Mixed Matrix Membranes based on PPO and graphene for gas separation

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Introduction

Novel composite Mixed Matrix Membranes (MMM) were fabricated by dispersion of different loadings of graphene nanoparticles (from 0.3 to 15 % weight percentage) in a dense permeable glassy polymer, poly (2,6-dimethyl-1,4-phenylene oxide), PPO, by solvent casting procedure. The permeability, selectivity and diffusivity of helium, nitrogen and carbon dioxide have been measured at two different temperatures, 35° and 65°C and the effect of graphene loading was studied. (R. Rea et al. 2018)

Material and Methods

Solid PPO and chloroform as solvent (purity > 99.5 %) were purchased by Sigma Aldrich, two different types of graphene were used (XT6 and XT7, characteristics in Table 1) and provided by Graphene XT . The polymer was dissolved in chloroform and, after the graphene addition, the suspension was sonicated, 15 minutes for XT6 and 1 hour for XT7, and then stirred for one day. The casting was done in a glass Petri dish at 50°C. To remove residual solvent and to stabilize the transport properties the membranes were treated at 200°C for one day in vacuum condition.

Results and Discussion

In figure 1a and 1b the permeability of MMMs, and that of pure PPO, are reported as function of graphene loading. At 35°C the helium and nitrogen permeabilities are increased for graphene percentage up to 1% while CO_2 seems not affected in that range of concentration. For higher concentrations a decrease of permeability is shown for all gases. As it can be seen in figure 2a and 2b, the He/CO_2 selectivity is enhanced by the presence of graphene at both the temperatures investigated, while the CO_2/N_2 selectivity is lower than the pure PPO both at 35°C and at 65°C. The third case, the He/N_2 selectivity, is among these two opposite situations since for 35°C is lower than pure polymer and it is higher at 65°C.

Table 1. Name, weight percentage and geometric characteristics of graphene types used

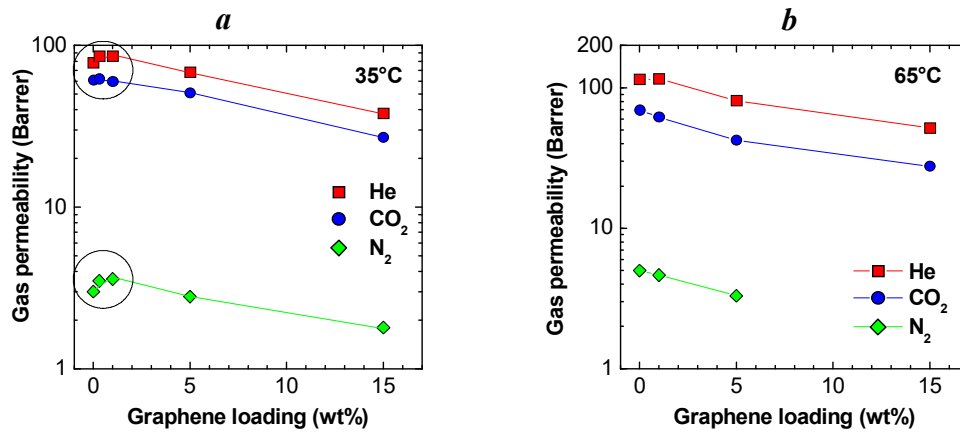| Graphene type	%$_{wt}$ graphene in polymer	Lateral Size (μm)	Thickness (nm)
XT7	0.3	20	2
XT6	1 / 5 / 15	5	6 - 8

Figure 1. Gas permeability as function of graphene content measured at 35°C (a) and 65°C (b).
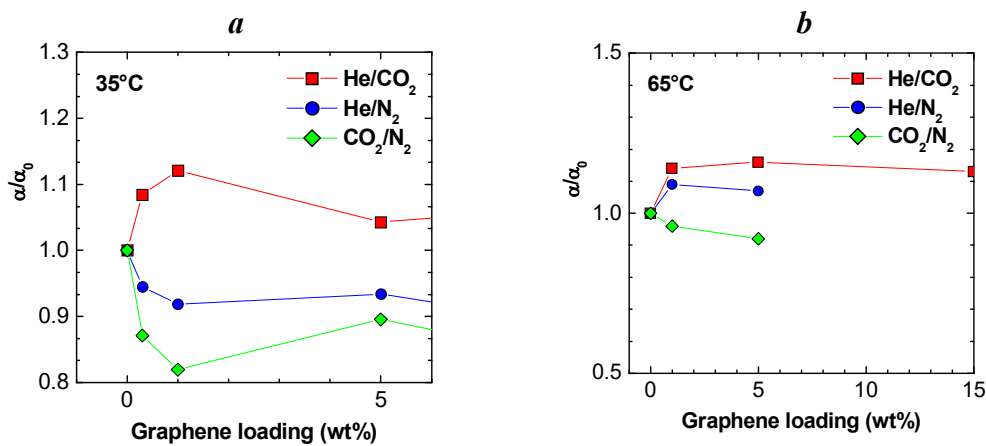

Figure 2. Ideal selectivities ratio at 35°C (a) and 65°C (b), α_0 is the pure PPO selectivity.

Conclusions

The increase in additional free volume at the polymer-graphene interface could explain the permeability enhancement observed by adding small amounts of graphene to PPO while, for higher loadings, the increase in tortuosity plays a predominant role and it is responsible of the permeability drop. The incorporation of filler nanoplatelets in the polymeric structure inhibits the chains mobility, as PPO exhibits a smaller dependence of permeability on temperature.

References

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