



Effect of the acetate group content on gas permeation through membranes based on poly(ethylene-co-vinyl acetate) and its blends



Aleksandra Wolinska-Grabczyk*, Piotr Kubica, Andrzej Jankowski

Centre of Polymer and Carbon Materials, Polish Academy of Sciences, 34 M. Curie-Skłodowska Str., 41-819 Zabrze, Poland

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ABSTRACT

The transport of gases through poly(ethylene-co-vinyl acetate) (EVA) of vinyl acetate (VAc) content ranging from 25 to 70 wt%, and through the respective EVA blends was studied. The both types of materials exhibited the same order of decreasing permeability $\text{CO}_2 > \text{He} > \text{O}_2 > \text{N}_2$. However, the membranes prepared from EVA copolymers were found to be more permeable than those obtained from the blends, showing a maximum of P value at 46 wt% of VAc, while the composition dependence of P for the blends was observed to comply with a rule for miscible blends. The observed differences in permeation behavior were correlated with physical properties of the membrane materials such as density, T_g , crystallinity, and FFV. All the membranes studied exhibited high selectivities (α) for CO_2/N_2 , and the low separation ability for O_2/N_2 . The values of α for the blend materials were found to be larger than those for the copolymers with the same VAc content, and to increase more sharply with the increasing amount of VAc. These results indicate that polymer blends may offer advantages over single component polymer system in the approach of increasing membrane separation performance by using favorable interactions of polar groups with CO_2 .

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1. Introduction

Membrane gas separation technology, after emerging in the late 1970s, has become a competitive separation technology over the last 15 years. Now, it is recognized as a very significant unit operation able to decrease costs of many industrial processes, and to reduce their environmental impact. Moreover, this technique is expected to facilitate the development of new technologies necessary for the sustainable growth [1]. Some examples of membrane gas separation processes already introduced into industry include the separation of oxygen from nitrogen, the separation of helium from nitrogen, the separation of hydrogen from hydrocarbons in refinery industry, or, recently, the removal of carbon dioxide from natural gas. Another area of increasing importance is the capture of carbon dioxide from flue gases generated by the combustion of fossil fuels and other human activities in order to reduce the amount of greenhouse gas emission to the atmosphere.

Commercial gas separation membrane processes utilize mainly polymers showing good processability. However, to develop membrane technology into new commercial areas as well as to make already existing applications more competitive, new

polymeric materials with higher permeability and selectivity are required. Unfortunately, polymeric membranes which have high gas permeability exhibit low selectivity and vice versa. This behavior has been demonstrated by Robeson, who expressed it in a form of an upper bound relationship between the log of the separation factor versus the log of the permeability of a faster permeating gas [2,3]. Those empirical relationships were shown to be valid for several gas pairs. Moreover, they were found to be in agreement with the ones theoretically predicted by Freeman [4]. Therefore, it is generally recognized that the upper bound relationship creates the limit for achieving the desired result of a high separation factor along with a high permeation rate for a given gas pair. Since the first publication concerning the upper bound, a large number of studies has been carried out to exceed this limit. Among them, the approaches involving heterogeneous membranes, surface modified membranes, and molecular sieve membranes were found to be quite successful [1,3,5]. This can easily be explained because those membranes form a separate class of membrane materials, which fall beyond the group of pure polymeric films utilized for establishing the upper bound relationship. Along with this approach, there has also been observed in literature significant development in the gas separation performance resulting from the introduction of rigid ladder-like polymers [5,6] or perfluorinated polymers [5,7,8]. The first group of polymers has structural characteristics similar to molecular sieving systems, whereas for the second group different solubility

* Corresponding author. Tel.: +48 32 271 60 77x784; fax: +48 32 271 29 69.

E-mail address: aleksandra.wolinska@cmpw-pan.edu.pl

(A. Wolinska-Grabczyk).

characteristics may be responsible for their unusual transport properties.

In this work we tried to exploit the idea of using the solubility selectivity as a tool to achieve higher selectivity/permeability combination. In general, addition of polar groups such as ethers, nitriles and acetates to a polymer is known to increase its solubility parameter [9]. Although the presence of these groups decreases free volume and increases polymer chain rigidity that in turn decreases gas diffusion coefficient, it can improve sorption of polar gases because of their affinity to them [10]. That should result in higher solubility selectivity for polar/non-polar gas pair. The presence of polar groups like fluorinated groups [11], carbonyl groups [10,12], nitrile groups [13], or oxyethylene groups [14] in a polymer chain has already been reported to be highly selective for CO₂ separation. Therefore, a focus of these studies has been on developing correlations between transport properties and the polar groups content. To achieve this we have studied both random copolymers of a variable composition and the respective miscible blends. The commercially available ethylene-co-vinyl acetate (EVA) polymers with different vinyl acetate group (VAc) content have been chosen for this purpose. Although EVA copolymers are widely used in many industrial fields, because of their multiphase character, they have still been the focus of the extensive research concerning their structure and properties [15].

The transport of water vapor, and O₂ and CO₂ gases through EVA films with VAc content varying from 19 to 70 wt% was studied by Marais et al. [16,17] with the aim of selecting polymer materials, which exhibit high H₂O/CO₂ and CO₂/O₂ selectivity for food packaging applications. Based on the results obtained, the authors concluded that an increase in the VAc content led to the improved water vapor/gas selectivity, while the selectivity of CO₂/O₂ showed no significant variation for the EVA copolymers studied. However, the permeability of both gases has been demonstrated to vary significantly with the VAc content. Barrier properties required for packaging purposes of EVA modified low density polyethylene (LDPE) were also studied by Shi et al. [18], who found out that an increase of EVA content led to the deterioration of those properties. The permeation of pure N₂, O₂, CO₂, and CH₄ gases in membranes prepared via phase inversion method from EVA copolymers containing 18 and 28 wt% of VAc groups was studied by Mousavi et al. [19]. The results presented in their work indicate that both the membrane permeability and selectivity were not affected noticeably by the chemical composition of the EVA copolymers. However, the conclusions presented by the authors are rather confusing, and seem to be formulated based on the miscalculated selectivity data. The transport of N₂ and O₂ through membranes made of the EVA copolymer with 18 wt% of VAc was also analyzed by Kumar et al. [20], who investigated the effect of the crosslink density on membrane permeation behavior. Much earlier, Shur et al. [21] reported for O₂ and N₂ transport in PVC/EVA blends that at higher VAc group content rate of gas permeation and diffusion decreased. Thus, from the data reviewed above, it appears that results concerning gas transport behavior in EVA copolymers are as yet not only meager in literature but also seem to be not quite consistent with each other. It makes therefore difficult to predict if the incorporation of VAc groups into a polymer chain may significantly affect polymer transport properties. Obtaining systematic data on gas transport in the EVA copolymers is therefore needed for better understanding the relationship between structure and transport behavior of this group of polymers.

In this work, a study of the gas transport properties of various EVA materials ranging from copolymers with 25 wt% of VAc to those with 70 wt%, as well as of EVA based blends is presented. Along with the discussion on the dependence of gas permeability on the VAc group content, analysis of the results in terms of the structural changes introduced by those groups is performed.

2. Transport fundamentals

The permeability of a polymer membrane to a gas penetrant is defined as the rate at which the gas permeates through a standard membrane thickness under a standard pressure difference. This can be expressed as [22]

$$P = \frac{Ql}{p_1 - p_2} \quad (1)$$

where Q is the penetrant flux under the steady-state conditions, l is the thickness of a membrane, and p_1 and p_2 are the upstream and downstream penetrant partial pressures, respectively. Permeability coefficients are very often expressed in units of Barrers, where 1 Barrer = 10⁻¹⁰ cm³(STP) cm/(cm² s cmHg). The process by which gas molecules permeate through a nonporous polymer membrane is assumed to be described by the solution-diffusion model [23]. According to this model, in the first stage, permeating molecules dissolve into the upstream (feed) side of the membrane, then they diffuse through the membrane to its downstream (permeate) side, and in the third step, they desorb from the membrane surface. Such view of the diffusion of gases through polymers was first proposed by Graham [24]. According to this model, and when $p_1 \gg p_2$, permeability can be expressed as [22]

$$P = DS \quad (2)$$

where D is the concentration average diffusion coefficient, and S is the apparent solubility coefficient. The latter one is defined as the ratio of the concentration C_1 of the gas dissolved in the upstream side of the membrane to the gas upstream partial pressure p_1 :

$$S = \frac{C_1}{p_1} \quad (3)$$

The ideal selectivity of a membrane for gas A over B is the ratio of their pure gas permeabilities [22]

$$\alpha = \frac{P_A}{P_B} \quad (4)$$

3. Experimental

3.1. Materials and membrane preparation

The EVA copolymers studied were commercial products obtained in a form of pellets from two different companies. EVA 25 and EVA 40 were kindly provided by DuPont and EVA 31.5, EVA 46, and EVA 70 by the German Institute of Plastics Materials (Darmstadt). The structure of EVA is shown in Fig. 1.

Membranes were made by dissolving a respective copolymer or a mixture of copolymers in xylene (mixture of isomers, POCH, Poland) to obtain a 12% (w/w) solution, and by pouring it onto a Teflon plate. The polymer solutions were stirred for several hours, and before casting, they were stored at 60 °C for one week to assure the dissolution process was completed. The purity of a solvent was 99% and it was used as received. To obtain blends of a broader composition range, EVA 31.5 and EVA 70 from the same

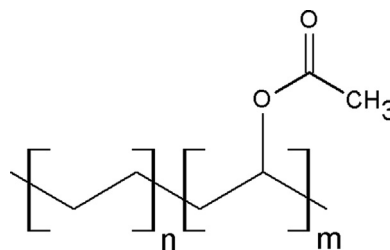


Fig. 1. Schematic representation of the EVA copolymer structure.

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