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# Study of the relationship between transport properties and free volume based in polyamide blends

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**Abstract**

Correlation between transport properties and free volume has been widely evidenced by several authors. We are showing through a positron annihilation study in a high barrier polymer that transport properties can be improved by means of antiplasticizers addition. We also are verifying in this paper the influence of both free volume hole size and free fractional volume in diffusion of gases, finding a relationship with solubility too.

*Keywords:* Positron annihilation; Antiplasticization; Free volume; Gas transport

## 1. Introduction

Diffusion is assumed to be a process in which polymer segments separate in front of a diffusion penetrant molecule, forming a hole through which the penetrant molecule can jump. The difference in diffusion rates for penetrants of different sizes has been attributed to a distribution of holes sizes or free volume in the polymer. According to the standard free volume theories of diffusion, there is, at each instant, a hole size distribution due to thermal density fluctuations. Each molecule can jump through any hole equal to or larger than its effective size. The probability that a volume large enough exists for such a jump could be described by the following Eq. (1) [1]:

$$P(V^*) = \exp\left(\frac{\gamma V^*}{V_F}\right) \tag{1}$$

where $P(V^*)$ is the probability of existence of a size hole of $V^*$, $\gamma$ the overlap factor that involves distinct penetrant molecules sharing free volume elements, and $V_F$ is the average free volume in the polymer matrix. This expression relates exponentially diffusion of penetrants and inverse of free volume. The major limitation of the quantitative use of this easy theory is the lack of a clear working definition of “free-volume”. There are modern theories of gas transport based in this theory, but their complexity limits their use [2–4].

Trying to improve selectivity or barrier properties in polymeric materials, often transport coefficients have been related to free fractional volume FFV, determined by density measurements and the group contribution method suggested by Bondi [5]. In this way, lineal correlations between inverse of FFV and logarithm of diffusion in gases [6,7] or vapours [8] have been reported; occasionally, the value of diffusion is not known and some authors have applied this theory to permeability coefficients. Despite of the fact that this has not much theoretical base, good results have been obtained, due to solubility staying almost constant for a penetrant in a large range of free volume [9].

However, some authors that have found a relationship between free volume and solubility of gases in polymers of the same family or similar families [7], though the relationship in this case is not very evident because it happens in a disperse stretch.

Over the last years, the positron annihilation lifetime spectroscopy (PALS) technique has been used to explore the size and number of molecular-scale voids in amorphous materials [10]. It has been found that void structures exhibit characteristics similar to those expected for the free volume in amorphous materials. A correlation has been reported between the void structure, as measured by PALS and by gas permeability of amorphous materials. Thus, correlations that have been reported point to very good fits

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[11], better than ones reported with free volume data according to the Bondi method, such us:

- Between logarithm of diffusion ($D$) and inverse of hole volume ($V_H$) [9] or orto-positronium lifetime in glassy polymers [12].
- Between logarithm of $D/T$, being $T$ temperature and the inverse of $V_H I_3$, that is, $\mathrm{FFV_{ap}}$ in our nomenclature, in rubbery polymers [13].
- Between $D$ and $\mathrm{FFV_{ap}}$ in norbonenes [14].
- Between the logarithm of $D$ and the inverse of $\mathrm{FFV_{ap}}$ in a series of polyimines [15].
- Or even a relationship between solubility coefficient and free volume hole size has been found [16] being narrower than the one found with FFV from Bondi [5].

Although the exact nature of the relationship between PALS, free volume and transport properties in polymers has not been established, the correlations found to date support claims that the PALS technique is a useful probe of the free volume that influences transport properties [17]. Thus, it is seen that positron annihilation measurements correlate well with permeability data and might even have predictive behaviour and, as more information becomes available, is expected to enhance the understanding of the relationship between molecular packaging and physical properties of the polymers [10].

Understanding the relationship between molecular packaging and physical properties of polymers is, roughly, the objective of this work. For this claim, we will compare transport coefficients (diffusion $D$, permeability $P$ and solubility $S$) with both size and fraction of free volume holes.

## 2. Preceding work

In a preceding paper [18] it has been shown a research of additives which can act as antiplasticizers in an amorphous polyamide, named Trogamid-T-5000™. Finally three additives have been chosen. There has been made a throughout analyze of their free volume behaviour with composition using density and positron annihilation spectroscopy. Polymer–additive systems have shown modification of free volume compared with pure Trogamid.

According to different measurements done in that work to determine free volume, in blends of 4,4′-(hexafluoroisopropanilidene)diphenol (HFBA) with Trogamid has been observed a plasticization effect of the additive in the polymer matrix, which means that additions of that compound increases the size of free volume holes ($V_H$) and the free fractional volume (FFV) as well as the mobility of chains, which is reflected in a descend in $T_g$ [18]. These changes usually affect the transport properties in an increase of diffusion [19] and solubility [20] coefficients.

However, studies of free volume in blends (of Trogamid) with different amounts of 1,5-dyhydroxynaphtalin (Ndiol) have shown an antiplasticization effect, with a decrease of $V_H$ and an anomalous behaviour of FFV.

Finally, blends with a polymeric additive, poly(4-vinylphenol) (PVPh) have pointed out an increase in free volume respect pure Trogamid, but with smaller hole size than pure Trogamid.

## 3. Experimental

Sample preparation and characterization have been explained previously [18]. Special care has been taken in having the same thermal history for all the blends. To determine transport, samples have been prepared the same way as described before but thinner than the ones used to determine free volume. Sorption kinetics of carbon dioxide have been carried out in a Cahn electrobalance which has been described elsewhere [21]. Experiments have been done with Trogamid and its blends at different compositions in the same pressure and temperature, in order to observe the change in behaviour in relation to kind and quantity of additive in the polyamide. Pure Trogamid has been conditioned at the same processes of heating, cooling and shearing that have been suffered blends for conforming it, in order to have identical thermal history. Kinetics have been carried out at 30 °C and $0.4559025 \times 10^5$ Pa (0.45 atm). This pressure is low enough to prevent an overshoot, but high enough to appreciate the gain of weight due to the gas sorption.

The absorbed gas concentration ($C$) was calculated from the equilibrium weight gain ($M_\infty$) of the membrane by means the following equation:

$$C\left(\frac{\mathrm{cm^3\ STP}}{\mathrm{cm^3}}\right) = \frac{22414 \cdot M_\infty}{44 \cdot V_{\mathrm{plm}}} \tag{2}$$

where $V_{\mathrm{plm}}$ is the volume occupied by the sample, in cm$^3$; $M_\infty$ is the total absorbed mass at equilibrium in g; and 44 is the molecular weight of the $CO_2$. Then, the solubility coefficient $S$ is given by this simple equation:

$$S = \frac{C}{p} \tag{3}$$

being $p$ the pressure. Moreover, diffusion coefficient, $D$, is available after an appropriate mathematical treatment of the kinetic data. In this sense, taking into account the so-called long times approximation (50–90% of $M_\infty$), the solution of the Fick's second law for a thin film geometry, the total mass uptake of the penetrant can be described by [22]:

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2}\exp\left(-\frac{D\pi^2 t}{l^2}\right) \tag{4}$$

where $M_t$ is the absorbed gas at $t$ time; $l$ is the film thickness; and $D$ is the diffusion coefficient (in cm$^2$/s). Thus, $D$ can be calculated from an adequate plot of sorption kinetic data. More details about transport magnitudes calculation procedures are given elsewhere [21].

Free volume determination has been carried out in a positron annihilation lifetime spectrometer described before as well [18]. Through this technique average free volume hole size ($V_H$) and apparent free fractional volume ($\mathrm{FFV_{ap}}$) have been obtained.