

HOW TO DESCRIBE AND PREDICT PLASTICIZATION IN GLASSY POLYMERIC MEMBRANES FOR GAS SEPARATION

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In glassy polymeric membranes, gas permeability shows different trends as upstream pressure increases, including the monotonous decline, a monotonous increase, as well as an initial decline followed by a subsequent increase after a minimum permeability value is reached. The minimum value, whenever present, occurs at a pressure conventionally indicated as the plasticization pressure. It is currently accepted that permeability behavior can be conveniently well described by a transport model only below plasticization pressure, while above that value the onset of additional phenomena at higher pressures are responsible of the observed increase in permeability and decrease in selectivity. On the other hand, the plasticization phenomenon has not been further inspected thus far, in terms of material property variations.

With the aim to reach to a deeper understanding of the phenomenon, we have experimentally inspected the behavior of Matrimid polyimide membranes, by analyzing both transport and mechanical properties. The permeability behavior and the "plasticization" effects induced by CO₂ have been studied by increasing the upstream pressure at different fixed values of downstream pressure. The mechanical properties studied include elastic modulus and viscoelastic response of samples saturated at different CO₂ pressures up to and above plasticization pressure. The trends obtained are rather interesting and actually not fully in line with what expected based on the current qualitative interpretation.

We also show that the observed gas permeability behavior can be described by considering only a solution-diffusion model in which the penetrant mobility varies with its concentration in the polymer matrix through an exponential law, with two adjustable parameters only. Diffusivity is thus taken as the product of molecular mobility and a thermodynamic factor, calculated by using the NELF model for thermodynamic properties of the glassy phase. It is observed that by fitting the only two adjustable parameters to the initial branch of the permeability isotherm, the above solubility diffusivity model allows the prediction of the plasticization pressure, at all values of downstream pressures used, without introducing any additional physical phenomenon.

The agreement observed between model calculations and experimental data of CO₂ permeability in Matrimid, as well as in various glassy polymers, is very satisfactory. That allows us to offer a deeper insight on the so-called plasticization phenomenon. The analysis of the permeability and the solubility isotherms, and the evaluation of concentration and swelling profiles in the membrane, show that in some cases the plasticization phenomena take place after part of the membrane has turned into rubbery phase. However, in other relevant cases as in Matrimid, the minimum in permeability is observed when the entire membrane is still glassy (and characterized by mechanical behavior comparable to the pure "dry" material), but with a polymer swelling sufficient for a permeability increase.

Finally, it is observed that all parameters used have a defined independent physical meaning, which might lead to the development of general correlations with both polymer and penetrant properties, based on which permeability predictions can be obtained.