Simultaneous WAXS/SAXS study of the morphological alterations induced by temperature and humidity in ethylene-vinyl alcohol copolymers as a function of the ethylene content

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Introduction
Ethylene-vinyl alcohol copolymers are a family of random semicrystalline materials with excellent barrier properties to gases and hydrocarbons, and with outstanding chemical resistance1. An important application of these materials is as barrier layer in multilayer structures to be used in various packaging designs for foodstuffs. In spite of the low gas permeation, EVOH copolymers generally show poor moisture resistance. The appetite for water of these materials, which results in a high water uptake, leads to deterioration of the gas barrier performance in high relative humidity environments.

Previous characterization of the effects on structure properties that combined temperature and humidity environments (typical industrial retorting conditions) have on EVOH32 (i.e. having a 32 mol percent of ethylene), demonstrated that apart from the extensive plasticization, a complete melting of the crystals take place during retorting 83ºC below the melting point of the sample2. In this context, the aim of these time-resolved simultaneous WAXS/SAXS experiments was to study another copolymer grades in order to check if the induced structural deterioration was a function of the ethylene content.

Experimental
Two commercial ethylene-vinyl alcohol copolymer grades (Soarnol®) with 26 and 44 mol% of ethylene (EVOH26 and EVOH44) and 10 microns thickness were supplied by The Nippon Synthetic Chemical Industry Co., Ltd. (NIPPON GOHSEI) (Japan).

Simultaneous WAXS and SAXS experiments vs. temperature were carried out at the synchrotron radiation source in the polymer beam A2 at Hasylab (DESY). Temperature scans were carried out at 5ºC/min on dry (sandwiched between aluminum foil) and in water saturation conditions for EVOH films in a liquid cell.

Relevant results
As previously observed for EVOH32, while in dry state the material melts around 183ºC, in the presence of pressurized water the crystallinity completely disappears around 100ºC.

The vinyl alcohol fraction of the copolymers is responsible for the sensitivity of these copolymers to water and, therefore it would be expectable that the copolymers with lower vinyl alcohol content could withstand better the retorting processes, as water is involved in this preservation process. In order to check if the structural deterioration was affected by the composition of the copolymers, a sample containing more vinyl alcohol (i.e. an EVOH26) and another containing more ethylene (i.e. and EVOH44) were temperature scanned in the presence of water and the melting temperature of the dry samples obtained by DSC (Tm [EVOH26] = 192ºC; Tm[EVOH44] = 163ºC) was compared with the melting of crystals during combined WAXS-SAXS in-situ retorting experiments.
Figure 2. WAXS and SAXS patterns of water saturated EVOH26 as a function of temperature.

In Figure 2 it is observed that both SAXS and WAXS patterns of EVOH26 disappear around 105°C, that is, 87°C below its melting point in dry state, which is a similar result to that obtained for the EVOH32.

In the case of EVOH44 the melting of the crystalline structure in the presence of water is again around 105°C, i.e. it is 58°C below the melting point of the dry copolymer (see Figure 3). The earlier melting of every copolymer at around 100°C, near to the water boiling point indicates that water vapour sorption is the mechanism which disrupts crystallinity in the polymer irrespective of ethylene content in the range from 26 to 48 mol% of ethylene.

Figure 2. WAXS and SAXS patterns of water saturated EVOH44 as a function of temperature.

This observations highlight the deleterious effect of retorting over EVOH structures, independently of their copolymer composition, which may have very important implications from an applied point of view.

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References