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Imparting antimicrobial activity in synthetic fabrics by high-temperature process

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Abstract

The present study introduces a coating approach for realization of antimicrobial textile surfaces that does not rely on nano-scale metal particles. Instead, bactericidal metal ions are used in place of elemental metal particles and are deposited in alginates that are adhered to the textile substrate through coating application. Antimicrobial finishing of polyester fabrics is challenging due to the limited permanence resulting from the hydrophobic nature of polyester fibers. A high-temperature (HT) derived process is now presented as a promising opportunity for introducing functions on polyester fabrics. For instance, an approach of antimicrobial finishing is presented; the applied antimicrobial agent consisted of a modified carbohydrate which cannot be bonded to the textile surface in a HT process. Therefore, different silane linker molecules were utilized, either comprising an alkyl or vinyl functional group. In terms of antimicrobial testing, the viability assay was carried out against the following pathogens, Escherichia coli and Staphylococcus aureus. Promising antibacterial results were witnessed and are likely to pave the way for future coating applications on textiles and other polymers substrates.

Keywords: HT-process, silane, alginate, metal complex, antimicrobial.

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1. Introduction

There is a lot of public debate about antimicrobial active materials, and this is made worse by the emergence of new bacteria or the emergence of resistance to antibiotics in well-known bacterium. Examples for these pathogenic microbes are Methicillin resistant Staphylococcus aureus (MRSA) and Enterohemorrhagic Escherichia coli (EHEC). For these pathogens, preventive hygiene is essential andactive antimicrobial materials can help in preventive measures. Antimicrobial finishes are often applied with nano-scale silver particles or other similar nano-scale metals, which have a high surface area to volume ratio. Silver ions can be released from these particles to act as the antimicrobial or biocidal agent (Mata et al., 2009). However, there are concerns about potential health risks caused by these particles; so antimicrobial finishing without nano-scaled particles may be more appealing to the customers. Antimicrobial finishing can be used for a variety of purposes;for example, it can help treat neurodermatitis in patients with diabetes mellitus. Additionally, it can reduce the risk of secondary wounds infections caused by diabetes mellitus. These infections can lead to serious complications when treating diabetic foot ulcers (Rouette., 2000). The 19th century witnessed the initial reference of the oligodynamic effect, which is the antibacterial action of certain metal ions. The exact mechanism of action of this phenomenon is still undetermined. Nonetheless, there are hints that metal ions, such as silver ions, alter the bacterial

membrane's sodium ion permeability. The bacterial respiratory chain enzyme NADH-quinone-reductase and NADH-ubiquinone-reductase is bound by silver ions, which moderates its impact. The gradient of sodium ion concentration across the cell membrane is lowered by the improved sodium permeability. This gradient typically powers the bacterial respiratory chain and a decrease in it may result in the death of the bacteria.

As known from high-temperature (HT) dyeing procedures, hydrophobic molecules can diffuse into the polymeric fiber during this kind of HT-treatment (Rouette., 2000). In this process the polymeric fiber is heated to its glass transition temperature which results in a higher mobility of the polymeric molecules. This allows hydrophobic molecules to diffuse into the polymer. After cooling down the polymeric matrix gets more rigid leading to an immobilization of the introduced molecules. Although this process is commonly used for dyeing it can also be applied for introducing other functions like antimicrobial properties on textile surfaces. The applied antimicrobial agent consists of a modified carbohydrate which cannot be bonded to the textile surface in a HT process. Therefore, different silane linker molecules were utilized, either comprising an alkyl or vinyl functional group (Deacon et al., 1980).

So, it is very likely that alkyl groups of a silane can also diffuse into a polymeric substrate heated above or to its glass transition temperature leaving their hydrophilic silanol groups on the surface of the substrate. In this study octyl-triethoxy-silane was used as alkyl functionalized silane.

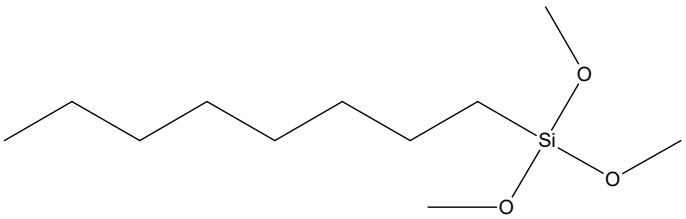

Figure 1: Octyl-triethoxy-silane

A second approach was conducted using vinyl-triethoxy-silane. In this case the mechanism is considered as a grafting reaction. For initiation of the radicalic reaction, dicumyl-peroxide was used as depicted in Figure 2.The initiated silane molecules are then grafted to the polyester substrate (Figure 3).

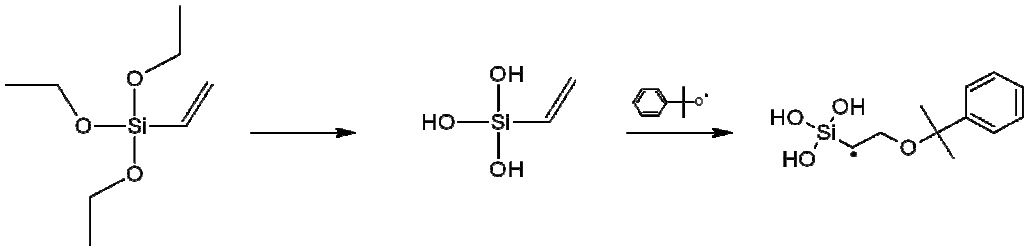

Figure 2: Preparation of radicalic initiated silane molecules

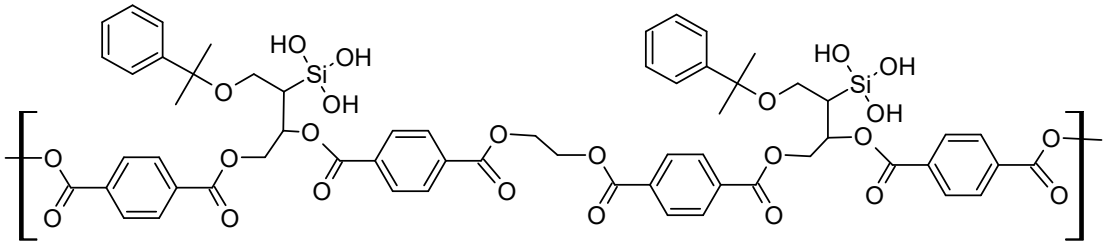

Figure 3: Grafted substrate of Polyester

2. Methods

With these two approaches of HT process, two different variations of silane mechanisms can be obtained and demonstrated as in figure 4A & 4B. Further different silane concentrations, viz. 0.1%, 0.5% and 1% were experimented at various processing times viz. 10 minutes, 20 minutes, 30 minutes, 60 minutes, 90 minutes and 120 minutes to demonstrate the differences and variations in the microbe viability results.In this way functionalized surface offers different reaction possibilities at the silanol site. For instance, antimicrobial active polymers can be immobilized on such a polymeric surfacelike polyester by means of surface functionalization.

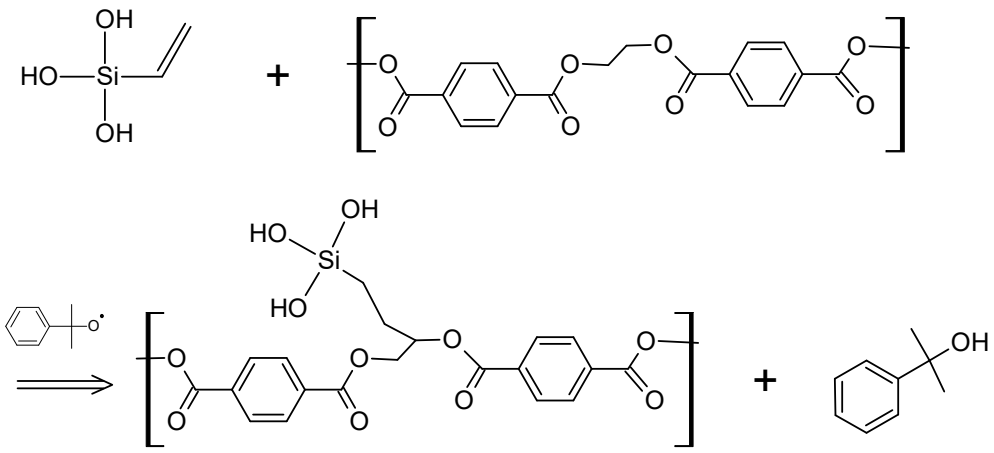

Figure 4a. Grafting reaction, initiated with dicumylperoxide, introducing reative silanol groups for further reaction with alginates

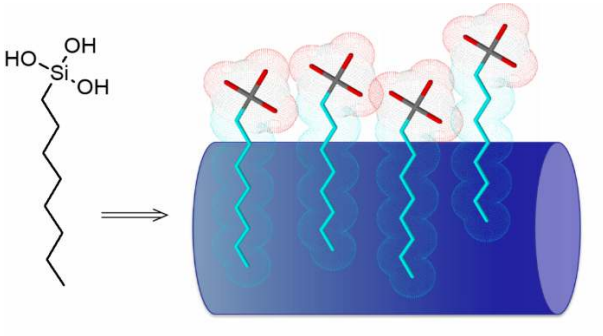

Figure 4b. Diffusion of alkyl residues into a polymeric fiber, immobilizing reactive silanol groups on the surface

In this work modified alginates were used as an antimicrobial/biocidal agent. The alginate was loaded with copper and zinc ions by an ion exchange reaction. Alginates consist mainly of β-D-mannuronic acid and α-L-guluronic acid. Sequences of polyguluronic acid in the polymer lead to a folded structure which allows coordinative bonding with bivalent cations in a chelate like complex (Figure 5).

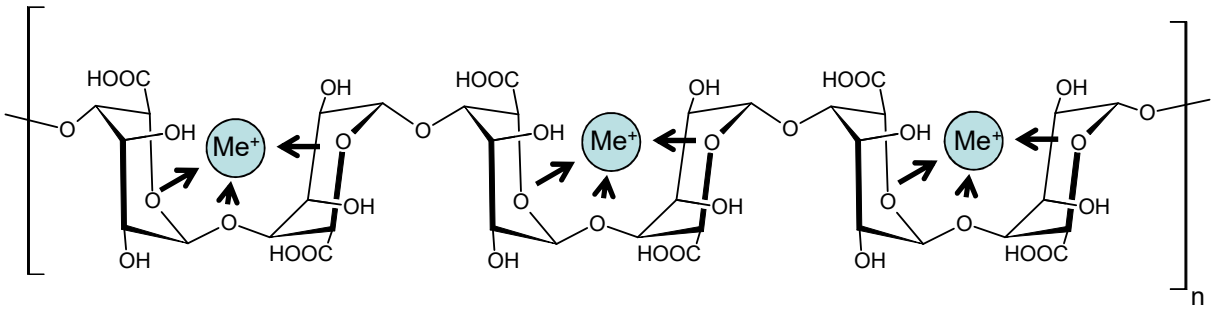

Figure 5: Pseudo chelate complex in a guluronic acid sequence

The coordinative bonding mechanism of the ions to the alginate can be investigated by FTIR spectroscopy due to a frequency shift of the asymmetric (asym.) and symmetric (sym.) stretching vibrations of the carboxylic groups (Papageorgiou et al., 2010). The antimicrobial effect of the alginate composite originates from the release of the introduced copper and zinc ions from the metal complex alginate. This effect is known as oligodynamic effect and is widely known. However, the mechanism is not fully understood. Some authors conclude the production of peroxides in a Fenton like reaction is responsible for the effect (Grass et al., 2011), others suggest it is because of some cationic changes in the sodium permeability of the bacterial cell membrane infringing the bacterial respiratory chain (Semeykina et al., 1990; Shrestha et al., 2009).

3. Experimental

The alginate composite was prepared by dispersing 22g sodium alginate in 60ml ethanol and adding 10ml of a solution containing 10g $Cu(NO_3)_2$ and 10g $Zn(NO_3)_2$(Balouiri et al., 2016; Christoph et al., 2000). The temperature of mixture was raised to 80°C from 40°C and allowed to cook for 90-100 minutes. Afterwards the solid substance was separated by centrifuging. Both the infusing reactions were conducted like a HT-dyeing process in a HT dyeing apparatus (Mathis Labomat, Niederhasli/Zürich, Switzerland). For this 0.1ml to 1ml silane was added to 100ml of a mixture of water and/or ethanol. Also, 4g of the modified metal complex alginate (after ion exchange) was added. The process was then conducted at 120°C for 10 minutes, 20 minutes, 30 minutes, 60 minutes and 90 minutes. The textile specimens were rinsed with the same process liquorafter finishing in which the material was treated under high temperature, containing silane and metal complex alginate and dried (Bogdanović etal., 2015). For comparison the samples were also prepared with bare$Cu(NO_3)_2$ and $Zn(NO_3)_2$ instead of the alginate composite (Gizdavic-Nikolaidis et al., 2011; Ramachandran et al., 2014).

For investigations of the surface topography of textile samples after finishing,Scanning Electron Microscopy (SEM) was used. For SEM investigations a microscope TM-3000 from Hitachi equipped with an EDS-unit (Quantax70 from Bruker) is used. This allows investigating the coating on the fiber surfaces and also to identify the copper and zinc content in the material. The acceleration voltage was 15 kV for SEM image acquisition and energy dispersive x-ray spectroscopy. To characterize the synthesized alginates, copper and zinc alginates were prepared separately. The materials were investigated by FTIR spectroscopy using an ATR assembly (Varian Excalibur 3100). The antimicrobial properties of the prepared textile samples were investigated using a viability assay against *Escherichia coli.* Glycerol stocks (10 µl) were grown over night in 75 ml LB medium. For testing their impact on viability, copper or zinc containing textile samples (circles of 6 mm diameter) were placed in sterile 48-multiwell cell culture plates together with 200 µl bacterial suspension (diluted 1:250 in LB medium) per well and incubated for 4h at 37°C, rotating at 120 rpm in an orbital incubator. Subsequent to treatment with the fabric samples, cellular viability was tested by measuring the reduction of methyl thiazolyl diphenyl-tetrazolium bromide (MTT). Briefly, cells were incubated with 0.01 % (w/v) MTT in culture medium, followed by lysis in isopropanol and determination of the absorption at 570 nm. Data are shown as % viability relative to bacteria in the absence of fabric samples. For each textile sample the measurement was conducted three times with different cutouts from the same sample (Mahltig et al., 2001).

4. Results

The prepared alginate composite exhibits significant peak shifts in the 1400 cm^{-1} and 1600 cm^{-1} region. Similar peak shifts were found (Papageorgiou et al., 2011; Song et al., 2022) indicating a complexation of the copper and zinc ions with the alginate (Qiang et al., 2021).

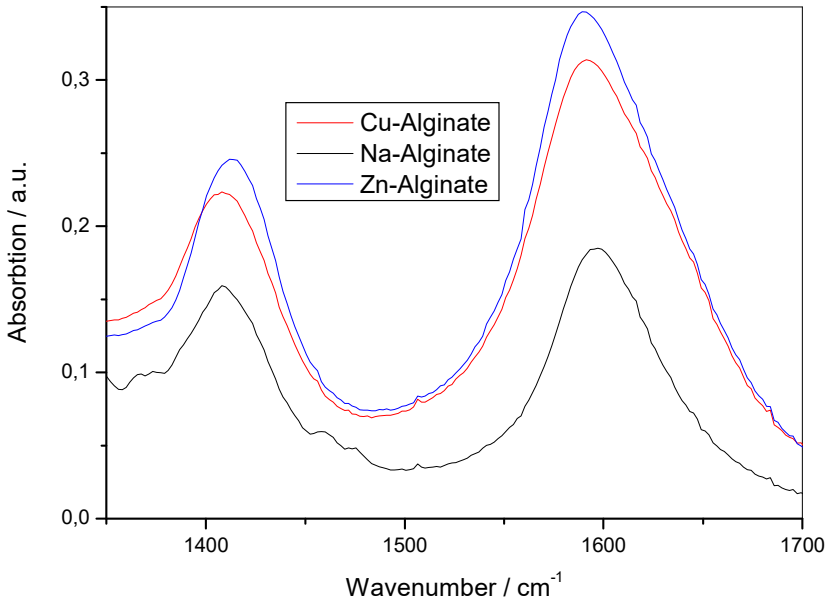

Figure 6: IR (ATR) Spectra of prepared alginates

	Reference [1]			This study		
	COO asym	COO sym	$\Delta\tilde{\nu}$	COO asym	COO sym	$\Delta\tilde{\nu}$
Na-alginate	1596.3	1404.3	192.0	1597	1408	189
Cu-alginate	1584.2	1402.1	182.1	1591	1408	183
Zn-alginate	1588.8	1407.3	181.5	1589	1412	177

Figure 7: Metal–carboxylate interactions in metal–alginate complexes studied with FTIR spectroscopy

The mechanism of the high temperature treatment with the alkyl silane was investigated by introducing nonanoic acid into polypropylene fibers in the mentioned process (Laourari, 2022). By EDX measurements, a significant oxygen content on the fibers was found after treatment and rinsing, which can only originate from nonanoic acid. Therefore, a similar mechanism in immobilizing amphiphilic substances like nonanoic acid or alkyl silanes is suggested as in the high temperature dyeing of polyester fabrics (Shemesh et al., 2015).

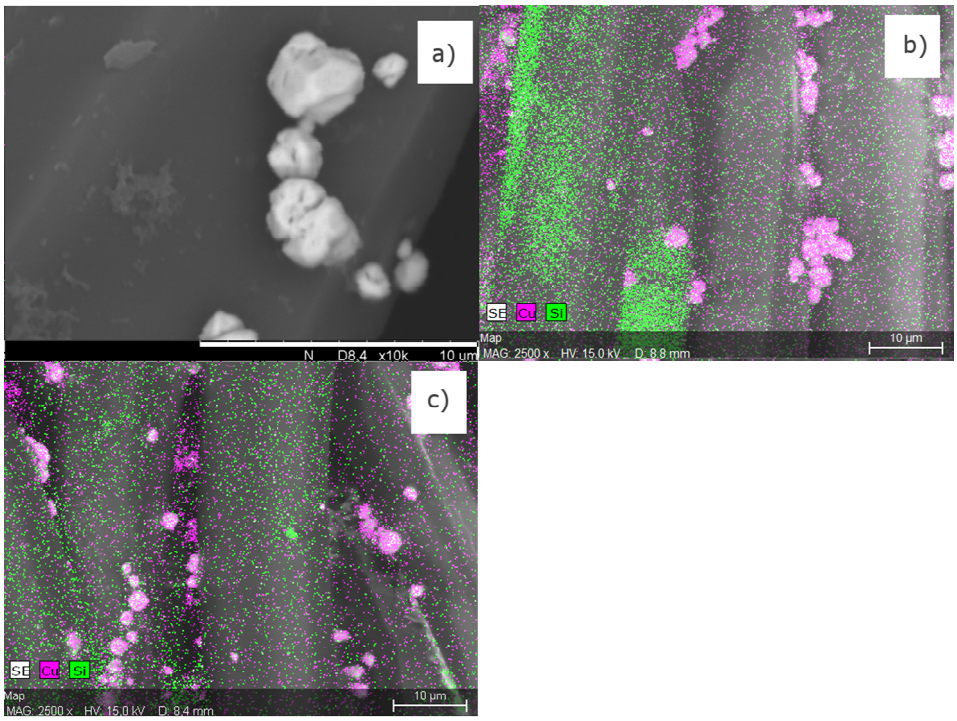

Figure 8a. SEM image of alginate particles on VTEO finished fabric; Figure 8b. EDX-Mapping: VTEO finished fabrics; Figure 8c. EDX-Mapping: OctEO finished fabrics.

On a comparative analysis from the results of the samples treated vinyl silane and alkyl silane at different temperatures and process duration, it was observed that the samples treated at 120°C for 90 minutes (both vinyl silane and alkyl silane) was likely to exhibit better antimicrobial function that was clear from the viability assay with E. coli. This may be because the samples treated at lower duration contained comparatively less volume of alginate-metal complex entrapped with silanes. This can be brought out as a correlation between the process duration and the volume of silanes that get infused which turns out to show that the process duration is directly proportional to the antimicrobial property and performance. But further prolonging of process duration to 120 minutes showed reduced antimicrobial property which might be because of the degradation of the metal complex alginates due to prolonged exposure to high temperature.

As depicted in Figure 9, the bactericidal properties of the alginate containing samples processed on the above parameters are significantly better compared to the control samples (Nitrate only). Furthermore, the antibacterial effect of the control group decreases after washing which is not visible in the alginate containing fabrics.

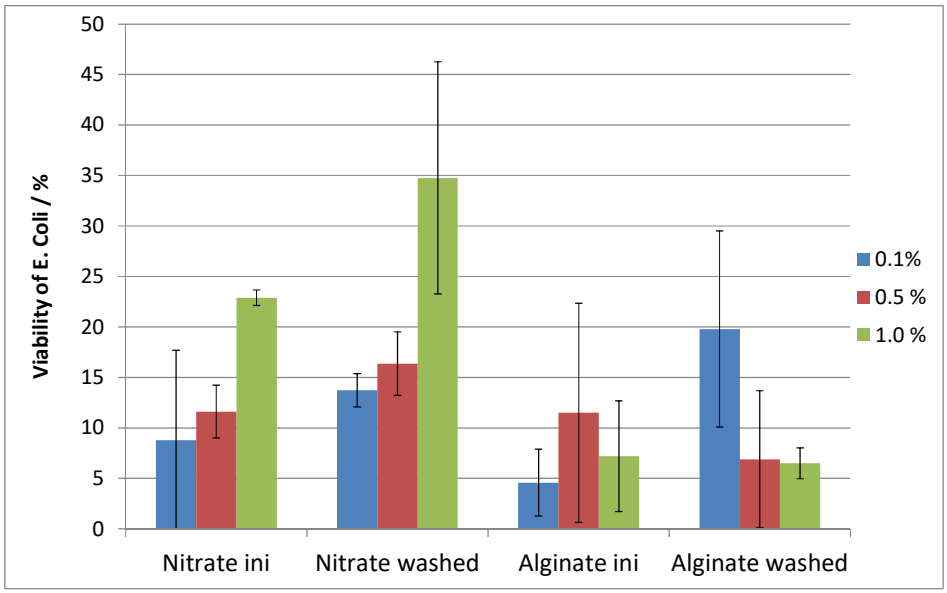

Figure 9: Antibacterial properties of fabrics finished with alkyl silane at120°C for 90 minutes, different silane concentrations (0.1% to 1%)

The use of vinyl silane instead of alkyl silane leads to slightly different results (Figure 10). The overall viability rates are lower in all cases compared to the alkyl silane mediated process (Figure 9). However, the washing fastness of the alginate finished samples is most significant by using the lowest silane concentration. The influence of the silane concentration is more crucial in this case than in the case of alkyl silane finished fabrics (Schierholz et al., 1997). However, the bactericidal effect even after washing of the vinyl silane finished fabrics is more evident than in every alkyl silane finished ones.

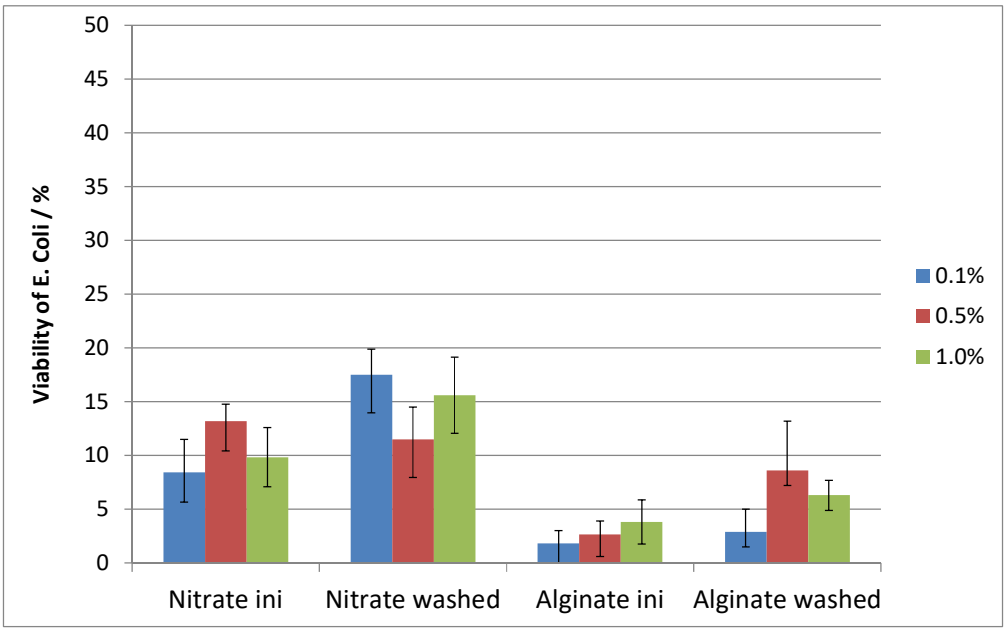

Figure 10: Antibacterial properties of fabrics finished with vinyl silaneat 120°C for 90 minutes, different silane concentrations (0.1% to 1%)

5. Discussion

Copper and zinc complexated alginates might be promising antimicrobial additives for textile finishing. Gelling of the alginate in the process was not observed, but the complexation could be confirmed by infrared spectroscopy. Furthermore, the release of the bactericidal ions in the finished fabrics is retarded, providing a long lasting and efficient antibacterial effect even after washing(Cyphert et al., 2020; Zhang et al., 2017). The process is favorable conducted with vinyl silanes leading to better bactericidal effects and higher washing fastness. Also, a less amount of silane is needed.

6. Conclusion

The prepared antimicrobial agent was applied on polyester substrate by the afore-mentioned HT-process. The resulting textile specimens exhibit bactericidal properties which was confirmed by viability assay against *Escherichia coli*.The presented approach shows an alternative option to introduce bactericidal effects in polyester fabrics. Therefore, HT finishing exhibits the ability to introduce anchor groups by the use of functionalized silanes which can be bonded permanently to the polyester substrate. The process was demonstrated by creating antibacterial functions but might also be promising for introducing other functions permanently on polyester or other hydrophobic polymeric fibers.

References

[1] RouetteH.-K., 2000, H - Polyester Dyeing, Encyclopedia of Textile Finishing, pp. 51-52.ISBN:978-3540650317
[2] Mata Y., Blázquez M., Ballester A., Gonzalez V and Munoz J., 2009, Biosorption of cadmium, lead and copper with calcium alginate xerogels and immobilized Fucus vesiculosus, Journal of Hazardous Materials, Vol. 163, pp. 555-562. https://doi.org/10.1016/j.jhazmat.2008.07.015
[3] Deacon G., Phillips R., 1980, Relationships between the carbon-oxygen stretching frequencies of carboxylato complexes and the type of carboxylate coordination, Coordination Chemistry Reviews, vol. 33, pp. 227-250. https://doi.org/10.1016/S0010-8545(00)80455-5
[4] Papageorgiou S K., Kouvelos E., Fawas E., SapalidisA., Romanos G., Katsaros F., 2010, Metal–carboxylate interactions in metal–alginate complexes studied with FTIR pectroscopy, Carbohydrate Research, vol. 345, pp. 469-473. https://doi.org/10.1016/j.carres.2009.12.010
[5] Grass G., Rensing C., SoliozM., 2011, Metallic Copper as an Antimicrobial Surface, Applied and Environmental Microbiology, vol. 77(5), pp. 1541-1547. https://doi.org/10.1128/aem.02766-10
[6] Semeykina A. L., Skulachev V. P., 1990, SubmicromolarAg(+) increases passive Na(+) permeabilty and inhibits the respiration-supported formation of Na(+) gradient in Bacillus FTU vesicles, FEBS Letters, vol. 269, pp. 69-72, https://doi.org/10.1016/0014-5793(90)81120-D
[7] Shrestha R., Joshi D. R., Gopali J. Piya S., 2009, Oligodynamic Action of Silver, Copper and Brass on Enteric Bacteria Isolated from Water of Kathmandu Valley, Nepal Journal of Science and Technology, pp. 189-193. https://doi.org/10.3126/njst.v10i0.2959
[8] Mahltig B., Reibold M., Gutmann E., Textor T., Gutmann J., Haufe H., HaaseH., 2001, Preparation of silver nanoparticles suitable for textile finishing processes to produce textiles with strong antibacterial properties against different bacteria types, Zeitschrift für Naturforschung B - Chemical Sciences, vol. 66B, pp. 905-919. https://doi.org/10.1515/znb-2011-0907
[9] BalouiriM., SadikiM., IbnsoudaS K., 2016, Methods for in vitro evaluating antimicrobial activity: A review,Journal of Pharmaceutical Analysis, vol. 6(2), pp 71-79. https://doi.org/10.1016/j.jpha.2015.11.005.
[10] ChristophF., KaulfersP M., Stahl-BiskupE., 2000, A Comparative Study of the in vitro Antimicrobial Activity of Tea Tree Oils s.l. with Special Reference to the Activity of β-Triketones, Planta Med, vol. 66(6), pp 556-560. https://doi.org/10.1055/s-2000-8604
[11] GizdavicNikolaidisM R., BennettJ R., Swift S., EastealA J., AmbroseM., 2011, Broad spectrum antimicrobial activity of functionalized polyanilines,Acta Biomaterialia,Vol. 7(12), pp 4204-4209. https://doi.org/10.1016/j.actbio.2011.07.018.
[12] Ramachandran R., Chalasani A G., LalR., RoyU., 2014, A Broad-Spectrum Antimicrobial Activity of Bacillus subtilis RLID 12.1, The Scientific World Journal, vol. 2014, Article ID 968487, 10pp. https://doi.org/10.1155/2014/968487
[13] BogdanovićU., VodnikV., MitrićM., DimitrijevićS., ŠkapinS D., ŽuničV., BudimirM., StoiljkovićM., 2015,Nanomaterial with High Antimicrobial Efficacy—Copper/Polyaniline Nanocomposite, ACS Applied Materials & Interfaces,vol. 7 (3), 1955-1966. https://doi.org/10.1021/am507746m
[14] LaourariI., LakhdariN., BelgherbiO., MedjiliC., BerkaniM., VasseghianY., GolzadehN., LakhdariD., 2022, Antimicrobial and antifungal properties of NiCu-PANI/PVA quaternary nanocomposite synthesized by chemical oxidative polymerization of polyaniline,Chemosphere, Vol. 291(2),132696. https://doi.org/10.1016/j.chemosphere.2021.132696.
[15] SchierholzJ M., PulvererG., 1997, Development of a New CSF-shunt with Sustained Release of an Antimicrobial Broad-spectrum Combination,Zentralblatt für Bakteriologie, Vol. 286(1), pp 107-123. https://doi.org/10.1016/S0934-8840(97)80082-5.
[16] ZhangY., ZhangL., LiB., HanY., 2017, Enhancement in Sustained Release of Antimicrobial Peptide from Dual-Diameter-Structured TiO2 Nanotubes for Long-Lasting Antibacterial Activity and Cytocompatibility, Applied Mater Interfaces, vol. 9(11), pp9449–9461. https://doi.org/10.1021/acsami.7b00322
[17] CyphertE L., LuC., MarquesD W., LearnG D., RecumH A., 2020, Combination Antibiotic Delivery in PMMA Provides Sustained Broad-Spectrum Antimicrobial Activity and Allows for Postimplantation Refilling, Biomacromolecules, Vol. 21(2), pp854-866. https://doi.org/10.1021/acs.biomac.9b01523
[18] ShemeshR., KrepkerM., NatanM., Danin-PolegY., BaninE., KashiY., NitzanN., VaxmanbA., SegalE., 2015, Novel LDPE/halloysite nanotube films with sustained carvacrol release for broad-spectrum antimicrobial activity, RCS Advances, vol. 5 (106), pp.87108-87117. http://doi.org/10.1039/C5RA16583K

[19] SongJ., YuanC., JiaoT., R. XingR., YangM., AdamsD. J., YanX., 2020, Multifunctional Antimicrobial Biometallohydrogels Based on Amino Acid Coordinated Self-Assembly, Small, vol. 16, 1907309. https://doi.org/10.1002/smll.201907309
[20] QiangM., Jin-LongS., FeiH., JingW., PeiW., Ya-FeiZ., FengW., Chu-FanM., 2021, Antibacterial Peptide HHC-36 Sustained-Release Coating Promotes Antibacterial Property of Percutaneous Implant, Frontiers in Bioengineering and Biotechnology, Vol. 9. https://doi.org/10.3389/fbioe.2021.735889

Biographical notes

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