viscose canvas containing dolomite and ZnO NPs in the coating is suitable as bookbinding canvas for use in the book collections in libraries and archives.

ACKNOWLEDGEMENTS

This work was supported by the project No. DF13P01OVV004 Exploration, conservation and care of modern library collections - materials and technologies provided by the Ministry of Culture within the Program of applied research and development of national and cultural identity (NAKI).
Special thanks to Mrs. Jitka Neoralová, Mrs. Jana Grabmüllerová and Dr. Mohanapriya Prasad.

REFERENCES

[1] MERRILL-OLDHAM, J., PARISI, P. A. *Library Binding Institute standard for library binding*. American Library Association, 1990.

[2] GREENFIELD, J. *Books: their care and repair*. HW Wilson, 1983.

[3] SAWAI, J., YOSHIKAWA, T. Quantitative evaluation of antifungal activity of metallic oxide powders (MgO, CaO and ZnO) by an indirect conductimetric assay. *Journal of applied microbiology*, 2004, vol. 96, no. 4, pp. 803-809.

[4] DOBSON, J. W., CASHION, J. P. *Glycol solution drilling system.* U.S. Patent No. 6103671 A, 2000.

[5] RAGHUPATHI, K. R., KOODALI, R. T., MANNA, A. C. Size-dependent bacterial growth inhibition and mechanism of antibacterial activity of zinc oxide nanoparticles. *Langmuir*, 2011, vol. 27, no. 7, pp. 4020-4028.

[6] JIN, T., HE, Y. Antibacterial activities of magnesium oxide (MgO) nanoparticles against foodborne pathogens. *Journal of Nanoparticle Research*, 2011, vol. 13, no. 12, pp. 6877-6885.

[7] EN ISO 1421:2016. Rubber - or plastics-coated fabrics - Determination of tensile strength and elongation at break.

[8] EN ISO 5470-2:2003. Rubber - or plastics - coated fabrics - Determination of abrasion resistance - Part 2: Martindale abrader.

[9] EN ISO 12947-1:1998. Textiles - Determination of the abrasion resistance of fabrics by the Martindale method - Part 1: Martindale abrasion testing apparatus.

[10] EN 14119: 2003. Testing of textiles - Evaluation of the action of microfungi.