Functional Polymer Materials for Energy Applications

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This entry provides insight into the recent energy applications of polymers.

polymer/functional polymer applications | energy | solar cells | fuel cells | supercapacitors | Enhanced oil recovery

1. Background

An increasing interest in the development of functional materials has led to the appearance of so-called smart polymers, which have demonstrated their practical performance in a wide range of application fields. These technical polymers are successfully gaining a growing number of recipients in the field of renewable energies, medical diagnostics, water treatment, pollution control, environmental protection, and food safety, thanks to their high sensitivity, diversity, specificity, and capacity for analysis in real time [1][2][3][4][5][6][7]. Some polymers are active and functional in nature, but others need to be modified to improve their impact and functionality. Several recent methods and techniques have been developed for the functionalization of the surfaces of synthetic and natural polymers [8][9][10][11][12]. Indeed, the terminal groups of the surface of a polymer could be linked or modified by reactive functional groups. Secondly, different molecules, oligomers, or active/bioactive polymers can be grafted to the surface, thus offering new desired properties which match the requirements of a targeted use [13][14][15][16][17]. Because of their inert character, polymeric surfaces need to be pre-activated before proceeding to their functionalization. This pre-treatment will give them an active surface for the immobilization of the various active agents. This surface activation could be performed chemically by grafting different active functions and branches, or physically, via different techniques, such as plasma treatment, laser treatment, UV irradiation, ozonolysis, electron beams, etc. [18][19][20][21][22][23][24]. Functionalization of polymeric surfaces is generally provided chemically either via covalent bonds and low energy interactions [25][26][27], or by non-covalent physical attraction, such as the adsorption of pollutants [28][29], antibacterial biomaterials [30][31][32], and drug delivery systems [33][34][35]. Covalent chemical functionalization remains the most interesting and the most advantageous. Indeed, it ensures a good durability of the active ingredients and a good stability of the active principle before and after its applied action. The chemical grafting of polyfunctional molecules or macromolecules and the functionalization via spacer compounds increases the efficiency of the polymeric surfaces by conferring them more active and spaced functions, therefore making them more effective and relevant.

Below is an overview of recent advances in polymers and functional polymeric materials and their exploration in the development of various applicative fields and industrial equipment (**Figure 1**).

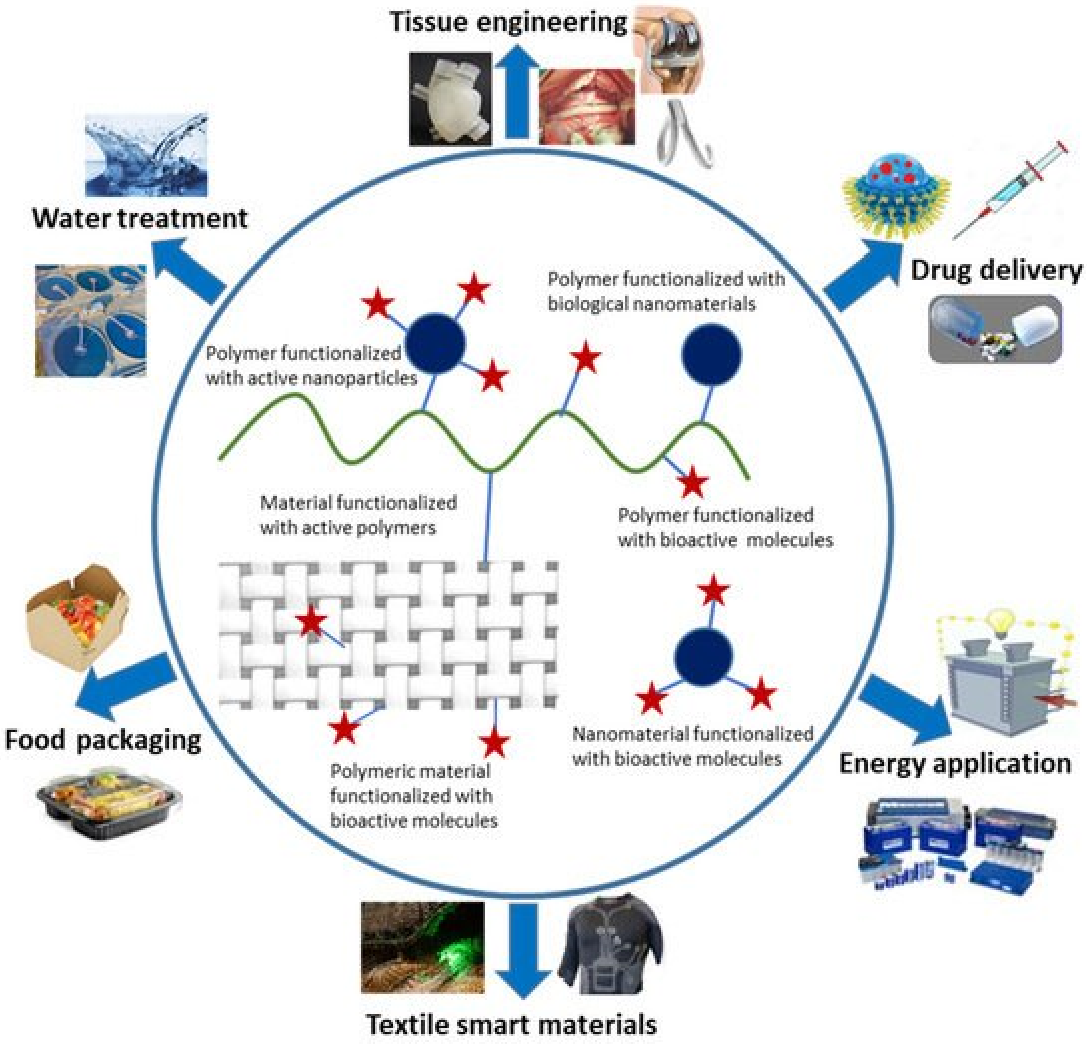

Figure 1. Applicative fields related to functional polymeric materials.

2. Energy Applications of Polymers

Currently, energy and sustainable energy have increasingly gained a leading position as the most important global concerns in view of the increased depletion of fossil fuels. Material and nanomaterial-based polymers and their composites are investigated in many various applications related to energy storage and production (**Figure 2**), including batteries, solar cells, super-capacitors, domestic tools, vehicles, fuel cells, biomedical equipment, and surgical appliances [36][37][38][39][40][41][42][43][44]. Conducting polymers are organic polymers that can conduct electricity, and they also may be used as semiconductors. Generally, the class of polymers known as characteristically conducting polymers, or electroactive conjugated polymers, were developed about 20 years ago, and their ability to conduct electricity is due to the occurrence of delocalized molecular orbitals. In addition to their conduction properties, they also exhibit interesting characteristics, such as electronic, magnetic, wetting, optical, mechanical, and microwave absorption properties. Conducting polymers (CPs) have received a lot of attention due to their economic importance, good environmental stability, and electrical conductivity, as well as their useful mechanical, optical, and electronic properties. Generally, conducting polymers have different nanostructures with a higher specific capacitance and may constitute an alternative in the development of new-generation energy storage devices [45][46][47][48][49][50]. There are many types of conducting polymers that have the ability to conduct electrical current. These conducting polymers generally are classified into three principal groups: ionic conducting polymers [51][52][53], intrinsically conducting polymers (ICPs), which also are known as synthetic metals [54][55][56] and conducting polymer composites [57][58][59][60].

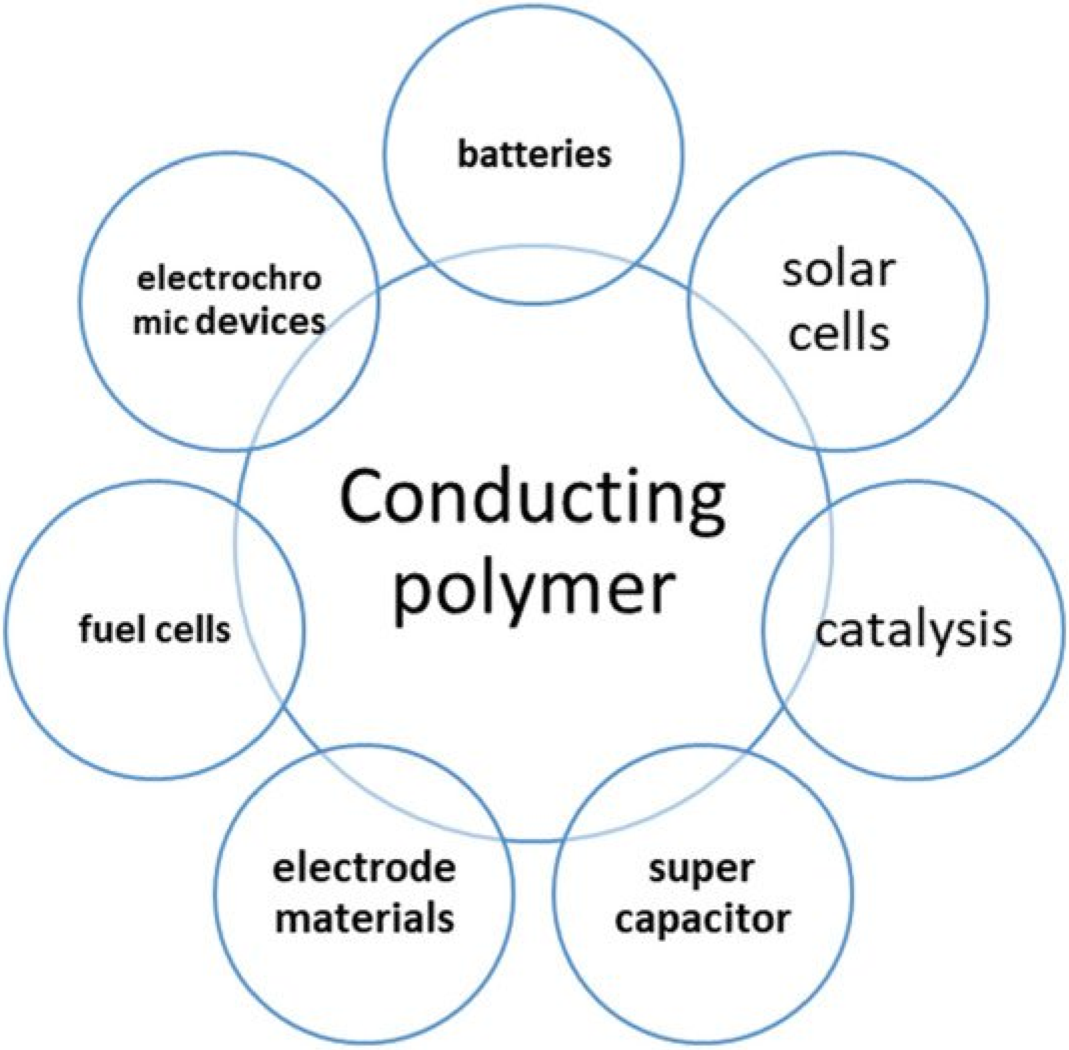

Figure 2. General applications of conducting polymers.

This distinctive type of polymer has been used in many important applications in the fields of the production and storage of energy, such as in energy assembly, energy storage, solar cells, batteries, photocatalysis materials, electrode materials, electrochromic devices, dye-sensitized electric cells, light emitting and sensing devices, and perovskite electric cells. They also have been used in other important applications, including as p-type conducting parts in thermoelectric generators, as well as being the polymer composites that are used in thermoelectric generators, piezoelectric materials, triboelectric generators, and super capacitors [61][62][63][64][65][66][67][68][69][70][71][72][73][74]. **Figure 2** shows the general applications of these conducting polymers.

Polyacetylene, polypyrrole, polythiophene, and polyaniline are examples of intrinsically conducting polymer ICPs. Among the existing conducting polymers, polyaniline has attracted considerably more attention than other types of polymers in recent years because of its superior properties, which include its ease of synthesis, unvarying conduction mechanism, and superior resistance to the effects of oxygen and water [75][76][77].

Recently, new types of conducting polymers have appeared and have proven to be effective in several fields and applications.

2.1. Batteries as an Energy Storage Application of Polymers

Many organic polymers can retain and store energy when they charged with electric current, and this energy can be used when it is needed, making it a general area for continuous and sustainable investment in both the short term and the long term. Currently, the most common battery systems are based on the Li-ion technology. This technology was proposed by M. S. Whittingham in 1976, and it was commercialized by SONY in 1990. Additionally, in the 1980s, conducting polymers were extolled as promising materials for the next generation of environmentally benign and efficient batteries. In the late 1980s, Bridgestone-Seiko and VARTA/BASF initiated their sales of commercial batteries that were based on polypyrrole and polyaniline, respectively [78]. One of the most intensively studied conjugated polymers for energy storage applications is polypyrrole, which also was used as an anode material to manufacture an aqueous Li-ion battery in conjunction with a $LiCoO_2$ cathode [79][80]. Polythiophene has been of interest to electrochemists for decades. The first battery with polythiophene as an active material was produced and described in 1983. Recently, poly(3′-styryl-4,4″-didecyloxyterthiophene), with a maximum capacity of 45 Ah kg^{-1}, and poly(4,4″-didecyloxyterthiophene), with a maximum capacity of 95 Ah kg^{-1}, were used as anode materials in combination with a polypyrrole cathode. Another type of polymer that was used in an earlier period consisted of polyaniline (PANI) pellet electrodes with different redox states. In addition, polyacetylene usage for anodes and cathodes and a PEO-based electrolyte were presented in 1981. Also, as recently shown by Zhu et al. [81], the bipolar active material known as poly(para-phenylene) can act as both a cathode and an anode. Many organic polymers can retain and store energy when charged with electric current, and the energy can be used when needed, making it a general area for continuous and sustainable investment in the short and long term. The ultrafast high energy density, long-term stability, and charge–discharge behavior are unique features of supercapacitors, which have attracted considerable attention recently. Different supercapacitors have emerged as efficient energy storage devices, showing wide applications in several fields, including electric vehicles and continuously automatic production power supplies, etc. [82][83][84][85][86]. These supercapacitors exhibit a higher specific power when compared to lithium-ion batteries. The electrodes of these supercapacitors are materials that are based on metal oxides but mainly on conductive polymers [87][88][89][90]. These conductive polymers have shown an excellent specific capacity and their low cyclic stability has been lately overstated by the investigation of nanocomposites which was based on conducting polymers [91][92][93].

2.2. Solar and Fuel Cells as an Energy Production Application of Polymers

Natural resources will be exploited for a clean environment and a good life in different countries. The importance of solar cells in the production of clean and sustainable electric power is attributed to places that government services do not reach or when the production of energy from the sun becomes cheaper than other sources. Silicon solar cells are widely used, but there is considerable research being done with the aim of providing less expensive solar cells, such as polymer solar cells and perovskite solar cells. [94][95][96][97].

Polymer solar cells, also known as plastic solar cells, use conjugated polymers as light absorbers, electron donors, electron acceptors, and/or hole transport materials, and these solar cells have been investigated for twenty years. A typical polymer solar cell contains a donor/acceptor bulk-heterojunction, a light-harvesting layer that is sandwiched between the electron and hole extraction layer, then the anode and the cathode. When polymer solar cells were first developed, their structure was similar to a conventional silicon-based solar cell with a planar junction. People believe that this device works as a P-N junction solar cell, based simply on its organic p-type and n-type semiconductor material coatings. At this point, the polymer functions as a photoactive layer for light absorption, charge generation, and transport [98][99].

Nowadays, various electrochemical reactions have been investigated in the direct conversion of chemical energy into electricity, in the context of fuel cells. These fuel cells have recently experienced great progress in their application for the production of electric vehicles [100][101]. Indeed, direct methanol fuel cells (DMFCs) have shown great potential in various energy applications, due to their energy conversion performance, high fuel portability, and eco-friendly aspects [102][103][104]. Several parameters influencing the efficiency of DMFCs have been reported, and the effects of the electrocatalysts used have been widely studied. These electrocatalysts are mainly conducting polymers, having primarily 1D and 2D nanostructures [105][106][107][108][109][110].

3. Oil and Gas Applications

Enhanced oil recovery (EOR), also known as tertiary recovery, is the most commonly used method to extract crude oil from an oil field when it cannot be extracted otherwise [111][112]. EOR can extract 30 to 60% or more of the oil from a reservoir. Due to the decrease in the discoveries of oil over the past few years, it is believed that enhanced oil recovery technologies will be vitally important, by ensuring the extended use of oil to generate energy. One of the reasons for this is due to the shortage of current oil resources and the difficulty associated with identifying new oil fields. Polymers have an important role in the application of enhanced oil recovery technology, especially surfactant and hydrogel polymers. Surfactant polymers are injected into the reservoir to reduce the interfacial tension between oil and water, which allows recovery of the oil that is trapped by the rocks in the reservoir, thereby increasing the production of oil. A hydrogel polymer is injected into the reservoir to increase the viscosity of the fluid that contains water, making that fluid more difficult to flow than the oil, thereby increasing the production of oil. The most common polymer that is used for this application is one or more of the polyacrylamide group [113][114]. A typical polymer flood project involves the mixing and injecting of polymer over an extended period of time until about 30 to 50% of the pore volume of the reservoir has been injected. The addition of polymer into the reservoir increases the viscosity of water and reduces the relative permeability of the water in the reservoir, thereby increasing the recovery of oil due to the increase in the fractional flow.

Hydrogel polymers have been used for many years to control the mobility of the injected water during enhanced oil recovery applications. These polymers are non-Newtonian (also called pseudoplastic) fluids because their viscosities are a function of the shear rate. They usually are used with surfactants and alkali agents to increase the sweep efficiency of the tertiary recovery floods [115][116][117]. It is important to select the appropriate polymer for a given area. Thus, the permeability of the reservoir and the viscosity of the oil are used to determine which polymer has the optimum molecular weight. The composition of the rock and the extent of adsorption of the polymer are used to determine the best degree of hydrolysis.

3.1. Polyacrylamides

The synthetic polymer used in enhanced oil recovery applications is almost always one of the polyacrylamides. A variety of these products is available from several manufacturers. In general, the performance of a polyacrylamide depends on its molecular weight and its degree of hydrolysis [113][114][118]. Partially hydrolyzed polyacrylamide (HPAM) is one of the polyacrylamide group, and it has the shape of a straight chain polymer of acrylamide monomers, some of which have been hydrolyzed. The HPAM is the polymer most often used in enhanced oil recovery applications, due to its relatively low price and good viscosifying properties [119].

3.2. Xanthan Gum/Biopolymer

Xanthan gum is a manufactured polysaccharide that is generally referred to as a biopolymer. It is produced by the microbial action of xanthomonascampestris on a substrate of carbohydrate media, with a protein supplement and an inorganic source of nitrogen. It is well known that xanthan gum has an excellent performance in high salinity brine. It is relatively compatible with most surfactants and the other injection fluid additives which are used in tertiary oil recovery formulations. The biopolymer is usually injected along with an effective biocide, to prevent microbial degradation [120]. Recently, a supramolecular system by self-assembly of xanthan gum with anionic or cationic surfactants and β-cyclodextrin has been developed. This composite polymer system has shown thermal and bio-stability, and greater viscoelasticity in brines, and thus confirmed its potential as a promising tool for enhanced oil recovery applications [121].

3.3. Superabsorbent Polymer Composites for Enhanced Oil Recovery

Superabsorbent polymer composites are three-dimensionally crosslinked hydrophilic polymers reinforced by clay, and they are capable of swelling and retaining huge volumes of water in this swollen state [122][123]. Superabsorbent polymer composites have been used as plugging agents in some oil fields in China to meet the need of enhanced oil recovery [124]. After operating for a year, in which water flooding was a perpetual problem, the water content in the crude oil increased, and this decreased the oil output. The high water content in crude oil can cause many problems, such as increased corrosion, increased amounts of sand, and the formation of emulsions that must be disposed of. Based on the results of this research, it was concluded that, when compared to the existing polymer, the superabsorbent polymer composite had good mechanical, thermal, and rheological properties. Recently, pH-sensitive poly (acrylamide-co-methylenebisacrylamide-*co*-acrylic acid) hydrogel microspheres immobilizing silica nanoparticles have been synthesized by reverse suspension polymerization. The prepared hybridized polymeric composite exhibited a significant improvement in the swelling property as a function of the change in pH and showed a 23% increase in the oil recovery factor [125]. Even so, additional advanced studies should be done to determine whether these different polymers could be used effectively for enhanced oil recovery [126].

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