The Journal of Supercritical Fluids 133 (2018) 30–37

Contents lists available at ScienceDirect

The Journal of Supercritical Fluids

journal homepage: www.elsevier.com/locate/supflu

Durable crosslinked omniphobic coatings on textiles via supercritical carbon dioxide deposition

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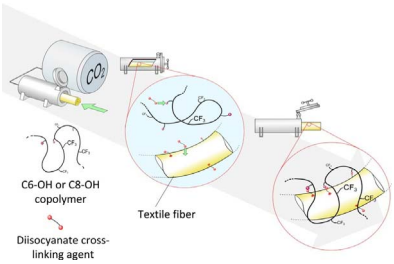
GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Supercritical carbon dioxide
Durable water repellent
Superhydrophobic
Omnifobic
Coating

ABSTRACT

A novel method of creation durable water- and oil- repellent coatings on flexible substrates (such as textiles) by simultaneous deposition of perfluoroalkyl methacrylate/hydroxyalkyl methacrylate statistical copolymers with a diisocyanate crosslinking agent from solutions in supercritical carbon dioxide (SC CO_2) is proposed. The morphology of fluropolymer films deposited on nylon fibers from 1,1,2- trichlorotrifluoroethane and from SC CO_2 with/without hexamethylene diisocyanate as a crosslinking agent is compared using scanning electron microscopy. Repellent properties of the films are analysed by water contact angle measurements and by performing standard water spray test as well as hydrocarbon resistance tests before and after multiple home laundry cycles. Enhanced uniformity of the SC CO_2 deposited coatings results in improved durability and liquid repelling properties in comparison to coatings deposited from a liquid solvent.

1. Introduction

Partially fluorinated copolymers are widely used for creating water-, oil-, and stain- repellent coatings on various substrates [1–4]. Such polymers usually contain perfluoroalkyl sidechains with CF_3 terminal groups, which arrange at the solid/air interphase. Repellent properties of the coating depend on its surface energy, which is determined by the orientation of the fluorinated sidechain fragments and has a lower limit of about 6–7 mN/m for the surface of densely packed CF_3 groups [5]. Reaching this limit and obtaining a thin film with uniformly aligned hydrophobic sidechains is not an easy task. The polymer films are usually applied by liquid phase techniques, which have certain fundamental limitations caused by surface tension of liquid solvents. Surface tension and corresponding capillary effects lead to formation of coating nonuniformities [6] and defects, which increase surface energy thus deteriorating repellent properties and coating durability. Moreover,

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http://dx.doi.org/10.1016/j.supflu.2017.09.020
Received 24 July 2017; Received in revised form 15 September 2017; Accepted 15 September 2017
Available online 18 September 2017
0896-8446/

using liquids as deposition media in industrial processes such as, for instance, padding process commonly used for water repellent finishing of textiles, leads to additional environmental issues. In such a process fabric is padded through a bath with a water-based dispersion of hydrophobic copolymer and is then passed through a squeezing roller into a dryer. The process consumes huge amounts of water as well as energy on the drying stage [7].

However, the abovementioned problems may be solved simultaneously by switching from liquid phase methods of polymer coatings application to dry deposition from supercritical CO_2. Indeed, it is a cheap, non-toxic, non-flammable fluid with high diffusivity, low viscosity and no surface tension driven effects [8]. CO_2 solvent quality can be controlled by changing pressure, which allows to purify and recycle this solvent easily by decompressing it and then compressing again. Recently, DyeCoo has demonstrated that it is possible to use SC CO_2 as a medium for dry industrial textile dyeing process [9], which allowed to decrease energy and chemicals consumption as well as to solve the waste waters problem.

It has been shown previously that SC CO_2 deposition allows to obtain uniform films of polymers with perfluorinated main chain such as Teflon AF amorphous copolymer on various substrates, including textiles [10–13]. However, such coatings lack durability due to weak adhesion of fluorinated polymer chains to the substrate and are wetted by oils due to yet relatively high surface energy of CF_2 film. Moreover, the applied polymers dissolve in SC CO_2 at relatively high pressures and temperatures, which limits the possibility of their practical application. On the other hand, fluorinated acrylic polymers, are readily soluble in CO_2 even in a liquid state [14,15] and can be easily applied from SC CO_2 solutions on substrates with complex morphology.

In the present article a novel process of creation of durable crosslinked water and oil repellent coatings on porous flexible supports via simultaneous deposition of fluorinated acrylic copolymers containing functional groups and crosslinking agent directly from SC CO_2 solutions is proposed. Morphology, performance and durability of coatings deposited on nylon fabric from supercritical carbon dioxide solutions of fluorinated homopolymers poly(perfluorohexyl ethyl methacrylate) (C6), poly(perfluorooctyl ethyl methacrylate) (C8) and their copolymers with hydroxypropyl methacrylate (referred to as C6-OH and C8-OH, correspondingly) are studied.

2. Experimental

2.1. Materials

Perfluorohexyl ethyl methacrylate was provided by Chemours (Capstone 62-MA intermediate, > 96% purity). Hydroxypropyl methacrylate (> 95% purity), perfluorooctyl ethyl methacrylate (> 97% purity), toluene-2,4-diisocyanate (TDI, > 98% purity) and hexamethylene diisocyanate (HMDI, > 99% purity) were bought from Sigma-Aldrich. Azobisizobutyronitrile (AIBN, > 99% purity) was provided by Chemical Line. A roll of TIC 300 spun nylon 6.6 plain weave fabric was provided by SDL Atlas. All chemicals were used as received without any further purification.

2.2. Polymer synthesis

Radical polymerization of homopolymers and copolymers was performed in SC CO_2 using methodology developed by DeSimone [16]. AIBN was used as an initiator [17]. Polymer synthesis proceeded as follows. For fluorinated acrylic homopolymers C6 and C8, 3 g of the corresponding monomers were placed into 20 ml stainless steel reactor with 1 wt.% of AIBN. The reactor was then filled with CO_2 until the pressure reached 100 bar. After that the reactor was heated to 60 °C and the pressure increased to 330 bar. After 48 h the reactor was decompressed and opened, polymer was removed from the reactor. For partially fluorinated acrylic copolymers with functional hydroxyl groups, specified amount of hydroxypropyl methacrylate was added to the reactor along with C6 or C8 and AIBN. The resulting products were collected, dissolved and precipitated from 1,1,2- trichlorotrifluoroethane (F-113). All synthesized polymers were dispersed solid powders.

Product yields were determined gravimetrically using A & D GR-200 analytical balance. Yields were calculated as a ratio of weight of a soluble in SC CO_2 part of the polymerization products to a total mass of monomers placed inside the high-pressure vessel.

The products of perfluoroalkyl methacrylate and hydroxypropyl methacrylate copolymerization contained two polymer fractions with different amount of hydroxyl groups: the first one with lower amount of hydroxyl groups was soluble and the second one was insoluble in F-113. The soluble component was separated from the insoluble one by means of dissolution-precipitation in F-113 and used in further experiments.

Copolymer composition was analyzed by FTIR-spectroscopy using a VERTEX 70 v FTIR spectrometer (Bruker, Geormany). IR spectra were registered in the range of 4000–400 cm^{-1} with spectral resolution of 4 cm^{-1} in the attenuated total reflection (ATR) mode using a GladyATR console (PIKE, USA) with a diamond working element. ATR spectra correction was performed using a standard spectrometers software. The amount of OH-containing units in the copolymers was estimated by comparison of relative intensity of OH stretching vibration peaks in the range of 3000–3700 cm^{-1}. For that three OH-spectra was used each time: IR-spectra for both fluorine-containing and OH-containing homopolymers and IR spectrum of the copolymer. The quantitative estimation was also performed by using normalized integral intensities of stretching vibration peaks for C = 0 (~1730 cm^{-1}) and both CH_2 and CH_3 (1200–1300 cm^{-1}).

H^1 NMR spectra were obtained for C6-OH copolymer using a Bruker AVANCE™ 400 device (Germany) with Freon-113 as a solvent. Integral intensities were used to estimate the ratio of fluorine-containing side-chains in a copolymer. GPC were performed for both C6 and C6-OH polymers using PLgel MIXED-C and PLgel MIXED-D columns (Agilent, USA) with α,α,α-trifluorotoluene as a solvent. GPC for polymers with 8 fluorinated carbon atoms could not be obtained due to poor solubility of such polymers in this solvent.

Phase diagrams of polymer/CO_2 system were obtained in order to analyse solubility of synthesized polymers by measuring cloud points in a variable volume optical cell with two sapphire windows produced by Sitec. Cloud points were observed visually by slowly decreasing the pressure at 0,5 bar s^{-1} and noting the moment when the solution becomes turbid due to occurring liquid–liquid phase separation [14].

2.3. Coating deposition

Required amount of polymer (2% of fabric weight, corresponding to approximate polymer concentration of 3 mg/ml in solution in SC CO_2) was distributed uniformly on the surface of the 19 × 19 cm^2 piece of fabric. The fabric was then rolled and placed in a 50 ml cylinder shaped stainless steel reactor. For crosslinked coatings HMDI was used as a crosslinking agent. 25 µl of HMDI was added to the reactor prior to placing a roll of fabric in it. The reactor was filled with CO_2 until the pressure reached 200 bar. The reactor was then heated up to 90 °C, the corresponding pressure was about 675 bar. After 3 h of the exposure at the SC conditions, the reactor was put into thermostatic bath at 50 °C and decompressed slowly (~5 bar per minute). The reactor was then opened and the fabric was retrieved.

For comparison, the coatings of the same composition were prepared by dip-coating of 19 × 19 cm^2 pieces of fabric in the vessel with 30 ml of solution of corresponding polymers in liquid F-113. The polymer concentration in the solution was 0.07 g/ml. For obtaining the crosslinked coatings HMDI was additionally dissolved in the polymer solution. Its concentration was 1 µg/ml.

After immersion of fabric pieces in the solution for 180 min they were allowed to dry at room temperature for 3 h and then baked in vacuum oven at 90 °C for 1 h.