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Electrospun fibers based on Arabic, karaya and kondagogu gums

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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 fibers whose morphology and physicochemical properties were evaluated. The mass ratios of 70:30 to 90:10 for PVA: GA, PVA: GK and PVA: KG were observed to establish an optimum blend solution ratio in order to fabricate uniform beadless nanofibers with an average diameter of 240 ± 50, 220 ± 40 and 210 ± 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.

1. Introduction

Electrospinning is a versatile method for making nanometer to micrometer size range fibers for a variety of molecules in synthetic, natural and biological polymers. Electropsun fibers 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 fibers 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 fibers 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

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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 & hyalyronic 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 fibers 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_3O_4) 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 fibre 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 1 M NaOH. $NaHB_4$ (1.0 M) 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 1 M 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].