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## Electrospun Fibers Based on Arabic, Karaya and Kondagogu Gums

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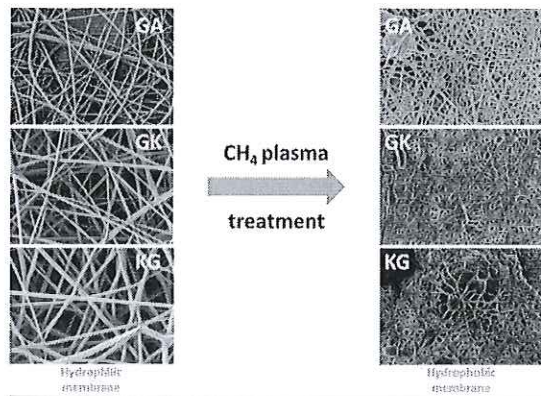
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## Graphical abstract



## Research Highlights

- Arabic, Karaya and Kondagogu gums nanofibers were prepared via electrospinning.
- Electrospun fibers were modified by methane plasma treatment.
- Plasma treatment resulted in enhancing the various properties of the fibers.

## Abstract

Nanofibers of natural tree polysaccharides based on three gums namely Arabic (GA), Karaya (GK) and Kondagogu (KG) have been prepared for the first time using electrospinning.

Electrospinning solutions were prepared by mixing gum solutions of GA, GK & KG with eco-friendly polymers such as polyvinyl alcohol (PVA) or polyethylene oxide (PEO). The present study focuses on the effect of electrospinning blended solutions of GA, GK or KG

with PVA or PEO, additives which influence system parameters and process parameters. This has important effects on the electrospinning process and the resulting fibres whose morphology and physicochemical properties were evaluated. The mass ratios of 70:30 to 90:10 for PVA: GA, PVA: GK and PVA: KG was observed to establish an optimum blend solution ratio in order to fabricate uniform beadless nanofibers with an average diameter of  $240\pm 50$ ,  $220\pm 40$  and  $210\pm 30$  nm, respectively. Various structural and physicochemical properties of the electrospun fibers were investigated. Furthermore, the comparisons of various functionalities of the untreated and plasma treated electrospun fibers were assessed. The methane plasma treated nanofibers were shown to be of extremely specific surface area, improved water contact angle, high surface porosity and roughness and superior hydrophobic properties compared to untreated fibers.

**KEYWORDS:** Tree gums; Electrospinning; physico-chemical properties

## 1. Introduction

Electrospinning is a versatile method for making nanometer to micrometer size range fibres for a variety of molecules in synthetic, natural and biological polymers. Electrospun fibres have been used into various technological areas due to their peculiar properties such as low density of nanofibers, large specific surface area, small pore size, high porosity, good breathability, excellent mechanical properties in proportion to weight and the possibility of incorporating different additives [1-3]. Electrospun fibres have been used in many applications in fields as diverse as filtration, acoustics, medical, drug delivery, tissue engineering, wound healing, solar cells, battery separators, catalysts, environmental and antibacterial [4-7]. Many system parameters (viscosity; concentration; conductivity; surface tension; molecular weight and distribution and topology - branched or linear - of the polymer or polymer blends) and process parameters (electric potential; flow rate of the polymer solution; distance between the capillary-end and target/collection screen; ambient parameters including temperature, humidity and air velocity in the chamber; motion of the target screen and internal diameter of the nozzle/capillary) have important effects on the electrospinning process and affect the resulting fibre morphology and properties [8-12].

Recent research on electrospinning of natural polymers (mainly focussed on biopolymers) has been augmented due to their biocompatibility, economic and non-toxic benefits in comparison with synthetic polymers [13]. The application of electrospun natural polymeric fibres has increased tremendously of late in the biomedical (e.g. tissue engineering scaffolding, wound dressing and drug delivery), environmental and antibacterial fields [1, 14]. The major task for electrospinning of natural polymers - such as chitin, chitosan, collagen, cellulose, silk fibroin, hyaluronic acid and alginates - mostly relies upon the selection of good solvent systems, molecular weight distributions and electrospinning

conditions [15-22]. Natural polymers such as tree gums (gum arabic, karaya and kondagogu) are important natural resources and there has been no comprehensive reporting on the electrospinning of these polymers in the literature. The underlying challenges facing electrospinning of these tree gums relates to their high molecular weights, reduced solubility, swelling nature and the proper selection of electrospinning solvent systems. It has been reported that natural polymers such as gellan gum, alginate, green seaweed (*Ulva Rigida*), tragacanth gum, guar gum and chitosan were successfully electrospun by blending them with poly (ethylene oxide) or poly (vinyl alcohol) [5, 17, 23-26].

Exudate gums (extracted from trees) are hydrocolloids with complex molecular structures that are hydrophilic in nature. They are widely used in the food, pharmaceutical, adhesive and textile sectors to stabilize emulsions and enhance thickening, just as they have been employed in numerous 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 out on various aspects of these tree gum polysaccharides. This includes studies on their availability, molecular weight distributions, chemical structures & food and non-food applications [27-31]. GA is obtained from the stems and branches of *Acacia Senegal* and *Acacia seyal* and being a branched polysaccharide, it exhibits unique structural and physico-chemical properties [32-36]. Consequently, it is widely used in food and pharmaceutical applications [37-40].

The physico-chemical properties, structural, rheological, occurrence, production, food and non-food applications of GK (*Sterculia urens*) have been widely studied by different research groups [41-47]. GK is a partially acetylated polysaccharide, has a branched structure and high molecular mass of  $\sim 16.0 \times 10^6$  Da [28]. It is grouped under substituted rhamno-galacturonoglycan (pectic) type tree gums [45]. This gum contains about 60% neutral sugars (rhamnose and galactose) 40% acidic sugars (glucuronic acid and galacturonic acids) and 8%

acetyl groups [48, 49]. GK is a good emulsification agent due to its acid stability, high viscosity and suspension properties and water binding attributes [50]. Recently, GK has been employed for the construction of copper oxide nanoparticles and its DDSA (Dodecenyl Succinic Anhydride) derivatives as potential antibacterial agent [51, 52].

Extensive research work has been carried out on KG (*Cochlospermum gossypium*) - a gum extracted from the Kondagogu tree which is grown in India - including evaluating its morphological, physico-chemical, structural, rheological, pharmaceutical and emulsifying properties [29, 53-56]. Furthermore, this gum can also be used as a biosorbent for the removal of toxic metal contaminants from aqueous environments and also utilised as environmentally friendly materials (in the twin roles of stabiliser and reducing agent) in the synthesis of metal/metal oxide nanoparticles [57- 62]. The toxicological evaluation of KG has established that this gum was non-toxic and has potential application as a food additive [63]. Structural analysis of this biopolymer has shown that it contains sugars such as arabinose, rhamnose, glucose, galactose, mannose, glucuronic acid and galacturonic acid [29, 53].

Developing the electrospinning process using aqueous based solvents or water soluble reagents to produce nanofibers will make the process eco-friendly and open up the way for industrial production. Biopolymers such as polysaccharides (cellulose, chitin, chitosan, alginate, dextrose & hyaluronic acid); proteins (collagen, gelatin, silk & fibrinogen); DNA; as well as some biopolymer derivatives (cellulose acetate & hydroxypropyl cellulose) and composites (cellulose acetate/PVA & cellulose acetate/hydroxyapatite) have been successfully electrospun into ultrathin fibers [64-70]. Biopolymeric nanofibrous mats have shown potential for applications in the medical and pharmaceutical fields. For example, nanofibers can be used to fabricate wound dressings and to construct tissue engineering scaffolds for drug delivery as well as other medical devices [71-76]. Recently, the emphasis on electrospun fibres based on natural polymers specific to

areas including biotechnology, food, water, the environment and energy has increased tremendously due to their attributes such as biocompatibility, non-toxicity, resource renewability and biodegradability [77-82]. Our research groups have recently reported the fabrication of plasma treated nanofibers based on KG and GK and their specific applications for the removal of metal/metal oxide nanoparticles (Ag, Au, Pt, CuO and Fe<sub>3</sub>O<sub>4</sub>) from water and potential anti-microbial membranes [83-86].

In the present investigation, we fabricated tree gum based nanofibers from GA, GK and KG by electrospinning their corresponding aqueous solutions blended with biodegradable polymers such as PVA or PEO in order to produce 'green electrospun fibers'. The influence of the system and process parameters on the nanofibers (based on fiber size, porosity, surface area and morphology) were systematically investigated. In addition, the enhancements of physico-chemical properties of the nanofibers were studied using methane plasma treatment. Various functionalities of the untreated and plasma treated fibers were ascertained using SEM, ATR-FTIR, stability, porosity, water contact angle, and BET analysis.

## **2. Materials and methods**

### **2.1 Materials**

GA and GK were procured from Sigma-Aldrich Company Ltd. KG was obtained from Girijan Co-operative Corporation (GCC), Hyderabad, India.

### **2.2. Methods**

#### ***2.2.1. Preparation of GA***

GA (10 g) were accurately weighed and dispensed into clean glass beakers containing one litre of deionised water. The gum solutions were placed on magnetic stirrers at room temperature and gently stirred overnight after which they were allowed to stand at room temperature for 12 h, so as to separate out any un-dissolved matter. The resulting gum



solution was subsequently centrifuged to obtain clear solutions and were freeze-dried and stored until further use.

### **2.2.2. Preparation of deacetylated GK and KG**

Deacetylated GK and KG were prepared with slight modification of the methods reported for deacetylation of polysaccharides such as *Sterculia striata*, *Sterculia urens* and alginates, [43, 44, 87, 88]. In brief, both GK and KG powders (1 g each) were accurately weighed and dispensed into clean glass beakers containing one litre of deionised water. The gum solutions were placed on magnetic stirrers at room temperature and gently agitated overnight after which they were allowed to stand at room temperature for 12 h, so as to separate out any undissolved matter. The resulting gum solutions were subsequently centrifuged to obtain clear solutions. Three volumes of each of the gum solutions were deacetylated by mixing with one volume of 1M NaOH. NaHB<sub>4</sub> (1.0M) was added to the reaction mixture to prevent the beta elimination reaction from occurring on any unprotected reducing ends of GK and KG polysaccharides, as reported for other polysaccharides under alkaline conditions [89]. After incubation for 6 h at room temperature with gentle agitation on a magnetic stirrer, one volume of 1M HCl was added to neutralise the solution (to a final pH of 7.0). The resulting solutions were dialysed (dialysis tubing DTV 12000.09.000; Mw range; 12 - 14 kDa, Medicell International LTD, London) extensively against deionised water to remove any residual salts. The gum solutions were then centrifuged and the so obtained clear solutions were freeze-dried and stored until further use. The deacetylation of GK and KG were monitored by FTIR analysis [29, 52].

### **2.2.3. 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<sub>3</sub> (0.1 M) containing 0.005% sodium azide (biocide) was used as the

eluent and the solution filtered using a GSWP 0.22  $\mu\text{m}$  filter (Millipore) and degassed by means of a vacuum degasser (CS615/Cambridge Scientific Instruments) before use. The samples of native GA (0.2 wt. %), deacetylated GK (0.2 wt. %) and deacetylated KG (0.2 wt. %) were prepared in 0.1 M  $\text{NaNO}_3$  solution and left overnight on a roller to complete dissolution of the samples. The GPC system consisted of a Suprema 3000 column with these specifications [dimensions: 300 mm  $\times$  8 mm; bead size: 10  $\mu\text{m}$  and pore size: 100  $\text{\AA}$ ]. The column was protected by a guard column (Polymer Standards Service GmbH). The flow rate was set to 0.5 ml/min. using a Waters Corporation HPLC pump in conjunction with a Rheodyne 7125 model injection system (loop volume 200  $\mu\text{L}$ ). A Dawn DSP Laser Photometer and OPTILAB DSP Interferometric Refractometer (Wyatt Technology Corporation) were used as detectors. The gum samples were filtered through 0.45  $\mu\text{m}$  syringe filters before being injected into the HPLC column. All measurements were performed in triplicate. The molecular mass distributions and rms radius moments of the gums were determined using the designated Astra software for Windows (4.90.08, QELSS 2. XX). The data was fitted using a first-order polynomial and the Zimm method. The refractive index increment ( $dn/dc$ ) values for GA, GK and KG were determined to be 0.141, 0.140 and 0.140 mL/g respectively for the three gums [29, 40, 54]. These values are in close agreement with those in the literature.

#### ***2.2.4. Electrospinning Solutions***

GA (10 wt %), GK and KG (both deacetylated) [3 wt. %] were prepared by dissolving them separately in deionised water. The PVA or PEO (10 wt. %) were prepared by heating at 90°C in a magnetic stirrer for 4 h. Then, the PVA or PEO solutions were mixed with the GA, solution (10 wt. %) and GK and KG (3 wt. %) in different ratios viz. 50/50, 60/40, 70/30, 80/20, 90/10 and 100/0 (PVA/GA; PVA/GK; PVA/KG; PEO/GA; PEO/GK and PEO/KG weight ratios) to test for electrospinning to make beadles and uniform size nanofibers.

Conductivity and viscosity of the electrospinning solutions were recorded using a Toledo FG3 electric conductivity meter (Mettler, USA) and a rotational viscometer (Brookfield Engineering Laboratories, USA). The surface tensions of the electrospinning solutions were determined using a tensiometer (KRUSS GmbH, Germany). All of the measurements were repeated three times and the values were reported as a mean  $\pm$ S.D (n = 3).

#### ***2.2.5. Preparation of nanofiber membranes and their treatments***

The electrospinning was carried out on a Nanospider electrospinning machine (Elmarco, NS IWS500U, Liberec, Czech Republic) with interchangeable electrode systems, working with both water or non-water soluble polymers. The details of the electrospinning conditions were as follows: spinning electrode width of 500 mm, effective nanofiber layer width of 200 – 500 mm; spinning distance of 130 – 280 mm, substrate speed of 0.015 – 1.95 m/min, voltage of 0–55 kV and process air flow of 20 – 150 m<sup>3</sup>/h.

#### ***2.2.6. Methane plasma treatment***

The methane plasma treated fibers were prepared in a 13.56 MHz radio frequency (RF) plasma reactor (BalTec Maschinenbau AG, Pfäffikon, Switzerland). The plasma chamber was thoroughly purged with a continuous flow of the gas used during the treatment to reduce trace amounts of air and moisture. During the treatment, the gas flow was adjusted in order to keep a constant pressure of 20 Pa inside the chamber. The plasma conditions and process parameters were as follows: voltage of 300 V; power 20W; time of 5 minutes; plasma gas purity of 99.997%; electrode area of 48 cm<sup>2</sup>; inter-electrode distance of 50 mm, and chamber volume of 1,000 cm<sup>3</sup>.

#### ***2.2.7. Characterizations of untreated and plasma treated electrospun fibers***

The measurement of the water contact angle ( $\theta$ ) was used to determine the surface wettability of both untreated and plasma treated fibers using the sessile drop method. Measurements

were performed using OCA20 equipment (Data Physics, Germany) and SCA-20 software. The presented data are the average of three measurements. The thicknesses of the plasma treated and untreated electrospun fibers were determined using the micrometer screw gauge method (SOMET CZ s.r.o, Bilina, CZ). The surface areas of the fibers before and after plasma treatment were analyzed using the Brunauer-Emmett-Teller (BET) technique (Autosorb iQ, Quantachrome, Florida, USA). The apparent densities and porosities of nanofibers were calculated using the equations (1) and (2), respectively.

$$\text{Apparent density} = \frac{\text{Membrane mass (g)}}{\text{Membrane thickness (cm)} \times \text{membrane area (cm}^2\text{)}} \quad (1)$$

$$\text{Porosity} = 1 - \frac{\text{Membrane apparent density (g cm}^{-3}\text{)}}{\text{Bulk density of mixture (g cm}^{-3}\text{)}} \quad (2)$$

#### **2.2.8. SEM analysis**

The surface morphologies and average diameters of the nanofibres were also investigated by a scanning electron microscope (ZEISS, Ultra / Plus, Germany) with ZEISS image software using 50 different points from the SEM images.

#### **2.2.9. ATR- FTIR spectrometry**

Attenuated Total Reflectance-Fourier Transform Infrared Spectroscopy (ATR-FTIR; NICOLET IZ10, Thermo Scientific, USA) was used to characterise the functional groups of

GA, GK, KG and their corresponding untreated and plasma treated nanofibers. The spectrometer is equipped with a multi-reflection, variable angle horizontal ATR accessory.

### 3. Results and discussion

#### 3.1. *Molecular mass distribution of GA, GK and KG*

The estimated molar mass distributions (weight average,  $M_w$ ; number average,  $M_n$ ; z-average molecular mass,  $M_z$ ) and rms radius moments [number-average mean square radius ( $R_n$ ), weight-average mean square radius ( $R_w$ ) and z-average mean square radius ( $R_z$ )] in nm of GA, GK and KG using GPC/MALLS and data fitted with a first-order polynomial using the Zimm method are presented in Table 1. The elution profile of GA, GK and KG using GPC and refractive index for determining molecular mass distributions are also shown in Fig.1 a, b & c, respectively. In the case of GA, the weight average molecular mass,  $M_w$   $5.013 \times 10^5$  g/mol and number average,  $M_n$  was found to be  $2.5313 \times 10^5$  respectively. These values are very close to those reported in the literature for GA [37, 90]. The weight average molecular weights of GK and KG were determined to be  $1.827 \times 10^6$  (Mw) and  $1.144 \times 10^6$  (Mw), respectively. The highest weight average Molecular weight (Mw) was obtained for GK, compared to values for KG and GA (Table 1).

#### 3.2. *Electrospinning properties of tree gum solutions*

The electrospinning of tree gums (GA, GK and KG) and other natural polymers are complex processes due to their solution behaviour, high molecular weight and viscosity. Several parameters such as viscosity, polymer concentration, solubility in various solvents and electrical voltages have been examined for producing uniform and beadless nanofibers. From the various parameters monitored, the viscosity, surface tension, polymer blend ratio and conductivity appear to have influenced the production of gum nanofibers by electrospinning. Table 2 shows that the solution parameters such as polymer blend concentrations, viscosity,

surface tension and conductivity of the electrospinning solutions of PVA (GA, GK and KG) were optimized. GA is water soluble up to 25 wt. %, compared to GK and KG (1 wt. %), but after dacylation, the solubilities of GK and KG were found to have improved (3 wt. %). Furthermore, due to chemical deacetylation [91], the solubility of both GK and KG were found to have increased, resulting in polymers with a more expanded conformation which improved the electrospinnability of these gums.

In our present work, 10 wt. % of GA and 3 wt. % of GK and KG (deacetylated) samples were used for blend solutions with PVA or PEO (10 wt. %). The selection of PVA or PEO for the successful electrospinning of tree gums (GA, GK and KG) was due to the high solubility of tree gums in PVA or PEO and the maintenance of both viscosity and surface tension of the blend solutions. The mixtures comprising PEO with GA, GK or KG respectively (in 50/50 to 90/10 ratios) have resulted in non-uniform nanofibers and beaded structures. PEO, as a non-monoenic flexible chain polymer, is thought to interact with tree gums (GA, GK and KG) through hydrogen bonding. The oxygen atoms in the PEO backbone could contribute to chain entanglement that interacted with tree gum intermolecular interactions, thus facilitating spinnability. Uniform diameter and beadless nanofibres could not be generated because of the weak hydrogen bonding interactions between PEO and tree gums (GA, GK and KG). Furthermore, the low polymer concentration of tree gums was not sufficient to lead to appropriate chain entanglement necessary for electrospinning. Due to these problems, PEO is not suitable as a proper polymer for making blends with tree gums for the electrospinning process. A similar problem was reported in the case of green seaweed (*Ulva Rigida*) with PEO blend solutions [23]. These solutions could not be electrospun owing to weak hydrogen bonding interactions and insufficient chain entanglement between the *Ulva Rigida* polymer chains with PEO that is necessary for the smooth production of nanofibers [23].

### **3.3. Morphological characterization of nanofibers**

The electrospun fibres of PVA blended with GA [(PVA/GA weight ratio of 50/50, 60/40, 70/30, 80/20, 90/10 and 100/0 (pure PVA)] are presented in Fig. 2 (a, b, c, d, e and f). PVA is a polar, biodegradable polymer with a large number of hydroxyl groups in its backbone structure, capable of interacting with tree gums to form hydrogen bonds and thereby disrupting intermolecular interactions of the gums - resulting in the production of uniform diameter smooth nanofibers by electrospinning. Our findings indicated that addition of PVA to tree gums resulted in viscosity reduction and thus enhanced the electrospinning abilities of the polymer blend solutions (Table 2 and Fig 2, 3 & 4). The decrease in viscosity with addition of PVA in PVA/Gum solutions is due to inter and intramolecular hydrogen bonding interactions between hydroxyl groups of PVA with carbonyl groups of tree gums. This observation was corroborated by FTIR analysis (Fig. 6) and the electrospinning properties of, gellan gum, *Ulva Rigida* as chitosan reported earlier [5, 23, 92]. The current work indicated that PVA was a better partner polymer than PEO for making blend solutions with tree gums. The mixed PVA/GA, PVA/GK and PVA/KG solutions (with respective ratios of 50:50 to 90:10 of PVA: GA; PVA: GK and PVA: KG) resulted in uniform morphology and defect-free nanofibers (Figs. 2, 3 & 4), respectively. The mass ratios ranging from 70:30 to 90:10 for PVA: GA, PVA: GK and PVA: KG were observed to ascertain the optimum blend solution ratios required to fabricate uniform beadless nanofibers with average diameters of  $240\pm 50$ ,  $220\pm 40$  and  $210\pm 30$  nm, respectively.

### **3.4. Comparison of plasma treated and non-treated electrospun fibers**

The SEM images methane plasma (2.0 min. treatment times) treated nanofibers of GA, GK and KG (P-GA, P-GK and P-KG) are presented in Fig. 5.

For the untreated samples (U-GA, U-GK and U-KG) of the same composition (PVA: GA/GK or KG; 90:10) (Fig. 2e, 3e and 4e) the smooth surfaces of the nanofibers are clearly observed, whereas the P-GA, P-GK and P-KG are remarkably roughened by the methane plasma (treatment time; 2.0 min.) treatments, as seen in Fig. 5 (a, b & c), respectively. Typically, plasma treatment modifies the surface by grafting hydroxyl (–OH), carbonyl (–C=O), and carboxylate (–COOH) groups [93-95]. A comparison of the physicochemical and structural properties of plasma treated and non-treated fibres of GA, GK and KG are presented in Table 3. The contact angles of U-GA, U-GK and U-KG are 50.5°, 60.4° and 61.5° respectively, these untreated fibers displaying hydrophilic properties. However, for the methane P-GA, P-GK and P-KG, the values of the water contact angle are 105.8°, 110.6° and 112.6° respectively, which imply hydrophobic properties (Fig. 5 a, b and c). In the plasma treated fibers, the crosslinking reaction induced by the esterification between carboxylic groups of the GA, GK or KG and hydroxyl groups of PVA was also confirmed using ATR-FTIR analysis (Fig. 6). The results show the effect of methane plasma treatment, not only on improving the hydrophobic properties of the nanofibers but also the size of the surface area. The BET measurement of methane P-GA, P-GK and P-KG are observed to be  $8.9 \pm 0.5$ ,  $9.5 \pm 0.6$  and  $9.8 \pm 0.8 \text{ m}^2\text{g}^{-1}$ , which is almost 70% more than the corresponding untreated nanofibers (Table 3). The degree of stability (DS %) of the plasma treated nanofibers are higher than that of the untreated fibers. The plasma treated nanofibers were observed to have better stability than the untreated fibers. Our results are in agreement with the water stability of electrospun chitosan nanofibres which have been prepared and used for the removal of toxic metals from water [96].

### 3.5. ATR-FTIR spectroscopy

The ATR-FTIR spectra of PVA, GA, GK and KG and untreated (U-GA, U-GK and U-KG) and plasma treated fibers of GA, GK and KG (P-GA, P-GK and P-KG) are presented in



Fig. 6. Spectra of GA, GK and KG showing peaks at  $3300\text{ cm}^{-1}$  related to the OH group and also at  $1159$ ,  $1082$  and  $1014\text{ cm}^{-1}$  (in the fingerprint region) corresponding to  $\text{-C-O-C-}$  stretching vibrations of various sugar moieties present in the gums [29, 90]. The band at  $2923\text{ cm}^{-1}$  represents the characteristic vibration of C-H stretching while the peaks at  $1430\text{ cm}^{-1}$  and  $1326\text{ cm}^{-1}$  are characteristic of the C-H deformation vibrations in PVA, respectively. The absorption peak at  $1000\text{--}1100\text{ cm}^{-1}$  can be assigned to the C-O stretching and O-H bending vibrations arising from the PVA chain, respectively. The appearance of a new peak at  $1563\text{ cm}^{-1}$  in the U-GA, U-GK and U-KG represents the deformation vibration of the OH group. The H bond suggests that a hydrogen bond forms between the PVA and U-GA, U-GK or U-KG to form PVA-GA, PVA-GK or PVA-KG blends (Fig. 6). Similar observations have been reported in the case of gum Tragacanth / PVA nanofiber formation and the generation of hydrogen bonding between  $\text{-OH}$  groups of PVA and  $\text{-COO}$  and  $\text{-OH}$  groups of gum Tragacanth [24]. GA, GK and KG have abundant hydroxyl groups in their structures. Hence on blending with PVA, hydrogen bonding interactions between GA, GK, and KG with PVA occurred and this is reflected in both untreated and plasma treated fibers. The additional functionality observed in plasma treated (P-GA, P-GK and P-KG) nanofibers (Fig. 6) is due to the surface modification by grafting of hydroxyl ( $\text{-OH}$ ), carbonyl ( $\text{-C=O}$ ), and carboxylate ( $\text{-COOH}$ ) groups.

#### 4. Conclusions

Tree gum (GA, GK and KG) hydrocolloid based nanofibers were fabricated for the first time in aqueous solutions of gums with PVA by electrospinning. The PVA was found to be a better partner solvent (in comparison with PEO) in gum solutions for electrospinning processes. The effects of various parameters such as solution properties and process factors, on the structure and morphology of the fibres were investigated. Plasma treatment was found to be an efficient and environmentally friendly method of enhancing the structural

and physicochemical properties of the electrospun fibres. The interactions between gums functional groups with PVA in the PVA/Gum blend solutions and after plasma treatment were demonstrated using ATR-FTIR. The present study focuses on development of plasma treated electrospun nanofibers based on natural polymers for potential applications in food and environmental areas.

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**Figure Captions:**

**Figure 1:** Refractive index and weight average molecular gel permeation chromatography elution profiles of (a) GA; (b) GK; and (c) KG, respectively.

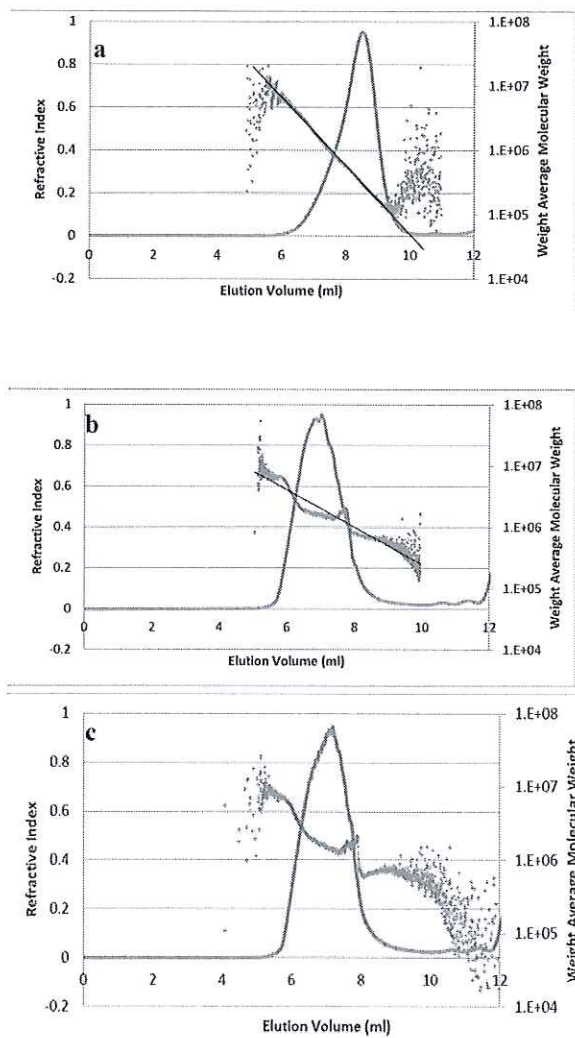
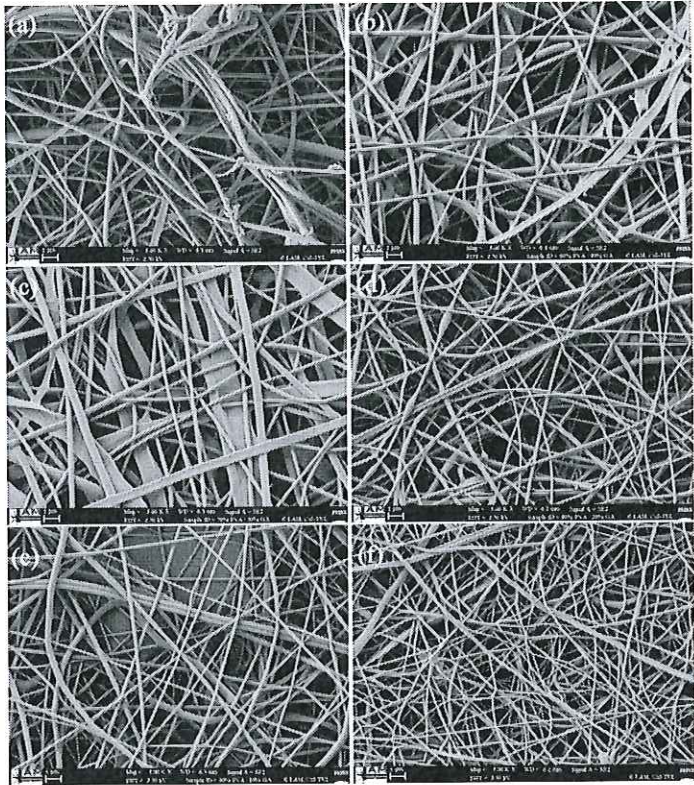
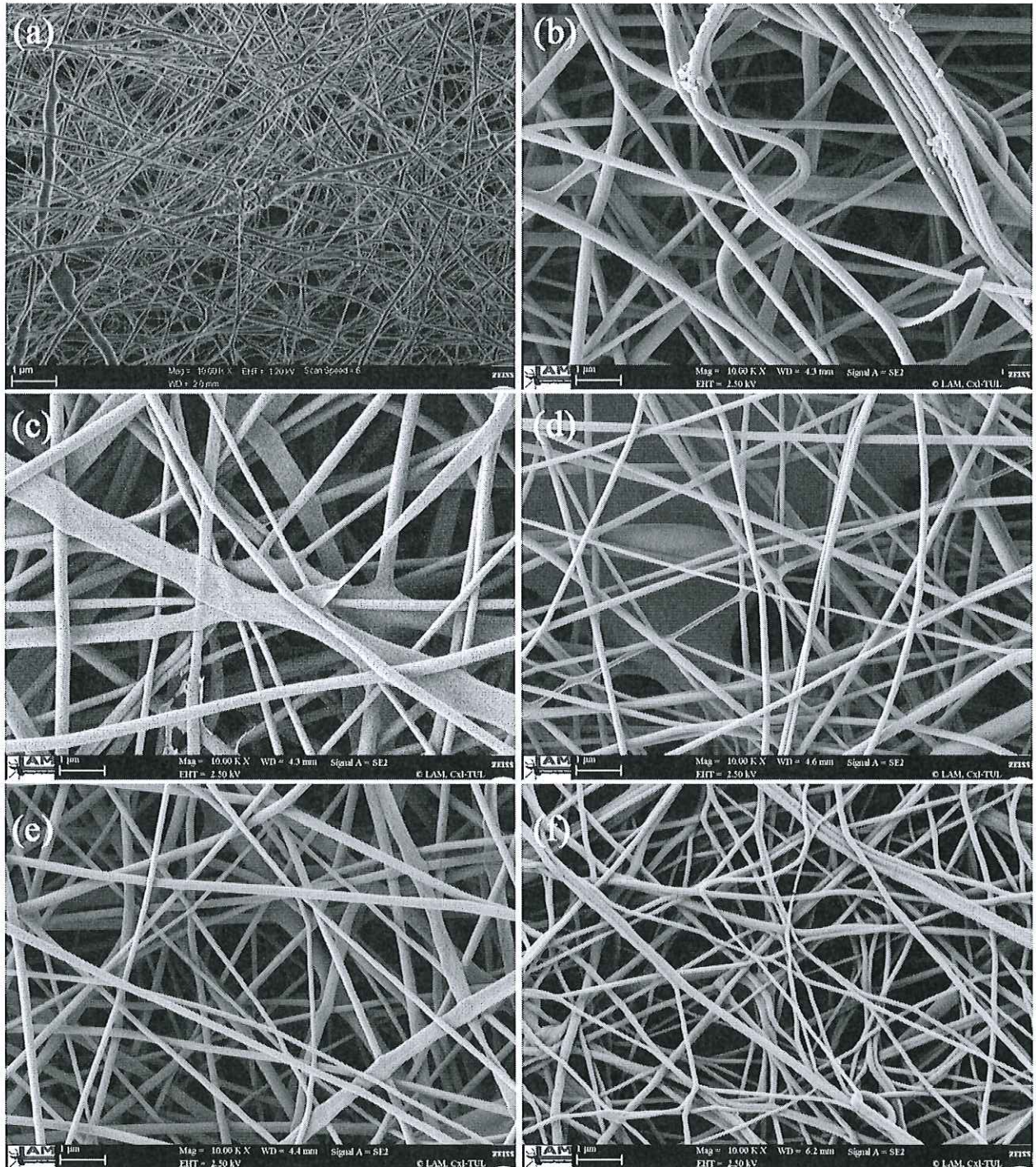


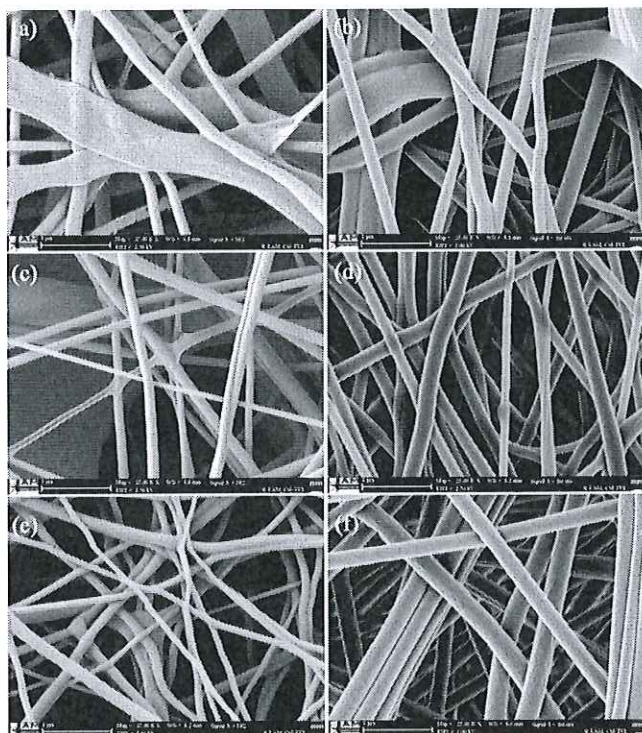
Figure 2: SEM photographs of nanofibers with different weight ratios of PVA to GA ( PVA/GK weight ratios of (a) 50/50, (b) 60/40, (c) 70/30, (d) 80/20, (e) 90/10 and (f) 100/0 (pure PVA).



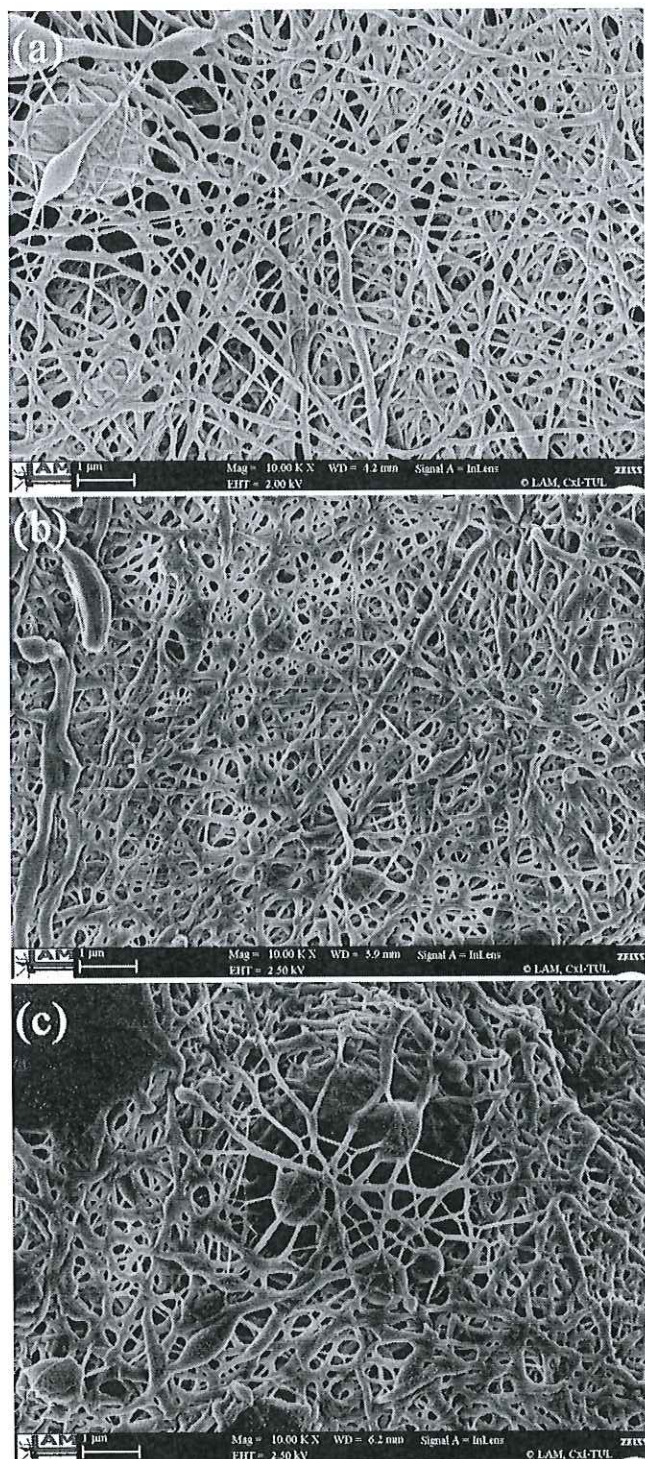
**Figure 3:** SEM Morphology of the PVA/GK nanofibers fabricated at varying PVA: GK ratios in the blend solutions (a) 50:50, (b) 60:40, (c) 70:30, (d) 80:20, (e) 90:10 and (f) 100:0 (pure PVA)



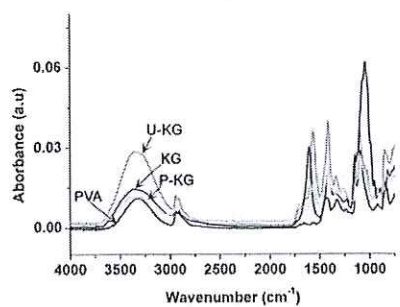
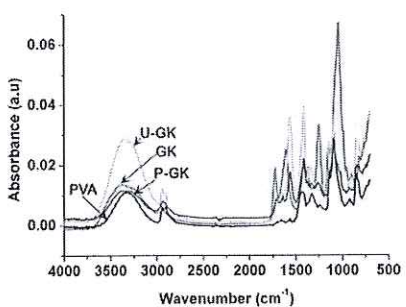
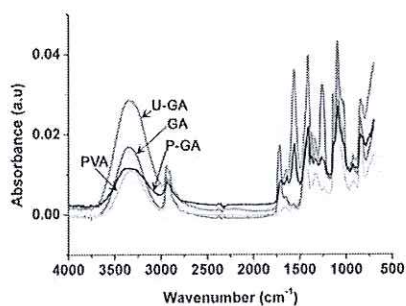
**Figure 4:** SEM Morphology of the PVA/KG nanofibers fabricated at varying PVA: KG ratios in the following blend solutions (a) 50:50, (b) 60:40, (c) 70:30, (d) 80:20, (e) 90:10 and (f) 100:0 (pure PVA).



**Figure 5:** SEM morphology of (a) Plasma treated nanofibers of GA; (b) GK; and (c) KG, respectively.



**Figure 6:** ATR-FTIR spectra of PVA, GA, GK and KG and their respective untreated and plasma treated nanofibers. Abbreviations: U-GA, U-GK and U-KG represent untreated nanofibers of GA, GK and KG, respectively and P-GA, P-GK and P-KG represent the methane plasma treated nanofibers of GA, GK and KG, respectively.





**Table 1:** The estimated molar mass distributions and rms radius moments (nm) of GA, GK and KG using GPC/MALLS and data fitted with first-order polynomial using the Zimm method (*eluant: 0.1 M NaNO<sub>3</sub>; flow rate: 0.5 mL/min.; dn/dc: for GA, 0.141 mL/g; for GK and KG; 0.140 mL/g*)

<b>Gum Type</b>	<b>M<sub>n</sub> (g/mol)</b>	<b>M<sub>w</sub> (g/mol)</b>	<b>M<sub>z</sub> (g/mol)</b>	<b>R<sub>n</sub> (nm)</b>	<b>R<sub>w</sub> (nm)</b>	<b>R<sub>z</sub> (nm)</b>
GA	2.5313 x 10 <sup>5</sup>	5.013 x 10 <sup>5</sup>	1.260 x 10 <sup>6</sup>	12.1	17.3	26.8
GK	1.537 x 10 <sup>6</sup>	1.827 x 10 <sup>6</sup>	2.062 x 10 <sup>6</sup>	87.0	91.8	95.3
KG	8.294 x 10 <sup>5</sup>	1.144 x 10 <sup>6</sup>	1.423x 10 <sup>6</sup>	82.9	90.7	96.3

**Table 2: Electrospinning composition and solution properties of GA, GK and KG with PVA blend solutions**

Electrospinning Polymer solutions		Solution properties <sup>a</sup>		
<u>GA/PVA</u>	<u>GA+ PVA</u>	Viscosity (mPaS)	Surface Tension (mN/m)	Conductivity (mS/cm)
(Solution mass ratio)	(Resulting blend conc. wt. %)			
50:50	10	2547±86.8	55.7±0.08	4.7±0.05
40:60	10	2200±59.8	54.2±0.05	4.6±0.05
30:70	10	1850±38.5	52.4±0.04	4.3± 0.04
20:80	10	1580±26.5	50.2±0.03	4.1±0.04
10:90	10	1387±20.4	49.2± 0.04	3.8±0.02
<hr/>				
<u>GK/PVA</u>	<u>GK+PVA</u>	Viscosity (mPaS)	Surface Tension (mN/m)	Conductivity (mS/cm)
(Solution mass ratio)	(Resulting blend conc. wt. %)			
50:50	6.5	4569±125.6	52.5±0.08	4.4±0.06
40:60	7.2	4008±89.9	50.6±0.07	4.2±0.05
30:70	7.9	3010±78.8	48.6±0.05	3.8±0.04
20:80	8.2	2540±45.6	46.4±0.05	3.6±0.03
10:90	9.3	2056±34.8	45.2±0.04	3.4±0.04
<hr/>				
<u>KG/ PVA</u>	<u>KG+PVA</u>	Viscosity (mPaS)	Surface Tension (mN/m)	Conductivity (mS/cm)
(Solution mass ratio)	(Resulting blend conc. wt. %)			

50:50	6.5	5025±205.6	54.5±0.09	4.2±0.04
40:60	7.2	4600±275.8	53.5±0.08	4.0±0.05
30:70	7.9	3500±150.6	52.0±0.06	3.6±0.04
20:80	8.2	2800±100.5	48.5±0.05	3.3±0.04
10:90	9.3	2100±56.4	46.6±0.04	3.2±0.02

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<sup>a</sup> Values = Mean ± S. D (n=3)

**Table 3: Comparison of physicochemical and structural properties of plasma treated and untreated tree gum electrospun nanofibers\***

Fibers	Thickness ( $\mu\text{m}$ )/ Surface Texture	Apparent density	porosity	BET surface area	Water contact angle	Degree of stability (%)
U-GA	25 $\pm$ 5; smooth	0.45 $\pm$ 0.08	65- 67	5.2 $\pm$ 0.4	50.5 $\pm$ 0.4	80
U-GK	35 $\pm$ 7; smooth	0.58 $\pm$ 0.06	70-72	5.8 $\pm$ 0.5	60.4 $\pm$ 0.5	90
U-KG	37 $\pm$ 6; smooth	0.60 $\pm$ 0.08	73-76	6.1 $\pm$ 0.4	61.5 $\pm$ 0.8	92
P-GA	32 $\pm$ 5; rough	0.56 $\pm$ 0.05	70-72	8.9 $\pm$ 0.5	105.8 $\pm$ 0.5	95
P-GK	45 $\pm$ 8; rough	0.68 $\pm$ 0.8	79-82	9.5 $\pm$ 0.6	110.6 $\pm$ 0.8	97
P-KG	50 $\pm$ 6; rough	0.71 $\pm$ 0.8	82-84	9.8 $\pm$ 0.8	112.6 $\pm$ 0.6	98

\*Data presented are representative of three independent experiments; Values= Mean  $\pm$  S.D (n=3); Abbreviations: P-GA, P-GK and P-KG and U-GA, U-GK and U-KG represents plasma treated and untreated fibers of GA, GK and KG respectively.

Due to the plasma treatment, the P-GA, P-GK and P-KG have shown much higher surface area, porosity, membrane thickness, apparent density, water contact angle and stability compared to untreated fibers. This can be ascribed to the hydrophobic surface generated by plasma treatment and the improved surface wetting attributes of the fibers [94, 95]. These results indicate that the prepared plasma treated fibers of tree gums have a higher potential for many applications.