Piezoelectric PVDF/cellulose nanocomposite membranes for energy harvesting

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INTRODUCTION

Energy harvesting captures and stores energy in ambient environment including kinetic, solar, wind and thermal forms for powering small devices such as wireless monitoring devices and wearable electronics.

Polyvinylidene fluoride (PVDF) is a semi-crystalline thermoplastic fluoropolymer with chemical composition of $(CH_2\text{-}CF_2)_n$ [1]. PVDF has three forms of phases depending on chain conformations of trans (T) or gauche (G) linkages: α (TGTG'), β (TTTT), and γ (TTTGTTTG'). The β phase in PVDF is thermodynamically more stable and is piezoelectric [2,3].

PVDF is normally mechanically stretched to orient molecular chains then poled under tension to achieve piezoelectric properties. In this work PVDF is processed using electrospinning to manufacture PVDF nanofibre membranes in form of suspension [4,5]. In addition, microcrystalline cellulose (MCC) and nanocrystalline cellulose (NCC) are incorporated as enhancement for mechanical and crystalline properties of the PVDF membranes.

The effects of the cellulose inclusion are characterised for piezoelectric, crystalline, mechanical and morphological properties. Influence of inclusion of stabiliser such as polyethylene glycol (PEG) on stability of the cellulose suspension (in PVDF/Acetone/DMAc) and on the properties of the membranes is also studied.

AIM AND OBJECTIVES

Aims:

This work is to achieve understanding of the influence of cellulose incorporation on piezoelectric, crystalline and mechanical properties of the membranes.

Objectives:

Using the PVDF solutions without cellulose inclusion as bench mark and varying cellulose type and concentration as well as inclusion of PEG (for suspension stability), this work is to investigate the effect of adding different types and concentrations of cellulose on structure (thicknesses and morphology of the nanofibre membranes, diameters of nanofibres and dispersion of the cellulose) and properties of electrospun PVDF/cellulose nanocomposite membranes (piezoelectric, crystalline and mechanical properties).

METHODOLOGY

Formulations:

A mixed solvent (Acetone and N,N-Dimethylacetamide (DMAc) with a volume ratio of approximately 2:1) is used to prepare the base PVDF solution (at a concentration of 0.096 g/ml).

1 wt% and 5 wt% MCC and NCC are incorporated in the PVDF solution with addition of 1 wt% PEG as a stabiliser in the PVDF/cellulose suspensions.

Preparation of suspensions

(1) The PVDF is dissolved in Acetone. DMAc is divided into two portions and is added into PVDF/Acetone and to prepare a cellulose/DMAc suspension, respectively. When PEG is incorporated, DMAc is divided into three portions and is added into PVDF/Acetone, MCC and the PEG powder respectively;

(2) The PVDF solution (and PEG/DMAc solution) is ultrasonicated till becoming clear;

(3) The PVDF solution is then added into cellulose/DMAc suspension drop by drop using a syringe while being magnetically stirred. For PEG inclusion, the PEG/DMAc solution is mixed with the cellulose/DMAc suspension and then the PVDF solution;

Electrospinning process

The principle of electrospinning process is illustrated in Fig. 1a [6]. The suspensions prepared are electrospun using a purpose built equipment (Fig. 1b).

Figure 1a

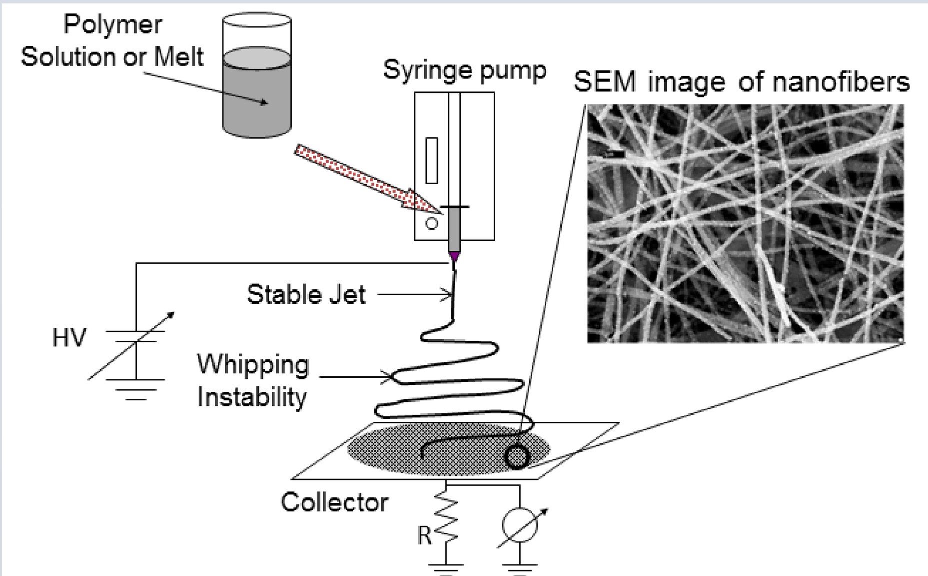


Figure 1b

Additional information: MCC20, MCC50 and MCC90 are microcrystalline cellulose with particle sizes of 20, 50 and 90 μm, information of NCCs is shown in Table below:

Cellulose ID	Resource	pH	Form	Additional Information
NCC20-2	MCC20	acidic	nanocrystalline (white gel)	needs high speed centrifuge and neutralising
NCC20-3	MCC20	neutral	nanocrystalline (white gel)	water content around 15%
NCC50	MCC50	acidic	nanocrystalline (white gel)	needs high speed centrifuge and neutralising
NCC50-2	MCC50	neutral	nanocrystalline (white gel)	water content around 15%
NCC90-2	MCC90	neutral	nanocrystalline (white gel)	water content around 15%
NCC90-12.87%	MCC90	neutral	nanocrystalline (white gel)	water content around 12.87%

Characterisations of the electrospun membranes:

(1) Piezoelectric properties: power output test and d_{33} meter measurement;

(2) Crystalline properties: X-ray diffraction (XRD);

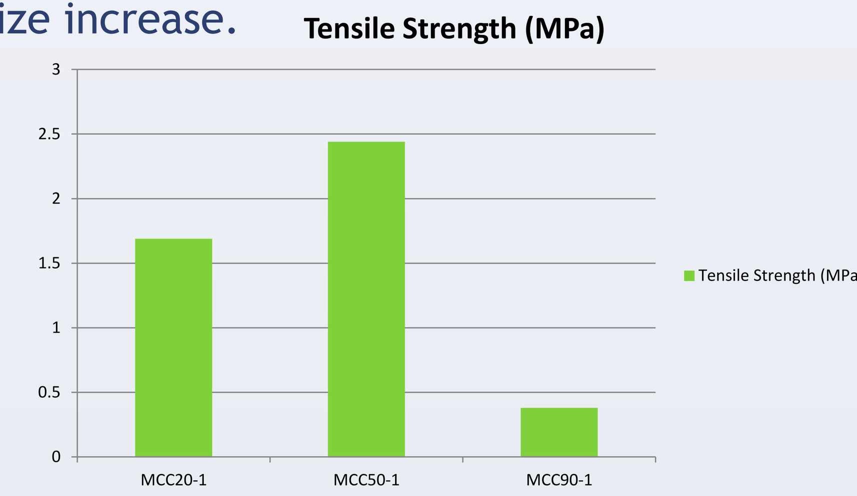
(3) Mechanical properties: tensile test;

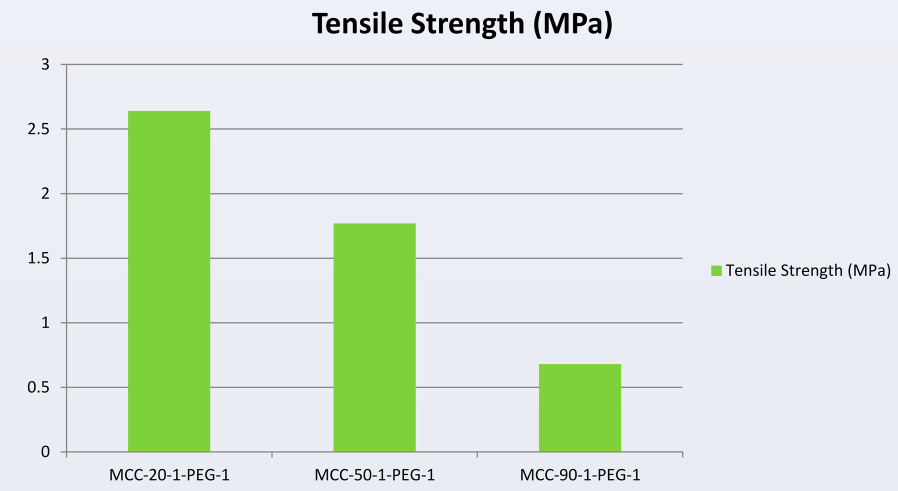
(4) Morphology: optical microscopic analysis, scanning electron microscope (SEM), micrometer for thickness and MATLAB for diameters of nanofibres.

PRELIMINARY RESULTS

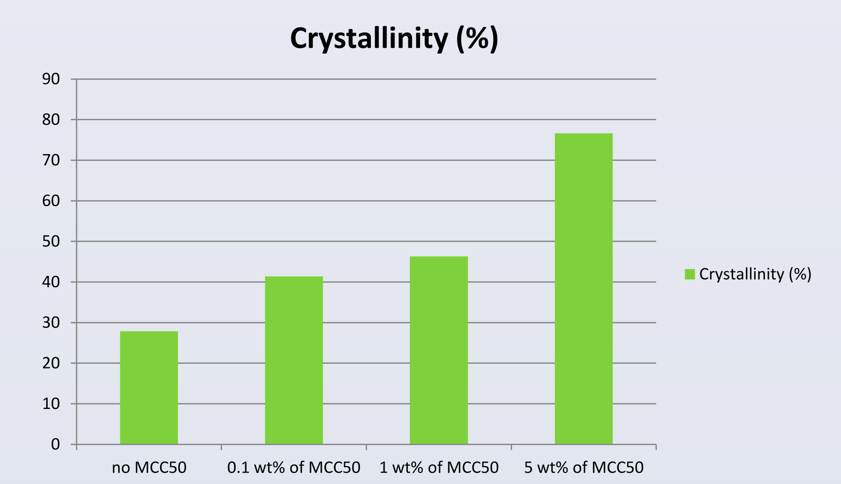
When 5 wt% MCCs are incorporated, sample with MCC50 has the largest crystallinity while sample with MCC90 has the smallest.

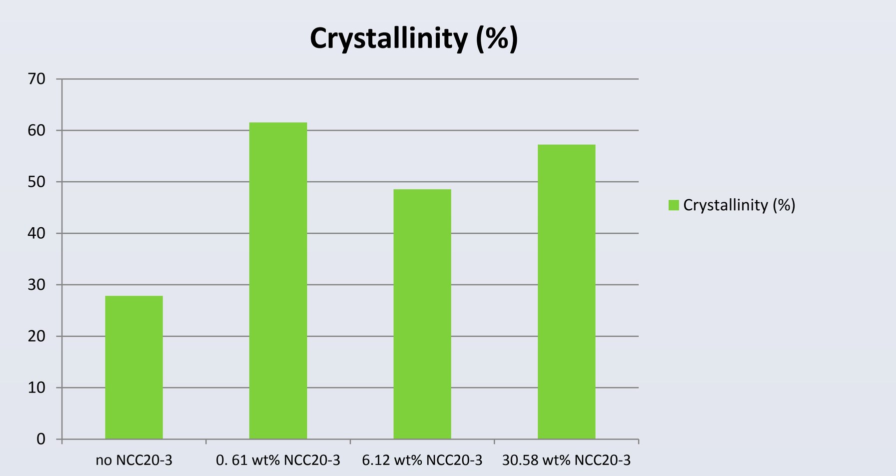
When 5 wt% MCCs are incorporated, membrane thickness decrease with MCC particle size increase.





From the figure on the left above we can see that when 1 wt% MCCs are incorporated, sample with MCC50 has the biggest tensile strength while sample with MCC90 has the smallest which is very weak. From the figure on the right we can see that when 1 wt% PEG is included, a clearer trend that tensile strength decrease with MCC particle size increase appears, strength of sample with MCC90 is still very poor.





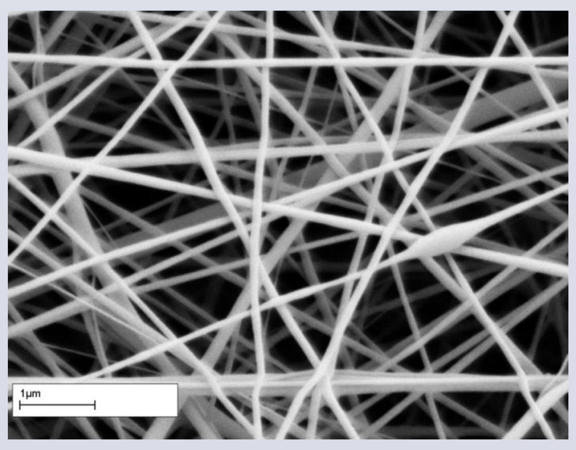
For samples with MCC20, MCC50 and NCC20-2, crystallinities increase with concentrations of cellulose increase, for samples with MCC90, NCC20-3 and NCC90-2, incorporation of certain concentrations are effective to enhancement of crystallinity and adding more cellulose is not helpful for improvement of crystallinity.

When 1 wt% PEG is included, crystallinity of samples with MCC20, MCC90 and NCC20-3 decrease.

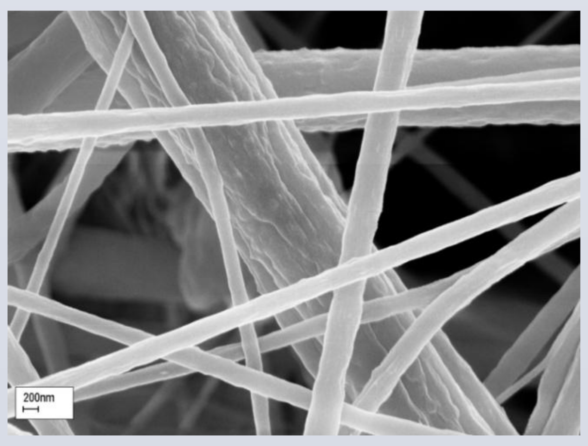
When 1 wt% PEG is included, tensile strength of sample with 1 wt% MCC20 and MCC90 increase, and one of MCC50 decrease. No matter PEG is included or not, tensile strengths of samples with MCC20 and MCC50 are improved comparing with pure PVDF, but for samples with MCC90, tensile strength decrease greatly when cellulose is incorporated.

Morphology of nanofibres is observed by using SEM, example SEM pictures of samples with MCC20 are shown below:

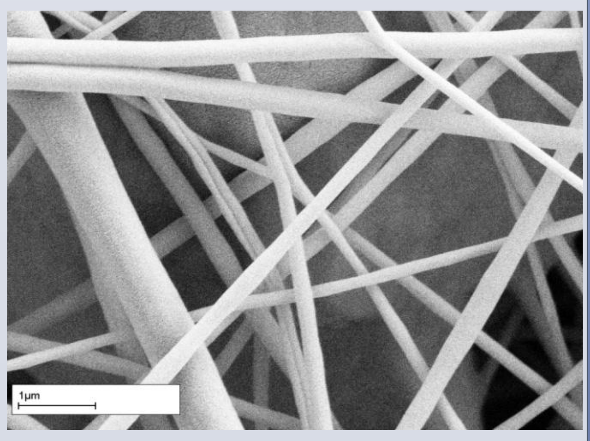
Pure PVDF:



MCC20-5:



MCC20-1-PEG-1:



FUTURE WORKS

Further characterisation of the materials include: Piezoelectric Coefficient (d_{33}) measurement, power output in a vibrational test rig and TEM for cellulose dispersion in the composites. New types of filler will be identified for performance enhancement of PVDF membranes.

REFERENCE

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