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Physical aging and plasticization of thick and thin films of the thermally rearranged *ortho*-functional polyimide 6FDA–HAB

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ABSTRACT

It was recently shown that the rate of the thermal rearrangement process of an *ortho*-functional polyimide is thickness dependent. Here it is shown that the gas separation properties of thermally rearranged (TR) polymer films are also affected by thickness. In this work, the physical aging and plasticization behavior of TR polymers were tracked using thin (~1–2 μm) and thick (~15–20 μm) films derived from an *ortho*-functional polyimide based on 2,2′-bis-(3,4-dicarboxyphenyl) hexafluoropropane dianhydride (6FDA) and 3,3′-dihydroxy-4,4′-diamino-biphenyl (HAB) over hundreds of hours. The thin films experienced a much greater rate of physical aging than the thick films, as indicated by the rapid decline of gas permeabilities and the gradual increase of ideal selectivities. As the thermal rearrangement temperature was increased, the aging rate of the resultant thin film did not increase extensively and the plasticization curves of the thin and thick films became closer. Long term exposure of the TR films to CO_2 at 32 atm over 500 h shows that the CO_2 permeability of the thick TR films did not show significant decline over time; whereas, the CO_2 permeability of the thin TR films increased over the first several hours and decreased rapidly during further exposure time. Finally, the response of thick TR films to C_2H_4, C_2H_6 and C_3H_8 over long term exposure shows that physical aging is greatly accelerated when the polymer matrix is severely plasticized by the more condensable gases.

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1. Introduction

Membranes have emerged as an effective technology for certain gas separations [1–3]. Over the past several decades, different types of materials, including metals, ceramics, carbons and polymers, have been used to fabricate membranes [4–8]. Polymers generally have the advantages of affordability and the ease of processability, and these attributes among others have made them the materials of choice in most cases [9–11].

Recent studies have shown that glassy polymer films behave very differently as their thickness decreases toward the submicron or nanometer range [12–19]. Monitoring gas permeation properties over thousands of hours indicates that thin films undergo physical aging much more rapidly than the thick films, with the same thermal history, typically used in most laboratory studies [12,14,15,20,21]. In addition, plasticization induced by highly condensable gases, like CO_2, has also been found to be thickness dependent. As compared to thick films, thin films (~200 nm) experience more extensive and faster plasticization with short exposure to CO_2 at elevated pressures. Horn and Paul showed that the plasticization pressure of a thin Matrimid® film was much lower than that of a thick Matrimid film [22]. In addition, when the Matrimid® films were exposed to CO_2 at 32 atm for hundreds of hours, no significant change of CO_2 permeability was observed for thick films; whereas, thin films showed a rapid initial increase of CO_2 permeability, indicating that the thin film is plasticized to a greater extent than its thick counterpart [16,17], followed by a decline in permeability apparently owing to physical aging.

Thin film studies have been reported for numerous glassy polymers including commercial polyimides, polysulfone (PSF), poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) and experimental 6FDA-based polyimides [14,15,21]. The extent of physical aging and plasticization effects vary widely from one material to another. For example, thin PPO films age much faster than thin PSF films, while the thin PSF film exhibits better plasticization resistance than thin PPO films [13,17]. Therefore, it is important to further extend systematic studies of thin films to other polymers and, in particular, to the high performance materials developed in recent years.

The high performance materials known as thermally rearranged (TR) polymers have attracted much interest for future

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industrial applications in gas separation [23–27]. During thermal rearrangement, the precursor polymer, usually an *ortho*-functional polyamide or an *ortho*-functional polyimide, is thermally converted to a heterocyclic structure such as polybenzoxazole upon thermal treatment under an inert atmosphere [24,28]. The gas separation performance of such TR films is strongly affected by the degree of conversion to the rearranged structure [29,30].

Our recent work on TR polymers has shown that the degree of chemical conversion is also affected by film thickness and a higher degree of conversion is attained as the film becomes thinner [31]. We were also interested in exploring how the gas transport properties of TR films depend on their thickness. Therefore, this work aims to systematically investigate the physical aging and plasticization phenomena in thin and thick TR membranes. Three different treatment temperatures, 350 °C, 370 °C and 390 °C, were used to thermally rearrange an *ortho*-functional polyimide films so as to achieve different degrees of conversion. The pure gas permeability of the resultant TR films was tracked over more than 1000 h. The responses of these TR films to CO_2 at elevated pressures and long term exposure at 32 atm were also studied. In addition, light hydrocarbons with different condensabilities were used in long term exposure experiments so as to explore the effect of gas condensability, which affects the solubility in the polymer, on physical aging and plasticization.

2. Experimental

2.1. Polymer synthesis and film preparation

The *ortho*-functional polyimide, 6FDA–HAB, was synthesized from 2,2′-bis-(3,4-dicarboxyphenyl) hexafluoropropane dianhydride (6FDA) and 3,3′-dihydroxy-4,4′-diamino-biphenyl (HAB). During chemical imidization, acetic anhydride was used as the dehydration agent; thus, the hydroxyl group at the *ortho* position was converted to an acetate structure. Details of monomer purification and polymer synthesis are described elsewhere [23,32].

The film casting solutions were prepared by dissolving the polymer in anhydrous cyclohexanone. Prior to film casting, the solution for thin film casting were filtered through PTFE filters of 0.45 μm, 0.2 μm and 0.1 μm pore size successively to remove insolubles or impurities. Owing to the very high viscosity, the solution for thick film casting was only filtered by PTFE filters of 5 μm and 1 μm.

The pristine 6FDA–HAB films were prepared by the knife casting method. Thin films of around 1 μm were obtained by casting a 2.8 wt% polymer solution using a knife clearance of 40 μm, while thick films of 15 μm were cast from an 8 wt% polymer solution at a knife clearance of 150 μm. The polymer solution was first cast on an annealed black glass plate; then the glass plate with polymer solution was put into a conventional oven at 80 °C for 1 h to remove the solvent. Afterwards, different procedures were applied to further dry the thin versus the thick films.

The nascent thin film was cut into pieces and peeled off from the glass plate by using deionized water and then annealed on a copper wire frame as described elsewhere [13,31]. The freely standing films were then dried in a vacuum oven at 80 °C overnight.

The nascent thick film was not peeled off immediately, since it may contain residual solvent and immersing this film into water may affect the membrane morphology, e.g., pore formation. After solvent evaporation in the conventional oven, the thick film while still on the glass plate was transferred to a vacuum oven for further drying. The vacuum oven was ramped at 25 °C/h from 75 °C to 200 °C and held at 200 °C for 24 h to remove the residual solvent. After naturally cooling down to room temperature, the thick film was peeled off the glass plate by using deionized water, followed by drying in a vacuum oven at 80 °C overnight. The resultant thin and thick films had thicknesses of 1.1 ± 0.2 μm and 13 ± 2 μm, respectively.

2.2. Thermal rearrangement procedures

Thermal rearrangement of the pristine 6FDA–HAB films was conducted in an oven, modified from an Agilent 6980 Gas Chromatography system, under continuous nitrogen purge. Three temperatures, 350 °C, 370 °C and 390 °C, were chosen for thermal rearrangement.

The oven was ramped from room temperature to 200 °C and held there for 30 min to remove the sorbed moisture and any residual solvent in the films. Subsequently, the oven was heated from 200 °C to the target temperature and held for 30 min for the thermal arrangement reaction. Afterwards, the oven was quenched to 50 °C over about 5 min, and the resultant TR films were removed. The time at which the films were taken out was recorded as time zero for physical aging.

It is very important to note a major difference in protocol from much of our prior work. For glassy polymers with glass transitions below where decomposition reactions might occur, we have in prior work heated the film above the T_g briefly to erase prior history and to give a well-defined time zero for subsequent aging studies. For a variety of reasons, this was not feasible here, so it is important to recognize that the behavior reported here for these TR films is affected to some degree by the prior history used to form the film including the thermal rearrangement process itself.

After being thermally rearranged, the films become thicker and the increase of film thickness is more pronounced the higher the treatment temperature. In general, the film treated at 390 °C is thicker than that treated at 350 °C. In addition, the final TR film thickness is also strongly affected by the thickness of the starting pristine film, which cannot be exactly controlled. Thus, due to these factors, it was not possible to prepare films for permeation testing of exactly the same thickness. In all the figures and tables, the thickness indicated refers to the thickness of the final TR film, unless otherwise stated.

2.3. Pure gas permeation test

The pure gas permeation properties were measured using a constant-volume variable pressure system. Measurements were conducted at 35 °C and 2 atm of trans-membrane pressure. Prior to a measurement, the system was evacuated under high vacuum. In an aging test, the permeabilities of H_2, O_2, N_2 and CH_4 were monitored over 1000–2000 h. After one run of measuring the four gases, the film was stored in a dry box (RH ~ 26%) at 25 °C.

3. Results and discussion

3.1. Thermogravimetric analysis (TGA)

During thermal rearrangement of 6FDA–HAB, several volatile compounds are generated and released [34]. In order to track the amount of weight loss incurred, isothermal TGA analyses were conducted following the exact thermal rearrangement protocol used to prepare the films for gas permeation measurements. The initial sample weight in the TGA pan was controlled at 5 ± 0.5 mg to reduce the variation caused by the different sample sizes. Fig. 1 shows the isothermal TGA curves for 6FDA–HAB films of different thicknesses treated at different temperatures.

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