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Preparation of membranes with polysulfone/polycaprolactone blends using a high pressure cell specially designed for a CO_2-assisted phase inversion

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Abstract

Herein we report the preparation of polysulfone/polycaprolactone (PS/PCL) blend membranes using a CO_2-assisted phase inversion method. Membranes containing from 0 to 50 wt.% of PCL were prepared and analysed in terms of morphology, miscibility, hydrophilicity, transport properties and mechanical performance. Membrane porous structures were characterised by scanning electron microscopy (SEM), showing that significant changes in the morphological characteristics were obtained upon the addition of PCL. The water flux measurements confirmed higher porosity and permeability for membranes with higher PCL weight ratio but contact angles indicated that the hydrophobic nature of the surfaces was increased. Differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA) experiments showed that PCL addition increased the pores non-homogeneity, improved the damping properties of the membranes and decreased the elastic behaviour.

Keywords: Membrane formation; Supercritical CO_2; Phase inversion; Polysulfone; Polycaprolactone; Porous material

1. Introduction

The majority of porous flat membranes are prepared by the wet-phase inversion method in which a homogeneous polymer solution (polymer plus solvent) is cast on a suitable support and immersed in a coagulation bath containing a non-solvent [1].

Unfortunately many organic solvents used in membrane preparation are volatile, flammable and may pose a risk to health and to environment. In addition to not being environmentally benign, the solvent contaminates the porous material and often needs to be removed by intensive post treatment processes. For medical and pharmaceutical applications, totally solvent free membrane materials are required. Alternative approaches are being developed, and one with growing areas of application is the use of supercritical fluids, of which the most common is carbon dioxide (CO_2) [2].

It has been well established that the properties of the membranes prepared using a CO_2-assisted phase inversion method can be modified by changing the conditions of pressure, temperature, composition of the casting solution, depressurization rate, etc. [2–7]. In this work, we have developed a new strategy to manipulate the properties of the membranes combining two techniques – foaming with a blowing agent and membrane preparation with polymer blends, which opens a new dimension in the control of membranes morphology and properties [8].

Polymer foaming using environmentally friendly physical blowing agents in their supercritical or nonsupercritical state has become of significant interest in the past decades [9] especially for membrane preparation [10]. In this process the samples are saturated with supercritical CO_2 ($scCO_2$) reducing the glass transition temperature (T_g) and/or the melting temperature (T_m) of the mixture, liquefying the polymer. Upon depressurization the CO_2 rapidly expands, causing voids and precipitation of the polymer matrix.

Polysulfone (PS) is a very important synthetic membrane material which displays excellent mechanical and thermal stability as well as good film-forming properties required for the

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preparation of membranes [11]. One of the major applications of this type of membranes is haemodialysis [12], were biocompatibility with human blood is an issue. Clinical and experimental studies have suggested that membrane biocompatibility may adversely affect the outcome of patients with acute renal failure requiring haemodialysis [13,14].

PCL is a biocompatible and biodegradable aliphatic polyester that is bioresorbable and non-toxic for living organisms. Because of its unique combination of biocompatibility, permeability, and biodegradability, PCL, has been widely applied in medicine as artificial skin, artificial bone, and containers for sustained drug release.

Herein we report the preparation of membranes with PS/PCL blends using a CO_2-assisted phase inversion method. The CO_2 capability to swell PCL, and decrease the T_m [15,16] was used to produce and control the porosity and the properties of the membranes. To the best of our knowledge this is the first attempt to combine CO_2 foaming ability with phase inversion process for membranes production with polymer blends.

The membranes produced were analysed in terms of morphology, hydrophilicity, transport properties and mechanical performance. Membrane hydrophilicity is an important parameter because it can significantly contribute to enhance blood compatibility and reduce fouling [11,12]. One of the primary factors enhancing the adsorption of the protein is hydrophobic interactions between membrane surfaces and protein molecules [17,18]. Information about the mechanical performance of membranes is important in many applications, where the systems are required to support mechanical loads. Dynamic mechanical analysis (DMA) is a popular technique that enables to decouple the elastic and viscous components of the viscoelastic properties of materials. In this work, DMA will be used to detect the influence of the PCL content in the viscoelastic features of the porous membranes.

2. Experimental

2.1. Materials

Polysulfone (molecular weight 67,000) and polycaprolactone (molecular weight 65,000) were obtained from Sigma–Aldrich in pellet form. Chloroform was also purchased from Sigma–Aldrich (purity ≥99.8%) and used without any further purification. Carbon dioxide was obtained from Air Liquide with 99.998% purity.

2.2. Membrane preparation

A detailed description of the apparatus and the experimental procedure can be found in our earlier publication [2]. In this work, a new high pressure cell, schematically represented in Fig. 1, was developed in order to increase membrane area and allow visual inspection of all production process.

This cell was fabricated in 316 stainless steel using standard machining techniques. In the core it has a porous structure that supports a bed of Raschig rings, which allows the homogeneous dispersion of CO_2 in the top of the casting solution. All the equipment was tested with pressures up to 30 MPa and no signs of failure were observed.

In a typical procedure, the casting solution, normally 15% (w/w) of polymer in chloroform is loaded into a teflon cap (with a diameter of 68 mm and 1 mm height) and placed inside

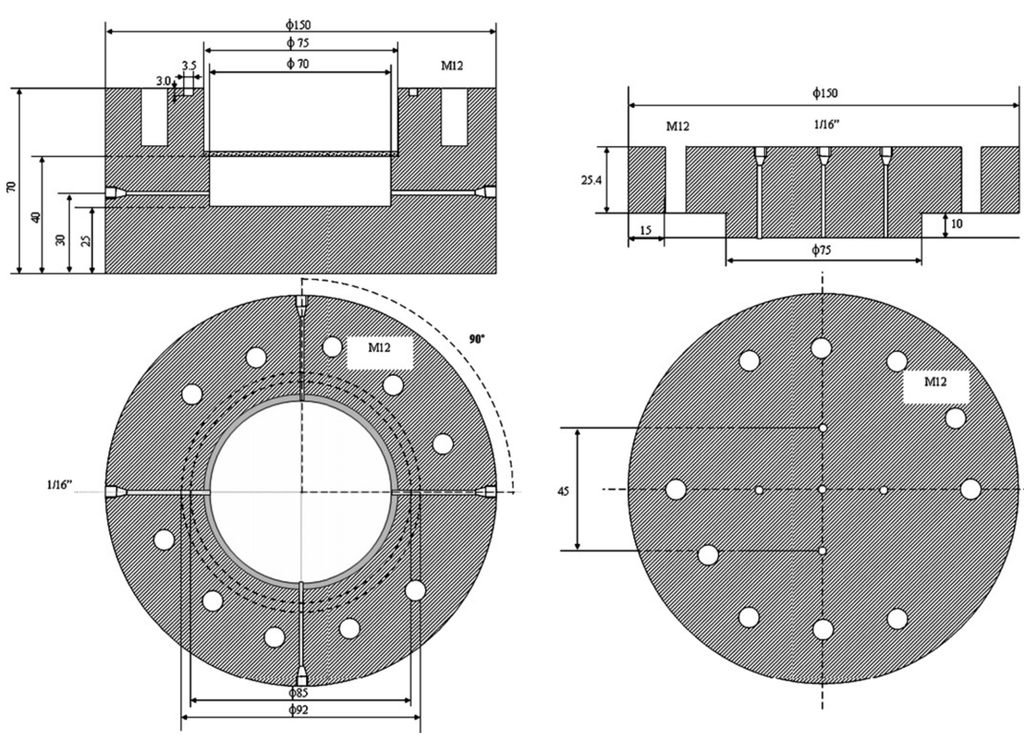

Fig. 1. Schematic representation of the new high pressure cell used for membrane preparation.