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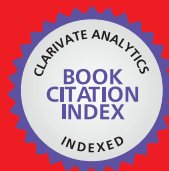
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Impregnation of Materials in Supercritical CO₂ to Impart Various Functionalities

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

Abstract

Supercritical CO₂ (scCO₂) 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, scCO₂ is the most environmentally acceptable solvent possessing many advantages compared with the conventional aqueous and solvent-based processing. scCO₂ 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 scCO₂ as impregnation medium to develop various functional materials and it is intended to stimulate further research into the application of scCO₂ to textile functionalization. It mainly focuses on applications related to textiles and some polymeric films.

Keywords: supercritical CO₂, 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 (CO₂) 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, CO₂ 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 $> 374^\circ\text{C}$ and pressure $> 22 \times 10^6$ Pa) and other organic solvents. Moreover, at least 90% of the CO₂ 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 CO₂ (scCO₂) is an attractive alternative to conventional organic solvents used in polymer impregnation [6].

scCO₂ 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, scCO₂ 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, scCO₂-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 scCO₂ dyeing and impregnation processes to develop products for various functional applications are reviewed. The chapter focuses on studies related to scCO₂ 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 scCO₂

Various studies utilizing scCO₂ as impregnation medium of textiles and polymers have been reported in the literature. Generally, scCO₂ impregnation of additives can be performed based on two mechanisms. The first mechanism works if the solute molecule is readily soluble in scCO₂ solvent. When polymers are introduced into scCO₂ bath containing solutes, the small CO₂ 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 CO₂ 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 scCO₂ dyeing and impregnation of drug molecules into polymers [8]. Therefore, the impregnation process is feasible when the active principle (solute) is soluble in scCO₂ or the partition coefficient is favorable toward the polymer charging enough solute, and the polymer itself is well swollen by the scCO₂ solvent [6]. The general steps of impregnation of polymeric fibres in scCO₂ 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 scCO₂ medium containing

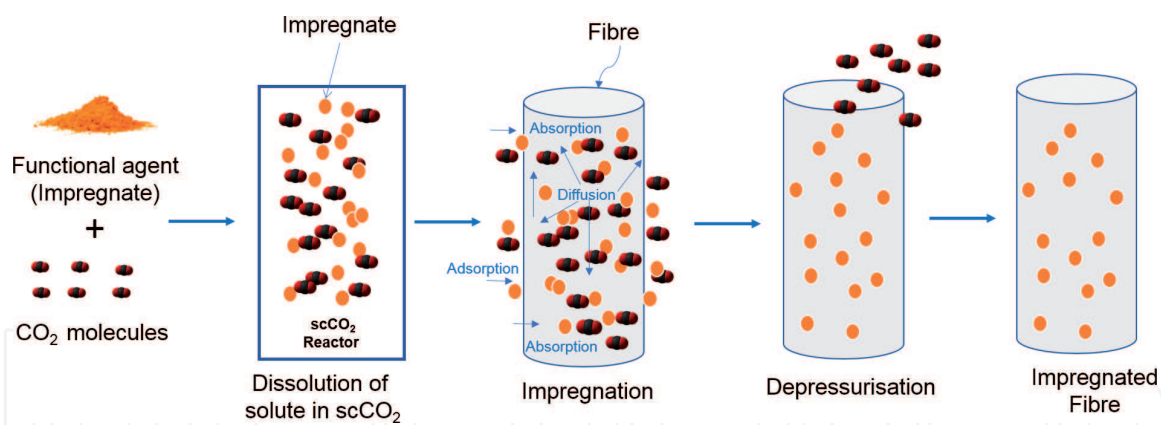


Figure 1. Schematic of impregnation mechanism of polymeric fibres with functional agent in scCO₂.

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 scCO₂

The most important property for the design of processes in scCO₂ medium is the solubility of the compounds in scCO₂ 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 scCO₂ solvent. The solvent character of scCO₂ 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 scCO₂ bath. Furthermore, the solvent power of scCO₂ 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 scCO₂ [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 scCO₂, but only two classes of polymeric materials such as fluoropolymers and silicones showed appreciable solubility in scCO₂ at a readily accessible temperature and pressure [19]. Thus, future research should focus on studying the solubility of functional compounds in scCO₂.

4. Functionalization in scCO₂

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 scCO₂ 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 CO₂-philic biocidal fluorinated pyridinium silicon and applied to cotton yarn using scCO₂ 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 scCO₂ 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 scCO₂. 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 scCO₂ medium to fabricate a durable water and oil repellent coatings [32]. A uniform, highly repellent, and durable coating was obtained by scCO₂ 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 scCO₂ processing method for functionalization of textiles and polymeric materials.

4.3 Natural functional compounds

Supercritical CO₂ 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 scCO₂ to develop different functional materials. They studied the solubility of thymol in scCO₂ 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 scCO₂ solvent, and impregnation process was successful. All the samples prepared using scCO₂ impregnation exhibited strong antimicrobial effect against a wide range of bacteria strain. The same research group also used scCO₂ 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 scCO₂ 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 scCO₂ 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/TiO₂ onto silk fabric using scCO_2 impregnation technique. Co-deposition of photocatalytic TiO₂ 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 scCO_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 scCO₂ 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 scCO₂ has the potential to replace the current water and solvent-based textile chemical processes in the future.

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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
<i>Pa</i>	pascal
PCL	polycaprolactone
PCL-HA	polycaprolactone hydroxyapatite
PE	polyethylene
PET	polyester
PLA	polylactic acid
<i>Pt</i>	platinum
QAS	quaternary ammonium salt
scCO ₂	supercritical carbon dioxide
<i>T_g</i>	glass transition temperature
TiO ₂	titanium dioxide
TMP	2,2,6,6-tetramethyl-4-piperidinol

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