

# NEW POLYMERIC MATERIALS FOR CO<sub>2</sub> CAPTURE FROM FLUE GAS STREAMS

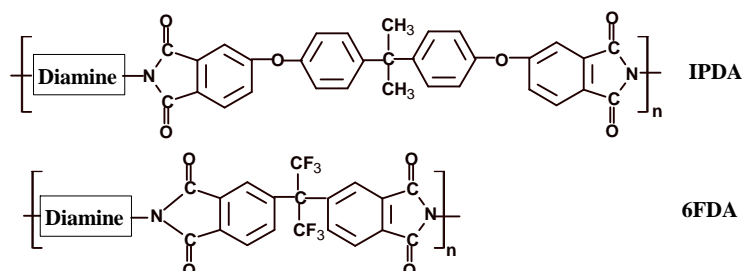
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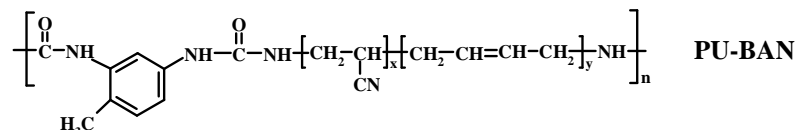
Carbon capture and storage receives wide recognition as a promising way against global warming caused by CO<sub>2</sub> emissions. Since the CO<sub>2</sub> capture is the most expensive step in the sequestration, there is need for new more efficient separation processes to be applied, which allow cost reduction. Membrane separation has potential to be an alternative to conventional processes for carbon dioxide capture, such as reversible solvent absorption or pressure swing adsorption. In particular, membrane technology offers potentially higher energy efficiency and it is environmentally friendly. In addition, the required process equipment is simple, compact, and relatively easy to operate and control. Moreover, this equipment is modular and can be easily scaled up. There are several factors which are important in designing an economical membrane separation process; however the most important one is the membrane performance. For a membrane to be useful for the capture of carbon dioxide from flue gases it should possess high CO<sub>2</sub> permeability and CO<sub>2</sub>/N<sub>2</sub> selectivity, it should provide good mechanical and thermal stability, as well as the ability to be manufactured into different membrane modules. Generally, two types of polymeric membranes are used commercially for gas separations. Glassy membranes operate below their glass transition temperature, whereas the rubbery ones above it. Glassy polymeric membranes dominate industrial membrane separations because of their high gas selectivities. They also meet the demand for highly thermally and chemically stable polymers. On the other hand, the interest in membranes prepared from rubbery polymers has been increasing recently. It can be noted that the present CO<sub>2</sub>/N<sub>2</sub> upper bound relationship involves two rubbery polymers, modified PDMS and modified polyphosphazene, as the key data points [1].

The present work investigates the permeability and morphological properties of new membrane materials from the both types of polymers. The first group of glassy polymers studied comprises a series of structurally different polyimides (PI), and the second one poly(butadiene-co-acrylonitrile)-based elastomeric polyurethanes.

Polyimides have been extensively investigated for gas separation membranes [2]. Many of them exhibit good selectivity but at the expense of modest permeability. PIs with relatively high permeability consist of 6FDA (4, 4'-(hexafluoroisopropylidene)diphtalic anhydride) based units. Therefore, selected diamines were used in this work for polycondensation with 6FDA to obtain PIs. To get more information on structure-permeability-selectivity relationships of polyimides, the PI materials were also prepared from IPDA, 4,4'-(4,4'-isopropylidene-diphenoxy)bis(phtalic anhydride) and the same diamines.



For elastomeric polyurethanes, the adopted strategy was to obtain membranes with improved performance due to the increased solubility of CO<sub>2</sub>, and as a consequence, increased CO<sub>2</sub>/N<sub>2</sub> selectivity. It was accomplished by incorporating of polar acrylonitrile groups into the polyurethane chain. To study effect of polar group concentration on CO<sub>2</sub>/N<sub>2</sub> separation ability, polyurethanes with different acrylonitrile content were synthesized.



The polymers from both groups were characterized by means of FTIR spectroscopy and elemental analysis. The thermal behavior of polymers was characterized by DSC, TGA, and DMA analysis. The average interchain distance, calculated based on X-ray diffractograms of the polymers, and the determined polymer densities were used as physical parameters to be related to chain packing density. The permeability of pure CO<sub>2</sub> and N<sub>2</sub> was measured using constant pressure/variable volume method at a feed pressure of 6 atm and at 30<sup>0</sup>C.

The results of the present study have shown that the applied structural modifications allowed polyurethanes to be obtained with gas separation properties being closer to the CO<sub>2</sub>/N<sub>2</sub> upper bound defined by Robeson. Although these data comprise the position below the upper bound, they appear on the top edge of the data points cloud. In case of the synthesized polyimides, it has been demonstrated that by varying the structure of the diamine used, it is possible to move up and down in the Robeson's log-log diagram. However, no significant improvement in gas separation performance comparing to that of the other PIs listed in literature was noticed. A correlation between diamine and dianhydride structure and gas permeability have been found and discussed with respect to the behavior observed for structurally different polyimides.

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1. Robeson, L.M. The upper bound revisited, *J. Membr. Sci.* **320**, 390-400 (2008)
2. Powell, C. E., Qiao, G. G. Polymeric CO<sub>2</sub>/N<sub>2</sub> gas separation membranes for the capture of carbon dioxide from power plant flue gases. *J. Membr. Sci.* **279**, 1-49 (2006).