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Temperature effect on water desorption from methylcellulose films studied by thermal FT-IR microspectroscopy

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Abstract

Temperature-induced desorption behavior of water from methylcellulose (MC) film was investigated by a novel microscopic Fourier transform infrared (FT-IR) spectroscopy equipped with thermal analyzer (thermal FT-IR microscopic system) and thermogravimetric analysis (TGA). The result indicates that the weight loss of water from MC film was markedly correlated to the IR spectral changes of OH stretching (3000–3800 cm^{-1}) and bending (1649 cm^{-1}) modes of water molecules. The shift of OH stretching mode from 3461 to 3481 cm^{-1} was accompanied with the water loss from MC film induced by temperature effect. Two stages of water desorption from MC film were proposed: the first stage within the 35–65 °C had a dramatic IR peak shift from 3461 to 3477 cm^{-1} and accompanied with a largest weight loss of water from MC film, which might be mainly due to the desorption of free water with minor weakly hydrogen-bonded water; the second stage beyond 65 °C would be desorption of moderately hydrogen-bonded bound water, due to the gradual IR spectral shift from 3477 to 3481 cm^{-1} and a slower weight loss of water from MC film. The changes in peak area ratio of 1649 cm^{-1}/1374 cm^{-1} with the temperature also confirmed the IR spectral peak shift of the OH stretching mode via the water loss from MC film. The temperature-dependent dissociation of intermolecular and intramolecular hydrogen bonds within water molecules and/or between water/MC interaction might be responsible for the desorption kinetics of water from MC film.

Keywords: Methylcellulose; Water desorption; Thermal FT-IR; TGA; Hydrogen bonding

1. Introduction

Methylcellulose (MC) is one of the simplest cellulose derivatives known for a long time. The temperature-related inverse solubility and gelation behavior of aqueous MC solution are the unique characteristics, which are markedly associated with the ratio of hydrophobic zones to hydrophilic zones in MC backbone [1,2]. Since MC has excellent film-forming property, lipid barrier function, and low oxygen as well as moisture vapor transmission rate, thus it has been extensively used in food and pharmaceutical industries [3,4]. In the food industry, MC film is always used as a protective and edible film to reduce water vapor, oxygen, lipid and flavor migration between food components, and between food and the surroundings [3,5]. In addition, MC is also widely used in the pharmaceutical fields as thickener, protective glue, auxiliary emulsification agent, binder or film-coating forming agent for different dosage forms [4,6]. In particular, MC can prolong drug release by rapidly forming a protective viscous layer around the surface of tablet or pellet when exposed to aqueous fluids [7].

There has been an increasing interest in the diffusion of solvents through the polymeric film, in which water diffusion is of particular importance to affect the shelf-life of inner component, such as stability of drug, flavor and texture of foods [3,8,9]. Once water penetrates into polymer, it

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can easily interact with the polymer through hydrogen bonding [10,11], leading to possessing different states in polymer, particularly for hydrophilic polymer [12]. When water is absorbed into a hydrophilic polymer, its thermodynamic property is different from that of water in the bulk liquid state [13,14]. Based on the extent of interaction occurred between water and polymer, three states of water in hydrophilic polymer have been proposed: (i) free water, which may be crystallized at 0 °C, (ii) freezing bound water, which is crystallized below 0 °C, and (iii) non-freezing bound water, which does not crystallize even at lower temperature [14,15]. The bound water in polymer network is mainly presented by hydrogen-bonding the water molecules with the polar groups of the polymer. Since MC has many hydrophilic hydroxyl groups capable of interaction with water through hydrogen bonding in MC polymeric texture, resulting in plasticizing the MC film and influencing its physico-chemical properties [15].

Although many analytical methods such as differential scanning calorimetry (DSC), thermogravimetry (TG), dilatometry, nuclear magnetic resonance (NMR) have been used to investigate the content of free or bound water in the polymer film, there is an intrinsic shortcoming for each method [16]. However, infrared (IR) spectroscopy seems to be the optimal technique to determine the free or bound water in different samples such as polymer film, gel polymer, and protein via the sensitive vibrational frequency [17–19]. A novel microscopic Fourier transform infrared (FT-IR) spectroscopy equipped with thermal analyzer (thermal FT-IR microscopic system) has been used in our previous studies to simultaneously determine the correlation between the thermal response and the structural change of solid-state intramolecular cyclization of drugs or drug–polymer interaction, and the polymorphic transition of trehalose dihydrate in the dehydration and rehydration processes [20–22]. This one-step synchronous operation is fast, simple, sensitive, precise and reproducible. In the present study, we try to develop a non-destructive method to examine the *in situ* water content by using this novel thermal FT-IR microscopic system. Although the interaction of the water molecules adsorbed onto/into the solid MC film has been isothermally studied by IR spectroscopy in the different relative humidity (RH) levels at a room temperature [11], there is scant study for water desorption behavior from MC film by non-isothermal effect.

2. Materials and methods

2.1. Materials

The pharmaceutical grade of methylcellulose (MC, Metolose SM-100) was purchased from Shin-Etsu Chemical Co. Ltd. (Tokyo, Japan), and used without further purification. Aluminum foil and anhydrous ethanol were obtained from Reynolds Metals (Richmond, Virginia, USA) and Sigma Chemical Co. (St. Louis, MO, USA), respectively.

2.2. Preparation of MC film cast on aluminum foil

Two percents (w/v) of MC solution dissolved in double distilled water were prepared with constant stirring for 24 h. The MC aqueous solution was dropped on an aluminum foil (10 mm × 10 mm), and then quickly centrifuged by rotator with 50 rpm. All samples cast were dried at room temperature (25 °C, 70% RH) for 72 h. The thickness of MC film cast on the aluminum foil was about 20 μm determined by a digital micrometer (Mitsutoyo Manufacturing Co. Ltd., Tokyo, Japan).

2.3. Thermal reflectance FT-IR microscopic study

The MC film cast on aluminum foil was carefully cut to 6 mm × 6 mm in size. This foil was put directly on a micro hot stage (DSC microscopy cell, FP 84, Mettler, Greifensee, Switzerland). The DSC microscopy cell was then placed on the stage of the microscope in the FT-IR microspectrometer (Micro FTIR-200, Jasco, Tokyo, Japan) with a mercury cadmium telluride (MCT) detector. The temperature of the DSC microscopy cell was monitored with a central processor (FT80HT, Mettler), also calibrated with indium [20–22]. The polystyrene film was used as a wave number calibrator of FT-IR microscopic spectrometer. The heating rate was controlled at 3 °C/min. The thermal FT-IR microscopic system was operated in the reflectance mode and carried out from 25 to 200 °C under 68% RH condition. The reflectance IR spectra were collected at an angle of incidence centered at 30° and taken with a resolution of 4 cm^{-1}. Generally, 20 scans, after subtracting out an air blank, were accumulated to get a reasonable signal to noise ratio. The experiment was repeated three times to confirm the reliability.

2.4. Thermogravimetric analysis (TGA)

The weight loss of MC film cast on aluminum foil was also determined by using a thermogravimetric analysis (TGA; TGA-951, TA Instruments Inc., New Castle, DE, USA) at a heating rate of 3 °C/min from 25 to 200 °C. The water loss from MC film with the increase of temperature was calculated using the following expression:

$$\mathrm{WC_T}\ (\%) = (W_\mathrm{T} - W_\mathrm{FT}/W_\mathrm{T}) \times 100$$

where $\mathrm{WC_T}$ is the water content of MC film at the prescribed temperature, W_T is the total weight of MC film at the prescribed temperature, W_FT is the dry weight at 200 °C. Triplicate studies were performed and the mean was obtained.

3. Results and discussion

Three-dimensional plots of thermal-dependent reflectance FT-IR spectra of MC film cast on aluminum foil are displayed in Fig. 1. A strong peak at 3448 cm^{-1} and a shoulder at 3257 cm^{-1} might be due to the OH