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# Novel polysulfone–spray-dried silica composite membrane for water purification: Preparation, characterization and performance evaluation

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ABSTRACT

Development of composite membrane using organic polymer and inorganic nanoparticles is an emerging field of water purification process. Here we report the preparation, characterization and performance of a novel composite polymeric membrane prepared using composite of spray dried silica granule and polysulfone. We investigate the structure and performance of the membranes prepared using N-methyl-2-pyrrolidone or N,N-dimethyl formamide as solvent for the composite material. Such polymer-nanocomposite membrane shows significant enhancement of water permeability without sacrificing for the separation performance. In order to establish the structure–function correlation, we probed the mesoscopic structure of polymer casting solution and final membranes using small-angle scattering, atomic force microscopy and contact angle measurements. We put forward a plausible mechanism in support of the enhanced performance of the composite membranes.



## 1. Introduction

Ultrafiltration using polymeric membrane is an important separation process used nowadays in various industries such as, food, chemical, and nuclear [1–3]. The utilization of such membranes has increased manifold in last decade because of its use in separating colloidal and suspended matters from two major water sources, namely, surface water and sea water. The separation characteristic of such membrane is primarily controlled by its pore size and the physicochemical properties of its skin layer. At the same time, the physicochemical properties of the skin layer decide the fouling tendency [4] of the membrane. This includes the chemical nature of the surface, surface roughness, porosity as well as the void morphology of the support layer [5]. The structure and morphology of UF membranes are tailored [5,6] by modifying several parameters such as, composition of the casting solution and addition/incorporation of additives, thermodynamic environment during casting, relative humidity, etc. The efficiency of any filtration membrane is grossly characterized by its two functional characteristics namely, permeability and rejection of desired species. Often, the efficiency enhancement of one of the above characteristics results an efficiency reduction of the other characteristic.

In last few years, nanocomposite membranes [7] have attracted a great attention in the field of water purification because of their improved permeability without sacrificing much of separation capability and having better fouling resistance [8–18]. Various nanoparticles e.g. silica, silver, metal oxide, zeolites, etc., have been used as filler in the nanocomposite membranes. In some cases hollow microspheres have also been introduced [19]. In recent past, nanocomposite membranes have been studied using common polymers like polysulfone [6,8,20,21], polyvinylidene fluoride [22,23], cellulose acetate [24,25] and polyacrylonitrile [26] to tailor made various membrane properties. It has been found from such studies that the structural, mechanical, interfacial, and separation characteristics of ultimate nanocomposite membranes varies with the types of nanoparticles and their size, polymer, interaction of the nanoparticles with the components of the casting mixture, etc. Latest studies have indicated that the degree of dispersion of nano-materials in polymer matrix determined the mechanical strength of composites and membrane performances [26]. The interfacial interactions between the nano-filler and polymer matrix have been the key to fabricate nanocomposite membrane. It is worthy to mention that due to small size and large available surface area, the nanoparticles often agglomerate and this hinders [27] in achieving the enhanced property of the membranes.

Assembly of nano-colloids by solvent evaporation through spray-drying has been recognized [28–46] as fast and one step procedure to realizing intriguing structures consisting of correlated nanoparticles. In recent past, assembled granules with spherical as well as deformed doughnut like morphology comprising of assembled nanoparticles have been synthesized [35–37,39–41]. In brief, in spray-drying process, liquid colloidal droplets are passed through a hot zone where liquid evaporates. Attractive

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capillary force between the nanoparticles at some instant overcomes the repulsive Coulomb force and eventually interlocking of the particles takes place, which forms correlated nanostructured granules. One of the important structural aspects of such granules is that due to the inherent nature of the particle assembling process, the irregular fractal like agglomerates of the constituent nanoparticles are strictly avoided, which otherwise is ubiquitous for loose nanopowders.

Further, the interstice voids between the assembled nanoparticles can act as porous channels as far as the transport of fluid is concerned. Considering such structural novelty, spray-dried nanostructured silica granules have been incorporated in the polysulfone membranes through casting. In later part, it will be demonstrated that incorporation of such granules in polymeric ultrafiltration (UF) membranes indeed enhances significantly the pure water permeability of the membrane without sacrificing the separation characteristics.

In the present work, the effects of incorporation of such spray-dried nanostructured silica granules into Polysulfone membranes have been investigated for the first time to the best of our knowledge. Micro-structural investigations using small-angle scattering, atomic force microscopy have been performed to correlate the structure and the enhanced performance. It is worthy to mention that small-angle scattering is an important nondestructive tool to probe the morphological features and correlations in mesoscopic structures in condensed matter in a quantitative way. While such scattering technique [47] provides statistically averaged quantitative information, the microscopic techniques e.g. SEM, AFM provides direct evidence but over small zones. Thus scattering techniques and microscopic techniques are complementary in nature for obtaining detail structural information.

## 2. Materials and methods

### 2.1. Materials

Polysulfone (PSf) polymer is obtained from M/S. Solvay Specialities India Pvt. Ltd. N-methyl-2-pyrrolidone (NMP) and N,N-dimethyl formamide (DMF) of analytical grade is received from M/S. Sisco Research Lab. Pvt. Ltd., India and used as such without further purification. Polyethylene oxide with molecular weight of $10^5$ (PEO-100K) is obtained from M/s. Sigma–Aldrich. Silica dispersions (LUDOX® SM-30, Sigma–Aldrich) were obtained for spray-drying purpose.

### 2.2. Spray drying

Spray-dried granules were prepared[35] from 2 wt% aqueous silica dispersion (SM 30) using a spray-drier LABULTIMA LU228. Inlet temperature was fixed at 170 °C. Air compressed nebulizer was used to generate colloidal droplet for an atomizing pressure of 2 kg/cm$^2$. The feed rate was kept at 2 ml/min. Droplets were passed through a hot chamber. The diameter of the drying chamber was ~20 cm and its length was 60 cm. Aspiration rate was fixed at 50 m$^3$/h. Spray-dried powders were collected in cyclone separator. Spray dried powder granules were mixed well in polymer solution (PSF in DMF/NMP) before casting of the membranes.

### 2.3. Membrane preparation

Polymeric membranes have been prepared by dissolving 18 g PSf beads in 82 mL of solvent (either DMF or NMP) in airtight glass bottles. For preparation of mixed matrix membrane, 3.0 g of the Spray dried silica powder was dispersed in solvent followed by 18 g of polysulfone. The suspension was then stirred well for several hours until complete dissolution of polymer was achieved. This casting solution was spread with a knife-edge over a glass plate and subsequently it was immersed in laboratory de-ionized water for gelling. After 30 min, the polysulfone–nanocomposite mixed matrix films were removed from the water bath and were separated from the glass plate. The membrane was washed thoroughly with de-ionized water and stored in de-ionized water in a laboratory refrigerator at 6 °C before the use for experiments. The membrane thickness was 60 μm over 100 μm nonwoven polyester spun bonded fabric support (Viledon grade H1006 obtained from M/s. Freudenberg Nonwovens India Pvt. Ltd.).

### 2.4. Membrane characterization

Hydrophilicity of all the membranes is determined by measuring pure water contact angle using the sessile drop method on a standard drop shape analysis system (DSA100, KRüSS GmbH, Germany). At least eight equilibrium contact angles were obtained for each membrane, where the average of left and right contact angles defined the equilibrium contact angle. Average roughness of the membranes were measured using an atomic force microscope, AFM (NT-MDT-Multimode 3, Ireland), equipped with standard silicon nitride cantilever. Air-dried membrane samples were fixed on a specimen holder and 10 μm × 10 μm areas are scanned by tapping mode in air. The estimated tip radius was less than 10 nm. The cantilever length is 125 μm and force constant was about 5 Nm$^{-1}$. Roughness was quantified by the average roughness. Small-angle X-ray scattering (SAXS) measurements were performed on the dope and the cast membranes using a laboratory based SAXS instrument. Scattering intensity was recorded as a function of wave vector transfer $q$.

The performance of membranes has been evaluated in a cross-flow filtration system (active area of 20 sq. cm). These membranes have been initially pressurized with de-mineralized water at 50 psi until they have achieved constant flux. Subsequently, these pre-pressurized membranes have been used for ultrafiltration experiments at 30 psi. After collecting pure water permeability data, the feed has been changed to 200 mg/L PEO-100 K aqueous solution in order to evaluate the rejection of PEO-100 K. The separation of PEO-100 K has been determined by measuring total organic carbon of feed and permeates samples for all the membranes.

## 3. Results and discussion

### 3.1. Results

It has been seen that PSf gets dissolved well both in NMP and DMF. The dispersion remains slightly more transparent (Fig. 1) in case of NMP than DMF. The trend remains identical even after adding spray-dried silica granules in the polymer dispersion. Scanning electron micrograph (SEM) for the spray-dried granules comprising of silica nanoparticles is depicted [35] in Fig. 2. It is seen that the assembled granules are mostly spherical. SAXS measurements have been performed because of the fact that the scattering measurements are the best solution to probe the structure and correlation of assembled nanoparticles in such granules. The scattering intensity profiles of the spray-dried self-assembled silica nanostructured granules are shown in Fig. 3. It is worthy to mention that for such spray-dried granules, with two levels of mesoscopic structure, the scattering signal at higher $q$ is primarily dominated by the scattering from individual nanoparticles (smaller length scale) in the granules and the scattering signal at lower $q$ is primarily due to density fluctuation due to the existence of the overall granule (larger length scale). The detail analysis scheme for small-angle scattering data has been elaborated [35–37,39]