

sintered microsphere scaffolds had a total pore volume between 28% and 37% with median pore size in the range 170-200 microm. The compressive modulus and compressive strength of the scaffolds were in the range of trabecular bone, making them suitable as scaffolds for load-bearing bone tissue engineering.

Shalumon *et al.* have produced a fibrous scaffold consisting of chitosan and poly(ϵ -caprolactone) (PCL), which was electrospun from a solvent mixture made up of formic acid and acetone [121]. Chitosan concentration was varied from 0.5% to 2% with a fixed PCL concentration of 6%. Selected chitosan concentration (1%) was further blended with 4–10% PCL to obtain fine nanofibers. The mix composition was selected as 25/75 (1/3), 50/50 (1/1) and 75/25 (3/1) of chitosan/PCL. Lower concentrations of PCL resulted in beaded fibers while higher percentages of PCL (more than 8%) yielded fine nanofibers.

Nie *et al.* fabricated konjac glucomannan (KGM) scaffolds by electrospinning its aqueous solution [137]. They reported that the stability of KGM based scaffolds was improved after alkali treatment at a low concentration without any other chemical crosslinking agents involved. Meanwhile, KGM/chitosan bicomponent nonwoven membranes were also easily obtained from their dilute acidic solution, and the average fiber diameter was decreased with the increase in chitosan content. In addition, nanofibrous scaffolds improved the biocompatibility of chitosan materials.

Han *et al.* reported that Methoxy poly(ethylene glycol)-grafted chitosan (PEG-g-CS) was synthesized by mild Michael addition reaction of chitosan and methoxy polyethylene glycol monoacrylate [138]. Blend nanofibers of PEG-g-CS and poly(ethylene oxide) (PEO) were fabricated by electrospinning.

Ma *et al.* prepared Hyaluronic acid/chitosan polyelectrolyte complexes nanofibers by electrospinning [139]. They are expected to be used as biomedical materials in tissue engineering.

Nirmala *et al.* reported on the preparation of polyamide-6/chitosan composite nanofibers [140]. These composite nanofibers were prepared using a single solvent system via electrospinning process. The resultant nanofibers were well-oriented and had the good incorporation of chitosan.

Table V includes a summary of the electrospinning settings for some systems of chitosan/S.P. nanofiber blends [69, 80, 86, 125-127, 129, 141, 142].

As a general conclusion in electrospinning of chitosan blends, it can be said that the concentration of electrospinning solution and the molecular weight of chitosan have significant effects on decreasing the diameter of electrospun nanofibers and their quality. Figure 11 shows SEM of Chitosan/PVA blend nanofibers with different chitosan molecular weights. It illustrates that lower molecular weight chitosan leads to high quality nanofibers and higher molecular weight.

Apart from what is reported in Table V, there are successful efforts on producing chitosan blend nanofibers using other secondary polymers or additives such as poly

(L-lactic acid), silk, Zein, hydroxyapatite and montmorillonite [6, 107, 143- 145].

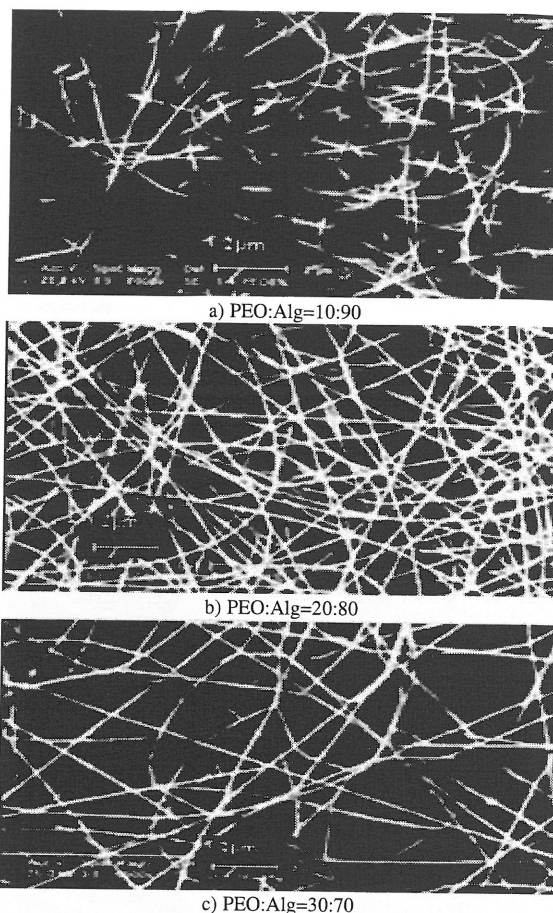


Fig. 8. The effect of PEO:Alg mass ratio on the diameter of electrospun nanofibers; 8% w/v PEO-2% w/v Alginate.

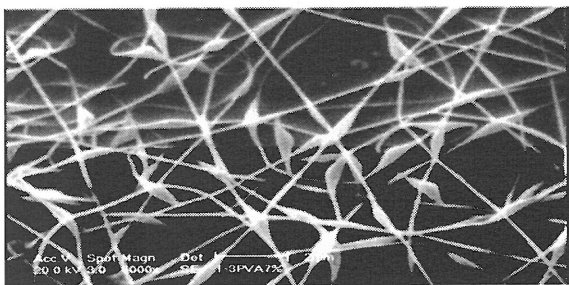
V. CHALLENGES AND PERSPECTIVES

In recent years, there has been a marked interest in biodegradable materials for their use in packaging, agriculture, medicine, and other areas. In particular, biodegradable polymer materials are of interest. As a result, many researchers have focused on modifying traditional materials to make them more user-friendly, and design novel polymer manufactures out of naturally occurring materials. The belief is that biodegradable polymer materials can reduce the need for synthetic polymer production (thus reducing pollution) at a low cost, thereby producing a positive effect both environmentally and economically.

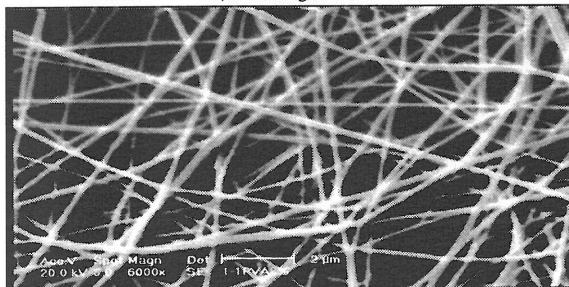
The integration of our current knowledge on biopolymers, with new material architecture such as nanostructured material has led to a family of potent and versatile products with a remarkable spectrum of applications. The unique characteristics of biopolymers such as biodegradability, biocompatibility, particular physical and chemical behavior of biopolymers and nanoscale materials have created a big demand for these products, mainly in medical applications such as tissue engineering, drug delivery and wound healing.

TABLE IV
OPTIMUM ELECTROSPINNING CONDITION LEADING TO DESIRED ALGINATE BLEND NANOFIBERS

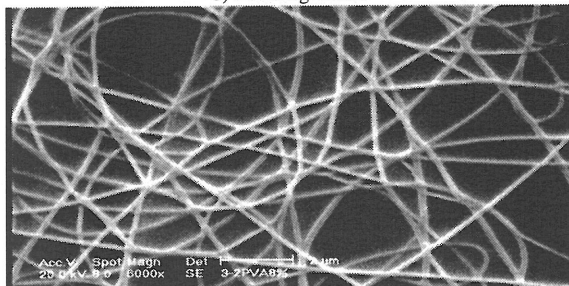
S.P. in blend	Sodium alginate viscosity (cps)	S.P.: Alg (solutions concentration wt%)	Applied voltage (kV)	Flow rate of the solution (mm ³ /hour)	Tip-collector distance (cm)	Nanofiber diameter (nm)
PEO ($\overline{M}_w = 100$ kDa)	1741	1/1 (overall 3%)	15	0.5	20	228
	1741	1/2 (overall 3%)	15	0.5	20	266
PEO ($\overline{M}_w = 300$ kDa)	700-900	10/90 w/w 8% PEO-2% Alg	11	3	10	109
	700-900	20/80 w/w 8% PEO-2% Alg	12	3	10	99
		10/90 w/w 8% PVA-2% Alg				
	700-900	22/78 w/w 8% PVA-2% Alg	12	3	10	66



a) PVA:Alg=10:90



b) PVA:Alg=20:80



c) PVA:Alg=30:70

Fig. 9. The effect of PVA: Alg mass ratio on the diameter of electrospun nanofibers 8% w/v PVA-2% w/v Alginate.

Biopolymers usually have a very complex rheology and electrodynamic behavior due to their complex molecules, high molecular weight, crystallinity and morphological characteristics. On the other hand, the technology of electrospinning is relatively young and unknown. Many of the achievements made in electrospinning are practical and the techniques of electrospinning (along with all other techniques used for the production of nanoscale materials) need essential studies to be more controllable and reproducible.

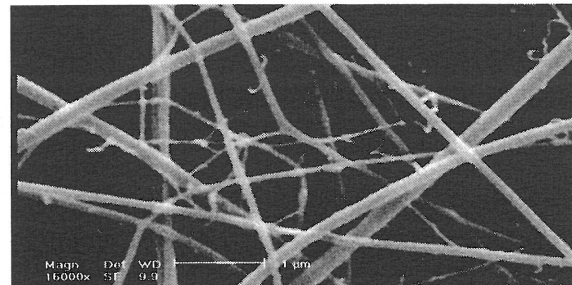
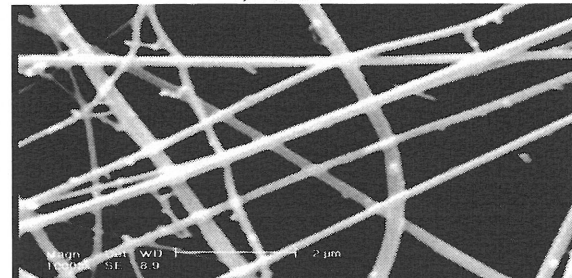
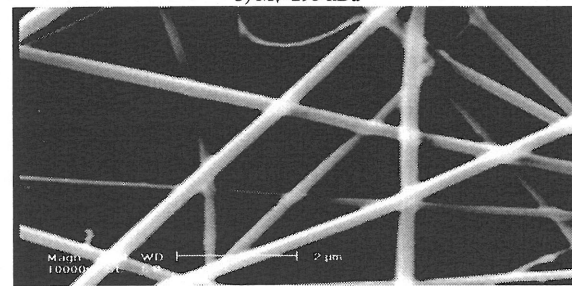
a) $M_v=645$ kDab) $M_v=293$ kDac) $M_v=104$ kDa

Fig. 10. SEM of Chitosan/PVA: 70/30 nanofibers for chitosan with different molecular weights.

However the fact is that apart from the notable advantages being already achieved, in studies on electrospinning of biopolymers, further researches are obviously required to improve the properties and behavior of nanoscale biopolymer material in both fields of biopolymers and nanostructured material (mainly electrospun nanofibers which have been widely used in recent studies). A better understanding of the relationship between structure and electrospinnability of biopolymer would be interesting for future work.

TABLE V
OPTIMUM ELECTROSPINNING CONDITIONS LEADING TO DESIRED CHITOSAN BLEND NANOFIBERS

S.P. in blend	Chitosan characteristic	Solution system	S.P./ CS (solutions concentration wt%)	applied voltage kV	Flow rate of the solution (cm ³ /hour)	Tip-collector distance (cm)	Nanofiber diameter (nm)
PMMA $\bar{M}_V = 5000$ kDa;	$\bar{M}_V = 1400$ kDa 80%DDA	Acetic Acid	25/75 (1.4wt%)	30	4.8	15	132
	$\bar{M}_V = 100$ kDa 70-80%DDA	Acetic Acid	25/75 (1.4wt%)	30	4.8	15	421
Collagen $\bar{M}_V = 80 - 100$ kDa	$\bar{M}_V = 1000$ kDa	HFP/TFA v/v=90/10	90/10(10wt%)	20	0.8	13	300-500
PEO $\bar{M}_V = 900$ kDa	$\bar{M}_V = 190$ kDa 85%DDA	Acetic Acid 0.5M	10/90 (2.1wt%)	20-25	N.R.	17-20	40<
	$\bar{M}_V = 148$ kDa 82%DDA	Acetic Acid 90%	3 wt %/4wt%	15	3	15	250
	$\bar{M}_V = 1000$ kDa 82%DDA	Acetic Acid 50-90%	3/1 (1.6wt%)	20	1.2	10	50 to 130
PVA $\bar{M}_V = 94$ kDa 96% hydrolyzed	$\bar{M}_V$: N.R. 78%DDA	Acetic Acid 3wt%	30/70(7.4wt%)	15	N.R.	15	125
PVA $\bar{M}_W = 124 - 186$ kDa 87-89% hydrolyzed	$\bar{M}_V = 1600$ kDa 82.5%DDA	Acetic Acid 2% v/v	17/83 (6wt%)	18	N.R.	25	20 to 100
PVA $\bar{M}_V = 70$ kDa 98% hydrolyzed	$\bar{M}_V = 293$ kDa >75%DDA	Acetic Acid 98%	70/30 (5.9wt%)	17	0.24	13.5	167
PVA $\bar{M}_W = 70$ kDa 97.5-99.5% hydrolyzed (10wt%) + Hydroxybenzotriazole monohydrate (HOBt- H ₂ O)	$\bar{M}_W = 110$ kDa 85%DDA	Distilled water	HOBt/CS=1/1 (2wt%) PVA/(HOBt:CS)=90/10-to 50/50	15	N.R.	15	282 to 190

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