Membranes based on poly(trimethyl silyl propyne) (PTMSP) and graphene nanoplatelets for gas separation and CO_2 capture

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Polymeric membranes for gas separation show a trade-off between permeability, related to the process productivity, and selectivity, associated to the separation efficiency: an increase in permeability is accompanied by a decrease of selectivity and vice versa.[1] The upper bound of membrane performance established by Robeson for many gas/gas separations represents a limit against which all selective materials must be judged.[1] The performance of high free volume glassy polymers lies very close to such upper bound, in the region characterized by high permeability and moderate selectivity. However, the majority of glassy membranes shows physical ageing, that is a molecular redistribution of the polymeric chains with time, which ultimately results in a reduction of free volume and gas permeability: such drawback, which arises from the non equilibrium state of glassy systems, somehow limits their applicability in real cases. [2]
The performance of polymeric membranes can be improved by incorporating inorganic fillers to form Mixed Matrix Membranes, MMMs.
We fabricated mixed matrix membranes based on PTMSP and 1 wt% of different types of graphene-based nanoplatelets: two graphenes (IND G and M60), and one GO. The membrane preparation procedure was carefully optimized to avoid filler precipitation and obtain good homogeneity and flexibility.
The films were analyzed for He, N2, CH4 and CO2 permeability. Gas permeability was studied over 9 months, in order to monitor the ageing, and after a mild (200°C) thermal treatment, that accelerates ageing.
In particular, as far as the permeability and ideal selectivity are concerned one can observe that:
- the addition of GO nanoplatelets (lateral dimension 2 micron, thickness 1.1 nm) to PTMSP enhances the permeability of all gases, by a factor equal on average to 8%, and the selectivity for the couple CO2/He and CH4/He. The solubility coefficient at 1 atm and 30°C is almost unvaried, while the diffusivity is enhanced by addition of GO filler. Such effects are attributed to a modification of the polymeric chain packing induced by the presence of nanoplatelets during casting, that creates additional free volume, similarly to what happens in the case of nanosilica-based membranes.
-The addition of a research grade of graphene (M 60) (lateral dimension 5 micron, thickness 2-8 nm) to PTMSP lowers the permeability by factors varying from -5% to -20%; the permeability of the smaller gases is more strongly reduced, thus the ideal selectivity for the couples CO2/He and CH4/N2, CH4/He, is enhanced. Such effects can be attributed to a reduction of the polymer free volume due to the presence of nanoplatelets during solvent evaporation; the phenomenon seem to affect more the small free volume domains than the large ones, and to enhance the vapor-selective behavior of PMTSP, that is more permeable to large and more condensable molecules. Permeability variations are mainly due to diffusivity changes, as it was tested with separate solubility and diffusivity experiments on CH4 and CO2 which show that solubility is almost unvaried, while the diffusivity is reduced by addition of M60 to PTMSP.
- the addition of graphene IND G (lateral dimension 0.2 micron, thickness 2-20 nm) to PTMSP lowers the permeability by a factor equal to about -24-30% for all gases. The

selectivity for the couple CO2/He, CO2/N2, CO2/CH4 is enhanced with respect to pure PTMSP. Such results may be due to a substantial reduction of free volume induced by IND G addition to PTMSP-based membranes.
The most interesting findings are those related to the effect of filler addition on the ageing behavior of PTMSP, which can be summarized as follows:
-Addition of GO slows down the ageing process: the initial loss of N2, CH4 and CO2 permeability is reduced with respect to pure PTMSP. For CO2, also the final, equilibrium permeability loss is mitigated by addition of GO, as verified by accelerating ageing via a thermal treatment at 200°C. Moreover, the response of the GO-MMM to a thermal treatment at 200°C, that partially reduces GO, is comparable or even better than that of the PTMSP membrane subject to the same treatment, indicating a good chemical stability of such composite structure.
-Addition of M60 slows down the ageing process of PTMSP, reducing the permeability loss with time for all gases. Addition of IND G, characterized by different morphology, does not affect the ageing of PTMSP, with the exception of He permeability, that decreases more slowly with respect to pure PTMSP .
Therefore, GO and M60 fillers modify the relaxation time of the polymer chains, by reducing their mobility and mitigating the ageing process, in some cases such effect is gas selective and can be exploited to tune the selectivity.
In conclusion, the addition of certain types of graphene nanoplatelets to PTMSP in small amounts is a promising strategy to adjust permselectivity and reduce ageing.

References

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