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polymer

Polymer 46 (2005) 5433–5436

www.elsevier.com/locate/polymer

Polymer Communication

Age dependent CO_2 sorption in Matrimid® asymmetric hollow fiber membranes

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Received 23 October 2004; received in revised form 27 April 2005; accepted 28 April 2005
Available online 23 May 2005

Keywords: CO_2 sorption; Asymmetric hollow fiber; Membranes

Asymmetric hollow fibers consist of a thin (~0.1 μm), selective skin layer supported on a macroporous substructure. This is the preferred membrane morphology for industrial gas separations, because the fiber geometry offers the ability to achieve an extremely high surface-area to volume ratio, and the thin, selective skin offers high productivity. Interestingly, the sub-micron skin thickness typical of asymmetric hollow fibers and the rapid quench process through which they are formed imbue hollow fibers with gas transport properties that are age-dependent. Recent work has shown that the permeance of asymmetric hollow fibers experiences a substantial decline from the initial value obtained immediately after fiber formation [1]. Previous work showed a similar effect in free-standing thin films (~1 μm) [2] and is believed to result from the loss of free volume due to physical aging [3,4].

In our laboratory, in some cases, a significant enhancement in CO_2 sorption has been observed for Matrimid® asymmetric hollow fibers exposed to pressures of CO_2 greater than ~450 psia compared to CO_2 sorption in a thick (~25 μm), dense Matrimid® film. This enhanced sorption of CO_2 in asymmetric hollow fiber was found to be age dependent. After storage in ambient laboratory conditions for a 144-day period, the CO_2 sorption isotherm of the hollow fibers approaches that of the dense film within experimental uncertainty. This age dependent behavior is shown in Fig. 1 with curves labeled as sample A-28 days, sample A-48 days, and sample A-144 days. These sorption isotherms were collected via a standard pressure-decay technique [5]. The sorption of CO_2 was normalized by the pure polymer density, which in the case of Matrimid® is 1.24 g/cm^3.

This quite dramatic upturn in CO_2 solubility was replicated by another researcher in our laboratory with a separate batch of Matrimid® fibers, and is labeled as sample B-55 days in Fig. 1. At this time, fibers cannot be consistently produced that show the behavior shown in Fig. 1. Besides of the fibers tested in Fig. 1, all other Matrimid® fibers spun in our laboratory exhibit a more traditional CO_2 sorption isotherm, which is in close agreement with the CO_2 sorption capacity measured for a thick, dense film. We report these results here, because the dramatic difference seen in the data in Fig. 1 would have a major impact on membrane performance, and we do not believe the results are artifacts of poor experimental procedure. This point is explored later in the paper.

The Matrimid® fibers produced in our laboratory are unique because they are characterized by a thin, defect-free skin layer, which achieves a selectivity of at least 95% of the observed selectivity in a thick, dense Matrimid® film. These defect-free fibers are spun from a quaternary solution, which contains a volatile solvent, tetrahydrofuran (THF), to facilitate skin formation. Traditionally, for industrial use, hollow fiber membranes are spun from ternary solutions, which do not contain a volatile solvent. These commercial fibers typically have defective, poorly selective, skins, which are post-treated by caulking to fill the defects. Interestingly, the fibers labeled as sample A in Fig. 1 were spun from a solution containing no THF, while the fibers labeled as sample B were spun from a solution containing 5.9% THF. A more thorough description of the hollow fiber

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doi:10.1016/j.polymer.2005.04.072

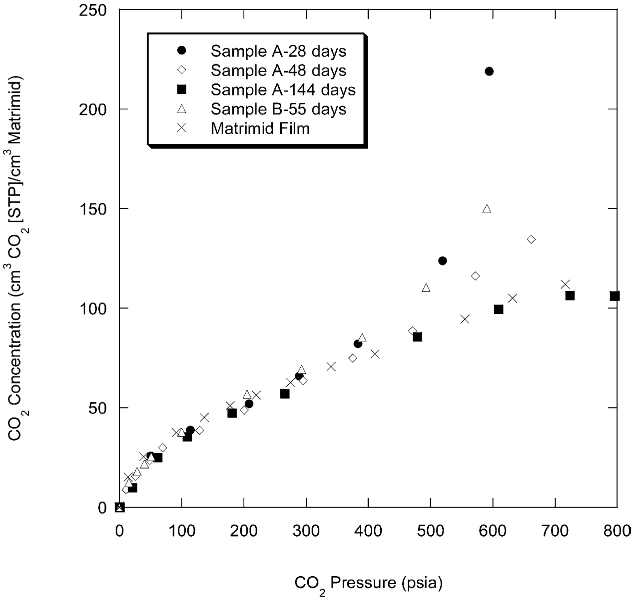

Fig. 1. Enhanced, age dependent sorption of CO_2 in Matrimid® asymmetric hollow fibers (samples A and B) compared to sorption in a thick, dense Matrimid® film.

spinning process used in our laboratory is available elsewhere [6].

The dry-jet/wet-quench spinning technique used in our laboratory produces a water saturated fiber. These water saturated fibers are solvent exchanged and dried under vacuum prior to sorption testing. The standard solvent exchange process used in our laboratory involves three 20-min washes in methanol, followed by three 20-min washes in hexanes, a 30-min air dry, and final drying at 120 °C under vacuum for 1 h. This solvent exchange process preserves the delicate asymmetric morphology and removes any residual chemicals left in the fibers from the spinning solution (i.e. THF, ethanol, *N*-methylpyrrolidinone).

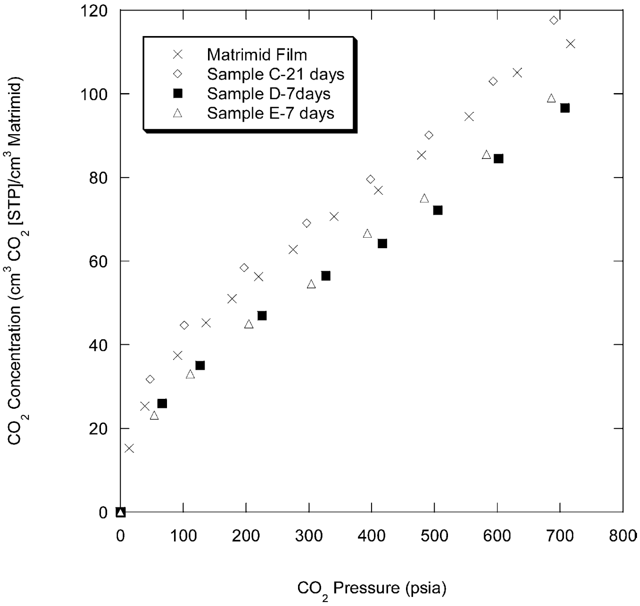

Fig. 2. Effect of solvent exchange and drying procedure on CO_2 sorption in Matrimid® asymmetric hollow fibers. Sample C was fully exchanged and dried. Sample D was not solvent exchange but dried under vacuum at 120 °C for 1 h. Sample E was not solvent exchanged and was only air dried.

The possibility of residual solvent or water left in the fibers, due to a poor solvent exchange, leading to the behavior shown in Fig. 1 was investigated. Three fiber states were spun and underwent varying solvent exchange processes. One fiber state was solvent exchanged using the normal procedure as described above and is labeled as sample C-21 days in Fig. 2. Another fiber state was not solvent exchanged with methanol and hexanes but was dried at 120 °C for 1 h under vacuum and is labeled as sample D-7 days in Fig. 2. The final fiber state was simply air dried after spinning and is labeled as sample E-7 days in Fig. 2. These fibers were tested by thermo-gravimetric analysis and had a mass loss of 1.1, 1.4, 5.9%, respectively, after heating to 400 °C at a rate of 10 °C/min. Even though the poorly solvent exchanged states showed a greater mass loss, their CO_2 sorption isotherms do not reflect the behavior shown in Fig. 1. Note that the mass uptake of CO_2 in Fig. 1 for sample A fibers that are 28-days old approaches 35 wt%, so the small differences in residual solvent should not be adequate to cause the large and time dependent trends observed.

As shown in Fig. 2, the CO_2 sorption isotherms of the poorly solvent exchanged fibers actually lie below the sorption isotherm of the properly solvent exchanged fibers and that of the thick, dense Matrimid® film. This behavior is believed to occur because residual solvent or water is occupying sorption sites in the poorly solvent exchanged fibers and thereby lowering the overall CO_2 sorption.

As noted previously, at this time, the behavior shown in Fig. 1 cannot be controllably replicated, and we believe this behavior is not simply an artifact. The enhanced sorption of CO_2 by Matrimid® asymmetric hollow fibers was observed by two different researchers working with two separate batches of fibers (samples A and B) and in two different sorption cells that have repeatedly given conventional results. Moreover, only CO_2 appears to show this odd response; no upturn in N_2 sorption was observed. Unfortunately, other high-sorbing penetrants were not tested and it is unknown if a different highly sorbing penetrant would show a similar response to that observed for CO_2. It is important to note, that sorption isotherms with a large inflection have been observed previously in other high-sorbing systems, where extreme plasticization leads to an actual glass transition at high activity [7]. However, it is hard to explain how extreme plasticization would lead to the type of age dependent sorption shown in Fig. 1.

Since, the above series of samples in Fig. 2 shows that residual solvent in the fibers is not a cause of the greatly enhanced CO_2 solubility shown in Fig. 1, we suspect but cannot prove that the effect may reflect an unusual morphological feature of the asymmetric structure. We suspect that the behavior captured in Fig. 1 is the result of trapping the fiber initially in a highly non-equilibrium state

Table 1
Effect of physical aging on the permeation properties of low-sorbing gases in Matrimid® asymmetric hollow fibers

Aging time (days)	N_2 permeance (GPU)	O_2 permeance (GPU)	He permeance (GPU)	O_2/N_2 selectivity	N_2/He selectivity
2[a]	0.93	6.49	82	6.97	88
254[b]	0.62	4.18	63	6.74	101
407[b]	0.39	2.88	45	7.38	115

[a] Measurement taken at 27 °C.
[b] Measurement taken at 35 °C.

due to the rapid quench experienced during hollow fiber formation. The quench rate can be approximated by considering that the polymer while in the spin dope exists in a state above its glass transition, and upon removal from the quench bath, the polymer exists as a vitrified fiber. With a take-up rate of 50 m/min, the time required for the polymer to pass through the quench bath is approximately 1-s. For Matrimid with a T_g of 305 °C, this translates to a quench rate of 280 °C/s. However, this estimate of the quench rate is extremely conservative, since from observation we know that the polymer vitrifies almost instantaneously upon contact with the water quench bath. This initial, highly non-equilibrium state and the small characteristic dimension of the hollow fibers allows for physical aging to affect a dramatic redistribution of the free volume in a relatively short period of time leading to the observed age-dependency in CO_2 sorption.

It is well known that physical aging of the selective skin results in significant age-dependent permeation properties in thin films and asymmetric membranes. As shown in Table 1, the Matrimid® fibers investigated in this study also show significant reductions in permeance over time when probed with non-interacting, low-sorbing gases.

The reductions in permeances and increases in selectivities shown in Table 1 are traditionally described as the result of a densification of the selective skin layer due to physical aging. The physical aging manifests significant reductions in permeance over an observable timescale because of the thin selective layer thickness. In the case of hollow fibers, the rapid quench experienced during formation most likely traps the selective skin layer in a highly non-equilibrium conformation, which may further accelerate the effects of physical aging. From examination of Fig. 3, it is apparent that the characteristic dimension, the nodule diameter, of the porous substructure is of the same order of magnitude as the thickness of the selective skin. Due to this observation, it is our contention that the porous substructure of an asymmetric hollow fiber may also undergo accelerated physical aging.

While the effects of physical aging in the selective skin are readily observed by permeance measurements, the effects of physical aging throughout the fiber, including the substructure, would be manifested in sorption measurements. As stated previously, we believe the behavior shown in Fig. 1 is the result of quenching the entire fiber, both skin and substructure, into a highly non-equilibrium state which is able to rapidly age away as a result of the fiber's small characteristic dimension. Unfortunately, the hollow fiber spinning process is so dynamic that quenching the fiber along the precisely same pathway to achieve the same initial glassy state is very hard to replicate. Generally, the effects of differences between similar non-equilibrium quenching trajectories are not so extreme. It may be that a vary narrow set of parameters (spinneret temperature, quench bath temperature, draw ratio, etc.) lead to the highly non-equilibrium initial state, while a much wider window of these variables leads to an initial state much more akin to that seen in the dense film. At the present time, however, we cannot reliably capture these variables in a reproducible manner.

Acknowledgements

The authors would like to acknowledge Mohammed

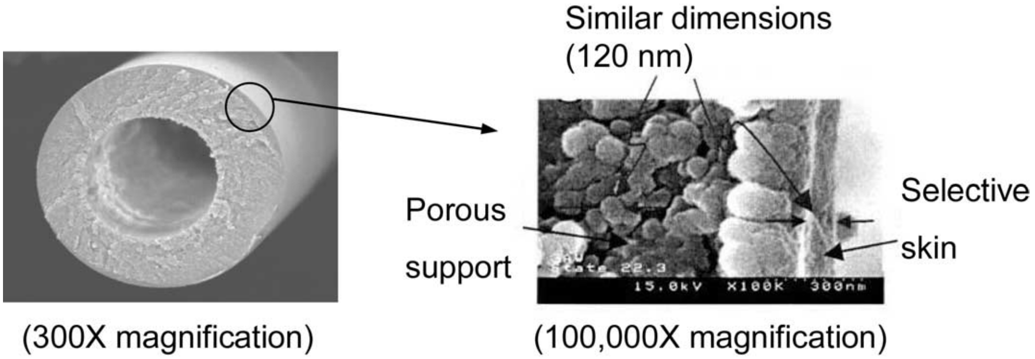

Fig. 3. SEM images of Matrimid® hollow fibers. Characteristic dimensions of the nodular, porous support layer are similar in size to the skin thickness.

Al-Juaied for providing data used in this study and financial support from MEDAL L.P.

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