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Effects of random defect distributions in the barrier coating on the gas permeability of multilayer films

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ABSTRACT

The influence of barrier coating defectiveness on the overall permeating flux through a bilayer film is considered with particular attention to the effect of spatial defect distribution. To that aim, the diffusion equations for the permeating species have been solved in a large number of 3D geometries, built to simulate a bilayer structure with defects randomly distributed on the coating surface. A numerical approach based on finite volume method was used and, for each value of defectiveness considered, ranging from 0.25 to 10%, a minimum number of 200 different geometries were analyzed, in order to obtain statistically meaningful results.
The numerical simulations results, which for regular arrays of defects also compares rather well with data available in the open literature, showed that the average flux obtained for each different defectiveness is not a fixed value, but rather shows substantial variations due to the randomness of the defect distribution. In particular, when few defects are present on the surface, differences higher than 10% have been observed in the flux calculated, while deviation lower than 3% with respect to the average value were obtained when the defects fraction on the surface was about 10%.
Interestingly, the random distribution of defects on the surface gives average flux which are always smaller than the corresponding ordered geometry and does not result in a Gaussian distribution of the permeate flux. Distributions close to the normal one were indeed observed only for higher defectiveness while, for lower defect fractions, flux distributions with a clear tail towards the lower permeation rates were obtained.

1. Introduction

Global packaging market is continually growing [1]; according to the World Packaging Organization, it reached 799 billion $ in 2012, considering both final products and industrial machinery, with an estimated increase to 1 trillion $ in 2018 [2]. That involves several different applications from food and pharmaceuticals [3–6] to vacuum insulation panels (VIPs) [7] and flexible organic electronic devices (LCD displays, integrated circuits, solar modules) [8–11]. In general, all these fields share the need of packages endowed with high barrier properties to protect their products from environmental contamination, with major focus on the penetration of oxygen and water vapor. The research on better and cheaper barrier materials is continuously progressing looking for new solutions able to fulfill the market and producer more demanding requests. A better understanding of the relationships between the structure of the barrier films and their final properties would, therefore, be of great help in giving guidelines for the design of new barrier materials, as well as to offer indications for quality control of the production lines.

Nowadays high barrier properties are created mainly in two different ways: through nanocomposite materials, created by using high aspect ratio impermeable fillers to increase diffusive path inside the materials [12–17]; or through multilayer composites where virtually impermeable thin films, of the order of few nanometers thickness, are coated on a cheap permeable support (usually PE or paper) two, three order of magnitude thicker than the coating itself [3,8,18–26].

Focusing the attention on the latter systems, they have become rather popular in recent years thanks to aluminum metallized polymer films and, more recently, to transparent barrier coatings such as AlO_x, SiO_x films which are slowly replacing the former solution in view of the advantages due to transparency, microwave compatibility and recyclability [19,21,22].

Gas barrier properties of these bilayer systems are affected by different factors, including permeability and thickness for both support and coating layer. However, to all practical purposes the latter can be often considered as completely impermeable, so that the residual permeation values, found experimentally and in literature, must be attributed to the presence of cracks and defects in the thin coating layers [20–27]. The defects are often created directly during the coating procedure or during the final product processing, since these very thin layers are easily damaged by the presence of defects in the support layer as well as by dust

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particles or other impurities during formation or, finally, by mechanical stresses during subsequent processing steps [23,28,29].

Whatever may be the type and origin of the defects on the coating, they are practically unavoidable and it is therefore of interest to understand their effect on the overall permeability of the final multilayer material. To that aim several different approaches are present in the literature to model the influence of defect fraction, size and shape on the final coating permeability. Analytical relationships are also available to describe the permeation through materials with circular [30,31] and as well as rectangular [24] defects located on the coating surface, which usually hold under the following particular simplifying assumptions:

i. $\lambda = \frac{polymer\ \ thickness}{defect\ \ radius}$ either $\gg 1$ or $\ll 1$;
ii. high distances among different defects, in order to avoid mutual concentration gradients interferences;
iii. regular and orderly defect arrangement (Fig.1-a).

Prins and Hermans [30] for example developed analytical relationships for the steady state permeate flux of a component *i* through cylindrical defects, as a function of thickness of the support layer, diffusivity, defect radius and fraction of the uncoated surface. In particular they obtained a linear relationship between permeate flux and the ratio between support thickness and defect radius when the latter parameter is larger than 0.3 and fraction of the defect area is much smaller than unity.

Rossi and Nulman [31], on the other hand, addressed the same type of problem finding analytical relationships for two limiting cases, one for support thickness much larger than defect radius and the other for support thickness much smaller than the defect radius. In the first case, of particular interest here, the total mass of permeant crossing the defect per unit time is linear with defect radius and, remarkably, independent of the support thickness. Yanaka et al. [24] developed theoretical models for defect shape in the form of long cracks or rectangular holes in a finite 3D system and found, as previous authors [30,31], manageable analytical approximate expressions for effective diffusion coefficient only in the case of large distance between defects.

Roberts et al. [32] proposed a model able to account separately for the permeation through three different pathways: amorphous oxide lattice, nano-defects and macro-defects. This was necessary to explain experimental data which do not fit purely macro-defect models presented by previous authors [24,30]. The relative importance of each path depends on permeant molecule size so the authors, considering a typical permeant size of 0.2–0.3 nm, defined the following different pathways for the diffusing substance: lattice (0.2–0.3 nm), nano-defects (0.3–1 nm), and macro-defects (> 1 nm). In conclusion they found a final relationship for the permeation in composite material in which two terms are present: one for the permeation through macro-defects (from refs. [31] or [24] depending of defect shape) and the other, based on a modified Knudsen expression, for the hindered permeation through lattice and nano-defects.

Several authors, [20,23,24,31,33] also considered numerical approaches to describe more general situations including different defect shapes and, more relevant, the effects due to interaction among defects on the permeating flow. Also in those works, however, only the special case of regular and orderly defect arrangement were generally considered. In such regular geometrical configurations, the changes in permeability due to defect-defect distance and support thickness, as well as the effect of the coating position in three-layers and multilayer structures [20,33] were studied and some semi-empirical relationships were obtained from numerical simulation, to describe the behavior of the system [23,33].

Such ordered geometries, however, are still far from real materials configurations where defects are not regularly nor orderly distributed but rather randomly placed onto the coating surface generating interaction and, consequently, permeating fluxes potentially very different from those observed in ordered geometries. To better elucidate this fact, the principal focus of this work is to study the effect of defectiveness on permeability of multilayer systems, when the spatial distribution of defects is random as, for example, in Fig. 1-b. The final aim is to reach a better insight on the actual behavior of the multilayer systems and possibly to obtain useful information and guidelines for the production of better barrier materials.

The complexity of analyzing random distribution of defects in a given structure is in general too high to be studied through mere analytical solutions and usually requires a numerical approach, which allows for an efficient solution of transport equation in a complex geometry [34–37].

In the present work, therefore, the use of a mathematical tool was chosen, based on finite volume method, to solve the mass transport problem in different geometries, with randomly distributed defects. This solver was then coupled with an automated system capable to process a rather large numbers of different geometries, which is a fundamental prerequisite to obtain statistically meaningful results.

Thanks to this approach, it was possible to obtain the behavior of permeating flux in systems endowed with random defect distribution and to describe their barrier properties as a function of defectiveness, mean distances among defects and permeability ratio between the two layers.

2. Theoretical background and numerical approach

The mass transport through a packaging material usually obeys the general rules of continuum mechanics and can be described through the use of local mass balance equations coupled with suitable constitutive laws for the relevant properties of the materials.

The general material balance equation for component *i* in a multicomponent system is the following:

$$\frac{DC_i}{Dt} = -\underline{\nabla} \cdot \underline{J}_i + \dot{n}'''_{gi} \tag{1}$$

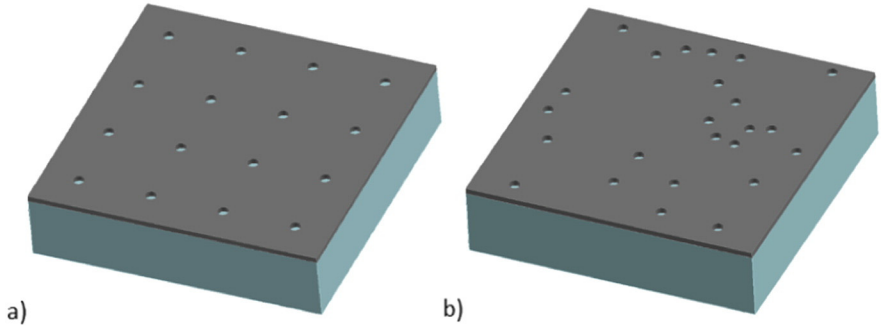

Fig. 1. a) Ordered defect distributions studied in previous works; and b) random defect distributions considered in this article.