Synthesis of Polymers for Electrospun Nanofiber Membranes

Subjects: Polymer Science

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The use of nanofiber a filtering medium is well established, and the electrospun nanofiber have several applications such as electrospun fibers for air purification and air filtration media. The different characteristics of nanofibers as morphologies, mechanical and optical properties, thermal stability, electrical conductivity, photocatalytic activity and bioactivity underlie their macromolecular structure and chemical composition.

Keywords: electrospinning ; air purification ; filtration

1. Polymethyl Methacrylate (PMMA)

The PMMA is a transparent thermoplastic polymer, obtained from methyl methacrylate (MMA) and an ester of poly(methacrylic acid) [1]. This polymer is usually synthesized by the radical polymerization of MMA, and anionic initiations, polymerization by the addition and atoms transfer radical polymerization (ATRP) are also available [2][3]. The polymeric chain contains hydrophobic (methylene) and hydrophilic (carbonyl) groups in each monomeric unit [3]. This polymer could be modified to enhance the capture of VOCs [4] using cyclodextrins (as α-cyclodextrin (α-CD), β-cyclodextrin (β-CD) and γ-cyclodextrin (γ-CD)) due the ability to form host-guest inclusion complexes). In addition, the PMMA shows potential as an encapsulation material due its high chemical stability, biocompatibility and nontoxicity [5].

2. PVP Polyvinylpyrrolidone

Polyvinylpyrrolidone (PVP), polyvidone or povidone is a water-soluble polymer synthesized from monomers of N-vinylpyrrolidone [6]. The Reepe's reaction is a convenient process that allows people to obtain soluble polyvinylpyrrolidone. The synthesis strategy initially uses acetylene and formaldehyde to obtain 1,4-butine diol, which is later hydrogenated to butane diol. Butyrolactone is obtained by oxidative cyclization and the subsequent reaction with ammonia afford, pyrrolidone. Finally, the vinyl group is introduced using acetylene to form N-vinyl-2-pyrrolidone-2.

The radical polymerization in water or 2-propanol, using hydrogen peroxide, AIBN or organic peroxide as initiators, is the main mechanism of synthesis. Give that the molecular weight of PVP is regulated by the concentration of hydrogen peroxide, the concentration of alkali hydroxide and copolymerization processes can be obtained with a lower molecular weight, insoluble polyvinylpyrrolidone (Crospovidone) and vinylpyrrolidone-vinyl acetate copolymer (Copovidone), respectively [7][8].

PVP is a versatile polymer with interesting and convenient features, it has an excellent solubility in solvents of different polarities, and it is used to stabilize suspensions and emulsions. PVP is a polymer recognized as safe by the Food and Drug Administration (FDA), it is a biocompatible and non-toxic polymer widely used in food industry, medicine, pharmaceutical and biomedical applications [8][9][10]. In particular, PVP showed effective particulate matter ($PM_{2.5}$) capture in a transparent air filter, and development was by the electrospinning method. The study of PM capture evidences a correlation between the type of polymer and the dipole moment where PVP (2.3 D) and PAN (3.6 D) have a better capture of PM 2.5 [11].

3. Polyacrylenitrile (PAN)

PAN and copolymers of PAN are polymers with versatile and multipurpose applications. Due to its high carbon yield (up to 56%), PAN is used as a carbon fiber precursor, and taking into account that it has interesting chemical, mechanical and thermal properties that allow for electrospun nanofibers and prepare carbon nanostructure microspheres. Nanocomposite fibers and polyacrylonitrile blends can be used in the manufacture of protective materials, technical textile, air filtration material, antimicrobial nanofibers spun for water treatment, electrochemical sensors, drug delivery, among others [12][13]. PAN can be synthesized by free radical vinyl polymerization, heat or by a catalyst from acrylonitrile monomer and was marketed by DuPond as-spun fiber around 1941 [12]. This polymer can also be synthesized by atom transfer radical polymerization, radicals catalyst and anionic polymerization with butyllithium that yield atactic polymers [13][14][15][16]. Due to its high carbon yield (up to 56%), PAN is used as a carbon fibre precursor, nanoparticles by the dispersion/emulsion polymerization process, electrospun nanofibers and carbon nanostructure microspheres with several applications such as antimicrobial nanofibers spun for water treatment, electrochemical sensors, supercapacitors materials, drug adsorption and air filtration media [16][17][18][19][20][21].

4. Polystyrene (PS)

PS is an aromatic hydrocarbon polymer that results from the addition of polymerization of the styrene monomer [22]. Modern PS production began in the 1970s due to the continued utility of the product and several applications ranging from food and medical packaging to home insulation [23]. Structural properties such as tacticity, molecular weight, mechanical strength, water and oxygen barrier, dimensional stability and thermal stability have attracted great interest from academicians and industrialists. Nevertheless, the disposal of these products creates environmental pollution because of their nondegradable nature. In this sense, a series of reviews and new technologies propose their recycling and reuse by mechanical (new nanocomposites), chemical (photodegradation and photostabilization) and thermal recycling (pyrolysis) [24][25][26][27]. Particularly, PS allow to build by electrospinning process fibers and nanofibers from polymer solution. The effect of PS concentration, applied voltage and spinning distance generate several morphologies of fibers with convenient mechanical properties [28][29][30]. Some of the applications based on PS include the nanofiber membrane with superhydrophobicity and superoleophilicity for the selective separation of water and low viscous oil [31], functionalization with acrylamide using plasma by development electrospun PS nanofibers [32], electrospun PS nanofibers as novel adsorbent to transfer an organic phase from an aqueous phase [33][34], grooved PS fibers by electrospinning and their effect in solvents [35] and PS nanofibers applied in the filter media [36].

5. Polyvinyl Alcohol (PVA)

PVA is a water-soluble synthetic polymer, prepared by the hydrolysis of polyvinyl acetate in ethanol with hydroxide [37], unlike most vinyl polymers, where the polymerization is developed by the corresponding monomer (vinyl alcohol). PVA is a biocompatible polymer used in biodegradable packing for food preservation, skin care applications and potential biomedical applications [38][39]. However, the tendency to absorb moisture limits its use under high moisture conditions. In this sense, several studies seek to improve its properties development blends with other polymers and additives such as citric acid, succinic acid, and tartaric acid [40][41].

6. Polypropylene (PP)

The synthesis of PP from propene by chain-growth polymerization has been known since the 1950s and was initially studied by Hogan and Banks. The potential applications of PP show a dependence on mechanical properties and thermal resistance that were improved by relevant advances of Natta and Ziegler, who developed a stereospecific polymerization using organometallic catalysts arising isotactic PP [42]. Considering that PP is a cheap polymer with excellent processability, chemical resistance, and moisture barriers, the chemical development favored the global industrial production of PP, which was 50 Mt in 1976 and grew to 360 Mt in 2018 [43]. However, the synthesis and functionalization of PP is an interesting current study area, where the obtention of novel polymers with different tacticity allow for potential applications in textile, automotive, cosmetics, and consumer packaging. In this sense, the polydispersity and molecular weight are controlled using transition metal (N,N-dietil hafnio) and metal alkyl chain transfer agent as $ZnEt_2$ to produce amorphous atactic polypropylene (a-PP) with narrow polydispersity and molecular weights of 12.6 kDa to 111 kDa [42]. Moreover, PP shows interesting and convenient mechanical properties as polyethylene–polypropylene blends and polypropylene nanocomposite fibers [43][44].

7. Polylactic Acid (PLA)

Lactic acid is the building block for the polymerization of PLA. The synthesis can be performed by different methods as direct condensation polymerization and polymerization through lactide formation and azeotropic dehydration condensation [45][46]. The enantiomers of lactic acid (L-(+)-LA and D-(-)-LA) are employed indistinctly in industrial production, and the polymer obtained is classified as an aliphatic polyester due to ester bonds that connect the monomer units. This structural characteristic plays a key role in non-toxic degradation process, applications in biomedical field and development of renewable and biodegradable materials [47]. However, the convenient mechanical and thermal properties allow for the development of nanofibers prepared by electrospinning that have morphological and structural features for biological applications like a scaffolds for tissue engineering, nanofibers of thin films of PLA/paclitaxel as molecular carriers for the sustained release of cancer therapeutics and electrospun PLA-cyclodextrins composite for Simultaneous High-Efficiency PM and VOC Removal [48][49][50][51].

8. Acrylonitrile Butadiene Styrene (ABS)

ABS is a thermoplastic copolymer consisting of three different monomer units, acrylonitrile (ACN), butadiene (BTD) and styrene (STE) [52], where their proportions can vary from 15% to 35% CAN, 5% to 30% BTD and 40% to 60% STE. The monomers in the polymeric chain play a different role, the nitrile group provides strength, ACN contributes hardness, rigidity and heat deflection temperature, and butadiene provides toughness and ductility at low temperatures. In this sense, ABS combines the resilience of polybutadiene with the hardness and rigidity of polyacrylonitrile and polystyrene [53]. Two methods are used for the preparation of ABS copolymer, the mechanical blending of styrene-acrylonitrile resin (SAN) with a butadiene base elastomer butadiene/acrylonitrile rubber and grafting of styrene and acrylonitrile onto PB [54]. The preparation of ABS membranes is an interesting field of study due the permeate flux, rejection of the pollution indices and thermal resistance, flowability, and emissions of volatile organic compounds (VOCs) [55][56]. Moreover, electrospun ABS nanofiber films have been developed as a nanosorbent for head space thin film microextraction of HAPS with applications in samples of water or urine, and showed excellent extraction efficiency and nanofibers membranes for air filtration media [57][58].

9. Polyurethane (PU)

PU are synthesized in a single step by reacting diisocyanates, polyols and catalyst as DABCO, metallic soaps or dibutyltin dilaurate [59][60]. The main aliphatic isocyanates for the synthesis of PU are diphenylmethane diisocyanate (MDI) or toluene diisocyanate (TDI), hexamethylene diisocyanate (HDI) or isophorone diisocyantate (IPDI). However, the polyols can be polyether polyols and polyester polyols as ethylene glycol, propylene glycol, poly-ethylene propylene oxide, 1,4-butane diol and 1,6-hexane diol [61]. PU shows important types of applications and the development of versatile materials as thermoplastics, foams, powder coatings, paints, elastomers, and insulators [62][63][64]. However, the preparation of polyurethane nanofibers by electrospinning is a field of interesting study, due to vast possibilities for functionalization with high surface area to volume or mass ratio, ease of use, adaptability and potential applications in biomedical, filtration technologies, sensors and nanoweb lamination based on electrospun PU polymer nanofibers [61][65][66][67].

10. Polyethylene Glycol (PEG)

PEG, also known as polyethylene oxide (PEO) or polyoxyethylene (POE), depending on its molecular weight, is an polyether polymer, initially produced by the reaction of ethylene oxide with water, ethylene glycol, or ethylene glycol oligomers [68]. The reaction is a catalyst by alkalis or metal oxides that affect the low polydispersity and growing polymer chain in the polycondensation process [69]. Additionally, these polymers also are considered green organic solvents, and are promising solvents for sustainable organic synthesis [70] and have been used for the development of eco-friendly reactions [71]. PEG have also been used to prepare novel PEG derivatives as PEGylated−peptide biopolymer conjugates, hydrogels of PEG/DEPEG, PEG-tosylate, -mesylate, -bromide or aldehyde and HS–PEG–alkyne [69][72][73][74][75].

In combination with other polymers, they have been used for different applications, for example, electrospun nanofibers of polyamide-PEG have been used for headspace solid-phase microextration, blend with polycaprolactone (PCL) and poly(ethylene glycol) have been used to improve materials of human osteoblast maturation, hydrophilic–hydrophobic terpolymers containing PEG for tissue engineering and electrospun cellulose acetate butyrate/polyethylene glycol (CAB/PEG) composite nanofibers biodegradable that enhanced the cell adhesion [76][77][78][79][80].

11. Polyethylene Terephthalate (PET)

PET is a thermoplastic polymer widely used to make plastic bottles, polyester yarn, microfiber towels, cleaning cloths and a wide variety of plastic products. PET can be synthetized by the direct reaction of Fischer esterification between terephthalic acid and ethylene glycol or transesterification reaction where one ester is transformed into another by reacting dimeth ylterephthalate with ethylene glycol [81]. A big problem with the production of PET is that it uses large amounts of derivatives of petroleum, making it an environmentally unfriendly polymer [82][83]. In response to the potential polymer pollution several applications have been proposed by chemical and mechanical recycling [84][85][86][87]. In this sense, recycling of PET has been studied for the development of aggregates such as the synthesis of copolyesters

(PET/poly-Ɛ-caprolactone), synthesis of PET from biomass-based in ethylene glycol and glycolysis [88][89][90][91]. Different types of PET nanofibers have been developed with different applications, for example PET/SiO_2 nanofibers membrane for applied to needle-felt filters, PET nanofibers loaded with silver nanoparticles for antimicrobial applications, PET nanofibers chemically modified with silane molecules for electroless deposition methods with copper and PET nanofibers as new adsorbent for micro-solid phase extraction of chromium(vi) in environmental water samples [92][93][94][95].

12. Polyamide-6 (PA-6)

PA-6 is a versatile thermoplastic polymer, very popular for the excellent mechanical properties such as impact strength, stiffness and high thermal degradation temperature, due the strong interchain attraction derived from the polarity of amide groups [96]. Among the different types of polyamides, nylon 6,6 is one of the most well known and commercialized aliphatic polyamides [97]. Several methods of polymerization have been used to synthetize PA-6, among them the transesterification by combination [98], direct polycondensation with triphenylphosphine melt-polymerization of block copolymers consisting of PA6 and Poly(N-cyclohexylmaleimide) (PCHMI) [96] and anionic ring-opening and condensation reactions [99]. In the same way, different monomers can be used, such as poly(4,4′-diphenylsulfone terephthalamide) (PSA), poly(*p*-diphenyl oxide terephthalamide) (POA), poly(*p*-diphenylmethane terephthalamide) (PMA), and isophthaloyl chloride (IPC) to obtain nylon 6,6 copolymers [100]. Several applications have been developed taking into account PA-6 as an air filter for multi-level physical sieving of airborne particles via sequential electrospinning [98], as well as PA-6 nanofibrous nonwovens membranes, useful for separation systems with good mechanical properties, such as a high-tensile strength and elongation [101].

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