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Study of Surface Modification of Electrospun Polyethylene Oxide Composite Fibre

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Abstract

Functionalization of polymers had gained attention because of advance applications as sensor, energy devices, membrane, etc. This present study is aimed at studying surface modification as a result of electrospinning functionalized polyethylene oxide (PEO) with zinc ion. Zinc chloride was added in various proportions to PEO solution then electrospun at various voltage. Fibres resulted into various shapes; belt, rod, mat and thread which differs from the primary PEO. The mechanism for the morphology modification was studied and the optimum conditions which retain the fibrous morphology were noted. This functionalized PEO can be used as energy device.

Keyword: Polyethylene oxide, Modification, Fibre, Composite, Functionalized

Introduction

Composite materials are referred to as wonder material due to low weight, corrosion resistance, high fatigue strength, modified structures and faster assembly (Josmin, et al., 2012). They are materials that consist of two or more interfaces which are different in term of chemical and physical properties. They have found applications in various areas: electronic, automobile, construction, medical, etc. (Josmin, et al.,2012) 2012). Many viable composites are found in nature; wood is a natural composite of cellulose fibre in a matrix of lignin, connective tissues in mammals is a polymer composites which comprises fibrous protein and collagen (Josmin, et al., 2012). Fibrous composites can be divided into natural/bio fibre and synthetic composite fibre. Synthetic composite fibres are obtained from non-natural materials which can be co-polymers, metal-polymer, inorganic-organic fibre. Polymer based composite fibre can be obtained using techniques such as drawing, template synthesis, phase separation, self assembly and electrospinning (Buchko, Kozloff, & Martin, 2001) (Fujihara, Lim , Ma, Ramakrishna, & Teo, 2005) (Zheng-Ming, Zhang,

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Kotaki, & Ramakrishnab, 2003). Electrospinning process is the only process that can be scaled up for mass production of continues fibre (Fujihara, Lim , Ma, Ramakrishna, & Teo, 2005) (Zheng-Ming, Zhang, Kotaki, & Ramakrishnab, 2003), it is simple and versatile method to generate ultrathin fibre. The name electrospinning was derived from electrostatic spinning, which involves the application of high voltage to a polymer solution in which charges are induced with resultant fibre production. Ultrathin fibre electrospun had been reported from over fifty polymers (Fujihara, Lim , Ma, Ramakrishna, & Teo, 2005), co-polymers (Fujihara, Lim , Ma, Ramakrishna, & Teo, 2005) (Zheng-Ming, Zhang, Kotaki, & Ramakrishnab, 2003), polymer-inorganic, inorganic oxides and ceramic (Zheng-Ming, Zhang, Kotaki, & Ramakrishnab, 2003) (Chronakis , 2005) with fibre diameter in the micro and nano dimension. Fibres greater than 1μm are micro-fibre while 1-1000nm are referred to as nano fibre. Composite materials made from micro fibres had been reported to have superior structural properties such as high modulus, strength to weight ratio in comparison with parent composite (Fujihara, Lim , Ma, Ramakrishna, & Teo, 2005). Nanofibre had advantages over microfibre based on higher surface area. Composite materials containing nanofibres are called nanocomposites.

Several composite fibre had been reported from electrospinning technique: (Kim & Reneker, 1999) studied the reinforcing effect of electrospun nanofibres of polybezinidazole in an epoxy and rubber matrix, Bergshoef et. al. (Bergshoef & Vancso, 1999) fabricated nanocomposite using Nylon-4, 6 nanofibre non woven membrane. Also composite ceramic hollow nanofibre through electrospinning had been fabricated.

PEO has been reported to be used as an anti-foaming agent in food (US Government – Food and Drug Agency, 2011), insulator (Ueno, et al., 2008), potentiator (Harmening, 2005), lubricatant coating (Nalam, Clasohm, Mashaghi, & Spencer, 2009), membrane, surfactants, packaging material (Rossi, 2006) (Geisbert, et al., 2010), laxatives (Palma Di, Cleveland, McGowan, & Herrera, 2007)and drug delivery while Zinc chloride is used as flux for soldering (Harmening, 2005), catalyst (Cooper, 1955) (Shriner, Ashley, & Welch, 1955), fire proofing agent, textile processing, smoke grenades (Sample, 1997), finger print detection and disinfectant (Watts, 1869).

Considering the numerous potentials of composite electrospun fibre, this present study aims at investigating the morphological rearrangement which will occur when polyethylene oxide (PEO) is functionalized with zinc ion in electrospinning experiment, functionalized nanofibres are applicable for use as membrane, sensors, protective clothing, drug delivery, etc (Zheng-Ming, Zhang, Kotaki, & Ramakrishnab, 2003)

Methodology

10% of 300,000g/mol PEO solution was prepared in distill water while 40%, 45% and 50% of PEO/$ZnCl_2$ solutions were prepared in distill water in the ratio of 0.5:0.2, 0.5:0.3,0.5:0.4 and 1:1 respectively. The solutions were stirred for 12 hours then filled into the spinneret and spun between 10-30 kV. A schematic diagram of the electrospinning set up is shown in Fig. 1. The fibres were characterized using scanning electron microscope. Chemicals used were of analytical grade.

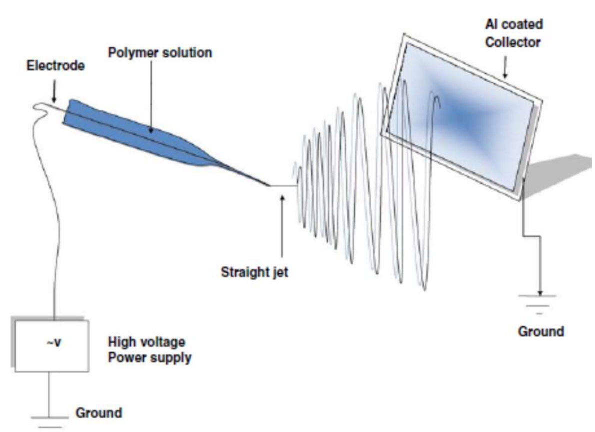

Fig. 1: Electrospinning set up

Results and Discussions

Figure 2 shows electrospun 25% PEO solution, the fibre was bead free with 0.65μm functionalized PEO solution electrospun at 30, 28 while figure 3 shows the micrographs of 40% and

24 kV. There was complete change in the fibre morphology in comparison with Figure 2. Spherical crown was observed in figure 3 (a) at 30kV but higher magnification (Figure 3(b)) revealed that the crown was made up of regular shaped flakes with fibre growth at the root. The average length of the flakes was 7.07μm. Furthermore, Figure 3 (c and d) shows a complete and incompletely formed spherical crown at 28kV. Figure 3(d) reveals an irregular shaped flake which makes up figure 3(c). At a lower voltage 24kV an array of incompletely formed flakes was observed (figure 3(f&g)). The incompletely formed spherical crown was observed to be made up of moist particles rather than fibre, with no fibre root. Figure 4 (a-g) shows micrograph of electrospun of 45% functionalized PEO solution at different voltages. A hollow tube with average diameter of 13.23μm was observed at 28 kV (Figure 4 (a-b)) while fibre with rough surface with average size of 1.26μm was obtained at 26 kV (Figure 4(c-d)). At lower voltage non-hollow

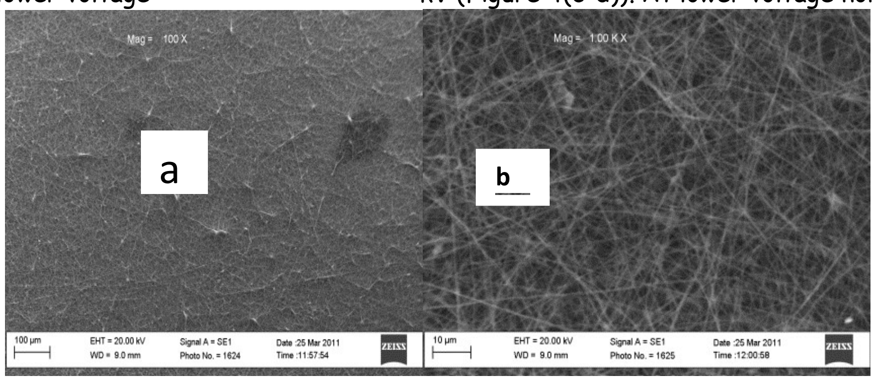

Figure 2: Scanning Electron Micrographs of PEO (a) at 1000x (b) at 100x

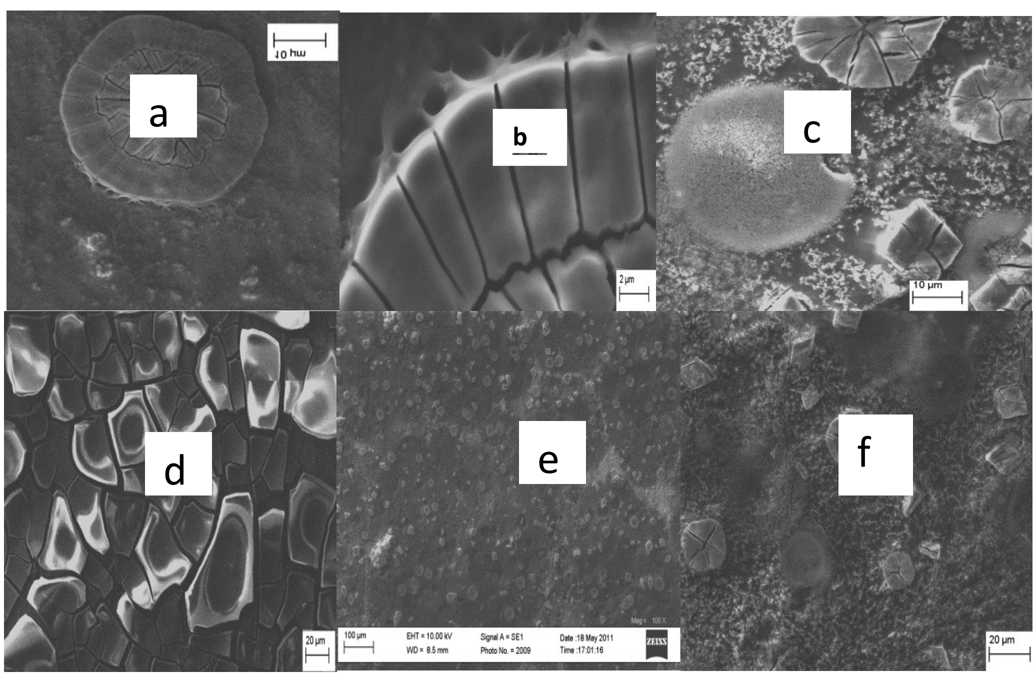

Figure 3: Scanning Electron Micrographs *of Electrospun 40 % PEO/ZnCl$_2$ (a) 30 kV at 1000x (b) 30 kV at 1500 kV (c) 28 kV at 1740x (d) 28kV at 1000x (e) 24 kV at 100x (f) 24 kV at 500x*

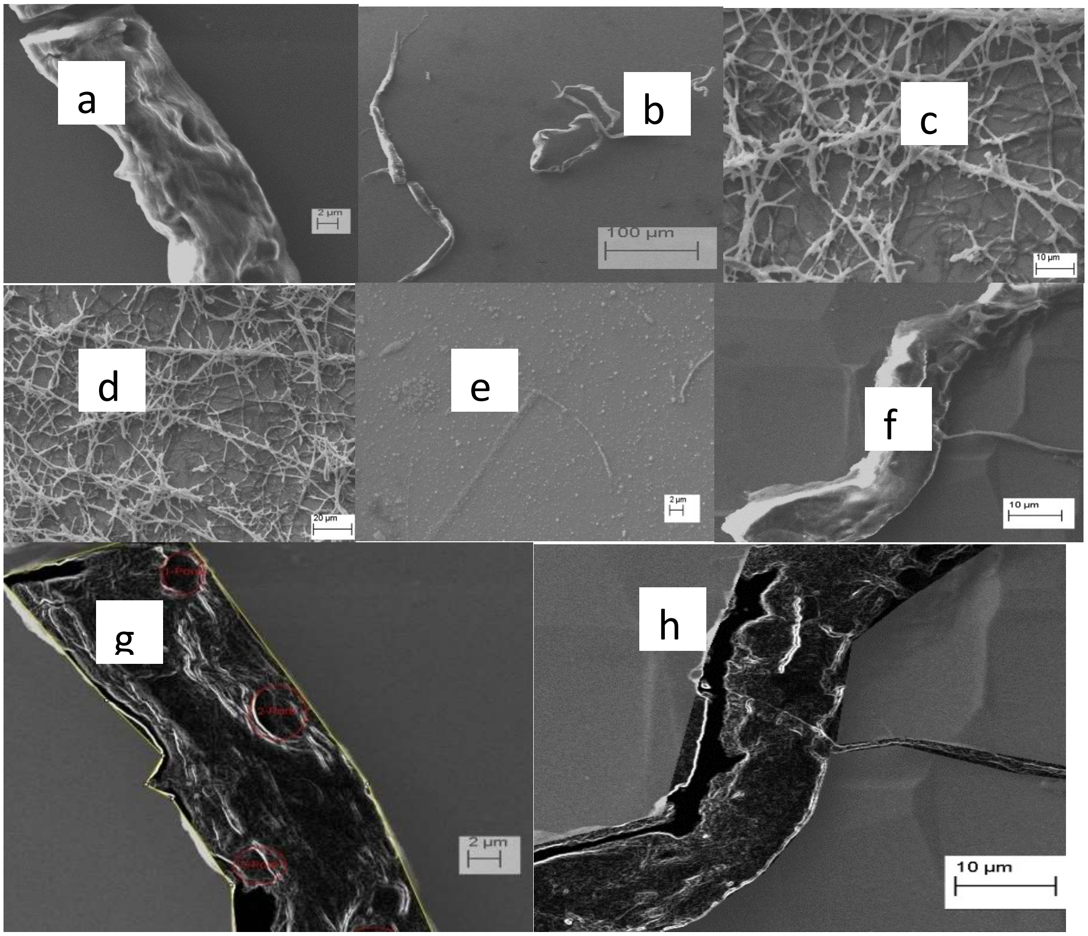

Figure 4: Scanning Electron Micrographs *of Electrospun 45% PEO/ZnCl$_2$ (a) 28 kV at 2000x (b) 28 kV at 100x (c) 26kV at 1000x (d) 26 kV at 500x (e) 24 kV (f) 22 kV (g) 28 kV at 2000x modified (h) 22 kV modified*

tube was observed which has an average diameter of 13.60μm. Further analysis of hollow and non-hollow tube formed showed that the tubes were made of fibre (Figure 4 (g and h)). Figure 5 (a-d) shows morphology of 50% solution fibre at 30kV, 26kV and 24kV. At 30kV, fibre presented a belt-like morphology with an average width of 29.61μm (Figure 5(a-b)), while at 24 and 26kV, a mat-like morphology was obtained as shown in Figure 5 (c and d). A notable experimental parameter which was responsible for change in surface morphology of this functionalized PEO solution is voltage. In electrospinning process, voltage plays a prominent role in the determination of resultant morphology (Zheng-Ming, Zhang, Kotaki, & Ramakrishnab, 2003). At high voltage, essential charges in the solution together with the external electric field will be initiated when the surface tension of the solution is overcome be electrostatic force (Zheng-Ming, Zhang, Kotaki, & Ramakrishnab, 2003). In the case of these functionalized PEO solutions with same viscosity, as voltage increases, the amount of charges remove will cause the jet to accelerate faster and volume of solution which will be drawn from the tip of the spinneret will simultaneously increase resulting in smaller and less stable Taylor cone (Buchko, Kozloff, & Martin, 2001; Zheng-Ming, Zhang, Kotaki, & Ramakrishnab, 2003; Fujihara, Lim , Ma, Ramakrishna, & Teo, 2005;). Also, stretching and acceleration of the jet are factors which are dependent on voltage supplied as well as resultant electric field, stretching of the polymer solution will increase with voltage due to columbic forces

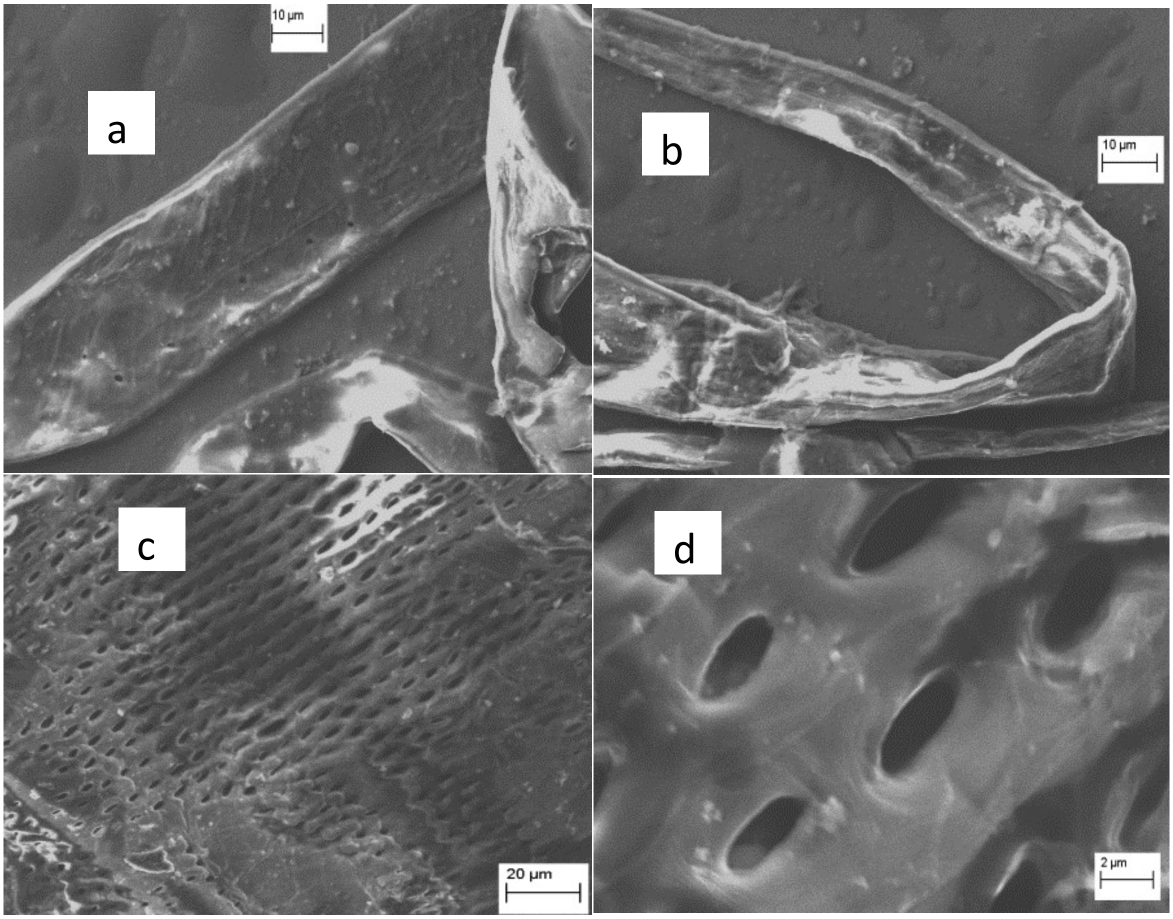

Figure 5: Scanning Electron Micrographs *of Electrospun 50% PEO/ZnCl$_2$ (a) 30 kV at 2000x (b) 30 kV at 500x (c) 26 kV (d) 24 kV*

in the spinneret which increase with electric field. Hence higher voltage favours the evaporation of solvent yielding a dry fibre obtained in figure 3(a&b), hollow fibre (figure 4(a,b&g)) and belt (figure 5(a&b)).
Another factor under the polymer concentration which is crucial in modification of the composite morphology is viscosity. The difference in surface morphology can also be attributed to difference in viscosity across the concentration while similarity was observed within solutions of same viscosity. Increase in the solution concentration will increase the viscosity while decrease in solution concentration will decrease viscosity. Larrondo et al., (Larrondo & Manley, 1981) showed that viscosity was crucial when they electrospun fibres from melt. Viscosity affects fibre morphology because at very low viscosity polymer particles are formed, electrospraying occurred rather than electrospinning. This factor is responsible for difference in morphologies.

Conclusion
Due to different applications (membrane, drug delivery, sensor, energy, etc) of
electrospun functionalized polymer fibre, it is important that reaction condition must be optimized in which the surface modification of the composite must remain fibrous. In view of this, the optimum condition for fibrous morphology was 45% PEO/Zn2$^+$ at 26kV. Other morphologies obtain will be useful as membrane (porous fibres), biomedical scaffold and sensors.

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