



# Biodegradable and biocompatible temperature sensitive triblock copolymer hydrogels as draw agents for forward osmosis



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## ABSTRACT

Recently, polymer hydrogels have been studying as a draw agent in forward osmosis (FO) due to their low toxicity, reusability and dewatering abilities. In this research work, we studied five triblock copolymer hydrogels as draw agents in FO process. Hydrogels were synthesized by ring opening polymerization of monomers D,L-lactide, Glycolide, methyl ether poly ethylene and stannous octane as catalyst. Prepared hydrogel named as “poly(ethylene glycol-[DL-lactic acid-co-glycolic acid]-b-ethylene glycol) (PEG-PLGA-PEG).” Different weight percentages i.e., 0.09 and 0.18 wt% of Graphene oxide (GO) and Graphene (Gr) were incorporated in hydrogels and named as “PEG-PLGA-PEG/GO-0.09 wt%, PEG-PLGA-PEG/GO-0.18 wt%, PEG-PLGA-PEG/G-0.09 wt% and PEG-PLGA-PEG/G-0.18 wt%.” Different types of characterization technique were used to characterize the prepared hydrogels i.e., H NMR spectrophotometers, Fourier transform infrared spectrometer (FTIR), Scanning electron microscopy (SEM), Molecular weights (MWs) measured Gel Permeation Chromatography (GPC), X-ray diffraction (XRD) and thermogravimetric analysis (TGA). All the five prepared hydrogels were tested as draw agents in FO process to check the effect of GO and G on swelling properties, water fluxes, and water recovery. After FO experiments results advocate, GO incorporation in polymer hydrogels increase the swelling ratios and thus yields higher water fluxes among all hydrogels. By using PEG-PLGA-PEG/GO-0.09 wt% and PEG-PLGA-PEG/GO-0.18 wt% hydrogels as draw agents, deionized (DI) water and 2000 ppm NaCl as feed solutions, the average water fluxes obtained are 0.68 LMH, 0.57 LMH and 0.55 LMH, 0.48 LMH, respectively. All prepared hydrogels remained active up to two times regeneration and these hydrogels were shown negligible reverse solute diffusive flux through the FO membrane.

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## 1. Introduction

One of the most significant challenges of this century is fulfilling the increasing water demand for drinking water supplies, food production and other industrial needs to support the enormous population growth [1,2]. To meet fresh water demand there is a need to find out the best process with energy efficient that should give water with drinking standards. Lots of research is going on membrane based separation processes. For this purpose reverse osmosis (RO) is currently the most commonly used desalination technologies because of its many merits over other conventional thermal desalination technologies [3]. RO requires large amounts of electricity and extremely high hydraulic pressures to force water across the membrane while rejecting salt and other contaminants. Drinking water production and industrial necessities water from

waste or contaminated water is a major challenge because it will helpful to reduce volume of waste water. Forward osmosis (FO) can do better than RO in terms of energy consumption and fouling [4].

Forward osmosis (FO) being a membrane based separation process; it deploys osmotic pressure difference to be the driving force for water permeation. In which semipermeable membrane acts as a separation medium [5]. A typical FO separation involves the feed solution, i.e. saline water, passing through a semipermeable membrane in another section containing draw agent (having high osmotic pressure in comparison with saline water/feed water) which flows on the other side of the membrane. Water gets transported from the feed side to the draw agent side through the membrane because of the osmotic pressure difference [5,6]. However, the separation of water from draw agent to retrieve pure water and regenerate draw agent is also important in FO. Hence there is a niche of developing a good drawing agent [4].

One of the key challenges in FO process is the limited choice of efficient and economic draw agent. While selecting the draw agent,

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it is desired to meet basic criteria i.e., high water permeation rate, it should generate high osmotic pressure, easy water recovery, reusable, non toxic, compatible with membrane surface, and cost effective [6,7]. Development of a novel draw agent has attracted attention of science community so far with incorporation of inorganic and organic salts [7–12]. Ammonia-carbon dioxide among them appears to be promising [13,14]. Few studies have been conducted with novice compounds such as hexavalent phosphazene salts [15], strong polyelectrolytes [16] and 2-methylimidazole-based compounds [17] to counteract with the problems such as low regeneration energy efficiency and counter diffusion. In spite of elevated osmotic pressure, their separation/regeneration/recycle, viscosity, or dissociation, etc. are the pitfalls [15–17].

Cross-linked by polymer chains with three-dimensional network structures is the characteristic of polymer hydrogels. Presence of a large number of hydrophilic groups is the reason of why polymer hydrogels absorb a lot of water [5]. The presence and dissociation of ionic species within the polymer hydrogel are responsible to swell and develop a higher internal osmotic pressure. Water absorbing properties of the networks results from the presence of functional groups such as Carboxylic ( $-\text{COOH}$ ), Hydroxylic ( $-\text{OH}$ ), Amidic ( $-\text{CONH}$ ) and Sulphonic ( $-\text{SO}_3$ ) [2].

Recently, researchers are focusing on polymer hydrogels as a draw agent in FO process. Smart polymer hydrogels exhibit sensitivity towards various parameters like temperature, pH, magnetic field, electric field, ionic strength and light [18–22]. A novel class of draw media, thermosensitive polymer hydrogels is sensitive to heat [23]. Polymer hydrogels have been claimed to provide a sufficient driving force to draw water from high salinity seawater across membrane by virtue of high osmotic pressure (2.7 MPa at 27 °C). Swollen hydrogel was dewatered at 50 °C and no by-product was produced, making it a great advantage during regeneration of drinking water. Polymer hydrogel series hence gained a stature of effective draw agent ever since in FO processes [5,23–27]. Synthetic polymer hydrogels are having following disadvantages like non-biodegradability, high energy consumption for water recovery [28], toxicity and non-biocompatibility. Hence, bio polymer based hydrogel will be highly required to overcome the above disadvantages.

Temperature sensitive triblock copolymer hydrogels are good in biodegradability and temperature responsive properties. A new species called “triblock copolymers”, consisting of A block covalently bonded (by ester link) with B-Block and vice versa form an ABA and BAB type hydrogel. Copolymer exhibits variable viscosity, it flows freely at low temperature and may form a gel at 35–40 °C. Poly([DL-lactic acid-co-glycolic acid]-*b*-ethylene glycol-[DL-lactic acid-co-glycolic acid]) (PLGA-PEG-PLGA) or poly(ethylene glycol-[DL-lactic acid-co-glycolic acid]-*b*-ethylene glycol) (PEG-PLGA-PEG), are a kind of block copolymers composed of hydrophobic poly(DL-lactic acid-co-glycolic acid) (PLGA) segments and hydrophilic poly(ethylene glycol) (PEG) segments. Copolymer molecules remain in solution because of hydrophilic PEG which is associated with hydrophobic PLGA segments by crosslinks. PEG and water molecules form hydrogen bonds association at lower temperature and hence favor aqueous solution. At higher temperature, hydrophobic forces of PLGA dominate the hydrogen bonds cause solution-gel transition. Unlike to the homopolymers of lactic acid (polylactide) and glycolic acid (polyglycolide), which show poor solubility. Thus, this makes it a suitable candidate to be used in the synthesis of various thermo responsive hydrogels [29,30].

The high molecular weight along with high PLGA contents makes the block polymer insoluble in water, although they tend to swell in aqueous media. Block copolymers with hydrophilic and hydrophobic blocks are capable of forming physical crosslink in water by means of hydrophobic interaction, crystalline micro domains or chain entanglement [31]. Hydrophobic domains,

because of physical interaction, retain micro domains swollen and together maintaining the integrity of polymer network in aqueous media. The elastic and viscoelastic properties make these copolymers soft for easy casting and thermally curable in spite of weak and reversible physical associations.

Graphene oxide is a two-dimensional carbon material with a large number of hydrophilic oxygenated functional groups i.e., carboxyl groups, epoxy, hydroxyl and carbonyl, etc. These groups enhance miscibility with polymer matrix and make more hydrophilic composites. Moreover, the thermal stability and mechanical strength of the hydrogels may be improved due to the outstanding thermal resistance and mechanical properties of graphene [32].

In literature, many papers are available on “PEG-PLGA-PEG hydrogel”. But all are used only in the pharmaceutical field as drug targeting systems. This combination is never used in forward osmosis (FO) as a draw agent. Therefore, an attempt was made to evaluate the performance of these (biodegradable and biocompatible) graphene and graphene oxide incorporated PEG-PLGA-PEG hydrogels in FO instead of synthetic polymer based hydrogel. We prepared five different hydrogels with incorporation 0.09 and 0.18 wt% of Graphene (G) and Graphene oxide (GO) i.e., (PEG-PLGA-PEG), PEG-PLGA-PEG/GO-0.09 wt%, PEG-PLGA-PEG/GO-0.18 wt%, PEG-PLGA-PEG/G-0.09 wt%, PEG-PLGA-PEG/G-0.18 wt%. These hydrogels were characterized by different techniques like, H NMR, FTIR, SEM, GPC, XRD, swelling ratios, water fluxes, water recovery and regeneration.

## 2. Materials and methods

### 2.1. Materials

Monomer D,L-lactide (3,6-Dimethyl-1,4-dioxane-2,5-dione) was purchased from Sigma-Aldrich, USA. Glycolide ( $\geq 99\%$ ) (1,4-Dioxane-2,5-dione) was purchased from Sigma (Life science), Netherlands. Methylene polyethylene glycol (mPEG, Mn 550 g/mol) and Dibutyltin Diacetate were purchased from Aldrich, USA. Polymerization catalyst used as stannous 2-ethyl-hexanoate (92.5–100%) was purchased from Sigma (Life science), Japan. Coupling agent as hexamethylene diisocyanate (HMDI) ( $\geq 99\%$ ) was purchased from Sigma (Life science), Germany. Solvents used in this study; diethyl ether, hexane, and anhydrous toluene were purchased from RANKEM, India. Graphene Oxide (GO) and Graphene were purchased from Adnano Technologies, India. Size of GO was between 0.8 and 1.6 nm and surface area was 400 m<sup>2</sup>/g. Graphene size was between 5 and 10 nm and surface area was 310 m<sup>2</sup>/g. For FO tests, sodium chloride (NaCl) purchased from FINAR chemicals Ltd, India. Commercial FO membrane purchased by Hydration Technologies Innovations (HTI) (Albany, OR) was used to test the performance of prepared hydrogel in forward osmosis process. This FO membrane was made of cellulose triacetate with an embedded polyester screen mesh. Deionized (DI) water produced by milliQ, Millipore-India was used for the experiments.

### 2.2. Synthesis of triblock copolymers

The synthesis of pure PEG-PLGA-PEG triblock copolymers was performed through a ring-opening copolymerization. A dried three-neck round-bottom flask was used, which equipped with a condenser. Poly(ethylene glycol) (2 g,  $M_w$  550 g/mole), D,L-lactide (5 g), and glycolide (1.66 g) were polymerized and catalyzed by 0.03 g of stannous 2-ethyl hexanoate, followed by elevation reaction temperature at 150 °C up to 8 h. Diethyl ether was used to wash (thrice) PEG-PLGA products followed by vacuum drying at room temperature. PEG-PLGA copolymer triblock synthesized by dissolving PEG-PLGA copolymer having terminal hydroxyl groups

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