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# Impregnation of corona modified polypropylene non-woven material with thymol in supercritical carbon dioxide for antimicrobial application

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ABSTRACT

This study discusses the possibility of impregnation of polypropylene (PP) and corona modified PP non-woven material with thymol in supercritical solvent in order to fabricate eco-friendly antimicrobial textile material. Carbon dioxide was used as a working fluid. The morphological changes on the PP fiber surface induced by corona treatment at atmospheric pressure as well as the presence of thymol on the fiber surface after impregnation were confirmed by FESEM analysis. Chemical changes were assessed by FTIR analysis. Antimicrobial activity of the modified PP non-woven material was tested against Gram-positive bacterium *Staphylococcus aureus*, Gram-negative bacterium *Escherichia coli* and fungus *Candida albicans*. Although both PP non-woven material impregnated with thymol and corona activated PP impregnated with thymol provided maximum microbial reduction, corona pre-treated material was much faster wetted, which could be an advantage in wound healing.



## 1. Introduction

Growing number of hospital acquired infections (HAI) became one of the major concerns of contemporary medicine. It is estimated that around 10% of all hospital patients are being infected by HAI during their hospitalization [1,2]. The major problem in the struggle against HAI is that many pathogens which caused HAI became resistant to antibiotic treatment. Consequently, it is difficult to control their spreading particularly if we keep in mind that most of the Gram-positive bacteria can persist around one month on the dry inanimate surface, Gram-negative bacteria somewhat longer while fungal pathogens may survive up to 4 months [3].

Textiles are suitable substrates for bacterial and fungal growth under the appropriate moisture and temperature conditions [2]. Textiles as common materials in the hospitals could be a substantial source of pathogens that may infect the patients, personnel or environment. Therefore, it is strongly recommended to use hospital textiles with adequate antimicrobial activity.

Antimicrobial agents such as metal salts, quaternary ammonium compounds, polyhexamethylene biguanides, triclosan, *N*-halamine, peroxyacid, metal (Ag, Cu) and metal oxide ($TiO_2$, CuO, ZnO) nanoparticles were exploited for introduction of antimicrobial properties to different textile materials [4,5]. In recent years the research interest is oriented more towards efficient, eco-friendly and low-cost natural bioactive agents. Biopolymer chitosan provides good antimicrobial properties on textile material [5]. Due to natural origin, biodegradability, bacteriostatic and fungistatic properties herbal plants and their essential oils seem to be very attractive for antimicrobial finishing of textiles.

Essential oils and their active components have already been used as food additives, in food packaging or cosmetic industry [6]. Recent reports confirmed that herbals and their extracts could be efficiently utilized for fabrication of antimicrobial textiles [7–12]. Hui et al. [7] made efforts to impregnate cotton fibers with chitosan/alginate microcapsules filled with traditional Chinese herbs–PentaHerbs extracts which could be employed in atopic dermatitis healing. Lee et al. [8] suggested that textile materials could be finished with Citrus unshiu's essential oil as a bioactive agent for skin healthcare. Polypropylene (PP) non-woven material activated by air plasma and coated with methanolic extracts of 11 medicinal herbs showed maximum bacterial reduction against bacteria *Escherichia coli* and *Staphylococcus aureus* [9]. Rukmani and Sundrarajan [10] reported that cotton material grafted with

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β-cyclodextrin and thymol possesses strong antibacterial activity against *E. coli* and *S. aureus*. Thymol could be applied as a promising antimicrobial agent for obtaining eco-friendly antimicrobial cotton material [11,12]. Milovanovic et al. [12] demonstrated that supercritical solvent impregnation (SSI) with carbon dioxide as a working fluid ensured loading of thymol on cotton gauze. Dissolution and loading of thymol on the textile material were performed in the same vessel indicating that there was no need for previous dissolution of thymol in appropriate solvent.

Supercritical carbon dioxide (SC-$CO_2$) has been already applied to textiles mostly for dying of synthetic fibers [13]. Due to environmentally friendly nature and low energy consumption, supercritical processes are increasingly exploited for cleaning and modification (coating, injection of functional agents, loading of nanoparticles) of natural and synthetic fibers [14–17].

Today PP non-woven materials are widely used in medical textiles like disposable surgical gowns, shoe covers, facemasks, drapes, head covers, etc [9]. Chemically inert nature of PP fibers can be altered by RF plasmas at low pressures and dielectric barrier discharge (DBD) or corona discharge at atmospheric pressure [18]. Plasma treatment leads to morphological changes on the PP fiber surface. Even more important, plasma oxidation results in introduction of polar groups on the fiber surface and hence, it becomes more hydrophilic and more reactive which facilitates its further processing.

This research was aimed to investigate the possibility of using SSI for loading of PP non-woven textile material with thymol in order to obtain desired level of antimicrobial activity. Corona discharge at atmospheric pressure was employed for modification of PP fiber surface prior to SSI of thymol. To our knowledge, this was the first attempt to combine corona treatment and impregnation in SC-$CO_2$ in finishing of textiles.

## 2. Materials and methods

### 2.1. Materials

PP non-woven fabric (40 g/m$^2$) was used as a substrate for thymol impregnation. In order to remove the surface impurities, the substrate was immersed in ethyl alcohol (Zorka, Serbia) for 10 min at liquor-to-fabric ratio of 40:1. Afterwards it was rinsed with tap and distilled water, and dried at room temperature.

Thymol (purity > 99%) was supplied by Sigma-Aldrich Chemie GmbH (Germany). Commercial $CO_2$ (purity 99%) was purchased from Messer-Tehnogas, Serbia.

The chemicals used for antimicrobial analysis were as follows: disodium hydrogen phosphate dodecahydrate (Centrohem, Serbia), sodium dihydrogen orthophosphate dihydrate (Fisher Scientific, UK) and sodium chloride (Lachner, Czech Republic). Tryptone soy broth, Agar and Yeast extract were provided by Torlak, Serbia.

### 2.2. Corona treatment

Corona treatment of the PP non-woven material (CPP) was performed at atmospheric pressure using a commercial device Vetaphone CP-Lab MK II. The PP samples were placed on the electrode roll covered with silicon coating, rotating at the minimum speed of 4 m/min. The distance between electrodes was 2.3 mm. The power was 700 W and the number of passages was set to 30.

### 2.3. Impregnation

Impregnation of the CPP non-woven material with thymol was performed in the high-pressure autoclave engineers screening system previously described in detail [12]. Thymol was placed at the bottom of the vessel and the substrate fitted in stainless steel support that was placed above it. Porous barrier was placed between the thymol and substrate in order to avoid possible splashing of thymol during decompression. Operational pressure was 15.5 MPa and temperature was 35 °C. Time of impregnation was 4 h. These parameters were selected on the basis of our previous investigation on thymol solubility in SC-$CO_2$ and cotton gauze impregnation [12]. The initial mass of thymol in the vessel was varied from 1.000 to 8.500 g, while the mass of PP and CPP material was 3.000 g. A slow decompression (0.33 MPa/min) was applied at the end of process. The mass of impregnated thymol was determined gravimetrically by measuring the impregnated sample. The percent (yield) of impregnation was calculated according to the following equation:

$$I(\%) = \frac{m_{th}}{m_{PP(CPP)+th}} \times 100 \quad (1)$$

where $m_{th}$ is the mass of impregnated thymol, and $m_{PP(CPP)+th}$ is the mass of impregnated PP (or CPP) sample with thymol.

### 2.4. FESEM and FTIR analyses

In order to investigate the influence of SC-$CO_2$ treatment on the PP and CPP fibers, the same procedure was performed in absence of thymol. The surface morphology of the PP and CPP fibers before and after SC-$CO_2$ treatment as well as after thymol impregnation was followed by field emission scanning electron microscopy (FESEM, Mira3 Tescan). The samples were sputter coated with a thin layer of Au/Pd prior to analysis.

Fourier transform infrared (FTIR) spectra of non-woven fabrics were recorded in the ATR mode using a Nicolet 6700 FTIR Spectrometer (Thermo Scientific) at 2 cm$^{-1}$ resolution, in the wavenumber range 500–4000 cm$^{-1}$.

### 2.5. Wetting time

The changes in wettabilty of investigated samples were evaluated via wetting time. The wetting time was measured in accordance with the procedure described in literature [19]. Five drops of deionized water (20 μL) were placed onto the fabric surface and wetting time was measured.

### 2.6. Antimicrobial analysis

Antimicrobial activity of the PP non-woven fabric, PP and CPP non-woven fabrics impregnated with thymol was evaluated against Gram-negative bacteria *E. coli* ATCC 25922, Gram-positive bacterial strains *S. aureus* ATCC 25923 and fungus *Candida albicans* ATCC 24433 using the standard test method ASTM E 2149-01 [20]. Microbial inoculum was prepared in the tripton soy broth, which was used as a growth medium for microbes while the potassium hydrogen phosphate buffer solution (pH 7.2) was used as a testing medium. Microbes were cultivated in 3 mL of tripton soy broth at 37 °C for 18 h (late exponential stage of growth). Fifty milliliter of sterile potassium hydrogen phosphate buffer solution (pH 7.2) was inoculated with 0.5 mL of a microbial inoculum. One gram of sterile PP or the PP and CPP samples impregnated with thymol cut into small pieces (sterilized in UV chamber for 30 min) was put in the flask which was shaken for 2 h. One milliliter aliquots from the flask were diluted with 9 mL of physiological saline solution and 0.1 mL of the solution was placed onto a tryptone soy agar. After 24 h of incubation at 37 °C, the zero time and two h counts of viable microorganisms were made.