



Pebax[®]/ZIF-67 mixed matrix membranes: effect of particle size and pressure on permeability and selectivity.

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Abstract

Pebax®/ZIF-67 mixed matrix membranes were produced by mixing Pebax® MH-1657 with two ZIF-67 particles, that were produced by different methods. Larger particles with 700 nm (RD) in size were produced by the hydrothermal method [1], [4], while smaller particles with 250 nm (RD-1) in size produced by the solvothermal method (Fig.1). The membranes were produced by solution casting and evaporation. The polymer was dissolved in a mixture of ethanol and water (70/30) at 363 K, and ZIF-67 particles were dispersed using an ultrasound bath separately in the same solvent mixture. After complete dissolution, ZIF-67 suspension was mixed with the polymer solution. Pebax®/ZIF-67 solution was poured on a Teflon petri dish that was placed in a vacuum oven at 313 K to remove the solvent. The membranes were dried at 313K to remove any residual solvent. Table 1 shows the permeability and ideal selectivity of Pebax®/ZIF-67 mixed matrix membranes. The results show that the incorporation of ZIF-67 particles increases gas permeability for all gases studied. The gas permeability for Pebax[®] and Pebax[®]/ZIF-67 membranes increases in the sequence CO₂>CH₄>N₂ [3]. The fact that CH₄ permeability is higher than N₂ permeability indicates that the permeability of Pebax[®] depends on gas solubility, and not only on diffusivity and kinetic diameter. Ideal gas selectivity depends on pressure, for the membranes prepared using ZIF-67 particles RD-1, the selectivity is higher at 1.5MPa while for the membranes produced from RD particles the best selectivity is obtained at 1.0 MPa. Increasing particle content does not improve the selectivity which could indicate the agglomeration of ZIF-67 particles. As shown in Fig. 2, CO₂ permeability increases for all mixed matrix membranes compared to neat Pebax, while ideal selectivity depends on upstream pressure and ZIF-67 content. The results are consistent with the work of Meshkat et al. [2] that obtained similar selectivity with higher ZIF-67 content. Based on the results it is possible to conclude that Pebax is more selective to N₂ than CH₄, and that the incorporation of ZIF-67 particles do not change that selectivity. Moreover, the properties of the mixed matrix membranes depend on upstream pressure and ZIF-67 content. Finally, the results indicate that ZIF-67 particles have a positive impact on Pebax permeability and selectivity.

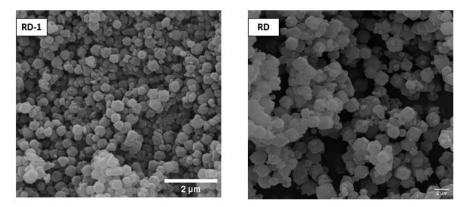


Fig. 1: Morphology of ZIF-67 samples. RD-1 was synthesized by the solvothermal method and RD was synthesized by the hydrothermal methods.

Table 1: Gas permeability and ideal selectivity of Pebax MH-1675 and Pebax/ZIF-67 mixed matrix membranes tested at 308 K.



P (MPa)	Sample	P N ₂ (Barrer)	P CH ₄ (Barrer)	P CO ₂ (Barrer)	a (CH4/N2)	α (CO ₂ /N ₂)	α (CO ₂ / CH ₄)
1.0	Pebax 1657	2±0,2	6±0,7	114±4	3±1,6	55±0,05	18±0,2
	1% RD-1	2,6±0,08.	-	152±0,2	-	59±1,9	-
	5%RD-1	3,2±0,02	-	136±2,4-	-	44±3,2	-
	1% RD	2,8±0,3	6,9±0,5	172,6±2	2,7±0,1	67,3±6,1	18,7±2,2
	5%RD	2,7±0,1	7,7±0,3	187,55±3,6	3±0,1	70±3,5	19,5±3,4
1.5	Pebax 1657	2±0,2	6±0,57	132±3,5	3±0,1	67±0,03	24±0,3
	1% RD-1	2,2±0,01	-	164±2,7	-	75±0,85	-
	5%RD-1	2,9±0,1	-	169±1,3	-	60±0,6	-
	1% RD	5,4±1	15,3±2,1	189,9±0,5	2,6±0,5	43,5±8	18,7±3,2
	5%RD	4,48±0,5	13,51±0,8	203±1,1	2,8±0,1	45,9±5,3	20±1,9

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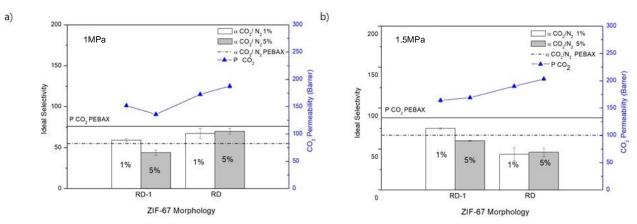


Figure 2: Permeability and ideal selectivity of mixed matrix membranes compared to Pebax. a) 1.0MPa and b) 1.5MPa

References

[1] Cravillon J., Münzer S., Lohmeier S-J, Feldhoff A., Huber K., and Wiebcke M., "Rapid Room-Temperature Synthesis and Characterization of Nanocrystals of a Prototypical Zeolitic Imidazolate Framework". *Chem. Mater.*, *21*, 1410–1412 (2019).

[2] Meshkat S, Kaliaguine S, Rodrigue D., "Mixed matrix membranes based on amine and non-amine MIL-53(Al) in Pebax[®] MH-1657 for CO₂ separation". *Sep Purif Technol*; 200: 177–190, (2018).

[3] Pacheco P., Zawadzki S. F., and Eiras D., "Influence of ZIF-67 drying temperatures on the structure and properties of PEBAX[®] MH-1657/ZIF-67 Mixed Matrix Membranes for Enhanced CO₂/N₂ Separation". *Materials Research* – accepted for publication.

[4] Yang F., Mu H., Wang C., Xiang L., Yao K. X, Liu L., Yang Y., Han Y., Li Y., and Pan Y.. "Morphological Map of ZIF-8 Crystals with Five Distinctive Shapes: Feature of Filler in Mixed-Matrix Membranes on C3H6/C3H8 Separation", *Chem. Mater.*, 30, 3467–3473 (2018).