Electrospun Nanofibrous Membranes

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Electrospinning is a versatile technique which results in the formation of a fine web of fibers. The mechanical properties of electrospun fibers depend on the choice of solution constituents, processing parameters, environmental conditions, and collector design. Once electrospun, the fibrous web has little mechanical integrity and needs post fabrication treatments for enhancing its mechanical properties. The treatment strategies include both the chemical and physical techniques. The effect of these post fabrication treatments on the properties of electrospun membranes can be assessed through either conducting tests on extracted single fiber specimens or macro scale testing on membrane specimens. The latter scenario is more common in the literature due to its simplicity and low cost.

Keywords: post-processing strategies ; electrospinning ; electrospun nanofibrous membrane ; mechanical properties

1. Introduction

Electrospinning is an attractive fiber fabrication technique specifically for the synthesis of nanoscale fibers and their membranes due to its simplicity and freedom to use a broad spectrum of polymeric systems. A range of parameters related to process, materials, environment and collector configuration have to be optimized in order to achieve successful electrospinning of a given polymer. Once this is done, these same parameters can be varied within the electrospinning window to alter the various properties of electrospun fibers including mechanical properties which have been the focus of this review paper.

2. Discussion

The effect of the variation of these parameters and their optimization can be gauged through the execution of mechanical tests. These tests can either be conducted on single fibers using advanced testing systems and protocols or alternatively on the membrane specimens which are in the form of web of interconnected fibers. The former needs special equipment and single fiber handling expertise, which are costly and time-consuming undertakings. The latter scheme is not only simpler and less costly, but can also give useful information about the effectiveness of the optimization scheme undertaken. The importance of such tests is twofold, as electrospun membranes often need post fabrication treatment and determination of the effectiveness of these treatments in relatively short spans of time is essential.

It has been observed that electrospun fibers collected in the form of an interconnected web or membrane either in random or aligned orientation lack structural coherence and strength needed for their effective exploitation in various application areas. This is so even though these membranes undergo an optimization at the manufacturing stage through the variation/alteration of various parameters as described earlier. A post fabrication strength enhancement strategy is therefore indispensable for all practical exploitation of electrospun fibrous membranes.

This literature survey has revealed a myriad of techniques available for the post fabrication strength enhancement of nanofibrous membranes. These include chemical as well as physical methods which can be adopted and tailored according to the requirements of the electrospun membrane in question.

Techniques like chemical crosslinking, thermal annealing, solvent dissolution, and stretching/drawing treatments are unassisted, as the first one is purely chemical, while the other three are solely physical. On the other hand, there are so called ‘assisted techniques’, such as hot pressing and hot stretching, which are thermally assisted mechanical treatment methods. These latter two lead to greater recrystallization and associated molecular rearrangement in the amorphous domains as well as fiber welding at inter fiber junctions, giving rise to higher crystallinity, alteration in fiber diameter, and improvement in structural integrity.

Following table gives a brief overview of various post fabrication treatments discussed in this study.

Table 1: Overview of post fabrication strategies for enhancement of mechanical properties of ENMs.

Nature of Treatment	Primary control Parameter	Secondary Control Parameter	Remarks
Crosslinking	Crosslinker concentration	Temperature	Crosslinker compatibility and reactivity are critical factors.
Annealing	Temperature	Duration	Temperature range should be maintained above crystallization temperature (Tc) and below melting point (Tm), which usually results in increased crystallinity. Temperatures maintained between Tg and Tm result in better strength. Temperatures maintained close to Tg result in improved elastic modulus.
Hot stretching	Temperature and stretching force	Duration	
Hot pressing	Temperature and applied pressure	Duration	Temperatures should be below Tm. Generally, temperatures lower than those used for annealing are employed. If temperature is too close to the melting point, the duration of treatment should be significantly reduced to preserve fibrous morphology.
Solvent welding	Vapor pressure	Duration	Solubility of polymer in the solvent is an important determinant, the criterion for which is: $\|\delta_s - \delta_p\| \le 2$ *.
Stretching/drawing	Draw ratio	None	In certain cases, an optional twist may also be applied.

* Hildebrand solubility parameter for solvent and the polymer are denoted as δ_s and δ_p, respectively[1] .

These changes work in tandem to improve mechanical properties such as tensile strength and modulus, while altering failure strain due to improved structural integrity in the membranes, which are among the most studied and compared parameters. At the same time, these post fabrication treatments should preserve fibrous morphology of the membranes.

Optimization of the properties during the execution of one of these chemical or physical schemes is carried out by carefully controlling the parameters and avoiding over exposure, which might result in the loss of fibrous morphology. Improvement in mechanical properties at the loss of fibrous morphology is avoided, as it results in simultaneous reduction in porosity and tortuosity in membranes. At the same time, inherent advantages associated with the use of ultrafine/nano fibers are also sacrificed. This is also one of the challenges in the selection and effective execution of one of the post fabrication strength enhancement techniques.

Certain generalized trends can be identified in the literature which help understand the effect of post fabrication treatments on morphological and mechanical properties of electrospun fibers. These findings have been summarized in Table 2.

A detailed discussion of testing protocols adopted in the literature for the comparison of untreated and treated membranes has also been provided. A uniform testing standard is far from available, and no uniform testing methodology has been adopted so far. Nevertheless, certain trends can be discerned, including a preference for uniaxial tensile testing on membrane specimens for a quick and meaningful comparative analysis of the effectiveness of the treatment scheme adopted. Single fiber testing protocols have rarely been adopted due to complexities and costs involved. A standardized testing procedure to bridge the gap between single fiber and membrane testing protocols while clearly establishing a link between the two is needed.

Table 2. Summary of the effect of post fabrication treatments on the properties of ENMs.

Nature of Treatment	**Effect of the Treatment on**					**Remarks**
	Diameter	**Crystallinity**	**Tensile Strength**	**Young's Modulus**	**Failure Strain**	
Crosslinking	No significant impact	Decreases	Increases	Increases	Usually decreases	Crosslinker concentration has significant impact on the overall properties.
Annealing	Depends on the type of polymer and annealing temperature selected (if fibers undergo melting as a result of heat treatment, diameter increases)	Usually Increases (when treatment carried out above crystallization temperature)	Increases	Increases	Depends on the type of polymer and annealing temperature selected	A range of temperatures selected between Tg and Tm or Tc and Tm can have diversely different effects on the properties of different polymers. If treatment is carried out at T>Tc, crystallinity increases.
Hot stretching	Decreases	Increases	Increases	Increases	Depends on the type of polymer and hot pressing conditions	

Hot pressing	Increases	Increases	Increases	Increases	Depends on the type of polymer and hot pressing conditions	
Solvent welding	Unaffected	Unaffected	Increases	Increases	Usually increases	Failure strain increases when plasticization effect of the solvent dominates.
Stretching/ drawing	Decreases	Increases	Increases	Increases	Decreases	

3. Conclusion

This study discusses in detail the control of key parameters during electrospinning which affect the mechanical properties of membranes, various testing protocols, and procedures which can be adopted to assess mechanical strength of the membranes followed by the post-processing strategies for the enhancement of mechanical properties of ENMs. It is expected that this review will enable more innovative research on post processing strategies of ENMs by providing thorough understanding of the comparative merits of these techniques for a particular electrospun fibrous membrane. An optimized treatment methodology may also be devised by hybridizing one or several of the schemes for greater crystallinity and enhanced mechanical properties while preserving the fibrous morphologies.

References

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