



# Study of the plasticising effect on polymer and its development in fuel cell application



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## ARTICLE INFO

### Keywords:

Plasticiser  
Ionic liquids (ILs)  
Ion exchange membrane  
Fuel cell

## ABSTRACT

Plasticisers have been widely used as additives in polymer applications, including pharmaceuticals, food processing, and electrochemical sensing, to improve the mechanical and physicochemical properties of the polymers. Recent developments using alternatives to the conventional phthalate ester plasticisers, such as water, ionic liquids (ILs) and deep eutectic solvents (DES), have opened new avenues for expanding plasticiser use into other potential areas such as ion exchange membranes. Owing to the unique properties of plasticisers that promote a higher amount of amorphous phase within the intermolecular structural of the polymer, combinations of plasticisers and polymers improve a polymeric film's ionic conductivity while maintaining film flexibility and thermal stability. Hence, this review paper intends to provide an insight on the applications of conventional and alternative plasticisers in various areas, as well as to address the working mechanism of plasticisers within polymer films. Most importantly, this paper highlights recent developments incorporating plasticisers in proton exchange membranes and the future potential of these materials. The outlook presented here demonstrates that some of the challenges faced during the fabrication of ion exchange membranes, which are alternatives to Nafion membranes, can be overcome.

## 1. Introduction

Proton exchange membrane fuel cells (PEMFC) are regarded as state-of-the-art energy generation devices, which will support the goal of meeting global demand while producing clean and efficient energy. PEMFCs were first introduced by the National Aeronautics and Space Administration (NASA) in the late 1950s with the evolution of fuel cell generators for manned space missions. Since then, the development of PEMFCs has accelerated rapidly. Extensive efforts have been paid to ensure the success of its commercialisation for various applications, including transportation, portable devices and stationary devices, after materials and system fine-tuning. This includes material selection for electrodes and electrolyte, as well as process control [1,2] to ensure proper functionality of fuel cell devices based on temperature, humidity and fuel flow. In essence, a PEMFC is an electrochemical apparatus that converts the chemical energy of a fuel into electrical energy without involving combustion. PEMFC technology is potentially attractive for automobile applications, mainly due to the high power density and low operating temperatures (80–120 °C) among many fuel cells. In addition, PEMFCs are advantageous because of their relatively short

start-up time, allowing an automobile functionality similar to combustion engine based vehicles with appropriate power integration [3]. Fig. 1 shows the typical structure of a PEMFC, consisting of an anode (fuel supply side), a cathode (oxidant supply side) and a membrane electrolyte (allowing the flow of ions between the anode and cathode) [4].

In a PEMFC, the central core component is the polyelectrolyte membrane, also known as the proton exchange membrane (PEM). It is a semi-permeable polymer membrane that acts as an electrolyte, providing ionic conduction between the cathodic and anodic electrodes, whilst also acting as a separator for the two reactant gases [5]. The conventional, commercially available PEM is the Nafion-117 membrane, comprised of sulfonic group side chains and a polytetrafluoroethylene backbone for facilitating proton conduction [6]. Despite Nafion membranes being used commercially as PEMs, the high fabrication cost of Nafion is a major drawback. Thus, several alternative materials are being studied with the goal of producing cost-effective PEMs to replace Nafion membranes. An appropriate candidate, would have the following properties [7]:

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- (a) High chemical and electrochemical stability during fuel cell operation.
- (b) High proton conductivity for supporting high current density with minimal resistivity losses.
- (c) Good water uptake.
- (d) Thermal and hydrolytic stability.
- (e) Low permeability to reactant species to maximise efficiency.
- (f) Low production cost.
- (g) Highly available in natural materials.

Subsequently, different classifications of polymer membranes have been studied, including fluorinated membranes, hydrocarbon membranes, aromatic membranes and hybrid/composite membranes [7]. Sulfonated poly(ether ether ketone) (SPEEK) is one of the many types of PEMs suggested as an alternative to Nafion, owing to the low cost and the good mechanical and thermal stability of SPEEK. The aromatic thermoplastic membrane is produced through a chemical modification with sulfonic acid that provides proton conductivity suitable for fuel cell applications [7]. These membranes possess most of the desirable characteristics stated above, which enables SPEEK membranes to be a potential substitute for Nafion. However, a SPEEK membrane was reported to demonstrate a gradual decrease in conductivity during low hydration conditions [8]. To address this issue, Trindade and co-workers [9] reported the further modification of a SPEEK membrane with ILs 1-butyl-3-methylimidazolium tetrafluoroborate (BMI-BF<sub>4</sub>) to enhance water retention, thereby preserving proton conductivity with a constant output of  $12.0 \times 10^{-2} \text{ S cm}^{-1}$  at an elevated temperature of 80 °C. The resulting output, which was  $17.0 \times 10^{-2} \text{ S cm}^{-1}$ , was comparable to outputs found with Nafion membranes for similar types of ILs and operating conditions [9].

Recently, biocomposite membranes have emerged as materials of interest because of the intrinsic advantages of biocomposites, which include low cost, biodegradability, abundant in nature, and substitution potential for some petrochemicals [10]. For these reasons, several biocompatible materials have been used as host polymers in biopolymer-based electrolytes, such as starch, cellulose, chitosan, chitin, lignocellulosic materials, polylactides, sago, and soy-based plastics [11–14]. Based on a study from Ma and co-workers [6], chitosan-based PEMs were intensively studied as alternatives for commercial Nafion membrane. Additionally, Smitha and co-workers [15] revealed that using sulfuric acid as a crosslinker for a chitosan membrane increases the structural stability of the sulfonated polysulfone-composite membrane, despite the coulombic interaction of the amino groups in chitosan with the sulfate ions, whilst the presence of sulfuric acid limits the water retention capacity of the system. Owing to these unique characteristics, chitosan-composite membranes potentially lead to better chemical and thermal stability in fuel cells [16].

As one can observe in Fig. 1, the fundamental material used to construct a PEM is the polymer itself. During fuel cell operation, the membrane will experience thermal expansion and contraction with changes in temperature and hydration level [17]. Thus, it is important to control and improve the characteristics of a PEM to avoid any possible device failure. Consequently, researchers are increasingly interested in using plasticisers as additives to polymeric membranes to improve the mechanical strength, thermal stability, and proton conductivity of the membrane [18]. Previously, plasticisers have been widely used in applications including, but not limited to, pharmaceuticals, food processing, and electrochemical sensing. To facilitate market demands, plasticisers in polymeric applications must have low production costs, be widely available and have a high degree of recyclability. However, the most widely used conventional plasticisers, often found in polyvinyl chloride (PVC) applications, are phthalate ester, which are considerably high in toxicity, particularly for paediatric exposure. Therefore, several alternatives have been proposed to replace conventional phthalate esters, such as water, ionic liquids (ILs) and deep eutectic solvents (DESs) [19–21]. Among the mentioned plasti-

cisers, the plasticising effect by ILs was shown to be most prevalent. Interestingly, the incorporation of ILs into a polymeric film integrates certain properties of ILs that have been shown to be beneficial in fuel cell membranes [22]. The extra ionic charges from an IL enhance the mobility of the polymer membrane, which can potentially lead to an increase in proton conductivity [18].

Although the precise nature of the molecular structure and bonding between the polymeric film and the plasticiser is unknown, plasticisers are known to promote as higher ratio of amorphous phase within the polymer, and thus leading to higher flexibility and thermal stability. In comparison, DESs are regarded as prospective materials which possess similar characteristics to ILs whilst being more cost effective and easier to synthesise. More recently, researchers have investigated DESs for compatibility and effectiveness towards plasticising of a polymer membrane.

Consequently, this review covers recent developments in plasticisers research while outlining the possibilities of using deep eutectic solvents (DESs) as potential plasticisers for fuel cell applications.

## 2. Characteristics of plasticisers

Plasticisers are additives used in the preparation of plastic membranes and are usually low molecular weight and inert organic compounds possessing low vapour pressures. These compounds are capable of shifting the glass transition temperature  $t_g$  and melting point  $t_m$  of polymers to lower values while preserving the rubbery properties of the polymers [23]. This aspect of plasticisers allows the polymer membranes to function under higher temperature while retaining flexibility [24].

The plasticisers for a polymer membrane can be differentiated into two categories: internal or external plasticisers. Generally, internal plasticisers have bulky molecular structures that create more intermolecular spaces and induce polymers to move around preventing polymer changes from coming closer together. Internal plasticisers usually involve the incorporation of monomers by either co-polymerising them into the polymer structure or reacting them with the original polymer, thus inducing a plasticising effect. One example would be the copolymerisation of vinyl acetate with vinyl chloride to achieve a lower glass transition temperature  $t_g$  [25]. In another example, polyethylene terephthalate (PET) modified using small amounts of polyether segments, forming segmented copolymers [26–28]. The bulky polymeric chains formed as a result of the internal plasticisation of PET with

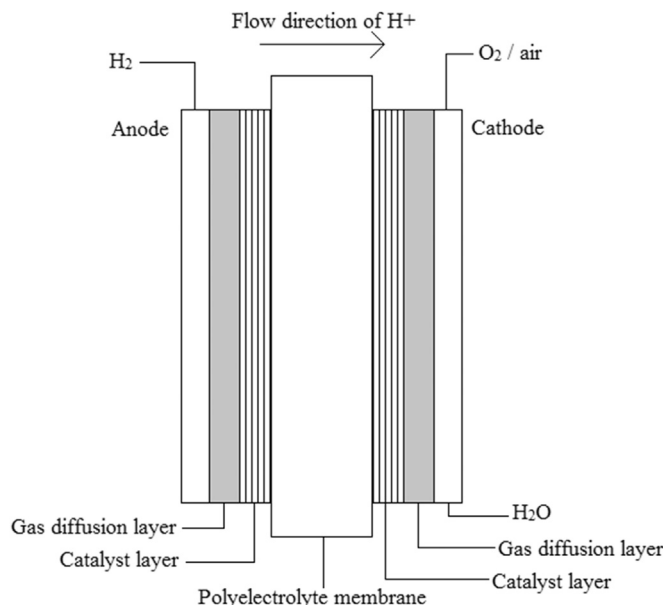


Fig. 1. Structure of a proton exchange membrane fuel cell (PEMFC) [4].

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