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Enhanced oxygen barrier property of poly(ethylene oxide) films crystallite-oriented by adding cellulose single nanofibers

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ABSTRACT

In this study, we investigated the influence of cellulose single nanofibers (CSNFs) added to poly(ethylene oxide) (PEO) on the microstructure and property to create high gas barrier films. The CSNF/PEO nanocomposite films were prepared by solvent casting. The PEO crystallite orientation was measured using wide-angle X-ray diffraction of the SPring-8 synchrotron radiation facility. The degree of crystallite orientation was evaluated from the reflections of the PEO (1 2 0) lattice planes to investigate quantitatively the effect of different amounts of the additive CSNFs. The crystallite orientation of PEO increased with the addition of the CSNF. Furthermore, the oxygen barrier property for each nanocomposite film was found to be higher than that of the pure PEO film. The 5 wt% addition of CSNFs was mostly effective in enhancing the PEO crystallite orientation and oxygen barrier.

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1. Introduction

Polymer crystals possess various properties such as high Young's modulus, strength, optical anisotropy, thermal conductivity, electrical conductivity, and gas permeability. For example, the gas permeability decreases with the increase of crystallinity and crystallite orientation. Generally, in polymer materials, small gas molecules enter amorphous regions more easily than crystalline regions. Polymer crystals, in which polymer chains are packed with each other, constitute a barrier for most molecules [1–4]. The path length of gas molecules depends on the volume fraction and the length and width of the crystalline regions [4,5]. Thus, the crystallite orientation is known to affect the gas permeability. Low oxygen permeability is favorable to preserve the quality of food and

medicines in packages. Therefore, developing technologies for controlling the degree and structure of the polymer crystallite orientation is very important.

Three methods to orient polymer crystallites are well established. First, the stretching method is widely used in industry [6]. Polymer films could be torn straight in one direction by stretching because polymer chains are elongated in the stretching direction. Therefore, food packages could be opened smoothly. The second approach is the multilayer method. The crystallizations for multilayered films of various combinations of polymers have been reported [7–12]. In these reports, coextruded films of poly(ethylene oxide) (PEO) and poly(ethylene-co-acrylic acid) were investigated for polymer crystallization in a confined space. The high orientation of PEO crystals in several dozen nm thickness caused a reduction in oxygen gas permeability [11]. This method has the advantage of prompting the polymer crystals to be oriented in every part of the film compared with the stretching method. However, producing uniform thickness of every layer in the multilayered film is difficult. In addition, the differences in the melt viscosities cause the delamination of the multilayered film. The third treatment employs composite fillers. Various fillers, such as fiber-form fillers, are used in polymer composites [13,14]. The crystallite orientation depends on the degree of crystallographic matching between the filler and

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the matrix (i.e., epitaxy) and on the nucleation density on the filler surface.

Recently, nanometer-sized fillers such as carbon nanotubes have received attention because they can improve the properties of the composites even at an extremely low filler content [15–18]. Cellulose single nanofibers (CSNFs) are also nanometer-sized fillers. Cellulose is a carbon-based material and is considered as a highly functional material due to its high Young's modulus, low thermal expansion, thermal stability, and chemical resistance [19,20]. Moreover, its raw materials are abundant in nature. Cellulose nanofibers have thus been used for the preparation of composites with numerous different polymers [21–23].

In our previous study, using a grazing incidence X-ray diffraction coupled with a two-dimensional (2D) detector, we observed that the addition of CSNFs improves the degree of crystallite orientation of the matrix resin [24]. We selected PEO as the matrix resin because it has a high affinity for cellulose and a reduction of the gas permeability of PEO-based nanocomposites is needed. For example, PEO is used to produce packages for food and medicines [25–27] and gas separation membranes [28,29]. PEO is a moisture sensitive material because PEO is a hydrophilic polymer. Films in packaging are not usually composed of only PEO. Hence PEO films including a moisture barrier and adhesion layer can be a package material. Therefore, our study to create high gas barrier PEO films will be important from the industry viewpoint. In this study, we investigated the relationship between the orientation of matrix resin crystals and the additive amounts of CSNFs, as well as measured the oxygen permeability.

2. Experimental

PEO (average molecular weight: 500,000 g/mol; Wako Pure Chemical Industries, Ltd., Osaka, Japan) was dissolved in distilled water by stirring and heating at 60 °C to obtain 1.0 wt% PEO aqueous solution. The CSNFs were made from pulp, and the aqueous CSNF dispersion consisted of mostly individualized nanofibers of 3–4 nm in width and a few microns in length, which was prepared by 2,2,6,6-tetramethylpiperidine-1-oxyl radical-mediated oxidation under moderate aqueous oxidation conditions as previously reported [30–32]. This aqueous CSNF dispersion was added to the aqueous PEO solutions to obtain PEO solutions containing 1, 2, 5, 10 wt% CSNFs. The film samples were prepared by solvent casting. The solvent was slowly evaporated at 60 °C, followed by further drying under vacuum at 60 °C for 2 d to remove the residual solvent. The film thickness was measured with a micrometer. The obtained thicknesses are listed in Table 1.

The melting temperature (T_m) and the degree of crystallinity (X_c) of PEO were measured by differential scanning calorimetry (DSC) (DSC 6100, Seiko Instruments, Japan). Approximately 5 mg of film samples were placed in aluminum pans. All DSC experiments were performed under nitrogen atmosphere. Each sample was heated from 25 °C to 160 °C at 5 °C/min and kept at that temperature for 10 min to perfectly melt the PEO crystals.

The crystal structures were evaluated by wide-angle X-ray diffraction (WAXD). WAXD measurements were performed at the BL03XU beamline of the SPring-8 synchrotron radiation facility [33]. The detector for diffracted X-rays was a flat panel detector (FPD), and the distance between the sample and the detector was 63.6 mm. The incident X-ray energy used was 12.4 keV. The X-rays were emitted from a direction almost parallel to the section of the films. Fig. 1a shows the image of the WAXD set up. The WAXD patterns were observed from the downstream.

The oxygen permeability of the films was measured on a MOCON OX-TRAN 2/21 apparatus (Modern Controls Inc., U.S.A.). The film samples were cut and sealed in an aluminum foil with a

Table 1

Composition, film thickness, and the thermal characteristics of CSNF/PEO nanocomposite films.

Sample ID	CP-00	CP-01	CP-02	CP-05	CP-10
CSNF (wt%)	0	1	2	5	10
Film thickness (μm)	84	72	117	57	53
T_m (°C)	66.5	66.8	67.3	66.1	66.7
X_c (%)	69.9	73.2	70.3	74.1	67.5

round-shaped open area of 5.0 cm². The permeability measurements were performed at 23 °C and 65% relative humidity with a test gas containing 100% oxygen. The oxygen permeability [$P(\text{O}_2)$] is given in (cm³ cm)/(cm² s cm Hg), which means the oxygen mass transfer rate in cm³/(cm² day) was multiplied by the thickness of the film and divided by the measurement time and the pressure difference of oxygen.

3. Results and discussion

The T_m of PEO was determined by the peak top of the melting behavior in the DSC heating curves of each CSNF/PEO nanocomposite. The X_c of PEO in the nanocomposite was calculated from the heat of fusion (ΔH_m), which is the area of the melting peak, using ΔH_m^0 for a pure crystalline PEO of 196.0 J/g [34].

$$X_c = \frac{\Delta H_m}{\Delta H_m^0}$$

The calculated thermal characteristics of CSNF/PEO composite films are listed in Table 1. The values of T_m for all samples were approximately equal. This suggests that the crystallite size is independent from the additive amount of CSNFs. Conversely, the X_c increased slightly on the addition of CSNFs (1–5 wt%), but reduced at an additive content of 10 wt% compared to the value of pure PEO sample as found in Table 1. We believe that CSNFs act as the crystal nuclei of the PEO crystals at that additive content due to the high-crystallinity surfaces and high affinity between CSNF and PEO [35,36]. Moreover, CSNFs prevent the PEO chains from crystallizing at additive contents higher than 10 wt% because the reflections from PEO crystals did not be observed at an additive content of 50 wt% by WAXD.

Fig. 1 shows the image of the WAXD measurement set up and the diffraction patterns of the CSNF/PEO nanocompositions (CSNF 0, 1, 5, 10 wt%). In the monoclinic unit cell of PEO, the polymer chains have 7/2 helix conformation with an orientation parallel to the c -axis. The unit cell parameters are $a = 0.805$ nm, $b = 1.304$ nm,

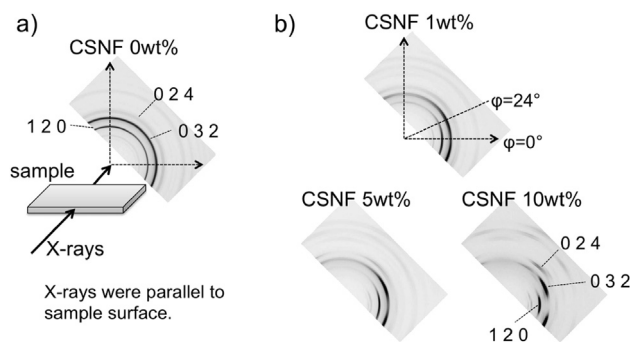


Fig. 1. a) The image of the WAXD set up at BL03XU. X-rays were emitted from a direction almost parallel to the section of the films. The pattern of the PEO film was observed from down stream. b) The WAXD patterns of CSNF (1, 5, and 10 wt %) / PEO films.

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