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Polysulphone/montmorillonite nanocomposite membranes: Effect of clay addition and polysulphone molecular weight on the membrane properties

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ABSTRACT

Polysulphone (PSf)/sodium montmorillonite clay (MMT) nanocomposite membranes were prepared via a congruence of the wet-phase inversion and the solution dispersion techniques, and a thermodynamic study, as well as an investigation of its morphological properties, hydrophilicity and membrane performance, were performed with respect to the PSf molecular weight and MMT content. An increase in both of these parameters contributed to a dislocation of the binodal curve to lower non-solvent contents. Exposure to 80% relative humidity of water vapour prior to immersion produced cylindrical defects in the surface and closed-cell morphology, whereas the membranes prepared by immediate immersion exhibited dense surfaces. In addition, there was competition between the thermodynamics and kinetics of the membrane formation. As the MMT content and PSf molecular weight increased, the membrane porosity increased due to a delayed liquid–liquid phase. The contributions from the acid–base interactions improved in the membranes with a higher PSf molecular weight. The membranes prepared by exposure to 80% relative humidity of water vapour exhibited high permeability values due to defects, and the membranes prepared by immediate immersion exhibited reduced permeabilities as the PSf molecular weight and clay content increased. Finally, these membranes, which have higher clay contents and PSf molecular weight, exhibited higher rejection values and were more selective to solute passage.

1. Introduction

An increase in the hydrophilicity of PSf membranes is highly desirable to increase filtered water production and membrane lifetime by reducing fouling formation. This phenomenon results in the reduction of the permeate flux as the pores are blocked by the residue, which increases energy costs since higher pressure is required to force the passage of the liquid through the membrane. Hence, increasing hydrophilicity is a strategy to reduce adsorption of substances and initial adhesion of microorganisms, as membrane absorbs more water molecules than foulant molecules [1,2]. Several techniques, including membrane surface modification [3–5] and aromatic electrophilic substitution [6–8], have been reported in the literature and were intended to improve this property. However, both techniques enhance this property without any additional gain or result in a decrease in the properties of the final material, such as thermal resistance [9].

Because polymer–clay nanocomposite technology has demonstrated that several material properties can be enhanced [10,11] (e.g., an increase in thermal and chemical resistance by restricting the segmental movement of the polymer results from the strong interactions between the polymer chains and clay mineral platelets [12–16]), this technology has been chosen to produce high performance materials.

The most used clays in nanocomposite science are the smectitic clays, such as hectorite, montmorillonite (MMT), and synthetic mica. These clays are composed of layers composed of two silica tetrahedral sheets with a central alumina octahedral sheet. These silicate layers are bound by common oxygen atoms and are filled with exchangeable cations, such as sodium, magnesium, and calcium ions, as well as water molecules. The clay mineral galleries are continuous in the *x* and *y* axis and stacked one above the other in the *z* direction (Fig. 1) [17]. To increase membrane hydrophilicity, the addition of sodium montmorillonite, which is a hydrophilic clay [18], can be used to improve material properties as well as the properties of the final membrane [19].

With respect to membrane science, the addition of a fourth component in the ternary system composed of polymer/solvent/non-solvent as well as the change in the polymer molecular

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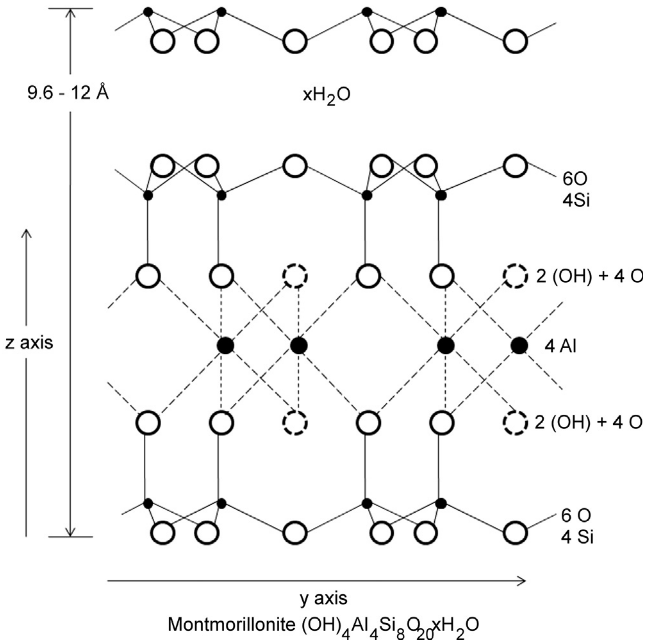

Fig. 1. Schematic representation of montmorillonite.

weight [20–22], which can improve pre-determined objectives, such as hydrophilicity, can significantly alter the membrane morphology, mechanical properties, lifetime and permeability [23–29]. There are a limited number of studies that report the use of clay as a fourth additive in the ternary system. Koh et al. [30] described the use of clay (Cloisite 15A, Cloisite 20A, Cloisite 30B, Cloisite Na^+) to prepare polyvinylidene fluoride–hexafluoropropylene (PVdF–HFP) nanocomposite membranes for application in lithium ion secondary batteries. With a retention time of 30 s, the clay addition promoted an increase in the porosity of membranes containing organo-modified clays. Another study involving the preparation of a PVdF/clay nanocomposite membrane has been reported. In this study, Nanomer 1.28 E natural Wyoming montmorillonite was used resulting in a substantially improved ionic conductivity with the addition of 2 wt% clay [31].

Five types of clay (i.e., raw MMT, Cloisite 15A, general MMT, hydrophobic MMT and hydrophilic MMT) were used to prepare polyetherimide (PEI) mixed matrix membranes for use in carbon dioxide removal. Due to high compatibility between the polymer matrix and the Cloisite 15A, a selectivity enhancement of 28% was obtained compared to that of neat PEI [32].

Ghamei et al. [33] prepared polyethersulphone nanocomposite membranes with organomodified montmorillonite. These membranes exhibited a thinner skin layer as well as a smaller surface pore size. With respect to their performances, the clay addition resulted in membranes with superior performance compared to that of a commercial NF membrane (NF45, Dow Filmtec).

The benefits of adding clay were also observed in polysulphone (PSf) nanocomposite membranes. In our previous studies [19,34], sodium montmorillonite was added to the PSf/NMP/water system, and the properties related to the formation of a nanocomposite structure as well as the mechanical and thermal properties were investigated with respect to the clay content and PSf molecular weight. The membranes with a lower clay content exhibited an exfoliated morphology whereas an increase in the clay content and PSf molecular weight decreased the number of pores and pore diameter and improved the thermal resistance because the weight loss decreased and the onset temperature of decomposition increased. An increase in the clay content up to 4.0 wt% and an increase in the PSf molecular weight enhanced the mechanical resistance.

Another study reported the preparation of polysulphone (PSf) nanocomposite membranes using organomodified montmorillonite, dimethyl acetamide as the solvent, water as the coagulant and PEG 400 as the pore forming additive in the casting solution. The addition of clay was responsible for the increase in the ratio of large pores in the skin layer as well as the increase in the porosity and permeability (from 0.095 $L\,m^{-2}\,s^{-1}$, 0 wt% clay to 0.106 $L\,m^{-2}\,s^{-1}$, 6 wt% clay) [35]. Ma et al. also prepared PSf nanocomposites membranes with the same system described above, except for the use of LiCl as a pore forming additive. An increase in the ratio of large pores in the skin layer and permeability were observed due to the addition of clay [36].

However, the studies related to polysulphone membranes until then carried out used organophilic clays, the water affinity of which is lower than that of hydrophilic clay. Hence, the novelty of this work consists in the use of hydrophilic clay, sodium montmorillonite, which, besides being able to improve thermal and mechanical properties as described previously [34], is able to increase membrane hydrophilicity. Furthermore, as far as the authors know, the researches that used clay as an additive in membrane preparation did not carry out a study related to the thermodynamics and kinetics of the resulting quaternary system and, therefore, membrane morphology understanding is more restricted. For this reason, the main aim of this research is an in-depth study of the thermokinetics so as to provide a complete understanding of the membrane properties.

Therefore, in this paper, the influence of the PSf molecular weight and clay content on the morphological properties, hydrophilicity and membrane performance is studied. The thermokinetic study allows us to investigate the membrane morphology with scanning electron microscopy and to evaluate the performance of these membranes based on changes in hydrophilicity by clay addition.

2. Experimental

2.1. Materials

PSf Udel® P-1700 and P-3500 were kindly supplied by Solvay Advanced Polymers. NMP was used as the solvent, and distilled water was the non-solvent. The fourth component added to the ternary PSf/NMP/water system was sodium montmorillonite from Wyoming (Sigma Co).

2.2. Suspension preparation

Suspensions consisting of 25 wt% PSf Udel® P-1700 and P-3500 and 0.0, 0.5, 1.0, 2.0, 3.0, 4.0 and 5.0 wt% MMT in NMP were prepared by mechanical stirring for 6 h according to a previously described protocol [19]. The viscosities of all of the dopes and suspensions were determined using a Brookfield viscosimeter (Model DV-III+CP 52) in a constant shear experiment at 25 °C. The samples were completely homogeneous and bubble-free during the rheological experiments. The extrapolation of shear forces measured for a zero shear rate provides the absolute viscosity.

2.3. Cloud point measurements

Cloud points were detected in triplicate by titration. For each MMT content (0.0, 2.0 and 5.0 wt%) and each PSf (P-1700 and P-3500), different suspensions were prepared where the PSf content was varied (1.0, 2.0, 3.0, 5.0, 7.0 and 10.0 wt%). Only low