Aging of Polyimides in High Temperature Environments

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Summary: Membranes made of high permeable fluorinated aromatic polyimide synthesized from 6FDA (4,4'-hexafluoroisopropylidene diphthalic anhydride) and 4MPD (2,3,5,6-tetramethyl-1,4-phenylene diamine) have been thermally treated to examine their aging behaviour at high temperature. The aging process was investigated by means of gas permeation tests, IR spectroscopy and thermogravimetric analysis combined with mass spectral analysis of the gaseous decomposition products. Up to around 400 °C thin films of the material show no major degradation but changes in color, flexibility and separation characteristics for O_2/N_2 were observed.

Keywords: aging; degradation; gas permeation; membranes; polyimides

Introduction

Aromatic polyimides with $-CF_3$ groups on the polymer backbone are stable in harsh chemical environments at room temperature, e.g. in gasoline or kerosene mixtures but they can be also used as high temperature packing/gluing materials in aircraft and space applications as well as in the electronic industry. In order to operate these polymers as membranes in separation processes at high temperature, it is necessary to investigate aging processes. One potential application at high temperature is the separation of hydrogen from reformate gas streams. For these processes it is important to figure out if under non-oxidative environments other degradation reactions take place than in air or oxygen.

Thermal treatments are well known methods in membrane preparation to improve the separation characteristics. Established methods for polyimides include annealing, quenching and carbonization.[1–3] Probably annealing of the material below its glass transition temperature T_g leads to an increase in density. As a result a lowered permeability and an increased selectivity compared to the native polymer is found.[4] Heating above the T_g followed by rapid quenching generally deletes the thermal history and causes higher fractional free volume.[1] In carbonization processes the membrane material degrades partially at higher temperature (depending on the material, e.g. at 500–800 °C) and builds up structures which can reach high permselectivity combined with very high permeability. Barsema et al. reported for Matrimid membranes an increase of oxygen permeability from 1.6 barrer (treated at 300 °C) to 40.2 barrer (treated at 525 °C) which is 25 times of the initial value. Simultaneously the selectivity for O_2/N_2 decreases from 8.2 to 4.6 which is a reduction of approximately 44%.[3]

With our setup it was not possible to perform permeation tests with hydrogen for security reasons. Therefore gas permeation experiments were carried out using O_2 and N_2. This method is often used to evaluate membrane separation characteristics as well as changes due to thermal treatments.

In this study an aromatic $-CF_3$ groups containing polyimide, the 6FDA-4MPD

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was annealed at temperatures between 300 and 400 °C for 24 hours to simulate applications at elevated temperatures.

As the 6FDA-4MPD investigated in this study shows extremely high permeability but rather low selectivity compared to other polyimides[5] it is desirable finding a new method to improve the selectivity with an acceptable loss in permeability. Therefore as a second aspect of this study it was investigated if short time accelerated aging at high temperatures could be a tool to increase the separation performance of 6FDA-4MPD similar to long time aging at low temperatures. Lin and Chung found that after aging for 280 days 6FDA-4MPD showed a decrease in oxygen permeability from 125 barrer to 80 barrer with an increase of O_2/N_2 selectivity from 3.52 to 3.75.[6]

Polymer Synthesis and Film Preparation

The material investigated is based on the aromatic dianhydride 6FDA (4,4'-hexafluoroisopropylidene diphthalic anhydride, Lancaster 99%) and the diamine 4MPD (2,3,5,6-tetramethyl-1,4-phenylene diamine, Fluka, 99%). The monomers were purified by sublimation (0.1 mbar) at 215 °C and 100 °C oil bath temperature respectively. DMAc (N,N-dimethylacetamide, Merck, >99%) was purified by fractional distillation after boiling several hours over calcium hydride.

The structure of the polyimide 6FDA-4MPD is shown in Figure 1. The polyimide was synthesized in a two step polycondensation reaction[7] under nitrogen atmosphere in a moisture free flask. In the first step 328.5 mg (2 mmol) of the diamine (164.25 g/mol) was dissolved in 2.66 mL DMAc then 888.5 mg (2 mmol) of the dianhydride (444.25 g/mol) was added as a solid. The reaction mixture was diluted with 2.66 mL DMAc until a concentration of approximately 20 wt% was reached.

After stirring the solution over night the polyamic acid was formed. For the chemical imidization, a mixture of 0.57 mL triethylamine and 0.84 mL acetic anhydride were added. The reaction mixture was then diluted with 6.74 mL of DMAc to lower the viscosity and heated up to 120 °C oil bath temperature for 30 minutes. After that it was cooled down to room temperature. The polymer solution was precipitated in water/ethanol and the solid polymer was milled, washed with ethanol and finally dried under vacuum (15–30 mbar) at 150 °C for three days. 1.05 g of dry polymer was obtained (yield: 91%).

Membrane samples for the investigation of gas permeability and gas selectivity were prepared by casting 1.6 wt% solutions of polymer in THF (Tetrahydrofuran, VWR Prolabo, >99.5%). In order to get defect free membranes, the polymer solution was filtered through a glass frit into a petri dish with a smooth surface. A funnel with some paper on top was used for covering the solution in order to avoid dust particles on the surface of the membrane and to build up a saturated atmosphere of THF, which evaporates slowly. After 8–16 hours the THF was vanished and the films could be stripped off with distilled water. The membrane samples were dried in a vacuum oven (15–30 mbar) at 150 °C for 24 hours. All samples were prepared this way. Those which were not treated thermally are mentioned as ''dried samples'' in the following paragraphs.

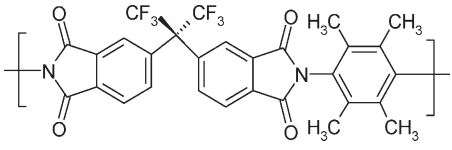

Figure 1.
Structure of the polyimide synthesized.

Annealing and Analytics

After the drying process described above some of the membranes were thermally treated in a metal cell with gas inlet, mounted in a muffle furnace. The cell

was set under nitrogen atmosphere and each sample was treated at a certain temperature in the range from 300 °C up to 370 °C for 24 hours. The temperature program was a single heating ramp with a heating rate of approximately 30–40 °C/min (automatic heating regulation by a fuzzy logic controller). The final temperature was then kept for 24 hours. After cooling down to room temperature, parts of the polymer film samples were laminated with aluminium foil on the outside region and glued with epoxy resin to prevent mechanical stress on the membrane created from the sealing of the permeation cell. Afterwards gas permeation tests of the treated films have been performed. The setup of the gas permeation apparatus is shown in Figure 2.

Permeation rates of oxygen and nitrogen (at 3 bar feed pressure and 35 °C) were measured using the pressure-rise permeation method.[8] The permeability is calculated in barrer according to equation (1)

$$1\,\text{barrer} = 10^{-10}\frac{cm^3(STP)\cdot cm}{cm^2\cdot s\cdot cmHg}. \quad (1)$$

From the single gas permeabilities the ideal gas selectivity for oxygen/nitrogen was calculated according to equation (2)

$$\alpha_{ideal\left(\frac{O_2}{N_2}\right)} = \frac{P_{O_2}}{P_{N_2}}. \quad (2)$$

Different dried samples without further treatment as well as polymer films thermally annealed were investigated in thermogravimetric analysis to estimate the mass loss in nitrogen atmosphere. Simultaneously the gaseous products were detected by mass spectrometry to get evidence of degradation reactions.

Dried and annealed membrane samples were also investigated by ATR-FTIR (attenuated total reflection fourier transform infrared spectroscopy) in order to examine whether degradation below 400 °C occurs. Further analysis by GPC (gel permeation chromatography) and ^{1}H-NMR could not be conducted because during thermal annealing, the solubility of the samples was drastically lowered.

Experimental Results

As outlined in the introduction the polyimide 6FDA-4MPD was tested for its performance as high temperature resistant

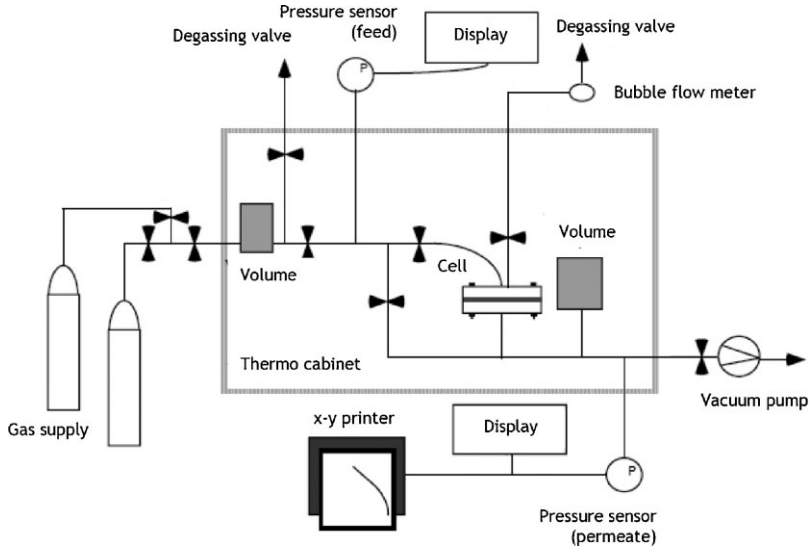

Figure 2.
Gas permeation test setup.

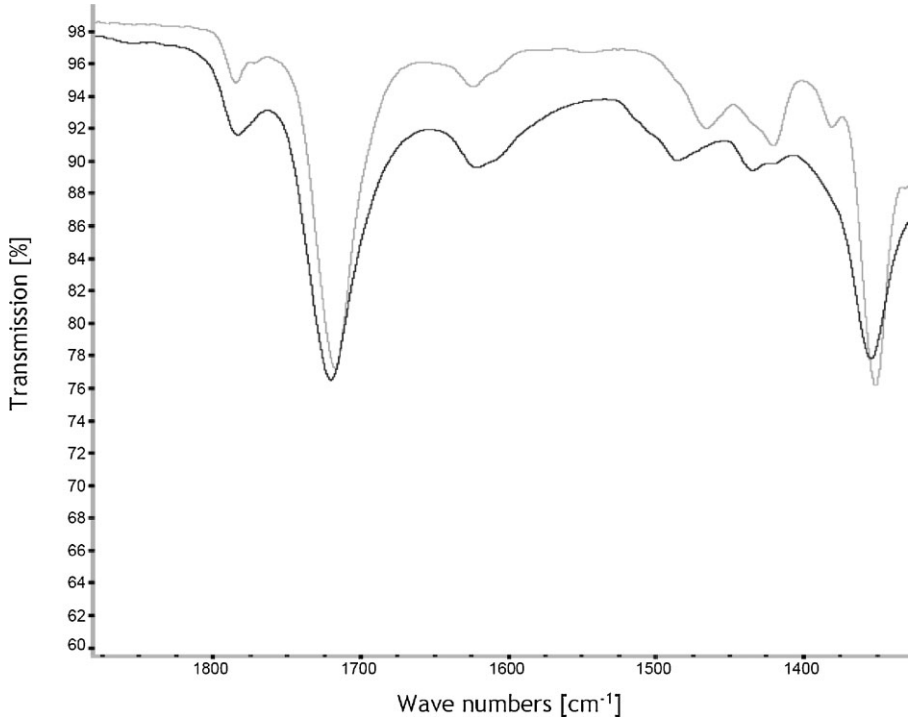

Figure 3.
ATR-FTIR spectra of dried (black) and at 380 °C annealed (grey) membranes.

membrane material after annealing has been performed. As shown in Figure 3, below 400 °C no radical degradation of the polymer backbone occurs. From the ATR-FTIR it is obvious that the sample annealed at 380 °C shows the same characteristic bonds C=O (1716 cm^{-1}, 1786 cm^{-1}) and C-N (1351 cm^{-1}) as the dried polyimide sample with no further annealing.

Further evidence was given by thermogravimetric analysis: The mass loss for 6FDA-4MPD at 400 °C is below 0.5%. At 500 °C the mass loss reaches 2.5% followed by faster degradation (Figure 4). From the

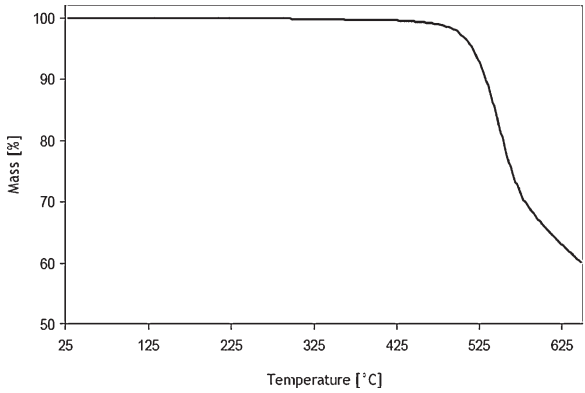

Figure 4.
Thermogravimetric analysis of 6FDA-4MPD under inert atmosphere.

mass spectroscopy of the gases derived from thermogravimetric analysis it can be seen that mostly fluorinated species occur as degradation products. At temperatures above 460 °C -CHF_2 is split off whereas at around 500 °C -CF_3 and at 546 °C -COF_3 fragments are found. This is in good agreement with the two decomposition pathways suggested for –CF_3 group containing polyimides by Turk et al.:[9] In oxidative atmosphere the main decomposition products are CO_2 and H_2O via cleavage of the main polyimide chain whereas under inert conditions the elimination of fluorocarbon radicals dominates.

For membrane based applications, permeation behaviour after annealing is very important and depends on different factors. Permeation can be influenced by compactation of the polymer, formation of charge-transfer-complexes, π-π stacking and radical cross-linking. The fact that the membrane material loses its solubility in THF and similar solvents could be evidence of radical cross-linking.

The permeation experiments show that the membranes which were annealed above 300 °C still had the mechanical strength to resist several bars of feed pressure although they changed their color (from nearly colorless to brown) and lost some flexibility. The thermal treatment significantly effected the permeability as well as the selectivity. The membranes dried at 150 °C without further annealing had an O_2 permeability of 120 barrer and an ideal selectivity for O_2/N_2 of 3.6. After annealing, the permeability dropped down to 70 barrer while the selectivity increased to 4.3 (Figure 5).

Conclusion

It has been shown that membranes made of 6FDA-4MPD can withstand high temperatures up to 400 °C without significant mass loss or structural damages under inert atmosphere. The membranes also possess sufficient mechanical stability for gas permeation applications. A reduced permeability and increased selectivity after annealing of the samples between 300 °C and 400 °C was found. Further experiments with higher annealing temperatures and different polymer structures are under investigation to prove the concept.

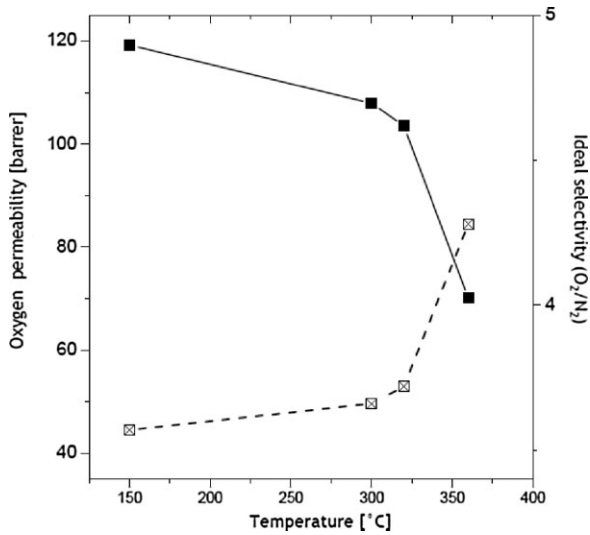

Figure 5.
Gas permeation characteristics of untreated samples (dried at 150 °C) and samples annealed at given temperatures. The solid line shows the permeability of oxygen at the given annealing temperature, the dashed line represents the ideal selectivity.

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