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Characterization of Extruded Ethylene-Vinyl Alcohol Copolymer Based Barrier Blends with Interest in Food Packaging Applications

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Summary: Based on previous work a number of optimum extruded blends with high contents of a high barrier ethylene-vinyl alcohol copolymer were selected and characterized in terms of phase morphology, water sorption and barrier properties. Blend components were an ethylene vinyl-alcohol copolymer (EVOH with 32 mol% ethylene), an amorphous polyamide (aPA) and a nylon-containing ionomer. A fine two phase structure was found for these blends in all cases. However, Raman spectroscopy results indicated a poor interface interaction between the blend components in the case of the EVOH/aPA blends. Higher interface interaction had been previously found in the dry EVOH/ionomer blends. Equilibrium moisture solubility and diffusion were found to be higher than expected from simple additivity. However, the oxygen transmission rate was found to be clearly lower than expected from the rule of mixtures, particularly under dry conditions, fitting closely a simple Maxwell model.

Keywords: blends, ethylene-vinyl alcohol copolymer, high barrier packaging

Introduction

Ethylene-vinyl alcohol copolymers are a family of random semicrystalline materials with excellent barrier properties to gases and hydrocarbons, and with outstanding chemical resistance.[1] These copolymers are therefore being increasingly used in the food packaging industry as barrier layers to protect foods from the ingress of oxygen and losses of flavours and

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consequently to increase package shelf-life.[2] In spite of that, EVOH copolymers are also largely affected by water and possess a number of processing associated problems, like deficient thermoformability, due to high rigidity and crystallization kinetics.[3] In addition to high water sensitivity, EVOH copolymers do not have a good compatibility (adhesion and miscibility) with other polymers whether of polar or non-polar nature.[4] The lack of good compatibility with other polymers is thought to be a consequence of the fact that EVOH copolymers are strongly self-associated, while the inter-association of the hydroxyl groups of EVOH with, for instance, the carbonyl groups of complementary polymers is comparatively weak. Even miscible systems have low LCST (Lower Critical Solution Temperatures) and phase separation is anticipated at processing temperatures. In order to avoid the deterioration of the physical and barrier properties by the uptake of water, these materials are usually sandwiched by coextrusion in multilayer structures where and inner and outer layers of hydrophobic materials, e.g. polyethylene, wrap up the barrier layer made up of EVOH. Blends of EVOH with other materials have been studied over the last years with the aim of boosting the barrier properties of low barrier performance materials, improving mechanical properties of EVOH and/or adhesion, etc.[5,6,7,8,9]

It is well known that the EVOH solid phase formability window, usually between 90°C and 110°C, does not overlap with that of many polymers used in coextrusion to form multilayer structures in the packaging industry. Blends of EVOH with low contents of amorphous PA have been claimed by manufacturers to broaden the forming capacity of EVOH with respect to temperature and draw ratios without sacrifice in gas barrier properties[3]. This is because the amorphous PA exhibits a much better forming capacity and its gas barrier performance[10] improves with increasing relative humidity as opposed to EVOH, which barrier properties deteriorate with increasing relative humidity.[11,12] Nylon containing, partially neutralized, ethylene-methacrylic acid copolymers (ionomer) are a family of materials highly transparent and with low hygroscopicity. These ionomers are thermoplastic materials ionically crosslinked and their properties vary with molecular weight and the amount of crosslinking. These materials are designed to be tumble-blended with EVOH in conventional equipment and are claimed[13] to provided a soft, clear, flexible film or sheet with improved flex resistance, excellent thermoformability, and gas barrier at high humidity, compared to films made of EVOH alone.

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Previous characterization studies carried out in melt-mixed compresion moulded specimens indicated a two phase structure with a fine distribution of the disperse phase within the EVOH matrix.[14,15] Better compatibility was observed in EVOH/ionomer blends, particularly for blends with higher contents of ionomer. Moreover, a thermofomability study[16] of the blends indicated that EVOH/aPA extruded blends did not improve the inherently poor formability of EVOH alone. In contrast, significant improvements in thermoformability were achieved by blending EVOH with a compatibilized-ionomer in the range 100-150°C. Optimum forming capacity was achieved in a ternary blend by addition of a compatibilized-ionomer to EVOH/aPA blends in the range of 140°C-150°C.

In this study, some additional results based on SEM, vibrational spectroscopy, moisture sorption and oxygen permeability are presented on extruded films of the blends, which permit us to characterize the properties of these barrier blends in the usual form in which they will be processed into food containers.

Experimental

Polymer sheets were obtained using conventional film co-extrusion equipment by extruding pelletised pre-extruded blends between polyethylene layers without adhesive. This allowed for an easy peeling off of the barrier blend film. The blends comprised EVOH-32 as main component and an amorphous PA (Selar PA UX-2034) and/or a Nylon-containing ionomer (Surlyn AM-7938) as minor components. The EVOH copolymer used was a commercial product (Soarnol DC3203) of Nippon-Gohsei (Japan) with 32 mol% of ethylene. The binary and ternary blends prepared were: EVOH/aPA (80/20), EVOH/ionomer (80/20) and EVOH/aPA/ionomer (80/10/10).

FT-Raman spectra were obtained using a FT-IR/NIR-FT-Raman Perkin-Elmer Spectrum 2000 instrument equipped with a diode pumped Nd:YAG laser PSU. Curve-fitting of the experiments was carried out with the Grams Research 2000 software package (Galactic

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Industries). Voigt line shapes (convolution of Lorentzian and Gaussian functions), no constraints, and linear baselines were used.

Scanning electron microscopy experiments were carried out in a Jeol JMS-6300. Samples were cryofractured and gold coated prior to SEM observations.

The kinetics of water sorption at 100% RH were obtained for the different samples by immersing dry specimens in distilled water and follow water uptake gravimetrically until saturation (equilibrium sorption).

Oxygen transmission rate was measured in an Oxtran MS (Modern Control Inc., Minneapolis, US) equipment with humidity control.

Results and Discussion

Previous characterization work in these blends by DSC, WAXS, DMA, SEM, microhardness and tensile testing indicated that the miscibility of this high barrier EVOH grade (with T_g at 59°C and T_m at 183°C) with the amorphous PA is very poor, and clear phase segregation throughout composition was shown by DSC, DMA and SEM.[14] Factors like geometric hindrance and chain stiffness of the amorphous PA (with a T_g around 127°C) could be responsible for this behaviour. A lack of good interaction between EVOH/aPA blend components was further supported by the negative deviation from the simple additive rule seen in the mechanical properties of these blends. A two phase structure was also observed in the EVOH/ionomer blends, but from the results a better phase compatibility was inferred. This compatibility increased in the ionomer rich blends and was thought to be enhanced by the presence of crystalline Nylon in the formulation of the ionomer.

Figure 1 shows SEM results carried out on extruded films perpendicular to the flow direction. From this figure, a fine particle dispersion with some debonding at the particles interface is observed. Similar observations were already reported in melt-mixed compression molded specimens.[14] However, while in the EVOH/aPA blends the dispersed phase is rather spherical in shape, this is clearly more elongated in the case of the EVOH/ionomer blend. The latter observation caused by the shear stress imposed during the extrusion procedure is probably a consequence of the lower viscosity and maybe of the phase interaction exhibited by the ionomer in this particular blend.

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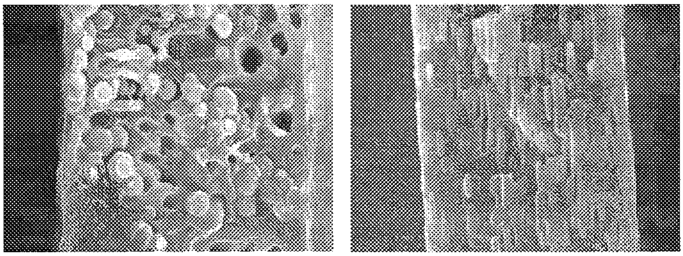

Fig. 1. SEM micrographs of films of EVOH/aPA (left) and EVOH/ionomer (right).

Figure 2 shows the Raman region centered at 1600 cm^{-1} containing some ring vibrations and the amide I mode at 1638 cm^{-1} for the aPA, water equilibrated aPA and EVOH/aPA 80/20 blend. This amide I mode is mainly due to CO stretching vibrations and contains two contributions one small due to free CO groups at 1671 cm^{-1} and another one at 1638 cm^{-1} originating from hydrogen bonded CO groups. Depending on the severity of the drying process the relative amount of free CO groups has been found to vary between ca. 10% and 16%.[17] In the presence of moisture however, the free CO band vanishes due to association of these free carbonyl groups with water molecules (see Figure 2, center). Therefore, the presence or absence of these free carbonyl groups, as well as the position of both of these contributions, can tell about potential interactions at a molecular scale. As EVOH is also capable of forming hydrogen bonding interactions via the hydroxyl groups present in the polymer chain, the disappearance of this free CO groups could then indicate phase interaction between EVOH and the aPA. Figure 2 also shows the amide I range in the EVOH/aPA 80/20 blend. From this Figure, it can be seen that free CO groups are still present, and therefore, there is no clear evidence of interaction between EVOH groups and the amide groups of the aPA. However, the position of the free CO contribution appears shifted towards lower wavenumber in the blend compared to the neat component. This could be attributed to a potential influence of the EVOH matrix over the free amide moieties. Consequently, Raman confirms the lack of a strong interaction between blend components in agreement with results gathered by other techniques for this particular blend. The

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spectroscopic analysis of the EVOH/ionomer blend is more complicated due to the compositional complexity of the ionomer, i.e. already a blend of an ethylene-methacrylic acid copolymers and a crystalline Nylon.

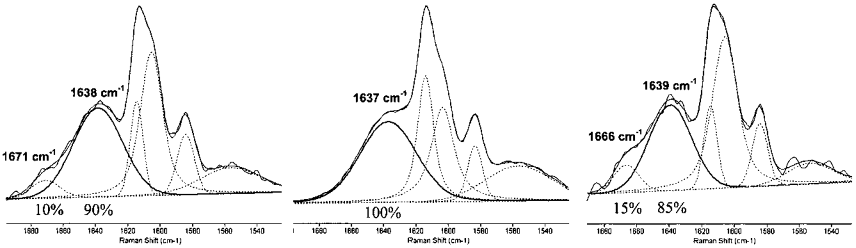

Fig. 2. Raman spectra in the range of the amide I mode for aPA (left), water equilibrated aPA (center) and the EVOH/aPA 80/20 blend (right). Percentages of the different contributions to the amide I envelop and positions are given.

The effect of moisture uptake was previously investigated in a number of melt-mixed compression molded blends by TGA, DMA, microhardness and tensile testing.[15] The study of the influence of water sorption on these blends is relevant to understand the gas barrier behavior of these materials under high relative humidity conditions; of concern, for instance, during typical industrial processes such as retorting of packaged food. From the results, water sorption was found to be in the order EVOH>aPA>>ionomer. The moisture was found to bind more strongly (higher temperature desorption by TGA) with EVOH than with aPA or ionomer. The T_g of water equilibrated aPA was still above room temperature, whereas it was well below room temperature in water equilibrated EVOH. Accordingly, EVOH showed increased plasticity and toughness at high relative humidity conditions. An intrinsic high stiffness and brittleness was measured for the aPA irrespective of the relative humidity. The ionomer showed low moisture dependence in the mechanical properties and much higher flexibility than aPA. In EVOH/aPA and EVOH/ionomer blends, the EVOH fraction was found to be fully plasticized. The phase compatibility suggested from earlier work for some EVOH/ionomer blends appeared to be eliminated by the effect of sorbed moisture on the potential interfacial adhesion via hydrogen bonding. In the mechanical properties of the blends exposed to moisture, EVOH/aPA blends showed an increase in stiffness, and in turn, of the fragility compared to EVOH alone, whereas high flexibility and toughness was still observed in EVOH/ionomer blends at high relative humidity conditions.

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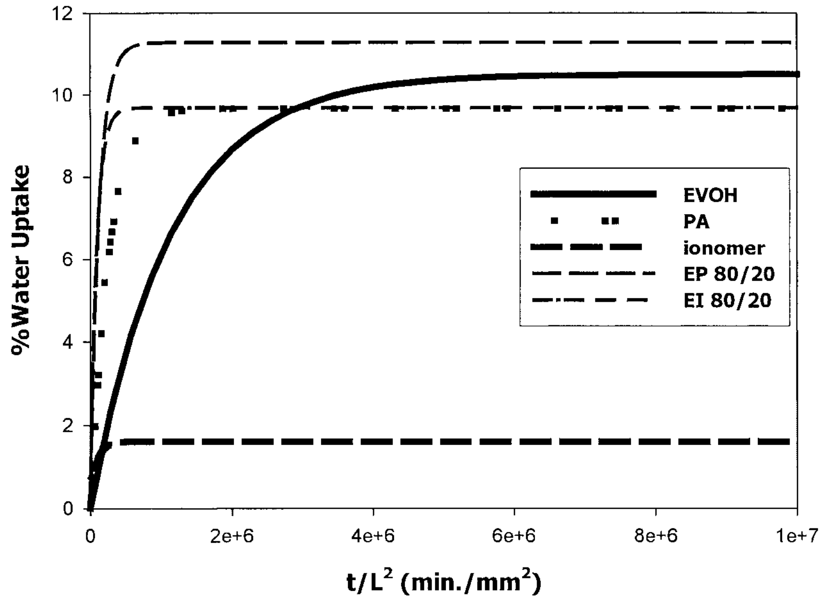

Fig. 3. Kinetics of water sorption at 100%RH for neat components and blends.

Figure 3 shows water sorption curves as a function of time at room temperature and at 100%RH for extruded specimens of the neat components and blends. From this figure, it can be seen that equilibrium sorption for the neat components is, as previously reported, in the order EVOH>aPA>>ionomer in the extruded specimens. However, from the isotherms it is also possible to observe that the diffusion of water is faster in the ionomer and slower for EVOH. In the blends however, it can be seen that solubility is higher than expected from simple additivity of those of the neat components; and so is the diffusion rate. A contribution to this observation could come from a slight decrease in crystallinity observed for the EVOH fraction in the blends during WAXS experiments; however this was not seen by DSC. Nevertheless, the cited effect must be largely attributable to lack of a strong interaction between components in the blends, which makes then the plasticized interface a preferential pathway for diffusion of moisture. In fact, if a more strong interaction was going to occur at the particles interface, that would have

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probably been disrupted by a more favorable interaction with moisture molecules, as was previously reported in EVOH/ionomer blends. Consequently, transport of moisture is observed to be higher in these blends than expected from simple additivity of the neat components.

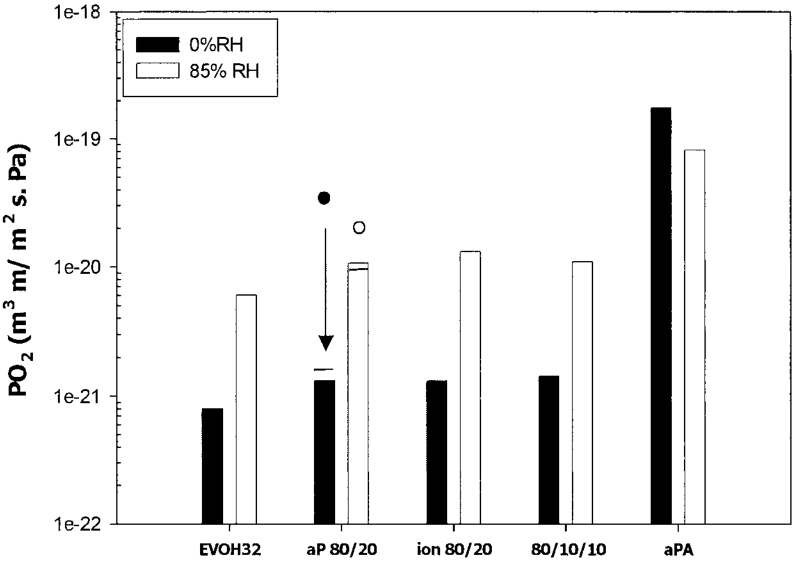

Fig. 4. Oxygen transmission rate at 0%RH and at 85%RH. Circles in the EVOH/aPA 80/20 blend correspond to parallel alignment of the two phases to permeant flow (simple additivity) and dashes to the Maxwell equation.[18]

Figure 4 shows the oxygen transmission rate results at 0%RH (dry) and at 85%RH in binary and ternary blends. A full map of the oxygen barrier properties across relative humidity is being currently measured and will be reported elsewhere. From the results, it can be seen that the oxygen permeability at 0%RH is lower for EVOH but is also very low for the blends. At high relative humidity (85% RH) the barrier properties of the materials are much higher in all cases, except for the amorphous PA. The latter material is known to have better barrier properties at high relative humidity due to its particular interaction with moisture. It has been recently found that moisture sorption does not disrupt the originally existing hydrogen bonding structure, but

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rather links to free amide moieties being the majority of the sorbed water under the form of clusters.[17] Clustered water is thought to fill the available polymer free volume, hence leading to a decrease in oxygen permeability on the bases of a competing mechanism. The barrier properties of the neat ionomer could not be measured because it could not be peeled off due to strong adhesion to the structural polyolefinic layers of the co-extruded sheets supplied. The deterioration in barrier properties of the blends at high humidity is consequence of the plastification of the EVOH continuous phase.

The barrier properties of the blends seem to follow a relationship (see equation 1) close to that proposed by Maxwell and extended by Roberson (see equation 1) for spheres of a low barrier phase dispersed in a high barrier continuous matrix (see dashes in Figure 4).[18] This simple model would appear to closely reflect, albeit with a slight positive deviation, the case of the dispersed morphology found for the EVOH/PA blend in Figure 1. The EVOH/ionomer blend could even present considerable better barrier than predicted from equation 1 due to the fact that particles are elongated (higher aspect ratio) in a direction normal to the permeation direction.

$$P_{EVOH/aPA} = P_{EVOH}\left[\frac{P_{aPA} + 2P_{EVOH} - 2V_{aPA}\left(P_{EVOH} - P_{aPA}\right)}{P_{aPA} + 2P_{EVOH} + V_{aPA}\left(P_{EVOH} - P_{aPA}\right)}\right] \quad (1)$$

The permeability of the blends consider here would then approach the permeability of a coextruded multilayer (series laminate normal to permeant flow, see equation 2) system comprising two layers, one made of a lower barrier disperse phase and the other of high barrier matrix; being therefore, the overall permeability close to the permeability of the neat high barrier matrix for a sufficiently high volume fraction of the matrix (V_{EVOH}). Equation 2 is a very favorable situation in terms of permeability for a non miscible blend.

$$P_{EVOH/aPA} = \frac{P_{EVOH}P_{aPA}}{V_{aPA}P_{EVOH} + V_{EVOH}P_{aPA}} \quad (2)$$

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The circles on the graph in Figure 4 represent the values of permeability obtained by application of a simple additive rule (layers parallel to permeant flow, see equation 3). This case would clearly be a very disfavorable situation in terms of permeability for these blends.

$$P_{EVOH/aPA} = P_{EVOH}V_{EVOH} + P_{aPA}V_{aPA} \quad (3)$$

At 85% RH the barrier properties of the blends are higher and approach closer the value for the simple additivity (equation 3) in the case of the EVOH/aPA blend. Nevertheless, they still show a reasonable close fit to equation 1, albeit with negative deviation. This observation may appeal for the application of not so simplified Maxwell models. This particular behavior is thought to be affected by the higher solution and diffusion of moisture at high humidity levels in these blends. Results for a ternary blend are also included. This blend has been found to provide optimum thermoforming performance.[16]

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