Journal of CO_2 Utilization 28 (2018) 107–116

Contents lists available at ScienceDirect

Journal of CO_2 Utilization

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

Molecular simulation aided design of copolymer thickeners for supercritical CO_2 as non-aqueous fracturing fluid

Baojiang Sun[a,*], Wenchao Sun[a,b], Haige Wang[b], Ying Li[c], Haiming Fan[a], Hao Li[a], Xiuping Chen[d]

[a] School of Petroleum Engineering, China University of Petroleum, Qingdao, 266580, China
[b] Engineering Technology Research Institute Company Limited of China National Petroleum Corporation, Beijing, 102206, China
[c] Key Laboratory of Colloid and Interface Chemistry of China's Ministry of Education, Shandong University, Jinan, 250100, China
[d] Study Institute of Oil & Gas Engineering, Tarim Oilfiled, PetroChina, Korla, 841000, China

ARTICLE INFO

Keywords:
Non-aqueous fracturing
Supercritical CO_2
Viscosity enhancement
Copolymer thickener
Molecular simulation

ABSTRACT

Molecular modeling of CO_2-polymer system was established to study the molecular behaviors and intermolecular interaction of copolymers in supercritical carbon dioxide (SC-CO_2) by all-atom molecular dynamics (MD) simulation. According to the simulation results, the correlations of the intermolecular interaction with the molecular structure and composition were explored. The effects of intermolecular interactions on the copolymer properties in SC-CO_2 were identified. A series of copolymers were synthesized with CO_2-philic monomer 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptadecafluorodecyl acrylate (HFDA) and CO_2-phobic monomer vinyl n-Octanoate (VOc), vinyl acetate (VAc), vinyl pivalate (VPi), respectively. The solubility and viscosification of the copolymers in SC-CO_2 were evaluated by cloud point pressure and relative viscosity measurements. It was found that P($HFDA_{0.49}$-*co*-$VAc_{0.51}$), which is the most effective thickener among the copolymers, could enhance the viscosity of SC-CO_2 by 62 times at 5 wt%. It was suggested that the thickening capability of the copolymers in SC-CO_2 may originate from intermolecular cross-links generated by associative groups. Combining the molecular simulation and experiment results, the structure-activity relationships of the copolymers in SC-CO_2 were revealed. It is believed that the molecular simulation aided design method for the SC-CO_2 copolymer thickener is reliable.

1. Introduction

The shale gas revolution brought by hydraulic fracturing technology has affected the oil & gas industry deeply. However, the environmental problems of water-based fracturing fluids, such as water shortage, drinking water pollution and flow-back water treatment, have caused more and more worries [1]. As an environment friendly solvent, supercritical carbon dioxide (SC-CO_2) has been used in many industrial processes [2,3]. In the exploitation of shale gas, SC-CO_2 has been considered to be a non-aqueous fracturing fluid with the potential to replace water [3–5]. Middleton and colleagues put forward that the advantages of SC-CO_2 fracturing include the avoidance of pore clogging caused by the expansion of clay minerals, the reduction of environmental problems caused by flow-back water, the wider fracture network [1,5]. Meanwhile, owing to its stronger interaction with the shale kerogen compared to CH_4, CO_2 could be used to exchange the CH_4 to enhance natural gas recovery and absorbed in the shale reservoir [5,6]. In addition, CO_2 is easy to return from the reservoir and be recovered after depressurization, the post-processing could be simplified [6–9]. CO_2 geological storage could be realized during this progress. The micro-cracks produced by SC-CO_2 fracturing could offer vast CO_2 storage potential. It was reported [1] that one shale gas well could absorb and store about $4.8 \times 10^5\ m^3$ of CO_2 under the reservoir pressure. Developing shale gas with CO_2 captured from industrial flue gas maybe a realistic choice of achieving carbon capture, utilization and storage to slow down the greenhouse effect [1,4,5,10], as shown in Fig. 1.

As fracturing fluid, one of the core functions of CO_2 is to transport the proppants into the fractures to prevent fracture closure, which was also illustrated in Fig.1. The low viscosity is the key issue of limiting the promotion of SC-CO_2 fracturing technology [1,2,10]. To make CO_2 an effective fracturing fluid, thickening agents are necessary to be added to enhance its viscosity and proppant carrying capability.

According to previous studies, small molecules were believed to be unable to thicken CO_2 effectively [11,12]. For polymers, the problem of their low miscibility with CO_2 must be solved by designing specific molecular structure [13,14]. Enick et al. [15,16] demonstrated that the

* Corresponding author.
E-mail address: sunbj1128@126.com (B. Sun).

https://doi.org/10.1016/j.jcou.2018.09.015
Received 17 December 2017; Received in revised form 31 July 2018; Accepted 20 September 2018

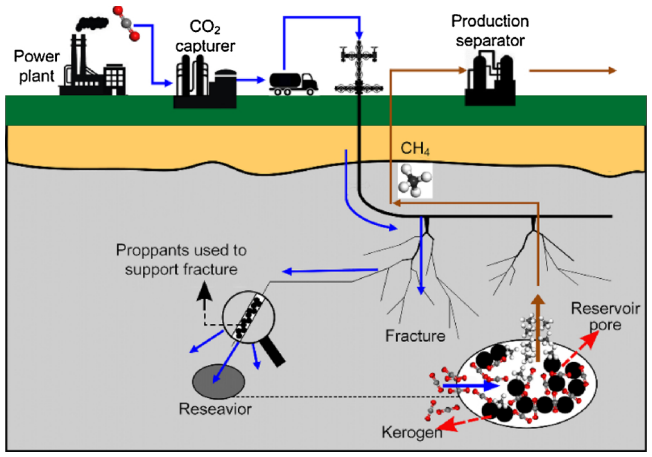

Fig. 1. Schematic industrial process of achieving carbon capture, utilization and storage in shale gas exploitation: SC-CO_2 fracturing, the displacement of CH_4 by CO_2 and the storage of CO_2 in shale. The blue arrow indicates the flows of CO_2 and the brown arrow indicates the flows of CH_4 (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

introduction of carbonyl group could improve the solubility of polyether in CO_2, and studied the effects of carbonyl group position. The advantages [17] of fluoropolymers in chemistry, thermodynamics and low surface energy make them used in optical waveguides, microelectronics and low-energy surfactants widely. Destarac and Marty et al. [18–21] have studied the relationship between fluoro-copolymer composition and the solubility in CO_2, exploring the role of intermolecular interactions and the entropy of mixing. Howdle et al. [22–25] pointed out the significant effect of the polymer-polymer interaction on the CO_2-phility of polymer. Fried et al. [26] have identified the specific interactions between CO_2 and the fluorinated groups in the polymers using ab initio molecular orbital calculations, and suggested that the dipole-quadrupole interaction played an important role in the intermolecular interaction. Wang et al. [27,28] have attempted to design new CO_2-philic materials by the ab initio modeling, but the experiment results do not fit with the computation results, since this modeling ignores the polymer-polymer interaction, temperature, entropy and structural effects.

On the other hand, polymers with good solubility in CO_2 do not always enhance the viscosity to a high degree. For example, the homopolymer Poly(fluorinated acrylate) only could thicken CO_2 to a low degree [29]. Enick and Beckman et al. [30–32] reported the thickening capabilities of the copolymers synthesized by HFDA and styrene, which could increase the viscosity of CO_2 at a high degree. They proposed that the copolymers containing CO_2-phobic groups may be able to thicken CO_2 effectively by π–π stacking, hydrogen bond or solvophobic interaction. The amphiphilic copolymer may be a kind of thickener for SC-CO_2 with potential. Compared to ab initio modeling, all-atom molecular dynamics simulation (MD) is an effective mean of designing polymer with special function, and has been used to design CO_2-philes. Liu and Hu et al. [33–35] have established the all-atom molecular modeling of the CO_2-polymer systems, such as CO_2-Poly (vinyl acetate), CO_2-Poly(vinyl acetate-alt-maleate), CO_2-Poly(vinyl acetate-CO-alkyl vinyl ether). They studied the phase behavior of the systems argued that, reducing the polymer-polymer interaction while maintaining the polymer-CO_2 interaction might be a promising strategy to improve the CO_2-phility of the polymer. To date little research about thickening mechanism of polymer in SC-CO_2 studied by all-atom MD simulation has been reported.

This paper aims to provide the method of selecting effective thickener from the alternative samples, by which the molecular simulation aided design could be realized and the ineffective experiment test could be reduced. The copolymers of CO_2-philic monomer HFDA with CO_2-phobic monomer VPi, VOc and VAc are taken as the research objects to study of structure-activity relationship. By investigating the intermolecular interaction energy, equilibrium conformation, radial distribution function (RDF), cohesive energy density (CED) and solubility parameter, the solubility and thickening capability of the copolymer in SC-CO_2 was identified. Six copolymers with different compositions were synthesized. The chemical structures of the copolymers were characterized by ^{1}H NMR. The cloud point pressures and the thickening effects of these copolymers in SC-CO_2 were measured. By examining the major factors impacting the solubility and the viscosification, the roles of associative groups and the structure-activity relationships of the copolymers in SC-CO_2 were revealed.

2. Computational section

The copolymers simulated in this paper were named P(HFDA$_a$-*co*-VOc$_x$), P(HFDA$_b$-*co*-VOc$_y$) and P(HFDA$_c$-*co*-VPi$_z$), respectively. The 'x', 'y', 'z' means the molar ratio of VOc, VAc, VPi in copolymers, respectively. The 'a'–'c' means the molar ratio of HFDA in the three kinds of copolymers, respectively. All the systems were simulated in COMPASS force field, which could predict the molecular structure, conformation, vibration and thermodynamic properties of condensed molecules accurately. The bond parameters of the molecule were calculated by ab initio calculation and the parameters of van der Waals non-bonding were calculated by the empirical method [36]. The all-atom molecular models of the CO_2 system with 2000 CO_2 molecules, the polymer systems with eight polymer chains and the polymer-CO_2 systems with eight polymer chains and 2000 CO_2 molecules was established by using the Material Studio package, as shown in Fig. 2.

The simulation boxes with different compositions were listed in Table 1. After the optimizations and the annealing calculations in the Forcite module, the MD simulations of the systems constructed by Amorphous Cell module were performed in NPT ensemble. The pressure was set to 25 MPa and the temperature was set to 308.2 K. The

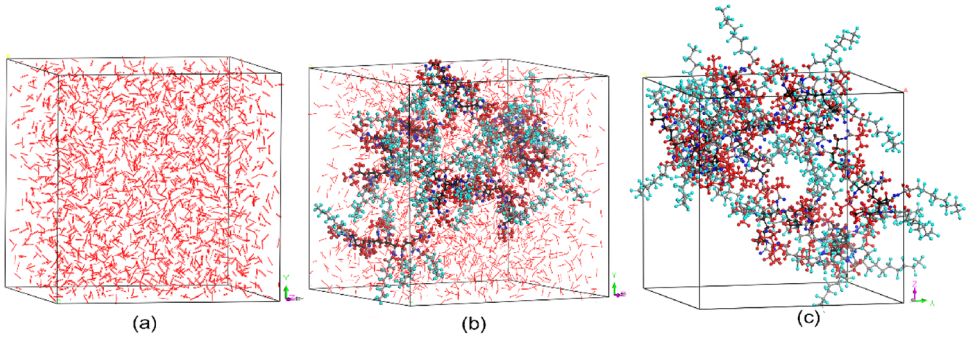

Fig. 2. Three kinds of systems established by all-atom molecular model. (a) the CO_2 system with 2000 CO_2 molecules; (b) the polymer-CO_2 systems with eight polymer chains and 2000 CO_2 molecules; (c) the polymer systems with eight polymer chains.