EMULSION TEMPLATED CROSSLINKED FIBROUS MEMBRANES *via* NEAR-GEL RESIN ELECTROSPINNING

Pramod Manikant Gurave

2018TTZ8478

ABSTRACT

Fibers have become essential to human civilization, starting with basic usage to advanced applications. The advancements in textile and polymer science led to the production of various forms of fibers such as yarns, fabrics, nonwovens, and three-dimensional spacer fabrics. Since decades, there has been a surge in interest in producing ultra-thin, one-dimensional structures of fibers, called as nanofiber. The nanofibrous material offers excellent properties such as high aspect ratio, interconnected porosity, flexibility, better mass transport, and enhanced surface area to volume ratio. Technologists have developed various techniques to produce nanofibers from natural and synthetic sources. Among them, electrospinning is the most facile and proven platform to produce transdisciplinary engineered fibrous materials. These nanofibers can then be combined to create advanced two- and three-dimensional structures, like membranes, nonwovens, foams, and aerogels etc. Electrospun fibers face constraints for scalability as the electrospinning process demands preformed polymer with high utilization of hazardous organic solvent for the dissolution of synthetic polymers, which lead to environmental concerns. Moreover, electrospun fibrous materials exhibit poor dimensional stability, against organic solvents at elevated temperature, and mechanical properties which restrict its utilization in real field applications. Crosslinked fibrous materials offer excellent dimensional stability and thermal resistance along with a wide range of applications in sorption, filtration, purification, and catalysis. Direct electrospinning of crosslinked polymers is not viable due to its restricted solubility in solvents. Previous reports highlight the adoption of post-electrospinning crosslinking techniques to produce crosslinked fibrous materials. Very limited options are available for post-crosslinking of electrospun fibers, additionally, this makes the whole process multi-steps and there is no control over morphology of fibers.

Very few reports are available on *in-situ* crosslinking of fibers during electrospinning process. The direct fabrication of crosslinked fibers from their monomeric form is scantly reported

in literature. Thus, there is an immense need and research prospects to generate robust electrospun fibrous materials from sustainably electrospinning techniques for real field applications.

In this study, we demonstrated and developed near-gel resin (nGR) electrospinning, through which crosslinked electrospun fibers were produced directly from styrene based monomeric mixtures. The mixture of styrene and divinylbenzene was polymerized using free radical polymerization under non-inert conditions until reaching the gel point, thereby forming a flowable resin. Subsequently, the resin was electrospun in various forms such as bulk, solution, or emulsion to directly produce crosslinked fibers. The effect of variation in crosslinking density on fiber morphology was evaluated. The challenges associated with nGR bulk and solution electrospinning in achieving high crosslinking density were overcome by emulsion electrospinning technique where crosslinked fibers up to 60% theoretical crosslink density were fabricated. As emulsion electrospinning has been referred to as green electrospinning, it minimized the use of organic solvent and promoted successful production of crosslinked polystyrene-based nanofibers in presence of polyvinyl alcohol (PVA). The crosslinked fibers with core-sheath morphology were obtained through precisely optimized parameters affecting emulsion electrospinning, such as template polymer concentration, emulsifier nature and concentration, volume of dispersed phase, and reaction conditions. Through nGR emulsion electrospinning, three generations of nanofibrous membranes were produced, namely, dual crosslinked membrane, silica composite membrane and metal organic frameworks (MOF) decorated nanofibrous membrane. Dual crosslinked fibrous membranes showed selective wettability toward oil and water as they were composed of fully crosslinked core-sheath fibers. Silica composite membrane was produced via forming Pickering nGR emulsion where silica nanoparticles were used as Pickering stabilizer for producing stable nGR emulsion as well as functional moieties to improve wettability of nanofibrous membrane. Fibrous membranes were enriched with MOF content to create multifunctional MOF-decorated membranes. The prepared membranes were tested as a separation membrane toward various oil/water mixtures and emulsions. All the membrane were thoroughly characterized to evaluate their wettability behavior, anti-fouling nature and oil sorption capacity. Overall, nGR electrospinning technique developed in this work paved a new and unique way to prepare polystyrene based crosslinked electrospun fibers and can be explored for other polymeric systems to produce nanofibrous membranes for advanced applications.