Review paper

Journal of High School Science

Polysulfones and their applications

Athipatla V

Submitted: April 11, 2023, Revised: version 1, June 8, 2023
Accepted: June 17, 2023

Abstract

Polysulfones are a group of high-performance thermoplastics with demonstrated utility in various industries such as medicine, pharmaceuticals, transportation, electronics, food and beverage, and water treatment. Polysulfones possess two primary forms in application: key structural components of various machines or thin membranes for filtration. Polysulfones are now integral to modern filtration housings and membranes for reverse osmosis, ultrafiltration and dialysis. Their inherent high bond dissociation energies make them resistant to hydrolytic attack in both acidic and basic environments, and at high temperatures. They are also biocompatible and have the capacity to adsorb endotoxins. Consequently, they are used in applications which call for constant exposure to water or harsh redox environments such as plumbing, implantable medical devices - including dialysis membranes, in steam autoclaves, to immobilize biosorbants and catalysts, and in waste water remediation. Their dielectric and insulating properties can be tuned to improve conversion of solar energy in perovskite solar cells, to increase current output in fuel cell proton exchange membranes at high temperatures and to increase the capacitance of supercapacitors. Their unique mechanical properties can be utilized in increasing and decreasing the crack resistance and propagation respectively in adhesive epoxy resins. Polyethersulfone blends with carbon or graphene nanosheets are more forgiving with regard to the trade off between gas selectivity and permeability, such that acceptable throughput may be obtained with high separation. For this reason, they are used in decarbonization technology, syngas composition optimization and separating hydrogen from hydrocarbons.

Keywords

Materials science, Polymers, Polysulfones, Polyethersulfone, Filter membranes, Water resources management, Thermoplastic, Dialysis membrane, Gas separation, Reverse osmosis

Vivek Athipatla, Carroll High School, 800 N White Chapel Blvd, Southlake, TX, 76092, USA. vivekathipatla@gmail.com

Introduction

Water is to the twenty-first century what oil was to the twentieth: the precious commodity that determines the wealth of nations (1). Over a billion people worldwide lack access to clean water, and as populations continue to grow, maintaining a clean and sustainable water supply is critical (2). Wastewater treatment and desalination are two primary water purification techniques to increase the available freshwater supply. As a result, there are over 58,000 wastewater treatment facilities (3) and 17,000 desalination facilities worldwide (4). The techniques and processes these facilities utilize rely on various polymer membranes to filter hazardous materials. While commodity plastics such as polystyrene and polyethylene are household names, these water treatment and desalination facilities rely on high-performance specialty plastics like polysulfones (5). Polysulfones are safe, energy-efficient and fulfill unmet needs in various industries, including those in water purification technologies. They play a central role in various applications from desalination techniques (6) to medicine (7), with potential for green energy harvesting (8). In this article, we review polysulfones and their uses and potential in both membrane and structural applications.

Discussion

Properties

Polysulfones are polymers composed of aryl and sulphonyl groups (9). They are commonly produced by polycondensation of the monomers, bisphenol A and dichlorodiphenyl sulfone (9), derived from natural gas and crude oil (10). The Diphenyl sulfonyl moiety imparts a high dissociation energy to chemical bonds leading to high-tensile properties and shielding from the effects of oxidizing agents (5). This chemical bond strength of polysulfones can be further enhanced physically by adding glass or carbon fibers (5). Polysulfones are classified as high-performance thermoplastics due to their ability to withstand temperatures above 150ºC, exhibiting relatively high glass transition temperatures (Tg) between 190ºC to 240ºC, and high heat deflection temperatures (HDT) (5). They are amorphous, semi-transparent, and possess low creep, electrical insulator properties, and self-extinguishing ability (5).

Polysulfones are highly resistant to most chemicals due to the diphenyl sulfonyl moiety, which offers chemical resistance by stability to oxidation since all electrons are shielded through resonance. However, outdoor exposure makes them susceptible to chemical degradation due to their aromatic ether backbone, although incorporating carbon, surface coating, or metalizing can mitigate such effects (11). They are also unsuitable for outdoor uses because of poor weathering and ultraviolet (UV) resistance. In addition, they are not resistant to low-polarity organic solvents (e.g., ketones and chlorinated hydrocarbons) and aromatic hydrocarbons.

Three primary variants of polysulfones are currently used: polysulfone (PSU), polyethersulfone (PES), and polyphenylene sulfone (PPSU). Their chemical structures differ in the functional groups between adjacent benzene rings (Figure 1). Though general properties are similar among all these high-performance thermoplastics, their differences manifest in unique ways, endowing one variant more utility over the others depending on the application.

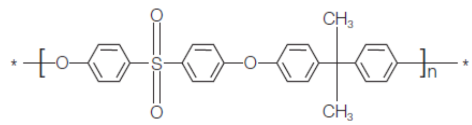
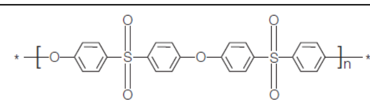
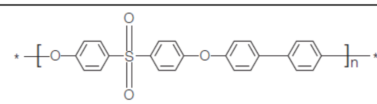
PSU	
PES	
PPSU	

Figure 1: Chemical structures of polysulfones (12).

PSU was the first to be developed and commercialized. It has the lowest density of all the polysulfones. Plastic resins are sold by unit weight but typically used by volume. Hence, PSU has the lowest price among all polysulfones. Comparing commercial variants, PSU offers the highest optical clarity and transparency (over 85% light transmittance) and absorbs the lowest amount of water among all polysulfones (absorbs less than 0.6% moisture by weight) (12-14). Therefore, PSU is preferred for implantable medical devices and filter housings.

PES possesses the highest concentration of sulfone moieties in the polymer's repeating unit. This polar moiety attracts water resulting in PES exhibiting the highest water absorption. PES is inherently flame resistant (oxygen index > 30), which can be further enhanced by adding flame-retardants. Structural differences lead PES to offer better chemical resistance, higher thermal capability, and improved mechanical properties than PSU (12-14). PES is preferred in the transportation industry due to these properties.

PPSU's biphenylene unit uniquely elevates its impact strength - its notched Izod is more than eight times greater than PSU or PES. PPSU has the highest HDT, over 30ºC greater when compared to PSU and 4ºC greater than PES. It also has superior chemical and hydrolytic resistance compared to PSU and PES. Hydrolytic stability is essential in plumbing applications where the plastic is in permanent contact with water. Because steam autoclaves are widely used to sterilize medical devices, resistance to steam sterilization is important as well. PPSU has steam autoclave resistance of over 1000 cycles when compared with 80-100 cycles for PSU and PES. PPSU also exhibits excellent resistance to chlorinated water at elevated temperatures. It is the most expensive polysulfone, limiting its use to where PSU and PES cannot satisfy requirements (12-14).

Membrane Technology

Polysulfones currently serve a prominent role in essential industries as both bulk structural components and membranes. Membrane applications of polysulfones are the fastest growing and poised to have significant potential to improve key aspects of human life, especially as a filter for medical applications and water treatment. In this section, we review filtration techniques that commonly utilize polysulfone membranes.

Microfiltration (MF) physically removes suspended solids from water by a membrane. The filters used in MF have a pore size of approximately 100 nm, physically preventing larger contaminants from passing through. As a result, bacteria and suspended solids are the only elements that can be removed through MF (15, 16). The dairy industry uses MF membranes for milk protein separation, fat, and microbial removal.

Ultrafiltration (UF) is an improvement upon MF in which slightly higher pressures and smaller pore sizes can block everything MF can. In addition, UF membranes also retain smaller contaminants and viruses. UF filters typically have a pore size of approximately 10 nm (15, 16). These are used in food and biopharmaceutical industries for enzyme concentration and removing endotoxins and pyrogens.

Nanofiltration (NF) membranes have a pore size of approximately 1 nm. They can typically remove 50% – 90% of monovalent ions such as chlorides or sodium. NF is often used to filter water with low amounts of total dissolved solids, remove organic matter, and soften water (15, 16).

Reverse Osmosis (RO) membranes are effectively non-porous and, therefore, exclude particles as well as many low molar mass species such as salt ions. RO systems have been successfully applied to desalinate saline groundwater, brackish waters, and seawater, as well as to remove inorganic contaminants such as radionuclides, nitrates, arsenic, and other contaminants (17). A cross-section of the RO membrane is shown in Figure 2 and has a pore size of approximately 0.1 nm. The relative pore sizes of different filtration membranes are shown in Figure 3.

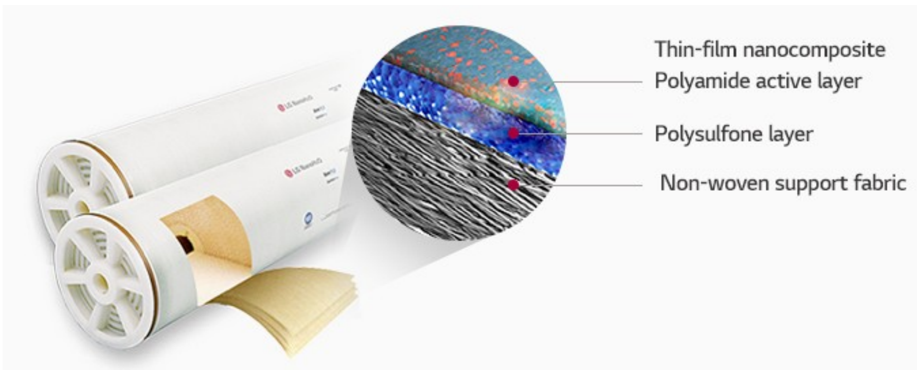


Figure 2. Cross-section of a Reverse Osmosis Thin Film Composite membrane (17).

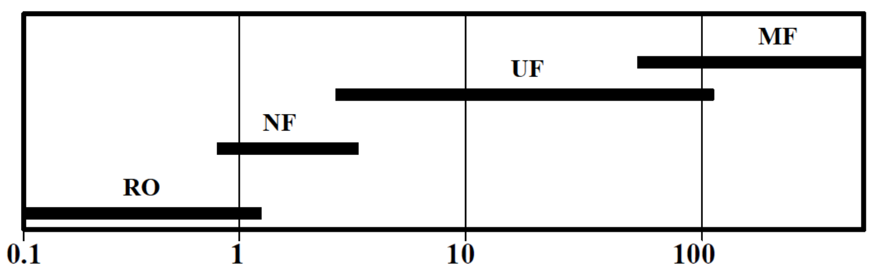


Figure 3. Pore diameters of filtration membranes (nm) (15).

Fouling is a limitation associated with the use of membrane technologies (Figure 4). Fouling occurs when contaminants collect on the surface or in the pores of a filtration membrane (18). Foulants restrict water flow through the membrane, resulting in consequences such as higher hydraulic resistance, greater energy consumption, and damage to the membrane and other system components. The hydrophobicity of polysulfones contributes to membrane fouling and is a significant disadvantage.

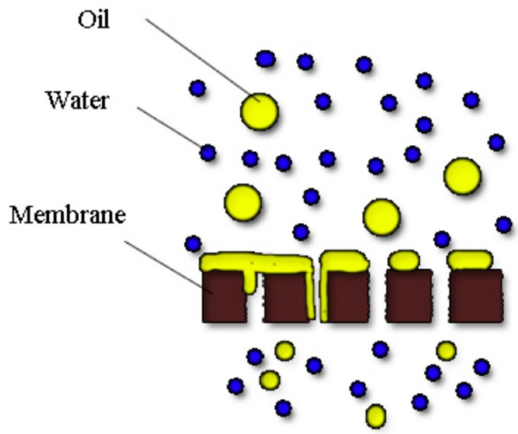


Figure 4. Simplified depiction of membrane fouling (19).

Achieving increased flow and reducing fouling has been an intense focus of research. Blended PSU/PES membranes enhanced antifouling property for separation of succinic acid from fermentation broth resulting in a flux recovery of 96% (20). Sulfonation of polysulfone with various agents at varying substitution degrees resulted in membranes with high flux quantities thus addressing the membrane fouling disadvantage of polysulfone membranes (21).

Applications

Polysulfones have many applications across several industries as both bulk structural components and thin membranes. However, polysulfones are used primarily in specialty applications due to their high raw materials and processing costs. They are often considered superior to polycarbonates, offering significantly better mechanical properties. At the same time, they are cheaper than other high-temperature engineering thermoplastics.

A major application of polysulfones is in the automotive industry. PES is utilized for its thermal and dimensional stability and oil resistance. It is a critical component of battery caps, carburetor or fuel injection parts and engine oil circulation systems. PSU and PES comprise parts of oil pumps, headlamp bezels, interior reflectors, and blade fuses (12-14). Due to their light weight compared to metals, polysulfones are increasingly being used in the design of aircraft interiors, comprising a major part of the honeycomb sandwich structures. Furthermore, they are an excellent choice for aircraft because they are fire retardant, a quality of utmost importance. Foams made of Ultrason® E (PES), patented by BASF, are approved for use in aircraft (22). Epoxy based composite materials are used to build aircraft exteriors and floors. Incorporation of polysulfones in epoxy resins is being studied to develop the next generation of composites. The phosphorus-containing polysulfone enhanced the thermal stability of epoxy resins optimizing flame retardancy while maintaining a high *Tg* (23).

In the electrical industry, PSU and PES comprise several critical components due to their excellent insulation properties, low creep resistance, and stable dielectric constant: coil formers, plug-and-socket connectors, injection molded printed circuit boards, circuit breaker components, and parts for contactors and relays. They also serve as transparent covers for signal lamps and switchboards, lamp bases and covers, heat shields, sensors, and battery seals (12). This utility extends to the construction industry, where polysulfones find usage in various electronic and mechanical components. They are also used in heating circulation pump rotors, thermostat components, hot-water meter components, and interior components for sanitary fittings where hydrolytic stability at high temperatures is necessary.

Polysulfones are utilized to enhance the mechanical and thermal properties of epoxy resins which are widely used in construction, machinery, aerospace, and other related fields (24). Epoxy resins are low cost adhesives and exhibit excellent bonding performance, easy processability, dimensional stability and superior thermal and chemical resistance. However, their high crosslinking density, large internal stress, and brittleness has limited their application in high-tech fields (24). The introduction of polysulfone (20 wt. %) into epoxy matrices significantly increases their crack resistance from 4 to 7 times and additional modification with an active diluent to reduce the viscosity of hybrid binders leads to a decrease in the resistance of matrices to crack propagation by 28–59% (25). Modifying epoxy resins with polysulfones not only enhances the overall toughness but also maximizes other important properties thus enhancing their potential in more sophisticated applications.

In the medical industry, polysulfones are extensively utilized as dialysis membranes. The first polysulfone membrane patent was issued in 1974 to Jack Bourganel (26). Since then, numerous modifications have been made to improve their selectivity and permeability. A US patent search returned nearly 50,000 results for polysulfone membranes. These membranes were first introduced for dialysis in 1984. Since then, they have replaced cellulose membranes because of their biocompatibility, ability to eliminate uremic toxins, promote solvent drag, and endotoxin adsorptive capacity. Polysulfones currently dominate the market possessing over 93% market share (71% PSU and 22% PES) (27). According to the 2021 report by the US Renal Data System, over half a million patients are on dialysis each year, demonstrating the value of these membranes (28). Filters for intravenous infusion sets also use PES membranes. Polysulfones are integral to chromatography and filtration membranes in pharmaceutical and biomedical laboratories because of their excellent film-forming properties and thermal and biological resistance (29). Use of PES membranes led to efficient amplification in both loop mediated isothermal amplification and thermophilic helicase dependent amplification compared to current paper-based diagnostics like cellulose chromatography paper providing optimal support for rapid molecular diagnostics for point of care applications (30). Polysulfone based membranes increased the separation of low-density lipoprotein from blood plasma to 75% and highlights their potential use in lowering cardiovascular disease risks (31). There also exist many uses for polysulfones in the medical industry beyond membrane applications. For example, PPSU is used to make sterilization trays for surgical and dental instruments, while heart valve sizers, outer shells of implantable ports, and transparent parts of anesthesia masks contain PSU (7).

Membrane technology is not restricted to medical applications and finds usage in the food industry where it is essential for food safety and quality. This has been applied to several production methods, including milk-solids separations in the dairy industry, juice clarification, and whey protein concentration due to good resistance to pH and temperature. Asymmetrical filter membranes are composed of a thin selective layer and a strong supportive layer. The supportive layer imparting mechanical strength to the filter membrane and assembly is usually made of polysulfone (32).

As previously mentioned, polysulfones play a critical role in water purification and desalination due to their desired properties, such as stability, high mechanical strength, and ease of modification (6, 33). Polysulfone membranes have been used extensively in water technologies due to their excellent combination of water flux (the rate at which water permeates a membrane) and solute rejection. Membrane-based desalination dominates the installed desalination capacity – in 2017 accounted for 95.6% of annual contracted capacity (34). PES is being studied to immobilize biosorbents. Biosorbent PES achieved a high removal rate of Pb^{2+} from water, reaching 98%, compared to neat PES, confirming that the biosorbent is responsible for the adsorption process. Dead bacterial cells were immobilized on a PES giving it the characteristics of a novel adsorptive membrane for the bioremediation of lead from wastewater (35).

Polysulfones are being actively studied in several clean energy segments such as the emerging fuel cell market. Fuel cells use the chemical energy of hydrogen or other fuels to cleanly and efficiently produce electricity. Several electric vehicles powered by proton exchange membrane (PEM) fuel cells have demonstrated the high potential of this technology. Currently, perfluorinated sulfonic-acid (PFSA) membranes called Nafion™ have been widely employed in PEM fuel cells. However, Nafion™ suffers reduced proton conductivity at high temperatures (over 80^0 C) (36). A series of PEMs based on sulfonated multiblock copolymers with different sulfonated PSU/PPSU ratios significantly improved proton conductivity at high temperatures as well as achieved significantly higher current density showing its promise as an electrolyte in fuel cells (36). Anion exchange membrane (AEM) electrolysers use a semipermeable membrane designed to conduct anions. AEMs are lower cost and have better mechanical/chemical characteristics compared to PEMs (37). AEM fuel cells yield high power output for a longer period of time when compared to PEM fuel cells and as a result are being widely researched as a viable alternative to PEM fuel cells. Significant enhancements to the fuel cell performance through increased water uptake, ionic conductivity, methanol permeability and alkaline stability have been demonstrated by the recent advancements in polysulfone-derived PEM/AEM (37). A series of quaternized polysulfones were successfully synthesized at a lower production cost and resulting in high power density of 300 mW/cm^2 ideally targeted for fuel cell applications (38).

The production of green hydrogen through water electrolysis is currently seeing strong interest as long-term option for storing electrical energy from renewable energy sources such as wind and sun and is essential for decarbonizing transport and industry. For this reason, it can be expected that water electrolysis technology will become increasingly important since the generated hydrogen can be used both in the mobility sector via fuel cells or as raw or auxiliary material for heavy industries such as chemical or steel industry. So far, PFSA-type membranes have mainly been used in PEM electrolysis due to their excellent chemical stability. PSU multiblock copolymer membranes have shown improved proton conducting performance compared to PFSAs and are being optimized for future PEM membranes (39).

A supercapacitor is another novel and eco-friendly energy storage option. Like an ordinary capacitor, a supercapacitor has two plates that are separated. The plates are made from metal coated with a porous substance such as powdery, activated charcoal, which effectively increases their surface area thus increasing their energy storage. Both carbon nanofibers (CNF) and porous carbon (PC) have large specific surface areas, hierarchical micro-meso pores, and perfect graphitization extents which results in high capacitance and strong stability when they are used as electrodes in supercapacitors. Polysulfone blended CNF and PC electrodes achieved high specific capacitances of ∼360 F g^{-1} and ∼290 F g^{-1} at 10 mV s^{-1} (40).

The use of perovskites for the manufacture of solar cells is an important advancement in photovoltaic devices. In these types of devices, the active organic layer is replaced by perovskites, which are ambivalent conductive materials that efficiently transport electrons and holes and attaining a high-power conversion efficiency. The electrical performance of polysulfones has been studied in terms of sulfonation percentage and thermal and ultraviolet (UV) post-treatment. As the sulfonation percentage was increased, better electrical performance (fill factor and power conversion efficiency) was obtained and UV treatment further improved overall performance by 24%. These optimized sulfonated polysulfones have promising applications in inverted hybrid perovskite solar cells (41).

Nuclear energy is a zero-emission clean energy source. Development of novel radiation and screening methods is necessary to ensure safe nuclear reactors for advancing nuclear energy. Types of radiation detectors include gas-filled detectors, solid-state detectors, and scintillators. Plastics without fluorescent-molecule doping have attracted increased attention as radiation detection components. PES has shown potential as a scintillation material in radiation detection (42). Transparent PES is resistant to environmental stress and responds rapidly to alpha particles despite its amber coloration (43). This will lead to future PES applications in radiation measurements.

Green chemistry is the design of chemical products and processes that reduce or eliminate the use or generation of hazardous substances. Immobilized catalysts are utilized in industrial processes to decrease metal contamination in products and waste streams. These catalysts can also be easily recovered and reused leading to a green chemistry approach. Cobalt composite immobilized on polysulfone fibrous network nanoparticles (CCPSF NPs) were used as catalysts in the oxidation of alcohols under microwave conditions. The high specific surface area of CCPSF NPs made it possible for it to be used as a green, efficient, and reusable nanocatalyst. Anticancer properties of these CCPSF NPs which are attributed to the presence of polysulfone and cobalt were evaluated on breast cancer cells (44).

Membrane-based gas separation is an energy-saving technology that is well-established and expanding. Gas separation technology using polysulfone hollow fiber membranes was developed by Permea (now a division of Air Products) for H_2 recovery and successfully commercialized as early as 1979. This was soon expanded to hydrogen/light hydrocarbon separations in refineries and hydrogen/carbon monoxide ratio adjustment in synthesis gas plants. The market has expanded very significantly over the past 25 years, and current sales are in the range of $1.0–$1.5 billion per year, but no large new application has been added (45). One of the key limitations for wider applications has been trade-off relationship between permeability and selectivity. PPSU based membranes have been shown to increase gas permeability while maintaining stable selectivity (46). This may provide a new approach to overcome the limitation and broaden the applications.

Continued and emerging applications of polysulfone membranes in filter technology depend on the ability to modify their properties to overcome inherent disadvantages. As a result, extensive research is being conducted on improving their properties. The performance of polysulfone membranes can be enhanced through various means. For example, fouling-related issues can be mitigated by incorporating hydrophilic functional groups at the surface, thus improving their performance. We review current modifications with considerable potential.

Plasma treatment is the process by which gas is ionized in a vacuum chamber to form plasma and alter the surface of a material. For example, oxygen plasma treatment is shown to change the hydrophobic PSU UF membrane to a hydrophilic membrane after just 20 seconds of treatment, ultimately increasing the flow rate (47). UV radiation of polysulfones, like plasma treatment, similarly affects surface structure and chemistry, significantly increasing their hydrophilicity. This has been achieved by exposing one membrane side to UV light at 254 nm (48). PSU and PES films exposed to UV radiation dramatically decreased their water contact angle on the irradiated surface, demonstrating increased hydrophilicity (49). While this process appears reversible, permanent hydrophilic surfaces were obtained by UV-assisted treatment in the presence of acrylic acid vapor (50). UV and plasma treatments were found to be equally effective (51). Membranes modified by these treatments can then become suitable for UF. Short term UV irradiation of thin polysulfone films in nitrogen atmosphere increased the dielectric permittivity of polysulfone (52).

Conclusion

Polysulfones have many applications as macroscopic structural components as well as thin membranes. They are used extensively as bulk structural components in a variety of markets such as automotive, electrical and construction industries. Their use in membrane applications exhibits the greatest future potential. Polysulfone membranes are currently used in important functions such as dialysis, water purification and waste water remediation, desalination, immobilized catalysis and biosorption. They are being actively evaluated in many new applications in the medical, food and clean energy segments. In the latter category, they are being investigated to improve conversion of solar energy in perovskite solar cells, to increase current output in fuel cell proton exchange membranes at high temperatures and to increase the capacitance of supercapacitors. New and innovative modifications and enhancements, such as the addition of carbon nanotubes and graphene oxide, have the potential to make polysulfones even more commercially appealing, such as improving the trade off between gas selectivity and permeability, to obtain acceptable throughput with high separation. For this reason, they are used in decarbonization technology, syngas composition optimization and separating hydrogen from hydrocarbons. The polysulfone field is rapidly evolving in applications and is well suited to mitigating many global challenges.

Acknowledgments
I sincerely thank Dr. Yuri Strzhemechny (Associate Professor and Chair) and Dustin Johnson (Graduate Student), Department of Physics and Astronomy, Texas Christian University, Fort Worth, TX, for their invaluable guidance and feedback.

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