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Regeneration of cellulose acetate nanofibrous mat from discarded cigarette butts

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Cellulose acetate present in the cigarette butts has been regenerated into nanofibrous mat. The developed mat is then characterized using various analytical tools. Uniform bead-free cellulose acetate fibre is obtained at 12 % w/v concentration of cellulose acetate. The mat thus obtained exhibits good antimicrobial property.

Keywords: Antimicrobial property, Cellulose acetate, Cigarette butts, Electrospinning, Nanofibrous mat, Silver nitrate

Pollution is undoubtedly a major threat to human beings and to the surrounding environment. Smoking the cigarettes causes air pollution leading to serious sickness to the users and passive smoking results in fatigue, headache and other chronic obstructive pulmonary diseases. Littering the cigarettes after consumption into the open space such as sidewalk, beaches, natural trails, gardens and other public places, causes water and soil pollution which in turn influences the environment by changing its physical, chemical and biological properties of the nature. The commercial cigarette comprises tobacco, paper, polyvinyl alcohol glue and 95% cellulose acetate. The cigarette filters are usually comprised of monofilament tow of cellulose acetate along with numerous chemicals and additives. The cigarette butt which holds a filter is about 30 % of whole cigarette's length and usually contains traces of tobacco. The accumulation of cigarette butts in the ecosystem is serious issue as the butt wastes are non-biodegradable[1]. They also affect ecosystem as it is carried out as runoffs from streets to drains, to rivers and ultimately to the ocean and then consumed by aquatic species[2]. Effective recycling of butts is one of the solutions to overcome the problem. At present, few limited works have been carried out to use cigarette butts as insecticide[3], filler in fired clay bricks[4] and energy storage devices[5]. Cellulose acetate is one of the preferred choices for preparing filters for water and air purification. This is due to the presence of acetyl groups in the structure of cellulose acetate. Electrospinning is a versatile tool to spin mat of preferred choice for filtration applications.

In the present work, it is planned to explore the possibility of regeneration of cellulose acetate by electrospinning and constructing a nanofibrous mat. Electrospinning is an emerging technique to produce fibres of nano dimensions. It is versatile, easy to use and can produce fibres with desired morphology. The fibre possesses advantageous of larger surface area to volume ratio, high porosity, pore size distribution, flexibility and superior mechanical properties. This technique uses the electrostatic forces to produce fine fibres by application of high voltage. The setup consists of three components such as capillary tube with needle, voltage supplier and collecting system. On application of voltage, electrostatic force overcomes the surface tension of the polymer solution and forms Taylor cone. On further increase in electric field, the polymer solution is ejected from the needle and solidified fibres are collected in the grounded collector after the evaporation of the solvent between needle and nozzle[6]. The produced electrospun web finds its application in various fields such as tissue engineering, drug delivery, filtration, separation, energy storage devices and sensors.

The present work is therefore aimed at regenerating the waste cellulose acetate collected from butts into nanofilament mat. The process parameters are optimized to achieve the desired result. Silver in the form of silver nitrate is doped with cellulose acetate as fibrous mat to functionalize the mat.

Experimental

Cellulose acetate (CA) was collected from discarded cigarette butts. Methanol, dimethyl formamide, acetone, and silver nitrate were purchased from Sisco Research Laboratories and then used as such for studies.

Extraction of Nicotine from Cellulose Acetate

The traces of nicotine were extracted from discarded cigarette butts by treating the butts with

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methanol in soxhelet apparatus for 12 h at 35° C . The nicotine was extracted and the fibres were dried and used for electrospinning process[7].

Electrospinning of Cellulose Acetate Fibres

Cellulose acetate solution was prepared by dissolving 8 %, 10 %, 12 % (w/v) of cellulose acetate in acetone and dimethyl formamide. The ratio of acetone to dimethyl formamide used was 2:1. The prepared solution was loaded into the 5 mL syringe fitted with 18G needles. The feed rate of the solution was set to 0.5 mL/h and the voltage was varied from 10 kV to 20 kV. The distance between the nozzle and the collector was kept at 15 cm. The randomly oriented nanofibres were deposited on a grounded aluminum foil after the evaporation of the solvents used in the solution[8]. Based on the best concentration at which uniform bead-free fibres were formed, silver nitrate at three different concentrations such as 1mM, 3mM and 5 mM was loaded and mixed thoroughly with ultra sonicator and further electrospun.

Characterization

The morphology of nanofibrous mat with and without silver nitrate was studied using scanning electron microscope. The samples were gold coated using sputter coating machine. Micrograph samples were taken at an accelerating voltage of 30 kV. To determine distribution of the silver nitrate particles in cellulose acetate membrane, a high resolution transmission electron microscopy (HRTEM) was used to obtain TEM images. X-Ray diffraction studies were carried out to understand the crystal changes in the samples. Thermogravimetric Analysis (TGA) measurements were carried out under nitrogen atmosphere in the temperature range from 50°C to 700° C at the heating rate of 20° C/min to understand the weight loss as a function of temperature. The antibacterial activity of the samples was tested through zone of inhibition testing with Gram negative bacteria (*E. coli*) and Gram positive bacteria (*S. aureus*).

Results and Discussion

In this study, efforts have been made to regenerate cellulose acetate from the cigarette butts in the form of nanofibres and explore its potential application. The SEM images of the cellulose acetate in the butt are given Fig. 1. Serrated cross-section of the fibres can be observed in the images. Mostly these fibres are present in the pleated configuration

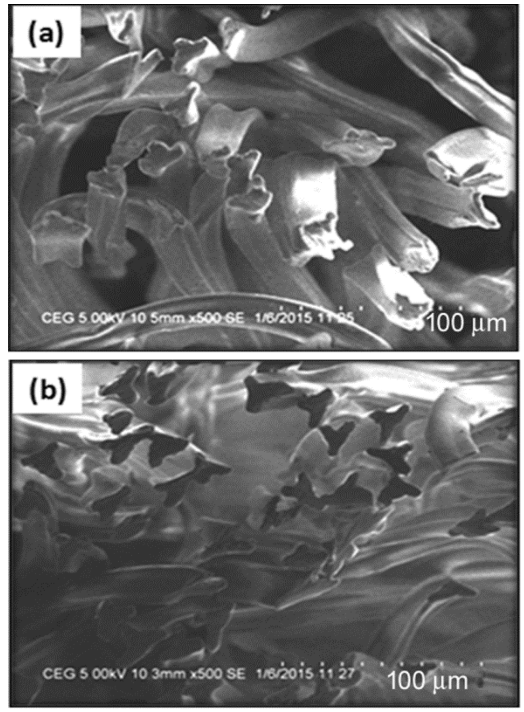

Fig. 1 — SEM images of cellulose acetate in the cross-section (a) before and (b) after removal of nicotine

Surface Morphology

The cigarette butts after usage contains traces of nicotine. The samples are electrospun as such without removal of nicotine and other impurities. The general observation during electrospinning of cigarette butts containing traces of nicotine is that the spinnability is difficult and at times it leads to formation of beads in the fibre structure. In order to overcome the above issue, it is planned to remove nicotine and other impurities from the butt using soxhlet apparatus. The SEM images of the samples prepared with presence and absence of nicotine are given in Fig. 2. Figures 2 (a), (c) and (e) show the sample without nicotine removal at 8, 10 and 12 w/v CA concentrations respectively. It can be seen from the images that beads are formed and the fibre morphology is not uniform. Figures 2 (b), (d) and (f) show the samples prepared after removal of nicotine. A uniform and bead-free fibre is obtained at CA concentration of 12 % w/v after the removal of nicotine. The diameter of the fibre ranges between 200 nm and 700 nm. At 12 % w/v CA concentration with an electrospinning voltage of 15kV, gap of 15cm and flow rate of 0.5mL/h, the uniform bead-free fibres are obtained.

To envisage a potential application for the regenerated cellulose acetate, it has been planned to dope the solution with silver nanoparticles. But

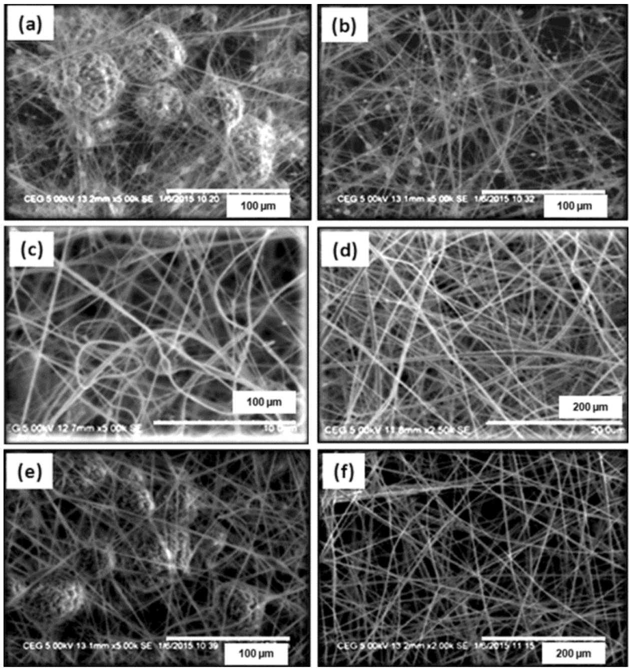

Fig. 2 — SEM images of samples (a) 8% w/v CA without extraction of nicotine, (b) 8% w/v CA after extraction of nicotine, (c) 10% w/v CA without extraction of nicotine, (d) 10% w/v CA after extraction of nicotine, (e) 12% w/v CA solution without extraction of nicotine, and (f) 12% CA extracted butt

addition of silver nitrate to the 12 %w/v cellulose acetate yields fibres in the thread form (Fig. 3). This may be due to increased conductivity and viscosity of the solution[9]. On reducing the CA concentration to 10 % w/v and on further incorporation of silver nitrate of concentration 1mM, 3mM and 5mM, uniform bead-free mat is obtained. The morphology of the fibres obtained is shown in Fig. 4. TEM images of samples are shown in Fig. 5. The images confirm the presence of silver particles on the surface of the fibres.

Thermogravimetric Analysis (TGA)

The TGA thermograms of the pristine cellulose acetate, regenerated cellulose acetate in the nanofibrous form, regenerated cellulose acetate doped with silver nitrate are given in Fig. 6. It can be seen that the onset degradation of pristine cellulose acetate starts at 320° C, whereas that of electrospun cellulose acetate starts at around 280˚. The interaction of the solvent combination with the polymer coupled with the application of high voltage during electrospinning has led to alteration of polymeric chain with the creation of residues. This leads to the faster onset of degradation in case of electrospun pure cellulose acetate. However on doping with silver nitrate the thermal stability increases and the onset of

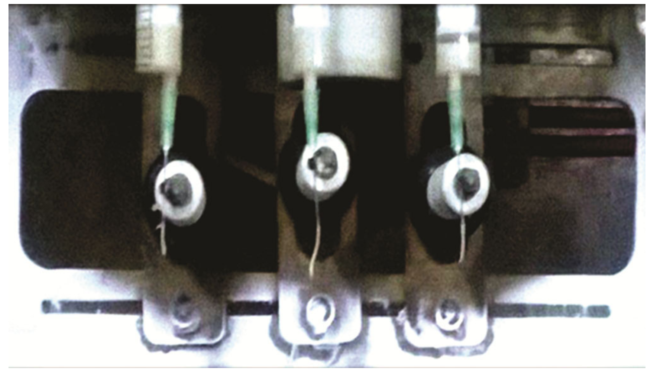

Fig. 3 — Thread like formation when 12% CA sample is electrospun

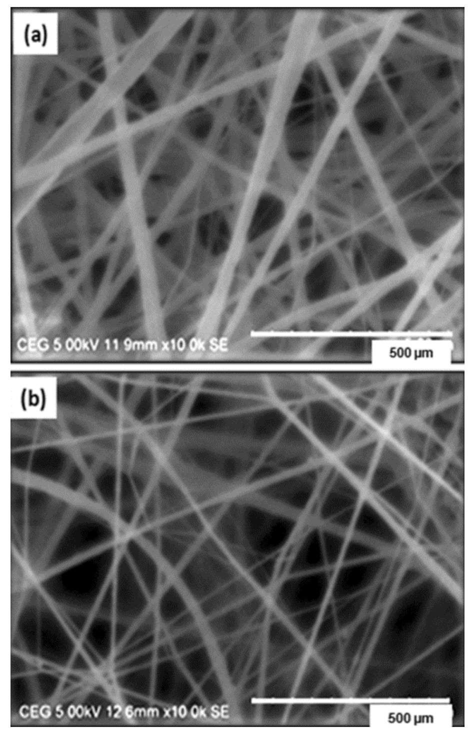

Fig. 4 — SEM of $AgNO_3$ incorporated electrospun CA mat (a) 1mM and (b) 5mM

degradation is shifted towards 320° C. The increased stability can be attributed to the presence of silver in the mat.

FTIR Analysis

FTIR of pure cellulose acetate, electrospun cellulose acetate with and without silver nitrate with optimized composition is shown in Fig. 7. The characteristic spectrum of pristine cellulose acetate shows broad absorption band at 3300 - 3500 cm^{-1} corresponding to the stretching of C-H groups. The absorption band at 2700 - 2900 cm^{-1} corresponds to the stretching of CH_2 groups and that of 1065 cm^{-1}

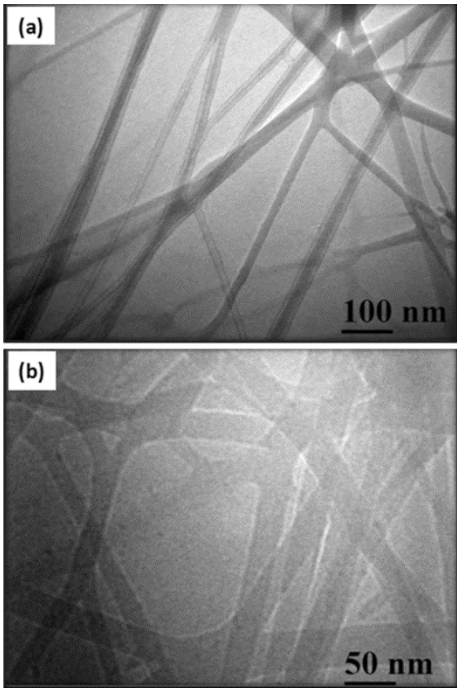

Fig. 5 — TEM images of $AgNO_3$ incorporated electrospun CA mat (5mM) at different magnifications (a) 100 nm, and (b) 50 nm

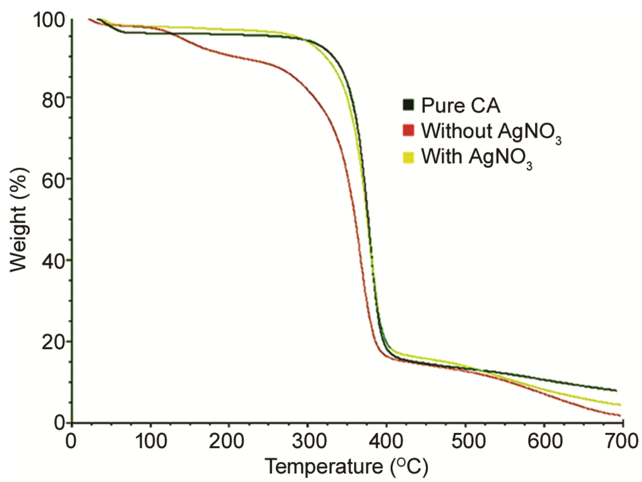

Fig. 6 — Thermogravimetric analysis of CA samples

corresponds to C-O-C (ether linkage) from glycoside units, whereas the peaks at 1650 cm^{-1} and 1500 cm^{-1} correspond to the stretching of C=O bonds[10]. The peaks at around 1450 cm^{-1} and 1300 cm^{-1} are assigned for scissoring of CH_2 group and bending of OH groups by vibration respectively. In case of electrospun pure cellulose acetate, the characteristic peak between 1000 cm^{-1} and 1500 cm^{-1} disappears due to the alteration of polymeric chains owing to application of high voltage during electrospinning. The characteristic peak of cellulose acetate is

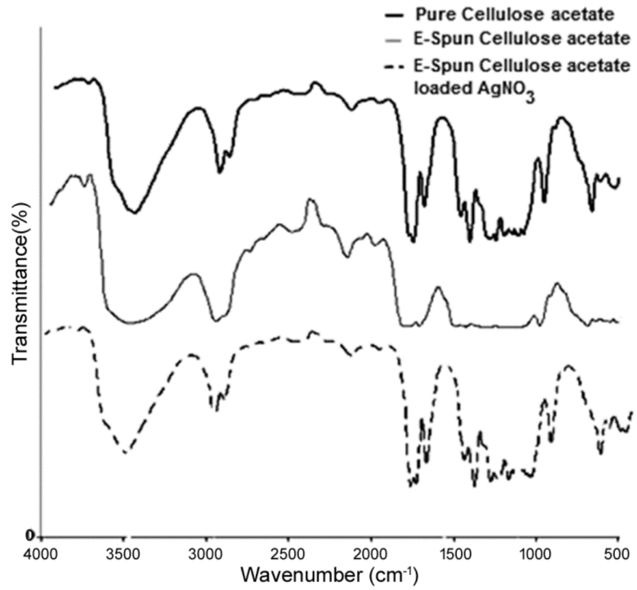

Fig. 7 — FTIR analysis of CA samples

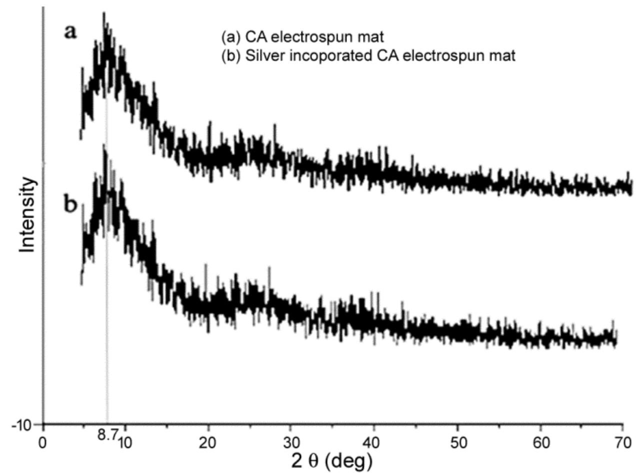

Fig. 8 — XRD graph for collected samples

seen in both regenerated and silver incorporated electrospun cellulose acetate web. This ensures that addition of silver to the solution does not make a significant change in the chemical structure of cellulose acetate.

XRD Analysis

The XRD pattern of pure nanofibrous cellulose acetate and cellulose acetate incorporated with silver nitrate mat is shown in Fig. 8. A characteristic crystalline peak at 8.7° 2θ is observed for both samples. The intensity of the peaks is not sharp and it can be attributed to the semi-crystalline nature of the samples. The electrospinning of samples results in fibres with increased amorphous content.

Table 1 — Zone of inhibition

$AgNO_3$, mM	Zone of inhibition, mm	
	E. coli	*S. aureus*
1	25	29
3	27	27
5	25	30

Zone of Inhibition

The zone of inhibition studies are carried out for Gram positive (*E.coli*) and Gram negative bacteria (*S. aureus*) as shown in Table 1. The zone of inhibition is found to be higher for Gram negative bacteria as compared to Gram positive bacteria [11]. However, no distinct variation could be observed for the increase in concentration of silver nitrate.

Cellulose acetate nanofibrous mat is produced using waste cigarette butts containing cellulose acetate polymer. At 12 % w/v concentration of cellulose acetate, a uniform bead- free fibre is obtained. The mat is functionalized by doping with silver nitrate. The mat exhibits good antimicrobial activity. An effective way for utilization of the disposed cigarette butts is provided.

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