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Polymer Processing with Supercritical Fluids

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Abstract—Supercritical fluids have a unique and valuable potential for the enhanced processing of many materials. This review describes research in the applications of supercritical fluids to polymer processing. The ability of supercritical carbon dioxide to swell and plasticize polymers is crucial to the impregnation, extraction, and modification of polymeric materials. This plasticization also reduces viscosity and facilitates the processing of polymers due to lower shear stresses. Spectroscopy plays an important role in probing these interactions at a molecular level and to follow *in situ* the processes of CO_2-induced plasticization and the crystallization of polymers. Opportunities exist for improving the processing of many polymeric-based materials ranging from textile to food and biomaterials. The implications of interactions between supercritical carbon dioxide and polymers for drying, dyeing, foaming and extrusion are also discussed with an outlook for further opportunities in this and related areas of polymer processing.

I. INTRODUCTION

Supercritical fluids (SCFs) have unique properties that may enhance many types of chemical process operations. An additional advantage of using SCFs stems from the fact that they may replace many environmentally harmful solvents currently used in industry. In particular, SCFs represent an attractive alternative to organic solvents for use as additives in polymer processing. For example, supercritical carbon dioxide ($scCO_2$), which is by far the most widely used SCF, is relatively cheap, nontoxic, and nonflammable and has zero ozone-depletion potential. Moreover, the fact that CO_2 is a gas under ambient conditions makes its removal from the polymeric product very easy, avoiding, for example, the costly processes of drying or solvent removal, which is very important in the processing of polymer-based materials.

But what are the properties of an SCF? A supercritical fluid is defined as a substance above its critical pressure and temperature. However, there is still no apparent distinction between a high-pressure gas and an SCF because, under all circumstances, such a fluid will occupy the full volume of its container, demonstrating the typical behavior of a gas. Nevertheless, such a fluid is usually not called a high-pressure gas but a supercritical fluid. The reason is that one cannot liquefy such a fluid under any pressure once it is heated above its critical temperature (it should be noted, however, that it can still be solidified at extremely high pressures!). No phase separation occurs for any substance at pressures or temperatures above its critical values, thus, one should never see a meniscus once the substance has become supercritical (Fig. 1). In other words, the critical point represents the highest temperature and pressure at which gas and liquid can coexist in equilibrium. However, it is very important to note that this definition is for a pure substance.

Once a small amount of another soluble substance is introduced into the SCF, its critical parameters could change depending on the concentration of the additive. In addition, the critical parameters of the fluid might

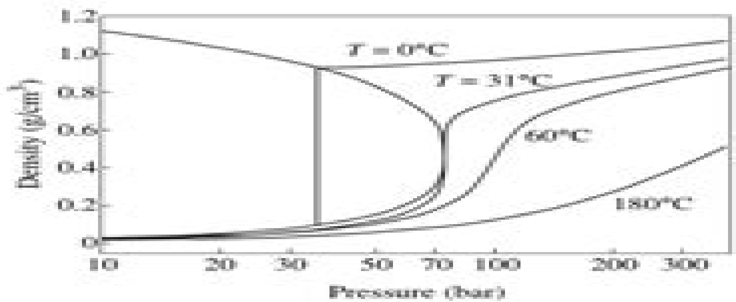

Fig. 1. Liquid–vapor phase diagram of carbon dioxide showing 4 isotherms: 0°C (below the critical temperature), 31°C (critical temperature), 60°C and 180°C (above the critical temperature). Note that at a temperature above 31°C and a pressure of 73 bar only one phase is present.

[1] This work was submitted by the author in English.

Polymer Procebing With Supercritical Fluids

Jin-Ying Zhang

Polymer Procebing With Supercritical Fluids:

Polymer Processing with Supercritical Fluids Vannessa Goodship,Erich Ogur,2004 SCFs are currently the subjects of intense research and commercial interest Applications such as the RESS rapid expansion of supercritical fluid solutions process are part of standard industrial practice In view of their ever growing importance in the polymer industry there is a need to fully comprehend how supercritical fluids interrelate with polymeric materials to realise the potential that can be gained from their use The authors review the basic principles of SCFs and their application within the polymer industry characteristics and properties extraction of unwanted residual products polymerisation solvents and polymer impregnation Processing applications such as plasticisation foaming and blending are also considered There is discussion of the potential within the polymer recycling industry for use of SCFs as cleaning agents or within supercritical oxidation processes Around 400 references with abstracts from recent global literature accompany this review sourced from the Polymer Library to facilitate further reading A subject index and a company index are included **Foaming with Supercritical Fluids** Ernesto Di Maio,Salvatore Iannace,Giuseppe Mensitieri,2021-11-06 Foaming with Supercritical Fluids Volume Nine provides a comprehensive description of the use of supercritical fluids as blowing agents in polymer foaming To this aim the fundamental issues on which the proper design and control of this process are rooted are discussed in detail with specific attention devoted to the theoretical and experimental aspects of sorption thermodynamics of a blowing agent within a polymer the effect of the absorbed blowing agent on the thermal interfacial and rheological properties of the expanding matter and the phase separation of the gaseous phase and of the related bubble nucleation and growth phenomena Several foaming technologies based on the use of supercritical blowing agents are then described addressing the main issues in the light of the underlying chemical physical phenomena Offers strong fundamentals on polymer properties important on foaming Outlines the use of supercritical fluids for foaming Covers theoretical points of view including foam formation of the polymer gas solution to the setting of the final foam Discusses the several processing technologies and applications

Polymer processing using supercritical fluids Elena Aionicesei,Željko Knez,Mojca Škerget,2009 The traditional methods for polymer processing use environmentally hazardous volatile organic solvents and chlorofluorocarbons Due to the increase of hazardous solvent emission and generation of aqueous waste streams there is an obvious need of finding new and cleaner methods for the processing of polymers Supercritical carbon dioxide scCO2 has attracted particular attention for these applications due to its tremendous potential as a plasticizer in polymer processing A particular interest is shown to the use of supercritical fluids for processing polymers destined for biomedical applications as microspheres microcapsules foams membranes polymer drug composites The method offers important advantages related to the absence of harmful organic solvents or when necessary the efficient extraction of solvents and impurities the mild processing conditions and the control of particle and foams morphology by simple variation of pressure and temperature Despite the huge potential of scCO2 as a green solvent for processing biocompatible and biodegradable polymers the phase equilibrium data essential for process design are quite scarce Optimum processing techniques and parameters pressure temperature still need consideration andstudy The data are especially scarce regarding the scCO2 processing of polymer ceramic composites for biomedical applications On this basis this thesis is aimed to open new perspectives over the use of scCO2 as a green solvent for the processing of biodegradable polymers and composites used as biomaterials Two biodegradable polymers were chosen for this study poly L lactide PLLA and poly D L lactide co glycolide PLGA Their composite with a bioactive ceramic powder hydroxyapatite HA was also studied The main idea followed by this thesis was the obtaining of porous polymeric or composite material scaffolds suitable for tissue engineering under mild temperature conditions and without the use of additional organic solvents The behavior of the two polymers under dense CO2 had been studied and explained More data about the polymer gas phase equilibrium necessary for understanding and optimizing the effect of processing parameters were obtained by determining the solubility and diffusion coefficients of CO2 in the polymers for certain values of temperature and pressure The solubility ofCO2 was measured for each polymer for three different temperatures 308 313and 323 K in the pressure range 10 30 MPa The temperatures were chosen higher than the critical temperature for CO2 but still low enough so as not to affect the bioactivity of any drugs or proteins that could be introduced in the system during processing The same range of temperature and pressure was employed for all tests involving the studied polymers or their composite materials The efficiency of mixing in the presence of scCO2 for obtaining composite materials from PLLA and HA and respectively PLGA and HA was studied by comparison with coprecipitation The solubility and diffusion coefficient of CO2 in the composite materials were afterward determined and the results were compared with the ones obtained for the polymer alone in order to determine the effect of the ceramic filler on the gas uptake The possibility of obtaining porous scaffolds was assessed by using a pressure quench technique using dense CO2 as blowing agent with and without the presence of aporogen The effect of pressure temperature depressurization rate and porogen on the final porous structure was investigated The experimental results were compared with literature data and with data obtained by mathematical modeling employing equations of state commonly used for polymersor polymer solvent systems The results indicate that gas foaming of biodegradable polymers represents a promising technique for obtaining tissue engineering scaffolds with the desired structure Still the processing parameters need to be studied and optimized according to the nature of the substrate and of the aimed final product

Supercritical Carbon Dioxide Maartje F. Kemmere,Thierry Meyer,2006-05-12 Recently supercritical fluids have emerged as more sustainable alternatives for the organic solvents often used in polymer processes This is the first book emphasizing the potential of supercritical carbon dioxide for polymer processes from an engineering point of view It develops a state of the art overview on polymer fundamentals polymerization reactions and polymer processing in supercritical carbon dioxide The book covers topics in a multidisciplinary approach starting from polymer chemistry and thermodynamics going through monitoring polymerization processes and ending with polymer shaping and post processing The authors are internationally recognized experts from different fields in polymer reaction engineering in supercritical fluids The book was initiated by the Working Party on Polymer Reaction Engineering of the European Federation of Chemical Engineering and further renowned international experts Supercritical Fluid Assisted Polymer Processing: Plasticization, Swelling and Rheology ,2000 The use of supercritical carbon dioxide scCO is a gas under atmospheric conditions it can be used as a processing aid and then easily removed from a polymer through evaporation to obtain the original physical properties of the unplasticized polymer matrix In addition CO has been shown to be more environmentally friendly in comparison to many of the traditional organic plasticizers However the biggest challenge hindering the widespread use of CO as a plasticizer involves a lack of understanding of and data quantifying its effect on polymer swelling and the concomitant reduction in material viscosity In this work a three step approach is used to investigate and quantify the physical phenomena associated with CO induced plasticization of polymer melts First a novel experimental apparatus was designed and constructed to measure equilibrium swelling swelling kinetics and diffusion of CO into a polymer melt It was found that diffusion of CO pressure had a negligible effect on the diffusion coefficient however the system temperature directly affected the diffusion coefficient Increased pressure was found to enhance the extent of swelling whereas a maximum was observed with increasing temperature at pressures above 15 MPa The Sanchez Lacombe equation of state was found to be in good agreement with the experimentally calculated variables and thus can be used as a predictive tool to obtain physical properties of the CO PDMS system Secondly a high pressure extrusion slit die rheometer was constructed to measure the viscosity of polymer melts plasticized with low concentrations of CO Polystyrene poly methyl methacrylate polypropylene low density polyethylene and poly vinylidene fluoride were all investigated CO was found to be an efficient plasticizer for all of these polymer materials generally lowering the viscosity of the melt 30 80% depending on processing conditions Predictive viscoelastic scaling models based on free volume principles and a p **Advances in Polymer Processing** S Thomas,Weimin Yang,2009-05-30 Processing techniques are critical to the performance of polymer products which are used in a wide range of industries Advances in polymer processing From macro to nano scales reviews the latest advances in polymer processing techniques and materials Part one reviews the fundamentals of polymer processing with chapters on rheology materials and polymer extrusion Part two then discusses advances in moulding technology with chapters on such topics as compression rotational and blow moulding of polymers Chapters in Part three review alternative processing technologies such as calendaring and coating foam processing and radiation processing of polymers Part four discusses micro and nano technologies with coverage of themes such as processing of macro micro and nanocomposites and processing of carbon nanotubes The final section of the book addresses post processing technologies with chapters on online monitoring and computer modelling as well as joining machining finishing and decorating of polymers With is distinguished editors and team of international contributors Advances in polymer processing From macro to nano scales is an invaluable reference for engineers and academics concerned with polymer processing Reviews the latest advances in polymer processing techniques and materials analysing new challenges and opportunities Discusses the fundamentals of polymer processing considering the compounding and mixing of polymers as well as extrusion Assesses alternative processing technologies including calendaring and coating and thermoforming of polymers **Supercritical Fluid Assisted Polymer Processing** Joseph Robert Royer,2000 Keywords Supercrtical fluids Viscosity reduction CO2 induced plasticization **Porous Polymer Science and Applications** Inamuddin,Mohd Imran Ahamed,Rajender Boddula,2022-05-02 Porous Polymer Science and Applications aims to provide recent developments and advances in synthesis tuning parameters and applications of porous polymers This book brings together reviews written by highly accomplished panels of experts working in the area of porous polymers It encompasses basic studies and addresses topics of novel issues concerning the applications of porous polymers Chapter topics span basic studies novel issues and applications addressing all aspects in a one stop reference on porous polymers Applications discussed include catalysis gas storage energy and environmental sectors making this an invaluable guide for students professors scientists and R D industrial experts working in the field of material science and engineering and particularly energy conversion and storage Additional features include Provides a comprehensive introduction to porous polymers addressing design synthesis structure properties and characterization Covers task specific applications of porous polymers Explores the advantages and opportunities of these materials for most major fields of science and engineering Outlines novel research areas and potential development and expansion areas Processing of Polymers Using Supercritical Fluids John J. Aklonis,Eric J. Amis,UNIVERSITY OF SOUTHERN CALIFORNIA LOS ANGELES DEPT OF CHEMISTRY.,1990 In the past most of the effort expended in the area of supercritical fluids and polymers has been devoted to chromotography and separation We propose to explore using supercritical fluids as solvents for the preparation of polymers and polymer blends in the form of fibers polymer sheets and perhaps irregularly shaped polymer solids It is well known that many of the most interesting new high tech polymers are exceedingly difficult to fabricate These polymers exhibit such highly desirable properties as electrical conductivity extremely high strength or remarkable thermal stability to name but a few In the supercritical regime one can vary and control the solvent power of fluids over ranges much broader than those accessible in the usual liquid regime We are attempting to take advantage of the high variability of solvent power of supercritical fluids with respect to processing of homopolymers as well as making polymer blends with unique properties Keywords Processing of polymers Supercritical fluids Fibers Solvents Light scattering studies PMMA JG *Supercritical Fluid Extraction* Mark McHugh,Val Krukonis,2013-10-22 Supercritical Fluid Extraction is a technique in which CO2 is used under extremely high pressure to separate solution e g removing caffeine from coffee Separations is basic to all process industries and supercritical fluid extraction is a specific type which is receiving a high level of attention The book will combine basic fundamentals with industrial applications The second edition has been expanded and updated and includes new chapters on chromatography and food processing this is an excellent book which is both instructive and amusing to read Its true value is neatly summarised in one of the closing sentences We have supplied you with the guidelines and criteria which you can now apply when considering supercritical fluids for your own needs Chemistry in Britain February 1995 **Polymer Process Engineering '99** Phil D. Coates,1999 Proceedings of an international conference held in June 1999 which was designed to address the issues Where is polymer processing going and What are the key trends in technology at the end of the 20th century in this vital international industry Papers cover leading edge developments in polymer processing technology in process measurements and process flow modelling and control *10th International Symposium & Exhibit on Supercritical Fluid Chromatography, Extraction and Processing* ,2001 **Advanced Polymer Processing** Lian Xiang Ma,Chuang Sheng Wang,Weimin Yang,2009-12-21 Selected peer reviewed papers from the Advanced Polymer Processing International Forum Qingdao China 19 21 August 2009 APPF 2009 *The 8th International Symposium on Supercritical Fluid Chromatography and Extraction* ,1998 *Modification and Processing of Polymers Using Supercritical Fluids* Paul B. Webb,2000 *Advances in Resist Technology and Processing* ,1995 **Polymer Science** ,2000 The English version will include two issues chemistry and the physics of polymers **Conference Proceedings** Society of Plastics Engineers. Technical Conference,1998 **Biomedical Polymers** Mike Jenkins,2007-09-10 A review of the latest research on biomedical polymers this book discusses natural synthetic biodegradable and non bio degradable polymers and their applications Chapters discuss polymeric scaffolds for tissue engineering and drug delivery systems the use of polymers in cell encapsulation their role as replacement materials for heart valves and arteries and their applications in joint replacement The book also discusses the use of polymers in biosensor applications Edited by an expert team of researchers and containing contributions from pioneers throughout the field the book is an essential reference for scientists and all those developing and using this important group of biomaterials **Handbook of Polymer Reaction Engineering** Thierry Meyer,Jos Keurentjes,2005

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