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Effect of humidity on mechanical, thermal and barrier properties of EVOH films

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ABSTRACT

The moisture content sensitivity of Ethylene-Vinyl Alcohol (EVOH) copolymers is a major problem for food packaging applications. Thus, the relationship between the hydration mechanism at molecular scale and the properties is a critical issue for barrier properties improvement of EVOH films. The aim of this study was to determine material structure-functional property relationships and inter-property correlations.

Firstly, mechanical, thermal, water sorption and oxygen barrier properties were determined for a wide range of water activity. The water sorption isotherm modelling with GAB equation, the evolution of the glass transition temperature applying Gordon-Taylor equation as well as the mechanical and O_2 barrier properties were studied. The results underlined the plasticization effect of water leading to a decrease of the cohesive energy density and a drastic loss of O_2 barrier properties of the EVOH copolymer from a critical point occurring when water activity was close to 0.5.

Secondly, an analysis of the experimental water sorption isotherm, expressed as the number of water molecules sorbed per repeating unit in the amorphous phase, associated with an analysis of the evolution of polymer chains mobility allowed to establish a relationship between the hydration mechanism at molecular scale and the properties. It was determined that the amount of water sorbed molecules dramatically increased at a critical point, corresponding to the moment from which one water molecule was linked in average every nine amorphous PVOH units. This point corresponded to the saturation of the monolayer and the beginning of the clustering phenomenon.

1. Introduction

Ethylene vinyl alcohol (EVOH) copolymers are a family of semi-crystalline copolymers of ethylene and vinyl alcohol that are widely used in food packaging, building and automotive applications. EVOH properties are mainly dependent on the copolymerization ratio of ethylene to vinyl alcohol [1]. In particular, the copolymers with low contents of ethylene (in concrete terms below 32 mol% ethylene) have outstanding barrier properties to oxygen, non polar solvents and food aromas under dry conditions, compared to other polymers [2–4]. For example polyethylene terephthalate (PET) presents an oxygen permeability that is 100 times higher than that of EVOH, while nonpolar polymers such as polyethylene (PE), polypropylene (PP) or polystyrene (PS) exhibit oxygen permeabilities over 4 orders of magnitude higher [5]. Moreover, EVOH copolymers exhibit a high transparency and interesting mechanical properties. The barrier and mechanical properties of EVOH under dry conditions are attributed to their semi-crystalline morphology and their high inter- and intramolecular cohesive energy. However, the major problem of EVOH copolymers is their moisture content sensitivity that causes a significant loss in their properties at high relative humidity environments [6,7]. This deterioration of properties is due to the water molecules sorbed by the copolymer which lead to a decrease of the inter- and intramolecular hydrogen bonding. As a result, the chains segmental motions enhance and the copolymer free volume increases [8]. The plasticizing effect of water has a direct impact on the copolymer glass transition temperature (T_g). Zhang et al. have shown a decrease of T_g value from 60 °C to − 5 °C with increasing of water activity from 0 to 0.94 [9].

Although the impact of hydration has been studied on chain mobility, and the mechanical and barrier properties of hydrated EVOH have been determined, according to our knowledge, no work had dealt with the establishment of inter-property relationships. Moreover, the relationships between the hydration mechanism at molecular scale and the properties had not been clearly established.

Thus, the control of all these properties appears to be preponderant for the varied barrier applications of the EVOH films, like in multilayer for food packaging for example [10,11].

The main objectives of this study were to perform a detailed analysis

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of the water sorption mechanism for a EVOH copolymer containing 32% mol ethylene, to get a better understanding of the water sorption at the molecular scale and to determine the consequences of the different sorption steps on the mechanical, thermal and oxygen barrier properties. This first step will then enable to establish the material structure-functional property relationships and inter-property correlations.

2. Experimental

2.1. Materials

The EVOH copolymer used in this work was commercialized by EVAL Europe under the name J102B. It was composed of 32% mol ethylene and had an average molecular weight, $\overline{M_W}$ close to 42,500 g mol^{-1}. Polypropylene (PP)-EVOH structures (PP/EVOH/PP) were obtained by coextrusion and the multilayer sheets were constructed without adhesive layer to get an easy separation of the EVOH layer from PP. It was checked that the coextrusion conditions used for the multilayer sheets preparation led to isotropic EVOH copolymer films (results not shown). The EVOH film thickness was 55 μm and the density (ρ_p) was 1.17.

Different salts were used to equilibrate the samples used for thermal and mechanical characterization at defined water activities (a_w). Potassium carbonate (K_2CO_3) was purchased from Merck, sodium chloride (NaCl), ammonium nitrate (NH_4NO_3) and potassium chloride (KCl) from Sigma-Aldrich. All salts were A.C.S. grade. Distilled water obtained from a MilliQ™ purification system with a water resistivity greater than 18 MΩ cm was used to prepare the salt solutions.

2.2. Preparation of samples equilibrated at different water activities

In order to get hydrated samples at different water activities, the films were placed in desiccators containing saturated salt solutions. Each salt solution was prepared by mixing between 50 and 100 ml of distilled water with an amount of salt equal to 2 times the salt solubility limit at 25 °C. The salts used for the study, namely K_2CO_3, NH_4NO_3, NaCl and KCl, allowed obtaining a water activity of 0.43, 0.62, 0.75 and 0.85, respectively at 25 °C [12]. The samples were conditioned for 4 days in order to reach the water sorption equilibrium conditions. EVOH copolymer films were also conditioned at a controlled room water activity (a_w = 0.27) for 4 days. Finally, films immersed in deionized liquid water (a_w = 1) during 48 h were also prepared.

2.3. Methods

2.3.1. Water sorption

Dynamic vapor sorption analyzer, DVS Advantage, was used to determine water sorption isotherms of the EVOH copolymer film. The vapor partial pressure was controlled by mixing dry and saturated nitrogen, using electronic mass flow controllers. The experiments were carried out at 25 °C. The initial weight of the sample was approximately 20 mg. The sample was pre-dried in the DVS Advantage by exposure to dry nitrogen until the equilibrated dry mass of the sample was obtained (m_0). A partial pressure of vapor (p) was then established within the apparatus and the mass of the sample (m_t) was followed as a function of time. The mass of the sample at equilibrium (m_{eq}) was considered to be reached when changes in mass with time (dm/dt) were lower than $2{\cdot}10^{-4}$ mg min^{-1} for at least 5 consecutive minutes. Then, vapor pressure was increased in suitable activity up to 0.9 by step of 0.1.

The value of the mass gain at equilibrium (G) defined as $\frac{m_{eq}-m_0}{m_0}$ for each water activity (a_w) was calculated and allowed to plot the water sorption isotherm. The precision on the values of G was estimated to be better than 5%.

2.3.2. Thermal analysis

Thermal analysis of the films was conducted through modulated differential scanning calorimetry (MDSC). The experiments were performed on a TA Instruments DSC QA 200, with hermetic pans containing between 5 mg and 10 mg of material. The scans were modulated at 1 °C/min. A first heating scan was performed from − 50 °C to 250 °C at 10 °C/min and then a cooling scan was set from 250 °C to − 50 °C at 10 °C/min. A second heating scan was at last applied using the same conditions as those used for the first one. Sample crystallinity was determined by subtracting the non-reversing heat flow from the reversing heat flow. The resulting melting enthalpy was divided by the theoretical 100% crystalline melting enthalpy of EVOH (ΔH^{∞} = 157,8 J/g) [13,14]. *Tg* value was determined as the temperature at the half-height value of the step-transition. Analyses were performed on dry and hydrated films.

2.3.3. Tensile tests

CRITERION (MTS Systems, Créteil, France) tensile testing machine equipped with a 500 N load cell was used to perform uniaxial tensile tests. The cross-head speed was adjusted to 10 mm/min and the gauge length at 10 mm. The tests were carried out on H3 type tensile specimens. Prior to mechanical tests, the samples were equilibrated at different water activities conditions ranging from 0.27 to 1. Values of tensile modulus (E), yield stress (σ_e), yield deformation (ε_e), breaking stress (σ_r) and deformation at break (ε_r) were determined from the stress–deformation curve. The values of the mechanical properties were the result of the arithmetic mean of the properties measured at least on three different specimens. The precision on the values of the mechanical parameters was estimated to be better than 10%.

2.3.4. Oxygen permeability

Oxygen permeability measurements were performed on a Mocon Oxtran 2/21 (Minneapolis, USA) equipped with a Coulox sensor. The open film testing area was 50 cm ^{2}. The test cell was composed of two chambers separated by the film. Nitrogen containing 2% of hydrogen (N_2/H_2) was used as the carrier gas and pure oxygen was used as the test gas. The water activity of the two gases was controlled by a humidifier. Prior to testing, specimens were conditioned in N_2/H_2 inside the unit for at least 4 days on the one hand to remove traces of atmospheric oxygen and on the other hand to be at the water uptake equilibrium condition of the films. Subsequently, oxygen was introduced in the upstream compartment of the test cell. Oxygen transferred through the film was conducted by the carrier N_2/H_2 gas to the coulometric sensor.

The oxygen permeability coefficient (P_{O_2}) was calculated considering the following equation:

$$P_{O_2} = \frac{J_{stat}.\,L}{\Delta p} \quad (1)$$

where L is the thickness of the film, J_{stat} the stationary flux and Δp the difference of pressure between the upstream and the downstream compartments. P_{O_2} values were expressed in Barrer (1 Barrer = 10^{-10} $cm_{STP}{}^3$ cm cm^{-2} s^{-1} $cm_{Hg}{}^{-1}$ = 3.36 × 10^{-16} mol m m^{-2} s^{-1} Pa^{-1}). Measurements were performed at controlled temperature (T = 23 °C) and for a water activity range from 0 to 0.9. The precision on the values of the permeability coefficient was estimated to be better than 5%.

Oxygen diffusion coefficients (D_{O_2}) were calculated from the permeation curves by using the following equation [15]:

$$D_{O_2} = \frac{L^2}{6.t_L} \quad (2)$$

where L is the thickness of the film and t_L is the time lag. t_L was defined by the time needed to reach J/J_{stat} = 0.6167, where J and J_{stat} are the flux and the stationary flux respectively. The precision on the values of the diffusion coefficient was estimated to be better than 5%.