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The impact of interfaces in laminated packaging on transport of carboxylic acids

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ABSTRACT

The permeability of oleic and acetic acid through low density polyethylene (LDPE) and ethylene acrylic acid (EAA) have been measured using diffusion cells. In addition, the permeability through combinations of LDPE and EAA in the form of laminates with different numbers of layers has been determined. Oleic acid shows an almost 30 times higher permeability compared to acetic acid, which was partly explained by the adsorption of oleic acid to the film surface during the permeability experiment. In addition, the permeability is lower for both oleic and acetic acid in the laminates compared to the pure films. The decreased permeability can be explained by the presence of crystalline domains close to the interface. This is supported by SAXS data which suggests an ordering of polymer chains in the EAA film close to the interface. In summary, the results show that it is possible to create barrier materials with decreased permeability, which is interesting for example in the packaging industry.

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1. Introduction

Food packaging materials function as barriers and aim to preserve and protect a food product from the surrounding environment [1]. Glass and metal have historically been used as barriers, and during the 20th century, plastics became popular to use as packaging materials, and a vast range of plastics with different properties has been developed to fulfill the various needs encountered. For example, low-density polyethylene (LDPE), which is a generically used plastic in packaging materials, is a good moisture barrier but a poor oxygen barrier [2]. Therefore, a plastic barrier is often combined with other materials i.e. other plastics or foil, often via co-extrusion, to create a laminate and an improved barrier. The natural result of the formation of a laminate is the creation of additional interfaces between the layers. The width and shape of the interface often vary and depend strongly on the polymers involved [3]. In addition, the interface properties often

differ from those of the bulk, which can affect the final barrier properties [4]. For example, molecular weight and polydispersity of a polymer have been shown to have impact on the interface, since high polydispersity and low molecular weight could result in the formation of a broader interface [5]. It has also been shown that shorter chains tend to assemble at the interface, hence lowering the interfacial tension [6] as a result of advantageous entropy gained by the system by excluding the longer chains from the interface [5]. The assembly of shorter polymer chains at the interface has also been shown to be responsible for the presence of a more ordered structural arrangement close to the interface, which is usually called transcrystalline layer [7–9]. A transcrystalline layer can also form between two immiscible polymers as a result of high polydispersity and the diffusion of shorter chains at the interface [9]. In that case, a decreased permeability for the laminate is expected due to the increased crystallinity at the interface.

Mass transport – or permeability – is directly connected to solubility and diffusivity of the permeant. However, the nature of the polymeric material (cross-linking, crystallinity, and substituents), possible addition of plasticizers, compatibilizers, stabilizers or fillers and temperature are all important factors

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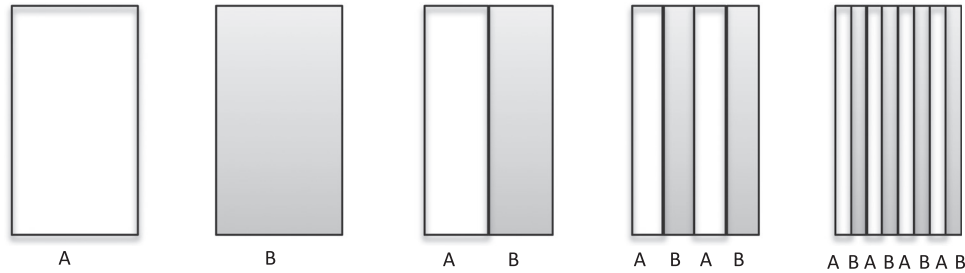


Fig. 1. Schematic representation of the pure films and the laminates, A=low density polyethylene (LDPE), B=ethylene acrylic acid (EAA).

influencing the permeability [10]. Crystalline parts in a polymeric material are often considered to be impermeable for small molecules. Hence, the mass transport of a permeant occurs mainly in the amorphous regions [11]. The mass transport can also depend on the free volume within the polymer and the segmental mobility of the polymer chains. Even though laminates are widely used in the packaging industry, only few studies are focused on the permeability of a liquid and what impact the interfaces may have on the total transport. There are many studies focusing on the permeability of gases through polymeric film materials, however [12–16].

In this study, we investigated the impact of the film layering on both the mass transport and the total permeability. Our hypothesis was that the presence of additional interfaces could drastically reduce the mass transport and total permeability of a permeant. To test this hypothesis, the permeability of oleic and acetic acid was measured for two pure polymer films; low density polyethylene (LDPE) and ethylene acrylic acid (EAA) as well as combinations of them consisting of up to eight layers (Fig. 1) while keeping the total film thickness constant. The structure of the film materials was investigated by small angle X-ray scattering (SAXS) and wide angle X-ray diffraction (WAXD), and the thickness of the interface was estimated using time-of-flight secondary ion mass spectrometry (TOF-SIMS). These results were further used to calculate an interfacial permeability and compare it to experimental values.

1.1. Theoretical basis

1.1.1. Diffusion through a polymeric film

For a barrier film without defects the primary mechanism for mass transport of a permeant from one side of a film to the other is diffusion, driven by the concentration gradient created in the experimental setup. Molecular diffusion in one dimension can be described by Fick's first law:

$$J = D \frac{dc}{dx} \quad (1)$$

where J is the flux, D is the diffusion coefficient of the permeant and dc/dx its concentration gradient. The diffusion coefficient is assumed to be independent of position and time. Furthermore, when it is assumed that steady state has been reached, i.e. when the concentration within the film does not vary with time, Eq. (1) can be rewritten into Eq. (2):

$$J = \frac{DA}{h}(c_1 - c_2) \quad (2)$$

where A is the area exposed to the permeant, h is the total film thickness, c_1 and c_2 are the concentrations at the surfaces of the films in Fig. 2a. In the case where the permeant is dissolved in aqueous solution surrounding the film barrier and thus not accumulated at the surface by an adsorption process, Eq. (2) presumes that the aqueous boundary layers on both sides of the film do not significantly affect the total transport process. Therefore, c_1 and c_2 can be related to the concentrations in the chambers by considering the partition coefficient, K , i.e. the ratio between the concentration in the chamber and at the surface of the film (Fig. 2a).

$$K = \frac{c_1}{c_d} = \frac{c_2}{c_a} \quad (3)$$

where c_d and c_a are the concentrations in the donor and acceptor regions respectively. Furthermore, Eqs. (2) and (3) can be rewritten into Eq. (4):

$$J_i = D_i K_i A \frac{(c_d - c_a)}{h} = P_i A \frac{(c_d - c_a)}{h} \quad (4)$$

The diffusion coefficient (D_i) times the partition coefficient (K_i) is equal to the permeability (P_i) for permeant i according to Eq. (4).

Fig. 2a shows the case when the partition coefficient K is equal to 1, i.e. the concentration of the interior film surface is the same as the concentration outside the film. However, for solid materials this is not always true, and Fig. 2b shows the situation when $K \ll 1$, i.e. the concentration within the film is lower than outside the

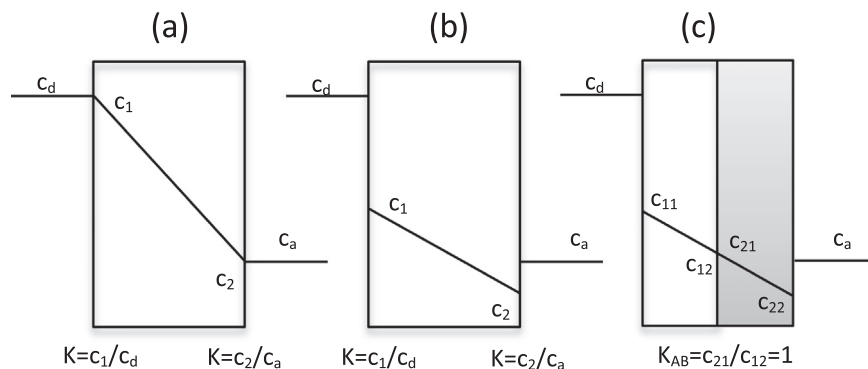


Fig. 2. One-layered film where steady state has been reached with (a) $K=1$, (b) $K \ll 1$ and (c) a two-layered film where $K_{AB}=K_B/K_A=1$, and where film A is white and film B is gray. Donor and acceptor chamber are on the left and right side, respectively.

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