GREEN COATINGS/PROCESSING USING LIQUID AND SUPERCRITICAL CO_2 WITH NON-FLUOROUS CO_2-PHILES

Thesis submitted to the
University of Calicut in partial fulfilment of
the requirements for the award of the degree of

DOCTOR OF PHILOSOPHY IN CHEMISTRY
under the Faculty of Sciences

by

ANU ANTONY

Under the guidance of
Dr. P. Raveendran

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“We stand now where two roads diverge. But unlike the roads in Robert Frost's familiar poem, they are not equally fair. The road we have long been travelling is deceptively easy, a smooth superhighway on which we progress with great speed, but at its end lies disaster. The other fork of the road — the one less travelled by — offers our last, our only chance to reach a destination that assures the preservation of the earth.”

— Rachel Carson in ***Silent Spring***

CERTIFICATE

Certified that the thesis entitled **"GREEN COATINGS/ PROCESSING USING LIQUID AND SUPERCRITICAL CO_2 WITH NON-FLUOROUS CO_2-PHILES"** is an authentic record of the research work carried out by **Ms. Anu Antony** under my guidance for the award of the degree of **Doctor of Philosophy** in Chemistry under the Faculty of Sciences, University of Calicut, Kerala, and that the same has not been submitted elsewhere for any degree or diploma.

Calicut University
17.12.2019

Dr. P. Raveendran
(Supervising Teacher)

CERTIFICATE

Certified that the thesis entitled **"GREEN COATINGS/ PROCESSING USING LIQUID AND SUPERCRITICAL CO_2 WITH NON-FLUOROUS CO_2-PHILES"** is an authentic record of the research work carried out by **Ms. Anu Antony** under my guidance for the award of the degree of **Doctor of Philosophy** in Chemistry under the Faculty of Sciences, University of Calicut, Kerala, and that the same has not been submitted elsewhere for any degree or diploma. I also hereby certify that the corrections/suggestions from the adjudicators have been incorporated in the revised thesis.

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17.12.2019

Dr. P. Raveendran
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DECLARATION

It is hereby declared that the thesis entitled **"GREEN COATINGS/PROCESSING USING LIQUID AND SUPERCRITICAL CO_2 WITH NON-FLUOROUS CO_2-PHILES"** submitted herewith is an authentic record of the research work carried out by me under the supervision of Prof. Dr. P. Raveendran, Department of Chemistry, University of Calicut, in partial fulfilment of the requirements for the award of the degree of Doctor of Philosophy in Chemistry under the Faculty of Sciences, University of Calicut, Kerala. The contents of this thesis have not been submitted to any other institute or University for the award of any degree or diploma.

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17.12.2019

Anu Antony

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Anu Antony

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LIST OF ABBREVIATIONS

Supercritical	:	sc
Supercritical Fluid	:	SCF
Volatile Organic Compound	:	VOC
Sucrose octaacetate	:	SOA
α-D-Glucose pentaacetate	:	AGLU
Poly(ethylene glycol)	:	PEG
Acetone	:	AC
Ethyl Acetate	:	EA
Urea	:	UR
Atenolol	:	AT

PREFACE

Utilization of liquid and supercritical (sc) CO_2 as an environmentally benign alternative solvent platform has been one of the major themes of green chemistry. Over the years, many novel and innovative industrial strategies using this solvent system have emerged by virtue of the inherent capabilities of this solvent system such as ease of solvent removal and tunability of solvent parameters. In addition to being abundant and inexpensive, this solvent system has many environmentally friendly attributes such as non-toxicity, non-flammability and importantly, easily attainable critical temperature and pressure, making this as an environmentally acceptable and economically viable solvent alternative for the chemical industry. In spite of its limitations in terms of understanding its full solvent capabilities, it has made inroads into several important areas such as fluoropolymer synthesis, dry cleaning, chemical separations and processing, pharmaceutical and textiles industry, microelectronic cleaning, extraction of natural products and synthetic organic chemistry. One of the major challenges in the area was the identification of non-fluorous and inexpensive CO_2-philes for enabling such applications. It was identified that one can develop CO_2-philes based on site-specific solute-solvent interactions such as Lewis Acid-Lewis Base interactions and was shown that simple functionalizations such as acetylation of carbohydrates can be employed for the design of inexpensive, non-fluorous CO_2-philes.

In this work we have employed three non-fluorous CO_2-philes, *viz*., α-D-Glucose pentaacetate (AGLU), Sucrose octaacetate (SOA) and Poly(ethylene glycol) (PEG; MW 1500). The first two belongs to the class of sugar acetates and the last one belongs to the class of oxygenated polymers.The integration of these CO_2-philes with liquid/scCO_2, for developing newer applications in the field of textiles, paper, wood, agricultural and pharmaceutical industries were investigated. Also, liquid/scCO_2 is compared with conventional solvents such as Acetone or Ethyl Acetate for the various applications studied.

The thesis is divided into eight chapters. Chapter 1 provides a detailed introduction to evolution and principles of green chemistry, alternative solvents, supercritical fluids, solvent attributes of scCO_2 and finally the specific objectives of the present work.

The specifications of various materials used, detailed description of supercritical CO_2 facility, methodologies adopted, and characterization techniques have been presented in Chapter 2.

Chapter 3 presents the results of our investigation on the sizing and desizing of cotton and polyester yarns using CO_2-philes as the size material and liquid/scCO_2 as alternative solvent. Sizing of yarns were also carried out in Acetone and Ethyl Acetate medium and compared.

Chapter 4 presents the sizing of paper using CO_2-philes as the size material and liquid/scCO_2 as the alternative solvent.

Chapter 5 deals with the study of the impregnation of wood using SOA in $scCO_2$ medium.

Chapter 6 discusses the preparation of composites of urea with CO_2-philes using $scCO_2$ as the solvent for the sustained release of urea. The results obtained are compared with the release kinetics obtained for composites prepared using Ethyl Acetate medium.

Chapter 7 presents the application of $scCO_2$ as the solvent for the preparation of drug-excipient composites for the sustained release of Atenolol. The results were compared with composites prepared using Ethyl Acetate medium.

Finally, the major conclusions of the work and the future outlook for extending these applications to an industrial level are presented in Chapter 8.