Chapter

Impregnation of Materials in Supercritical CO_2 to Impart Various Functionalities

Molla Tadesse Abate, Ada Ferri, Jinping Guan, Guoqiang Chen and Vincent Nierstrasz

Abstract

Supercritical CO_2 ($scCO_2$) impregnation has attracted growing interest due to its unique properties such as high diffusivity, low surface tension, and ease of solvent removal at the end of the process. In addition, $scCO_2$ is the most environmentally acceptable solvent possessing many advantages compared with the conventional aqueous and solvent-based processing. $scCO_2$ impregnation has a wide range of applications mainly used to incorporate various active principles such as pharmaceuticals, functional finishing agents, colorants, and other agents into a polymeric matrix. This chapter reviews some studies carried out so far about the application of $scCO_2$ as impregnation medium to develop various functional materials and it is intended to stimulate further research into the application of $scCO_2$ to textile functionalization. It mainly focuses on applications related to textiles and some polymeric films.

Keywords: supercritical CO_2, impregnation, functionalization, dyeing

1. Introduction

Supercritical fluid (SCF) is defined as a substance for which both its pressure and temperature are above the critical values simultaneously [1]. SCFs have been applied in many areas such as extraction, dyeing, impregnation, cleaning, polymerization, fractionation, formation of powdered polymers, and so on [2, 3]. Among the SCFs, carbon dioxide (CO_2) is the most popular as it offers several advantages including low toxicity, ready availability, low cost, non-flammability, environmental sustainability, and it is chemically inert under many conditions. In addition, CO_2 has an easily attainable critical temperature of 31°C and critical pressure of 7.4×10^6 Pa which are lower compared with other SCFs such as water (critical temperature > 374°C and pressure > 22×10^6 Pa) and other organic solvents. Moreover, at least 90% of the CO_2 introduced can be recovered and recycled at the end of the procedure, which is attractive from waste minimization viewpoint. This also reduces the production cost and avoids the undesirable solvent residue in the produced material [4].

Impregnation is the process of infusing or depositing solute molecules dissolved in a solvent into a polymer matrix to modify the property of the material by physically or chemically binding or absorbing impregnates to a bulk or surface [5].

The conventional aqueous or solvent-based impregnation processes have many drawbacks such as low diffusion rates, high temperature, limited penetration depth, very long contact time, use of hazardous solvents, consumption of high energy, water, solvents, and other additives. To solve these problems, several techniques have been developed, and it has been shown that supercritical CO_2 ($scCO_2$) is an attractive alternative to conventional organic solvents used in polymer impregnation [6].

$scCO_2$ has appeared to be the appropriate candidate to replace conventional impregnation using organic solvents due to several unique properties suitable for impregnation of polymeric materials. It has high diffusivity and low viscosity allowing faster penetration of molecules to the polymer matrix than in water. The absence of surface tension also improves the penetration of molecules into polymeric structures and avoids the unwanted distortion of delicate materials during processing. In addition, the possibility to recover high purity and dry product free from residual solvent is one key advantage especially important when considering the production of food and pharmaceuticals [6–8]. Furthermore, $scCO_2$ reduces the environmental pollution and the associated cost incurred for the removal of the residual solvent, cost of freshwater input, and wastewater treatment. Due to these important attributes, today, $scCO_2$-assisted impregnation has been used in many fields and it is a promising candidate to replace organic solvents in the future.

In this chapter, studies involving $scCO_2$ dyeing and impregnation processes to develop products for various functional applications are reviewed. The chapter focuses on studies related to $scCO_2$ impregnation of textile fibers and polymers and some polymeric films, made of similar polymers. The references used are not exhaustive, as many articles are published covering the same subject area, but only the most relevant ones for this chapter are presented.

2. Impregnation mechanism in $scCO_2$

Various studies utilizing $scCO_2$ as impregnation medium of textiles and polymers have been reported in the literature. Generally, $scCO_2$ impregnation of additives can be performed based on two mechanisms. The first mechanism works if the solute molecule is readily soluble in $scCO_2$ solvent. When polymers are introduced into $scCO_2$ bath containing solutes, the small CO_2 molecules penetrate to the free volume of the amorphous region and swell the material creating additional free volumes. This causes plasticization of the material due to a decrease in the glass transition temperature (T_g) [9]. Then, the dissolved solutes are transported to the fiber surface and subsequently penetrate and diffuse into the swollen polymer matrix. Finally, upon depressurization, the CO_2 molecules are removed by the shrinking polymer, and the impregnate molecules are trapped inside the polymer matrices [10]. The second mechanism applies for solute molecules, which are poorly soluble but having high affinity to the polymer. In this case, the solute molecules partition preferably toward the polymer matrix than the fluid because of their higher affinity to the polymer. This is the key mechanism by which polar dye molecules are incorporated into the polymer matrix in $scCO_2$ dyeing and impregnation of drug molecules into polymers [8]. Therefore, the impregnation process is feasible when the active principle (solute) is soluble in $scCO_2$ or the partition coefficient is favorable toward the polymer charging enough solute, and the polymer itself is well swollen by the $scCO_2$ solvent [6]. The general steps of impregnation of polymeric fibres in $scCO_2$ are illustrated in **Figure 1.**

Functional active principles such as functional dyes, antimicrobial agents, flame retardant, antioxidants, fragrances, pharmaceutical drugs, and others can be impregnated into a polymer by exposing the polymer to $scCO_2$ medium containing

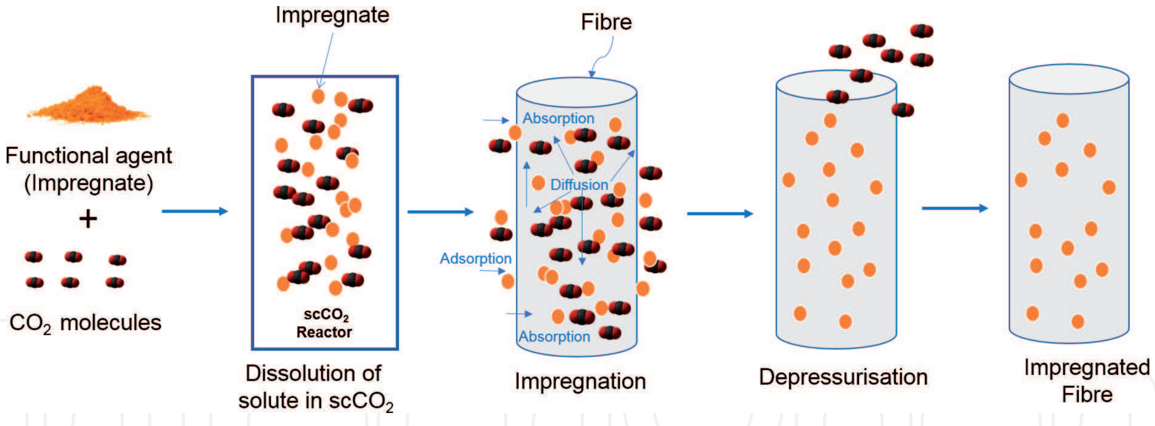

Figure 1.
Schematic of impregnation mechanism of polymeric fibres with functional agent in $scCO_2$.

these agents based on the mechanisms explained above [5]. It has been shown that pharmaceutical drugs can be impregnated into a swollen polymer matrix at operating temperature low enough to avoid thermal degradation of temperature-sensitive drugs. After impregnation and depressurization, the impregnated drug materials slowly diffuse out from the polymer matrix at a slower rate than the rate it was diffused into the polymer which can be used to form a novel controlled release of drugs [11]. The same principle works for deodorizing and antimicrobial agents as well.

3. Solubility of functional agents in $scCO_2$

The most important property for the design of processes in $scCO_2$ medium is the solubility of the compounds in $scCO_2$ fluid. For this reason, solubility data of many compounds including dyes are available in the literature [12–14]. The properties of the compounds such as molecular structure, size, and polarity are the main factors determining their solubility in $scCO_2$ solvent. The solvent character of $scCO_2$ is very much like a hydrocarbon solvent such as n-hexane [15], in which polar compounds are poorly soluble and nonpolar molecules such as disperse dyes have relatively higher solubility [16, 17]. To improve the solubility, polar co-solvents (also called entrainer or modifier), such as acetone or alcohols, are usually added to the $scCO_2$ bath. Furthermore, the solvent power of $scCO_2$ is a function of its density, and this density can be fine-tuned by changing the pressure and temperature of the system [18]. Disperse dyes are among the most investigated compounds, owing to acceptable solubility and suitable molecular size for dyeing polyester and other synthetic fibers in $scCO_2$ [13]. However, the solubility data of functional finishing agents commonly used for textile finishing are still scarce in the literature. According to reports, several non-ionic, low molecular mass organic materials are soluble in $scCO_2$, but only two classes of polymeric materials such as fluoropolymers and silicones showed appreciable solubility in $scCO_2$ at a readily accessible temperature and pressure [19]. Thus, future research should focus on studying the solubility of functional compounds in $scCO_2$.

4. Functionalization in $scCO_2$

In the conventional process, functional finishing agents are usually applied at the end of the process during dyeing or finishing stages. The common problems with these conventional finishing processes are the requirement of a higher amount of water, energy, and auxiliary chemicals, which generates toxic wastewater causing environmental pollution and increases production cost. Due to this, a new dyeing and impregnation process has been developed in which $scCO_2$ is used as a solvent and transport media owing to unique and important properties as explained earlier. In this section, attempts that have been made so far to functionalize different textile fibers and polymers using $scCO_2$ impregnation technique are reviewed. The functional finishing agents used in impregnating polymers are categorized as functional dyes based on natural and synthetic origin, silicon and fluoropolymer-based, natural functional compounds, and organometallic-based agents.

4.1 Functional dyes

One strategy that has been followed to functionalize textiles in $scCO_2$ is by using different dyes having additional functional property. In this method, the functional dyes are either prepared by modifying them to contain functional groups through molecular design or those dyes which inherently possessed the required functional property are directly used. In most of the cases, disperse dyes are modified to contain functional groups based on the needed functionality, and some of them are presented in this section. Fluorescence functional dyes, such as disperse fluorescent yellow 82 were used to dye polyester in $scCO_2$ with the aim to manufacture protective clothing [20]. Results showed that polyester fabric was successfully dyed in $scCO_2$ medium exhibiting better photostability and fastness properties, and no morphological change was detected. Abou Elmaaty et al. [21] synthesized new hydrazonopropanenitrile dyes and applied the new species to polyester fabric using $scCO_2$ for potential antimicrobial application. Efficient dyeing and excellent antimicrobial and fastness properties were obtained using $scCO_2$ dyeing procedure. A series of disperse azo dyes with potential antibacterial activity were also applied to nylon 6 fabric using $scCO_2$ technique and compared with aqueous dyeing [22]. The comparison showed that samples dyed under $scCO_2$ medium had excellent antibacterial efficiency and better color fastness properties compared with the conventional exhaust dyeing with the advantage of the elimination of auxiliary chemicals. Impregnation of polyester (PET) films and poly(hydroxybutyrate) (PHB) granules with curcumin natural dye in $scCO_2$ has been reported [23]. In this study, the impregnation process was successfully developed with different amounts of curcumin add-on depending on the dyeing conditions and no significant detrimental effect observed on the material properties. More recently, curcumin has been used to dye and functionalize polyester in $scCO_2$ in our research group [24]. Dyed samples exhibited excellent color strength and fastness properties with improved antibacterial, antioxidant, and UV protection properties. Thus, the strategy of utilizing functional dyes which are suitable for $scCO_2$ process is a promising approach toward the production of colored and functional material in a single step.

4.2 Silicon and fluoropolymer-based functional agents

As stated earlier, silicon and amorphous fluoropolymers are known to have appreciable solubility in $scCO_2$ solvent. Due to this, functional agents based on these compounds have been employed to functionalize various textiles, polymers, and films. Mohamed et al. used a modified dimethyl siloxane terminated with silanol groups (DMS) to functionalize cotton fabric in $scCO_2$ [25]. Different crosslinking agents were used for covalently bonding silicon and cellulose. The results confirm that $scCO_2$ medium provides good coating (thickness between 1 to 2×10^{-6} m) of the cotton surface with a 3D network of DMS compound and crosslinker. Chen et al. [26] synthesized CO_2-philic silicon-containing quaternary ammonium salt (QAS) and applied to cotton in $scCO_2$ to prepare antimicrobial fabric. The treated fabric exhibited potent antimicrobial activity with good durability against washing and UV irradiation. They also synthesized silicone-containing 2,2,6,6-tetramethyl-4-piperidinol (TMP)-based N-chloramine and applied to polyethylene (PE) fiber via $scCO_2$ impregnation technique. A uniform coating of TMP-based N-chloramine reaching up to 70×10^{-9} m was obtained using 28×10^{6} Pa pressure. The obtained PE modified with TMP-based N-chloramine imparted powerful and durable biocidal activity [27]. The same research group synthesized a CO_2-philic biocidal fluorinated pyridinium silicon and applied to cotton yarn using $scCO_2$ impregnation medium. Up to 50×10^{-9} m thickness of biocidal layer with pyridinium groups segregated on the top surface was attained at 24×10^{6} Pa and 50°C. The obtained material provided higher biocidal efficiency [28]. Furthermore, polyester fabric was treated with low molecular weight polytetrafluoroethylene in $scCO_2$ medium and a high degree of water repellency was consistently obtained [29, 30]. Xu and co-workers [31] prepared a water/oil repellent polyester fabric using a solution of organic fluorine in $scCO_2$. A uniformly distributed fluorine could be obtained with good water/oil repellency keeping good air permeability and improved strength. Recently, perfluoroalkyl methacrylate/hydroxyalkyl methacrylate and a crosslinking agent (diisocyanate) have used to treat nylon fabric in $scCO_2$ medium to fabricate a durable water and oil repellent coatings [32]. A uniform, highly repellent, and durable coating was obtained by $scCO_2$ treatment compared with a coating deposited from a liquid solvent. These studies show that silicon and fluoropolymer-based materials have been playing a key role in the application of $scCO_2$ processing method for functionalization of textiles and polymeric materials.

4.3 Natural functional compounds

Supercritical CO_2 has also been used to impregnate polymers with natural functional compounds to impart different functionalities. Zizovic and co-workers widely investigated the application of thymol to various textile-based substrates in $scCO_2$ to develop different functional materials. They studied the solubility of thymol in $scCO_2$ and its impregnation on cotton gauze [33], cellulose acetate [34, 35], corona modified polypropylene non-woven material [36], and polycaprolactone (PCL) and polycaprolactone hydroxyapatite (PCL-HA) composites. Thymol has been shown soluble in $scCO_2$ solvent, and impregnation process was successful. All the samples prepared using $scCO_2$ impregnation exhibited strong antimicrobial effect against a wide range of bacteria strain. The same research group also used $scCO_2$ impregnation medium for loading cellulose acetate beads with carvacrol in order to fabricate a biomaterial with antimicrobial properties obtaining considerable antibacterial effect [37]. Thymol has also been used to modify polylactic acid (PLA) [38] and linear low-density polyethylene (LLDPE) [39] films using $scCO_2$ impregnation technique with the aim to prepare active materials for a wide range of applications such as food packaging and others. Furthermore, thymol was applied along with quercetin, a natural bioactive compound, to a film and foam-like structure N-carboxybutyl chitosan (CBC) film and agarose (AGR) using $scCO_2$ impregnation technique to fabricate wound dressing material. Impregnation was performed with the help of ethanol as a co-solvent, and higher impregnation yield was obtained at higher pressure and temperature. The obtained materials also exhibited a sustained release profile based on the release kinetic study [40]. Goñi et al. used Eugenol, a well-known natural antioxidant, and antimicrobial agent, to impregnate LLDPE films to fabricate active food packaging material [41]. The obtained film presented a good level of antioxidant property with some degree of heterogeneity and a decrease in crystallinity when higher treatment pressure was used. In another study, Eugenol was also used to impregnate polyamide fibers to fabricate antibacterial dental floss, and inhibition of more than 99.99% has been achieved [42]. Recently, Pajnik and co-workers impregnated pyrethrum extract to polypropylene, polyamide, and cellulose acetate in the form of films and beads using $scCO_2$ to fabricate functionalized materials with repellent properties [43]. In addition, chitosan and derivatives have been used to impregnate polyester in $scCO_2$ bath [44]. Results showed that low molecular weight chitosan and chitosan lactic acid salt were successfully impregnated whereas no chitin could be impregnated. More recently, very low molecular weight chitosan and chitosan lactate have also been successfully incorporated to polyester fabric using $scCO_2$ dyeing technique in our research group obtaining good antibacterial activity [45]. Overall, natural-based functional agents have shown a huge potential for the fabrication of various functional materials using $scCO_2$ impregnation technique.

4.4 Organometallic-based functional agents

In addition to the agents mentioned above, impregnation of organometallic compounds into polymer matrices using $scCO_2$ has also been widely studied for various functional applications. Antifungal textiles have been produced via $scCO_2$ impregnation of cotton with silver, Ag (hepta), and Ag (cod), demonstrating measurable inhibition [46]. Boggess et al. produced highly reflective polyimide films for aerospace application with silver-containing additive using $scCO_2$ infusion and subsequent curing at 300°C [47]. They have demonstrated that silver additive was incorporated into a polyimide film creating a reflective surface on both sides of the film. Chiu et al. [48] produced a wearable photocatalytic device via integration of Ni-P/TiO_2 onto silk fabric using $scCO_2$ impregnation technique. Co-deposition of photocatalytic TiO_2 and electrically conductive Ni-P metallization layer was achieved through $scCO_2$-assisted electroless plating and silk fabric with higher corrosion-resistant, and photocatalytic activity was achieved. Metallization of silk with platinum (Pt) was also conducted in $scCO_2$ medium obtaining a smooth and compact layer with improved adhesion promoted by $sccCO_2$ metallization [49]. The results demonstrated its applicability in medical and wearable devices. Cotton fabric has been impregnated with palladium (II) hexafluoroacetylacetonate to fabricate conductive fabrics [50]. Hematite nanoparticles were loaded to cellulosic fiber under $scCO_2$ to fabricate a water repellent composite fiber [51]. Peng et al. used silver nanoparticles to coat wool fabrics in $scCO_2$, and the coated fabric exhibited excellent catalytic, antistatic, and antibacterial activities [52]. Polycarbonate has been impregnated with silver nitrate in $scCO_2$, resulting up to 99.9% bacteria reduction [53]. Belmas and co-workers [54–56] have used $scCO_2$ process to impregnate a range of organometallic complexes in a synthetic polymer prior to electroless copper plating to improve the adhesion of copper to the polymer. The adhesion between the copper and polymer was much improved after $scCO_2$ impregnation of the organometallic complexes. Polyacrylate has been impregnated with copper (II) hexafluoroacetylacetonate in $scCO_2$ followed by thermal decomposition of the copper. The formation of copper oxide was evident ensuring improved wear resistance of polyacrylate [57]. In conclusion, owing to nanoscale metal microparticles, organometallic compounds have been successfully used to modify polymers in $scCO_2$ solvent for various functional applications and might be one potential area that needs further investigations in the future.

5. Conclusions

From the studies reviewed in this chapter, it has been shown that $scCO_2$ is a viable technique for the fabrication of various functional materials if appropriate agents suitable for the process are used. It can be an attractive alternative to traditional aqueous or organic solvents as it avoids toxic auxiliary chemicals and the use of water. Further studies are still required in selecting suitable functional agents which works best under $scCO_2$ solvent through investigation of their solubility, compatibility, and process optimizations. Due to its environmental advantages, the scientific community and the industrial compartment would expect an increase in research in this area as $scCO_2$ has the potential to replace the current water and solvent-based textile chemical processes in the future.

Acknowledgements

All the universities collaborating on the program are gratefully acknowledged.

Conflict of interest

The authors declare no conflict of interest.

Nomenclature

Ag	silver
AGR	agarose
CBC	carboxybutyl chitosan
CO_2	carbon dioxide
DMS	dimethyl siloxane
LLDPE	linear low-density polyethylene
m	meter
N	nitrogen
P	phosphorus
Pa	pascal
PCL	polycaprolactone
PCL-HA	polycaprolactone hydroxyapatite
PE	polyethylene
PET	polyester
PLA	polylactic acid
Pt	platinum
QAS	quaternary ammonium salt
$scCO_2$	supercritical carbon dioxide
T_g	glass transition temperature
TiO_2	titanium dioxide
TMP	2,2,6,6-tetramethyl-4-piperidinol

Author details

Molla Tadesse Abate[1,2,3]*, Ada Ferri[1], Jinping Guan[3], Guoqiang Chen[3] and Vincent Nierstrasz[2]

1 Department of Applied Science and Technology, Politecnico di Torino, Corso Duca degli Abruzzi, Torino, Italy

2 Textile Materials Technology, Department of Textile Technology, The Swedish School of Textiles, Faculty of Textiles, Engineering and Business, University of Borås, Borås, Sweden

3 College of Textile and Clothing Engineering, Soochow University, Suzhou, Jiangsu, China

*Address all correspondence to: molla.tadesse_abate@hb.se; molla.abate@polito.it

References

[1] Nalawade SP, Picchioni F, Janssen L. Supercritical carbon dioxide as a green solvent for processing polymer melts: Processing aspects and applications. Progress in Polymer Science. 2006;**31**:19-43. DOI: 10.1016/j.progpolymsci.2005.08.002

[2] Knez Ž, Markočič E, Leitgeb M, Primožič M, Knez Hrnčič M, Škerget M. Industrial applications of supercritical fluids: A review. Energy. 2014;**77**:235-243. DOI: 10.1016/j.energy.2014.07.044

[3] Ramsey E, Sun Q, Zhang Z, Zhang C, Gou W. Mini-review: Green sustainable processes using supercritical fluid carbon dioxide. Journal of Environmental Sciences. 2009;**21**:720-726. DOI: 10.1016/S1001-0742(08)62330-X

[4] Saus W, Knittel D, Schollmeyer E. Dyeing of textiles in supercritical carbon dioxide. Textile Research Journal. 1993;**63**:135-142. DOI: 10.1177/004051759306300302

[5] Weidner E. Impregnation via supercritical CO2–what we know and what we need to know. Journal of Supercritical Fluids. 2018;**134**:220-227. DOI: 10.1016/j.supflu.2017.12.024

[6] Kikic I, Vecchione F. Supercritical impregnation of polymers. Current Opinion in Solid State & Materials Science. 2003;**7**:399-405. DOI: 10.1016/j.cossms.2003.09.001

[7] Barros AA, Silva JM, Craveiro R, Paiva A, Reis RL, Duarte ARC. Green solvents for enhanced impregnation processes in biomedicine. Current Opinion in Green and Sustainable Chemistry. 2017;**5**:82-87. DOI: 10.1016/j.cogsc.2017.03.014

[8] Kazarian SG. Polymer processing with supercritical fluids. Polymer Science Series CC/C of vysokomolekuliarnye soedineniia. 2000;**42**:78-101. DOI: 10.1002/3527606726.ch10

[9] Zhong Z, Zheng S, Mi Y. High-pressure DSC study of thermal transitions of a poly(ethylene terephthalate)/carbon dioxide system. Polymer. 1999;**40**:3829-3834. DOI: 10.1016/S0032-3861(98)00594-1

[10] Chakraborty JN. Dyeing in supercritical carbon dioxide. In: Chakraborty JN, editor. Fundamentals and Practices in Colouration of Textiles. 2nd ed. New Delhi, India: Woodhead Publishing India Pvt. Ltd.; 2014. pp. 356-364. DOI: 10.1016/B978-93-80308-46-3.50028-5

[11] Champeau M, Thomassin JM, Tassaing T, Jérôme C. Drug loading of polymer implants by supercritical CO_2 assisted impregnation: A review. Journal of Controlled Release. 2015;**209**:248-259. DOI: 10.1016/j.jconrel.2015.05.002

[12] Gupta RB, Shim JJ. Solubility in Supercritical Carbon Dioxide. 1st ed. Boca Raton, Florida, USA: CRC press; 2006. 960 p. DOI: 10.1201/9781420005998

[13] Banchero M. Supercritical fluid dyeing of synthetic and natural textiles - a review. Coloration Technology. 2013;**129**:2-17. DOI: 10.1111/cote.12005

[14] Škerget M, Knez Ž, Knez-Hrnčič M. Solubility of solids in sub- and supercritical fluids: A review. Journal of Chemical & Engineering Data. 2011;**56**:694-719. DOI: 10.1021/je1011373

[15] Hyatt JA. Liquid and supercritical carbon dioxide as organic solvents. The Journal of Organic Chemistry. 1984;**49**:5097-5101. DOI: 10.1021/jo00200a016

[16] Draper SL, Montero GA, Smith B, Beck K. Solubility relationships for

disperse dyes in supercritical carbon dioxide. Dyes and Pigments. 2000;**45**:177-183. DOI: 10.1016/s0143-7208(00)00008-5

[17] Gebert B, Saus W, Knittel D, Buschmann H-J, Schollmeyer E. Dyeing natural fibers with disperse dyes in supercritical carbon dioxide. Textile Research Journal. 1994;**64**:371-374. DOI: 10.1177/004051759406400701

[18] Montero GA, Smith CB, Hendrix WA, Butcher DL. Supercritical fluid technology in textile processing: An overview. Industrial and Engineering Chemistry Research. 2000;**39**:4806-4812. DOI: 10.1021/ie0002475

[19] McClain JB, Londono D, Combes JR, Romack TJ, Canelas DA, Betts DE, et al. Solution properties of a CO2-soluble fluoropolymer via small angle neutron scattering. Journal of the American Chemical Society. 1996;**118**:917-918. DOI: 10.1021/ja952750s

[20] Xiong XQ, Xu YY, Zheng LJ, Yan J, Zhao HJ, Zhang J, et al. Polyester fabric's fluorescent dyeing in supercritical carbon dioxide and its fluorescence imaging. Journal of Fluorescence. 2017;**27**:483-489. DOI: 10.1007/s10895-016-1975-0

[21] Abou Elmaaty T, Ma J, El-Taweel F, Abd El-Aziz E, Okubayashi S. Facile bifunctional dyeing of polyester under supercritical carbon dioxide medium with new antibacterial hydrazono propanenitrile dyes. Industrial and Engineering Chemistry Research. 2014;**53**:15566-15570. DOI: 10.1021/ie502088r

[22] Elmaaty T, El-Aziz E, Ma J, El-Taweel F, Okubayashi S. Eco-friendly disperse dyeing and functional finishing of nylon 6 using supercritical carbon dioxide. Fibers. 2015;**3**:309-322. DOI: 10.3390/fib3030309

[23] Herek L, Oliveira R, Rubira A, Pinheiro N. Impregnation of PET films and PHB granules with curcumin in supercritical CO2. Brazilian Journal of Chemical Engineering. 2006;**23**:227-234. DOI: 10.1590/S0104-66322006000200010

[24] Abate MT, Ferri A, Guan J, Chen G, Nierstrasz V. Colouration and bio-activation of polyester fabric with curcumin in supercritical CO2: Part I-investigating colouration properties. Journal of Supercritical Fluids. 2019;**152**:104548. DOI: 10.1016/j.supflu.2019.104548

[25] Mohamed AL, Er-Rafik M, Moller M. Supercritical carbon dioxide assisted silicon based finishing of cellulosic fabric: A novel approach. Carbohydrate Polymers. 2013;**98**:1095-1107. DOI: 10.1016/j.carbpol.2013.06.027

[26] Chen Y, Niu MQ, Yuan S, Teng HN. Durable antimicrobial finishing of cellulose with QSA silicone by supercritical adsorption. Applied Surface Science. 2013;**264**:171-175. DOI: 10.1016/j.apsusc.2012.09.165

[27] Chen Y, Wang YY, Zhang Q, Yang CY, Han QX. Preparation of silicone containing 2,2,6,6-tetramethyl-4-piperidinol-based N-chloramine for antibacterial polyethylene via interpenetration in supercritical carbon dioxide. Journal of Applied Polymer Science. 2019;**136**:1-9. DOI: 10.1002/app.47614

[28] Chen Y, Zhang Q, Ma YJ, Han QX. Surface-oriented fluorinated pyridinium silicone with enhanced antibacterial activity on cotton via supercritical impregnation. Cellulose. 2018;**25**:1499-1511. DOI: 10.1007/s10570-018-1657-y

[29] Prorokova NP, Kumeeva TY, Zavadskii AE, Nikitin LN. Modification of the surface of poly(ethylene terephthalate) fabrics by application of a water-repellent coating in

supercritical carbon dioxide medium. Fibre Chemistry. 2009;**41**:29-33. DOI: 10.1007/s10692-009-9121-2

[30] Prorokova NP, Kumeeva TY, Khorev AV, Buznik VM, Nikitin LN. Ensuring a high degree of water repellency of polyester textile materials by treating them with supercritical carbon dioxide. Fibre Chemistry. 2010;**42**:109-113. DOI: 10.1007/s10692-010-9233-8

[31] Xu Y-Y, Zheng L-J, Ye F, Qian Y-F, Yan J, Xiong X-Q. Water/oil repellent property of polyester fabrics after supercritical carbon dioxide finishing. Thermal Science. 2015;**19**:1273-1277. DOI: 10.2298/TSCI1504273X

[32] Zefirov VV, Lubimtsev NA, Stakhanov AI, Elmanovich IV, Kondratenko MS, Lokshin BV, et al. Durable crosslinked omniphobic coatings on textiles via supercritical carbon dioxide deposition. Journal of Supercritical Fluids. 2018;**133**:30-37. DOI: 10.1016/j.supflu.2017.09.020

[33] Milovanovic S, Stamenic M, Markovic D, Radetic M, Zizovic I. Solubility of thymol in supercritical carbon dioxide and its impregnation on cotton gauze. Journal of Supercritical Fluids. 2013;**84**:173-181. DOI: 10.1016/j.supflu.2013.10.003

[34] Milovanovic S, Stamenic M, Markovic D, Ivanovic J, Zizovic I. Supercritical impregnation of cellulose acetate with thymol. Journal of Supercritical Fluids. 2015;**97**:107-115. DOI: 10.1016/j.supflu.2014.11.011

[35] Milovanovic S, Markovic D, Aksentijevic K, Stojanovic DB, Ivanovic J, Zizovic I. Application of cellulose acetate for controlled release of thymol. Carbohydrate Polymers. 2016;**147**:344-353. DOI: 10.1016/j.carbpol.2016.03.093

[36] Markovic D, Milovanovic S, Radetic M, Jokic B, Zizovic I. Impregnation of corona modified polypropylene non-woven material with thymol in supercritical carbon dioxide for antimicrobial application. Journal of Supercritical Fluids. 2015;**101**:215-221. DOI: 10.1016/j.supflu.2015.03.022

[37] Milovanovic S, Adamovic T, Aksentijevic K, Misic D, Ivanovic J, Zizovic I. Cellulose acetate based material with antibacterial properties created by supercritical solvent impregnation. International Journal of Polymer Science. 2017;**2017**:9. DOI: 10.1155/2017/8762649

[38] Torres A, Ilabaca E, Rojas A, Rodríguez F, Galotto MJ, Guarda A, et al. Effect of processing conditions on the physical, chemical and transport properties of polylactic acid films containing thymol incorporated by supercritical impregnation. European Polymer Journal. 2017;**89**:195-210. DOI: 10.1016/j.eurpolymj.2017.01.019

[39] Torres A, Romero J, Macan A, Guarda A, Galotto MJ. Near critical and supercritical impregnation and kinetic release of thymol in LLDPE films used for food packaging. Journal of Supercritical Fluids. 2014;**85**:41-48. DOI: 10.1016/j.supflu.2013.10.011

[40] Dias AMA, Braga MEM, Seabra IJ, Ferreira P, Gil MH, de Sousa HC. Development of natural-based wound dressings impregnated with bioactive compounds and using supercritical carbon dioxide. International Journal of Pharmaceutics. 2011;**408**:9-19. DOI: 10.1016/j.ijpharm.2011.01.063

[41] Goñi ML, Gañán NA, Strumia MC, Martini RE. Eugenol-loaded LLDPE films with antioxidant activity by supercritical carbon dioxide impregnation. Journal of Supercritical Fluids. 2016;**111**:28-35. DOI: 10.1016/j.supflu.2016.01.012

[42] Mosquera JE, Goñi ML, Martini RE, Gañán NA. Supercritical carbon dioxide

assisted impregnation of eugenol into polyamide fibers for application as a dental floss. Journal of CO_2 Utilization. 2019;**32**:259-268. DOI: 10.1016/j.jcou.2019.04.016

[43] Pajnik J, Radetić M, Stojanovic DB, Jankovic-Častvan I, Tadic V, Stanković MV, et al. Functionalization of polypropylene, polyamide and cellulose acetate materials with pyrethrum extract as a natural repellent in supercritical carbon dioxide. Journal of Supercritical Fluids. 2018;**136**:70-81. DOI: 10.1016/j.supflu.2018.02.014

[44] Baba T, Hirogaki K, Tabata I, Okubayashi S, Hisada K, Hori T. Impregnation of chitin/chitosan into polyester fabric using supercritical carbon dioxide. Sen'i Gakkaishi (報文). 2010;**66**:63-69. DOI: 10.2115/fiber.66.63

[45] Abate MT, Ferri A, Guan J, Chen G, Ferreira JA, Nierstrasz V. Single-step disperse dyeing and antimicrobial functionalization of polyester fabric with chitosan and derivative in supercritical carbon dioxide. Journal of Supercritical Fluids. 2019;**147**:231-240. DOI: 10.1016/j.supflu.2018.11.002

[46] Gittard SD, Hojo D, Hyde GK, Scarel G, Narayan RJ, Parsons GN. Antifungal textiles formed using silver deposition in supercritical carbon dioxide. Journal of Materials Engineering and Performance. 2010;**19**:368-373. DOI: 10.1007/s11665-009-9514-7

[47] Boggess RK, Taylor LT, Stoakley DM, St. Clair AK. Highly reflective polyimide films created by supercritical fluid infusion of a silver additive. Journal of Applied Polymer Science. 1997;**64**: 1309-1317. DOI: 10.1002/(SICI)1097-4628(19970516)64:7<1309::AID-APP10>3.0.CO;2-S

[48] Chiu WT, Chen CY, Chang TFM, Hashimoto T, Kurosu H, Sone M. Ni-P and TiO2 codeposition on silk textile via supercritical CO2 promoted electroless plating for flexible and wearable photocatalytic devices. Electrochimica Acta. 2019;**294**:68-75. DOI: 10.1016/j.electacta.2018.10.076

[49] Chiu W-T, Chen C-Y, Chang T-FM, Tahara Y, Hashimoto T, Kurosu H, et al. Platinum coating on silk by a supercritical CO2 promoted metallization technique for applications of wearable devices. Surface and Coating Technology. 2018;**350**:1028-1035. DOI: 10.1016/j.surfcoat.2018.02.070

[50] Iwai Y, Sameshima S, Yonezawa S, Katayama S. Fabrication of conductive cotton by electroless plating method with supercritical carbon dioxide. Journal of Supercritical Fluids. 2015;**100**:46-51. DOI: 10.1016/j.supflu.2015.02.027

[51] Xu S, Shen D, Wu P. Fabrication of water-repellent cellulose fiber coated with magnetic nanoparticles under supercritical carbon dioxide. Journal of Nanoparticle Research. 2013;**15**:1577. DOI: 10.1007/s11051-013-1577-6

[52] Peng LH, Guo RH, Lan JW, Jiang SX, Li C, Zhang ZY. Synthesis of silver nanoparticles on wool fabric in supercritical carbon dioxide. Materials Express. 2017;**7**:405-410. DOI: 10.1166/mex.2017.1386

[53] Mölders N, Renner M, Errenst C, Weidner E. Incorporation of antibacterial active additives inside polycarbonate surfaces by using compressed carbon dioxide as transport aid. Journal of Supercritical Fluids. 2018;**132**:83-90. DOI: 10.1016/j.supflu.2017.02.009

[54] Belmas M, Tabata I, Hisada K, Hori T. Application of Dithiol compounds in supercritical carbon dioxide to improve the adhesive properties of copper-plated p-aramid fibers. Sen'i Gakkaishi (報文). 2010;**66**:229-235

[55] Belmas M, Tabata I, Hisada K, Hori T. Supercritical fluid-assisted Electroless copper plating of aramid film: The influence of surface treatment. Sen'i Gakkaishi (報文). 2010;**66**:215-221. DOI: 10.2115/fiber.66.215

[56] Belmas M, Tabata I, Hisada K, Hori T. Supercritical fluid-assisted Electroless metal plating onto aramid films: The influence of thermal treatment. Journal of Applied Polymer Science. 2011;**119**:2283-2291. DOI: 10.1002/app.32970

[57] Popov VK, Bagratashvili VN, Krasnov AP, Said-Galiyev EE, Nikitin LN, Afonicheva OV, et al. Modification of tribological properties of polyarylate by supercritical fluid impregnation of copper (II) hexafluoroacetylacetonate. Tribology Letters. 1998;**5**:297-301. DOI: 10.1023/a:1019110228703