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Development and characterization of cellulosic nanofibre matrix loaded with hexanal

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Abstract
An electrospun cellulosic nano-fibre matrix was developed using polyvinyl alcohol and β-cyclodextrin polymers and employed as a smart delivery system for a gaseous molecule (hexanal) which is known to extend shelf-life of fruits and vegetables. A laboratory study was undertaken to encapsulate hexanal in electrospun cellulosic nano-fibre matrices. In order to develop cellulosic matrix, a cellulosic paper with 399 µm thickness was chosen as a substrate to deposit elecrospun nano-fibre. The biodegradable nano-stickers developed and characterized. The high resolution imaging with SEM has shown that the diameter of nanofibre made of PVA + β-cyclodextrin before and after loading of hexanal were about 160 ± 10nm and 290 ± 10nm, respectively. The vertical sectioning was done to measure the thickness of deposited nanofiber over the substrate was 4.1µm. The internal features of the nano-fibres were visualized under Transmission Electron Microscope (TEM). The average diameter of the nanofibre before and after loading of hexanal was 53.4 and 166nm, respectively. The hexanal loaded into the fibre was measured as 73.6 nm. The XRD indicates the crystallinity of nanofibre before and after loading of hexanal.

Keywords: Nano-fibre, electrospinning, polyvinyl alcohol, β-cyclodextrine

Introduction
Electrospinning is one of the versatile and highly emerging technologies is electrospinning which is widely used in smart delivery of drugs, tissue engineering, environmental protection etc. Electrospinning is a classical traditional technique, patented by A. Formhals in 1934 used to synthesize Nano sized polymeric fibre by applying high voltage (Anton, 1934) [4]. When the polymer solution is subjected to an electrical field, an electric charge is induced on the liquid surface. When the applied electric field reaches a critical value, the repulsive electrical force overcomes the surface tension forces. Eventually, a charged jet of the solution is ejected from the tip of the Taylor cone and an unstable and a rapid whipping of the jet occurs in the space between the capillary tip and collector which leads to the evaporation of the solvent, leaving a polymer behind (Taylor, 1969) [10].
Hexanal is a naturally occurring volatile C-6 aldehyde formed via the lipoxygenase pathway in plants; precursor for formation of alcohols and esters in the production of aroma. Hexanal is a generally regarded as safe (GRAS) compound and an inhibitor of phospholipase D activity. Studies on the application of hexanal in climacteric fruits such as banana, plum, apple, tomato and pear delayed the ripening process and senescence of fruits and thereby playing an important role in shelf-life extension of fruits. Further, researches have proved that the activity of PLD can be inhibited by primary alcohols such as s hexanal (Paliyath *et al.*, 1999) [7]; (Tiwari *et al.*, 2011) [11-12]. Hexanal is found in nearly 300 natural sources including apple, apricot, banana, sweet and sour cherries, citrus peel oil and juices, berries, guava etc. with molecular formula C6H12O and molecular mass 100.1 a.m.u, present in a liquid state at Normal Temperature and Pressure (NTP). Hexanal exists in liquid state at room temperature (25 ºC). It has lower melting point of -20 ºC and higher boiling point of 120 ºC. Hence, it is highly stable and degrade in higher temperature during storage. But hexanal has very low vapour pressure i.e. 10mmHg at 20 ºC and thus easily volatilized when the temperature rises. Hence, there is a need for developing a novel delivery system for controlled release of hexanal to extend the shelf- life of fruits.

Materials and Method

Chemicals

Hexanal (98% pure) were purchased from Sigma Aldrich chemicals Bengaluru, Polyvinyl alcohol was purchased from Astron Chemicals, Ahmedabad and β-cyclodextrin (98% pure) was purchased from HIMEDIA Mumbai. All the chemicals used for this study were analytical grade and water was double distilled before use.

Preparation of electrospinning solution

Polyvinyl alcohol

Polyvinyl alcohol (PVA) solution of 10% was prepared by dissolving 1g of PVA in 10ml of double distilled water at 60 °C in borosil hot plate magnetic stirrer for 4 hrs at 200 rpm.

β cyclodextrin

The β cyclodextrin solution of 40% was prepared by dissolving 4 g of β cyclodextrin in 10 ml of double distilled water at 70°C in borosil hot plate magnetic stirrer for 4 hrs at 200rpm. The prepared 40% β cyclodextrin solution and 10% PVA solution were mixed well.

Cellulosic substrate

Filter paper Whatman No.3 were used as Cellulosic Substrate, purchased from Mehta Scientific Corporation, Chennai.

Result

Scanning Electron Microscope (SEM)

The diameter of the nanofibre made of PVA + β-cyclodextrin before and after loading of hexanal were about 160 ± 10nm (fig 1) and 290 ± 10nm (fig 2). The vertical sectioning was done to measure the thickness of deposited nanofiber over the substrate. The thickness of the substrate was 399µm (fig 3) and the thickness of nanofibre deposited over the substrate was 4.1µm (fig 4).

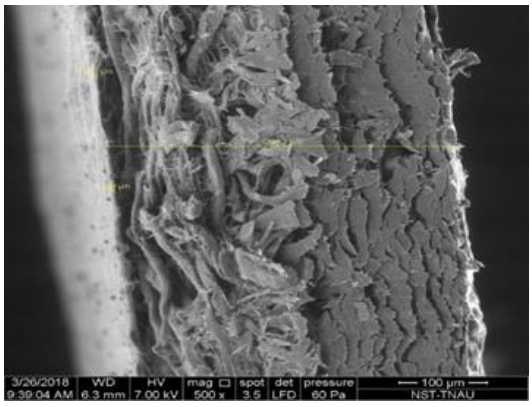

Fig 1: SEM image of Cellulosic substrate

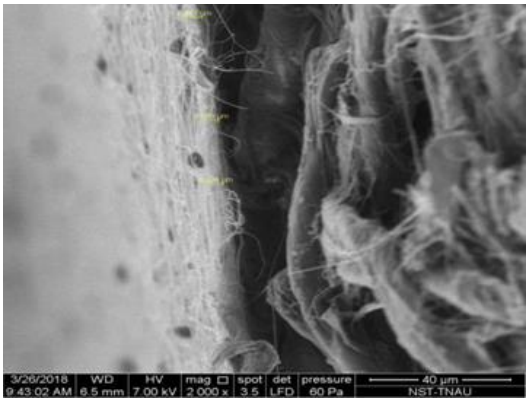

Fig 2: SEM image of nanofibre over substrate

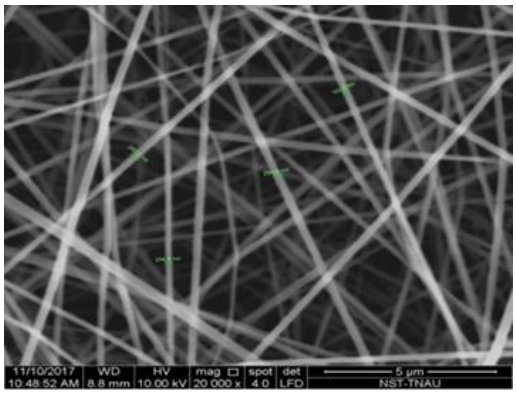

Fig 3: SEM image Nanofibre unloaded

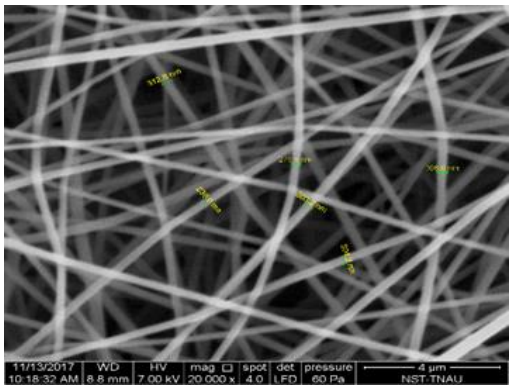

Fig 4: SEM image Nanofibre loaded with hexanal

Transmission Electron Microscope (TEM)

The internal features of the nano-fibres were visualized under Transmission Electron Microscope (TEM). The images have exhibited a clear view of formation of electrospun nanofibre and loading of hexanal in the fibre. The average diameter of the nanofibre before and after loading of hexanal was 53.4 (fig 5) and 166 nm, respectively. The hexanal loaded into the fibre was measured as 73.6 nm (fig 6).

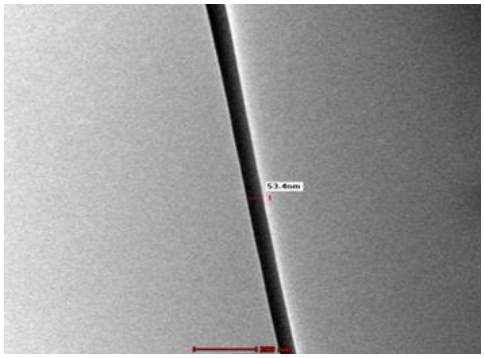

Fig 5: TEM image Nanofibre unloaded

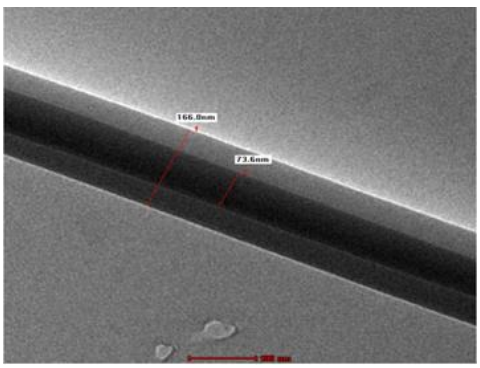

Fig 6: TEM image Nanofibre loaded with hexanal

X-Ray Diffraction (XRD)

The diffraction angles and peak intensity of XRD patterns can be used to verify the crystallinity of the samples. The XRD pattern of pure PVA showed a characteristic broad peak at 2θ ≈19.26° which corresponded to the PVA semi-crystalline phase. The β-cyclodextrin exhibited crystalline structure with distinct XRD peaks at 2θ angles viz. 9.15°, 12.64°, 12.85°, 19.74° and 23.07°. The results showed that the XRD pattern peaks at the 2θ angles in the electrospun fibers matrices before and after loading of hexanal were 12.20° and 10.32°, respectively (fig 7 & 8).

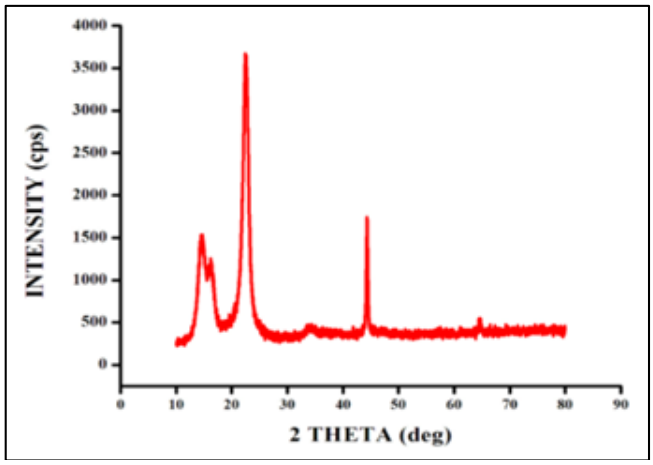

Fig 7: XRD PVA + β-cyclodextrine

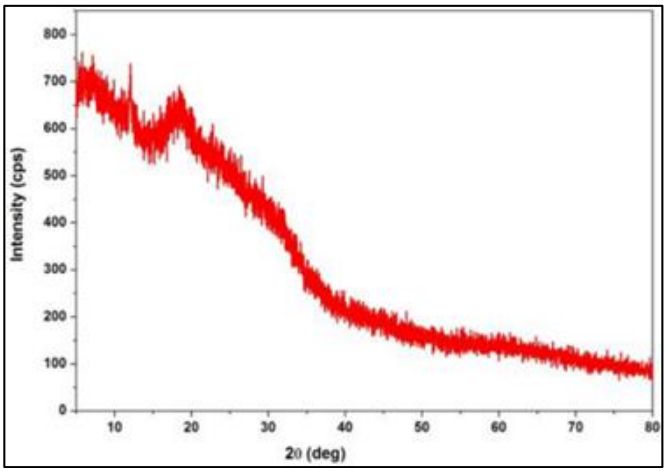

Fig 8: XRD PVA + β-cyclodextrine + Hexanal

Discussion

Scanning Electron Microscope (SEM)

The results exposed uniform, continuous and beads free fibre formation in different treatments. The average diameter of the nanofibre before and after loading of hexanal were about 160 ± 10nm and 290 ± 10nm, respectively. The vertical sectioning was done to measure the thickness of deposited nanofiber over the substrate. The thickness of the substrate was 399µm and the thickness of nanofibre deposited over the substrate was 4.1µm. The fibers produced in both the method of electrospinning methods indicated that hexanal had been completely entrapped inside the nano-fiber membrane. The results are in correspondence with findings of Jia *et al*. (2007) [5] and documented that the average fiber diameter increased monotonically from about 371 nm at a concentration of 6 percent to about 676 nm at a concentration of 9 per cent. They also suggested that the lower solution concentration facilitated to obtain thinner fibers. Maintaining other processing parameters, fiber diameter increased with increasing solution concentration. Alhosseini *et al*. (2012) [2] revealed that in PVA/ chitosan blend (weight ratio 90/10), the average fiber diameter was found to be 221 nm with a range of 94–410nm; while in PVA alone, the average fiber diameter was 744nm with a range of 395–1105nm. It should be noted that in electrospinning, the fiber diameter was dependent on the viscosity and charge of the solution. Furthermore, Taepaiboon *et al*. (2006) [9] also explained that columbic repulsion worked to stretch the charged jet and electrostatic force brought the jet to the target.

Transmission Electron Microscope (TEM)

Transmission electron microscope characterization of the present study justified that the nanofibers were fabricated as uniform and beads free. The average diameter of the nanofibre before loading of hexanal and after loading of hexanal was 53.4 and 166nm. The image clearly shown loading of hexanal in to the fibre was evenly distributed and the loading of hexanal in to the fibre was measured as 73.6nm. The image demonstrated that the intensity of electron falls over the fibre matrix bright and dark shadow images captured. The internal diameter of the hexanal loading was 73.6 nm that proved beyond doubt that the active molecule is effectively entrapped.

X-Ray Diffraction (XRD)

The result showed that pure samples of PVA, β-CD possessed numerous sharp XRD peaks, indicated that various crystalline forms were present in the samples. The pure PVA shows a significant crystalline peak at about 19.3°, indicated the occurrence of strong intermolecular and intramolecular hydrogen bonding. β-CD exhibited distinct XRD peaks appearing at 9.15°, 12.64°, 12.85°, 19.74°, and 23.07° at 2θ values. These numerous sharp XRD peaks of β-CD indicated that various crystalline nature of β-CD. However, these peaks disappeared from the patterns of the nanofiber matrices and new peaks were emerged. XRD pattern of hexanal loaded in PVA+β-CD, nanofiber matrix, the 2θ values occurred at 10.32°and 12.20°. In addition, hexanal loaded nanofiber matrices exhibited fewer and broader XRD peaks than the pure polymers, indicating that the crystallinity of the compounds decreased after nanofiber formation. Thus, hexanal loaded nanofibers had amorphous nature which significantly indicates the successful entrapment of hexanal into the nanofiber matrices.

The result on the X ray diffraction for of PVA, β-CD polymer and their loaded electrospun matrices with hexanal are in harmony with the findings of Prabu *et al*. (2015) [8], Mangolim *et al*. (2014) [6], Abdullah *et al*. (2015) [1], Zhang *et al*. (2015) [13] and Alwan *et al*. (2016) [3]. They reported the XRD pattern of PVA, that indicated that the crystalline size of PVA, β-CD polymer and their loaded complexes; HgS nanoparticles with PVA, Caffeine and curcumin with β-CD, ethyl butyrate and hexanal with (β-CD) exhibited reduction in crystallinity by the transformation of sharp peak to broad peaks. The lack of crystallinity was an additional confirmation for the formation of inclusion complex and led to increase the amorphous structures in the solid inclusion complex.

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