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Thermally stable polymers for advanced high-performance gas separation membranes

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ABSTRACT

Polymeric membranes can be used for the energy-efficient and low-cost gas separation. However, their inability to resist high temperatures limits their use in certain industries. Some polymer membranes can be operated at some levels of the unpleasant environments, but the energy- and cost-efficiencies are offset by the necessity to severely cool hot streams. In many cases, such implementation is impossible or altogether impractical. Therefore, numerous studies have been focused on modifying polymers to create synthetic polymeric membranes which survive at high temperatures. Polymer scientists introduced many thermally stable polymers mostly based on carbocyclic and heterocyclic aromatic polymers, which exhibit enhanced thermal stability. However, the major problem with these polymers is their low processability, which is mainly due to their insolubility or high phase transition temperatures. So far, there has been little success in processing the high-temperature-resistant polymers to make membranes with acceptable separation and performance characteristics. The aim of this study is to review efforts which have been made to produce high-performance polymeric membranes with a focus on the preparation procedure; whereby, the main limitations and challenges to be faced were explored. The key factors discussed include the type of polymer, membrane preparation method, thermal analysis results and application of the prepared membranes. The primary purpose of this review is to lay out the basics for selecting polymer, solvent, additives and the appropriate preparation method to produce thermally stable polymeric membranes for gas separation. The future direction of research and development to fully exploit the potential usage of thermally stable polymeric membranes to achieve commercially viable processes was also shown.

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1. Introduction

In recent years, membrane gas separation (GS) technology has become one of the fastest emerging technologies due to their distinct advantages over conventional techniques (mainly absorption by amines). In particular, membrane GS exhibits operational flexibility, easy scale-up, low operating costs, compact design, and high product quality [1–8]. One of the most important applications of membrane GS is to capture and recover CO_2 from gas streams. The concentration of carbon dioxide (CO_2) in the atmosphere has been increasing significantly over the past century. The average concentration of CO_2 in 2015 was 399 ppm which was about 40% higher than that in the mid-1800 s. The CO_2 emission has been intensified in the last decade with an average growth of 2 ppm/year [9]. This intense upward trend is primarily attributed to the growing worldwide energy demand from fossil fuels. The industrial sector is responsible for one-third of all the energy utilized globally and for almost 40% of CO_2 emissions [10]. Given the significant effect of greenhouse gas (CO_2 as the main component) emission on climate change and global warming, capture, and recovery of CO_2 has become a global issue [11–13].

There are several different types of membrane materials such inorganic materials (ceramics, metals, zeolites, carbons), organic materials (rubbery, glassy, and polymer blends) and porous hybrid materials (metal-organic framework (MOFs), zeolitic imidazolate frameworks (ZIFs)). Due to the high cost of inorganic membranes and porous hybrid materials [14,15], and their modularizing problem, numerous studies have been focused on modifying polymers to create synthetic polymeric membranes which survive at elevated temperatures. The polymer membranes are inexpensive and simply manufactured into large-scale modules. Treatment of gas streams using polymeric membranes has, therefore, become a common practice in many industries [16]. However, the major limitation of the current polymeric materials is their relative lack of tolerance to high temperatures. Many hot gas streams in all chemical industries must remain at high temperature during GS process. Many of these streams cannot be subjected to membrane-based separation processes. In some applications, the process streams are cooled solely to accommodate a membrane GS process, after which are heated back. This cooling followed by re-heating causes the waste of a considerable amount of energy [17].

Research in thermally stable polymers started in 1950 when carbocyclic and heterocyclic polymers were first discovered and the ability of the polymers to withstand high temperature was discovered [18]. Thermal stability of a polymer is variously defined as:

- Maintenance of the chemical characteristics of the polymer “above 300°C by Thermogravimetric Analysis (TGA) in air” [19], or,
- Maintenance of physical properties for long periods of time “at 280°C in air measured by Instrumental Gas Analysis (IGA) [19].”

These definitions could be construed as vague by some researchers, because the stability is subjectively defined in terms of a temperature where the polymer chemically denatures without specifying the period of operation, and the mechanisms for loss of thermal properties (deterioration) are not exactly addressed. The thermal stability of many “heat-resistant” polymers is also frequently described by such terms as “good” or “high” without quantification. These statements raise questions, such as, what is the environment at which the stability should be studied? How long is the polymer stable at a specific temperature in different environments? At what temperature does the polymer become unstable? What is the role of pressure or stress in addition to temperature? From a practical standpoint, thermal stability is the temperature or temperature range that a material can withstand and still retain useful properties in a given application [20]. This practical viewpoint is perhaps more useful for defining thermally stable membranes. In fact, for testing the suitability of membranes as filtration media at high temperatures, the membrane should be tested at high temperatures in a specific application for a long period instead of focusing on thermal analysis results.

In addition to stability, at least two other key factors exist that enter in the recipe for the success of high-temperature-resistant membranes. These are shown in Fig. 1 as the unification challenge. The concept of thermally stable membranes, developed by specialty polymers, involves three critical factors which determine their ultimate utility: stability, durability, and processability. The analysis of the long-term performance of membranes confirms the reliability of operation and the process sustainability. Failure analysis can be used as a tool to identify process sustainability and to develop actions to prevent failure occurrence. The first step is to know the membrane failure criteria which entirely depend on the application requirements. Generally, membranes must undergo a long-term operation at elevated temperatures and demonstrate quite a favorable trade-off relationship between selectivity and permeability [20].

Without getting into the mathematics, the reliability of a polymeric membrane is defined as a measure of the chance that the membrane will last long enough to perform the separation. In fact, it is a measure of the probability of remaining in-service to a certain point in time. Reliability of membrane can be affected by small changes in membrane material properties.

The primary challenge in the preparation of membranes from stable polymers is the difficulty in processing, as these polymers have a very low solubility in common solvents. In fact, there is an inverse relation between stability and tractability. Therefore, the

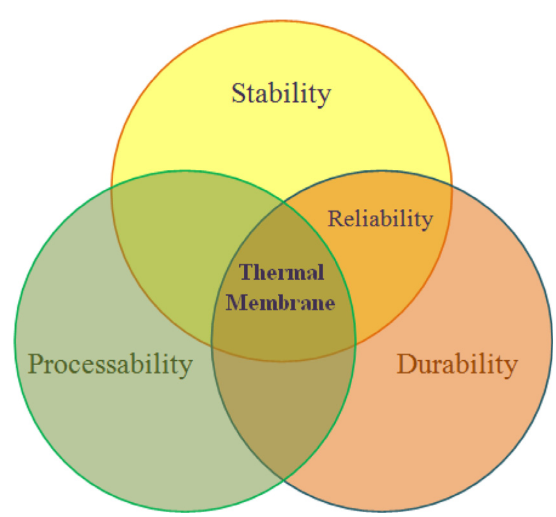

Fig. 1. The challenge of unifying stability, durability, and processability to produce thermally stable polymeric membranes.