Effect of Water Presence on the Sorption of Organic Compounds in Ethylene–Vinyl Alcohol Copolymers

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ABSTRACT: Sorption isotherms of methanol, ethanol, propanol, butanol, hexanol, ethyl caproate, and limonene in 4 ethylene–vinyl alcohol (EVOH) copolymers with different ethylene contents were determined by inverse gas chromatography (IGC) at 25°C and different relative humidity conditions. From sorption isotherms, solubility coefficients were determined and used as a tool for comparison. Besides affecting the morphology of the polymers by plastification, sorbed water seems to increase the polarity of the medium. Sorption of alcohols increases at high relative humidity; both plasticization and polarity cause this behavior. The effect is more important for the smaller alcohols and among polymers for those with low ethylene content. As the sorbant becomes nonpolar, plasticization and polarity effects become antagonistic. Indeed, the effect of water presence in sorption of hexanol is not significant, and sorption of limonene and ethyl caproate is even reduced at high water content. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 711–716, 1998

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INTRODUCTION

Knowledge of molecular mass transport processes through polymeric materials is essential for the design of packages, protective clothing, separation membranes, and chromatographic column fillings. Although based on the same thermodynamic principles, different mass transport phenomena have been described, depending on the source and destination of the transport, that is, migration, permeation, or sorption (adsorption, absorption, desorption, scalping, etc.).[1] Many articles, reviews, and books have been published about migration, especially with reference to food packaging applications, and the concerns here relate to toxicity or organoleptic changes, which may be induced in foods.[2,3] Similar comments can be made about permeation. This phenomenon is important in gas separation membranes, high barrier, and modified atmosphere packaging.[2–5]

Sorption is a mass transport phenomenon scarcely analyzed since the sorption effect in common polymer applications is not seen as being as dramatic as permeation or migration. Moreover, sorption experiments are more complex and time-consuming than those for migration or permeation analysis. Mass sorption may result in morphological changes, such as plasticization, and even in the swelling of the polymer.[6] In addition to the effect on the polymer itself, in some pack-

aging applications, the effect on the content is more important. This is the case with aromatic foods in which aroma sorption in the package (scalping) may result in a shorter shelf-life.[2,3]

In the last few decades, inverse gas chromatography (IGC) has become a powerful technique in the evaluation of many polymer properties.[7] Among other applications, this technique can evaluate sorption isotherms of volatile substances by simple injections of known samples using the polymer as a column filling.[8] The most common procedures consist of the polymer solution being applied as a coating on an inert support, glass beads, or the internal surface of a passivated capillary column.[9–11] In this way, the polymer presents a greater surface area-to-volume ratio. However, this destroys the mechanicothermal history of the material. In our study, columns were filled with strips of ethylene–vinyl alcohol (EVOH) films obtained by extrusion. Although the surface-to-volume ratio is not as great, this technique permits the utilization of IGC with polymers not easily soluble. IGC, in effect, is used as a comparative tool and not as a way of obtaining absolute values for the characterization of the sorption phenomenon.[12]

EVOH copolymers are used mainly as a gas barrier material for diverse applications. Packages for oxygen-sensitive foodstuffs are constructed with EVOH as a central high-barrier layer sandwiched between 2 layers of water barrier materials.[4] These layers protect EVOH from sorbing water. Its hydrophilic nature and the effect of water presence on different properties, such as T_g or oxygen permeability are well known. Despite the fact that EVOH is sensitive to water, it is used when the packaging structure is going to suffer a humid-thermal treatment, such as retorting.[4] In these cases, EVOH sorbs large amounts of water, which affect its properties even after drying.

EVOH copolymers are also excellent barriers against volatile organic substances. In a previous article, solubility of alcohols in EVOH (29% ethylene content) was determined at different temperatures. EVOH was found to have poor affinity for alcohols in spite of their high polarity.[13] The higher the polarity of the sorbate, the greater the sorption. In this article, the effect of water on the sorption of organic substances, including alcohols, is measured by IGC for 4 EVOH copolymers with different ethylene contents.

EXPERIMENTAL SECTION

Materials

Four EVOH copolymers with different ethylene percentages, 29 (EVOH-29), 32 (EVOH-32), 38 (EVOH-38), and 44% (EVOH-44), were studied in this work. Materials were supplied by Elf Atochem (CERDATO, Serquigny, France) in films of 20.5, 15.6, 18.9 and 21.9 μm thick, respectively. Due to EVOH hydrophilic nature, films cannot be obtained by single layer extrusion. Instead, three-layer films, polypropylene (PP)–EVOH–PP, were obtained in an Erwepa coextrusion machine. When this type of structure is desired, it is necessary to include 2 layers of coextruded adhesive since PP and EVOH are incompatible and the structure would suffer delamination. We took advantage of this property, and the structures were built without adhesives. By peeling off PP layers, EVOH films were obtained. This procedure was basically selected for the 2 following reasons: (1) EVOH films present a structure similar to that obtained industrially (the same mechanicothermal history); (2) during coextrusion and the posterior cooling process, the EVOH layers were protected from water uptake.

Methanol (MeOH), ethanol (EtOH), n-propanol (PrOH), n-butanol (BuOH), n-hexanol (HxOH), d-limonene (LIM), and ethyl caproate (EtCp) of analytical reagent quality (Sigma, Madrid, SPAIN) were selected as organic sorbants because of their different sizes and polarities. Sample preparation has been described already.[13] Injected mass varied from 2.5e-7 to 1.3e-5 g. MilliQ water was used to provide a water-enriched chromatographic carrier gas.

Chromatography

A description of the theoretical procedure to determine sorption isotherms was described in an earlier publication.[13] A Perkin–Elmer 8310 chromatograph equipped with a flame ionization detector was operated under isothermal conditions at 25°C. Before entering the column, carrier gas (He) bubbled in a glass washing bottle, and the outward stream was diluted with a dry stream, as Figure 1 shows. Since the column filling was not very compact, pressures at the column head were very low ($\Delta p < 0.01 \ atm$), and the use of glass equipment was not hazardous. Both streams were carefully controlled by precision Nupro needle valves (VCI, Barcelona, Spain) and Aalborg flow-
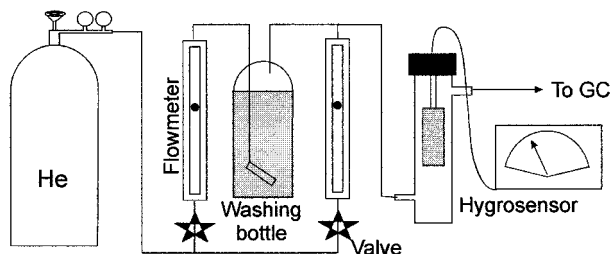
Figure 1 Diagram of the equipment used to create a carrier gas stream of known and controlled relative humidity.

Figure 2 Examples of the sorption isotherms obtained by IGC for 3 alcohols under 2 different conditions.

meters (Monsey, NY). A final stream of constant relative humidity and flow rate were obtained with this scheme. Measurements were taken around 0, 25, 50, and 75% RH values. Relative humidity of the carrier gas was constantly checked before it entered the column by a precision Hygrosensor type H-3 class A (Hygrodynamics, Jessup, MD). Experiments were performed between dry and humid conditions. RH was maintained constant ($\pm 1\%$) throughout a sorption isotherm determination. The flow rate of the carrier gas stream was in the range of 16 ± 2 mL/min for all experiments.

Stainless steel columns (60 cm long, 4.2 mm internal diameter) were filled with 2-mm wide strips of polymer films. Total weights of the fillings were 4.94 (EVOH-29), 6.1 (EVOH-32), 5.7 (EVOH-38), and 4.3 g (EVOH-44). This procedure avoids any effect of column preparation. Common coating on an inert support by polymer solution and evaporation destroys polymer history, and, consequently, polymer morphology differs from that of the original material. Moreover, this procedure is applicable to not easily soluble polymeric materials.

RESULTS AND DISCUSSION

Sorption isotherms at 25°C of lineal alcohols (C1 to C6) in 4 EVOH copolymers were determined by IGC. Figure 2 shows the isotherms of MeOH, EtOH, and HxOH in EVOH-29 at dry and high relative humidity conditions. Similar isotherms were obtained for the rest of systems studied. In the range of sorbate activity studied, all isotherms were linear, following Henry's law. Therefore, solubility coefficients were calculated to describe the sorption equilibrium and are presented in Figure 3.
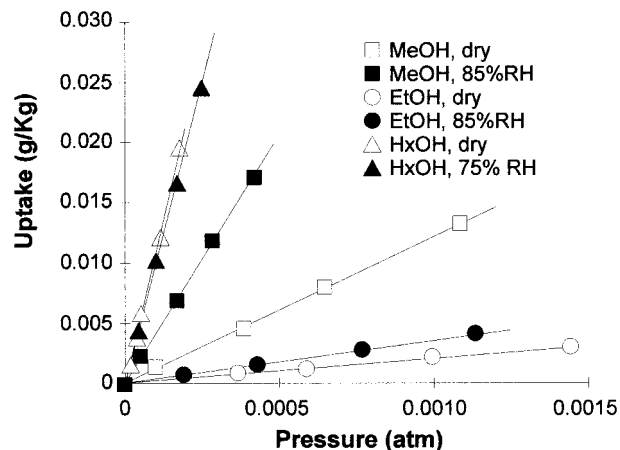
Many factors affect the sorption process between a volatile sorbate in gas phase and a solid polymeric phase. When sorption equilibrium of different sorbates with the same sorbant are compared, properties of the sorbates are responsible for different behaviors. High compatibility of sorbate and sorbant (same polarity and the presence of groups capable of H-bonding) increases the sorption. Sorbate condensability also facilitates better contact between them. These 2 properties are antagonistic in the case of lineal alcohols, and the longer the C-chain, the more the polarity decreases and condensability increases. Methanol sorption is higher than that of ethanol, with polarity being the dominant factor. From ethanol to hexanol, the sorption increases and condensability becomes dominant. The same profile was observed with the 4 copolymers under study and in EVOH-29 for temperatures below T_g,[13] confirming the utility of the new column filling procedure
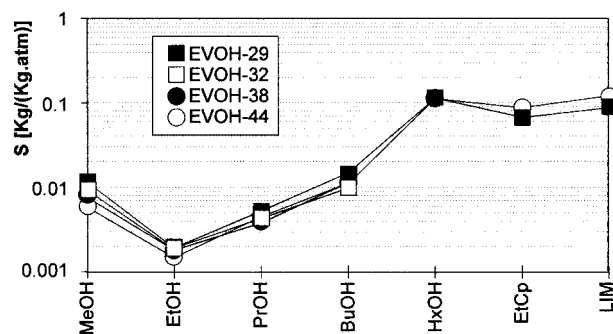

Figure 3 Solubility of organic substances in EVOH copolymers at 25°C and 0% RH.

as a comparative tool. For the same column filling, since chromatographic conditions were kept constant, any difference in sorption is exclusively due to different interactions between sorbate and polymer. In terms of absolute values, solubility coefficients should be compared with values obtained with a more adequate technique, such as gravimetry or permeability experiments since the reduction of surface-to-volume ratio may lead to an important reduction of sorption. In this article, Ss are below, though within the same range of magnitudes as those obtained in a previous article.[13] The solubility of hexanol in EVOH-44 was determined independently by an isostatic permeation experiment.[14] The value was 0.16 KgKg^{-1} atm^{-1}) also close to that obtained in this work. Consequently, the method is useful when comparing sorptions of different sorbates within the same column, and, in absolute terms, it provides a good approach to real values.

Two more sorbates, EtCp and LIM, were the subject of study. Their sorption values are close to that of hexanol. EtCp and LIM are sorbates with a large molecular volume and low polarity. The dominant factor may be condensability as HxOH. Indeed, vapor pressures at saturation of HxOH, EtCp, and LIM are very low, 0.0011, 0.0028, and 0.0022 atm, respectively.[15] LIM is less volatile (more condensable) than EtCp and is sorbed more by the copolymers. HxOH is both the less volatile and the most polar sorbate under study and has the greatest sorption. Similar effect of chain length on sorption was found for alcohols and alkanes in polyethylene.[16,17]

When the sorption equilibrium of a sorbate in different sorbants is compared, properties of the sorbants are responsible for different behaviors. Polymer properties affecting transport properties are free volume, density of cohesive energy, polarity, and crystallinity, and most of them related to the presence of empty spaces where sorbate molecules can get sorbed and to the mobility of chains within the matrix (or the inter-segment interactions).[18] In this study, those factors related to the chemical composition of the copolymers should vary with ethylene percentage in the same direction. The greater the number of alcoholic segments, the greater the polarity and the density of cohesive energy. Crystallinity, however, also depends on the thermomechanical history of the polymer. Moreover, IGC factors such as filling geometry can play an important role when sorption isotherms are compared.[9] Therefore, a comparison between values obtained with

different columns has to be made with care. Values of solubility seem to be very similar between columns, and the effect of EVOH ethylene content (within the studied range) is in general not very important. In a parallel study, sorption of water is being studied by gravimetry. We have found that the solubility increases as ethylene content decreases, although the differences are smaller than expected (unpublished data).[14] Sorption of methanol increases as ethylene content decreases (the copolymer is more polar and has more locations susceptible to H-bonding). The same behavior occurs, although reduced for EtOH, PrOH, and BuOH. Following this tendency, no difference was observed between the sorption of HxOH in EVOH-29 and EVOH-44. The 2 sorbates without OH groups are sorbed more in EVOH-44 than in EVOH-29. In these cases, the sorbates are nonpolar and, consequently, are more compatible with the copolymers with less OH groups.

When a large number of molecules enters a polymer matrix, they fill the polymer free volume and interact with the polymer in different ways. The consequences can range from plasticization to polymer swelling. Molecules may interact with the polymer, relaxing the interchain forces. This relaxation results in an increment of polymer mobility (decreasing the glass transition temperature) and, therefore, plasticization. If sorbate–polymer interactions are strong enough, the penetrant is preferred by the polymer, the number of molecules allowed to enter increases, and the polymer swells. These interactions may be stronger than polymer–polymer interactions. When this occurs, the polymer can be dissolved by the penetrant.

It is well known that EVOH copolymers are plasticized by water. This is clearly indicated by the decrease in the glass transition temperature as water content increases.[19] Sorbed water molecules may interact with the polymer by H-bonding and dipole forces, breaking part of the interchain bonds. In terms of mass transport processes, the effect of this morphological change can be observed by an increment in the diffusion coefficient values. Whether these changes also affect the equilibrium is not as clear. The presence of a penetrant in a polymer matrix is limited to the amorphous portions.[18] However, some authors indicate that the penetrant can change the crystallinity percentage of the polymer.[20] In a previous study, no effect of water sorption on EVOH crystallinity was found.[19]
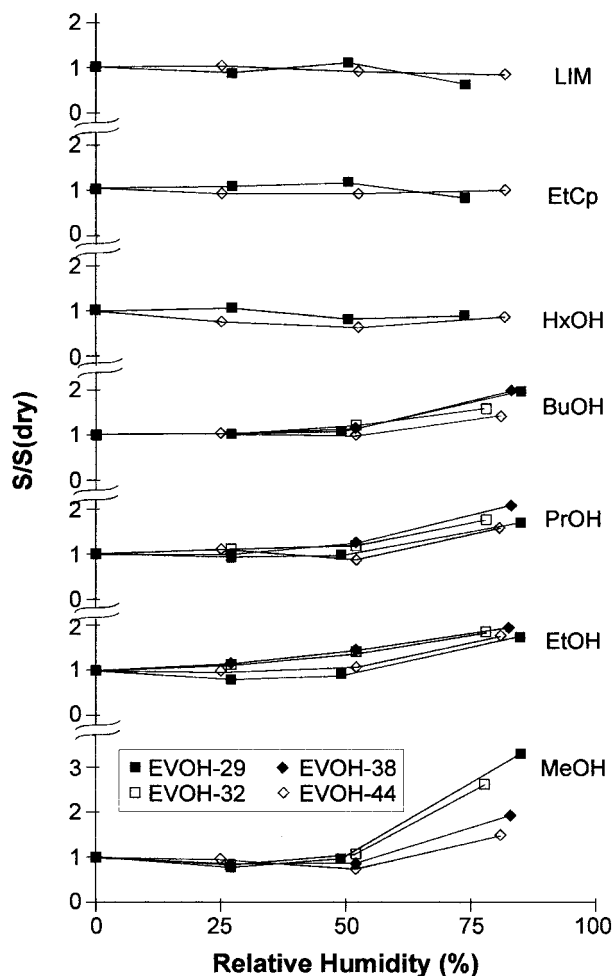
Figure 4 Effect of relative humidity on the solubility of organic compounds in EVOH's at 25°C (values in solubility over solubility in dry conditions).

The effect of water presence on the solubility of organic substances in EVOH copolymers was also studied. After the sorption analysis in dry conditions, IGC columns were conditioned at 3 relative humidities (from drier to wetter atmospheres). The results expressed as a ratio between the measured solubilities and that taken at dry (to make it more visual) are shown in Figure 4 for each sorbate as a function of relative humidity. It can be seen that the presence of water at low relative humidity scarcely affects the sorption values. Alcohol molecules interact with the polymer by H-bonding, dipolar, and dispersion forces. The presence of water molecules may be seen as alcohol competitors for the same interacting sites. Although not generally so, the value of S appears to decrease at low relative humidity, especially for the smaller alcohols according to this hypothesis.

On the contrary, the sorption of alcohols clearly increases at high RH. This effect is more obvious in the case of methanol, the most polar sorbate analyzed, becoming less important as the length of alcohol (and the apolarity) increases. This behavior is followed by the 4 EVOHs. Plasticization and swelling of the polymer could cause this increment in solubility.

While it appears that the sorption of alcohols increases, no effect (even the contrary effect) was observed for nonpolar sorbates, such as limonene or ethyl caproate. If plasticization and swelling opened the polymer structure (greater free volume), a similar behavior would be observed irrespective of the sorbate polarity. A hypothesis that may explain the different profile that sorption of polar and nonpolar sorbate presents with respect to RH is that the presence of water also increases the polarity of the polymeric media, which then becomes more compatible with polar sorbates. This hypothesis also explains why the sorption of LIM and EtCp in humid environments decreases more significantly in EVOH-29 than in EVOH-44 since the former is a more polar polymer, which sorbs more water than the latter.

CONCLUSIONS

The solubility of 5 alcohols, an ester and a terpene in 4 EVOH copolymers was evaluated by IGC at 25°C and at different relative humidities. Under dry conditions, solubilities in the same copolymer appear to be affected by the condensability and the polarity of the sorbate. These 2 factors are antagonistic in alcohols since as the molecule size increases, the condensability increases, and the polarity decreases. The effect of EVOH ethylene content on values of solubility is not as important, although it seems that as the ethylene content decreases (more polar copolymer), the sorption of polar sorbates increases, while that of nonpolar sorbates decreases.

The presence of water in EVOH copolymers appears to cause plasticization and swelling of the polymer as well as a polarity increment of the matrix. At high relative humidity conditions, the alcohols appear to be more soluble in the polymer, while the solubility coefficients of LIM and EtCp decrease.

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