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Surface Morphology Analysis and Mechanical Characterization of Electrospun Nanofibrous Structure

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Abstract The extraordinary properties of nanofibrous structure have gained ever-increasing appeal as an attractive candidate in a myriad of applications, especially for the water filtration. This type of structure has permeability due to its porous structure. Electrospinning is one of the most viable approaches in fabricating nanofibrous web that exhibits novel and outstanding performance in membrane separation as compared to those produced through conventional methods. Thus, the optimization of electrospinning processes is actively pursued by many researchers in order to obtain the best structure suitable for real-life applications. In this study, the surface morphology analysis and mechanical characterization of nanofibrous structure are addressed. For this purpose, polyvinylidene fluoride (PVDF) is considered. The polymeric nanofibrous structures are fabricated through electrospinning process were varied and the resulting morphology of the structure were observed using SEM. In addition, the macroscopic mechanical responses of the structure were probed by means of tensile tests with special attention given to membrane anisotropy and behavior under cyclic loading.

1. Introduction

Poly(vinylidene fluoride), or more commonly known as PVDF is a highly non-reactive material produced from the polymerization of 1,1-difluoroethylene. The possession of outstanding properties such as high chemical resistance, good thermal stability and excellent mechanical properties contribute to its popularity in many applications such as water treatment, pollutants removal, battery separator, membrane distillation, etc.

In recent years, electrospinning arises as a popular method for the fabrication of PVDF structure due to the ease of fabricating very fine fibers down to nanometer size. These polymeric nanofibers exhibit improved properties compare to fibers in the micron size where the structure consists of very large surface area to volume ratio as well as superior mechanical stiffness and strength compare to the larger fibers. Some other reasons that make electrospinning an advantageous method are its simple toolings requirement, cost-effectiveness and also versatility. Typical electrospinning process utilizes high voltage where ultra-thin fibers are continuously formed from the polymer solution through the electrostatic forces generated.

As far as concerned, several experimental works investigating the effects of processing parameters on the morphologies of electrospun PVDF fibers are available [1-3]. Zhao et al. (2005) [1] investigated on the effects of polymer concentration and solvent amount on the fiber surface morphology of the electrospun PVDF structure. Meanwhile, Cozza et al. (2013) [2] take into

consideration the influences of airflow rate and relative humidity during the electrospinning process, which are less likely to be explored by other researchers. Some other significant electrospinning parameters that should be highlighted include the solvent selection, feed rate, capillary-collector distance as well as the ambient temperature. On top of that, some researchers investigated the nanoscale mechanical properties of single polymer fiber [4,5] while some probed into the macroscale mechanical properties of the electrospun nanofibrous structure [1,6]. However, there are significantly less number of works focusing on the mechanical response of nanofibrous structures under cyclic loading in view of durability analysis.

Within this context, focuses of the present work are laid on the preparation and fabrication of PVDF nanofibrous structure using electrospinning technique. Moreover, the resulting surface morphology and mechanical response under cyclic loading were investigated. The paper is organized as follow. In Section 2, the experimental procedures are discussed including electrospinning, surface morphology analysis and mechanical tests. The results are presented and discussed in Section 3 while concluding remarks are given in Section 4.

2. Experimental Study

2.1 Materials. PVDF powder with an average molecular weight of 534,000 g/mol was sourced from Sigma Aldrich. N,N-dimethylformamide from Univar and Acetone from R&M Chemicals were utilized as solvents for polymer solution preparation. All chemicals were used without further treatment.

2.2 Preparation of PVDF Polymer Solution. N,N-dimethylformamide (DMF) and acetone functioned as solvents for the preparation of PVDF polymer solution. For this research, polymer concentration of 13 wt.% and 15 wt.% were investigated. PVDF powder of 13 wt.% and 15 wt.% were dissolved in a mixture of the two solvents where the ratio of DMF to acetone is fixed at 7:3. Syringe of 10 ml was used as the solution reservoir where a stainless steel needle tip was connected.

2.3 Electrospinning. An electrospinning labscale unit from Electroris was utilized for the electrospinning processes. Syringe containing PVDF polymer solution was connected to the high voltage supply while the capillary-collector distance was set to be 150 mm. A stationary electrically grounded collector covered with aluminium foil was utilized for the fiber deposition. Electrospinning started by subjecting a 13 wt.% PVDF polymer solution to a voltage of 10 kV for a duration of 10 hours to obtain sufficiently thick structure for further characterization. Subsequently, the electrospinning processes were repeated by utilizing 15 kV and 20 kV voltages. The entire process was repeated by replacing 13 wt.% with 15 wt.% polymer concentration, as indicated in Table 1.

Sample	Polymer	Voltage	DMF:Acetone	Feed rate	Capillary-collector
	concentration [wt.%]	[kV]	ratio	[ml/h]	distance [mm]
1A	13	10	7:3	0.5	150
1 B	13	15	7:3	0.5	150
1C	13	20	7:3	0.5	150
2 A	15	10	7:3	0.5	150
2B	15	15	7:3	0.5	150
2 C	15	20	7:3	0.5	150

Table 1: Six sets of processing parameters for the electrospinning of PVDF polymer solution

2.4 Characterization of PVDF Nanofibrous Structure

2.4.1 Surface Morphology Analysis. PVDF nanofibrous structures produced were examined under Scanning Electron Microscope (SEM) (Phenom ProX) to determine the surface morphology of the structures. Images of 1000× and 5000× magnifications were captured for each of

the sample for further analysis. The diameter of electrospun fibers was measured through $5000 \times$ images using ImageJ software. Subsequently, number of beads per unit area was calculated through $1000 \times$ images.

2.4.2 Mechanical Characterization. Mechanical testing was performed with Shimadzu Universal Tensile Testing Machine attached with 50 N capacity load cell. In this research, the PVDF structure with best surface morphology was subjected to mechanical testing. Subsequently, specimens with dimension of 60 mm \times 10 mm (length \times width) were cut in two perpendicular directions, i.e. horizontal and vertical from the structure and were labeled as X-direction and Y-direction respectively. Specimens from both directions were then subjected to monotonic tensile test and increasing cyclic loading test to determine the mechanical properties of the material.

3. Results and Discussion

3.1 Surface Morphology Analysis. In general, randomly oriented fibers were deposited onto the aluminium foil and the fibers morphology was observed under SEM. SEM images captured for the six PVDF structures are shown in Figure 1, for both of the polymer concentrations of 13 wt.% and 15 wt.%. Subsequently, the average fiber diameter and number of beads per unit area were obtained through the analysis of SEM images, as tabulated in Table 2.



Fig. 1: SEM micrographs of electrospun PVDF structures with 1000 × magnification.

Sample	Average Number of beads		Sample	Average	Number of beads			
	diameter	per unit area		diameter	per unit area			
	[nm]	[beads/ mm ²]		[nm]	[beads/ mm ²]			
1A	497 ± 49	320 ± 102	2A	777 ± 93	116 ± 7			
1B	295 ± 17	967 ± 27	2B	399 ± 27	695 ± 95			
1C	493 ± 36	238 ± 48	2 C	378 ± 22	129 ± 20			

Table 2: Average fiber diameter and number of beads per area for electrospun PVDF structures

By comparing the surface morphology of 13 wt.% PVDF structures (1A to 1C), sample 1B showed a distinct surface morphology where it possessed a high number of beads with very fine fibers. Similar phenomenon was observed when comparing 15 wt.% PVDF structures (2A to 2C), with sample 2B having greater bead defects and finer fibers. These results were also proven through appropriate analyses shown in Table 2.

It was suggested that an optimum range of applied voltage existed for every polymer solution which greatly depended on the polymer-solvent system [2,7]. Varying the electrospinning voltage produced similar trend on both 13 wt.% and 15 wt.% PVDF membranes. Thus, two optimum voltage ranges, i.e. 10 kV and 20 kV which promoted better surface morphology were determined.

Varying the polymer concentration appears to affect the number of bead defects as well as the fiber diameter of the electrospun membrane. Indeed, increasing polymer concentration decreases the formation of bead defect and at the meantime increases the average fiber diameter [7]. By comparing on samples with different polymer concentration but similar processing voltage (sample 1A with 2A; sample 1B with 2B; sample 1C with 2C), bead defects decreased as polymer concentration increased from 13 wt.% to 15 wt.%. Moreover, fiber diameter increased in accordance with polymer concentration except for sample 2C. This result might be due to the combination effects of increasing polymer concentration and processing voltage.

In summary, sample 2C appeared to possess the best surface morphology among the electrospun PVDF structures, due to its small average fiber diameter and low number of bead defects. For this reason, sample 2C was subsequently subjected to two types of mechanical testing, as discussed earlier in section 2.4.2.

3.2 Mechanical Testing. In this research, monotonic tensile tests were conducted on specimens from two perpendicular directions which were labeled as X and Y- directions. It was found that the resulting stress-strain characteristics of the membrane are independent of direction. Thus, the materials can be considered as initially isotropic in the plane. Due to the limitation of space, the stress-strain curve for monotonic tensile test will not be shown here.

In the next tests, specimens from X-direction were chosen for the cyclic loading tests with increasing maximum strain. During this displacement-controlled cyclic loading test, the specimen was brought back to the initial zero stress at the end of each cycle to prevent buckling of the specimen. The resulting stress-strain curve was illustrated in Figure 2(a). From Figure 2(a), elastic modulus ratio was computed and plotted against maximum strain for each cycle, as shown in Figure 2(b). Note that the elastic moduli were computed from the slope of each reloading curves. Moreover, the elastic modulus ratio was defined by the ratio between the elastic modulus of each reloading curve to the initial elastic modulus.

From Figure 2(a), two phenomena were observed as the specimen was stretched to higher strain values, which were the occurrence of permanent deformation and the increased in plastic yield limit. Meanwhile, the increase and decrease curve in Figure 2(b) indicated the changed in stiffness of the specimen as the material was stretched to a higher maximum strain. This observation suggested that two competing phenomena took place: fiber reorientation resulting to higher stiffness and the breakage of physical junctions leading to lower stiffness. Further works are needed to fully understand the observed phenomena.



Fig. 2: (a) Cyclic loading stress-strain curve, (b) Plot of elastic modulus ratio vs maximum strain.

4. Conclusion

PVDF nanofibrous structures had been successfully fabricated through electrospinning technique. Electrospun PVDF structures were subjected to surface morphology analysis where the structures were examined under Scanning Electron Microscope (SEM). Results showed that PVDF nanofibrous structure produced from 15 wt.% polymer concentration with feed rate of 0.5 ml/h, voltage of 20 kV and capillary-collector distance of 150 mm possessed the best surface morphology. The best structure was then chosen to undergo monotonic tensile test and cyclic loading test with increasing maximum strain. Monotonic tensile testing on specimens with perpendicular directions showed that the material was initially isotropic in the plane. Subsequent cyclic loading test highlighted significant permanent deformation on the material upon unloading and induced changes on the stiffness as the maximum strain increases.

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References

- Z. Zhao, J. Li, X. Yuan, X. Li, Y. Zhang and J. Sheng, Preparation and properties of electrospun poly(vinylidene fluoride) membranes. J. Appl. Polym. Sci. 97 (2005) 466-474.
- [2] E. S. Cozza, O. Monticelli, E. Marsano and P. Cebe, On the electrospinning of PVDF: influence of the experimental conditions on the nanofiber properties. Polym. Int. 62 (2013) 41-48.
- [3] Y. Liao, R. Wang, M. Tian, C. Qiu and A. G. Fane, Fabrication of polyvinylidene fluoride (PVDF) nanofiber membranes by electro-spinning for direct contact membrane distillation. J. Membr. Sci. 425-426 (2013) 30-39.
- [4] M. Boffito, E. Bernadi, S. Sartori, G. Ciardelli and M. P. Sassi, A mechanical characterization of polymer scaffolds and films at the macroscale and nanoscale. J. Biomed. Mater. Res. A 103 (2015) 162-169.
- [5] R. Inai, M. Kotaki and S. Ramakrishna, Structure and properties of electrospun PLLA single nanofibers. Nanotechnology 16 (2005) 2008-2213.
- [6] K. Hwang, B. Kwon and H. Byun, Preparation of PVdF nanofiber membranes by electrospinning and their use as secondary battery separators. J. Membr. Sci. 378 (2011)111-116.
- [7] J. M. Deitzel, J. Kleinmeyer, D. Harris, N. C. B. Tan, The effect of processing variables on the morphology of electrospun nanofibers and textiles, Polym. 42(1) (2001) 261-272.