Journal of CO_2 Utilization 19 (2017) 185–193

Contents lists available at ScienceDirect

Journal of CO_2 Utilization

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

Assessment of commercial poly(ε-caprolactone) as a renewable candidate for carbon capture and utilization

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ARTICLE INFO

Article history:
Received 15 January 2017
Received in revised form 16 March 2017
Accepted 27 March 2017
Available online xxx

Keywords:
Poly(ε-caprolactone)
Carbon dioxide capture
PFG-NMR
Adsorption
Renewable

ABSTRACT

Poly(ε-caprolactone) (PCL) is a cheap and sustainable polymer with long-term degradation (3–4 years) and low temperature transition ($T_m = \sim 60\,^{\circ}C$). We report on the investigation of PCL as a valid green candidate for Carbon Capture and Utilization (CCU). Studies were carried out by two complementary tools: a Sievert-type volumetric apparatus, to thoroughly analyse the CO_2 adsorption/desorption process inside the polymer, and Nuclear Magnetic Resonance (NMR) spectroscopy for a deeper study of the molecular dynamics and confinement effects through ^{13}C – pulsed field gradient (PFG) method (self-diffusion measurements), relaxation times (T_1) and spectral analysis. The morphology of the solid-state PCL was also investigated by Scanning Electron Microscopy (SEM). The effects of both the physical state and the adsorption process conditions on the PCL's CO_2 sorption capabilities were investigated as well as those concerning the cyclic life and the regeneration process. We find that two kind of adsorption sites are present in PCL matrix. Furthermore, PCL show a remarkable and complete thermoreversibility of the CO_2 adsorption process, a key condition in view of possible applications in this field.

1. Introduction

Global carbon dioxide (CO_2) growth rate is larger than the average of the last 10 years [1]. The Intergovernmental Panel on Climate Change (IPCC) has reported that the excessive emissions of greenhouse gases (GHG) to the atmosphere, mainly CO_2, are the primary source of modern global climate change and the consequent global warming of the Earth [2–4]. This increase of CO_2 in the atmosphere includes both natural and anthropogenic emissions, the latter due primarily to the combustion of fossil fuels, gas flaring and cement production [5,6]. For these reasons during recent years, an efficient reduction of GHG emissions is recognized worldwide as very important and is leading to increased efforts to reduce their environmental impact, including utilization of both preventive and remediation methods. The former are related to the incentive of renewable energies, while the latter have been linked to the implementation of systems for emission reduction in existing industrial plants producing enormous CO_2 discharges [7]. The carbon capture is an emerging technology to minimize CO_2 emissions adopted by several industrialized countries n capture is an emerging technology to minimize CO_2 emissions adopted by several industrialized countries [2]. Once captured from the anthropogenic or industrial sources, CO_2 can be stored indefinitely in geological media (Carbon Capture and Storage, CCS) or can be used as industrial feedstock in the production of chemicals, materials and fuels (Carbon Capture and Utilization, CCU) [8]. CCU does not always need to meet the CCS stringent conditions of high gas purity and high compression, therefore allowing a cheaper and more direct use of CO_2 [9–11]. The CCU economic aspect, combined with the recent advances in catalysis, is leading to the use of CO2 as a starting material capable of partially replacing crude oil, with beneficial side-effects on the environment [8]. Some examples of CCU are the employment of CO_2 in greenhouses, algae production, drink carbonation, welding, molding, fumigation, synthesis of hydrocarbons, carbonates (i.e. Carbstone durable bricks), carbamates, organic acids, urea and derivatives [9,12–14]. It is worth noting that the CCU products do not allow a permanent storage of

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http://dx.doi.org/10.1016/j.jcou.2017.03.017
2212-9820/

CO2 which will be eventually released into the environment, therefore a concerted work by CCU and CCS is required [8]. Currently, three are the main technologies for carbon capture: pre-combustion capture, oxy-combustion and post-combustion capture [6,15]. Among the three technologies of capture the post-combustion one is the most widely implemented, since the separation of CO_2 from the combustion exhaust is the most intuitive and easily applicable approach [16]. A wide range of CO_2 capture techniques from gas streams have been investigated, based on physical and chemical adsorption, absorption, cryogenic, microbial and membrane separation technologies [17–22]. Currently, amine-based technologies (i.e. chemical trapping in an aqueous solution, with the 0.409 mol CO_2/mol amine in the case of the benchmark reference monoethanolamine [23]) are the most advanced and cost-effective for CO_2 post-combustion capture [16]. However, such technologies suffer from solvent decomposition, toxicity, release of hazardous byproducts, corrosiveness toward the equipment and high energy consumption for solvent regeneration [24–26], and there is a need of new materials for carbon capture. Separation processes based on solid physical adsorbents are considered to be one of the most efficient approaches in terms of low cost and good cycle performance [27,28]. These require less energy to release the captured CO_2 and to recycle the sorbent, for example by using pressure/temperature swing adsorption, but there are a number of drawbacks: cost, sorbent lifetimes and excellent recyclability. Hence, the design of materials with tailored sorption characteristics is important [29]. Over the past few decades, a number of novel-structured porous solid physical adsorbents based on metal-organic frameworks (MOFs) [30], ordered mesoporous silica [31], zeolites [32], carbon-based materials (activated carbons, pyrogenic carbons, metal-carbon composites, carbon nanomaterials) [26,27], and microporous organic polymers (MOPs) [33] have emerged and are used as CO_2 adsorbents, showing high CO_2 capture capacity. MOPs, less frequently called with the more general, accurate name of porous organic polymers (POPs) [34] have been receiving considerable attention due to their exceptionally high porosity, chemical stability, versatility, functionalization possibilities [24]. Among the MOPs, different families have been synthesized over the past years and they include: hypercrosslinked polymers (HCPs) [35], conjugated microporous polymers (CMPs) [36], polymers of intrinsic microporosity (PIMs), [37] porous aromatic frameworks (PAFs) [38], porous polymer networks (PPNs) [39,40], covalent organic frameworks (COFs) [34]. MOPs are usually networks of polymeric chains packed together in a disordered open porous configuration and their synthesis commonly requires expensive catalysts and multistep synthetic methologies [4]. Moreover, although MOPs have been extensively studied for H_2 and CH_4 storage, only few reports have been published about their CO_2 capture [41,42]. However, each material has advantages and disadvantages and the quest for outstanding sorbents is still a growing, fast-paced, area of research [16]. Of the outmost importance is the regeneration energy of the sorbent, which is the economic key to the commercial application of the technology [4]. Polyesters are a class of biodegradable polymers characterized by the presence of ester moieties, along the chain, responsible of their high affinity towards CO2. Due to a plethora of monomers and a wide range of polymerization design and techniques available, it is possible to tune their mechanical, chemical and thermal properties, allowing these polymers to be extensively used in various fields: electronics, biomedical applications, drug-delivery, packaging, 3D printing, tissue engineering [43–48]. One of the most interesting things of polyesters is that they are, differently from most if not all MOPs, already commercially available.

Poly(ε-caprolactone) (PCL) is a sustainable semicrystalline polyester, easily synthesized by ring-opening polymerization of ε-caprolactone, largely used as resorbable/biocompatible polymer in the medicinal, materials and tissue engineering fields [49,50]. Its economicity, long-term degradation (compared to other polyesters, up to 3–4 years), biological and environmental friendliness, CO_2-philicity and low melting point transition (~60 °C) make it a very interesting candidate to be studied as carbon capture low temperature adsorbent [50]. Therefore, solubility and diffusivity data of CO_2 in PCL are important parameters for understanding the gas-polymer interactions and are retrievable from literature [51–54]. However, these values are generally determined for a wide range of temperatures and pressures using the gravimetric techniques and permeation curve respectively and they might be affected by several critical aspects that may be source of error [55,56]. Several papers have reported investigations of CO_2 sorption by PCL, but were performed either at high pressure (above 100 bar) [57–60] or only on the melted polymer (above 70 °C) [53,54,61–63]. To the best of our knowledge, no research was reported on the CO_2 sorption by PCL at room temperature (RT) and low pressure. Furthermore, there is a lack of knowledge on the effect on sorption in the transition from the solid to the molten polymer. We faced this study by two different and complementary techniques: an isothermal gas adsorption study using a Sievert-type (volumetric) apparatus at RT and in the range of $0 \div 15$ bar (solid polymer conditions) and the pulse field gradient (PFG) Nuclear Magnetic Resonance (NMR) spectroscopy. Concerning the latter method, it is a powerful and non-invasive spectroscopic technique that allows the direct measurement of the self-diffusion coefficients, D. Here it was used to measure the diffusion of CO_2 absorbed in the polymer, in the 20–60 °C temperature range i.e. from solid to molten polymer condition. Generally, this technique is employed for studies of molecular dynamics of fluids, such as water, in bulk or confined geometries [64–67], while literature on the gas diffusivity in nanostructured materials or composite membranes is rather scarce [56,68,69]. Confinement effects and molecular interactions with the polymer greatly influence the mobility of the gas molecules, and these PFG-NMR measurements have allowed to reveal two physical states of CO_2, associated with two diffusion coefficients. Finally, we investigated the regeneration effect also via Scanning Electron Microscope (SEM) on the recovered polymer.

2. Experimental section

2.1. Materials

Poly(ε-Caprolactone) (Mw = 80,000 Da, pellets) is a biodegradable polyester with a low melting point of around 60 °C and a glass transition temperature of about −60 °C, and was purchased from Sigma-Aldrich. For NMR study we used $^{13}CO_2$ (high purity carbon dioxide, 99% ^{13}C isotopic enrichment) purchased from Sigma-Aldrich.

2.2. Morphological study

Scanning electron images were collected employing a Quanta FEG 400 (FEI) Scanning Electron Microscope (SEM) equipped with Fast Fourier Transform (FFT) bandpass filter and using an electron beam in the range 2.0–15.0 keV in order to obtain typical morphological information. The PCL sample was manually cracked and the corresponding internal surfaces were observed.

2.3. CO_2 adsorption/desorption measurements

The CO_2 adsorption/desorption measurements were carried out at RT (~$21 \div 25$ °C) and in the $0 \div 15$ pressure range bar by using an