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### ELECTROSPUN NONWOVEN TEXTILE FROM POLYLACTIDE AND DERIVATIVE OF JEFFAMINE ED® AND 8-HYDROXY-QUINOLINE-2-CARBOXALDEHYDE AND ITS COMPLEX WITH Cu<sup>2+</sup>: PREPARATION AND ANTITUMOR ACTIVITY

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**Introduction:** 8-Hydroxyquinoline and its derivatives are very attractive for biomedical applications due to their beneficial biological properties - antimicrobial, antitumor, antioxidant and anti-inflammatory [1]. These compounds also had the ability to form complexes with biologically important transition metal ions ( $Cu^{2+}$ ,  $Fe^{2+}$ ,  $Fe^{3+}$ , etc.), which accounts for their biological activity. The incorporation of these biologically active compounds in electrospun nonwoven textile can impart favorable biological properties to the textile. In the present study, electrospun nonwoven textile of polylactide (PLA) containing a Schiff base from Jeffamine ED<sup>®</sup> and 8-hydroxyquinoline-2-carboxaldehyde (Jeff-8Q) or its complex with  $Cu^{2+}$  (Jeff-8Q. $Cu^{2+}$ ) of various designs were prepared. The influence of the composition of the obtained textiles on their antitumor properties was estimated.

**Experimental part**: Schiff base derivative of Jeffamine ED<sup>®</sup> and 8-hydroxyquinoline-2carboxaldehyde (Jeff-8Q) and its complex with Cu<sup>2+</sup> (Jeff-8Q.Cu<sup>2+)</sup> were obtained by the procedure described earlier [2,3]. The morphology of the fibrous materials was evaluated by scanning electron microscopy (SEM, Jeol JSM-5510 (Tokyo, Japan)). The antitumor activity of the mats was estimated using the MTT assay. Custom-made electrospinning equipment was used.

**Results and Discussion:** For the first time Jeff-8Q- or Jeff-8Q.Cu<sup>2+</sup>-containing fibrous materials of various designs were obtained by applying one-pot electrospinning (type "*in*") or electrospinning combined with dip-coating (type "*on*"). Electron paramagnetic resonance (EPR) analysis was performed to examine the complexation of Cu<sup>2+</sup> in the Jeff-8Q.Cu<sup>2+</sup>/*in*PLA and Jeff-8Q.Cu<sup>2+</sup>/*on*PLA mats. The *in vitro* release of Jeff-8Q or its complex with Cu<sup>2+</sup> from the type "*on*" electrospun nonwoven textile was more rapid than that of the type "*in*" textile. The performed MTT cell viability studies revealed that in contrast to the neat mats, the Jeff-8Q.Cu<sup>2+</sup>-containing fibrous materials (both types "*in*" and "*on*") displayed good cytotoxicity against human cervical HeLa tumor cells. Fluorescence microscopy analyses indicated that the induction of apoptosis is one of the major mechanisms of the antitumor efficacy of the obtained electrospun nonwoven textile.

**Conclusion**: The results suggest that the prepared novel electrospun nonwoven textile containing Jeff-8Q or Jeff-8Q. $Cu^{2+}$  are promising candidates for local application in the treatment of cervical tumors.

**Keywords:** Schiff base, 8-hydroxyquinoline derivative, electrospinning, antitumor activity **Acknowledgments:** Financial support from Bulgarian National Science Fund (Grant KP-06-N39/13/2019) is gratefully acknowledged.

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### ELECTROSPUN POLY (METHYL METHACRYLATE) - BASED COMPOSITES FOR PHOTOCATALYTIC WATER TREATMENT

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**Introduction** Electrospun materials are considered to be the most versatile candidates for the effective treatment of water, filtration, and separation because of their high surface area, high porosity, and light weight. In order to improve their applicability and performance for use in water treatment, metal oxide nanoparticles have been incorporated into materials. Thus, the key challenge in water treatment is to prepare appropriate electrospun composites with a high efficiency and low environmental impact.

**Experimental part** Poly (methyl methacrylate) (PMMA, average molecular weight ~ 350,000 g/mol) and titanium (IV) oxide (TiO<sub>2</sub> nanopowder, 99.7% anatase) were purchased from Sigma Aldrich. N,N-dimethylformamide and methylene blue B (MB) were purchased from Merck. All reagents were of an analytical grade of purity and were used as received without further purification.

**Results** Electrospinning was successfully used for the one-step fabrication of poly(methyl methacrylate) fibers loaded with an inorganic photocatalyst - TiO<sub>2</sub>. Besides the electrospinning conditions, the TiO<sub>2</sub> content in the PMMA solution was varied in order to fabricate PMMA fibers filled with significant amounts of TiO<sub>2</sub>. The morphology of the electrospun composites was affected by the amount of TiO<sub>2</sub> incorporated into the PMMA fibers. In addition, the inorganic photocatalyst had an impact on the wettability, thermal stability, and optical properties of the electrospun composites. In particular, the surface wettability of the composites was strongly influenced by UV light irradiation and from hydrophobic became superhydrophilic. Moreover, PMMA/TiO<sub>2</sub> composites had enhanced tensile strength. The optical properties, photocatalytic activity when using methylene blue as a model organic pollutant, and reusability of the composites were evaluated with respect to targeted application.



**Conclusion** PMMA/TiO<sub>2</sub> composites were successfully fabricated in one step by electrospinning. They preserve their photocatalytic activity almost completely after three uses in the presence of a model organic pollutant - MB. Thus, the proposed original and simple approach is very promising for the future development of highly efficient composites for photocatalytic water treatment.

**Keywords:** electrospinning; poly(methyl methacrylate); TiO<sub>2</sub>; UV-induced wettability; mechanical properties; photocatalysis.

Acknowledgments: This research was partially funded by the European Regional Development Fund within the OP "Science and Education for Smart Growth 2014 - 2020", grant number BG05M2OP001-1.001-0008-C01. Research equipment of Distributed Research Infrastructure INFRAMAT, part of Bulgarian National Roadmap for Research Infrastructures, supported by Bulgarian Ministry of Education and Science was used in this investigation.

## ONE-STEP FABRICATION OF POLYMER HYBRIDS CONTAINING MN-DOPED ZNSE/ZNS NANOCRYSTALS

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**Introduction** Semiconductor nanocrystals (NCs) doped with transition metal have intensively studied because of their unique optical properties and enormous applications. Among them, ZnS or ZnSe NCs doped with Mn-ions attracted much attention, because Mn-ions are easily incorporated into the II-VI host crystalline lattice. However, developing a method for simple and effective incorporation of highly luminescent NCs into appropriate polymer matrices for fabrication of solid-state lighting and flat-panel displays, still remains a great challenge.

**Experimental part** Commercially available zinc acetate (99.9%), manganese acetate (99.9%), 3mercaptopropionic acid (99%), selenium powder (99.5%), sodium sulfide, as well as polyacrylonitrile (PAN, 150000 g/mol) and poly(methyl methacrylate) (PMMA, 350000 g/mol) were supplied from Sigma-Aldrich. All chemicals were of analytic grade of purity and used as received without further purification.

Results In the present study, in order to fabricate fibrous polymer hybrids with predetermined high photoluminescence (PL) efficiency, Mn-doped ZnSe/ZnS (Mn : ZnSe/ZnS) core/shell NCs were synthesized and embedded into PMMA and PAN fibers, respectively. By varying the conditions for electrospinning, the optimal conditions for the formation of a Taylor cone were found for both PMMA and PAN spinning solutions. Thus, by one-step electrospinning of PMMA/NCs and PAN/NCs mixtures, fibrous polymer hybrids were prepared. Detailed morphology of the hybrids was observed by SEM, while the distribution and crystallinity of the embedded NCs were determined by TEM/SAED. Optical properties were also studied in details by photoluminescence spectroscopy. Finally, PL efficiency was evaluated to show the potential of prepared polymer



hybrids prospective for emitters-production as solid-state illumination sources and lighting devices.

**Conclusion** An appropriate conditions for successful embedding of Mn:ZnSe/ZnS core/shell NCs in PMMA and PAN fibers were found and by one-step electrospinning novel Mn:ZnSe/ZnS-in-PMMA and Mn:ZnSe/ZnS-in-PAN hybrids with enhanced luminescence were fabricated.

**Keywords:** Mn-doped ZnSe/ZnS core/shell nanocrystals, electrospinning, PAN hybrids, PMMA hybrids, photoluminescence.

Acknowledgments: This research was partially funded by the European Regional Development Fund within the OP "Science and Education for Smart Growth 2014–2020", grant number BG05M2OP001-1.001-0008-C01. Research equipment of Distributed Research Infrastructure INFRAMAT, part of Bulgarian National Roadmap for Research Infrastructures, supported by Bulgarian Ministry of Education and Science was used in this investigation.

### INNOVATIVE ANTIOXYDANT BIOPOLYMER/PLANT EXTRACT MATERIALS PREPARED BY ELECTROSPINNING

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**Introduction** Electrospinning has gained considerable attention due to its versatility for producing fibrous materials with outstanding characteristics, such as high porosity, small diameter, excellent pore interconnectivity, high surface-to-volume ratio, ease of functionalization for various purposes and superior mechanical properties. These useful characteristics make the nanofibrous materials perspective candidates for many applications such as scaffolds for tissue engineering and cell culture, wound dressings drug delivery cosmetics, protective clothing, filtration and thermal insulation, electronic and semi-conductive materials. Natural products can be obtained from four main sources: plants, animals, marine organisms and microorganisms. They exhibit tremendous chemical and structural diversity. Since ancient times, plant species had medicinal use with better patient tolerance and acceptance. Encapsulation of plant extracts, through electrospinning, can accelerate their remedial potential. This process increases the therapeutic potential by improving bioavailability and maintains a steady concentration of bioactive compound to the target area. The aim of the present study was to prepare and to characterize novel fibrous materials based on a biocompatible polymer containing a crude extract by electrospinning.

**Results and Discussion** The optimal process conditions for the preparation of defect-free fibers were found. The newly obtained fibrous materials were fully characterized by scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), X-ray diffraction analysis (XRD) and water contact angle measurements. It was found that the incorporation of the crude extract had significant effect on the average fiber diameter, thermal characteristics and structure of the obtained materials. Moreover, it was found that the electrospun PLA/P. oleracea materials showed high antioxidant activity.

**Conclusion** Extract-containing fibrous mats exhibited high antioxidant activity as estimated by DPPH free radical scavenging method. Therefore, the created innovative mats might have a practical use for wound healing applications, as well as in food industry.



Keywords: plant extract; biopolymer; electrospinning; high antioxidant activity

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### NOVEL POLYLACTIDE/PORTULACA OLERACEA FIBROUS MATERIALS FOR BIOMEDICAL APPLICATIONS

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**Introduction:** Health concerns associated with the side effects of synthetic compounds used in medicine, pharmacy, cosmetics, and food industry as well as the emergence of antibiotic resistance of pathogens has driven electrospinning research towards the development of fibers encapsulating plant extracts. Portulaca oleracea possesses a wide spectrum of pharmacological properties such as neuroprotective, antimicrobial, antidiabetic, antioxidant, anti-inflammatory, antiulcerogenic, and anticancer activities and therefore is used to relieve symptoms and treat a wide range of diseases, including gastrointestinal diseases, respiratory disorders, liver inflammation, kidney and bladder ulcers, fever, insomnia, inflammation and headaches. In the recent years great research interest has been directed toward encapsulation of bioactive plant extracts into electrospun fibrous materials. However, up to now there are no data in the literature focused on fabrication of fibrous electrospun materials loaded with P. oleracea extract.

**Results and Discussion:** The electrospinning of PLA solution (polymer concentration 10 wt%) under the selected conditions reproducibly resulted in obtaining uniform fibers with mean fiber diameter of  $1100 \pm 200$  nm. The addition of P. oleracea (1; 5 or 7.5 wt%) to the PLA spinning solution led to the preparation of fibers with larger diameters. XRD analyses revealed that the initial P. oleracea extract is in crystalline state. In the XRD pattern of PLA/P. oleracea fibrous materials characteristic diffraction peaks with high intensity corresponding to P. oleracea were not observed. DSC thermograms showed that the incorporation of the extract in the PLA fibers resulted in shifting of Tg and Tcc of PLA to lower temperatures accompanied with decrease in the degree of crystallization of the polyester. Moreover, P.oleracea



incorporated into PLA fibers exhibits antioxidant activity. The efficiency of the obtained fibrous materials to enhance the proliferation of mouse BALB/c 3T3 fibroblasts was evaluated. The obtain results show that the fibrous materials loaded with P. oleracea were biocompatible and no toxic to normal cells.

**Conclusion:** Thus obtained novel materials could be a potential candidate for tissue regeneration and wound healing applications.

Keywords: Portulaca oleracea; PLA; electrospinning; antioxidant activity, cell culture

Acknowledgments: This work was supported by Operational Program "Science and Education for Smart Growth" 2014-2020, co-financed by European Union through the European Structural and Investment Funds, Grant BG05M2OP001-1.002-0012 "Sustainable utilization of bio-resources and waste of medicinal and aromatic plants for innovative bioactive products". Research equipment of Distributed Research Infrastructure INFRAMAT, part of Bulgarian National Roadmap for Research Infrastructures, supported by Bulgarian Ministry of Education and Science was used in this investigation.



## COTTON FABRIC WASTE CONVERSION TO VALUBLE CHEMICALS

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Today, the circular economy is a powerful engine for new technology development. Besides the environmental benefits, the economic ones are also important. The strong incentive for recycling processes is the waste conversion into valuable products. Cotton is comfortable to wear and use, so the amount of scrap is significant. The sources of cotton waste are pre-consumer and post-consumer cotton. Recycling processes have considerable benefits when the waste fabric cotton is converted again into fibres or valuable chemicals. Biomass containing cellulose, including textile waste, is a promising raw material for a new generation of liquid fuels and chemicals such as 5-hydroxymethyl furfural (HMF).

After processing, cellulose is a source of glucose. There are many studies on the production of ethanol from waste textiles. Cellulose can be transformed into other valuable chemicals as HMF through a series of chemical reactions: hydrolysis of cellulose to glucose, isomerization of glucose to fructose, and dehydration of fructose to HMF. With the help of homogeneous and heterogeneous catalytic processes, HMF is converted into 2,5-dimethylfuran (DMF), 2-methylfuran (2-MF) and long-chain hydrocarbon alkanes. The latter have properties that make them potential substitutes for petroleum fuels. By HMF oxidative conversion can be obtained 2,5-furandicarboxylic acid (FDCA). This bio-based monomer is used for polyester, polyamides, etc. polymers production, finding application in different areas, such as textiles, packaging, and coatings, among many others.

The difficulties in these processes stem from the fact that textile waste cannot be converted in one step, the yield of glucose and HMF is low, and side products are produced that inhibit reactions, rehydration of HMF and polymerization between sugars and HMF. The other barrier to recycling cotton is the cellulose fibres' great strength and crystalline structure due to possible hydrogen bond formation. The fabrics are often a mix of materials, which makes separating cotton difficult. Each textile is further processed to improve its properties - colour, fire resistance and wrinkle, etc. These treatments make the waste conversion to glucose difficult, and pretreatment is necessary.

Various methods for this facilitate the hydrolysis of cellulose to glucose. These are mechanical, chemical (acidic or alkaline), hydrothermal, ultrasonic, microwave, enzymatic, etc. and their combination. An effective pretreatment method is the steam explosion, which uses steam, high temperature, and pressure. The sudden pressure reduction results in the mechanical processing of the hydrolyzed product. This method is also used in combination with other methods.

The present work aims to obtain glucose from cotton-based textile waste as a raw material for FURanbased chemical synthesis. The tasks to be performed in this plan are to select appropriate methods for the cotton waste pretreatment to obtain the highest possible glucose yields.

**Keywords:** cotton waste pretreatment, 5-hydroxymethyl furfural, 2,5-furandicarboxylic acid, glucose conversion

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### ANTIMICROBIAL PROPERTIES OF FLUORESCENT COTTON FABRIC, MODIFIED WITH CHITOSAN OR LAYER-BY-LAYER COATED WITH CHITOSAN AND ALGINATE

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**Introduction:** The cotton fabric modification with fluorescent hydrogel or coating organized layerby-layer is the way to obtain intelligent interfaces with controllable properties. These composite materials can find different biomedical, ecological, etc. applications. Natural polysaccharides such as chitosan and alginate are eco-friendly, biodegradable polymers. They can form films on the cotton surface via electrostatic interaction between their opposite charges. The modification of chitosan with 1,8-naphthalimide fluorophore enables the following swelling and erosion of the obtained hydrogel on the fabric surface via changes in its fluorescent emission.

This study aims to prepare and compare the antimicrobial properties of cotton fabric composites modified with cross-linked fluorescent chitosan with citric acid and the same material coated with alginate as a second layer.

**Experimental part:** Cotton fabric was impregnated with citric acid and with solution of chitosan and chitosan modified with 1,8-naphthalimide fluorophore. The second material was obtained as the previous one but as a last step the fabric was immersed in an alginate solution. The obtained materials have been characterized by optical and scanning electron microscopy and fluorescent, gravimetric and thermal analysis (TG-DTA-DTG). Their antimicrobial activity was investigated against Gram-positive Bacillus cereus and Gram-negative Pseudomonas aeruginosa used as model strains.

**Results and Discussion:** The surface morphology of composites, investigated by optical and scanning electron microscopy, shows that the chitosan layer wrapped the cotton fibres. The alginate treatment of the sample resulted in a denser layer with an uneven grain structure that bonded the fibres. On the fabric surfaces, irregularly scattered colour spots were observed due to the 1,8-naphthalimide-modified chitosan. The alginate layer application on the surface improved the thermal stabilities of cotton fabric with the residual chars increased. Swelling and erosion of hydrogel in phosphate buffer pH 7.4 at 37 °C caused a decrease in fluorescence emission, which was more pronounced in the sample with the alginate layer. The antimicrobial activity of the cotton samples has been evaluated against B. cereus and P. aeruginosa as model bacterial strains. The analysis showed that the sample containing only chitosan almost entirely inhibited the growth of both bacterial strains. The fabric covered with alginate inhibited the growth of P. aeruginosa and B. cereus by 63% and 92%, respectively.

**Conclusion:** Surface treatment of cotton fabric with cross-linked fluorescent chitosan and then with alginate as a second layer can modify its thermal and antibacterial properties due to a change in the layer structure and the positive charge of chitosan.

Keywords: chitosan, alginate, cotton fabric, 1,8-naphthalimide

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## ALTERNATIVE FUEL DESULPHURISATION METHODS

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The continuous growth of fossil fuels consumption led to a problem associated at first with the corrosive action of certain types of sulfur compounds and later with the negative impact of hetero atomic compounds in fossil fuels on the environment. In this regard, investigations related to the purification of petroleum products from sulphur compounds is important. In petroleum they are in the form of mercaptans, sulphides, disulfides, thiophenes and benzothiophenes. To remove sulphur compounds from fuels over the past few decades, refineries mainly use hydrodesulphurization (HDS). The process is carried out in conditions of high pressure and temperature, in the presence of a catalyst. In the literature, a large number of alternative methods of hydrodesulphurization are described, such as: oxidative desulphurization and its varieties; alkylation; extraction desulphurisation; conversion/extraction desulphurisation in different variants; desulphurisation by precipitation, biodesulfurization, etc.

Particular attention among the listed methods occupies the method of adsorption desulphurization. This is technologically not complicated, energy-efficient and at the same time one of the most effective methods for removing diverse pollutants from different environments. The method is based on the ability of the solid adsorbent to selectively adsorb organic sulphur compounds from fuels.

Various porous materials such as activated aluminium oxide, zeolites, carbon materials and others have been studied as adsorbents to remove organic sulphur compounds from model and real fuels. In recent years, biosorbents have increasingly been paid attention, as they are effective and with low cost. One of the promising raw materials for biosorbent synthesis are rice husks - waste, the annual accumulation of which creates serious environmental problems. Our research shows that an adsorbent obtained by pyrolyzed rice husks has good potential for adsorption desulphurization of liquid fuels. Its adsorption affinity decreases in the order: thiophen>benzothiophen>dibenzothiophene.

Of interest is an innovative study using composite material synthesized from textiles and metal organic frameworks (MOF) for adsorption purification of thiophen from model fuels [1]. An *in-situ* method for modifying cotton and wool with MOF by infrared technology was used. The reported results confirm expectations that the sorption capacity of the obtained textile materials increases after their modification. A decrease in the sorption capacity of composites has been observed after their regeneration, which is explained by a decrease in the amount of MOF on their surface. This study will open the way for using infrared radiation for preparing textile based MOF composite materials which are oriented in desulphurization application.

Keywords: bioadsorbents, desulphurization, fuels, textile composites.

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The authors acknowledge the support through Project No 12231 Purification of model fuels from sulphurorganic compounds using bioadsorbent. Adsorption isotherms.

### INFLUENCE OF COTTON FABRIC MODIFICATION ON ITS ABILITY FOR OIL-WATER SEPARATION

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**Introduction:** Spills of oil and oil products occur very often around the world, despite the measures taken to prevent them. Similar water pollution may also occur in the Black Sea and the Danube, and the reasons for this are port and ship operations. Hence, the development of methods and means to eliminate these contaminants from water continues to be relevant. Sorbent materials are one of the most effective, easy for application and inexpensive ways to clean up spills. The sorption rate and capacity of the material, its buoyancy, flexibility, hydrophobicity and water stability are some requirements for their successful application. The other environmental demands are the possibility of regeneration by concentrating the adsorbed oil, the reuse of the materials and their subsequent safe destruction. An ideal sorbent should be highly oleophilic and hydrophobic at the same time. Cotton fabric has many excellent properties suitable for this application. However, cotton is hydrophilic and has to be modified to perform oil sorption activity.

This study aims to prepare composite materials from cotton fabric modified with aldehyde functionalized chitosan and with added ZnO and to compare their properties to remove oil from water.

**Experimental part:** The first material contains a cotton fabric impregnated with chitosan solution and glutaraldehyde. In the second material preparation, Zn ions were added to chitosan and converted to ZnO particles. The third material was obtained with chitosan, modified with benzaldehyde, and crosslinked on cotton fabric. The fourth material was acquired as the third one and contained ZnO particles.

**Results and Discussion:** The materials were investigated as sorbents for crude oil in water. The largest sorption capacity for oil was obtained with the fourth sample, followed by the third sample. Slightly lower results were obtained for the second sample, containing unmodified chitosan. The possibility for the adsorption-desorption of oil and the reuse of the sorbents have also been investigated. All materials were regenerated successfully with hexane and reused for complete oil removal. In vitro antimicrobial activity was studied by finding the growth inhibition of model microbial strains (Grampositive bacteria Bacillus cereus, Gram-negative bacteria Pseudomonas aeruginosa and the fungus Candida lipolytica). The results have shown that cotton fabric obtained with benzaldehyde-modified chitosan has better antimicrobial properties than that obtained with chitosan alone. The presence of zinc oxide particles in the samples completely inhibited the growth of all three model strains.

**Conclusion:** The material's hydrophobicity was enhanced with the benzaldehyde chitosan modification, improving the oil sorption capacity. This material is easy to use, regenerate, and reuse and has good antimicrobial properties. The presence of ZnO refines the material performance.

Keywords: chitosan, benzaldehyde, oil-water separation, antimicrobial

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## ANTIMICROBIAL PHOTODYNAMIC ACTIVITY OF COTTON FABRICS MODIFIED WITH FLUORESCENT DENDRIMERS

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The adaptability of the pathogenic microorganisms caused by their rapid multiplication rate is responsible for their increased resistance to antimicrobials used in clinical practice. In relation to solving this problem, the search for new more effective compounds with improved antimicrobial properties is required. Scientists are now focusing their efforts on the design, synthesis and investigation of low and high molecular weight compounds (linear, branched, dendrimers) of different nature and structure, with the aim of discovering and developing new substances with antimicrobial activity.

The antimicrobial activity of dendrimers and hyperbranched polymers is due to their ability to bind to the bacterial cell surface, disrupting the permeability and integrity of the membrane. They can adsorb and form nanosized films on textile surfaces under various interactions.

The antimicrobial activity of cotton fabrics is influenced by several factors, such as mechanical retention of microbial cells on the fabric depending on the surface morphology; dispersion of the antimicrobial material on the textile surface; and change in the hydrophobic/hydrophilic nature of the materials, which can affect the degree of contact of the microbial inoculum with the fabric. The antimicrobial effect of treated textile fabrics is due to the slow release of biologically active substances into the medium or direct contact with microbial cells. Microbial adhesion as a first stage in biofilm formation can be limited by the interaction of dendrimers with the cell surface or with ions that stimulate microbial adhesion, resulting in a change in cell wall properties and preventing microbial attachment.In this case, the dendrimers inhibit the secretion of extracellular biopolymers, leading to the detachment of cells from the surface of the cotton tissue and thus to the prevention of biofilm formation. This



shows good prospects for the use of such compounds for the production of antibacterial textiles.

As photoactive compounds, these dendrimers, whose activity is retained even after deposition on textile materials, indicate that they are suitable candidates for application in antibacterial photodynamic therapy. This is a new area against the bacterial resistance to antibiotics used in the medical practice and future research should be directed in this area.

Keywords: cotton fabric, dendrimer. antimicrobial, photodynamic therapy, fluorescence

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### POSSIBILITIES FOR MODIFYING COTTON FABRICS WITH TITANIUM NANOPARTICLES. ADVANTAGES AND CHALLENGES OF THE PROCESS

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#### Introduction

Extraordinary photocatalytic activity, non-toxicity, high availability, biocompatibility, and low price make  $TiO_2$  nanoparticles particularly attractive for manufacturing of different high value-added products. During the past several years, many efforts have been made to immobilize  $TiO_2$  nanoparticles onto textile materials with an aim to produce goods with multifunctional properties such as UV protective, selfcleaning and antibacterial. The processing of textile materials with  $TiO_2$  nanoparticles is relatively simple, but insufficient binding efficiency between certain fibers and  $TiO_2$  nanoparticles imposes a problem concerning the stability and durability of nanocomposite systems during their exploitation. Therefore, recent studies were more oriented toward chemical and physico-chemical modification of fiber surfaces that may enhance the binding efficiency of  $TiO_2$  nanoparticles. This article looks at some latest advances in finishing of different textile materials with  $TiO_2$  nanoparticles.

#### The mechanism of TiO<sub>2</sub> action

The size, shape, crystalline structure and specific surface area determine the chemical, optical, and electrical properties as well as photocatalytic activity of  $TiO_2$  NPs. The exposure of  $TiO_2$  NPs to UV light with an energy that matches or exceeds its band gap energy leads to an excitation of electron from valence band into conduction band while the positive hole is left behind.

#### The application of $TiO_2 NPs$ to textile materials

The impregnation of textile materials with  $TiO_2$  NPs is typically conducted by dip-coating method. After being immersed in  $TiO_2$  NPs colloid or suspension for certain time, the fabrics are padded, dried and cured. Afterwards, they are usually rinsed with water and dried. This procedure is described here in rough outline.



Although the times of immersion in the colloid, padding pressures, temperatures and times of drying and curing as well as rinsing methodologies vary from author to author, the methods of coating are principally the same.

#### Conclusion

This review clearly indicates that huge potential of  $TiO_2$  nanoparticles could be efficiently utilized for imparting antibacterial, self-cleaning and UV-protective properties to various textile materials. Simple routs for processing of textile materials with  $TiO_2$  nanoparticles and the fact that small amount of this cheap, chemically and physically stable photocatalyst provide desired effects make  $TiO_2$  nanoparticles particularly attractive finishing agent which can find a broad application in textile industry.

**Keywords:** TiO<sub>2</sub> nanoparticles, textile materials, UV protection, photocatalytic activity, antibacterial activity

### STUDY ON THE APPLICATION OF DBD PLASMA IN FLAME RETARDANT TREATMENT FOR DYED COTTON FABRICS

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Introduction: Cotton is one of the most used textile fibres. However, it is a combustible material with a low LOI of 18.4% [1]. Therefore, flame retardant treatment for cotton fabrics, especially durable flame retardant, is an important requirement for many areas of use. Many studies have shown that Pyrovatex CP New (PCN) combining crosslinking agents such as trimethylolmelamine (TMM) or 1,3-dimethylol-4,5-dihydroxyethylene urea (DMDHEU) is a very good choice to create durable flame-retardant cotton fabrics. However, they release formaldehyde, and their mechanical strength is reduced compared with pre-treatments because the crosslinking reaction occurs at high temperature and requires the use of phosphoric acid as a catalyst [2-4]. In our recent studies, a new formaldehyde-free crosslinking agent (Knittex FFRC (K-FFRC)) was used as a replacement for the old one as a solution to reduce the release of free formaldehyde from fabrics [5, 6]. However, our research has shown that when treating cotton fabric with PCN and K-FFRC, for the treated fabric to be fire resistant (LOI > 25), the curing temperature must be greater than 170°C and the time curing must also be longer than 120 seconds. It is this condition that reduces the mechanical strength of cotton fabric [7]. To solve this problem, we pre-treated cotton fabric with DBD plasma for 90 s, plasma treated fabric then treated with PCN and K-FFRC. The results show that the fabric has been pre-treated with plasma, during the flame-retardant treatment it only needs to be cured at 160°C for 90 seconds to have a LOI > 25. To achieve this value, the normal cotton fabric must be cured at 180°C for 120s during flame retardant treatment [7, 8]. This study also shows that too strong plasma treatment conditions (high plasma power, prolonged exposure time) also adversely affect the mechanical performance of cotton fabrics. These studies are all performed on white cotton fabrics after pre-treatment, while functional finishing is usually carried LOI of 18.4% [1]. Therefore, flame retardant treatment for cotton fabrics, especially durable flame retardant, is an plasma power, prolonged exposure time) also adversely affect the mechanical performance of cotton fabrics. These studies are all performed on white cotton fabrics after pre-treatment, while functional finishing is usually carried out on dyed fabrics. In dyed cotton, some of the active radicals are usually occupied by dye molecules, so their level of reactivity is different from that of undyed fabrics. Therefore, in this study, DBD plasma was applied on dyed cotton fabrics before they were flame retardant treated with PCN and K-FFRC. The objective of this study was to clarify the effect of DBD plasma treatment on flame retardant treatment for the dyed cotton fabric. **Experimental:** *Procedure:* Dyed woven cotton fabric with mass of 242/m<sup>2</sup> was supplied by NASILKMEX -> APDBD plasma treatment with plasma power of 400 W (1 W/cm<sup>2</sup>) for 30s -> Flame retardant treatment with PCN and K-FFRC -> Flame retardant dyed cotton fabric -> Washing fabric according to ISO 6330 for 5 cycles. *Testing:* Flammability of fabric by ASTM D 6413 -2015 and determination of LOI of fabric by ASTM D 2863 - 97 befor and after flame-retardant treatment and after washing. Measument of color of fabric befor and after DBD plasma treatment.

plasma treatment.

**Result:** The results showed that the DBD plasma pre-treatment improved the efficiency of the flame retardant process for the dyed cotton fabric: the LOI of the fabric before and after washing were both improved compared to samples not pre-treated with DBD plasma. However, compared with the white fabric, the flame-retardant treatment condition for dyed cotton fabric needs to be stronger for the flame retardant treated fabric to have the desired flame retardant properties. The results also showed that plasma treatment also changed the color of dyed cotton fabrics. The color of the fabric tends to be lighter after plasma treatment. *Keywords*: Dyed cotton fabric, DBD plasma, Flame retardant, Pyrovatex CP new, Knittex FFRC

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### INVESTIGATION OF THE FRAGRANCE DURABILITY OF KNITTED FABRIC BAND COATED BY EUGRARIT RSPO MICROCAPSULES CONTAINED THE CINNAMON OIL ESSENTIAL

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The aromatherapy textile of cinnamon oil comes from a compound found in the essential oil called cinnamaldehyde. With the antibacterial and anti-inflammatory properties that can help treat certain metabolic, infectious, digestive or respiratory disorders, this compound is also very volatile. Moreover, cinnamon essential oil can help treat dermatitis, but the coumarin compounds found in essential oils can cause skin irritation. Therefore, encapsulation is currently the best solution to improve evaporation and keep the fragrance of essential oils on fabrics longer and reduce large amounts of pure essential oils in direct contact with the skin. In this study, we have investigated the odor fastness of Eugrarit RSPO microcapsules contained the cinnamon essential applied to the surface of interlock fabric knitted by Chief Value Cotton (CVC) yarn (60% cotton, 40% polyester). The fragrance durability of the knitted fabrics coated by pure cinnamon essential oil and the microcapsules contained cinnamon essential oil and the microcapsules contained contact by the microcapsule contained contained contact of the pressure of knitted fabric band coated by the microcapsule contained

cinnamon essential oil induced by extension levels of 21.25%, 57.5%, 68.75%, 83.75% had been studied. The fragrance durability evaluation was based on the combination of the expert method and diluted solution method. The results showed that the fragrance intensity of knitted fabrics treated by pure essential oil was stronger but the diminution of their fragrance was faster than these ones treated by the cinnamon essential oil microcapsules. Besides, the higher the extension applied on the fabrics band, the smaller their fragrance intensity had been maintained. The problem of long-term retention of essential oil on the fabric surface for the purpose of preserving fragrance or promoting the necessary properties of the essentiel oil for a long time was one goal of the works. Cinnamon essential oil contains many healthful compounds but it is quickly evaporatetes and coumarin compounds easily cause skin irritation when exposed to large amounts of skin. Using microencapsulation in this study showed the good effectiveness of microcapsules contained the cinnamon



essential oil for long-lasting fragrance on the fabric. Fragrance intensity of microcapsules contained the cinnamon essential oil was showed decreasing with the higher compressive force corresponding to the larger extension applied on the fabric band. Lberation of the active agent such as essential oil from the microcapsules coated on the knitted fabric band could be controlled by fabric extension. The results could be applied on the therapy textile field and medical textile as compression garment.

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**Keywords:** Microencapsulation, fragrance textile, healthcare textile, interlock knitted fabric, fabric extension.



### INVESTIGATION OF THE PROPERTIES OF TEXTILE MATERIAL WITH HYDROGEL CONTAINING ZINC OXIDE PARTICLES

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Microbial growth on textile fabric causes a number of changes in appearance - discoloration, loss of strength and elongation, bad smell. As a result of microbial adhesion to the surface of an infected textile material, it can cause undesirable consequences, lead to clinical complications and even death. Natural organic fibers such as cotton, linen and wool are easily attacked by microorganisms. This requires modification of their surface through chemical, physical or biological treatment in order to provide antimicrobial protection and prevent their spread.

In this study, an attempt was made to improve the properties of cotton fabric by impregnating it with gelatin hydrogel cross-linked with glutaraldehyde and containing ZnO nanoparticles. Three methods of ZnO synthesis were investigated by varying the components and processing conditions. The *in situ* method for obtaining ZnO nanoparticles on the surface of cotton fabric was successfully applied. The composite materials were examined by means of SEM, spectrophotometric analysis using UVA/VIS/NIR, and air permeability.

Morphological analyzes show the presence of spherical ZnO particles that have changed into a flower-like form. In other samples, the particles are covered by the collagen film, and in



others, they are scattered and agglomerated in certain places. The immobilization conditions and different synthesis sequence were found to affect the particle shape and morphology of the hydrogel on the cotton fabric surface. It has been proven that the composites obtained by one method show the best characteristics and promising results for antibacterial properties, which are the subject of future research. It is necessary in further research to characterize the biological properties of the obtained composite materials, as well as their possibility of use as an antimicrobial material. The cotton–gelatin–ZnO NPs biocomposite can be very effective for use as wound dressings, absorbing wound exudates and providing a perfect moist healing wound environment protected from the effects of microorganisms.

Keywords: biocomposites, cotton, gelatin, ZnO nanoparticles