TREE GUM BASED ELECTROSPUN NANOFIBRE MEMBRANES: PROCESS OPTIMIZATION, CHARACTERIZATION AND ENVIRONMENTAL APPLICATION

Vinod VELLORA THEKKAE PADIL & Miroslav ČERNíK*

*Department of Nanomaterials in Natural Sciences, Institute for Nanomaterials, Advanced Technology and Innovation(CXI), Technical University of Liberec (TUL), Studentská 1402/2, Liberec 1, 461 17; Telephone: +420 485 353 017; *Email: miroslav.cernik@tul.cz and vinod.padil@tul.cz*

Abstract

Tree gums such as gum arabic (GA), gum karaya (GK), and kondagogu gum (KG) are obtained as natural exudates and exhibit unique properties with a wide variety of applications in food, pharmaceutical, adhesive, paper, textile, beverage and other industries. A series of poly(vinyl alcohol) /gums (GA, GK and KG) blend nano fibres with different weight ratio of PVA/Gums were fabricated via electrospinning. Various parameters, such as effects of solvents, molecular weight, and solution properties on the electrospinning, were investigated. The mass ratios of 90:10 for PVA/Gums were established to be the optimum conditions for uniform nanofibre formation. The developed nanofibres were evaluated for the removal of micropollutants from water.

Keywords: Tree gums, Electrospinning, nanopollutants, Adsorption

1. INTRODUCTION

Exudates gums are hydrocolloids and have complex molecular structures, are hydrophilic in nature and extracted from tree. They are used in food, pharmaceutical, adhesive, textile, to stabilize emulsions, thickening, and other industries for centuries. The important tree gums available in the markets are gum arabic (GA), gum karaya (GK), gum tragacanth (GT) and kondagogu gum (KG). Extensive research has been carried in various aspects of these tree gum polysaccharides, which includes their availability, molecular weight distribution, chemical structures, food and non-food applications [1-3]. GA , obtained from the stems and branches of *Acacia Senegal* and *Acacia seyal* is a branched polysaccharide, exhibit unique physio-chemical properties and are use in food and pharmaceutical applications [4]. The extensive research on the structure-functional properties of GA has been reported in literature and it is recognized that GA is composed of arabinogalactan (AG), arabinogalactan-Protein (AGP) and glycoprotein (GP) [5]

Physico-chemical properties, structural, rheological, occurrence, production, food and non-food applications of GK (*Sterculia urens*) have been widely studied by different research groups [6-8] GK is a partially acetylated polysaccharide and has a branched structure and high molecular mass of ~16.0×10^9 Da and grouped under substituted rhamno-galacturonoglycan (pectic) type tree gums [9]. This gum contains about 60% neutral sugars (rhamnose and galactose) and 40% acidic sugars (glucuronic acid and galacturonic acids) and 8 % acetyl groups and is a good emulsification agent due to its acid stability, high viscosity and suspension properties and water binding properties [10].

Extensive research work has been carried out on KG (*Cochlospermum gossypium*), a gum extracted from the Kondagogu tree which is available in India, including its morphological, physico-chemical, structural, rheological, pharmaceutical and emulsifying properties[3, 11]. Further, this gum can also be used as a biosorbent for the removal of toxic metal contaminants from aqueous environments and also used as a environmental friendly stabilizing and reducing agent for the synthesis of metal/metal oxide nanoparticles [12, 13].

In the present investigation, the molecular distributions of GA were compared with deacetylated GK (DGK) and deacetylated KG (DKG) using gel permeation chromatography linked multi angle laser light scattering. Further, we have prepared blended solution of various gums with PVA and fabricated electrospun membrane via electrospinning. The effects of weight ratio and the concentration on many parameters, such as molecular weight, polymer and solution properties (viscosity, surface tension, chain entanglement and electrical conductivity) were evaluated. Morphology of the electrospun nanofibres using SEM analysis, and adsorption of NPs onto the nanofibres were also evaluated.

2. EXPERIMENTAL

2.1. Materials

Gum Arabic and Gum Karaya were procured from Sigma-Aldrich company LTD, USA, Kondagogu Gum (KG) sample were collected from Girijan Co-operative Corporation, Hyderabad, India. Poly (vinyl alcohol), Mw 88,000 (degree of deacetylation 88%), $AgNO_3$), $HAuCl_4.3H_2O$), H_2PtCl_6, and NH_4OH were purchased from Sigma- Aldrich, USA. De-ionized water was used in all experiments.

2.2. Methods

2.2.1. Determination of molecular mass distributions of GA, GK and KG

The molecular mass distributions of the GA, GK and KG were determined using the technique of GPC (gel permeation chromatography) linked to MALLS (multi angle laser light scattering). $NaNO_3$ (0.1 M) containing 0.005% sodium azide (biocide) was used as the eluent and the solution filtered using a GSWP 0.45 um filter (Millipore) and degassed by means of a vacuum degasser (CS615/Cambridge Scientific Instruments) before use.

2.5. Preparation of PVA/ Gums blend solution for electrospinning

An aqueous solution of PVA (12 wt %) was prepared by heating at 90 ^oC in water kept over a magnetic stirrer for 5 h. Aqueous PVA (12 wt %) was mixed with GA, DKG and DGK solution (5 wt %) in different weight proportions of PVA with GA, DGK and DKG (100/0, 50/50, 60/40, 70/30, 80/20, 90/10 and 0/100), to determine good spinnability and uniform sizes of nanofibers after electrospinning. The resulting mixtures were kept over a magnetic stirrer and stirred for 5h to ensure complete mixing.

2.6. Solution properties

A Fungilab viscometer (ALPHA R series, Barcelona, Spain) was used for the measurements of the solution viscosity of the blended solutions. The pH and conductivity of the electrospinning solutions were determined using a Multi 3430 Digital pH/conductivity meter (WTW GmbH, Weiheim, Germany). The surface tension of the blended solution was determined using a Tesiometer (K6, KRUSS GmbH, Hamburg, Germany). All the measurements were performed at 25 ^0C. The measurements were done in triplicate and the values reported as mean± S.D.

2.7. Electrospinning

All electrospinning was carried out with a Nanospider electrospinning machine (NS IWS500U, Elmarco, Czech Republic) under the following parameters: spinning electrode width = 500 mm, effective nanofiber layer width = 200-500 mm; spinning distance = 130-280 mm, process air flow = 20-150 m^3/h, and voltage 0-50 kV.

2.8. Crosslinking and stability of PVA/DKG nanofibers

The membranes were cross-linked by keeping the membrane in an oven at 150 ^{o}C for 1 h to 6 h. The initial and final weights (in mg) of PVA/Gums nanofibres were determined before and after heat treatment to confirm any loss in weight of the fibres during the heating process.

2.9. SEM analysis

The surface morphologies of the electrospun nano fibres were investigated using a scanning electron microscope (ZEISS, Ultra / Plus, Germany).

2.10. Adsorption study

Adsorption study was conducted using PVA/Gum nanofibres (PVA/GA, PVA/GK and PVA/KG) membranes (10 mg) added into 10 ml (2 x 10^{-4} M) of each NP solution (Au, Ag and Pt) in a separate flask. The whole mixture was kept for constant shaking (200 rpm) at room temperature. The experiment was carried out in different time points to determine the time taken for maximum adsorption. The adsorption efficiency and the adsorption capacity were calculated using standard equations. The initial and final concentrations of nanoparticles before and after adsorption were determined using ICP-MS analysis (NexION 300 Q, PerkinElmer, USA). The adsorption studies were also monitored by UV-vis spectroscopy (Cintra 202 UV-VIS spectrophotometer, GBC, Australia). All adsorption and experiments were done thrice and all value of results is presented as mean ±S.D.

3. RESULTS AND DISCUSSIONS

3.1. The molecular distribution of GA, GK and KG

The estimated molar mass distributions of GA, GK and KG using GPC/MALLS and data fitted with a first-order polynomial using the Zimm method (*eluant: 0.1 M $NaNO_3$; flow rate: 0.5 mL/min.; dn/dc: for GA, 0.141 mL/g; for GK and KG; 0.140 mL/g*) was determined to be Mw, 5.013 x 10^5 g /mol, 1.827 x 10^6 g /mol and 1.144 x 10^6 g/mol, repectively.

3.2. Electrospinning parameters of gums

In the present study, the solution parameters such as polymer concentration, viscosity, conductivity, surface tension and fibre diameter were optimised . The best ratio for fabrication of various PVA/Gums nanoofibres were found to be 90/10 wt % of PVA/Gums ratios (PVA /GA; 12 wt %: 25 wt%., PVA/GK; 12 Wt %: 5 wt%: and PVA/KG ; 12 wt%: 5 wt%) are presented in Table 1.

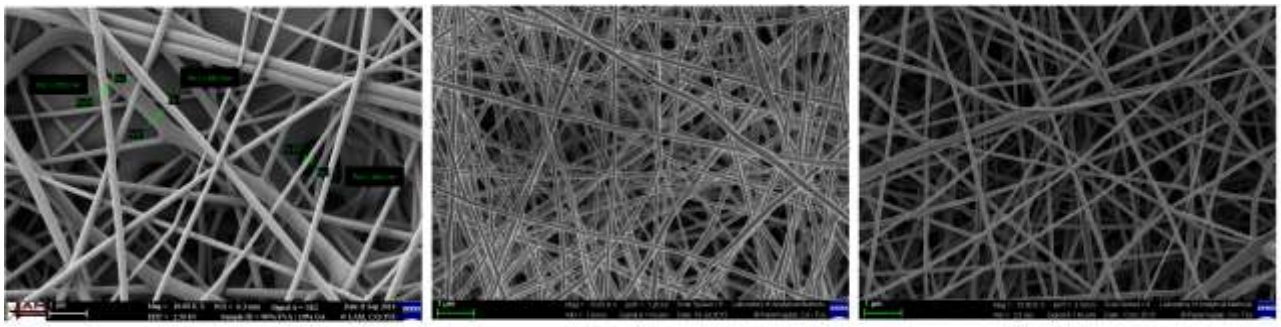

Fig. 1: Electrospun nanofibres of PVA/GA, PVA/GK and PVA/KG

Table 1: The composition , solution properties and fibre diameter of the electropsun PVA blended gum solutions.

	Gum	PVA	PVA/GUM Blend solution	Viscosity (mPaS)	Conductivity (mS/cm)	Surface Tension (mN/m)	Fibre diameter (nm)
GA	25 wt.%	12 wt.%	90/10 (PVA/GA)	1474±36	0.85±0.09	46.5±0.1	130 -430
KG	5 wt.%	12 wt.%	90/10 (PVA/KG)	4100±57	1.68±0.1	54.5±0.1	100-200
GK	5 wt.%	12 wt.%	90/10 (PVA/GK)	3480±50	2.75±0.08	48.5±50	100-200

3.3. SEM analysis of electrospun PVA/GA, PVA/KG and PVA/GK

Morphology of the electrospun nanofibres of PVA blended GA, GK and KG determined using SEM is presented in Fig 1. The PVA / gum weight ratio of 90:20 produced uniform nanofibres with diameters in the range of 100- 400 nm size. In the present investigation the PVA and gum in the ratio of 90: 20 wt % was to the optimum ratio to get uniform nanofibres.

3.4. Cross -linking and heat treatment of nanofibres

All the nanofibres were heat treated at 140 ^{o}C for cross-linking the polymers and the stability of the nanofibers were tested by immersing the nanofibres in water for 24 h. The Degree of stability (DS) of the PVA/GA, PVA/GK and PVA/KG were determined to be 95.8 %, 94.3%, and 93.5% respectively.

3.5. Adsorption of nanoparticles

The adsorption (%) and adsorption capacity (q_e) of the various PVA/Gum nanofibres (NF) are presented in Table 2. From Table 2 it can be observed that KG/PVA NF have a stronger affinity towards Ag, Au and Pt NP compared to GK/PVA and GA/PVA. Adsorption of NP onto the surface of the membranes can be explained by the interaction between the NP and the surface functional groups of the membrane. GA, KG and GK have an abundant number of functional groups, such as -OH, -COO and C=O groups, which can interact with NP and effectively remove them from water. These observations are similar to previously reported works on the toxic metal adsorption of KG and GK [14, 15].

The adsorption capacity of the Gum/PVA NF was calculated from the adsorption efficiencies and is presented in Table 2. From Table 2 it can be observed that the q_e value for Ag, Au and Pt varies in the order KG /PVA > GK/PVA >GA/PVA. These results are in agreement with earlier research works on functionalized electrospun PVA membranes which was used for extraction of NP from water [16].

Table 2: Comparison of adsorption efficiency, AE (%) and adsorption capacity q_e ($mg.g^{-1}$) of different nanoparticles (Ag, Au, and Pt) on PVA/GA, PVA/GK and PVA/KG NFs: Conditions; agitation speed; 3h: weight of gum/PVA NF, 10mg; volume of the solution; 100 mL; Temperature; 25.0±0.1 ^{0}C.

Gum/PVA NF	NPs used for Adsorption	Adsorption, AE (%)	Adsorption Capacity, q_e (mg/g)
GK/PVA	Ag	55.4±0.85	119.1±0.45
	Au	49.5±0.85	196.4±0.69
	Pt	60.3±0.48	236.5±0.98
GK/PVA	Ag	65.4±0.95	140.2±0.44
	Au	54.5±0.68	212.7±0.85
	Pt	65.3±0.55	254.7±0.68
KG/PVA	Ag	66.5±0.98	143.4±0.67
	Au	59.5±0.68	230.4±0.85
	Pt	69.3±0.55	270.4±1.25

4. CONCLUSIONS

Natural hydrocolloids GA, GK, and KG were blended with PVA in various ratios to produce nanofibres by electrospinning. The optimum ratio of PVA (12 wt %) and GA, GK and KG (25 wt %, 5 wt % each Gk and KG) to achieve a uniform distribution of nanofibres was 90/10. The electrospun PVA/GK nanofibres were cross-linked with heat to make them water insoluble. The membrane was successfully used to remove (Ag, Au, and Pt) nanoparticles from an aqueous solution. The adsorption efficiency (%) of NPs on the surface of the membrane varies in the following order Pt > Ag >Au, for PVA/KG, PVA/GK and PVA/GA, respectively. Results indicate that the major functional groups of hydroxyl (-OH), carbonyl (-C-O) and carboxylic (-COOH) present in the nanofibre surfaces are responsible for the adsorption of nanoparticles on the surface of the membrane. The polymer electrospun membranes consisting of PVA with gums are environmentally friendly and have a great potential for electrospun nanofibre membranes in applications such as biomaterials, water purification and medical devices.

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