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Study of the influence of water sorption in pure components and binary blends of high barrier ethylene–vinyl alcohol copolymer and amorphous polyamide and nylon-containing ionomer

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Abstract

The effect of moisture uptake has been investigated in 32 mol% ethylene–vinyl alcohol copolymer (EVOH), amorphous polyamide (PA), and nylon-containing ionomer and in a number of binary blends of these polymers by sorption, TGA, DMA, microhardness and tensile testing. Blends of these materials have been claimed by manufacturers to improve the thermoformability characteristics of EVOH while retaining/improving high gas barrier under high relative humidity conditions. From the results water sorption was found to be in the order EVOH $>$ PA $\gg$ ionomer. The moisture was found to bind more strongly (higher temperature desorption by TGA) with EVOH than with PA or ionomer, but the fraction of non-hydrogen bonded to the polymer (mostly clustered) moisture appeared to be lower for PA than for EVOH. The T_g of water equilibrated PA was 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 PA irrespective of relative humidity. The ionomer showed low moisture dependence in the mechanical properties and much higher flexibility than PA. In EVOH/PA 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/PA blends displayed increased stiffness but fragility compared to EVOH, whereas high flexibility and toughness was still observed in EVOH/ionomer blends at high relative humidity conditions.

Keywords: High barrier ethylene vinyl–alcohol copolymers; Water sorption; Polyamide-containing ionomer

1. Introduction

Ethylene–vinyl alcohol random copolymers are a family of semicrystalline materials with excellent barrier properties to gases and hydrocarbons, and with outstanding chemical resistance. EVOH copolymers are commonly produced via a post-polymerization reaction of a parent ethylene-*co*-vinyl acetate copolymer, whereby the acetoxy group is converted into a secondary alcohol. These materials are being increasingly used in the packaging industry as barrier layers to protect foods from the ingress of oxygen and the losses of flavors and consequently to increase package shelf-life [1]. Their barrier properties increase with the increase in the content of vinyl alcohol in the grade. In particular those grades with higher content of vinyl alcohol (≥68 mol%) have outstanding barrier to gases [1] like O_2, N_2 and CO_2 and to hydrocarbons [2]. Unfortunately, EVOH copolymers are markedly affected by water [2–4] and posses a number of processing associated problems, like deficient thermoformability, due to high crystallization kinetics [5]. 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. The deterioration of the barrier properties due to moisture uptake derives from the fact that the inter- and intra-molecular hydrogen bonding (so-called self-association) provided by the hydroxyl groups is intercepted by water molecules. This interaction strongly reduces interchain cohesion and mechanical integrity, increases the fractional free volume of the polymer (plasticization effect) and enhances the permeation through polymer packages. The poorer barrier performance of EVOH polymers under high relative humidity conditions is relevant because many food industry applications require retort processing for food sterilization. Thus, steam retorting of EVOH multilayer containers not

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only causes rapid oxygen barrier deterioration but also a permanent excess free volume that cannot be eliminated under normal storage conditions [6].

Blends of EVOH with low contents of amorphous polyamide are claimed by manufacturers to broaden the forming capacity of EVOH with respect to temperature and draw ratios without sacrificing the gas barrier properties at high relative humidity conditions [5]. Thus, amorphous PA is reported to have a particular interaction with moisture [7], which makes it to exhibit improved gas barrier performance [8] with the increasing relative humidity as opposed to EVOH, where barrier properties deteriorate with the increasing relative humidity. Nylon-containing ethylene–methacrylic acid copolymers (ionomer) partially neutralized with lithium ions are a family of materials highly transparent and with low hygrospicity. 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 [9] to provid 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.

In a previous paper [10], the phase morphology, crystallinity and mechanical properties of dry melt-mixed and extruded films of binary blends of EVOH and PA and a nylon-containing ionomer were studied by DSC, TGA, WAXS, SEM, microhardness and tensile testing. From the results, both types of blends were found to exhibit a biphasic nature, which implied lack of thermodynamic miscibility between blend components. Moreover, the compatibility between EVOH and amorphous PA phases was found to be poorer than that reported for EVOH/PA6 blends and the mechanical properties showed negative deviation from the simple additive rule and high brittleness. This behavior is possibly attributable to geometric hindrance and chain stiffness of the amorphous polyamide. On the other hand, a better phase compatibility was suggested for EVOH/ionomer blends. These blends showed increased flexibility and toughness with the increase in ionomer content and strain rate. Moreover, the intrinsic low solid phase thermoformability window of EVOH has recently been confirmed to be greatly enhanced and improved by blending EVOH with low contents of ionomer [11].

In this study we report about the effects of moisture on the above blends and pure components in terms of water sorption, phase morphology, glass transition temperature (T_g) depression and the resulting changes in the mechanical properties.

2. Experimental

2.1. Materials

A number of binary blends of commercially available ethylene–vinyl alcohol copolymer (EVOH with 32 mol% of ethylene, EVAL® LCF-101) from Kuraray Co. Ltd., amorphous polyamide (Selar® PA UX-2034, polymerized by condensation of hexamethylene diamine and a mixture of 70/30 isophthalic and terephthalic acids) and nylon-containing ionomer (Surlyn® AM-7938) from DuPont de Nemours Co. were prepared by melt mixing at 230°C for 10 min at 30 rpm in a Brabender mixer under an argon atmosphere. The random placement of the acid isomers in the polymer chain prevents crystallization in the amorphous PA. The ionomer is a crystalline nylon-containing ethylene methacrylic acid copolymer partially neutralized with lithium atoms. The type and content of the crystalline nylon present in the ionomer were not supplied by the manufacturer. Sample sheets were obtained by compression molding in a hot plate press at 220°C followed by quenching in water. Specimens of EVOH/PA blends were dried at 110°C for four hours before testing and EVOH/ionomer blends were dried at 70°C for 48 h in a vacuum oven due to the low melting point exhibited by the ionomer. Water equilibrated (100% RH) specimens of the blends were obtained by immersing dry samples in distilled water until they reached saturation. Saturation (equilibrium sorption) is defined as constant weight uptake for successive measurements. The following blend compositions in weight were prepared:

EVOH/PA: 80/20, 70/30, 50/50, 30/70.
EVOH/Ionomer: 90/10, 80/20, 70/30, 50/50, 30/70.

A selected number of high EVOH content blends of EVOH/PA and EVOH/ionomer were coextruded for tensile testing using conventional film coextrusion equipment. The extrusion of the blends was carried out using pelletised pre-extruded blends. LDPE top and bottom layers were coextruded (no tie layers were used) to sandwich the barrier (EVOH blend) layer. Before testing the multilayer system the PE layers were easily delaminated to release the inner EVOH blend film. These films were tested at 23°C and equilibrated (to constant weight) to three different relative humidity conditions namely, 0%RH (dry), 65% RH and 97%RH. 65% RH is the relative humidity in the laboratory and 97%RH was provided by a saturated solution of potassium sulfate [12].

2.2. Thermal analysis

TGA experiments were conducted in a thermogravimeter Setaram TGA92 equipment at 10°C/min on dry samples and water saturated samples.

Dynamic Mechanic Analysis (DMA) experiments were carried out on compression molded polymer bars in a Perkin–Elmer DMA7e at a constant frequency of 1 Hz from −100°C and at 5°C/min in the three point bending mode. Temperature calibration was carried out with water and indium. Water equilibrated samples were placed in the testing chamber, which had been previously set to the starting temperature (−100°C) in order to prevent water desorption before the scan.

2.3. Microhardness

A Vickers indenter attached to a Shimadzu microhardness tester was utilized for micro-indentation measurements at room temperature using a contact load of 0.49 N and a contact time of 25 s. The microhardness (MH) values (in MPa) were calculated from Eq. (2).

$$\mathrm{MH} = \frac{2\sin 68^{\circ} P}{d^2} \tag{2}$$

where P (in N) is the contact load and d (in mm) is the average of six measurements of diagonal length of the projected indentation area.

2.4. Tensile testing

Tensile testing up to failure of dry and water equilibrated melt-mixed blends was carried out at room temperature in an Instron 4400 Universal Tester. A fixed crosshead rate of 10 mm/min was utilized in all cases and the results were taken as the average of five tests. Dumb-bell shaped specimens were used according to the standard ASTM D638.

Tensile testing was also carried out at a crosshead rate of 50 mm/min on extruded films in the machine direction of selected blends of EVOH/PA and EVOH/ionomer.

3. Results and discussion

3.1. Water uptake by sorption and TGA

Equilibrium water content as a function of percent of EVOH in the blends is shown in Fig. 1. The equilibrium water content (sorbed water under 100% relative humidity conditions) is defined as the weight percent of water sorbed in water equilibrated specimens of the blends. Fig. 1 shows that the content of sorbed water in the neat components is 9.4% for quenched EVOH, 8.6% for amorphous PA and 1.7% for the ionomer. The EVOH/PA and EVOH/ionomer blends display a general trend of decreasing water content with the increasing ionomer and PA content, albeit this decrease is barely significant in the case of EVOH/PA blends due to similar water sorption exhibited by EVOH and PA. Lower water sorption is observed for the EVOH/ionomer blends due to low hygrospicity exhibited by the ionomer. This low hygrospicity is probably attributed to high ethylene content, a very low Nylon content and a low ionization rate of the methacrilyc acid comonomer. Interestingly, a positive deviation from the simple additive rule is generally seen to occur in both types of blends, particularly in EVOH/ionomer blends. This positive deviation seen in EVOH/ionomer blends is larger in blends with high content of EVOH. This result could arise from the lack of good interaction between blend components reported earlier [10], particularly for EVOH/PA blends and blends with high contents of EVOH. A lack of good interfacial adhesion or positive interaction between phases was suggested by SEM and tensile testing and could result in a free volume excess. Moreover, structural differences of the neat components in the blends could also take place. Thus, previous X-ray work [10] suggested that a slight reduction in the crystallinity of the EVOH fraction could occur in both types of blends. Accordingly, more free volume would become available to host water molecules in the increased amorphous fraction of the EVOH phase.

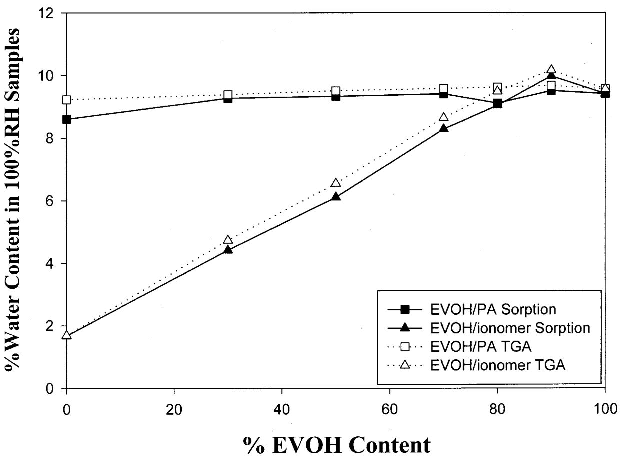

Fig. 1. Water content by sorption and TGA measurements as functions of EVOH content in EVOH/PA and EVOH/ionomer blends.

Fig. 2a shows the TGA weight loss curves of the neat blends components. From these curves, the weight losses associated with water desorption and polymer degradation processes can be monitored as a function of temperature. Fig. 2b shows the derivative of the weight loss in the temperature range in which moisture is released from the polymer. The overall weight loss associated with this desorption is also shown in Fig. 1. It is worthy to remark that the weight gain (water content in saturated specimens) as determined by sorption and the TGA weight loss measurements are both referred to the weight of equilibrated specimens and hence they should provide comparable results. Fig. 1 shows that indeed a similar trend and a good agreement is found between both measurements, being the TGA weight loss only slightly higher than the weight gained by sorption experiments. This discrepancy may just indicate that the dry samples could still have retained some moisture before undertaking the water uptake experiments or the release of some soluble polymer matter; albeit it should be stressed that the differences are small. Fig. 2 shows that in all cases the release of water spreads over a rather broad range of temperatures, albeit a large fraction of the water desorption is limited to a relatively shorter temperature range (represented by a sharp peak in Fig. 2b) for the materials. The fraction of the water loss corresponding to this peak is 61% for EVOH and 83% for the PA. Interestingly, most of the moisture represented by

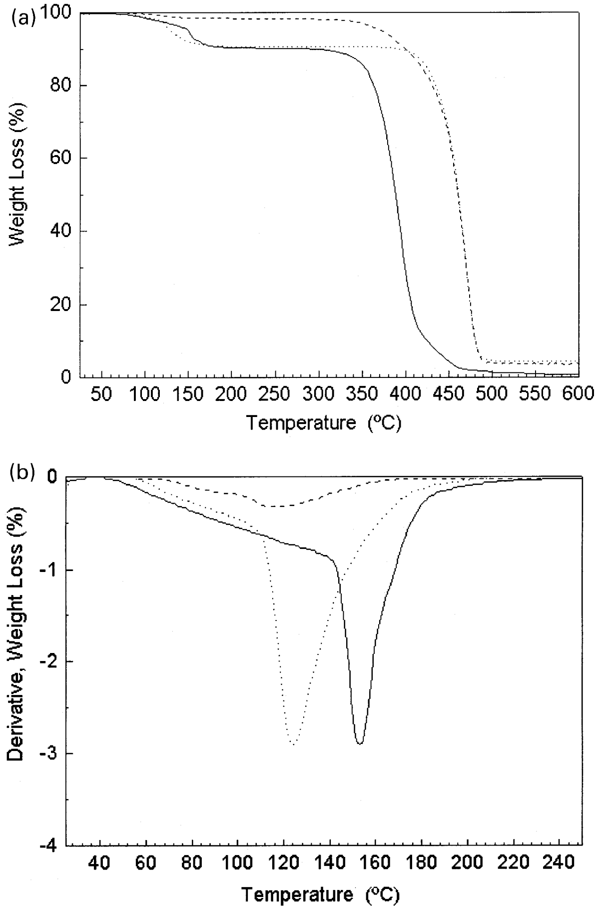

Fig. 2. (a) TGA weight loss and (b) first derivative curves of water equilibrated EVOH (continuous), PA (dotted) and ionomer (dashed).

this peak in EVOH associates more strongly with this polymer than it does with PA and ionomer, because it is released at a higher temperature. Despite the fact that EVOH and PA take up a large amount of water (see Fig. 1), moisture is not so strongly linked to the polyamide chains as it frees at a lower temperature. Water desorption is also completed at a lower temperature for the ionomer and, therefore, the association of the sorbed water molecules with this material is thought to be weaker. The strong association (affinity) of water with EVOH is known to arise from a strong hydrogen bonding interaction between the hydroxyl groups present in the polymer chain and water molecules, whereas the association of water with amide groups is comparatively weaker. It is worth realizing that the water loss begins at temperatures as low as ca. 45°C in all cases. This observation reinforces the hypothesis that water molecules may link to the polymer in different ways as suggested by Hodge et al. [13]. These authors evidenced for the case of polyvinyl alcohol (PVOH) that water can liaise with the polymer chains in three ways: (i) by hydrogen bonding to the alcohol groups, (ii) by hydrogen bonding to the already bonded water molecules (clustering) and (iii) water can also exist in a free state. The most effective plasticizing water for the polymer is the hydrogen bonded water because it reduces the interchain cohesion by intercepting the intermolecular hydrogen bonding provided by the hydroxyl groups. This form of bonding, strongly anchored to the polymer, is likely to be responsible for the water loss peaks recorded at higher temperatures, i.e. for the 61 and 83% of the water sorbed in EVOH and PA, respectively. When hydroxyl and amide groups have been occupied by hydrogen bonded water molecules, clustered and free water are likely to fill the remaining polymer free volume. These latter two forms of water uptake are also favored by the opening of the free volume induced by the plasticizing effect of the hydrogen bonded water and are likely to be responsible for the low temperature water loss. The theoretical weight percentage of moisture hydrogen bonded to amorphous EVOH (with 32 mol% of ethylene) can be easily calculated assuming the association of one water molecule per hydroxyl group: this is estimated to be of 24%. If we assume a mass crystallinity fraction for quenched EVOH of about 0.35 [10], then the experimental percentage of moisture sorbed in the amorphous phase of EVOH is around 15% (moisture is thought to be excluded from the crystals). This result indicates that not all the hydroxyl groups present in amorphous regions are associated with individual water molecules, but in fact much less. Moreover, if we take into account the broad temperature range in which water frees during the TGA runs, some of this water (around 39%) must be forming more labile structures like clusters as indicated above. As a result, it becomes apparent that the presence of hydrophobic ethylene segments and the strong inter-association (inter- and intra-chain) between hydroxyl groups in EVOH copolymers may attenuate the potentially higher detrimental effect of water considerably. A contributing factor to the peaks spread over temperature is indeed the dynamic character of the TGA experiments. Thus, the change in moisture diffusion coefficient across temperature during the heating scan is thought to influence the broadening of the peaks. In addition to the above, molecular heterogeneity in EVOH copolymers has been suggested in the literature [14]. This could also be partially responsible for the broad range in temperature seen for the water loss: If the distance between hydroxyl groups is longer than the average and/or some branching is present, a weaker interaction with water (local more apolar character) can be anticipated compared to that held by other chains with shorter olefinic sequences between hydroxyl groups. For amorphous PA the theoretically calculated percentage of water uptake is found to lay between 13 and 23%, depending on the assumptions made, i.e. on whether water molecules associate only with N–H groups or they do with both N–H and carbonyl groups, C═O. As both (i) the experimental percentage of moisture is found to be of only about 9%, in good agreement with previous work [7], and (ii) clustering is thought to occur for this polymer at water activities higher that 0.3 [7], moisture must only associate with some of the N–H groups. This argument is

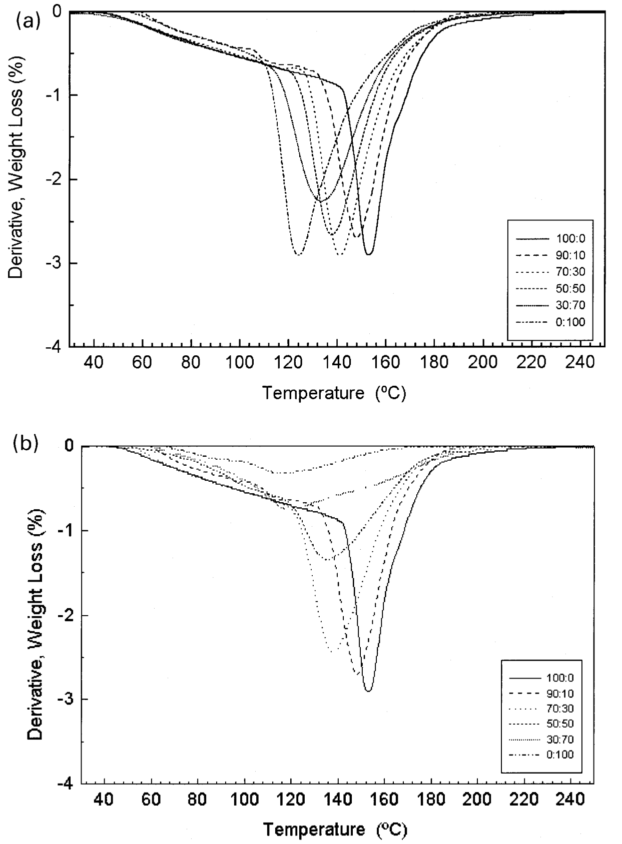

Fig. 3. First derivative of the TGA weight loss curves of (a) EVOH/PA blends and (b) EVOH/ionomer blends.

further substantiated by IR analysis [7]. From Fig. 2, clustering and free water are estimated to account for about 17% of the water uptake in the PA.

Fig. 3 shows the derivative of the water weight loss curves for the two types of blends. The temperature of the maximum of these curves is seen to decrease in the blends with the increasing EVOH content, which shows that the association of water with the blends becomes weaker as the content of EVOH decreases in the blend. Interestingly, a single peak shifted downwards in temperature is obtained in the blends with the decreasing EVOH content, especially in EVOH/PA blends, rather than a bimodal feature combination of two peaks arising from the two blend components. As thermodynamic miscibility does not occur in these blends, the moisture bound to one and the other blend component must be strongly influenced by each other during desorption in the TGA run, hence giving a rather single peaked desorption regime. Thus, it would appear as if the moisture bound to EVOH was trapping (retarding desorption) the moisture associated with the second blend component whereas on leaving the latter moisture would push on its way out the moisture associated with EVOH. Again, the dynamic character of the TGA experiments must also have an influence over the recorded shape of the peaks.

3.2. Glass transition temperature by DMA

Water is a very proactive molecule inducing property changes in a number of polar polymers. The interaction of water molecules with polymer chains comprising hydrophilic groups is in most cases detrimental for the barrier and mechanical performance of these materials, i.e. the so-called plasticization effect [15]. This is typically the case of nylons, polyvinyl alcohol, ethylene–vinyl alcohol copolymers and others. Polar polymers are often better barrier materials because they exhibit higher cohesive energy density [2], i.e. higher intermolecular association, provided by the polar groups comprising the polymer chains. It is this high cohesive energy density which is dramatically intercepted and reduced by the presence of moisture. The effect of reduction in barrier properties is usually accompanied by a depression in the glass transition temperature of the polymer. Such a reduction in T_g often causes a collapse in the mechanical properties of the material. As opposed to the above behavior, the amorphous polyamide studied here has been reported to show a favorable interaction with water under high relative humidity conditions, which results in the reduction of the oxygen permeability [8]. The molecular association mechanisms by which the oxygen barrier properties counterintuitively increase at high relative humidities for amorphous PA are not certain. Fig. 4 shows the DMA storage and loss modulus and the tan delta curves of dry and water equilibrated specimens of the neat blend components, and Table 1 summarizes the maximum of the loss modulus for the neat components and for some of the blends studied here. From Fig. 4 a dramatic drop in T_g can be observed for EVOH and PA materials. The PA appears to depress its T_g in a slightly greater quantity than EVOH under saturation conditions (see Table 1). This could be a result of the higher fraction of hydrogen bonded moisture to PA than to EVOH, i.e. 83% for PA vs. 61% for EVOH. Nevertheless, while the modulus of EVOH is clearly depressed in the water equilibrated sample at room temperature, the modulus of the equilibrated PA is almost unaffected until about 40°C. If a comparison is drawn between the shape of the dry and water saturated DMA traces, they are both very much alike for EVOH and PA, albeit shifted slightly downwards in modulus and considerably in temperature after water uptake. This observation does not support the presence of significant freezable water (free water molecules) but rather clustered in these two polymers as no additional transitions or features are observed. The water equilibrated ionomer exhibits a completely different relaxational behavior. Thus, two clear relaxations in the tan delta curve of the equilibrated sample, one at 50°C and the other at −19°C, can be seen, where before water saturation there was a broad feature centered at 20°C. It is well known that ionomers do often show two main relaxations or glass transitions. One is ascribed to the polymer matrix, i.e. amorphous short chain segments containing polyethylene branches and non-ionized carboxylate

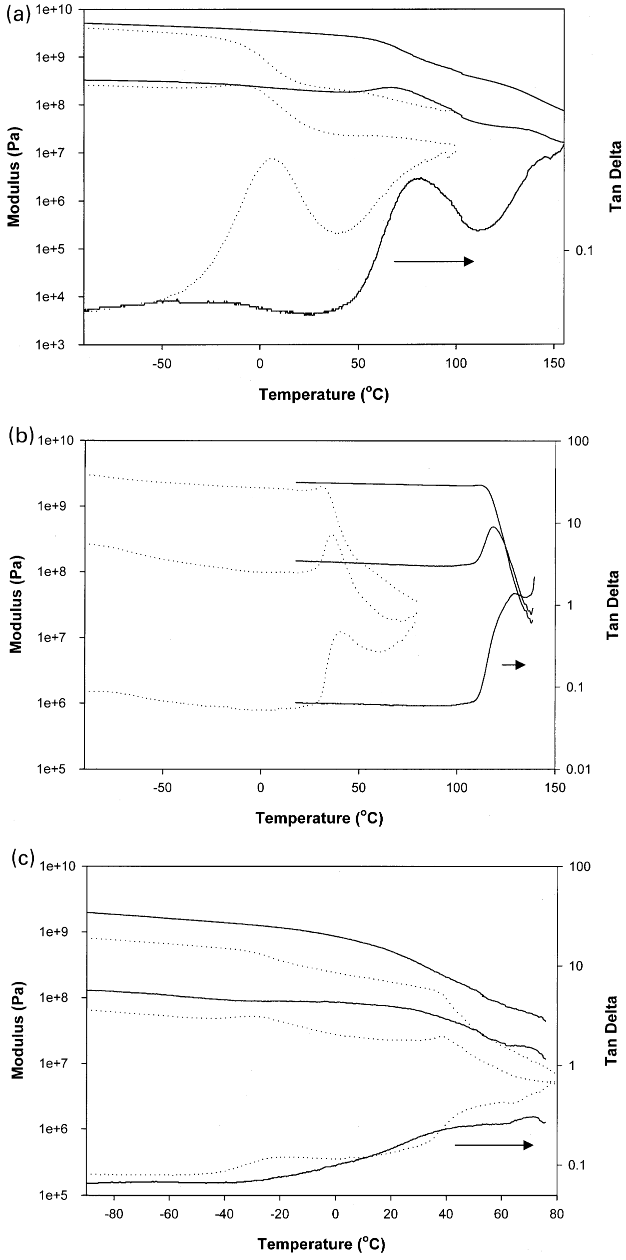

Fig. 4. DMA storage and loss modulus and tan delta of dry (continuous) and water equilibrated (dotted) specimens of (a) EVOH, (b) PA and (c) ionomer.

groups, and the other one to order–disorder transitions in the ionic cluster. An ionic relaxation at ca. 44°C assigned to order–disorder transition in the ionic cluster has been reported in the DSC run of a similar inomer, Zn^{2+} containing no Nylon [16]. These transitions are usually characterized by DMA although in some cases DSC is also able to discern them. The dry sample shows a rather broad feature centered at around 20°C, which could hide two or more relaxations very close to each other. In the wet sample these two transitions could be better resolved or become observable by the plasticization effect of water. Nonetheless, it is difficult to assign the described mechanical relaxations to one or the other feature as the methacrylic acid component of the matrix and the ionic cluster may be both affected by moisture to a different extent. In addition, the nylon fraction present does surely uptake water and, in case its T_g was contributing to the broad peak ranging from -20 to 60°C in the dry sample, it could drop to lower temperature in the equilibrated sample, hence also helping to resolve the DMA curves in the temperature range studied here.

In the 80/20 EVOH/PA blend of dry and water equilibrated specimens two relaxations are seen which are attributed to the neat polymers (see Fig. 5a). From a previous paper [10], dry EVOH/PA blends did not show thermodynamic miscibility and as a result the relaxations of the blend components are easily identified in the DSC and DMA traces of the blend. In the water equilibrated samples the T_g of the EVOH fraction in the blend appears at around the same position as in the equilibrated neat EVOH specimens. This observation indicates that the plasticization of EVOH is completed and occurs similarly as in neat EVOH. The relaxation ascribed to the PA fraction in the blends appears

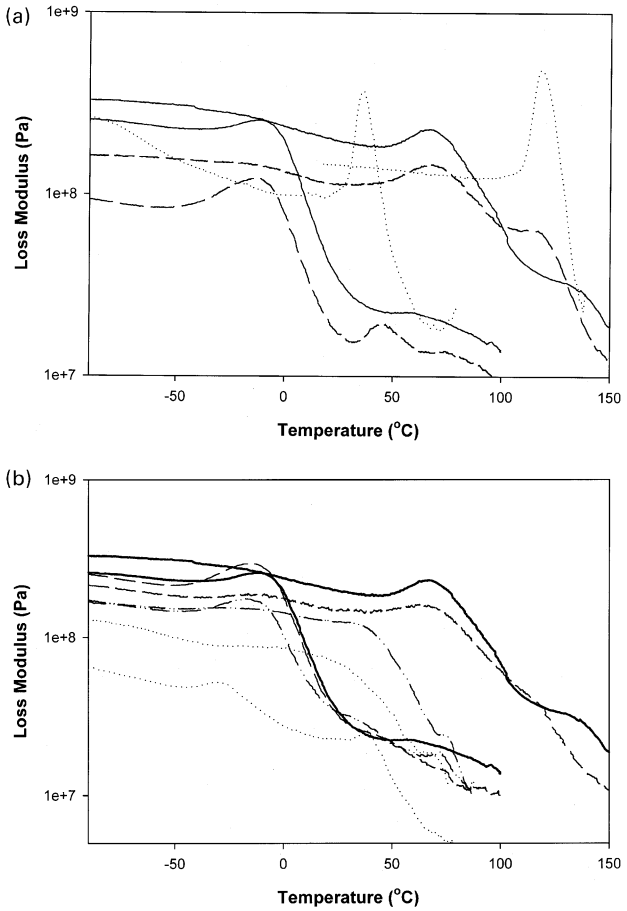

Fig. 5. (a) Loss modulus of dry and water equilibrated (peaks at lower temperature) specimens of EVOH (continuous), 80/20 EVOH/PA blend (dashed) and PA (dotted). (b) Loss modulus of dry and water equilibrated (peaks at lower temperature) specimens of EVOH/ionomer blends, 100/0 (continuous), 80/20 (dashed), 50/50 (dashed-dotted), 0/100 (dotted).

Table 1
Maximum (T_g) of the DMA loss modulus (E'') curves for a number of dry and water equilibrated specimens of the blends and the resulting water-induced temperature depression

	DMA T_g dry (°C)		DMA T_g water (°C)		T_g drop (°C)	
	E''_{EVOH}	$E''_{\text{PA or ion}}$	E''_{EVOH}	$E''_{\text{PA or ion}}$	$\Delta E''_{\text{EVOH}}$	$\Delta E''_{\text{PA or ion}}$
EVOH/PA blends						
100/0	67	–	−11	–	78	–
80/20	68	117	−12	45	80	72
0/100	–	118	–	36	–	82
EVOH/ionomer blends						
100/0	67	–	−11	–	78	–
80/20	65	–	−14	–	79	–
50/50	36	–	−16	–	52	–
0/100	–	20	–	−29 and 38	–	–

at a slightly higher temperature than in neat PA. The PA fraction appears, therefore, to be slightly less plasticized in the blend, perhaps influenced by the higher water affinity exhibited by EVOH. The EVOH fraction may act as a moisture scavenger in the blend. In EVOH/ionomer blends the transition of plasticized EVOH can be clearly seen in all the samples (see Fig. 5b). In the dry blends however, a lower EVOH glass temperature transition was reported with increasing ionomer content [10], which suggested a better compatibility between EVOH and ionomer particularly in the phase inversion blends. However, as the T_g of fully plasticized EVOH can be clearly distinguished in the equilibrated specimens studied here, the potential compatibility (induced by hydrogen bond-assisted interaction with the matrix and the ionic cluster) suggested for the phase inversion dry blends may be disrupted by the sorption of water. This would eventually lead to profuse plasticization of the EVOH fraction in the blend.

Table 2
Tensile modulus (E), strain to failure (ϵ_b) and toughness as functions of relative humidity for extruded blends at a strain rate of 50 mm/min

	%RH	E (MPa)	ϵ_b (%)	Toughness (MJ m^{-3})
EVOH/PA blends				
100/0	0	3137 ± 183	65 ± 20	52
	65	2579 ± 51	242 ± 53	123
	97	325 ± 21	325 ± 30	81
80/20	0	2929 ± 110	8 ± 1	5
	65	2032 ± 146	215 ± 11	87
	97	727 ± 104	204 ± 25	70
70/30	0	2810 ± 142	4 ± 0.3	3
	65	2090 ± 77	173 ± 7	71
	97	864 ± 42	133 ± 18	42
0/100	0	2831 ± 152	5 ± 0.5	3
	65	2793 ± 74	3 ± 0.1	3
	97	2682 ± 112	5 ± 0.2	3
EVOH/ionomer blends				
100/0	0	3137 ± 183	65 ± 20	52
	65	2579 ± 51	242 ± 53	123
	97	325 ± 21	325 ± 30	81
80/20	0	2671 ± 115	50 ± 14	37
	65	2159 ± 145	198 ± 18	77
	97	405 ± 49	302 ± 15	81
70/30	0	2208 ± 43	155 ± 26	84
	65	1724 ± 148	233 ± 15	86
	97	466 ± 50	273 ± 7	71

3.3. Mechanical properties

Tensile modulus and microhardness, and strain to failure and toughness were derived and are plotted as a function of composition in Figs. 6 and 7, respectively. From the comparison of Figs. 6a and b the first observation is the good correspondence between tensile modulus and microhardness measurements in dry and equilibrated samples as a function of EVOH content. Indeed, modulus and microhardness values for dry and water saturated blends showed a reasonable linear correlation with each other (see Fig. 8) that can be expressed by the following equation:

$$E = 20\,\text{MH}.$$

A lineal relation ($E = 10\,MH$) between these two parameters has been published recently for a range of polyethylene materials [17]. A linear relation between microhardness and yield stress has also been reported before [11,17]. The tensile modulus and microhardness of a low density polyethylene sample were also measured and shown in Fig. 8. Interestingly, this material did also fit very well within our linear trend (see Fig. 8). The discrepancy in the slope of the correlation could arise from the scatter shown by the polyethylene materials studied by Flores et al. [17] due to the narrower modulus range displayed by their materials. From the work of Flores et al. [17] and from our more recent results [11] it becomes apparent that microhardness can be linearly related to both yield stress and Young's modulus. This would be in reasonable accordance with models like the one proposed by Struik [18], which predicts a simple linear relation between yield stress and the elastic modulus. A further discussion concerning this topic is beyond the scope of the present paper and will be dealt elsewhere.

From the plots in Fig. 6, modulus and microhardness are

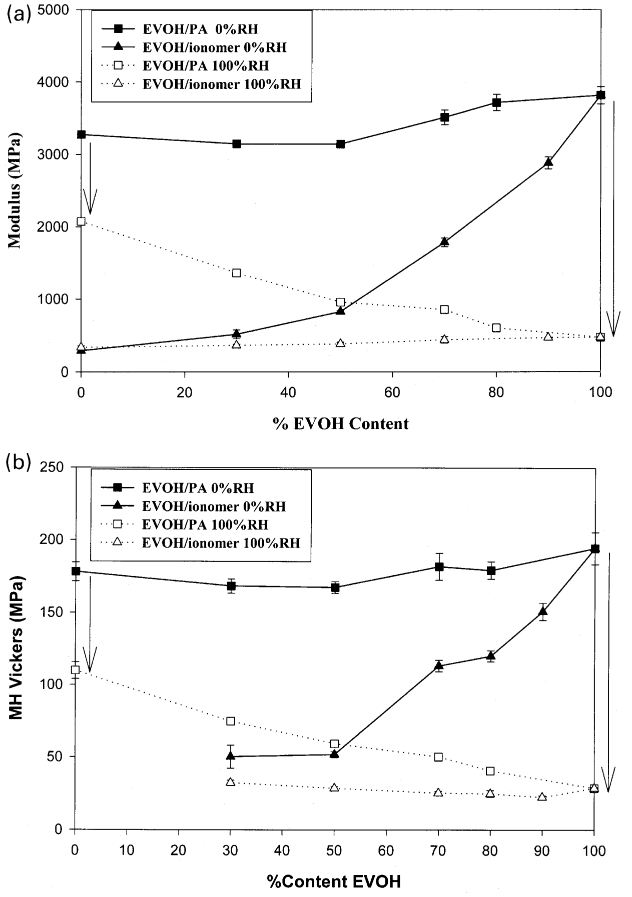

Fig. 6. (a) Tensile modulus and (b) microhardness as a function of EVOH content in dry and water equilibrated EVOH/PA and EVOH/ionomer blends.

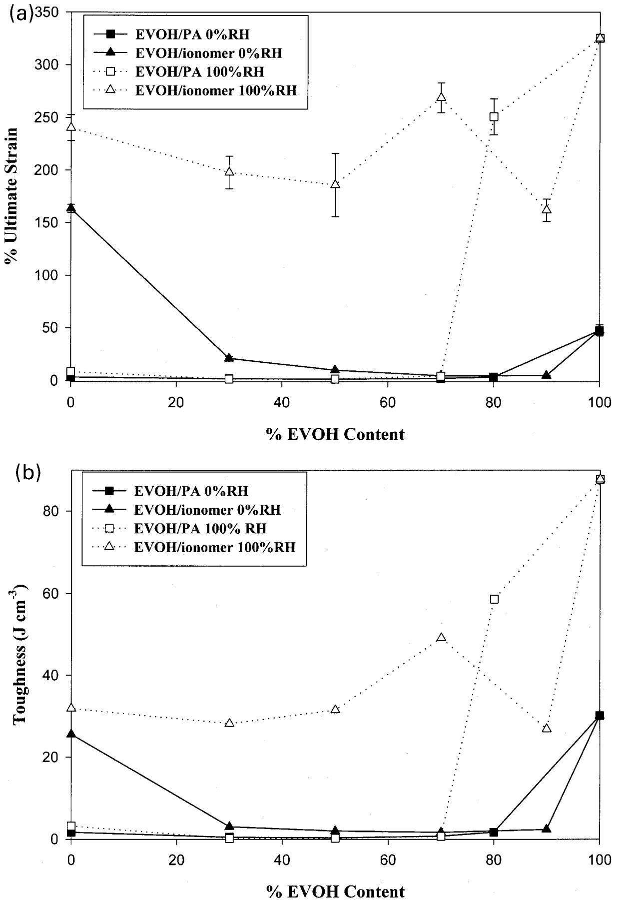

Fig. 7. (a) Ultimate strain and (b) toughness as a function of EVOH content in dry and water equilibrated EVOH/PA and EVOH/ionomer blends.

found to decrease in the dry blends with decreasing EVOH content, albeit more steeply for EVOH/ionomer blends. In the water equilibrated samples, both mechanical measurements increase in magnitude with the increasing PA content in the blend, whereas EVOH/ionomer blends hardly change. Thus, in the water equilibrated blends, EVOH/ionomer blends have in all cases increased flexibility, while the EVOH/PA phase inversion blends maintain high stiffness values even under high relative humidity conditions. Despite the fact that a similar amount of water sorption was measured for EVOH and PA materials, water induced plasticization (see arrows in Fig. 6) is affecting the mechanical performance of EVOH to a considerable greater extent. Nonetheless, direct comparison of water sorption for these two materials is misleading because the PA has virtually no crystallinity whereas EVOH has a mass crystallinity fraction between 35 and 55% depending on the obtaining procedure [10]. As water sorption is thought to be exclusively limited to the amorphous fraction of most polymers, it is clear that the effective uptake of water is at least one third larger for EVOH. More importantly, albeit the T_g of PA is indeed largely depressed by water sorption, it still falls above room temperature, i.e. above the temperature of the tensile testing experiments (see Table 1): from Fig. 4 it can be seen that the modulus of the water equilibrated PA only shows significant reduction at temperatures above 36°C.

Values of ultimate strain and toughness measured at a strain rate of 10 mm/min and at room temperature are shown in Fig. 7. From this it can be seen that under dry

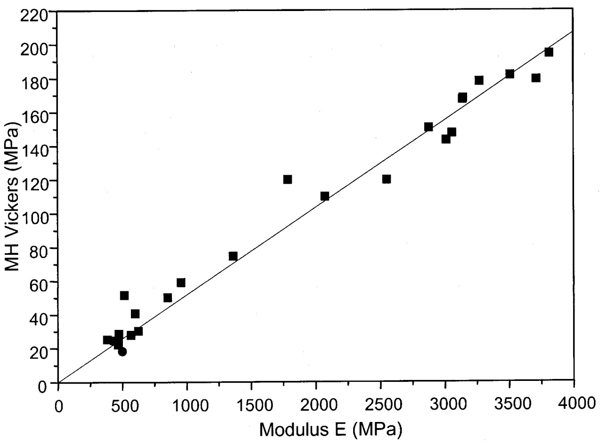

Fig. 8. Microhardness vs. tensile modulus for all dry and water equilibrated blends (square) and a LDPE (circle).

conditions EVOH/PA blends are extremely fragile. Somewhat higher plasticity is seen in the case of EVOH/ionomer blends under these testing conditions. Larger strain to failure and toughness can be generally measured in the equilibrated samples as a result of water plasticization, however those mechanical parameters are still seen very low in EVOH/PA blends.

Extruded films of high content EVOH blends were also tested in the machine direction in tensile experiments at three relative humidity conditions and at higher strain rate, i.e. 50 mm/min (see Table 2). It should be borne in mind that in order to keep up the barrier performance of these blends a high content of EVOH must be present, hence our interest in the performance of high EVOH content blends. From previous work [10], flexibility rose in dry EVOH/ionomer blends with the increasing ionomer content and strain rate. This observation was deemed to have significant relevance in the high temperature performance of the blends, e.g. during solid phase thermoforming. From Table 2 it can be seen that all blends generally exhibit decreased modulus and increased ductility and toughness in the presence of moisture; this is an unambiguous indication of the moisture-induced plasticization process occurred in the samples. Nevertheless, the presence of moisture has little effect on the extruded PA, which shows at room temperature high stiffness and low plasticity irrespective of relative humidity. Accordingly, at room temperature and at high relative humidity, EVOH/PA extruded blends display increased stiffness and reduced toughness with the increasing PA content in agreement with tensile results gained in melt mixed blends at a lower strain rate. On the other hand, EVOH/ionomer blends show an increased flexibility and toughness at 0%RH with regard to both neat EVOH and samples tested at a lower strain rate [10]. With the increasing relative humidity these blends still maintain a high degree of flexibility and toughness, showing a slightly higher modulus and lower strain to failure with regard to plasticized EVOH.

4. Conclusions

The effect of moisture has been investigated in EVOH, PA and nylon-containing ionomer and in a number of binary blends of these materials by sorption, TGA, DMA, microhardness and tensile testing. From the results it is clear that EVOH takes up a larger quantity of water (before and after correction for the crystallinity content) than PA and ionomer. Comparatively, the ionomer shows very low hygroscopicity. Moisture was found to bind more strongly with EVOH through hydrogen bonding than with PA, but the fraction of non-hydrogen bonded to the polymer (mostly clustered or self-associated) moisture was suggested to be lower for the PA. This may be a consequence of the comparatively more intense interaction of the hydroxyl groups. A result of the latter could also be the observation that the water-induced glass transition depression (polymer plasticization) is slightly smaller for EVOH than for PA. In spite of that, the T_g of the fully plasticized PA still shows above room temperature, whereas T_g of the fully plasticized EVOH lays well below room temperature. In the mechanical properties at room temperature, EVOH is found to be largely plasticized by moisture and displays much lower modulus and higher plasticity and toughness than under dry conditions. On the other hand, the mechanical integrity of both PA and ionomer is not so affected by moisture. Nevertheless, while the PA shows an intrinsic high stiffness and brittleness (irrespective of relative humidity), the ionomer shows much higher flexibility. More importantly, the flexibility of the latter material is found to be enhanced by the increasing strain rate. In blends, the water uptake was found to be slightly higher than that predicted by the simple additive rule and the EVOH fraction in the blends was found to be fully plasticized. The phase compatibility suggested from earlier work for some EVOH/ionomer blends appeared to vanish by the effect of sorbed moisture intercepting potential interfacial adhesion via hydrogen bonding. In the mechanical properties of the blends exposed to moisture, EVOH/PA blends displayed increased stiffness but fragility compared to EVOH, whereas high flexibility and toughness was still observed in EVOH/ionomer blends. The above observations may support recent experiments [11] from which the thermoformability characteristics of EVOH were found to be greatly improved in terms of temperature and draw ratio by adding ionomer, whereas these were in general poorer for EVOH/PA blends. Sorption and desorption isotherms and oxygen barrier properties as a function of relative humidity are now under study for these blends and will be reported elsewhere.

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