Polymers and the Water Crisis in Brazil: Opportunities for Technological and Environmental Development

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Abstract: At a global level, climate changes have been responsible for alterations in rainfall regimes. Numerous impacts resulting from such complex dynamics negatively affect peoples and nations. Desertification, sandification, floods, and droughts are some evident examples of the transformation the world is undergoing. In Brazil, the past few years have been characterized by long periods of drought in some regions. As a result, there have been considerable drops in the levels of reservoirs that supply important urban and economic axes in the country. Implications on the national economy and entire production chains aggravate the current scenario, along with two long years of the Sars-Cov-2 pandemic period. From this perspective, the present work aims to address the pressing need to adopt technologies and techniques for collecting and treating rainwater. To this end, specialized databases were accessed in order to evaluate ongoing research on the use of polymeric materials to achieve that goal.

Keywords: Membranes, water treatment, polymer surveys, climate.

1. INTRODUCTION

Although there is still disagreement about what has promoted extreme weather events - whether just a result of human action or a natural event stemming from the Earth's cycle - climate change is ever more visible, more intense, and more frequent. Event-related theories usually start with a disruption. An event depends on the level of experience - whether it is experienced in the present or constructed in retrospect - and is perceived as something that has changed dramatically [1, 2]. From this perspective, climate change is an event whose effects are felt like an extension or exacerbation of the weather pattern. Its developments are represented by timescales and oscillations, described over years, decades, and centuries [3]. Regardless of the time scale used as a reference, extreme events have become more impacting on humanity, no matter how they are reported by the local and/or the international media [4]. The consequences are manifold and sometimes immeasurable. But on a macro scale, the natural [5-11], economic [12-14], political, and also social [15-17] effects stand out. It is, therefore, necessary that political actors - from the organized civil society and private organizations -, researchers, and educators act responsibly in order to mitigate that scenario.

Studies project, for Brazil, climatic effects such as an increase in the average temperature in the central region [18], an increase in the number of days with temperatures above 34°C [19], an increase in the number of consecutive drier days and higher annual precipitation both in the western Amazon and southern regions of Brazil [20] and a decrease in rainfall rates for the Midwest and Northeast of Brazil [21]. The São Francisco River Basin, for example, had a considerable reduction in its baseflow, impacting the population and the product segments that rely on its waters [22].

Regarding research and development, numerous studies have been carried out worldwide to better understand extreme climate phenomena and also to circumvent their possible damage to society. To this end, different areas of knowledge are brought together to attain such a goal. Materials Engineering is one of them. Through the development and processing techniques of polymeric materials, many projects for water catchment and treatment have become feasible.

In this sense, the present paper aims to address the main polymers used in projects and research for rainwater catchment and treatment as a way of mitigating the effects of long droughts in some regions of Brazil.

2. METHODOLOGY

The present work is based on a survey of types of polymers used in manufacturing devices for collecting and treating rainwater. Articles submitted and published in well-recognized search platforms were analyzed. To this end, and due to its relevance in the production of academic materials, the Science Direct

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E-ISSN: 1929-5995/22

database was used. Keywords that converged on the topic of polymers used in water treatment were used. The searches focused on words appearing in the titles of the publications.

3. RESULTS

According to a recent Frost & Sullivan (2021) [23] survey on polymer markets and circular economy, the scarce potable-water scenario will demand efforts from major players (politicians or not) to adopt water treatment technologies. The same document also states that polymer membranes will play an important role in a market that is tending to grow. It is estimated that by 2027 the segment will mobilize around US$ 9 billion per year, at the global level. When compared to 2020, there will be a 4.2% growth rate per year. Data obtained by Frost & Sullivan reinforce that the demand for the next 10 years will be driven by the food and beverage industry, which requires treated water. But clinics and hospitals have also increased such demand, particularly for their dialysis and blood transfusion units [24-26].

Searches for articles on the ScienceDirect platform occurred without defining a time frame. By using the combination of the keywords 'polymer' and 'water', 3,366 articles were retrieved containing those words in their titles. However, many of them were not directly associated with water catchment and/or treatment technologies per se. In order to further refine the search and make it more precise to the proposed topic - namely, the development of research and technology in the area of water catchment and treatment using polymers -, periodicals with potential adherence to the theme were defined. To this end, the following journals were searched: *Polymer, Journal of Membrane Science, European Polymer Journal, Chemical Engineering Journal, Separation and Purification Technology, Polymer Science USSR, Water Research, Journal of Petroleum Science and Engineering, Desalination*. As a result of such filtering, the publications were reduced to a total number of 695, of which 645 (92.8%) were research articles, and the remainder divided among review articles (2.6%), book reviews (0.6%), conference (0.1%), discussion (0.1%), editorial (0.1%), errata (0.7%), and short communications (2.9%). Three journals that concentrated more than 100 publications were *Polymer* (176 publications), *Journal of Membrane Science* (142 publications), and *European Polymer Journal* (100 publications).

All publications went through a screening stage when their respective abstracts were read. From this stage on, it was possible to evaluate the relevance of the articles to the proposed topic. Articles referring to the use of polymeric materials in separation processes with no potential for human consumption or reuse were disregarded, as well as publications associated with polymerization and solubilization of polymers in water. The queries were performed between October 20 and October 25, 2021. In the first screening step,

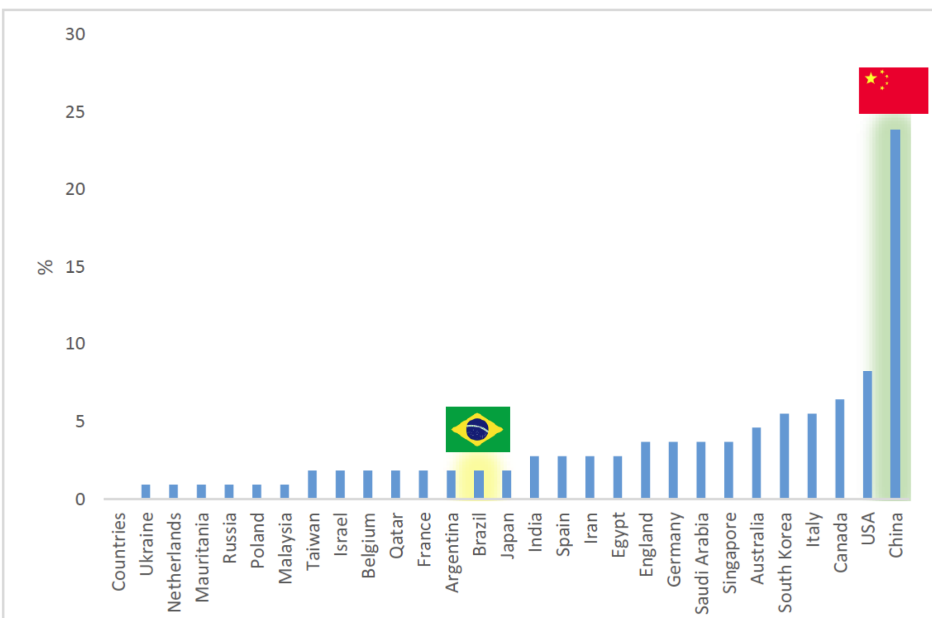

Figure 1: Percentage of academic publications, by country, on polymer membranes for water treatment. Search made in the ScienceDirect platform.

considering the relevance of the titles of the publications with the topic of the project, the search retrieved a total of 96 publications.

Figure **1** shows the percentage of world production on the topic.

The People's Republic of China has the largest number of published scientific articles, totaling almost 24% of the global publications. Despite the demand for treated and potable water, Brazil can be considered an intermediate research center on the subject, accounting for nearly 2% of the academic productions obtained from the research platform.

3.1. Polymers for Manufacturing Membranes for Filtration

The problems related to water pollution and its management have stimulated various studies on the development of technologies capable of promoting the reuse of that natural resource, whether potable or not [27-30]. One of the widely employed technologies for reusing contaminated water is filtration by polymeric membranes. Those materials can be used in various production industries: oil and gas, pharmaceuticals, food industry, medical applications, etc. [31-35]. The membranes are designed to be permeable to water and not to compounds that are removed from the feed stream and rejected [36]. Membranes for microfiltration, ultrafiltration, and nanofiltration can be able to filter out 0.5-5; 0.005-0.5 and 0.0007-0.005 micrometers particles, respectively [37].

Membrane separation processes are appealing for a couple of reasons: they are relatively simple to operate when compared to other processes in the market; they operate at room temperature and are useful when one of the currents is thermosensitive; they can be applied in different circumstances; there is no phase change [38].

The advantage of employing polymers as a membrane matrix lies in their chemical functionalization ability [39, 40] and the possibility of obtaining nanostructures that can act as barriers at the nanoscale. This procedure allows greater selectivity of the developed membrane, which can abstract a certain group of substances at the expense of others, at the level of particles, molecules, or ions [41]. In general, nanofiltration membranes are intended for the treatment of seawater and water contaminated with micropollutants [42-44].

Effective removal of trace organic contaminants has been one of the main applications of nanofiltration and reverse osmosis membranes for producing potable water. Polymer structures based on aliphatic-aromatic polyamide have been widely studied at bench and pilot scale levels for removing pesticides, pharmaceuticals, and other molecules that are present in water [41]. Also, according to the authors, those studies involved the analysis of only one organic solute. Organic compounds that were approximately the pore size of nanofiltration and reverse osmosis membranes and that had an ionizable functional group were rejected by electrostatic repulsion. Such repulsion occurs when the membrane surface and the solute present in the feed current have the same charge [45]. Studies have pointed out that the hydrophobicity of membranes strongly affects the separation of organic water molecules. Furthermore, the researchers concluded that hydrophobic membranes generally have a greater tendency to build up fouling than hydrophilic membranes.

In the survey on membranes tested for organic contaminant removal, Gohil and Ray (2017) [41] verified the percentage of rejection for particular membranes. The NF-70 type, for example, rejected beta zone, alachlor, chlordane, heptachlor, vinclozolin, and pirimicarb molecules by 100%. These membranes, designed by FilmTec Corporation, are negatively charged and used for nanofiltration processes.

3.1.1. Cellulose Acetate (CA)

Membranes produced from acetate and cellulose have high hydrophilicity, high water permeability, and a low tendency to form fouling [46, 47]. Li and colleagues (2006) [48] developed a CA-based membrane for water-oil separation. The results showed an oil retention level of over 99%, with a 10 mg/L oil content in the permeate.

In their studies regarding the synthesis and characterization of CA-based and nylon-66-based membranes, [49] obtained promising water-oil separation results. When compared to the evaluated commercial CA membranes (Merck Millipore, with a 0.22 μm pore diameter), whose permeate flow rate is 22 L/m^2.h and oil rejection of 70%, the modified membranes showed a permeate flow rate of 33 L/m^2.h and an oil rejection percentage close to 95%. The authors found that increasing the nylon-66 content in the membrane composition represented an increase in the oil rejection percentage. That is because polyamide conferred greater hydrophilicity to the membrane surface. The permeation properties were attributed to the homogeneous distribution of nylon-66 on the CA matrix. The modified membranes were produced using the cast molding method. The thermal and mechanical properties of the developed membranes proved to be better than their commercial counterparts. Thermogravimetric analyses, performed at 15°C/min over a temperature range between 300°C and 600°C under an inert atmosphere, showed that the membranes developed at laboratory scale were more resistant to high temperatures and had a lower mass loss. The authors attributed such behavior probably to the formation of extra hydrogen bonds, between CA and nylon, which will require greater energy to promote ruptures, increasing temperature.

3.1.2. Polysulphone (PSF)

PSF and CA were also jointly employed for developing membranes for water-oil separation. Mousa and co-authors (2020) [50] obtained, by electrospinning, different types of coaxial nanofibers, which were doped with zinc oxide (ZnO) nanoparticles and treated with an aqueous solution of sodium hydroxide (NaOH). Figure **2** shows the arrangement of polymeric structures in the fibers. The results revealed a tensile strength of up to 7.58 MPa, a modulus of elasticity of 0.2 MPa, and toughness of 23.4 $J.m^{-3}$. The nanofibers with the NaOH aqueous solution had increased hydrophilicity and, consequently, an increased water separation flux. This was attributed to the hydrogen bonds formed between NaOH and water molecules. The tests that were performed led to a water flow rate of 420 $L/m^2.h$ for the treated membranes, 1.6 times higher than that for the non-treated membranes.

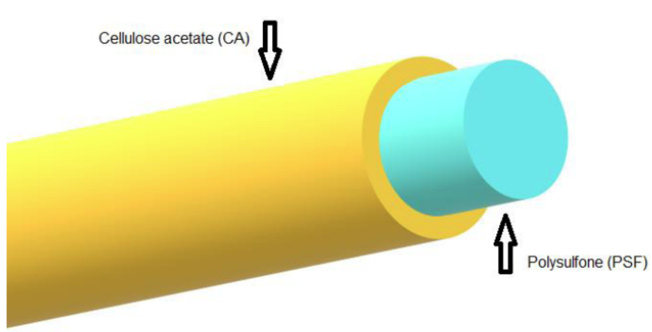

Figure 2: Scheme illustrating the coaxial nanofiber membrane.

In addition to those results, the authors concluded that the ZnO doped membranes presented some activity against *Escherichia coli*. According to the authors, the bactericide action can be attributed to two reasons: (a) interaction of ZnO nanoparticles with the microorganisms and (b) release of antimicrobial ions. Combined, these steps favor the formation of oxygen-based species, such as OH radicals, hydrogen peroxide, and O_2, which are capable of causing damage to *E. coli* cells. These studies complement the already known multifunction of ZnO in polymer composites, as an additive for improving roughness, permeability, and fouling resistance - already described in the literature [51]. Nanoparticles of titanium oxide, graphene oxide, diamond, and carbon nanotubes are also incorporated in the manufacturing processes of polyamide-based membranes aiming to improve the roughness and hydrophilicity of the material [52].

3.1.3. Polyvinylidene Fluoride (PVDF)

Polyvinylidene fluoride (PVDF) is a semicrystalline thermoplastic polymer with varied applications due to its unique properties such as chemical, thermal to UV radiation stability, oxidation resistance [53], biological resistance, and durability [54], with potential use in the manufacture of fibers for making some of those protective face-covers used during the Sars-CoV-2 pandemic period [55]. There are five crystalline phases (α, β, γ, δ, ε), with the β and γ being polar phases that present conditions to favor the piezo, pyro, and ferroelectric properties of the polymeric material [54]. The alpha phase is non-polar and easily obtained by polymerization.

In their studies related to water-oil separation processes, [39] developed a membrane-based on two polymers: PVDF and poly(N-acryloyl morpholine), PACMO, a non-ionic polymer. The aim was to obtain graphitized polymeric structures on a PVDF base, called PVDF-g-PACMO, and thus generate a membrane with lower fouling generation, based on the knowledge that hydrophilic polymeric bristles on membrane surfaces can reduce the formation of deposits during the water-oil separation process. Figure **3** illustrates the poly(N-acryloyl morpholine) structure anchored on the PVDF substrate.

The membranes were obtained with pore size control, via surface-initiated atom transfer radical polymerization (ATRP).

3.1.4. Poly(Piperazine Amide) (PIPA)

Many nanofiltration membranes are composite materials obtained from a thin layer of polyamide prepared by interfacial polymerization [56]. The

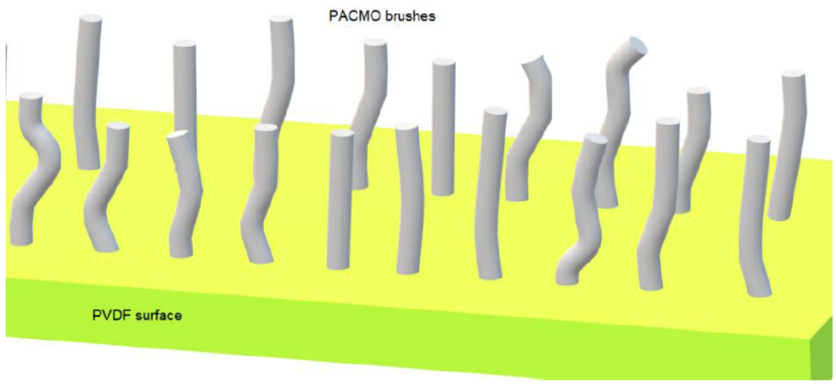

Figure 3: Schematic illustration of the PACMO structures anchored on the PVDF substrate.

performance of a nanofiltration membrane depends on many variables, such as the structure of the monomers that constitute the polymer and the preparation and post-treatment conditions [57, 58].

Polyamides derived from aromatic amines, such as 1,3-phenylenediamine, MPD; and aliphatic diamines, such as piperazine, PIP, have shown to be applicable for manufacturing reverse osmosis and nanofiltration membranes. One such polyamide is poly(piperizinamide), PIPA. Piperazine is a monomer widely used in interfacial polymerization processes that, when reacted with trimesoyl chloride (TMC), forms PIPA. Its molecular structure, shown in Figure **4**, contains crosslinked and uncrosslinked regions and has pendent carboxylic groups. These groups arise during the interfacial polymerization process, due to the partial hydrolysis of acyl chloride present in TMC. The content of carboxylic groups interferes with the water flow rate and the electrostatic repulsion between ions and charged molecules with the membrane surface [56].

Commercial membranes produced from such polymer exhibit high selectivity and pore size around 1 nm and are suitable for removing organic compounds [59].

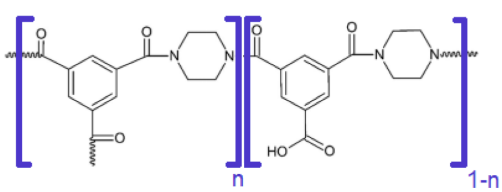

Figure 4: Molecular structure of *poly(piperazine amide),* PIPA.

3.1.5. Poly(Ethylene Terephthalate) (PET)

In addition to the development of new polymers - useful for manufacturing water treatment membranes -, the modification of already consolidated polymers proves to be promising in obtaining filtration properties. [60], for example, have assessed the filtration potential of PET fibers whose surface morphology has been altered by poly(ethylene glycol) PEG particles. Studies have shown that the incorporation of such particles helps in reducing the deposition phenomenon in membranes [61, 62]. PEG microspheres can be grafted onto the surfaces of a polymer matrix or else added as a blend [60]. In their studies, Regev and co-authors (2019) [60] polymerized spherical particles (1 to 10 μm diameters) of poly(ethylene glycol) methacrylate, PEGMA, onto PET fiber surfaces. Figure **5** illustrates flat PET fibers coated with PEGMA particles.

The results showed an increase in the efficiency of dirt removal from the water, with a decrease in its turbidity.

Currently, most commercial polymer membranes are of petrochemical origin, the presence of which will tend to grow in the market as the demand for membranes increases [63]. However, the same search for alternative and sustainable methods and materials will equally affect the membrane industry. In that regard, research in the area has also been carried out to develop biomaterials that can foster wastewater treatment with a capability equal to that of similar petrochemicals. Kim *et al* (2020) [64] developed biopolymers based on isosorbide, which has already been used by the productive sector as an additive to improve the thermal, mechanical, and optical properties of many polymers.

CONCLUSIONS

The growing demand for water for various applications, coupled with the imminent scarcity scenario of this natural resource, requires the adoption

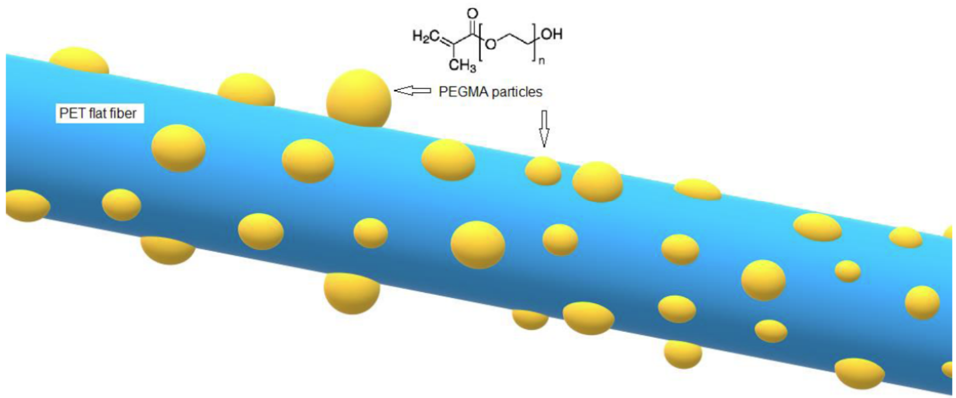

Figure 5: Schematic illustration of the fibers grafted with poly(ethylene glycol) methacrylate.

of water reuse technologies. All indications are that the development of membranes and filtration systems (ultra, nano, and microfiltration) depends on research in the domain of materials, especially in the area of polymers.

A bibliographical survey in specialized databases reveals a worldwide interest in the development of polymer membranes for water treatment. Although the studies were mostly conducted in the People's Republic of China, many other countries, including Brazil, are doing research on the subject, seeking to improve technologies and materials used in filtration units (ultra, micro, and/or nanofiltration). Despite the recent water crisis faced by Brazil, the country still lacks additional research and relevant publications on the development and/or improvement of polymer membranes for water treatment, evidencing a potential for the emergence of new research groups in the country.

Even with the robust consolidation of the commercial membrane industry, there is still room for further improvement of the membranes already in use. Chemical modifications through particle doping or interfacial polymerization techniques have proven to be viable alternatives to increase membrane performance, whether to reduce deposits or to increase the water flow.

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Received on 8-02-2022 Accepted on 09-03-2022 Published on 21-03-2022

https://doi.org/10.6000/1929-5995.2022.11.01