PENETRANT-INDUCED PLASTICIZATION IN GLASSY POLYMER MEMBRANES FOR GAS SEPARATION

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ABSTRACT

The present paper deals with the performance of glassy polymer membranes plasticized by penetrant gases. Penetrant-induced plasticization of gas separation membranes has been the subject of a number of recent investigations. Historically, plasticization can be attributed to the swelling stresses exerted by the penetrant molecules on the polymer network. It appears that carbon dioxide behaves as a plasticizing agent for many glassy polymers by expanding the polymer lattice and increasing the frequency of molecular motions. In glassy polymers, the permeability to carbon dioxide is pressure dependent. Permeability can either increase or decrease with increasing feed pressure. It was thought that the permeability of most glassy polymers to gases decreases with increasing pressure in accordance with the predictions of the dual-sorption theory. Presumably, the plasticizing action of CO_2 decreases the ability of the membrane to separate molecules thereby causing the reduction in selectivity. In gas separation membranes, plasticization effects are observed as anomalous sorption and permeation during measurements at elevated pressures. The alteration of a number of properties resulting from the polymer conditioning by the sorbed penetrant molecules was investigated. It has been demonstrated that high sorption of carbon dioxide results in a strong plasticizing effect on the properties of several polymers. Disentanglement of polymer chains at elevated pressure, the depression of the glass transition temperature by absorbed CO_2 molecules, the decreasing of activation energy for diffusion with increasing concentration visualize the plasticization effect of carbon dioxide on glassy polymers.

Keywords: Plasticization; Carbon dioxide; Gas separation; Glassy polymer membrane

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1. Introduction

Plasticization of polymers by highly sorbing gases has been the focus of numerous studies over the past decade [1-5]. It is known that CO_2 acts as a plasticizer at elevated pressures [6]. Several authors [7] indicated that CO_2 has a quadrupole moment and is expected to be more soluble in polymers with a polar matrix. Polar groups of the polymer are assumed to increase the tendency of a polymer to be plasticized because they may have dipolar interactions with the polarizable CO_2 molecules. The strong interactions between the CO_2 and the polymer material often affects flux and permselectivity properties. Presumably, the plasticizing action of CO_2 weakens the polymer material, which is observed as a considerable loss in separation ability of the membrane. Thus, it was thought that penetrant-induced plasticization may significantly spoil the membrane performance in high-pressure CO_2/CH_4 separations.

In Figure 1, the polymers show the decreasing permeability with increasing pressure at low feed pressures. Dual-mode considerations can explain the decreasing permeability behavior [8]. After going through a minimum, the permeability increases again when the plasticization effects are stronger than the decrease of the permeability. This is often referred to as plasticization and the pressure at the minimum permeability is called the plasticization pressure. In this case, plasticization of glassy polymers can be simply defined as the increase in CO_2-permeability as a function of feed pressure [9]. The increasing of the permeability occurs at sufficiently high CO_2-concentration to disrupt chain packing in the polymer. This results an increasing of the free volume and segmental mobility of the polymer matrix. Due to the

swelling of the polymer matrix and the enhanced chain mobility imply an increase in gas diffusion. The permeation of CH_4 is accelerated and as a consequence the polymer looses its selectivity.
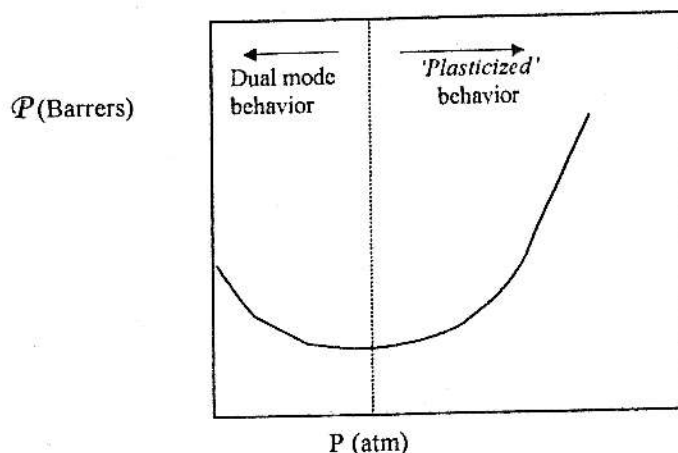
FIGURE 1: Generic Permeation Behavior of Glassy Polymers. Dual-mode Considerations Explain the Decreasing Permeability Behavior and the Increase in Permeability at Elevated Pressures is Referred to Plasticization.

The permeability of glassy polymers to CO_2 can either increase or decrease with increasing penetrant pressure. One possible explanation by Sanders [2] about the decrease in permeability with pressures is that the solubility coefficient decreases with pressure more rapidly than the diffusion coefficient increases with concentration. On the other hand, for polymers in which the permeability increase with pressure, the diffusion coefficient increase with concentration much more rapidly than the solubility coefficient decrease with pressure. However, the permeability is no longer constant but increases in time (Fig.2). Wessling has studied on the permeability of a polymer above the plasticization pressure and the phenomenon of plasticization during permeation [5].

Recently, Bos et al. [1] have investigated CO_2-induced plasticization phenomena in several different glassy polymers by single gas permeation and sorption experiments. Furthermore, they found that the permeability increases with the increasing of free volume which is in agreement with the findings of Lee [10]. They observed that the number of carbon dioxide sorbed is important in causing plasticization and not its polar character. From the experiment results show that polysulfone, polyethersulfone and polyetherimide have shown high plasticization pressures compared to the other polymers. Investigation of asymmetric cellulose acetate membranes which revealed anomalous permeation behavior for carbon dioxide and methane have been explained by the plasticization phenomena [11].
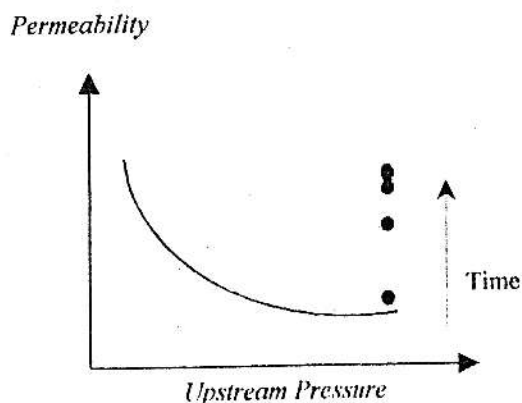
FIGURE 2: CO_2 Permeability in a Glassy Polymer Depending on the Upstream Pressure Value and on Time.

Plasticization of polyimide membranes by CO_2 have documented in the literature [12-14]. White et al. [15] reported that asymmetric membranes prepared by a precipitation process are more sensitive to plasticization effects of CO_2 compares to dense one due primarily to different microstructure and morphology of the asymmetric membranes. The asymmetric film has a smoother surface than the dense film via Atomic Force Microscopy (AFM). Generally, most of the reported permeability properties for polymers are from dense films because they provide values that can be considered as upper limits for the selectivity. Hence, many investigaters have been reported the plasticization phenomena on homogeneous dense films.

Some researchers compared the plasticization behaviour of a polyimide film at different operating temperature [9,16]. A higher permeability is expected at increasing temperature because the solubility of carbon dioxide in the glassy polymer become lower at higher temperatures [1,17-19] and the diffusivity increase with increasing temperature. Wessling et al. [20] found that it is a difference of plasticization behaviour between thin films and thick films prepared from the same polymer. Work has been carried out to investigate the phenomenon of accelerated plasticization properties of thin–film composite membranes used in gas separation.

The purpose of the present communication is to study the fundamental understanding of CO_2-induced plasticization on the performance of polymeric membrane for gas separation. The effect of exposure to high-pressure CO_2 on the physical properties of glassy polymers has also been discussed.
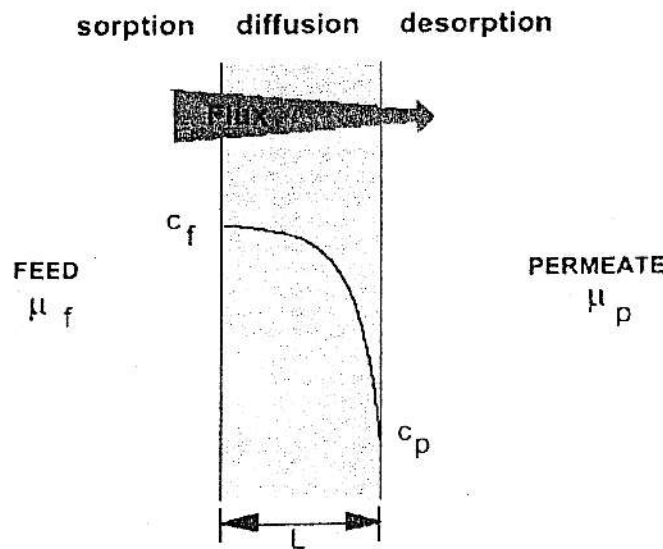
2. Background

FIGURE 3: Permeation through membrane via solution-diffusion mechanism.

It is well known that transport of penetrant through a glassy polymer membrane occurs by a solution-diffusion mechanism [21]. Permeants dissolve in the polymer film and then diffuse through the polymer film and then diffuse through the membrane down a concentration gradient (Fig.3).

$$P = [D][S] \tag{1}$$

where D is an average diffusion coefficient, and S is a solubility coefficient [22]. According to the solution-diffusion model, the product DS is referred to as the permeability (P) of the gas in the membrane material. The ability of a membrane to separate a gaseous mixture of A and B may be characterized by the ideal permselectivity, α, which is defined by

3

$$\alpha_{AB} = \frac{[P_A]}{[P_B]} \qquad (2)$$

For the sorption of penetrant molecules into glassy polymers, a number of different models have been developed. The most widely used model is the dual-mode sorption model [23]. The Figure 4 illustrate the procedure for determining parameters by the dual sorption model. This theory postulates the existence of two types of sorption mechanisms in a glassy polymer:

(1). Gas molecules dissolved by an ordinary dissolution process according to Henry's law, the concentration of the molecules C_D is related to the pressure

$$C_D = k_D p \qquad (3)$$

where k_D is the Henry's Law solubility coefficient and

(2) gas molecules absorbed at fixed sites in microcavities "frozen" into the polymer matrix. The concentration of these molecules is related to presssure p by the Langmuir isotherm:

$$C_H = C_H'bp/(1+bp) \qquad (4)$$

where C_H' is the hole saturation constant and b = the hole affinity constant which represents the ratio of the rate constants of gas adsorption and desorption in the microcavities or defects.

The total penetrant concentration C in a glassy polymers is then given as a function of p by the expression:

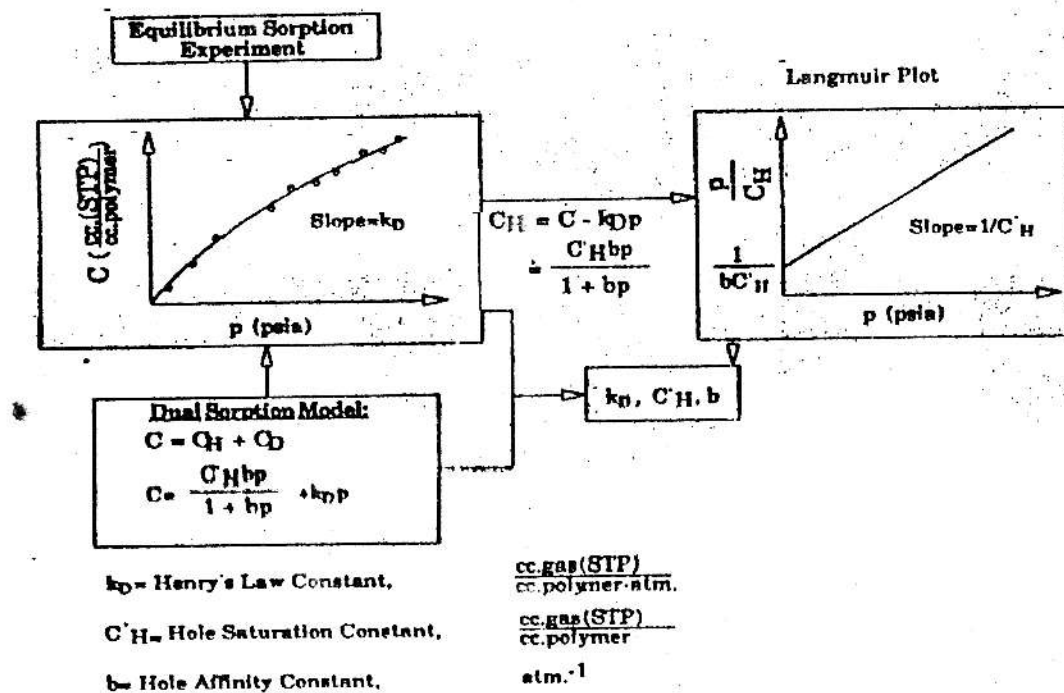$$C = C_D + C_H = k_D p + C_H'bp/(1+bp) \qquad (5)$$

FIGURE 4: Diagram Illustrations Procedure for Determining Parameters by the Dual Sorption Model.

3. Effects of sorbed CO_2 on the properties of glassy polymers

Sorption of significant quantities of CO_2 results in a strong plasticizing effect on the properties of several polymers [1]. However, the magnitude of plasticization depends on the amount of the gas sorbed [2]. In the following subsections, the alteration of a number of physical properties resulting from the polymer conditioning by the sorbed penetrant molecules will be described.

3.1. Depression of the glass transition temperature

It has been recognized for several years that the sorption of carbon dioxide by polymers can cause significant plasticization resulting a depression in the glass transition temperature. The swelling of the polymer matrix lossened the structure of the polymer matrix and as a consequence polymer chains become more flexible. Many studies elucidate the increase in chain mobility can be observed by a depression of the glass transition temperature of the polymer-penetrant mixture [2-3,5,24-27]. As was shown by Simha and Boyer [28], a higher Tg correlates with an increasing chain stiffness. The lower Tg of the membrane film may be attributed to a more flexible polymer matrix as a result of a less efficient packing (lower density). Thus, CO_2 at modest pressures can cause significant reductions in the glass transition temperature of glassy polymers which have high CO_2 solubility [5]. The decrease in Tg and/or increase in chain mobility may arise from the modification of the interchain energy interaction by the penetrant as well.

Chiou et al. [3] observed that sorption of CO_2 by different polymers can cause significant plasticization resulting in decrease of Tg of 32°C for polystrene, 51°C for polycarbonate, 18°C for poly(vinyl chloride) and 22°C for poly(ethylene terephthalate). Wessling et al. [5] observed that 6FDA-based polyimides showed Tg-depressions of 198°C at 50 bars CO_2. Sanders [2] studied the CO_2-induced changes in polyethersulfone (PES). Houde et al. [29] indicated that the depression in Tg in the case of polysulfone was 18°C.

3.2. High pressure dilation kinetics

The plasticization effect is the introduction of increased free volume which is opposite to the effect of thermal annealing [30]. Wessling et al. summarized that swelling occurs at low and high pressure levels in different ways. Since the dilation kinetics increase with increasing the temperature, it was noteworthy that the loosening of denser packed entanglement is a thermally activated process [4]. A study has also been made by Sefeik and Schaefer [25] that small concentration of CO_2 can significantly increase the frequency of main-chain motions. Hence, the sufficient highly carbon dioxide concentration in the polymer film disrupts the chain packing, thereby leading to a larger free volume and enhanced rates of segmental motions.

3.3. Activation energy for diffusion

The activation energy for diffusion, E_d is the kinetic component of the temperature dependence of permeation and is primarily dependent on penetrant size and shape of a polymer [18]. It can be defined as the energy required to separate polymer chains for a diffusional jump. Thus, the polymer matrix swells upon sorption of CO_2 results in a decreasing activation energy with increasing of penetrant molecules concentration in the polymer film. This shows that less energy is required for the blending of polymer chains in order to create new void volume [4].

4. Conclusion

In high-pressure CO_2/CH_4 separation problems arise due to plasticization. This phenomenon is most frequently observed for separations involving CO_2 such as natural gas upgrading, enhanced oil

recovery (EOR), and landfill gas cleaning. High level sorption of CO_2 in glassy polymer can cause a dilation of the polymer matrix and significant change its characteristics.

Several investigations have been reported the impact of the plasticization on the gas separation process and its suppression method. Recent research in Membrane Research Unit, University Technology of Malaysia has focused on investigating the plasticization effect on the performance of asymmetric membrane for gas separation. Futhermore, an attempt is made to find correlations between the plasticization and the membrane performance in order to minimize this phenomena.

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