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An investigation of the interaction of supercritical carbon dioxide with poly(ethylene terephthalate) and the effects of some additive modifiers on the interaction

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Abstract

In order to investigate the interaction between supercritical carbon dioxide ($scCO_2$) and poly(ethylene terephthalate) (PET) and the effect on this interaction of some additive modifiers such as alcohols, the swelling behaviors of PET in $scCO_2$/modifier systems were examined. A special apparatus equipped with two observation windows was constructed. The change in the dimension of the PET yarn in the $scCO_2$/modifier was monitored using a CCD camera pointing through one of the windows. It was confirmed that the swelling of PET due to $scCO_2$ is accompanied by the crystallization of PET, but the crystallization induced by $scCO_2$ can be prevented by adding specific modifiers to the fluid. The equilibrium swelling of PET in $scCO_2$/modifier increased as the solubility parameter of the fluid approached to the solubility parameter of PET.

Keywords: Supercritical carbon dioxide; Poly(ethylene terephthalate); Crystallization; Swelling; Cosolvent effect

1. Introduction

Supercritical fluid is defined as a substance existing above its critical temperature and pressure. Supercritical fluid is a highly compressed fluid, which has properties typical of both gas and liquid [1]. The density of the fluid can be controlled over a wide range by changing the temperature and pressure conditions. Therefore, the solvent property of the fluid, which depends on the density of the fluid, can be also controlled [2,3]. In addition to these properties, $scCO_2$ has the capacity to plasticize hydrophobic polymers. The sorption of CO_2 into the polymer results in the swelling of the polymer, causing changes in the mechanical and physical properties of that polymer [4].

Thus, $scCO_2$, which has such advantageous properties as compared to conventional solvents, has been used in the extraction industry for many years, e.g., for extracting caffeine from coffee or essential hop oil from hops. On the other hand, $scCO_2$ has been receiving wide attention due to its wide potential application in several fields of polymer processing, such as impregnation, foaming, dyeing and so on, in addition to the environmental benefits [4]. The advantage of almost all of these new technologies, as compared to the conventional polymer processing technologies, is due to the plasticizing capacity of $scCO_2$, in addition to the properties peculiar to supercritical fluid [4]. Therefore, to fully exploit $scCO_2$ in these new technologies, it is important to understand how $scCO_2$ interacts with materials and to investigate the ways in which materials can be plasticized in $scCO_2$. In investigating a polymer/$scCO_2$ system, it is important to study the kinetics of CO_2 sorption into the polymer and the structural changes in the polymer induced by $scCO_2$.

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PET is industrially one of the most important candidates for $scCO_2$ processing. As such, the swelling of PET and the changes in its mechanical and physical properties in $scCO_2$/PET systems have been reported previously [5–10]. According to these reports, PET swells by absorbing CO_2 molecules and is then plasticized in $scCO_2$; this results in a reduction of the glass transition temperature and the promotion of its crystallization, among other things.

On the other hand, it has been reported that the solvent property of $scCO_2$ is drastically changed by the addition of a small amount of polar solvent as a modifier [11–13]. For example, it is reported that the solubility of disperse dyes in $scCO_2$ is significantly increased by the addition of a small amount of ethanol or acetone, due to the increase in the affinity between the disperse dye and $scCO_2$ [11]. The effect of the addition of the modifier can be considered to apply to polymers as well as to disperse dyes in $scCO_2$. The solubility of CO_2 in the polymer will increase if a small amount of organic solvent is added to $scCO_2$ as a modifier, because the addition of the modifier leads to an increase in the affinity between a polymer and $scCO_2$. Thus, the polymer-plasticizing capacity of $scCO_2$ is expected to increase if a modifier is added to $scCO_2$.

In this study, the interaction between $scCO_2$ and PET and the effects of some additive modifiers such as an alcohol to the $scCO_2$/PET system were investigated by measuring the amount of swelling of the PET. The swelling behavior and the structural changes in PET immersed in $scCO_2$ were investigated under various conditions.

2. Experimental

2.1. Materials

PET fibers were used to investigate the interaction with $scCO_2$ and the effects of various modifiers. Undrawn gut yarns with a diameter of 2.05 mm and containing titanium dioxide were supplied by Toray Industries, Inc. The carbon dioxide gas used in all of the experiments was purchased from Uno Sanso Co., Ltd. (99.5% pure). Several organic solvents were used for modifying the solvent property of $scCO_2$; all of them were guaranteed-grade reagents from Nacalai Tesque, Inc.

2.2. Methods

2.2.1. Measurement of the swelling

A schematic diagram of the apparatus used for measuring the swelling behavior of PET is shown in Fig. 1. The pressure vessel has two sapphire glass windows to allow observation inside the vessel. In all experiments, the gut yarn, 2.05 mm in diameter and about 40 mm in length, was suspended in the sample holder in the vessel. The length and diameter of the gut yarn were measured to within 0.05 mm with a caliper square.

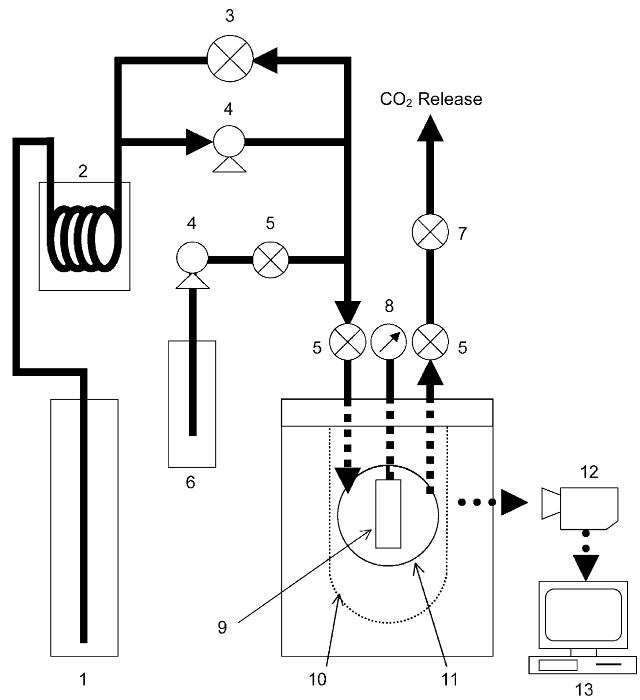

Fig. 1. Schematic diagram of the experimental equipment used for measuring the swelling of the PET samples: (1) CO_2 cylinder, (2) cooler, (3) back pressure valve, (4) pump, (5) stop valve, (6) modifier cylinder, (7) flow control valve, (8) pressure gauge, (9) sample holder, (10) high-pressure vessel, (11) observation window, (12) CCD camera and (13) personal computer.

The system was evacuated with a vacuum blower. After the evacuation, to render the temperature inside the vessel stable and uniform, the vessel was heated to the measurement temperature and the temperature was held there for 2 h. Carbon dioxide was then introduced, and the desired pressure was maintained. If a modifier was added to the system, an organic solvent was injected into the vessel after the introduction of the carbon dioxide. In case the pressure in the vessel decreased slightly due to the mixing of CO_2 and the organic solvent, both CO_2 and the organic solvent were newly injected into the vessel at the given ratio, in order to ensure a constant pressure inside the vessel. The beginning of the measurement of the swelling of PET ($t = 0$) was defined as the moment at which carbon dioxide started to be introduced into the vessel. A CCD camera took enlarged pictures of the sample in the vessel through the observation window at regular intervals for 27.8 h; these images were then imported into a personal computer. Finally, the change in dimension of the sample as a function of time was determined to a precision of $\pm 20\,\mu m$ based on enlarged pictures of the sample. The change in yarn length and diameter gave almost the same percentage values. However, the measurement error of the change in the yarn diameter was too large (within ca. 20%) to evaluate. We assumed that the swelling of the undrawn PET gut yarn was isotropic, and therefore only the change in yarn length was followed. Assumptions like this for the undrawn gut yarn can be found in other research papers [14].