Microcellular open porous polyester membranes from thiol-ene polymerisations of high internal phase emulsions

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ABSTRACT

A high internal phase emulsion templating procedure is applied for the preparation of membranes which exhibit an open porous morphology with interconnected macro pores and open porous surfaces. A doctor blading procedure is used to cast the high internal phase emulsion onto glass substrates. Continuous phase of the emulsions contain divinyladipate and pentaerythritol tetraakis(3-mercaptopropionate) which are photopolymerised using the thiol-ene click chemistry to yield polyester type polymer network. The resulting polymer morphology features primary pores as a result of emulsion’s droplet phase, with diameters between 7 and 14 µm and interconnecting pores as a result of polymerisation shrinkage, with diameters between 1.6 and 2.2 µm. The highly porous and interconnected morphology mirrors the precursor emulsion structure with a dense packing of internal (aqueous) phase droplets. Doctor blades with different slit dimensions are used for casting thus producing membranes with different thicknesses while in all cases typical polyHIPE morphology is observed. Mechanical tests show a dependence of tensile modulus and tensile strength on the membrane thickness and also on pore size distribution.

Introduction

Porous polymeric membranes are an increasingly important class of materials due to the applications not only in the field of separation but also other fields like biomedical applications, energy storage, sensoric systems, etc. There are different methods available for the preparation of porous membranes and approaches used depend on the type of morphology and the size distribution of pores required.[1] While a large number of preparation procedures utilise casting of polymer solution and subsequent membrane formation resulting in membranes with isolated pores, a smaller number of synthetic processes are known producing through porous membranes with an interconnected cellular morphology. Among the methods for preparation of polymers with interconnected macroporous structure and pore sizes of micrometre scale, emulsion templating is increasingly popular due to the possibilities of preparation of polymeric material in various forms and due to relative ease of precursor emulsion preparation. To obtain material with connected pores, a high volume ratio of droplet to continuous phase is normally used, typically over 74 vol.%. [2] By polymerising the monomer containing continuous phase, a polyHIPE (poly High Internal Phase Emulsion) is produced which has a morphological structure of micrometre-sized pores (cavities), connected by a number of interconnecting channels. A large variety of porous polymers have been prepared in this way demonstrating the applicability of this method.[3,4] Typically, monomers are included in the continuous phase of the emulsion resulting in a monolithic material while polymers prepared from emulsion containing different monomers in both phases have also been demonstrated.[5,6] While it is possible to obtain various shapes and forms of a polyHIPE material simply using different moulds for HIP emulsions, preparation of thin films of polyHIPEs have so far proven more difficult. Zhao et al. have used a stamping method for the preparation of 4-vinylbenzyl chloride (VBC) based polyHIPE membranes.[7] Films with thicknesses from around 150 to 760 µm were obtained, however problems regarding uneven surface and pin holes were reported. We have introduced a doctor-blading approach for HIP emulsions with the use of glass substrates.[8] Apart from VBC-based membranes, styrene [9] and glycidyl methacrylate [10] based membranes were prepared with this method, controlling the thickness, porosity and morphology. Highly porous membranes with excellent mechanical properties and functionalisable, to yield ion-exchange groups for protein separation were prepared.

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of open-cell macroporous membranes made by the ring opening metathesis polymerisation (ROMP) of a mixture of norbornene and dicyclopentadiene, which can be used as a separator in lithium-ion batteries, has also been demonstrated.\[11\] On the other hand, Menner et al. reported on the preparation of flexible porous polyHIPE membranes by an emulsion printing technique.\[12\]

Free radical polymerisation, usually using thermal initiation, is the most common way of polymerising a HIP emulsion while the use of step growth polymerisation mechanism is less frequently used, mainly due to sensitivity of emulsions to higher temperatures.\[13–17\] Recently, thiol-ene chemistry has been demonstrated as a useful polymerisation procedure within high internal phase emulsion templating.\[18–20\] Furthermore, using photopolymerisation of a thiol/alkene based HIP emulsions macro structuring is possible by the use of additive manufacturing technologies.\[20,21\] Multifunctional thiols and alkenes with additional functionalities are available commercially facilitating the synthesis of polymers via the thiol-ene reactions. »Click« nature of the thiol-ene reaction also facilitates the HIP templating approach since no side products are formed during the reaction.

Herein we demonstrate the combination of a high internal phase emulsion templating with the doctor blading for emulsion casting onto a substrate and subsequent photopolymerisation of the continuous phase containing divinyladipate and pentaerythritol tetrakis(3-mercaptopropionate).

Experimental part

Materials

Pentaerythritol tetrakis(3-mercaptopropionate) (tetrathiol, TT, Sigma Aldrich), divinyladipate (DVA, TCI Europe), toluene (TOL, Sigma Aldrich), Irgacure 819 (I819, BASF), calcium chloride (CaCl₂, Sigma Aldrich), poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) (Pluronic L-121, HLB = 1.5, Sigma Aldrich) and ethanol (Merck) were all used as received.

Preparation of emulsions and membranes

To organic phase, consisting of DVA and TT (with ratio of vinyl to thiol groups 1:1), initiator (Irgacure 819; 1 wt.% to monomer), surfactant Pluronic L-121 (15 vol.% to monomer), and toluene (50 vol.% to monomer) were added dropwise to the aqueous phase (1% solution of CaCl₂, 85 vol.% of total volume). The mixture was stirred with an overhead stirrer at 250 rpm during the addition of aqueous phase and for further 30 min after the addition of all aqueous phases. To prepare membranes, emulsions were transferred to a doctor blade (slit between 300 and 1000 μm) which was used to spread the HIP emulsion onto a polished glass substrate (180 x 200 x 10 mm). The spread of the emulsion was polymerised in a UV chamber (Intelliray 600, Uvitron) at 80% intensity for 140 s. After the polymerisation, the membrane was removed from the glass substrate by dipping the substrate with membrane into a vessel with deionised water which allowed easy removal from the glass substrate. The membrane was then washed with deionised water and ethanol by immersing it in the solvent for 24 h with periodical solvent exchange (10 times) and air dried. Resulting membranes are denoted as M300 to M1000, the number standing for the thickness of slit of doctor blade (in μm).

Mechanical testing

Tensile properties of prepared polyHIPE materials were measured using an Instron 5800 testing machine (Instron Limited, MA, USA) at a test speed of 5 mm min⁻¹. The measurement was performed at room temperature. The dumbbell specimens for tensile testing (type 5B according to the ISO 527 standard) were die-stamped from the polymerised materials. The reported values are averages obtained from at least five specimens.

SEM observation

Membranes were broken into sample size pieces (approx. ½ cm²) in liquid nitrogen and coated with Pd. The samples were observed with a scanning electron microscope (Philips XL-30) operated at a voltage of 15 kV.

The average diameters of cavities and interconnecting pores in the samples were determined from SEM image analysis, namely by averaging over 50 measurements taken from the images corrected with a correction factor 2/√3 to account for random cutting of the samples.

Structural characterisation

FTIR spectra were recorded on an IRAffinity-1 Fourier Transform Infrared Spectrophotometer (Shimadzu Corporation, Japan) spectrometer using ATR adapter.

Results and discussion

Membrane preparation and morphology

The efficiency of thiol-ene click polymerisation and the possibility for photoinitiation \[22\] makes it a very appropriate pathway for use in combination with emulsion templating. Using functional monomers, a polymer network
can be obtained, while altering the thiol to alkene ratio can result in different polymer structures. Using monomers with ester functionalities can result in the formation of degradable material. Furthermore, vinyl esters in comparison to acrylates exhibit lower cytotoxicity.[23]

Polymerisation of pentaerythritol tetrakis(3-mercaptopropionate) (TT) with DVA in the presence of a radical initiator and an equimolar ratio of vinyl to thiol groups will result in a polymer network (Figure 1). We have previously successfully used emulsion templating in order to prepare highly porous monolithic material from either DVA and TT [24] or DVA only.[25]

To prepare thin films of DVA/TT based polyHIPEs, simple casting of the emulsion (a part of the technique frequently used for the preparation of asymmetric membranes by phase separation) [26,27] was used (Figure 2). A doctor blade can be used to spread the emulsion over the supporting substrate if the emulsion viscosity is appropriate. An emulsion with a composition optimised for monolithic DVA/TT polyHIPEs was used.[24] It was initially found that for preparing thin films, the composition of emulsion used for the preparation of monoliths was not appropriate. A change in the surfactant system was therefore applied, using only polymeric surfactant (poly(ethylene glycol)/
poly(propylene glycol) (15 vol.% per organic phase). Higher surfactant concentrations resulted in slow polymerisation and consequentially emulsion phase separation for which the reason might be in the initiator being dispersed more in the surfactant semi-phase.

Observing the prepared membranes in cross-sections, (Figure 3) it can be seen that in all cases, typical polyHIPE morphology with primary pores (cavities in place of the droplets of internal phase), which are connected with a number of interconnecting pores is produced exhibiting cavities with diameters between 7 and 14 µm and interconnecting pores with diameters between 1.6 and 2.2 µm. As previously found,[8] the substrate for emulsion casting is important in terms of surface morphology. In our case, the casting of emulsions was done on a polished glass substrate and the use of such substrate yielded surface open morphology which is an important parameter considering possible applications of the membranes. Besides the cross section of prepared membranes, the surface was also examined by SEM (Figure 3). The images show the open cellular structure even on the surface of the membrane which was in contact with the glass substrate. The diameters of primary pores are similar to the ones observed in cross section of the membranes. It was found that the dimension of the blade slit does not have a significant effect on the morphological features, pore size and pore size distribution; all membranes have primary pores with diameters between 7 and 14 µm. Homogeneity of morphology (in terms of pore size distribution) is relatively high, as seen from pore size distribution graphs (Figure 4).

**Figure 3.** SEM of prepared membranes.
Mechanical properties

From results of testing the mechanical properties of individual samples summarised in Table 1, following conclusions can be drawn. First, the tensile modulus, which is a measure of stiffness, increases with increasing specimen thickness. Second, the ultimate tensile strength is comparable for all samples, but it tends to depend on the average cavity diameter (Table 2). Third, the deformability of the membranes (ultimate strain), is given by the pore diameter at the surface, i.e. by the average interconnecting pore diameter. From the performed tensile tests it is evident that the macroscopic tensile behaviour reflects both the cavity and interconnecting pore diameters as well as the specimen thickness. Before discussing the individual effects separately it has to be mentioned that the deformability of the polymer film is of significant importance when a specific usage requests the film to be folded or stretched. Produced sheets of membrane with the molar ratio between DVA and TT were 2:1 and the nominal porosity of 85%. The membranes were very flexible and it was possible to deform the thin films in both directions. In all cases, the thickness of obtained membranes correlated to the thickness of the slit of the doctor blade used (Table 2). The thickness of the membrane was lower than the slit of the doctor blade which can be attributed to the relatively high viscosity of the emulsion and thus the thickness of spread does not completely follow the slit during the doctor blading procedure.

The most sensitive to the specimen thickness is the value of modulus, i.e. a measure of stiffness. It increased with an increasing membrane thickness. It could be ascribed to the skin-core morphology of the materials. It seems that the material in the bulk (core) exhibits higher stiffness than the material in the skin (in the surface layer). When assuming that the thickness of the skin layer is the same in all the cases, the increase in the modulus with increasing thickness can be ascribed to increasing core-to-skin ratio.

All the samples exhibit sufficient ultimate strength, which slightly correlates with core diameter in the bulk. Thus, the samples with smaller cavity diameters show higher ultimate-strength values. On the other hand, the deformability as expressed with ultimate strain values, reflects the consequence of the cavity size and the interconnecting pore diameter, i.e. size of the pores in between individual cells. Thus, the thinnest sample with

| Sample ID | Modulus (kPa) | Ultimate strength (kPa) | Ultimate strain (%) |
|-----------|---------------|-------------------------|---------------------|
| M300      | 380 ± 75      | 320 ± 23                | 75 ± 5              |
| M600      | 560 ± 110     | 335 ± 90                | 100 ± 20            |
| M900      | 820 ± 35      | 360 ± 50                | 110 ± 20            |
| M1000     | 895 ± 90      | 286 ± 30                | 115 ± 35            |

Figure 4. Pore size distribution charts for membranes.

Figure 5. FTIR spectra of monomers and M300.

Chemical structure and polymerisation were monitored by FTIR (Figure 5). The disappearance of carbon double bonds in DVA (1648 and 857 cm⁻¹) and thiol groups (2580 cm⁻¹) is visible.
the largest cavities (cells) and the highest interconnecting pore diameter exhibits significantly lower ultimate strain value. Finally, it has to be mentioned, that all the prepared samples have sufficient mechanical properties for possible membrane applications.

In order to evaluate the hydrophilicity of the surface of prepared membranes, contact angle measurement by a water-drop method was performed. For all samples, water drop quickly spread on the surface suggesting a strong hydrophilic character of the membrane surfaces.

**Conclusion**

We have demonstrated that applying a combination of doctor blading and high internal phase emulsion templating results in thin films with open porous morphology which is also exhibited on the surface. Thiol-ene click chemistry was used for the fast preparation via photocopolymerisation and this is particularly advantageous in the case of emulsion templating for thin films as the emulsion structure is fixed quickly allowing the formation of open porous morphology. The membranes have thicknesses depending on the doctor blade used. Thiols and alkene used allow for degradation via ester linkages and give the membranes elasticity.

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**Disclosure statement**

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**Table 2. The film thickness and the diameter of pores in cross section of membranes.**

| Sample ID | Thickness (mm) | CDa (µm) | IDb (µm) |
|-----------|----------------|----------|----------|
| M300      | 0.151          | 13.6     | 2.2      |
| M600      | 0.439          | 9.7      | 1.7      |
| M900      | 0.689          | 7.2      | 1.6      |
| M1000     | 0.759          | 11.4     | 1.8      |

*a*Average cavity diameter.  
*b*Average interconnecting pore diameter.
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