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Review

Supercritical fluids and polymers – The year in review – 2014

Erdogan Kiran

Department of Chemical Engineering, Virginia Tech, Blacksburg, VA 24061, USA

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ABSTRACT

A critical overview of publications on applications of supercritical fluids in polymer formation, modification and processing is presented. The review is focused on publications that appeared in 2014 only with the intent of providing an in-depth look at the activity in the most recent year to gain insights on the more recent trends and opportunities. The articles have been grouped under ten different application areas which include (1) polymer solutions and phase behavior, (2) polymerizations, (3) particle formation/micronization/drug delivery systems, (4) films, (5) fibers, (6) membranes, (7) nanocomposites, (8) porous materials – foams/scaffolds, (9) organogels, and (10) lignocellulosic polymers. In each category, articles are discussed under specific polymer or polymer type to better highlight those polymers that are receiving the greater level of attention. In 2014, more polymers were explored for their foamability, and for generation of nanocomposites. Poly(ε-caprolactone), poly(lactic acid) and poly(lactide-co-glycolide) were the most frequently investigated polymers for their porous matrix formation, or particle formation features using supercritical carbon dioxide because of their biomedical significance as biodegradable platforms for tissue engineering scaffolds and drug delivery devices. Poly(ethylene oxide), poly(lactic acid), and poly(methyl methacrylate) were the polymers that were explored in multiple application areas.

Based on the close examination of these publications, the review provides specific observations on the advances that are made toward improved understanding of the factors that affect the miscibility of polymers in carbon dioxide, and for further understanding of the synergistic or other effects of components in polymer blends and composites, including the consequences of the presence of crystalline versus amorphous domains and morphological differences, or the consequences of the presence of nanofillers in different applications. New perspectives that are emerging in each application area are presented.

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E-mail address: ekiran@vt.edu

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1. Introduction

This review article is the first in a new series of focused articles that will appear in the Journal of Supercritical Fluids in the coming years. The primary objective of these reviews will be to present in-depth analyses of the publications in a given specific application area that had appeared in the most recent year and provide insights for the future directions and opportunities. We are now presenting a critical overview of the publications that appeared in 2014 that pertain to the various applications of supercritical fluids in the field of polymers.

Polymers and polymer related applications constitute one of the more active areas of research for supercritical fluids-based technologies which has experienced an almost exponential growth since about 1990. The Journal of Supercritical Fluids, which had started in 1988, has witnessed this remarkable growth, having served as the medium for many of the publications in the area.

A search of the Web of Science with the broad key word "supercritical" shows that there have been nearly 50,000 articles published since 1974, 96% of which (47,818) having been published since 1988. Of this total, 3374 were published in 2014. The corresponding numbers for the 1974–2014 period when conducted with the combined key words "supercritical" + "carbon dioxide" are 18,438 and 1262. These are given in Table 1 which provides more detailed information on the publications specific to polymers and their different application areas with the key words "polymer" + "supercritical" and also with the key words "polymer" + "supercritical" + "carbon dioxide". With a total of 4596 publications that have appeared since 1974, polymers account for nearly 10% of all the publications, a ratio that appears to have been sustained in 2014 as well. What is further interesting is that 411 articles, representing nearly 10% of all polymer related publications, have appeared in the Journal of Supercritical Fluids.

It is also important to note that of the 4596 total publications related to polymers, only 30 had been published prior to 1990. However, the number of publications during the five-year intervals that followed (from 1995 to 1990; 2000 to 1995; 2005 to 2000; and 2010 to 2005) showed a remarkable increase, with numbers going from 30 to 200; 503; 889 and 1374, respectively; corresponding to an average yearly publication numbers of 2, 40, 101, 178 and 275 during these years. This is shown in Fig. 1. As for the current five-year interval, the number of publications from 2010 to the end of 2014 has been 1285, of which 326 were published in 2014 alone. Fig. 1 suggests that the total number for the period 2010–2015 will most likely reach 1900, increasing the average yearly publication for the most recent five-year period to about 380.

Among the specific topical areas, Table 1 shows that polymerizations and polymer solutions, along with their associated phase behavior have been the ones most explored. It is however important to recognize that the total number of publications cannot yet be as large in some of the areas which are themselves relatively new. For example research pertaining to tissue engineering applications did not start until after 1990s. Recognition that supercritical fluids could be employed in membrane formation was also after 1990s. The research trends in these newer areas are better assessed if viewed over the past 10–15 year period. Table 2 shows the trends in the number of articles published in a given year in some of the focus areas in 1995, 2000, 2005, 2010, and 2014. The steady increase in activity in foaming, film formation, composites, drugs, and in crystallization is immediately noted while activity in areas such as polymerization, as well as studies on the broad areas of solubility and phase equilibria have remained relatively steady.

Another indicator of the continual growing activity is the number of review articles that have appeared each year especially since 1995. Since 1974, Web of Science indicates that 342 reviews have been published, of which 28 appeared in 2014 alone. Even though not all of these review articles have sufficient supercritical fluids content or focus, several authors [1–12] provide valuable status report in the various activity areas until 2014 including foaming and nanoporous materials [1–3], particle formation [4,5], membranes [6], polymer synthesis [5,7–9], aerogels [10,11] and chromatography [12,13]. Selected review articles from 2013, 2012, 2011, and 2010 provide additional overviews of the earlier literature in the areas of foaming [14–16] nanocomposites [17], drug delivery and biomedical applications [18,19].

It is important to emphasize that our focus in the present review is on the activity in 2014 alone. In the preparation of this review, a genuine attempt was made to access all the articles that showed up in the Web of Science search. The review is however not an annotated bibliography and publications that did not have sufficient supercritical fluids content, or those articles for which the full texts were not easily accessible have not been included in the review. Furthermore, no attempt was made to provide background literature prior to 2014, other than the selected references to the review articles that have been mentioned above. I do hope that those who have published on a given topic in other (earlier) years will not feel that they have been overlooked as this review is a "snap shot" of activity in 2014 alone.

The present review and discussions are presented in 10 parts with the following subheadings:

Part 1. Polymer solutions/phase behavior
Part 2. Polymerizations
Part 3. Particle formation/micronization/drug delivery systems
Part 4. Films
Part 5. Fibers
Part 6. Membranes
Part 7. Nanocomposites
Part 8. Porous materials – foams/scaffolds
Part 9. Organogels
Part 10. Lignocellulosic polymers

In each part, a brief introduction is provided that highlights the key parameters that need to be considered and the challenges that each topical area presents for effective utilization of supercritical fluids. In the discussions of the publications, a specific polymer or polymer type was chosen as the common denominator to group the articles. This grouping provides a quick assessment of the polymers that are of current interest for exploring supercritical fluid-base processing strategies. To the extent possible a brief statement has been included with each polymer as to their use areas to provide a snap shot perspective as to why a given polymer should be of any interest for their explorations with supercritical CO_2.

2. Part I. Polymer solutions and phase behavior

Along with the progress being made in diverse utilization areas of supercritical fluids, efforts are continuing for generation of new data as well as modeling of phase behavior in polymer solutions for more targeted applications. There is a growing appreciation of the need to document the changes in the thermophysical properties (such as the glass transition or the melting temperature) of polymers that are exposed to supercritical fluids undergo in a given process. There is also the appreciation of the significance of the role of amorphous versus crystalline domains in semicrystalline polymers play in influencing the solubility of supercritical fluids in a given polymer matrix which affect the morphological changes that follow. In this respect, significant amount of activity has been directed to assessing the extent of solubility and sorption of carbon dioxide in polymers and the associated changes in the properties of polymers. This is not surprising since carbon