

Rheological evaluation of the influence of polymer concentration and molar mass distribution on the formation and performance of asymmetric gas separation membranes prepared by dry phase inversion

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Abstract

Asymmetric gas separation membranes were prepared by the dry-casting technique from PEEKWC, a modified amorphous glassy poly(ether ether ketone). The phase inversion process and membrane performance were correlated to the properties of the polymer and the casting solution (molar mass, polymer concentration, solution rheology and thermodynamics). It was found that a broad molar mass distribution of the polymer in the casting solution is most favourable for the formation of a highly selective membrane with a dense skin and a porous sub-layer. Thus, membranes with an effective skin thickness of less than 1 μm were obtained, exhibiting a maximum O_2/N_2 selectivity of 7.2 and a CO_2/CH_4 selectivity of 39, both significantly higher than in a corresponding thick dense PEEKWC membrane and also comparable to or higher than that of the most commonly used polymers for gas separation membranes. The CO_2 and O_2 permeance were up to 9.5×10^{-3} and $1.8 \times 10^{-3} \text{ m}^3/(\text{m}^2 \text{ h bar})$ (3.5 and 0.67 GPU), respectively.

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1. Introduction

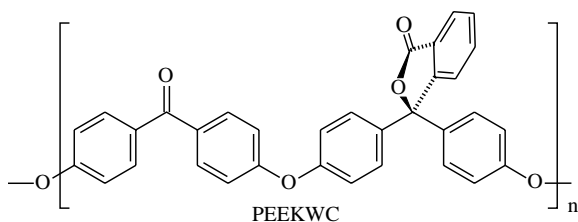
Polymeric membrane formation is a complex process which depends on a great variety of parameters. In the dry-wet phase inversion technique, the most common technique for the preparation of flat membranes, many different factors such as the type and concentration of polymer used, the type of solvent, nonsolvent and additives used in the casting solution and/or coagulation bath, the casting temperature, and for instance the interval between casting and coagulation determine the membrane properties. These factors determine whether the membrane will become dense or porous, symmetric or asymmetric, whether it will have a dense or porous skin and macrovoids or not, and whether it will have a finger-like, sponge-like, cellular or particulate morphology

[1–3]. Under different preparation conditions the same polymer may give membranes suitable for different types of separation processes, ranging from microfiltration, ultrafiltration to gas separation, depending on the particular morphology obtained.

In our lab we have studied the membrane forming properties of a glassy poly(ether ether ketone), modified with a cardo group in its backbone (PEEKWC, Scheme 1). The particular structure of PEEKWC makes this polymer, in contrast to the normal PEEK, readily soluble in various common organic solvents at room temperature. It also has good thermal and mechanical properties and is therefore suitable for use as a membrane material [4,5]. This polymer has previously been studied for the preparation of flat [5–7] and hollow fibre membranes [8,9] by wet phase inversion, yielding porous membranes in most cases. Dense PEEKWC is also suitable for gas separation [10,11], and the reported O_2/N_2 selectivity of about 6, and the CO_2/CH_4 selectivity of 33 locate this polymer [5,12–14] above the average in the famous Robeson plot [15].

Most of the polymers commonly used for gas separation membranes are mainly soluble in nonvolatile solvents such as

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Scheme 1. Structure of the PEEKWC repeating unit.

N,N-dimethylacetamide (DMA), *N,N*-dimethylformamide (DMF), dimethylsulfoxide (DMSO) and *N*-methylpyrrolidone (NMP), and membrane preparation methods usually require a wet coagulation step to remove the solvent. In contrast, PEEKWC is also soluble in highly volatile solvents like chloroform, dichloromethane and tetrahydrofuran, enabling film formation by solvent evaporation under mild conditions [7,10,16,17]. Solvent evaporation usually gives relatively thick dense membranes which can be useful for accurate determination of the gas diffusion and solubility coefficients by time lag and/or sorption measurements, but such films are of relatively little practical importance as actual membranes because of their low permeance.

Recently we have presented the preparation of asymmetric PEEKWC membranes with a thin dense skin by the dry phase inversion technique [16,18]. In this method phase inversion is induced by evaporation of the solvent from a ternary mixture of polymer, volatile solvent and nonvolatile nonsolvent and no coagulation bath is required to obtain the asymmetric morphology [3]. It was found that with PEEKWC, using chloroform as the solvent and a series of alcohols as the nonsolvent, the boiling point of the solvent rather than its polarity determines the success of the dry phase inversion technique [16]. In this study it was shown that a less polar and high-boiling nonsolvent gives membranes with a more open porous sublayer and a thinner dense skin than a polar low-boiling nonsolvent. Furthermore, the overall thickness and porosity of the sublayer increases and the skin thickness decreases with increasing nonsolvent concentration in the casting solution, which has its maximum limit at the position of the binodal demixing curve. Besides the casting solution composition, several external parameters determine the membrane formation process. The casting and evaporation temperature acts on the thermodynamics of the phase inversion process through the position of the binodal demixing curve, and on the kinetics of the process through the evaporation rate of the solvent, through the diffusion rate of all species, and through the pore nucleation and growth rate. For the PEEKWC/chloroform/butanol mixture it was found that higher temperatures result in a thicker dense skin [18]. Forced air circulation above the nascent membrane has the same effect, increasing the solvent evaporation rate and reducing the relative pore nucleation and growth rate.

Remarkably the effect of the molar mass distribution (MMD) on the membrane formation and membrane properties has received little attention in the literature, in spite of

its strong influence on the properties of the polymer solution. To the best of our knowledge the influence of the MMD has never been studied in the dry-casting process and only few times in the wet-casting or the thermally induced phase separation (TIPS) process, usually in relation to the membrane formation and membrane morphology. In the dry-wet casting of cellulose acetate membranes, a fractionated sample with low molar mass gives denser morphology with courser and less interconnected pores than a sample with high molar mass [19]. Exactly the opposite results were observed by Cheng et al. for polyurethane (PU) membranes prepared by dry-wet casting from a solution in DMF [20]. A high molar mass PU gave a completely dense membrane, both in water and in octanol as the coagulation bath. A low molar mass sample gave a cellular morphology upon coagulation in water and a particulate morphology upon coagulation in octanol. For the PU membranes the limitation of the solvent/nonsolvent exchange at higher molar mass was given as the main reason for the formation of the dense membranes, whereas differences in pore growth kinetics were held responsible for the influence of molar mass on the morphology of the cellulose acetate membranes. In TIPS the morphology was found to change from a cellular structure at low molar mass of the polymer to a sponge-like structure with small, highly interconnected pores at high molar mass [21]. Differences were mainly caused by a strong shift in the cloud point curve and to a faster liquid–liquid phase separation rate; the crystallization temperature remained nearly unaffected by the molar mass. If the differences in molar mass concern the pore forming polymer additive instead of the membrane forming polymer, the effect depends on different factors [22]. If the pore forming polymer has a strong influence on the overall solution viscosity, then for kinetic reasons a high molar mass sample is likely to reduce macrovoid formation. If, on the other hand, the pore forming polymer does not strongly modify the solution viscosity, then its effect as a nonsolvent may dominate and it may promote macrovoid formation. With respect to the final membrane properties, an increase in the molar mass improved the mechanical resistance of a dense chitosan reverse osmosis membrane [23], and it strongly reduced swelling of the dense skin by CO₂ in an asymmetric polyimide gas separation membrane [24].

In the present work we investigated how the MMD and the polymer concentration in the casting solution influenced the dry-casting process and the membrane morphology, and how this could be related to the rheological behaviour of the casting solution. The importance of the polymer solution rheology is evident for continuous membrane preparation processes such as hollow fibre spinning, where flow-induced orientation may be frozen in during the coagulation step [25,26]. In the present work we found that the morphology can be correlated with the MMD and the casting solution rheology even for flat membranes formation through dry-casting, where flow-induced effects are negligible. The aim is to optimize the membrane selectivity and maximize the gas flux, minimizing the skin thickness.

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