Processing and Properties of Polysulfone Hollow Fibre Membranes for Gas Separation Filled with Sub-micron Carbon Fibres

Sergey A. Gordeyev, Iain D. Sharpe, Simon J. Shilton*

Department Chemical and Process Engineering, University of Strathclyde, James Weir Building, 75 Montrose St., Glasgow G1 1XJ, UK

Summary: Polysulfone hollow fibre membranes, of the type produced previously with enhanced gas separation properties, were filled with vapour grown carbon fibres (VGCF) of sub-micron diameter. The effect of filler content on mechanical and gas permeation characteristics was studied. Hollow fibre membranes filled with up to 2.8 vol. % of VGCF were produced using forced convection dry jet/wet spinning. Fibre stiffness increased with increasing VGCF filler content. The fibres with the highest concentration of filler were about 30 % more stiff than unfilled membranes. The addition of VGCF lead to a rise in permeability and some decrease in selectivity.

Introduction

All polymers are permeable to gases and vapours to different extents. Permeability is a physical property of great importance in a variety of applications: separation of gas mixtures, food packaging, protective coatings (paints and varnishes), biomedical devices, substrates for microelectronics, etc. Polymers are commonly used in these applications in the form of nonporous membranes: films or sheets, hollow fibres or capillaries.

Hollow fibres (Figure 1) are the most favoured membrane geometry owing to high surface area per unit volume of a membrane module. In the last decade, much effort has been devoted to understanding the fundamental scientific aspects of gas separation hollow fibre membrane processing. This has enabled gas separation by polymeric membranes to become an economically viable technology.

A forced convection dry jet/wet spinning process for manufacturing of asymmetric polysulfone hollow fibre membranes with selectivities that surpass the recognised intrinsic value of the polymer has been developed recently in our group [1]. The results, achieved in laboratory scale spinning, were exciting. However, the membranes produced are delicate and suffer from poor mechanical performance. This problem is addressed in the current study by introducing a filler material into the membrane matrix.

 CCC 1022-1360/00/$ 17.50+.50/0

The most common approach to reinforce a polymer material mechanically is to fill it with stiff elongated inclusions such as chopped glass or carbon fibres. Assuming that filler particles are distributed evenly in the matrix and have a good cohesion to the polymer, an increase both in tensile strength and stiffness can be achieved. Efficiency of reinforcement depends primarily on filler concentration and orientation distribution of the inclusions.

An important condition of efficient reinforcement is that the maximum dimension of inclusions has to be much smaller than the minimum dimension of the composite. For hollow fibres, the thickness of the wall is the critical dimension. The wall thickness of the membranes studied here is about 200 μm. Both glass and conventional carbon fibres are continuous and have diameters of several microns. Such fibres can be chopped to a minimum length of about 200 μm and are thus unsuitable to reinforce the current membranes.

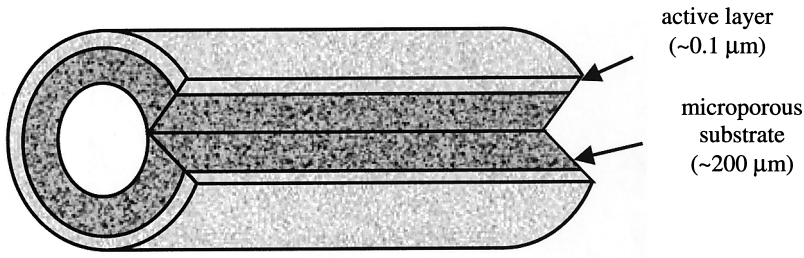

Figure 1. Typical morphology of an asymmetric hollow fibre membrane

Vapour-grown carbon fibre is a new class of material, which is different from other types of carbon fibre in its method of production, its unique physical characteristics and the prospect of low-cost fabrication [2]. VGCF is similar to fullerene tubes in the nano-scale domain of initial formation and in the highly graphitic structure of the initial fibril. Processing conditions and treatments affect their properties greatly.

Table 1. Physical properties of VGCF [3].

Fibre Diameter/Length	0.1/100 μm to 10/10000 μm
Tensile Strength	2.7 to 7.0 GPa
Tensile Modulus	400 to 600 GPa
Strain at Break	0.5 to 1.5 %
Density	1.8 to 2.1 g/cm^3
Electrical Resistivity	$1 \cdot 10^5$ to $2 \cdot 10^6$ S/m
Thermal Conductivity	20 to 1950 W/(m·K)

Table 1 shows ranges of physical properties achieved for VGCF. Nowadays VGCF is commercially available and there is the perception that it could allow the development of a new generation of advanced composite materials with unique combinations of mechanical, electrical, thermal and other properties. In particular, it has been shown that due to the sub-micron diameters and moderate lengths, these carbon fibres can easily be incorporated into polymer fibres [4]. Thus, VGCF with sub-micron diameter and length below 100 μm are considered as the most appropriate filler for mechanical reinforcement of polysulfone hollow fibre membranes.

In the present study, we offer preliminary results of a feasibility study on the processing of polysulfone hollow fibre membranes reinforced with sub-micron VGCF. The main purpose was to produce mechanically enhanced membranes, robust enough for real industrial applications.

Experimental

Polysulfone (Amoco Chemicals, Udel P1700, M_w=35 400) was used in this work. The VGCF were supplied by Applied Science Inc. (USA). Their average diameter was about 200 nm and the length was in the range of 5 μm to 60 μm. An optimised four component dope comprising polysulfone (22% (w/w)), N,N dimethylacetamide (31.8% (w/w)), tetrahydrofuran (31.8% (w/w)), ethanol (14.4% (w/w)) was used to spin the unfilled membranes [1]. Composite spinning solutions comprising this standard dope and, respectively, 0.6, 1.4, and 2.8 vol. % of VGCF with respect to the amount of polysulfone were prepared for the study. To aid their distribution, the VGCF were pre-dispersed in THF (about 10% of the THF required for the dope was used). The dispersion of VGCF was mechanically stirred at room temperature for 30 min and then placed in an ultrasonic bath for another 30 min to break down pellets of loosely aggregated curved filaments (the state in which the VGCF were obtained from the

manufacturer). After that, the dispersion was poured into the vessel with the rest of the dope components and stirred vigorously for 30 min. Before spinning, the composite dopes were passed through a 230 μm filter (stainless steel gasket, mesh) to remove any remaining large aggregates of carbon fibres. The three filled dope compositions, together with unfilled standard dope, were then spun at the same conditions using the forced convection dry jet/wet technique [1].

The gas permeability of the membranes was evaluated by fixing a fibre module into a pressure chamber, pressurising and then measuring the resulting gas transmission rate. The hollow fibres for this test were coated with a highly permeable elastomeric silicone polymer [1] to heal any surface pinholes or imperfections, which diminish gas separation performance of the membranes. Two pairs of test gases were used in this work: oxygen – nitrogen and carbon dioxide – methane. The pressure difference Δp across the membrane modules in the tests was 5 bar. Permeability P is given by:

$$P = \frac{Q}{A\,\Delta p}, \tag{1}$$

where Q is flow rate, A is membrane surface area. Membrane selectivity Ω with respect to any two gases, i and j, is the ratio of permeabilities:

$$\Omega^{i}_{j} = \frac{P_i}{P_j} \tag{2}$$

Tensile properties of the samples were measured using an Instron 1122 tensile testing machine. A sample gauge length of 50 mm and a cross-head speed of 10 mm/min were used throughout. Dynamic modulus measurements were performed at 10 Hz using a Rheovibron instrument. All mechanical tests were carried out at room temperature.

To study membrane morphology hollow fibre specimens were cut using a fresh razor blade and mounted on sample stubs. These were then sputter coated with palladium before being viewed with a scanning electron microscope (SEM).

Results and discussion

The levels of VGCF studied here did not adversely affect the spinnability of the dope. Although the samples for this study were manufactured at the conditions that were optimised in previous trials with the standard dope to achieve the best selectivity characteristics [5], it was found that stable spinning is possible with the composite dopes over a range of extrusion rates, stretch ratios and nitrogen flow rates.

Table 2 shows the tensile properties of the membranes. While tensile strength was found to be almost insensitive to VGCF content, tensile modulus and elongation at break show a trend typical for fibre reinforced thermoplastics: stiffness is increased and ductility is decreased upon VGCF content. The increase in tensile modulus indicates that these carbon fibres adhere well to polysulfone. Elongation at break falls from 47.7% for the unfilled sample to 22.2% for the sample filled with 2.8 vol.% of VGCF. However, even in the case of the composite with the highest filler concentration, sample failure occurs well above the yield point. This suggests that the VGCF inclusions are distributed evenly in matrix and that they do not produce weak points in the material at low extensions. The insensitivity of tensile strength to amount of inclusions suggests that the matrix morphology (for instance, size distribution of pores) plays the key role in the sample failure mechanism.

Table 2. Tensile properties of the composite membranes (static).

VGCF content (vol.%)	Tenacity (MPa)	Modulus (Mpa)	Strain at break (%)
0.0	22.6	815.3	47,7
0.6	22.2	876.9	42,7
1.4	22.7	944.2	36,1
2.8	23.1	1005.6	22,2

The mechanical response of the membranes at low deformations is more pertinent for gas separation applications than the tensile characteristics at break. The dynamic modulus values display the same trend as the static moduli obtained from the tensile tests (Fig. 2). However, the mechanical reinforcement effect derived from the dynamic measurements is greater. A 29% increase in dynamic modulus (over unfilled membranes) was found in the composite with the highest VGCF content, in comparison to 23% for the static tensile modulus. Dynamic modulus measurements are performed in the linear elastic region of deformation and hence the influence of relaxation processes in the polymer and also possibly in the interface regions has been eliminated. Thus, the dynamic modulus can be considered as more a reliable characteristic concerning this particular application.

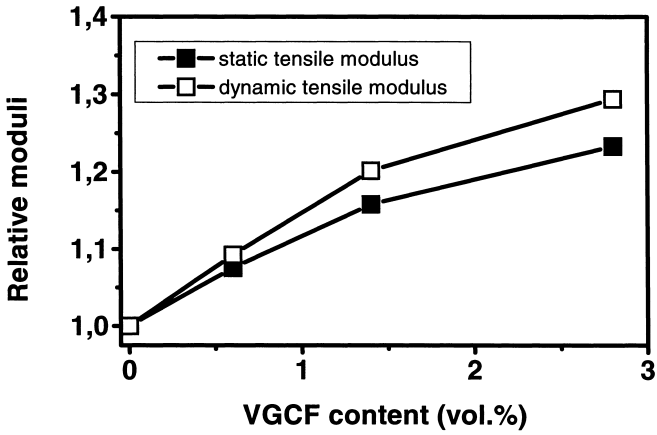

Figure 2. Static and dynamic moduli versus VGCF content

Table 3 shows a rise in permeability for all gases as VGCF content is increased. The lowering of selectivity suggests an increase in the surface porosity (amount of imperfections in membrane surface) as VGCF is introduced. However, it is striking that even at the highest VGCF content, the membranes still have a selectivity of about one third of the recognised intrinsic value for polysulfone for both gas pairs [6].

Table 3. Gas permeation properties.

VGCF content (vol.%)	P_{O_2}	P_{N_2}	$\Omega^{O_2}_{N_2}$	P_{CO_2}	P_{CH_4}	$\Omega^{CO_2}_{CH_4}$
0.0	10.10	1.50	7.46	58.20	1.54	40.10
1.4	14.08	3.18	4.43	75.73	4.23	17.89
2.8	16.93	7.48	2.26	67.64	9.79	6.91

Permeability or pressure-normalised flux x 10^6 (cm^3 (STP)/(s cm^2 cm Hg), measured at 25°C and a pressure differential of 5 bar.

SEM photographs show the general asymmetric structure of the membranes (Fig. 3). No substantial distinction in morphology was detected between the composite and unfilled membranes. All membranes have relatively dense wall regions and large voids in the middle where the two coagulation fronts meet each other during phase inversion.

The gas permeation performance of the hollow fibres is determined by the structure and quality of the active layer at the outer surface of the membrane. The active layer is too thin to be detected with SEM and its thickness can only be estimated from gas transmission modelling [7]. However, some useful information can be derived from observations of the outer surface of the membranes. The unfilled membranes (Fig. 4a) have relatively few surface defects, which can be sealed easily by the silicone coating. However, in the composite hollow fibres (Figs. 4b, c), some of the carbon fibres can be seen protruding from the membrane surface. They create extra damage to the active layer resulting in an increase in membrane permeability and a decrease in selectivity. The results of the gas permeation tests may also suggest that the carbon fibre sections sitting proud of the membrane surface were not completely covered with silicone coating.

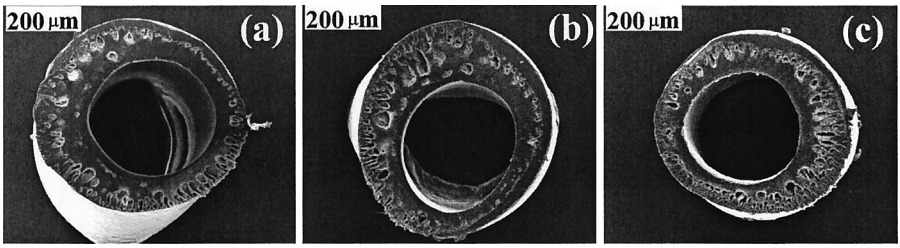

Figure 3. Cross-section of polysulfone hollow fibres filled with various content of VGCF: (a) 0 vol.%, (b) 1.4 vol.%, (c) 2.8 vol.%.

The images of the surface of the composite membranes provide more evidence of strong interfaces between the filler and the polysulfone matrix and also provide evidence of an even distribution of carbon fibres in the matrix. As it can be seen in Figure 4, that there are no voids adjacent to the carbon fibres protruding from the membrane skin. The SEM photograph (Fig. 4c) also shows that there is a strong preferential orientation of VGCF in the extrusion direction (along the diagonal of the photograph).

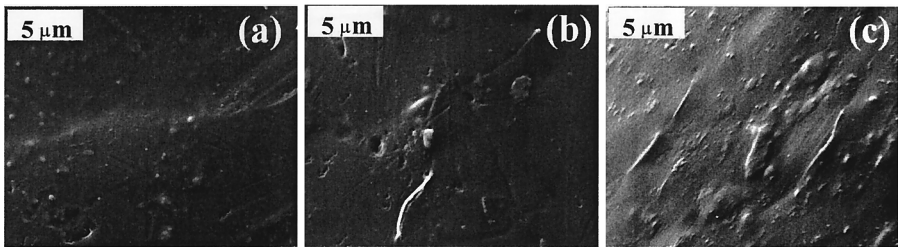

Figure 4. Outer surface of polysulfone hollow fibre membranes filled with various content of VGCF: (a) 0 vol.%, (b) 1.4 vol.%, (c) 2.8 vol.%

The detrimental effects of VGCF on membrane selectivity experienced in this study could be overcome by a more close consideration of composite fibre processing. First of all, the VGCF used in this work have a very broad length distribution. It can be seen in Figure 4b, c that only large VGCF disturb the membrane surface. Therefore, using smaller VGCF with a narrow length distribution should be considered as a way to reduce surface damage. Secondly, the requirements of the coating material may be different for composite membranes compared to unfilled membranes. The thickness of the silicone coating may be insufficient to cover completely the sections of the carbon fibres proud of the surface. Coating with a more concentrated silicone polymer solution could be another means to improve the selectivity of composite membranes. Finally, the amount of free solvent in the composite dope may not correspond to that in the standard dope due to absorption into the carbon fibres. This reduction in effective solvent concentration in the dope may change the conditions of the active layer formation. This probable effect should be investigated in future studies.

Conclusions

1) Polysulfone gas separation hollow fibre membranes filled with up to 2.8 vol. % of VGCF can be produced using forced convection dry jet/wet spinning.
2) Using VGCF with sub-micron diameter as a filler enhanced the mechanical performance of polysulfone hollow fibre membranes. A 29 % increase in tensile stiffness was achieved at the highest VGCF content of 2.8 vol.% studied in this work.
3) The addition of VGCF leads to a rise in permeability and a decrease in selectivity of polysulfone membranes. This is due to the protrusion of sections of the larger carbon fibres from the membrane outer skin.

4) Further work to prevent formation of defects in the active layer and hence enhance the selectivity of the composite membranes would lead to highly robust and productive gas separation membranes.

References

[1] A. F. Ismail, I. R. Dunkin, S. L. Gallivan, S. J. Shilton, *Polymer* **40**, 6499 (1999)
[2] M. L. Lake, *in Proceedings of NATO ASI Workshop "Carbon filaments and nanotubes",* Budapest, June 19-30, 2000, Chapter X
[3] Pyrograph III®, *Technical Bulletin, Applied Sciences*, Inc., Cedarville, Ohio, (1998)
[4] C. A. Bernardo, S. A. Gordeyev, J. A. Ferreira, *in Proceedings of NATO ASI Workshop* "Carbon filaments and nanotubes", Budapest, June 19-30, 2000, Chapter XIV
[5] I. D. Sharpe, A. F. Ismail, S. J. Shilton, *Separation and Purification Technology*, **17**, 101 (1999)
[6] I. Pinnau, W. J. Koros, *J. Appl. Polym. Sci.,* **43**, 1491 (1991); R. T. Chern, W. J. Koros, H. B. Hopfenberg, V. T. Stannett, in "Materials Science of Synthetic Membranes", D. R. Lloyd (Ed.), *A.C.S. Symp. Ser.,* 25-46, (1985)
[7] S. J. Shilton, G. Bell, J. Ferguson, *Polymer*, **37**, 485 (1996)