

# Water Effect on the Morphology of EVOH Copolymers

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**ABSTRACT:** The effect of water on the morphology of four ethylene vinyl alcohol copolymers (EVOH) with different ethylene contents was studied by differential scanning calorimetry (DSC). EVOH film samples equilibrated in controlled atmospheres at different relative humidities (RH) and 23°C were analyzed. Under dry conditions, the glass transition temperature ( $T_g$ ) was unaffected by copolymer ethylene content. As RH increases,  $T_g$  decreases. It seems that the presence of water within the polymer matrix results in plasticization of the polymer.  $T_g$  varies from around 50°C (dry) to below room temperature. EVOH copolymers are glassy polymers when dry and rubbery polymers at high RHs. Fox and Gordon–Taylor's equations well describe  $T_g$  depletion at low water uptake, although severe water gain results in a considerable  $T_g$  decrease, which is not predicted by these theories. Melting temperature,  $T_m$ , and enthalpy,  $\Delta H_m$ , were also analyzed. When dry,  $T_m$  decreases as ethylene content increases. No significant water effect was found on either  $T_m$  or  $\Delta H_m$ . Hence, crystallinity seems to be unaffected by water presence. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 74: 1201–1206, 1999

**Key words:** EVOH; water effect; DSC;  $T_g$ ;  $T_m$ ; melting enthalpy

## INTRODUCTION

It is well known that polymers allow the transport of low-molecular weight substances. This phenomenon is a complex process, including sorption and molecular diffusion of substances through the amorphous portion of the polymer matrix. Mass transport is a very important phenomenon in many polymer applications (membranes, packaging, packing of chromatographic columns, etc.).

Ethylene vinyl alcohol copolymers (EVOH) are commonly present in food packaging. They are

used as permanent gas-barrier materials for those foods that are sensitive to certain levels of oxygen or carbon dioxide. However, EVOH properties, including barrier properties, are greatly affected by water content.<sup>1,2</sup> Because water is always present in a food packaging system (it forms part of the external atmosphere and is a main constituent of many foodstuffs), EVOH films are always sandwiched between polyolefin layers (barrier to water) to protect EVOH. In some cases, both package and food are subject to thermal treatments such as pasteurization or retorting. High temperatures and high relative humidities (RH) result in EVOH sorption of large amounts of water and consequently considerable changes in the EVOH properties.<sup>3</sup>

Water effect was also observed in other hydrophilic polymers such as polyamides<sup>4,5</sup> and polyesters.<sup>6–8</sup> Marked decreases in the glass transition temperatures ( $T_g$ ) of Nylon 6<sup>9</sup> and poly(ethylene terephthalate)<sup>6</sup> (PET) caused by water sorption were measured. The concept of a hydrogen bond network in polyamides and the disruptive effects

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of water on this, with particular reference to water molecules becoming firmly bound to the polar groups in these polymers, is prevalent in the literature.<sup>10,11</sup> However, how water affects polymers is still not clear. It is known that the presence of low-molecular weight molecules in the polymer matrix induces some plasticization (this is the effect of plasticizers on polyvinyl chloride). An excellent review on polymer plasticization by water was recently published.<sup>12</sup> Low-molecular weight molecules are supposed to be positioned in the amorphous part of the structure, interacting with the polymer and relaxing interchain attractions. This results in an increase in chain mobility and consequently a reduction in mechanical and barrier properties. It is controversial whether or not mass transport also affects the crystalline part of the polymer. Some authors suggest that mass transport may be limited to the amorphous part of the matrix, but it may also affect the polymer crystallinity.<sup>13</sup>

In this article, we report on the effect of water on polymer morphology in four EVOH copolymers of different ethylene contents by differential scanning calorimetry (DSC). The analysis includes glass transition and melting of polymer films from dry to 100% RH at 23°C.

## EXPERIMENTAL

Four EVOH copolymers (Soarnol D2908, DC3203, E3808, and A4412) with 29, 32, 38, and 44% ethylene contents were studied and are referred to as EVOH-29, EVOH-32, etc. Polymeric films were kindly supplied by Cerdato (Elf Atochem, Serquigny, France). They were obtained in an Erwepa coextruder by coextrusion of a polypropylene (PP)/EVOH/PP structure. The multilayer sheet was constructed without adhesives for easy separation (by peeling) of the EVOH layer from PP. In this way, polymer morphology was similar to EVOH obtained industrially and EVOH films were protected from water during the cooling process at the exit of the coextruder die. Other effects related to contact between PP and EVOH in the molten state are not taken into account because of their immiscibility and the brevity of their contact. Film thickness values measured in a micrometer (Metrotec, Spain) were  $20.5 \pm 1.1$  (EVOH-29),  $15.6 \pm 1.3$  (EVOH-32),  $18.9 \pm 1.3$  (EVOH-38), and  $21.9 \pm 1.2$   $\mu\text{m}$  (EVOH-44).

Circular samples of 5-mm diameter were obtained using a paper punch. Samples consisting of

eight circular films weighed approximately 0.004 g. These samples were equilibrated at different RHs in desiccant containers with standard salt-saturated solutions of NaBr (28.3% RH),  $\text{Mg}(\text{NO}_3)_2 \times 4\text{H}_2\text{O}$  (57% RH), and  $(\text{NH}_4)_2\text{SO}_4$  (75.5% RH). The humidity maintained in each container was evaluated by a high-precision Hygrosensor hygrometer (Newport Sci., Jessup, MD). Dry samples were obtained in a desiccant container with silica gel at room temperature, and 100% RH was achieved in a desiccant container with MilliQ water. In all cases, samples were maintained for at least two months to ensure equilibrium.

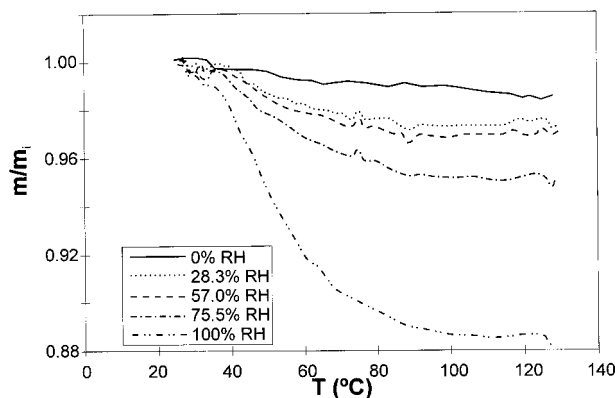
Thermal analysis was carried out in a Mettler TA Instruments 4000 thermal analyzer. The instrument had DSC and thermogravimetry (TG) capabilities. The instrument assembly was equipped with a dual-sample cell, TC11 TA processor, control and evaluation unit, and DSC30 and TG50 measuring cells.

DSC analysis was performed using the DSC30 cell. Samples were put into open pans (40- $\mu\text{m}$  aluminum sample pans, Mettler). Commercial samples of indium (99.999% purity) were used as a calibration standard of  $T_m = 156.6^\circ\text{C}$  and  $\Delta H_m = 38.4$  J/g. The heating chamber was purged with a dry nitrogen stream (15 ml/min) to avoid moisture condensation. The temperature rose from  $-40$  to  $240^\circ\text{C}$  at  $20^\circ\text{C}/\text{min}$ . Thermograms were analyzed to obtain  $T_g$ ,  $T_m$ , and  $\Delta H_m$  by using the manufacturer's software.  $T_g$  values were determined by the onset method because the end of the transition was not always clear. Values of  $T_g$ ,  $T_m$ , and  $\Delta H_m$  shown in this article are the average  $\pm$  the standard deviation of at least three samples.

The TG50 cell was used for TG analysis. Samples were heated from 25 to  $240^\circ\text{C}$  at  $20^\circ\text{C}/\text{min}$  in open pans to determine the amount of sorbed water present in the polymer after equilibrium in each atmospheric condition.

## RESULTS AND DISCUSSION

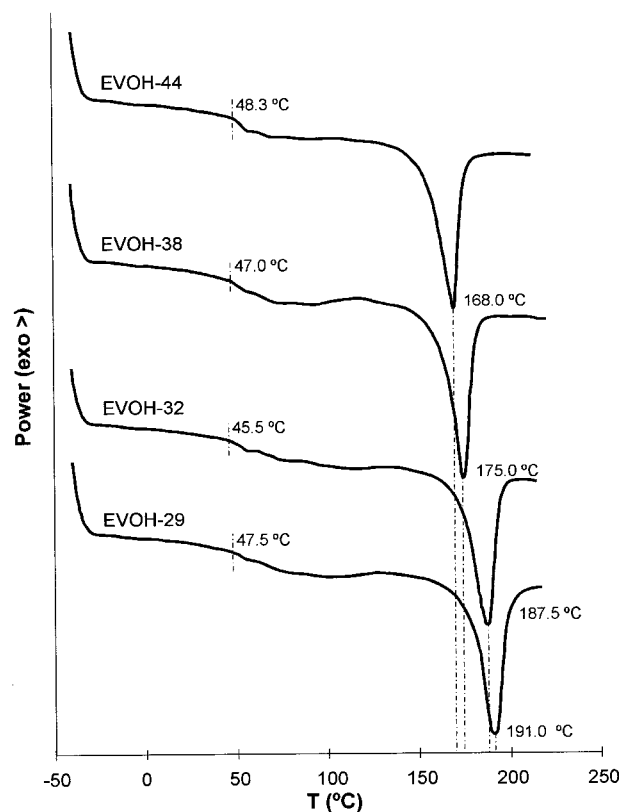
Water content of EVOH samples under different RH conditions was determined by TG and is presented in Figure 1 (for EVOH-29) and Table I. Apart from water, other components may desorb during the heating process. The thermograms of the dry samples were initially used as a baseline; however, this was reconsidered after noticing that there was a depression over the temperature range corresponding to that at which water evap-



**Figure 1** TG thermograms of EVOH-29 samples conditioned under different humidity conditions.

orates in the wet samples. This was confirmed by DSC analysis. It seems that sorbed water is so strongly associated with the polymer chains that even after two months under dry conditions, water is still present. Probably a portion of the sorbed water is firmly bonded to the polymer following a Langmuir-type of sorption. In a previous article,<sup>14</sup> the sorption of water by a semicrystalline polyamide was found to be bimodal. The initial part of the isotherm was described by Langmuir's equation, whereas the rest of the isotherm agreed with the Flory–Huggins' equation.

The evaporation of water was measured by a sample weight change from room temperature to 130°C. Obviously, sorbed water increases with RH. Sorbed water at high humidities surpasses 10% of EVOH weight, confirming their high affinity for water. It is important to mention that the loss of water was not abrupt but extended over a broad temperature range as Figure 1 shows. This is probably due to the absence of free water in the polymer and strong interactions between water molecules and —OH groups via H bonding. In spite of the different levels of ethylene, water sorption did not differ substantially between EVOH copolymers.

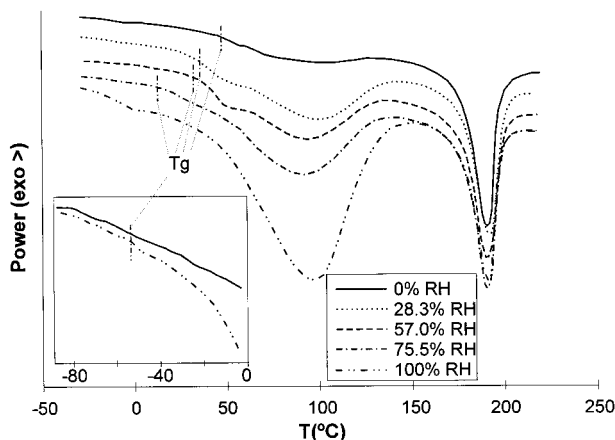


**Figure 2** DSC thermograms of dry EVOH samples showing the values of  $T_g$  and  $T_m$ .

Figure 2 shows the DSC thermograms of the four EVOHs studied under dry conditions.  $T_g$  values were obtained by the onset procedure because the end of the transition was not obvious for wet samples, and  $T_m$  values were determined from the peak of the transition. The melting temperatures of EVOH copolymers were intermediate between those of the homopolymers [polyvinyl alcohol (PVOH) and linear low-density polyethylene (LLDPE),  $T_m$  (PVOH) = 230°C and  $T_m$  (LLDPE) = 100°C].<sup>15</sup> As expected, the higher the alcohol content, the higher the melting temperature. The temperature variation profile versus ethylene

**Table I** Percentage (average  $\pm$  standard deviation) of Water Sorbed by EVOH Copolymers Under Different Relative Humidity Conditions Obtained by Thermogravimetry

RH (%)	EVOH-29	EVOH-32	EVOH-38	EVOH-44
0	0.6 $\pm$ 0.6	0.9 $\pm$ 0.9	0.4 $\pm$ 0.4	0.6 $\pm$ 0.6
28.3	3.7 $\pm$ 0.7	4.3 $\pm$ 1.2	4.1 $\pm$ 0.9	3.2 $\pm$ 0.9
57.0	3.9 $\pm$ 0.7	4.5 $\pm$ 1.2	4.7 $\pm$ 1.0	3.7 $\pm$ 0.9
75.5	6.0 $\pm$ 1.0	5.8 $\pm$ 1.3	5.3 $\pm$ 1.0	5.0 $\pm$ 1.0
100	12.9 $\pm$ 0.6	13.0 $\pm$ 1.1	11.0 $\pm$ 1.0	12.4 $\pm$ 1.2



**Figure 3** DSC thermograms of EVOH-29 samples conditioned under different humidity conditions.

content approached a straight line. By contrast, the  $T_g$ 's varied only slightly with ethylene content, despite the considerable difference in  $T_g$  between PVOH (80°C) and LLDPE (−130°C).<sup>15</sup>

Figure 3 shows the DSC thermograms of EVOH-29 at different RHs. As can be seen in the thermograms, the presence of water yields a wide peak with a maximum near 100°C, which corresponds to the evaporation of water. The thermogram of the dry sample also presents the same peak indicating that the water is still present in samples conditioned at 0% RH, in agreement with TG analysis. It is interesting to note that melting ice was not observed except in the samples at 100% RH, and even in that case, the peak was too small for a sample containing over 10% of water. This may indicate that water molecules are not free but bonded to polymer chains, possibly by H bonding with the —OH groups. This hypothesis also explains the width of the peak assigned to water evaporation.<sup>14</sup> Similar behaviors were observed with the other three copolymers.

The presence of water also appeared to affect the location of  $T_g$ . As was explained in the experimental section,  $T_g$  was determined by the onset method because water evaporation hid the end of the transition. Figure 3 shows the decrease in  $T_g$  from 50 to 10°C as RH increases. The sample conditioned at 100% RH did not show the glass transition within the temperature range assayed. For this reason, a new DSC test was performed starting from a lower temperature on both the dry and the 100% RH samples. A thermal transition appeared around −60°C for the wet sample that was not seen in the dry sample. This transition was assigned as the glass transition of the wet

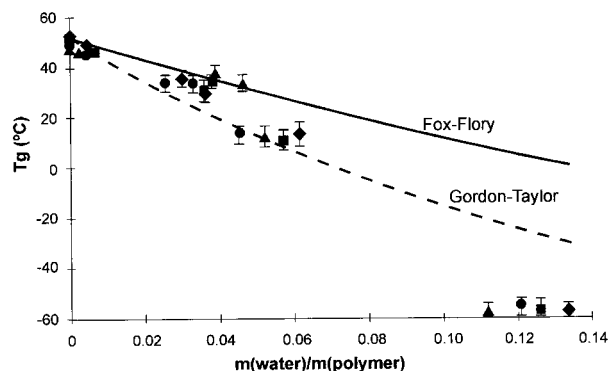
sample. Figure 4 presents the plot of  $T_g$  as a function of water content for all copolymers. The reduction of  $T_g$  by organic liquids, plasticizers, and monomers is well documented. There are also some interesting reports on the plasticizing power of water in different polymers. PET fibers containing 7% of water showed a  $T_g$  value 16°C below that when dry. The more hydrophilic Nylon 6 showed a  $T_g$  decrease of 72°C after gaining 6% of water.<sup>16</sup> The correspondence between  $T_g$  and the start of water evaporation may indicate a relationship between  $T_g$  values and water presence. Water sorbed in the polymer matrix strongly interacts with the chains, breaking the interchain attractions, and consequently plasticizing the polymer.

Many expressions relating  $T_g$  to the presence of a plasticizer were reported in the literature. Among them, the equation proposed by Fox and Flory<sup>17</sup> is the most commonly used,

$$\frac{1}{T_g} = \frac{w_p}{T_{gp}} + \frac{w_s}{T_{gs}} \quad (1)$$

This expression was successfully used to describe the effects of many plasticizers and even water in small amounts.<sup>4</sup> The behavior of different polymer/solvent systems was well described by the Gordon–Taylor equation in which an empirical parameter,  $k$ , was introduced<sup>17</sup>

$$T_g = \frac{w_p T_{gp} + k w_s T_{gs}}{w_p + k w_s} \quad (2)$$



**Figure 4** Experimental glass transition temperatures of EVOHs under different relative humidity conditions: (◆), EVOH-29; (■), EVOH-32; (●), EVOH-38; and (▲), EVOH-44. Values predicted through (—), Fox–Flory's equation, and (---), Gordon–Taylor's equation with  $k = 5$ .

**Table II Average and Standard Deviation Values of Experimental Melting Temperatures for EVOH Copolymers Under Different Relative Humidity Conditions**

RH (%)	EVOH-29	EVOH-32	EVOH-38	EVOH-44
0	191.0 ± 1.5	187.4 ± 2.0	174.7 ± 1.0	168.2 ± 0.3
28.3	191.9 ± 1.2	187.6 ± 0.9	176.1 ± 1.3	167.2 ± 1.8
57.0	189.7 ± 1.6	187.2 ± 3.2	176.5 ± 1.4	168.3 ± 2.8
75.5	191.2 ± 2.0	187.3 ± 3.1	176.9 ± 2.0	168.7 ± 0.7
100	189.6 ± 2.1	186.9 ± 1.2	175.3 ± 3.5	168.2 ± 2.9

In eqs. (1)–(2),  $w_i$  is the weight fraction of component  $i$  ( $i = p$ , polymer;  $i = s$ , sorbate),  $T_{g_i}$  is the glass transition temperature of pure  $i$  component. Equations (1) and (2) were used to describe the change in  $T_g$  due to the presence of water using 135 K as the water–glass transition.<sup>18</sup> However, it was necessary to obtain the value of  $T_g$  of samples without water. New experiments were carried out as follows. Samples were heated to 240°C, then cooled to –40°C, and finally heated to 240°C at 20°C/min. Despite the thermal history of the copolymers being destroyed, water was also removed from the sample, and therefore, a more accurate evaluation of  $T_g$  was obtained. The results were 52 ± 2 (EVOH-29), 50 ± 3 (EVOH-32), 46 ± 1 (EVOH-38), and 45 ± 2 (EVOH-44). Introducing these data in eq. (1) and including an empirical value for  $k$  in eq. (2), the theoretical effect of water on  $T_g$  was obtained. The value of  $k$  in eq. (2), which agreed better with the experimental values, was 0.2. Some authors<sup>19</sup> related the value of  $k$  to the heat capacity increments at the glass transition of the pure components ( $k = \Delta C_p^p / \Delta C_p^s$ ). Values close to that obtained here were published.<sup>19</sup> As Figure 4 shows, both equations provide a good description of experimental data for low water uptakes. As water content increases, eq. (1) shows considerable deviations. The Gordon–Taylor approximation showed a larger decrease in  $T_g$  with water uptake, al-

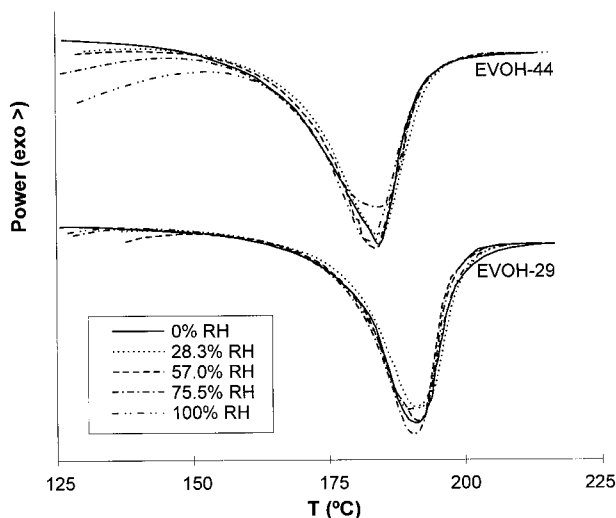
though the values were far from those experimentally obtained at 100% RH.

The melting behavior of EVOH copolymers was also determined under different RH conditions. As Table II shows,  $T_m$  values were not significantly affected by RH. The only variation found was the expected decrease in  $T_m$  values as ethylene content increased.

The invariability of melting temperature with water content clearly indicates that (a) there was no phenomenon of crystalline perfection during the heating process, and (b) the water initially present is removed from the sample before the melting process starts, otherwise there would be a depression of  $T_m$  (the higher the water content the greater the depression). In contrast, the melting enthalpy values listed in Table III (corrected to discount sorbed water mass) did show significant changes. Enthalpy values for EVOH-29 and EVOH-32 were unaffected by RH, indicating that the crystallinity was almost unchanged. However, the enthalpy values corresponding to the EVOH-38 and EVOH-44 melting processes clearly decreased as water content increased. Initially, this profile could be associated with a reduction in crystallinity. However, it was difficult to explain why these two samples were affected, whereas the other two were not. The melting peaks of EVOH-29 and EVOH-44 (corrected to 1 g of sample) were plotted and presented in Figure

**Table III Average and Standard Deviation Values of Experimental Melting Enthalpies for EVOH Copolymers Under Different Relative Humidity Conditions**

RH (%)	EVOH-29	EVOH-32	EVOH-38	EVOH-44
0	71.8 ± 0.7	67.9 ± 2.2	70.2 ± 2.1	63.8 ± 0.4
28.3	71.1 ± 3.6	67.7 ± 2.3	69.2 ± 2.9	59.8 ± 0.4
57.0	72.8 ± 3.2	70.9 ± 1.0	65.8 ± 1.4	60.6 ± 2.2
75.5	73.3 ± 1.3	69.4 ± 3.6	64.5 ± 1.8	55.2 ± 0.4
100	71.4 ± 0.2	65.5 ± 0.8	59.0 ± 0.1	51.9 ± 0.9



**Figure 5** Melting peak profiles of EVOH-29 and EVOH-44 at different relative humidities.

5. As can be seen, the difference between samples occurs at the beginning of the transition. The end of water evaporation appears to hide the start of polymer melting, hence the integration of the melting peak is not complete. As the ethylene content decreases, the EVOH melting temperatures increase, and polymer melting and water evaporation appears as two separate peaks. Consequently, we believe that the presence of water does not affect the percentage of crystallinity.

We are presently conducting DSC studies by using closed capsules to examine the influence of water content on the crystallization/melting behavior of these copolymers.

## CONCLUSIONS

Sorption of water by four EVOH copolymers of different ethylene contents under different RH conditions at 23°C was characterized by thermal analysis. EVOH copolymers sorbed large amounts of water, presumably within the amorphous portions of the matrix. Sorption increases as the ethylene content of EVOH decreases. Water is not free but strongly interacts with the polymer as shown by the absence of peaks at 0 and 100°C in the DSC thermograms.

The presence of water results in the plasticization of the polymer. Indeed, the  $T_g$  decreases as the polymer films are exposed to progressively

more humid environments. No water effect on copolymer melting temperatures was observed.  $T_m$  values and melting enthalpies were invariable with RH, indicating that crystallinity is not affected by the transport of water within the polymer.

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