FUNCTIONALIZATION OF POLY (ETHER SULFONE) (PES) AND POLYSULFONE (PSF) MEMBRANE

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Abstract: Functionalized PolyEtherSulfone (PES) and PolySulfone(PSf) membranes exhibit superior properties, but their permeability and retention remain same to certain extent. Numerous graft polymerization techniques have been developed for the modification of PolyEtherSulfone (PES) and Poly(Sulfone) (PSf) membranes. Modification of ultrafiltration membranes through graft polymerization of some selected molecules has been used to increase membrane surface hydrophilicity as a means of decreasing fouling during filtration. Desired membrane properties, such as higher solute retention, higher permeability, and lower propensity to fouling, can be obtained while maintaining desired membrane rejection. The modifications increase membrane stability and make their regeneration easier, unlike cellulose membranes. Some known techniques like UV-assisted graft polymerization using certain monomers were reviewed and conclusions based on the techniques and their results were made. The results showed that functionalizing the membranes with suitable monomers or molecules improved their filtering properties significantly.

Keywords: Membrane, Functionalizing, Ultrafiltration, PES, PSf, UV-assisted graft polymerization

Introduction

Nowadays numerous techniques have been used to modify the filtration properties of polymer membranes. Membrane filtration has been considered a technically important separation process over the years. Several processes using membranes have been developed for many applications such as microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), reverse osmosis (RO), pervaporation (PV; using porous or non-porous membranes), membrane distillation (MD), and membrane contactor (MC). The surface functionalization of membranes has become a key point in membrane science and technology. It can enhance the performance of the existing membranes, i.e., by minimizing membrane fouling or by introducing novel functionalities.

A generally applicable research strategy for the introduction of functional groups at inert polymer membrane surface is the current area of interest among many scientists. In the last few years functionalization of polymer membranes has been valued as a vital tool to improve their properties. Functional groups like hydroxyl, ketone and carboxylic acid groups have been used to tailor the surface of membranes. These groups are generally used to improve chemical bonds between substrates and adhesives. Functionalization of the membrane surface is one of the efficacious techniques that can endow these materials with unique properties and transform them into valuable finished products.

Functionalization improves properties such as hydrophilicity,hydrophobicity, biocompatibility, anti-fouling, antibacterial properties etc. while keeping the core structure and some native properties of the membrane intact.

Case Studies and Discussion

Exhaustive research was conducted through which the enhancement of the surface properties of the membranes was observed. The following case studies are enumerated for analysing the intricacies of the same. Some case studies and their results are reviewed in chronological order.

I. J. Kilduff et al. (2000)[4] studied the modification of Poly(ether sulfone) and sulfonated poly(sulfone) nanofiltration membranes by UV irradiation and UV-assisted graft polymerization of N-vinyl-2-pyrrolidinone (NVP) in an attempt to mitigate fouling caused by naturally occurring organic compounds (NOM) found in surface waters.

The aim of functionalization is to lower contact angles, corresponding to a hydrophilic surface that will not promote the adhesion of hydrophobic or amphoteric materials, (Cellulosic membranes which have low contact angles (< 30 °, and sometimes < 20°), are less likely fouled by proteinaceous solutions). Hence, UV irradiation was used for grafting which had a significant effect on surface energy, lowering contact angles significantly.

II. B. Kaeselev et al. (2001)[5] conducted a research on Photoinduced grafting of ultrafiltration membranes: comparison of poly(ether sulfone) and poly(sulfone).

It consisted of UV-assisted graft polymerization of three hydrophilic monomers,N-vinyl-2pyrrolidinone (NVP), 2-acrylamidoglycolic acid monohydrate (AAG) and 2-acrylamido-2-methyl-1-propanesulfonic acid (AAP) on both poly(ether sulfone) (PES) and poly(sulfone) (PSf). These ultrafiltration (UF) membranes were modified using the dip method with 300 nm wavelength lamps. The concentration of monomer and irradiation energy supplied to the membranes was varied.

The main objective of this work was to synthesize modified membranes with filtration properties superior to that of the base membranes.

Best results were obtained at the highest monomer concentrations and lowest radiation energy. For best properties the degree of grafting required was unusually low. PES was found to be more sensitive to UV-assisted graft induced polymerization and needs lesser energy for grafting than PSf.

III. J.Y. Park et al. (2006)[6] studied about amphiphilic graft copolymers having polysulfone (PSf) backbones grafted with poly(ethylene glycol) (PEG) side chains which were synthesized via reaction of an alkoxide formed from PEG and a base (sodium hydride) with chloromethylated polysulfone. The reaction of poly(ethylene glycol) alkoxide with chloromethylated polysulfone is used for forming hydrophilic polysulfone membrane which remains water insoluble.

PolySulfone membranes grafted with polyethylene glycol formed a porous network-like surface structure with higher porosity, wettability and resistance to protein adsorption as compared to PSf membrane. PSf-g-PEG (PolySulfone membranes grafted with polyethylene glycol) modified membranes can be useful for hemodialysis, cell encapsulation etc.

IV. **Nanwen Li et al. (2012)**[12] conducted a research on anion exchange membrane (AEM) which were prepared from polysulfone (PSf) membrane by functionalization with tertiary amines via lithiation chemistry. The PSf membranes containing bis-(phenyldimethylamine) substituents were then quaternized to obtain bis(phenyltrimethylammonium) (PTMA) polymer with hydroxide-conductive properties.

The resulting modified membrane exhibited unusually low water swelling and methanol permeability but high hydroxide conductivity.

V. S.H. Choi et al.(2012)[2] conducted a research for the removal of endocrine disrupting chemicals (EDCs), such as di-(2-ethylhexyl) phthalate (DEHP), from potable water. Cyclodextrin (CD) which was prepared was used in polysulfone (PSf/CD) hollow fiber membranes. Cyclodextrin (CD) was modified with fatty acid chlorides to produce amphiphilic CDs. In the membrane formation process, the amphiphilic CDs migrated to the membrane surfaces.

It was visible from results that the DEHP removal efficiency of PSf/CD membrane increased considerably with the amount of CD. These results also show that PSf/CD membranes can be used in eco-protective water treatment system. Thus it could be inferred from the results that PSf/CD hollow fiber membranes can effectively remove DEHP from aqueous solutions and provide good water permeability.

Applications

An important application is the anion exchange membrane fuel cells (AEMFC), which has the ability to transcend the performance of proton exchange membrane fuel cells due to facile oxygen reduction kinetics and a number of catalyst choices [13].

Also, functionalised Polysulfone (PSf) is widely used material in membranes for applications like haemodialysis etc.

Polysulfone/poly(ethylene oxide) block copolymers, PSf-g-PEO, can be used to improve resistance to platelet adhesion. The adhesion properties can be enhanced by blending a sulfonated PEO acrylate diblock copolymer into PSf . PEO is a widely used biomaterial due to its excellent resistance to protein adsorption and biocompatibility.

Further benefits are that functionalization results in high performance membranes with adjusted interface characteristics and also gives rise to binding functional groups attached to the surface[14]. Retaining the desired native properties and pore structure are of importance. However, such modifications always changed the membrane formation process.

Photochemical surface functionalization of polymers has advantages like the reaction can be done under mild reaction conditions and low temperature. High selectivity can be made feasible by choosing specific reactive groups and certain excitation wavelengths. Lateral structures can also be produced by using UV excitation light.

Conclusion

Surface Modification (functionalization) of membranes by graft polymerization by chemical grafting, UV induced grafting and high energy radiation initiated grafting is currently the interest of many researchers. The modified membranes have more functions than just being selective barriers with high performance. Along with conventional grafting processes, the controlled living radical polymerization is gaining popularity among researchers since it is fast and polymers formed have regulated molecular weight and low polydispersity. This method can be used to create graft polymer chains with a well-defined structure. These membranes are capable of achieving controlled functions in varied applications. Hence, surface modification of membranes with controlled living graft polymerization will gain more and more importance in the future.

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