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Swelling behavior of polyester in supercritical carbon dioxide

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ABSTRACT

The present study aimed to investigate the effects of different supercritical CO_2 conditions on the swelling of polyester. We employed a Box-Behnken design to discuss three variables governing the polymer swelling: system temperature, system pressure and treatment time. The obtained results showed that the system temperature and pressure played significant influence on the swelling of polyester samples. The second-order polynomial formula developed provided accurate predictions for the experimental data, with coefficient of determination R^2 0.9938. The theoretical maximum for the swelling of polyester was 0.725 mm under the optimum treatment condition with a system temperature of 140 °C, a system pressure of 26 MPa and a treatment time of 60 min. In addition, it is proposed that the swellability of polyester was dependent upon the polymer plasticization in supercritical CO_2 and the intermolecular interactions between the CO_2 and the carbonyl groups in polyester.

1. Introduction

Industrial and academic researchers have shown convincingly that CO_2 can be used as a green dyeing medium instead of water in textile dyeing due to the significant economical and ecological benefits, such as nontoxicity, nonflammability, low energy consumption, no water consumption, and recyclability [1–3]. In supercritical state, CO_2 displays numerous unique properties, for example, high diffusivity and solubility, zero surface tension, and almost no risk of heat deformation with relatively low critical temperature and pressure [4,5].

In recent years, great interest was given to the dyeing of synthetic fibers in supercritical CO_2 with the aim to achieve their eco-friendly production by manipulating the dyeing temperature, pressure and time [6–8]. During supercritical dyeing process, CO_2 fluid near or slightly above its critical points (T_c = 31.10 °C, P_c = 7.38 MPa) produces substantial polymer swelling because of the dissolution of CO_2 in polymers [9]. This provides a good possibility to control the dyeing quality of polymer since the swelling of fibers is directly connected with their dyeability. Therefore, the swelling behavior of polymers in supercritical CO_2 is the emphasis of current research.

To probe polymer swelling under supercritical CO_2 state, interferometric dissolution rate monitor was used by C. Ober, and estimated that the maximum swollen film thickness for tetrahydropyranyl methacrylate was 35 mol% at 45 °C for pressures ranging from 12.8 MPa to 19.7 MPa [10]. K. P. Johnston measured the swelling of a 50 nm monodisperse polystyrene latex by dynamic light scattering at 25 °C at pressures up to 35 MPa, and found that the polystyrene (PS) latex swelled by up to 1.6 times as much as bulk PS at the higher pressures [11]. T. Tassaing investigated the polymer swelling in situ at 40 °C from 2 MPa to 15 MPa by employing an FT-IR microscope, and determined the swelling of polyethylene oxide was highly dependent on the polymer crystallinity [12]. A. Gibaud reported the swelling properties of confined poly(n-butyl methacrylate) (PBMA) films at 8 MPa and 35 °C using X-ray reflectivity technique, and found that PBMA films exhibited a greater amount of swelling than do PS films (bulk $T_g \approx 100$ °C) owing to the lower glass-transition temperature (bulk $T_g \approx 29$ °C) [13]. It is also proved that Associated Lattice Fluid Equation of State (ALF EOS) is able to predict the extent of swelling of the polymer due to CO_2 using a single parameter obtained from one solubility isotherm [14]. In addition, R. Dohrn summarized the experimental high-pressure phase-equilibrium data in the periods between 2000 and 2008, which provided essential references for the solubility (sorption) of volatile components in polymers [15,16]. However, to date, swelling data of polymers at higher CO_2 temperatures and pressures are rather rare, although they are directly related to the fibers' dyeability in supercritical CO_2.

The current study aims to develop an in situ visible method for polyester swelling in supercritical CO_2. The effects of major process parameters including temperature, pressure, and time on the swelling of polyester were studied using the response surface methodology. A swelling model for polyester in supercritical CO_2 was established, and its effectiveness was validated. Furthermore, swelling mechanism of

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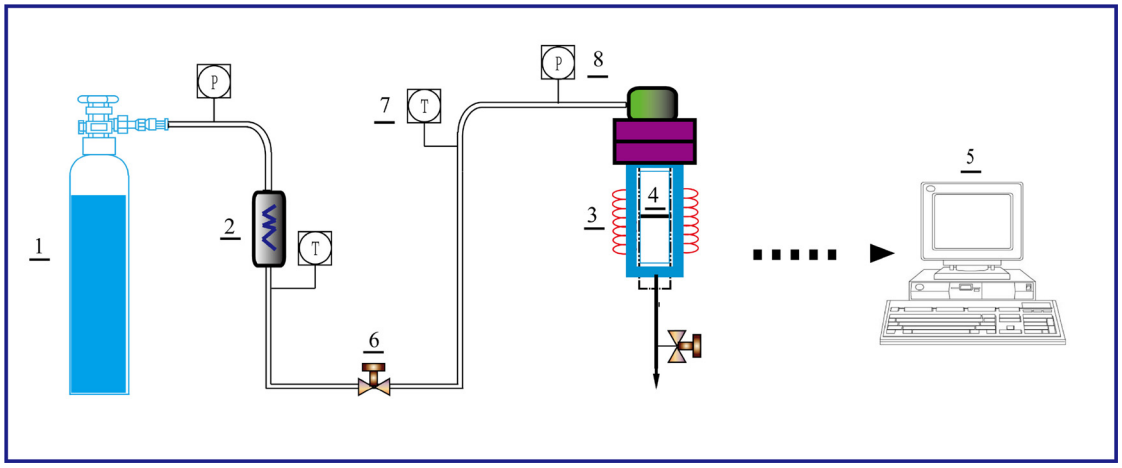

Fig. 1. Schematic representation of the supercritical CO_2 apparatus used for the swelling measurement: (1) CO_2 reservoir; (2) filter; (3) heater; (4) high pressure chamber; (5) control terminal; (6) micrometering valve; (7) temperature gauge; (8) pressure gauge.

polyester in supercritical CO_2 was also proposed.

2. Experimental

2.1. Materials

Polyester yarns (0.47 mm) in this study were obtained from Liaoning Chaoyi Industry & Trade Group (Fuxin, China). CO_2 gas was purchased from China Haohua (Dalian) Research & Design Institute of Chemical Industry Co., Ltd., with a purity of 99.90%.

2.2. Swelling detection

Swelling of polyester was analyzed and detected optically inside a phase equilibria apparatus (T_{max} = 140 °C, P_{max} = 40 MPa) purchased from Waters in USA. Schematic representation of the supercritical CO_2 apparatus is presented in Fig. 1. Polyester was fixed on a shelf, and loaded into a high pressure chamber. The chamber was sealed and CO_2 in a reservoir was discharged through a syphon, and filtered with a filter to remove the impurities. The liquid CO_2 was then injected into the high pressure chamber to increase system pressure. The system temperature was controlled by a heater rolled around the chamber to make CO_2 reach supercritical state. During test, the system pressure and temperature in the chamber were regulated within 0.1 MPa and 0.1 °C.

Polyester diameter change in supercritical CO_2 because of swelling was observed in situ through the high pressure view chamber equipped with a monochromatic light source and a CCD video camera, as displayed in Fig. 2. A halogen lamp connected with an optical fiber was located in a sapphire window to illuminate the interior of the chamber. Digital pictures of the polyester yarns under different supercritical CO_2 conditions were recorded using the CCD video camera in order to calculate the swelling data.

2.3. Experimental design and analysis

A class of the Response surface methodology (RSM) called Box-Behnken design was employed for investigating the supercritical CO_2 experiments to ascertain the effect of the three independent parameters including system temperature, system pressure and treatment time on the swelling of polyester. The optimum ranges of system temperature (100–140 °C), system pressure (22–26 MPa) and time (30–60 min) were determined according to our preliminary experiments [7]. A 3^3 full factorial design is generated as shown in Table 1. To express the swelling data as a function of the independent variables, a second-order polynomial equation (Eq. (1)) was used as follows [17]:

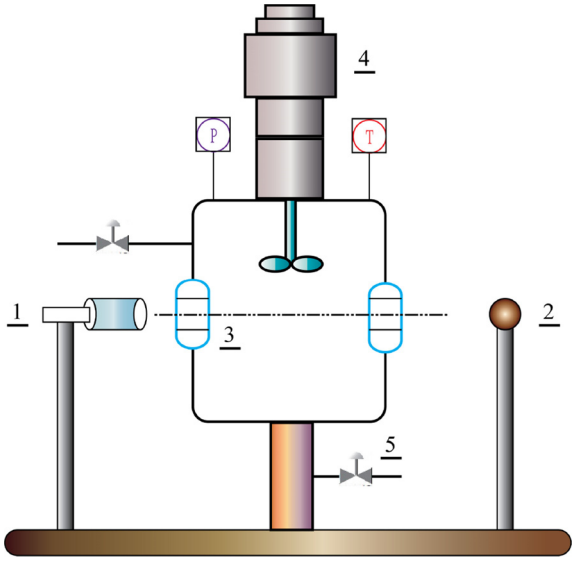

Fig. 2. Schematic representation of the high pressure chamber in supercritical CO_2 apparatus: (1) CCD camera; (2) light source; (3) visible window; (4) magnetic stirrer; (5) gas pipeline.

Table 1
Variables and levels in the 3^3 design.

Symbol	Factor	Level 1	Level 2	Level 3
X_1	Temperature (°C)	100	120	140
X_2	Pressure (MPa)	22	24	26
X_3	Time (min)	30	45	60

$$Y = \beta_0 + \sum_{i=1}^{n} \beta_i x_i + \sum_{i=1}^{n} \beta_{ii} x_i^2 + \sum_{i=1}^{n} \sum_{j=2}^{n} \beta_{ij} x_i x_j + \varepsilon \quad (1)$$

where x_i, x_j are the independent variables; Y is the predicted response value; β_0, β_i, β_{ii}, β_{ij} are the regression coefficients for intercept, linear, quadratic and interaction effect, respectively; ε is the random error, and n is the number of variables.

The three independent experimental parameters were assigned as X_1 (temperature, °C), X_2 (pressure, MPa) and X_3 (time, min). The variables and levels in the 3^3 design were listed in Table 1. A second-order polynomial model containing these three independent variables was established as follows (Eq. (2)):