Journal of CO_2 Utilization 27 (2018) 289–296

Contents lists available at ScienceDirect

Journal of CO_2 Utilization

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

Surface wettability of supercritical CO_2 - ionic liquid processed aromatic polyamides

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ARTICLE INFO

Keywords:
Aromatic polyamides
Modification
Supercritical CO_2
Ionic liquid
Wettability

ABSTRACT

Wettability of aromatic polyamides (aramids) was investigated after exposed to the binary system of 1-Butyl-3-methylimidazolium hexafluorophosphate and supercritical CO_2, which was performed at a pressure of 30 MPa for 60 min by varying the treatment temperature between 80 °C and 120 °C. Dynamic contact angle analysis for the original and treated aramids was conducted to determine the correlation between the surface treatment and the polymer wettability. It is confirmed that the water contact angles for aramids were reduced significantly from 139.8° to 83.0° in the supercritical CO_2-ionic liquid systems, and the hydrogen bonding structure between the amide linkages in aramids and the PF_6^- in [BMIM][PF_6] was proved to form, which is conducive to the improvement of wettability. SEM observations revealed more and more pleat-like wrinkles appeared on the surface of aramid, accompanied by the notable fiber swelling in the supercritical CO_2-ionic liquid systems. In addition, XRD and TG analysis indicated that the crystallinity and the maximum decomposition temperatures of aramids were decreased gradually with ionic liquid treatment while those of aramids were increased with the temperature rising by adding ionic liquid in supercritical CO_2. Overall, this proves to be an more effective and ecofriendly approach for aramid modification by supercritical CO_2-ionic liquid systems.

1. Introduction

Aromatic polyamides (aramids) are one of the most important high performance polymers, and have attracted increasing commercial and academic interest because of the outstanding properties, such as low density, high strength, excellent thermostability and flame resistance [1,2]. Thus, aramids are widely used in the field of aerospace, automotives and textiles [3,4].

However, some drawbacks also present in the application processes of aramids due to the hydrophobic and chemically inert surface by the hydrogen-bond interactions of amide groups in polymer macromolecule [5]. Extensive investigations have been conducted and various techniques have been developed to improve the interfacial properties of aramid fibers. These studies mainly focused on chemical treatment [6,7], plasma discharge [8–10], ozone irradiation [11], ultrasonic treatment [12], and other modification methods. Wang reported a grafting modification approach for meta-aramid by using bioinspired dopamine self-oxidative polymerization and epoxy functionalized silane KH560, and found that the interfacial adhesion between fibers and rubber was improved by 62.5% [13]. Yin investigated a continuous online aramid modification method by employing air DBD plasma, and demonstrated that the oxygen/carbon atomic ratio of polymer is enhanced from 15.99% to 27.15% due to the implantation of oxygen-containing groups [14]. Although the above modification methods improve the interfacial properties of fibers through chemical grafting or physically etching, they are rarely used in practice because of the stringent reaction conditions and complicated work procedures. Development of new technologies to improve the wettability of aramid is becoming the primary goal for researchers [15,16].

Supercritical CO_2 fluid technique has achieved considerable progress during the past few years, which displays the characteristics of water free and energy preserving [17–19]. At present, employing supercritical CO_2 instead of water and other solvents has been revealed to be potential for the surface modification of materials as supercritical CO_2 offers the advantages of excellent plasticity and high diffusivity to polymers [20–22]. Zheng investigated the effect of supercritical carbon dioxide on the surface morphology changes of yak hairs, and observed remarkable etching effect was generated on the covering scales of fibers at high temperature and pressure because of the hydrolysis to the disulfide bonds in cystine [23]. Sumita analyzed the crystallization properties of PLLA/PMMA under high-pressure CO_2, and found that crystallization behavior of PLLA/PMMA can occur even at 0 °C, accompanied by three times larger strain at break than the amorphous and cold-crystallized film [24].

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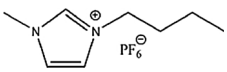
https://doi.org/10.1016/j.jcou.2018.08.006
Received 5 May 2018; Received in revised form 21 July 2018; Accepted 9 August 2018

Table 1
The ionic liquid used in supercritical CO_2.

Ionic liquid	Formula	Molecular weight	Chemical structure
[BMIM][PF_6]	$C_8H_{15}F_6N_2P$	284.18	

This work aimed to develop an more effective and ecofriendly approach for aramid modification. An hydrophobic ionic liquid, 1-Butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF_6]), has been applied to the modification process of aramid under supercritical CO_2 condition. The wettability of aramid was evaluated by the static water contact angle measurements and was related to surface morphology of fibers. Moreover, the chemical composition, crystalline structure and thermal stability of the aramid were also measured by Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD) and Thermogravimetric (TG) analysis.

2. Experimental

2.1. Materials and supercritical carbon dioxide treatment

Meta-aramid supplied by Dandong Unik Textile Co., Ltd. (China) was used in this study. The fabric weight is 220.0 g/m^2. [BMIM][PF_6] was purchased from Energy Chemical Co., Ltd. (China), and its chemical structures is shown in Table 1. The analytical reagent grade acetone was purchased from Tianjin Kemiou Chemical Reagent. To remove the waxes and oils on fiber surface, aramid samples were cleaned with acetone at room temperature for 20 min, and they were then dried by employing an air oven at 100 °C for 30 min.

The scoured aramid were dipped into [BMIM][PF_6] for 5–10 min, making its liquid rate 100%. After that, the fabrics were fastened onto a porous distributor which was positioned into a treatment vessel (6) during modification process. CO_2 gas in a cylinder (1) was purified firstly through a filter (2), and was liquefied using a refrigerator (3). The liquid CO_2 was injected into the treatment vessel by employing a syringe pump (4). At the same time, CO_2 was heated by employing a heat exchanger (5) to tune fluid into supercritical state. When the request condition was reached, aramid fabrics in the treatment vessel were treated at a pressure of 30 MPa for 60 min with different temperatures. During the experiments, system pressure was regulated by an electric back pressure valve (8), and [BMIM][PF_6] was separated from CO_2 gas in a separator (7). Decompression operation was conducted by adjusting the relief valves after the treatment process was finished, and the obtained aramid fabrics were removed for further analysis. In addition, aramid samples with a liquid rate of 100% were treated at 80 °C, 100 °C and 120 °C in an oven for 60 min to compare with those samples treated in supercritical CO_2. A schematic diagram of the treatment apparatus was shown in Fig. 1.

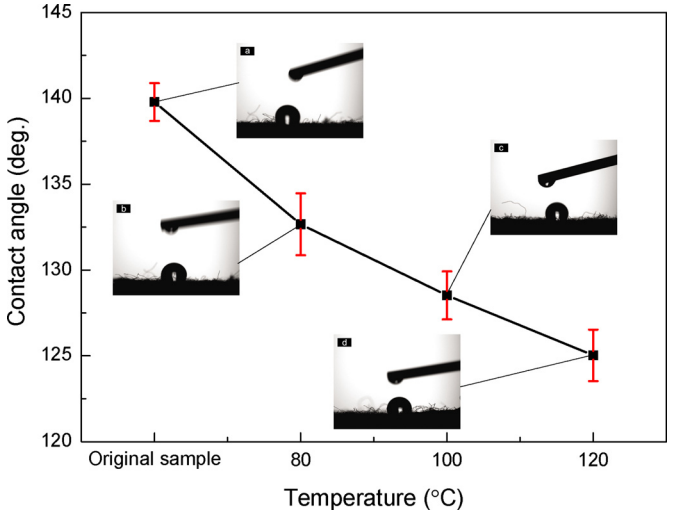


Fig. 2. Contact angles of the original aramid (a), and treated at 80 °C (b), 100 °C (c), and 120 °C (d) in supercritical CO_2.

2.2. Characterization

The surface wettability of aramid was observed by employing a DCA-322 W contact angle meter (Thermo Cahn, USA) by measuring the static water contact angle. The aramid samples were firstly placed on a sample stage, and a drop of deionized water was deposited on the fabric

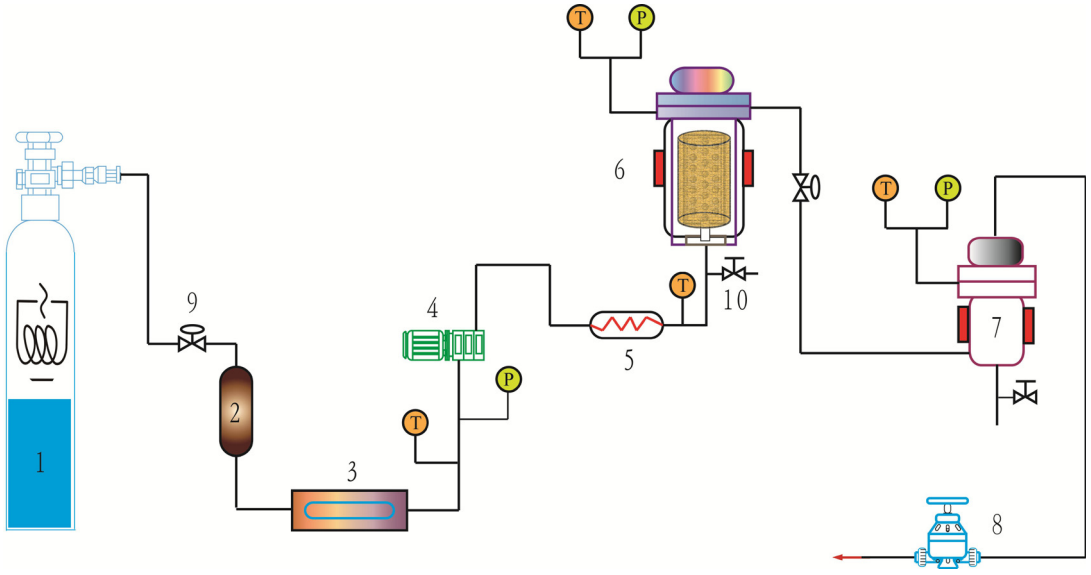


Fig. 1. Schematic diagram of the supercrtical CO_2 fluid apparatus.
(1) CO_2 cylinder, (2) Filter, (3) Refrigerator, (4) Syringe pump, (5) Heat exchanger, (6) Treatment vessel, (7) Separator, (8) Electric back pressure valve, (9–10) Relief valve.