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Modelling of gas permeation based on the morphology of a natural polymer material

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This work aims at relating gas transport mechanisms through natural polymers with the morphology characteristics of the polymer.

The use of natural polymers has increased significantly in recent years, encouraged by their sustainability. This interest has been also extended to their use as membrane materials and thin films. Natural polymers have been studied and used for the last years on the transport and separation of liquid and gas mixtures. The case study of this work is natural cork, which attracted attention since it is a renewable and sustainable raw material that has been used for many centuries. Its gas permeation properties and thermal insulation potential are also responsible for the commercial interest in this biopolymer.

First of all, a characterisation of the natural polymer under study was performed. Cork was characterised in this work in terms of its sorption and permeability data in relation to various gases with different molecular mass: He, O_2, N_2 and CO_2. In order to characterise natural cork in terms of type of polymer behaviour, its gas transport properties are compared with selected synthetic polymers reported in the literature. With the purpose of covering a large range of situations, the behaviour of natural cork is compared with polymers with diverse viscoelastic properties, from glassy to rubbery polymers. Particularly, natural cork behaviour is compared to polycarbonate, PTFE (Teflon AF2400) and PDMS. The permeability of different gases through natural cork and also through the other selected polymers is plotted *versus* the Lennard-Jones diameter, d_{LJ} [Å], a molecular collision diameter, as shown in Figure 1.

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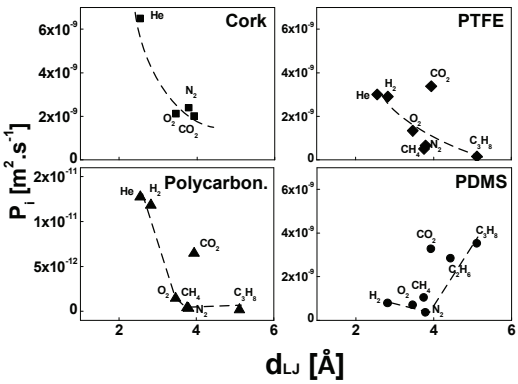

Figure 1: Permeabilities of various gases, P_i [$m^2.s^{-1}$], in natural cork (23ºC, 1 atm), in low free volume polycarbonate and in the high free-volume PTFE, Teflon AF 200 (25ºC, 3.4 atm) [1] and in PDMS (35ºC, 1 atm) [2], as a function of the Lennard-Jones collision diameter, d_{LJ} , expressed in Å (10^{-10}).

Natural cork exhibited a typical behaviour of a rigid glassy polymers and low affinity to the gases, like polycarbonate, which was not expected due to its low density [3] and free volume, higher than 70% [4], associated to a high flexibility of the material as a whole. The polymer behaviour of natural cork was also characterised in terms of the Young modulus, a measurement of the stiffness of the material, in the cork as a whole (low value of Young modulus, so flexible) and specifically in the material of the wall of the cork cell of cork (very high value of Young modulus, so very rigid).

A detailed characterisation of the structure of the polymer was also obtained from scanning electron microscopy, SEM, and transmission electron microscope, TEM. Although natural cork has a regular cell structure with small, empty, closed cells with a hexagonal prism shape, a diversity of structural parameters is observed, so the variation of each relevant structural parameter was quantified. And a special attention was given to the structure of cork cell walls.

Finally, a mathematical model was developed based on the morphology data previously obtained, taking into account variations of each relevant structural parameter. The model considers that gas permeation occurs through the plasmodesmata, which are channels, with approximately 100 nm of diameter, that cross the cell walls of the cork cells. The model also considers that gas followed Knudsen transport, which was experimental validated by the gas permeabilities behaviour with increasing gas molecular weight (similarly to Figure 1), by the low gas sorption data and by the calculation of the correspondent Knudsen numbers.

A good agreement was observed between estimated and experimental values of gas permeabilities through cork, valid in an interesting range of values of gas molecular weights. This similarity between experimental data and estimated results also proves that the transport mechanism present is indeed a Knudsen diffusion type. Hence, it allowed an identification of the relevance of sorption and diffusion phenomena, in this case a transport through the polymer controlled by diffusion.

To our knowledge this structure / function approach has not been developed for studying transport through natural materials. A transport model supported on this approach is expected

to contribute for the understanding of the underlying phenomena, opening also perspectives for the use of identical methodology for studying gas transport in other complex natural materials.

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