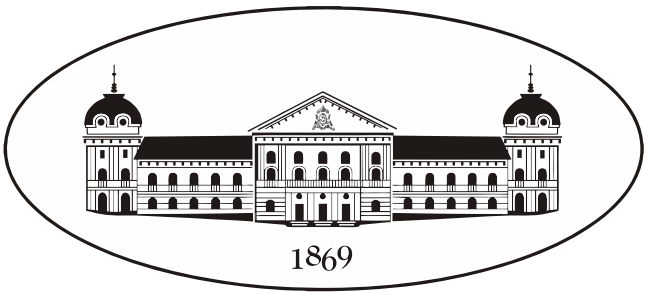
# Topic № 1
# FIBRES AND YARNS; CHEMICAL TECHNOLOGIES; NANOTECHNOLOGIES

*678*

*Industry of High Molecular Substances. Rubber industry. Plastic industry.*


ТЕХНИЧЕСКИ УНИВЕРСИТЕТ
СОФИЯ


1869

# LEATHER PRINTING AND OTHER DECORATION METHODS

10.53230/tgm.1310-912X.2020.0010.01

**D. ZHELEVA[1], A. TONEVA[1]**
[1] University of Chemical Technology and Metallurgy - Sofia, Bulgaria
Department Textile and Leather,
e-mail: darinajeleva@abv.bg

Leathers differ from other materials in dyeing or printing due to their diverse structure. The dyeing process results in a monochrome background, while the printing processes can reproduce multicolored patterns on the face of the material using different printing techniques. The printing of patterns, symbols and ornaments on materials is a form of decoration that is more common in the textile industry than in the leather industry. Modern printing technologies offer fast printing on leather and other materials with different structure and color, which stimulates designers to develop their graphic designs for prints and patterns digitally.

The aim of the present work is to study and analyze the methods and techniques for printing and decoration on leather.

The interaction of dyes or printing inks with the protein substances of the skin tissue and the hair cover is a complex process. The reasons is the different structure and properties of the printing inks and the different application of the main component of the dyed material - collagen and keratin, depending on the pre-treatment of the leather, tanning and finishing processes.

Printing on leather can be done by screen printing, transfer, inkjet, digital and other types of printing. The special ink, developed for leather, made it possible to apply high-quality, multi-colored motifs. The requirement is to use dyed smooth leather, as a transparent cover layer is applied to prevent the paint from being erased by sealing the ink layer.

Leather printing processes include the stages of preparing an image with a monochromatic or polychromatic character, printing the image using one or more inks on a sheet of paper (so-called transfer printing) and transferring them to the leather.

The ability to print white ink, UV printing makes it possible for advanced printing on leather based on shadows. This suggests that it can also be printed on dark leather goods.

Conclusions:

- There are various printing techniques in the leather industry, many of which are taken from the textile printing technique;
- The interaction of dyes and printing inks with the protein substances of the skin tissue and hair cover is a complex process and requires a specific approach to each material;
- Most of the applied techniques of printing on leather are described as patents;
- Laser printing has also entered the leather industry, creating a diverse palette of colors and designs.
- Many different decoration techniques are applied to leather products: stamping, engraving, perforation, embroidery, etc.

**Key words:** leather, printing techniques, inks, decoration techniques

# EXTRACTION AND ANALYSIS OF KERATIN HYDROLYSATES OBTAINED FROM SHEEP WOOL

10.53230/tgm.1310-912X.2020.0010.02

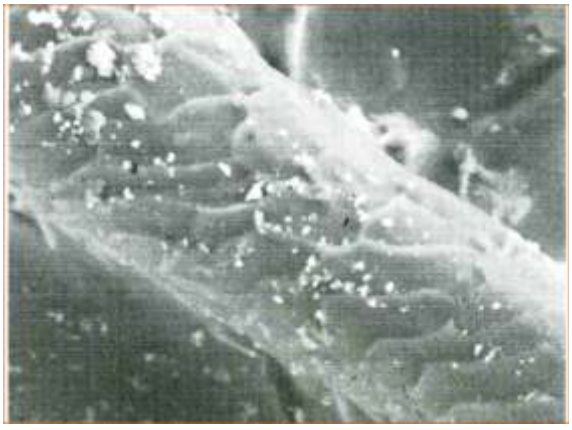
**Margarita KOLEVA[1], Darina ZHELEVA[1]**
[1]University of Chemical Technology and Metallurgy, Textile and Leather Department,
8 Kl. Ohridski bul., 1756 Sofia, Bulgaria
e-mail: mkoleva2103@abv.bg

***Introduction***

Keratin in wool is a potentially important natural source of protein with many applications. Wool keratin is a strong resistant, insoluble biomaterial that can play a major structural role in many biological systems. The aim of the present study is to obtain and analyse keratin hydrolysates from sheep wool, respectively native and alkaline pre-treated, using different oxidation and reduction methods.

***Experimental part***

The raw materials for the extraction of keratin hydrolysates in our research are samples from the hair cover of sheepskins, respectively in native form and obtained after lime sulfide unhairing. The wool, which is lime sulphide pre-treated, is obtained after the process of unhairing of sheepskin under certain conditions. The methods used for the hydrolysis of keratin-containing materials are the following: with thioglycolic acid and urea; by sulphitolysis with sodium pyrosulphate and with sodium hydroxide.



The obtained hydrolysates were characterized by qualitative reactions, spectrophotometric and infrared analysis.

***Results and discussion***

The hydrolyzates obtained by lime sulfide unhairing process have shown a high concentration of polypeptides in the sample and rupture of the disulfide bonds in their chains. The highest degree of hydrolysis was achieved for the pre-treated samples. It was proved that the method of hydrolysis with NaOH is the most appropriate for sheep wool and to a much greater extent for the alkaline treated wool than for the native. Therefore, pre-treatment of hair samples facilitates the hydrolysis process and makes it easier to break disulfide bonds. The data from the IR analysis completely correlate with the quantitative and qualitative analyzes and show the degree of rupture of the disulfide bonds depending on the intensity of the adsorption bands.

***Conclusion***

Three methods were used for the hydrolysis of keratin from the hair cover of sheep skins, respectively of native wool and that obtained by lime sulfide unhairing. NaOH has the best hydrolyzing effect on disulfide and peptide bonds. Pre-alkaline treatment of the wool by reducing agent increases the degree of hydrolysis compared to the native wool. It has been proven the presence of keratin protein in some of the hydrolysates as well as the rupture of disulfide bonds.

**Keywords:** sheep wool, keratin hydrolysates, methods of analysis

# STRUCTURAL CHANGES OF THE HYDROGEL FOR TEXTILE MODIFICATION DEPENDING ON THE INTENDED APPLICATION

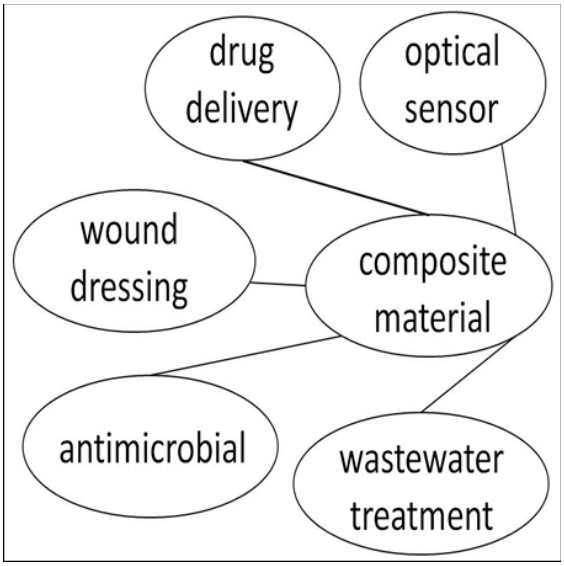
10.53230/tgm.1310-912X.2020.0010.03

**Daniela ATANASOVA[1], Desislava STANEVA[1], Ivo GRABCHEV[2]**
[1] University of Chemical Technology and Metallurgy, 1756 Sofia, Bulgaria
[2] Sofia University "St. Kliment Ohridski", Faculty of Medicine, 1407 Sofia, Bulgaria
e-mail: d.atanasova1@abv.bg

In the recent years, we have conducted several studies related to the modification of textile materials with hydrogel, and included or not inorganic nanoparticles. Some of the properties and applications of these composites are antimicrobial; optical sensors; wastewater treatment materials; wound dressings or delivery of biologically active substances. The aim of this study is to summarize the results in terms of the factors that affect the properties of the respective composite materials and how their modification allows achieving a suitable application.

The modification of cotton or polyamide fabrics with hydrogel was performed by surface-initiated photopolymerization. Photosensitive dye (eosin Y) in combination with a co-initiator (N-methyl diethanolamine) was used to initiate radical polymerization. It was found that the greater amount of photoinitiator and the simultaneous presence of three monomers affect the polymerization process and, accordingly, the properties of the pH sensor. The controllable swelling of the hydrogel is an important parameter for suitable loading and releasing of drugs with minimal burst effect. The amount of the crosslinking monomer and the hydrogel on the cotton surface has been changed to find the most suitable structure providing adequate loading and releasing of vitamin B12 under appropriate physiological conditions (temperature and pH).

The composite material cotton fabric with hydrogel and silver nanoparticles is a suitable material for production of wound dressings. A key point that affects the obtained properties is again eosin Y, as it is an intermediate link in the simultaneous conduct of photoreduction of silver ions to nanoparticles and hydrogel polymerization. It has been found that other metal ions can also be used for the production of materials with antimicrobial properties. The conversion of zinc ions to zinc oxide is done by varying the quantity of co-initiator of photopolymerization N-methyl diethanolamine. The higher concentration of zinc ions and amine increases the concentration of ZnO nanoparticles and the antimicrobial properties of the material. The immobilization of iron oxide nanoparticles with polyacrylamide hydrogel on the polyamide fabric can be used as a heterogeneous Fenton catalyst for purification of real wastewater upon dyeing. The material obtained at a higher Fe(II) ions concentration is more efficient in the degradation of this dye.




***Keywords:*** textile, hydrogel, nanoparticles, applications

***Acknowledgments:***
The authors acknowledge Grant № КП-06-КОСТ-23/2019, Fund "Scientific Research", Ministry of Education and Science of Bulgaria.

# COTTON FABRIC MODIFIED WITH CHITOSAN AND ZINC OXIDE

10.53230/tgm.1310-912X.2020.0010.04

**Desislava STANEVA[1], Vesislava TOTEVA[1], Ivo GRABCHEV[2]**
[1] University of Chemical Technology and Metallurgy, 1756 Sofia, Bulgaria
[2] Sofia University "St. Kliment Ohridski", Faculty of Medicine, 1407 Sofia, Bulgaria
e-mail: grabcheva@mail.bg

***Introduction***

The fulfillment of the circular economy goals is closely connected with finding various possibilities for the application of the already used materials. The growing consumption of cheap and second-hand clothes decreases the possibility of their reuse as wearable textiles. Another possibility is to utilize the textiles for cleaning or become a raw material for other industries. In the recycling, additional processing is often required to create the appropriate characteristics of the new product that suit the desired use. The composite materials integrating the specific textile properties with biodegradable renewable biopolymers and inorganic nanoparticles can find applications as sorbents and filters for the treatment of wastewater or oil spilling.

The aim of this study is to prepare a composite material from cotton fabric modified with cross-linked chitosan and zinc oxide nanoparticles.

***Experimental part***

Three samples, containing different concentrations of zinc oxide were obtained (Ch, ChZn, ZnChZn). In the first sample (Ch) cotton fabric was impregnated with a water solution of chitosan and glacial acetic acid, and next was crosslinked with glutaraldehyde. In the second sample (ChZn) the solution of chitosan and zinc nitrate was applied on the fabric and successively treated with glutaraldehyde and NaOH. The sample (ZnChZn) was obtained by irrigation with water solution of zinc nitrate, next with chitosan and zinc nitrate solution, and finally with glutaraldehyde and NaOH.

***Results and Discussion***

The surface of the composite materials has been compared with the initial cotton fabric by using a scanning electron microscope. In the sample (Ch) the individual fibers are glued together by a thin layer of chitosan. In the ChZn material, the surface of the fabric is covered with an almost uniform film, in which defects and cracks are observed. Evenly distributed small white grains of zinc oxide are included throughout the structure of the film. The morphology of the samples in dry and wet state was evaluated by optical microscope. The increased amount of zinc oxide results in a denser layer on the surface of the fibers and impedes water penetration and the macro-gaps in the fabric structure are still visible. The modification of cotton fabric with chitosan and its crosslinking was confirmed by FT-IR analysis and the appearance of the new characteristics bands.

***Conclusion***

A film of chitosan containing in situ formed zinc oxide nanoparticles on the surface of a cotton fabric has been successfully obtained. The resulting composites have the potential use as antimicrobial, self-cleaning materials with suitable sorption properties.

***Keywords:*** composite materials, chitosan, cotton fabric, zinc oxide particles

***Acknowledgments:***

The authors acknowledge the support through Project № КП-06-Н37/27 provided by the National Science Fund, Ministry of Education and Science of Bulgaria.

# NOVEL ANTIOXIDANT ELECTROSPUN NONWOVEN TEXTILE FROM POLYLACTIDE AND 8-HYDROXYQUINOLINE DERIVATIVE AND ITS COMPLEX WITH $Cu^{2+}$

10.53230/tgm.1310-912X.2020.0010.05

**Milena IGNATOVA[1], Nikoleta STOYANOVA[1], Nevena MANOLOVA[1], Iliya RASHKOV[1], Rositsa KUKEVA[2], Radostina STOYANOVA[2]**

[1]Laboratory of Bioactive Polymers, Institute of Polymers, Bulgarian Academy of Sciences, Akad. G. Bonchev St, Bl. 103A, BG-1113 Sofia, Bulgaria

[2]Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, Akad. G. Bonchev St, Bl. 11, BG-1113 Sofia, Bulgaria

e-mail: ignatova@polymer.bas.bg

***Introduction***

8-hydroxyquinoline and its derivatives are well known for their high antimicrobial, antioxidant and antitumor activity [1]. It is assumed that their biological activity is related to their chelating ability against transition metal ions ($Cu^{2+}$, $Fe^{2+}$, $Fe^{3+}$, etc.) of biological importance [2]. When included in electrospun fibrous materials, such compounds may impart them beneficial properties. The purpose of this work was to investigate the possibility for the preparation of novel electrospun nonwoven textile containing 8-hydroxyquinoline derivative or its complex with metal ion of diverse design, as well as to study the impact of the fiber composition on the antioxidant activity of the fibrous materials.

***Experimental part***

8-hydroxyquinoline derivative - Schiff base from Jeffamine ED® and 8-hydroxyquinoline-2-carboxaldehyde (Jeff-8Q) and its complex with $Cu^{2+}$ (Jeff-8Q.$Cu^{2+}$) were prepared as described earlier [3,4]. Custom-made electrospinning equipment was used. The morphology of the fibrous materials was observed by scanning electron microscopy (SEM) using a Jeol JSM-5510 SEM (JEOL Co. Ltd, Japan). The antioxidant activity of the mats was evaluated using the DPPH assay.

***Results and Discussion***

Novel nonwoven textile from polylactide (PLA) and Jeff-8Q or its complex with $Cu^{2+}$ of various design was successfully prepared. To achieve this, one-pot electrospinning (type "*in*") or combining the electrospinning and dip-coating techniques (type "*on*") were applied. The morphology of the mats and chemical composition of their surface were studied by scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS). The coordination of $Cu^{2+}$ in Jeff-8Q.$Cu^{2+}$ complexes incorporated into electrospun nonwoven textile or deposited on its surface was studied by electron paramagnetic resonance spectroscopy. It was found that for the type "*on*" mats the *in vitro* release of Jeff-8Q (Jeff-8Q.$Cu^{2+}$) was more rapid as compared to type "*in*" mats. The performed DPPH radical scavenging assay showed that Jeff-8Q.$Cu^{2+}$-containing fibrous materials (both types "*in*" and "*on*") exhibited higher antioxidant activity than that of Jeff-8Q-containing mats.

***Conclusion***

In this study it was shown that Jeff-8Q and its complex with $Cu^{2+}$ might successfully be incorporated in the electrospun nonwoven textile from polylactide. This novel nonwoven textile is promising for biomedical applications.

***Keywords*****:** 8-hydroxyquinoline derivative, electrospinning, dip-coating, antioxidant electrospun nonwoven textile

***Acknowledgments***: Financial support from Bulgarian National Science Fund (Grant KP-06-N39/13/2019) is gratefully acknowledged.

[1] Al-Busafi S.N., Suliman F.E.O., Al-Alawi Z.R., *Research & Reviews,* Journal of Chemistry 3, 1-10 (2014)

[2] Prachayasittikul V., Prachayasittikul S., Ruchirawat S., Prachayasittikul V., *Drug Design, Development and Therapy* 7, 1157-1178 (2013)

[3] Mladenova R., Ignatova M., Manolova N., Petrova T., Rashkov I., *European Polymer Journal* 38 989-999 (2002)

[4] Ignatova M., Stoyanova N., Manolova N., Rashkov I., Kukeva R., Stoyanova R., Toshkova R., Georgieva A., *Materials Science and Engineering C* 116, 111185 (2020)

# NOVEL ELECTROSPUN NONWOVEN TEXTILE CONTAINING BIOACTIVE COMPOUNDS OF PLANT ORIGIN WITH ANTIOXIDANT AND ANTIBACTERIAL PROPERTIES

10.53230/tgm.1310-912X.2020.0010.06

**Milena IGNATOVA[1], Nevena MANOLOVA[1], Iliya RASHKOV[1], Velizar GOCHEV[2]**
[1]Laboratory of Bioactive Polymers, Institute of Polymers, Bulgarian Academy of Sciences, Acad. G. Bonchev St, Bl. 103A, BG-1113 Sofia, Bulgaria
[2]Department of Biochemistry and Microbiology, Plovdiv University Paisii Hilendarski, Plovdiv, 4000, Bulgaria
e-mail: ignatova@polymer.bas.bg

***Introduction***

In recent years, the incorporation of bioactive compounds of plant origin in electrospun nonwoven textile intended for biomedical applications is increasing. The specific properties of the electrospun fibrous materials related to their nanoscale size provided a possibility for extended release of bioactive compounds resulting in enhancement of the therapeutic effect of the compounds, diminishing their cytotoxicity and improving their bioavailability. Essential oil from Salvia spp. and polyphenolic compounds of plant origin are highly attractive for application in biomedicine and pharmacy due to the set of their beneficial biological properties (antioxidant, antimicrobial and anticancer activities).Therefore finding routes to incorporate these bioactive compounds in electrospun nonwoven textile is of great interest.

***Experimental part***

Fibrous materials containing essential oil from Salvia spp. and individual bioactive polyphenolic compound were fabricated by electrospinning. The morphology of the fibrous materials was evaluated by scanning electron microscopy (SEM) with Jeol JSM-5510 (Jeol Ltd., Japan). The antioxidant activity of the electrospun nonwoven textile was studied by the DPPH radical scavenging method.

***Results and Discussion***

Novel nonwoven textile from biocompatible and biodegradable aliphatic polyester (PE) and nonionogenic water-soluble polymer (polyvinylpyrrolidone (PVP)), containing essential oil from Salvia spp. and individual bioactive polyphenolic compound were successfully prepared by electrospinning. The obtained fibrous materials were defect-free and cylindrical. The incorporation of essential oil from Salvia spp. and bioactive polyphenolic compound into the fibrous materials does not affect significantly their thermal stability. Antioxidant activity test showed that nonwoven textile containing essential oil and bioactive polyphenolic compound displayed high antioxidant activity. The microbiological screening demonstrated that incorporation of essential oil and bioactive polyphenolic compound in the fibers led to inhibition of the growth of Gram-positive bacteria S. aureus, Gram-negative bacteria E. coli and fungi C. albicans by the fibrous materials.

***Conclusion***

This novel nonwoven textile has potential as wound dressing materials.

***Keywords:*** essential oil from Salvia spp., individual bioactive polyphenolic compound, nonwoven textile, electrospinning, antioxidant properties, antibacterial activity

***Acknowledgments:*** This work was supported by the Bulgarian Ministry of Education and Science (Grant D01-217/30.11.2018 and D01-323/18.12.2019) under the National Research Programme "Innovative Low-Toxic Bioactive Systems for Precision Medicine (BioActiveMed)" approved by DCM #658/14.09.2018.

# INFLUENCE OF THE SURFACE MASS IRREGULARITY ALONG THE WIDTH OF THE FABRIC ON THE DYEING AFFINITY AND COLOUR DEVIATION

10.53230/tgm.1310-912X.2020.0010.07

**Desislava STANEVA[1], Vania JORDANOVA[2,3] and Ivelin RAHNEV[3]**
[1]University of Chemical Technology and Metallurgy, 1756 Sofia, Bulgaria,
[2]South-West University "Neofit Rilski" - Blagoevgrad
[3]E. Miroglio EAD - Sliven
e-mail: grabcheva@mail.bg

The uniform dyeing of light fabrics implies adjustment and maintenance of the already optimized technological mode, in terms of temperature and duration of the process.

In practice, it turns out that in order to achieve maximum uniformity of colour on the surface of the fabric; the corresponding uniform dye affinity is required.

In cases where the fibrous composition of the fabrics is uniformly distributed, only the density can affect the uniform penetration of the dye solution between the fibres.

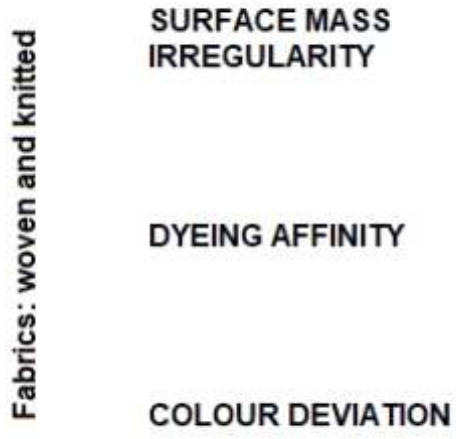
The density of the fabric or surface mass is generally evenly distributing due to its negligibly small thickness relative to the width, and especially the thickness.

In fact, in woven fabrics there is a difference in the surface mass between the edges and the middle of the fabric. This is largely due to the different tension of the main threads gripped by the wide holders and the rest. Any other differences in the setting of the weaving loom and geometric unevenness cause deviations in the distribution of the area mass.

In a similar way, the setting of circular knitting or warp knitting machines causes a difference in the density or area of the knitted fabrics.

The problem is to determine the critical level of unevenness by surface mass of the fabric already produced, which would cause a difference in dye affinity, which in turn would lead to divergence and declassification of the fabric as a non-compliant product.

In this case, the solution lies in the synchronization of three technological indicators with clearly expressed numerical values.




In the first place is the analysis of textile physical metrology, which will assess the uniformity of the surface mass across the fabric.

In second place is the recipe and the mode of dyeing the fabric.

Third is the generalized assessment of the conformity of the colour along the width of the fabric to the set value. Such a numerical estimate is obtaining from a spectrophotometer.

The subject of this article is the comparison of the non-uniformity of the surface mass of knitted fabrics and the estimation of the colour deviations, flattened by means of a spectrophotometer.

The aim of the development is to establish the limit level of mass non-uniformity on the acceptable colour deviation in the width of the fabric.

***Keywords:*** textile fabrics, mass irregularity, dyeing affinity, colour deviation.

***References:***

[ 1] Datacolor | Color Management Solutions: Tools for the Most Accurate Color

# PREPARATION AND CYTOTOXICITY OF NOVEL BIOACTIVE COMPOUND-CONTAINING POLYMERIC NANOSIZED MATERIALS

10.53230/tgm.1310-912X.2020.0010.08

**Milena IGNATOVA[1], Selin KYUCHYUK[1], Nikoleta STOYANOVA[1], Nevena MANOLOVA[1], Iliya RASHKOV[1], Reneta TOSHKOVA[2], Ani GEORGIEVA[2]**

[1]Laboratory of Bioactive Polymers, Institute of Polymers, Bulgarian Academy of Sciences, Acad. G. Bonchev St, Bl. 103A, BG-1113 Sofia, Bulgaria

[2]Institute of Experimental Morphology, Pathology and Anthropology with Museum, Bulgarian Academy of Sciences, Acad. G. Bonchev St, Bl. 25, BG-1113 Sofia, Bulgaria

e-mail: selin.erdinch@polymer.bas.bg

***Introduction***

It is well known that 8-hydroxyquinoline, its derivatives and berberine chloride (Brb) manifest a set of beneficial biological properties: antimicrobial, antioxidant, antitumor, etc. [1,2]. The incorporation of these bioactive compounds in polymeric nanosized materials (electrospun nonwoven textile and nanoparticles (NPs)) can impart advantageous properties to the materials. Therefore finding routes to prepare 8-hydroxyquinoline derivatives- and Brb- containing polymeric nanosized materials and to explore the effect of the composition of the obtained materials on their cytotoxicity is of great interest.

***Experimental part***

8-Hydroxyquinoline derivative and its complex with Cu2+ were prepared as described earlier [3,4]. Custom-made electrospinning equipment was used. The in vitro cytotoxicity of the obtained nanosized materials against HeLa human cervical tumor cells and non-tumor BALB/c 3T3 mouse fibroblast cells was assessed by the MTT assay. The morphology changes in the cells cultured in the presence of nanosized materials were assessed by fluorescent staining methods.

***Results and Discussion***

Novel nonwoven textile from polylactide and 8-hydroxyquinoline derivative (Schiff base from Jeffamine ED® and 8-hydroxyquinoline-2-carboxaldehyde (Jeff-8Q)) or its complex with Cu2+ (Jeff-8Q.Cu2+) of diverse design was fabricated by one-pot electrospinning or electrospinning combined with dip-coating. Stable aqueous dispersions of NPs based on complexes of Brb and poly(methacrylic acid) or poly(acrylic acid), were also successfully prepared by mixing their dilute aqueous solutions. The morphology of the fibrous mats and NPs were studied by scanning electron microscopy (SEM) or transmission electron microscopy (TEM). In vitro cell viability studies and used fluorescent staining methods demonstrated that the prepared Jeff-8Q- or Jeff-8Q.Cu2+-containing fibrous materials and Brb-containing NPs displayed a higher cytotoxicity against HeLa tumor cells than against non-tumor BALB/c 3T3 mouse fibroblast cells. It was found that the observed antitumor effect against HeLa cells is mainly due to the induction of apoptosis.

***Conclusion***

These properties render these novel polymeric nanosized materials promising as potential candidates in the drug delivery systems in the treatment of cervical tumors.

***Keywords:*** 8-hydroxyquinoline, Schiff base, complex with Cu2+, berberine, electrospun nonwoven textile, nanoparticles, cytotoxicity of nanosized materials

***Acknowledgments:*** Financial support from Bulgarian National Science Fund (Grant KP-06-N39/13/2019) is gratefully acknowledged.

[1] Song Y., Xu H., Chen W., Zhan P., Liu X., Medicinal Chemistry Communications 6, 61-74 (2015)
[2] Imanshahidi M., Hosseinzadeh H., Phytotherapy Research 22, 999-1012 (2008)
[3] Mladenova R., Ignatova M., Manolova N., Petrova T., Rashkov I., European Polymer Journal 38 989-999 (2002)
[4] Ignatova M., Stoyanova N., Manolova N., Rashkov I., Kukeva R., Stoyanova R., Toshkova R., Georgieva A., Materials Science and Engineering C 116, 111185 (2020)

# POLYMER MEMBRANES FROM BIODEGRADABLE POLYMER AND CHEMICAL FUNGICIDE PREPARED BY ELECTROSPINNING

10.53230/tgm.1310-912X.2020.0010.09

**N. NACHEV[1], M. SPASOVA[1], N. MANOLOVA[1], I. RASHKOV[1], M. NAYDENOV[2]**
[1]Laboratory of Bioactive Polymers, Institute of Polymers, Bulgarian Academy of Sciences, Acad. G. Bonchev St, bl. 103A, BG-1113 Sofia, Bulgaria
[2]Department of Microbiology, Agricultural University, BG-4000 Plovdiv, Bulgaria
mspasova@polymer.bas.bg

***Introduction***

Esca is one of the earliest described diseases in grapevines that cause trunk damages and sudden wilting of the entire plant. It is known that esca is caused mainly by species Phaeoacremonium chlamydospora and Phaeoacremonium aleophilum. However, there are no known curative approaches for fighting with esca directly. Novel approaches and agents for solving the problem can be provided by developing innovative fibrous polymer membranes containing biologically active chemical fungicides.

***Experimental part***

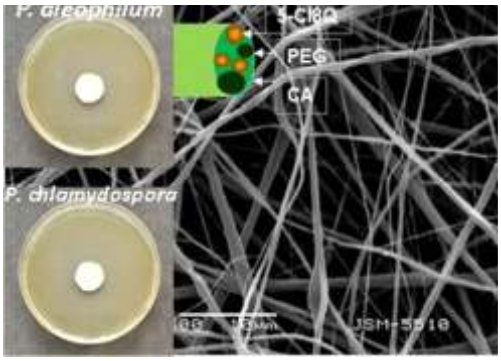
Cellulose acetate (CA, 30 000 g/mol and DS 39.8%), polyethylene glycol (PEG, Mr = 1 900-2 200 g/mol) and 5-chloro-8-hydroxyquinoline (5-Cl8Q) (Sigma-Aldrich) were used. Acetone (Sigma-Aldrich) of analytical grade of purity was used.

***Results***

Fibrous membranes of CA, CA/5-Cl8Q, CA,PEG and CA,PEG/5-Cl8Q were obtained by electrospinning. Electrospinning of CA solution (10wt%) reproducibly resulted in obtaining continuous defect-free fibers with mean fiber diameter of 780 ± 100 nm. The addition of PEG into the spinning solutions resulted in decrease of the average fiber diameter (531 ± 80 nm). The addition of 5-Cl8Q (10 wt%) to the spinning solutions led to the preparation of fibers with diameters 750 ± 90 nm for the CA/5-Cl8Q fibrous membranes and 446 ± 60 nm for the CA,PEG/5-Cl8Q membranes. The antifungal activity of the electrospun membranes was assessed as well. The incorporation of 5-Cl8Q in the membranes that were placed in contact with P. chlamydospora and P. aleophilum resulted in complete inhibition for all fungi.

***Discussion***

The observed decrease in fiber diameter of CA,PEG and CA,PEG/5-Cl8Q fibers may be explained by the decrease in the solution viscosity by adding a lower molecular weight polymer (PEG) to the spinning solution. The observation of wide zones of inhibition around all membranes containing 5-Cl8Q is evidence that the incorporated bioactive compound impart antifungal activity to the prepared novel fibrous membranes.




***Conclusion***

Polymer membranes from CA - a biodegradable polymer and a chemical fungicide - 5-Cl8Q were successfully prepared by electrospinning. The incorporation of 5-Cl8Q in the membranes imparted a considerable antifungal effect against P. chlamydospora and P. aleophilum. These features indicate that the obtained novel fibrous membranes are suitable candidates for application in agriculture for plant protection against two main causative agents of esca disease.

***Keywords:*** electrospinning; cellulose acetate, chemical fungicide, Phaeomoniella chlamydospora; Phaeoacremonium aleophilum;

***Acknowledgment:*** The authors thank the National Science Fund of Bulgaria for the financial support (Grant number KP-06-OPR03/2 (14.12.2018).

# DESIGN OF ECO-FRIENDLY ELECTROSPUN MATERIALS WITH FUNGICIDAL ACTIVITY AGAINST P. CHLAMYDOSPORA

10.53230/tgm.1310-912X.2020.0010.10

**O. STOILOVA[1], M. SPASOVA[1], N. MANOLOVA[1], I. RASHKOV[1], M. NAYDENOV[2]**
[1]Laboratory of Bioactive Polymers, Institute of Polymers, Bulgarian Academy of Sciences, Acad. G. Bonchev St, bl. 103A, BG-1113 Sofia, Bulgaria
[2]Department of Microbiology, Agricultural University, BG-4000 Plovdiv, Bulgaria
e-mail: stoilova@polymer.bas.bg

***Introduction***

Electrospinning is a cutting-edge nanotechnology that allows facile fabrication of fibrous materials with unique features. The suitable combination of biocompatible and biodegradable poly(3-hydroxybutyrate) (PHB) with nanosized TiO2-anatase capable to generate singlet oxygen by using electrospinning alone or in conjunction with electrospraying, is expected to enable the creation of innovative polymer composites with varied design able to protect mechanically damaged vines from entering the spores of P. chlamydospora, i.e. to protect vineyards from Esca - the most devastating disease of grapevines.

***Experimental part***

Poly(3-hydroxybutyrate) (PHB, 330000 g/mol), titanium (IV) oxide (TiO2, 99.7% anatase nanopowder, <25 nm), chitosan oligomers (COS, 3000-5000 g/mol), chloroform (CHCl3) and N,N-dimethylformamide (DMF) were of analytical grade and used without further purification.

***Results***

Fibrous TiO2-in-PHB materials were obtained by electrospinning of a mixture of PHB solution with TiO2 (7% w/v). Fibrous TiO2-on-PHB materials were prepared by using a PHB spinning solution (14% w/v) for electrospinning and TiO2-COS dispersion for electrospraying. For this purpose, an aqueous COS solution (0.5%) was added to TiO2 (10% w/v) dispersion in ethanol. Electrospinning was performed at 25 kV voltage, tip-to-collector distance of 25 cm and 1500 rpm collector rotation speed. In order to study the antifungal activity against P. chlamydospora of the fibrous materials, 20 ml conidia suspension (with final concentration 107 conidia/ml) was passed through each fibrous material by using a filtration device.

***Discussion***

One-pot electrospinning of a suspension of TiO2 in PHB solution resulted in materials in which TiO2 was incorporated within the fibers (design type "in"). Simultaneous electrospinning of PHB solution and electrospraying TiO2-COS dispersion enabled the preparation of materials consisting of PHB fibers on which TiO2 was deposited on the fibers' surface (design type "on"). It was shown that TiO2-on-PHB exhibited complete inhibition of fungal growth of P. chlamydospora.

***Conclusion***

The obtained eco-friendly fibrous materials based on PHB and TiO2 are promising candidates for plant protection against penetration and growth of main causative fungi causing Esca disease.

***Keywords:*** antifungal activity, electrospinning, electrospraying, PHB, TiO2.

***Acknowledgment:*** The authors thank the National Science Fund of Bulgaria for the financial support (Grant number KP-06-OPR03/2 (14.12.2018).

# ANTIOXIDANT ACTIVITIES OF NOVEL QUERCETIN-LOADED ELECTROSPUN FIBROUS MATERIALS

10.53230/tgm.1310-912X.2020.0010.11

**Nikoleta STOYANOVA, M. SPASOVA, N. MANOLOVA, I. RASHKOV**
Laboratory of Bioactive Polymers, Institute of Polymers, Bulgarian Academy of Sciences,
Acad. G. Bonchev St, bl. 103A, BG-1113 Sofia, Bulgaria
e-mail: mspasova@polymer.bas.bg

***Introduction***

Quercetin occurs abundantly in a variety of fruits and vegetables. This biologically active compound exhibits remarkable antioxidant, anti-inflammatory, antibacterial and anti-tumor activities. Quercetin incorporation in fibrous polymer matrices is of interest when its biomedical and pharmaceutical applications are intended.

***Experimental part***

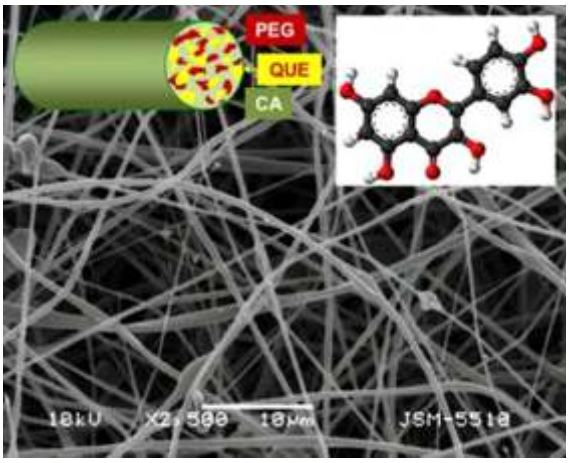
Cellulose acetate (CA, 30 000 g/mol and DS 39.8%), polyethylene glycol (PEG, Mr = 1 900-2 200 g/mol) and quercetin (QUE, ?95%; Sigma-Aldrich) were used. Acetone (Sigma-Aldrich) of analytical grade of purity was used.

***Results***

Electrospinning of CA solution (10 wt%) resulted in obtaining defect-free fibers (780 ± 80 nm). It was found that the incorporation of PEG resulted in decrease of the mean fiber diameter (530 ± 150 nm). Further decrease in the mean fiber diameters to 390 ± 150 nm was observed in the case of CA/PEG/QUE fibrous materials. The addition of a water-soluble polymer - PEG led to reduction of the contact angle value from 120° for the CA mat to 0° for the CA/PEG and CA/PEG/QUE mats. The antioxidant capacity of CA/PEG/QUE mats using 2,2-diphenyl-1-picrylhydrazyl (DPPHo) radical scavenging assay was evaluated. It was found that CA/PEG mats exhibited very low antioxidant activity. In contrast, after 30 minutes of contact with DPPH solution, QUE-containing mats exhibited high antioxidant activity (DPPHo absorption decreased by approximately 94.4%). The colour of the DPPH solution changed to pale yellow upon contact with CA/PEG/QUE mat.

***Discussion***

No peak corresponding to the melting point of QUE was observed in the DSC thermogram of CA/PEG/QUE fibers, which evidenced that the QUE incorporated in the fibers was in amorphous state. Moreover, quercetin-containing fibrous mats exhibited high antioxidant activity as estimated by DPPH free radical scavenging method.



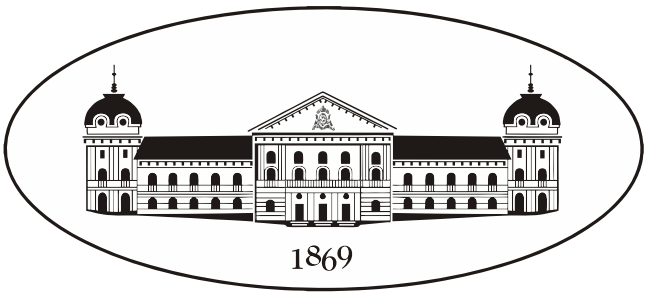

***Conclusion***

Novel fibrous materials with antioxidant activities based on cellulose acetate, polyethylene glycol and quercetin were successfully obtained by electrospinning It was found that the incorporation of PEG in the polymer matrix led to hydrophilization of the material and facilitated the release of the biologically active compound - quercetin. In addition, it was shown that the quercetin-containing fibrous materials exhibited high antioxidant activity.

***Keywords:*** quercetin, electrospinning, antioxidant activity, cellulose acetate fibers

***Acknowledgment:*** The authors thank the Bulgarian Ministry of Education and Science (Grant D01-217/30.11.2018) under the National Research Programme "Innovative Low-Toxic Bioactive Systems for Precision Medicine (BioActiveMed)" approved by DCM # 658/14.09.2018.


ТЕХНИЧЕСКИ УНИВЕРСИТЕТ
СОФИЯ


1869