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Encapsulation of vanillin/cyclodextrin inclusion complex in electrospun polyvinyl alcohol (PVA) nanowebs: Prolonged shelf-life and high temperature stability of vanillin

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ABSTRACT

We produced functional nanowebs, containing vanillin, having prolonged shelf-life and high temperature stability facilitated by cyclodextrin (CD) inclusion complexation. Polyvinyl alcohol (PVA) nanowebs incorporating vanillin/cyclodextrin inclusion complex (vanillin/CD-IC) were produced via electrospinning technique. The vanillin/CD-IC was prepared with three types of CDs; α-CD, β-CD and γ-CD to find out the most favourable CD type for the stabilization of vanillin. PVA/vanillin/CD-IC nanofibres, having fibre diameters around ~200 nm, were successfully electrospun from aqueous mixture of PVA and vanillin/CD-IC. Our results indicated that vanillin with enhanced durability and high temperature stability was achieved for PVA/vanillin/CD-IC nanowebs due to complexation of vanillin with CD, whereas the PVA nanofibres without CD-IC could not effectively preserve the vanillin. Additionally, we observed that PVA/vanillin/γ-CD-IC nanoweb was more effective for the stabilization and slow release of vanillin suggesting that the strength of interaction between vanillin and the γ-CD cavity is stronger when compared to α-CD and β-CD.

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1. Introduction

Cyclodextrin inclusion complexes (CD-IC) are widely used in the food industry in order to achieve prolonged shelf-life and high temperature stability for volatile or unstable flavours and other food additives (Del Valle, 2004; Hedges, 1998; Marques, 2010). Cyclodextrins (CDs) are cyclic oligosaccharides having a truncated cone shape molecular structure, and CDs have unique ability which they can form non-covalent host-guest inclusion complexes with a variety of molecules including food additives (Del Valle, 2004; Hedges, 1998; Marques, 2010). In CD-IC, the CD cavity provides stabilization and protection to the guest molecules from evaporation, degradation and oxidation; in addition, the release of the guest molecules can be controlled and/or delayed by the CD-IC (Hădărugă et al., 2006; Kant, Linforth, Hort, & Taylor, 2004; Wang, Cao, Sun, & Wang, 2010). The three most common CDs used are α-CD, β-CD, and γ-CD having 6, 7, and 8 glucopyranose units in the cyclic structure, respectively (Fig 1). The depth of the cavity for these CDs is same which is ~8 Å, but, the size of the cavity is different for α-CD, β-CD, and γ-CD, which are ~6, 8 and 10 Å, respectively (Szejtli, 1998). The formation and stability of the CD-IC strongly dependent on the size/shape fit between the host CD and guest molecule, therefore, different types of CDs (α-CD, β-CD, and γ-CD) would show different capabilities to form inclusion complexes with the same guest molecule and the resulting CD-IC would have different stability (Rekharsky & Inoue, 1998).

Recently, electrospinning has received great attention since this technique is quite versatile and cost-effective for producing nanofibres/nanowebs having several unique characteristics, such as a very large surface-to-volume ratio, and moreover, functional additives can be effectively incorporated into the nanofibre matrix during the electrospinning process in order to produce multifunctional nanofibres/nanowebs (Greiner & Wendorff, 2007; Li & Xia, 2004). It has been reported that the electrospun nanofibres/nanowebs having unique properties and the multi-functionality nature can be quite applicable in various areas such as tissue engineering, wound healing, controlled/sustained release systems, filtration/membranes, functional textiles, etc (Bhardwaj & Kundu, 2010; Ramakrishna et al., 2006). Electrospinning of nanofibres has also received some interest in functional food and active food packaging (Kriegel, Arrechi, Kit, McClements, & Weiss, 2008; Vega-Lugo & Lim, 2009), since electrospun nanofibrous matrix having exceptionally high surface area and high encapsulation efficiency, can be effective for the stabilization of active food additives.

Food additives such as flavours and antioxidants are mostly sensitive to heat, oxygen and light, however, cyclodextrin inclusion complexation is very effective for the stabilization/protection and controlled/sustained release of these functional additives (Koontz, Marcy, O'Keefe, & Duncan, 2009; Wang, Cao, Sun, & Wang, 2011).

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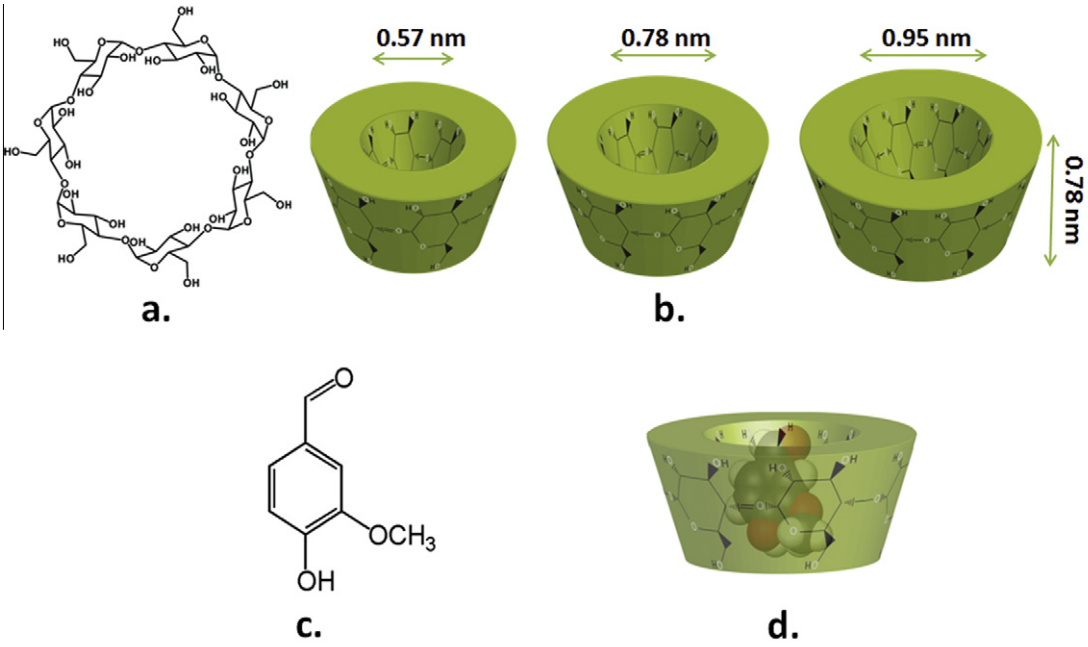

Fig. 1. (a) Chemical structure of β-CD; (b) approximate dimensions of α-CD, β-CD, and γ -CD; (c) chemical structure of vanillin and (d) schematic representation of vanillin/CD-IC.

Therefore, incorporation of CD-IC into electrospun nanofibrous matrix would improve the shelf-life, stability and slow release of such food additives. For instance, very recently, we have reported the electrospinning of the polymeric nanowebs containing menthol/cyclodextrin inclusion complexes (menthol/CD-IC) (Uyar, Hacaloglu, & Besenbacher, 2011; Uyar, Nur, Hacaloglu, & Besenbacher, 2009). We observed that nanofibres without menthol/CD-IC could not preserve menthol due to its volatile nature; yet, the high temperature stability for menthol, up to 300 °C, was achieved for nanofibres containing menthol/CD-IC.

In this study, we have produced functional polyvinyl alcohol (PVA) electrospun nanofibres containing vanillin having long-lasting durability and high temperature stability, facilitated by cyclodextrin inclusion complexation. Vanillin is widely used as a flavour and fragrance and it is also used as a food preservative due to its antioxidant properties in food industry (Karathanos, Mourtzinos, Yannakopoulou, & Andrikopoulos, 2007). However, vanillin has a short shelf-life because of its volatile nature, therefore, the stabilization of vanillin is very important for its prolonged functionality. Here, PVA nanofibres incorporating vanillin/cyclodextrin inclusion complex (vanillin/CD-IC) were successfully electrospun by using three types of CDs (α-CD, β-CD, γ-CD). Encapsulation of vanillin/CD-IC in PVA nanofibre matrix yielded vanillin with enhanced durability and high temperature stability but the PVA nanoweb without the CD-IC could not preserve the vanillin effectively. We also observed that the type of CD used is quite important to improve the shelf-life of vanillin in the PVA nanofibre matrix. The encapsulation of CD-IC in electrospun nanowebs is particularly attractive since such functional nanowebs containing CD-IC of flavours/fragrances would be quite applicable in functional foods and active food packaging.

2. Experimental

2.1. Materials

Polyvinyl alcohol (PVA) (M_w: 85,000–124,000, Aldrich, 87–89% hydrolysed) and vanillin (99% purity, melting point: 81–83 °C, Sigma-Aldrich), deuterated dimethylsulphoxide (DMSO-d6) (Merck, deuteration degree min. 99.8% for NMR spectroscopy) were used in this study. Cyclodextrins (α-CD, β-CD, and γ-CD) were purchased from Wacker Chemie AG, Germany. All materials were used without any purification. The water was from Millipore Milli-Q ultrapure water system.

2.2. Preparation of the solutions

The inclusion complexes of vanillin with α-CD, β-CD, and γ-CD were prepared by mixing equimolar (1:1 molar ratio) amount of vanillin with CDs in water. In the solutions, the vanillin content was 5% (w/w) with respect to the PVA content and the CD amount was adjusted to 32% (w/w) for α-CD, 37% (w/w) for β-CD and 43% (w/w) for γ-CD, with respect to PVA. The α-CD and γ-CD were dissolved in water at room temperature, whereas β-CD was dissolved in water at 75 °C for 5 min because of its low water solubility, and then, the vanillin was added to the aqueous solutions of CDs. After mixing the solutions overnight at room temperature, the vanillin/α-CD solution became slightly turbid, the vanillin/β-CD solution became clear and the vanillin/γ-CD solution became highly turbid. PVA solutions were prepared separately by mixing PVA pellets in water for 2 h at 75 °C, and the solutions were cooled down to room temperature. Then, the vanillin/α-CD and vanillin/γ-CD inclusion complex solutions were added to the polymer solutions and stirred for additional 4 h at room temperature. On the other hand, total water amount was used to dissolve β-CD, so PVA pellets were directly added to vanillin/β-CD-IC aqueous solution and stirred 2 h at 75 °C. In all cases, the PVA concentration was 12% (w/v, with respect to solvent (water)) in PVA/vanillin/CD-IC solutions. PVA/vanillin/CD-IC nanofibres were subsequently electrospun from the resultant solutions at room temperature. For comparison, we also have electrospun nanofibres from the solution of PVA and PVA/vanillin without CDs. The compositions of the solutions used for the electrospinning are summarised in Table 1.

2.3. Electrospinning

The prepared solutions were loaded individually in a 3 ml syringe. The syringe (needle inner diameter = 0.8 mm) was fixed hor-

Table 1
The solution compositions and the morphological characteristics of the resulting electrospun nanofibres.

Solutions	% PVA[a] (w/v)	%, CD type[b] (w/w)	% Vanillin[b] (w/w)	Viscosity (Pa.s)	Conductivity (μS/cm)	Average fibre diameter (nm)	Fibre morphology
PVA	12	–	–	0.157	798	185 ± 50	Bead-free nanofibres
PVA/vanillin	12	–	5	0.662	784	245 ± 45	Bead-free nanofibres
PVA/vanillin/α-CD-IC	12	32%, α-CD	5	0.233	667	180 ± 35	Bead-free nanofibres
PVA/vanillin/β-CD-IC	12	37%, β-CD	5	0.588	489	190 ± 40	Bead-free nanofibres
PVA/vanillin/γ-CD-IC	12	43%, γ-CD	5	0.192	536	140 ± 20	Nanofibres with CD-IC crystals

[a] With respect to solvent (water).
[b] With respect to polymer (PVA).

izontally on the syringe pump (Model: KDS 101, KD Scientific, USA) and the solutions were electrospun by using high voltage power supply (AU Series, Matsusada Precision, Japan). The electrospinning of the solutions was performed at the following parameters; applied voltage = 15 kV, tip-to-collector distance = 10 cm and the solution flow rate = 1 ml/h. A grounded stationary cylindrical metal collector covered by a piece of aluminium foil was used as a collector for the fibre deposition. The electrospinning setup was enclosed in Plexiglas box and the electrospinning was carried out at 24 °C, at 30% relative humidity. The nanowebs were dried at room temperature in the suction hood for 24 h in order to let the uncomplexed vanilllin evaporate if any present.

2.4. Measurements and characterisation

The viscosity of the solutions was measured with rheometer (Physica MCR 301, Anton Paar) equipped with a cone/plate accessory (spindle type CP 40-2), at a constant shear rate of 100 s^{-1}, at 22 °C. The conductivity of the solutions was measured with Multiparameter meter InoLab® Multi 720 (WTW) at room temperature. The morphology and the fibre diameter of the electrospun nanofibres were analysed by scanning electron microscope (SEM) (Quanta 200 FEG, FEI). The nanofibre samples were coated with 5 nm Au/Pd (PECS-682) prior to SEM imaging. The average fibre diameter (AFD) for the samples was calculated by analysis of around 100 fibres from the SEM images.

The X-ray diffraction (XRD) (PANalyticalX'Pert Powder diffractometer) data for the CDs, nanowebs and vanillin were collected by using Cu Kα radiation in a range of 2θ = 5–30°. Thermal properties of the samples were investigated by using differential scanning calorimeter (DSC) (Q2000, TA Instruments) and thermogravimetric analyzer (TGA) (Q500, TA Instruments). For DSC analyses, the samples were initially equilibrated at 25 °C and then heated to 250 °C at a 20 °C/min heating rate under nitrogen gas. TGA measurements were performed for electrospun nanowebs after 1 day of their storage. The TGA data were recorded from room temperature to 600 °C, at a heating rate of 20 °C/min, under nitrogen atmosphere. The proton nuclear magnetic resonance (^{1}H-NMR) (DPX-400, Bruker) spectra were recorded at 400 MHz at 25 °C. About 20 g/l nanoweb sample was dissolved in DMSO-d6 in order to determine the presence of vanillin in the nanoweb samples.

2.5. Stability test

PVA/vanillin and PVA/vanillin/CD-IC nanowebs were stored in the open air in the laboratory (22 °C at 25% relative humidity) for a certain period of time. After 1 and 8 days of their storage, small samples of nanowebs were analysed by TGA in order to determine the amount of the remaining vanillin in the samples. The amount of vanillin present in the nanowebs was calculated from the TGA data, that is, the % weight loss took place between 80–175 °C and 100–200 °C in TGA thermogram of PVA/vanillin and PVA/vanillin/α-CD-IC and PVA/vanillin/β-CD-IC was considered as the % weight of vanillin present in the samples, respectively. In the case of PVA/vanillin/γ-CD-IC, the weight loss was continuous between 125 and 250 °C, therefore, the calculation of the % weight of vanillin was kind of difficult since there was an overlapping of PVA degradation as well starting from 250 °C, so, to be on the safe side, % weight loss took place up to 240 °C was considered as the % weight of vanillin present in this sample.

The nanowebs were also analysed by TGA after 50 days of their storage, but, the weight loss between 80 and 225 °C was insignificant and the interpretation of the TGA data was difficult. Therefore, the presence of vanillin in the nanowebs after 50 days of their storage was detected by ^{1}H-NMR studies. The quantity of vanillin in the nanowebs was calculated by integrating the peak ratio of the characteristic chemical shifts corresponding to vanillin and CD. The integration of the CD peak at 5.8 ppm and vanillin peak at 9.8 ppm were taken into account in order to calculate the stoichiometry of the vanillin and the CD molecules in the nanowebs. The % weight of vanillin in the nanowebs was calculated from the molar stoichiometry between the vanillin and the CD determined from the ^{1}H-NMR spectra. It was assumed that the initial amount of CD was preserved before and after the electrospinning, that is, the amount of CD in the PVA solution before the electrospinning was considered same as the amount of CD in the PVA nanowebs after the electrospinning.

3. Results and discussion

In this study, encapsulation of vanillin/cyclodextrin inclusion complexes (vanillin/CD-IC) in polyvinyl alcohol (PVA) nanoweb was achieved via electrospinning technique. PVA nanofibre matrix was chosen since PVA is a biodegradable and non-toxic synthetic polymer, and PVA is applicable in food packaging (Chiellini, Cinelli, Chiellini, & Imam, 2004; Tripathi, Mehrotra, & Dutta, 2009; Wu, Wang, & Chen, 2010). Several studies have also shown that PVA has good electrospinnability, in which drugs (Taepaiboon, Rungsardthong, & Supaphol, 2006), enzymes (Ren et al., 2006) or nanoparticles (Park et al., 2010) can be easily incorporated in electrospun PVA nanofibres.

The PVA nanofibres containing vanillin/α-CD-IC, vanillin/β-CD-IC and vanillin/γ-CD-IC were electrospun from the aqueous solution mixture of PVA and vanillin/CD-IC. For a comparison study, PVA and PVA/vanillin nanofibres without CD were also electrospun. Table 1 summarises the solution compositions and the morphological findings of the electrospun nanofibres. The representative SEM images and the fibre diameter distribution, along with average fibre diameter (AFD) of pure PVA, PVA/vanillin and PVA/vanillin/CD-IC nanowebs are depicted in Fig 2. Uniform and bead-free nanofibres were obtained from PVA, PVA/vanillin PVA/vanillin/α-CD-IC and PVA/vanillin/β-CD-IC systems. In the case of PVA/vanillin/γ-CD-IC nanoweb, the nanofibres were mostly uniform, but, in some areas, it was observed that aggregates of vanillin/γ-CD-IC crystals were present and distributed in the fibre matrix. Mostly, the fibre diameters were between 100 and 250 nm for

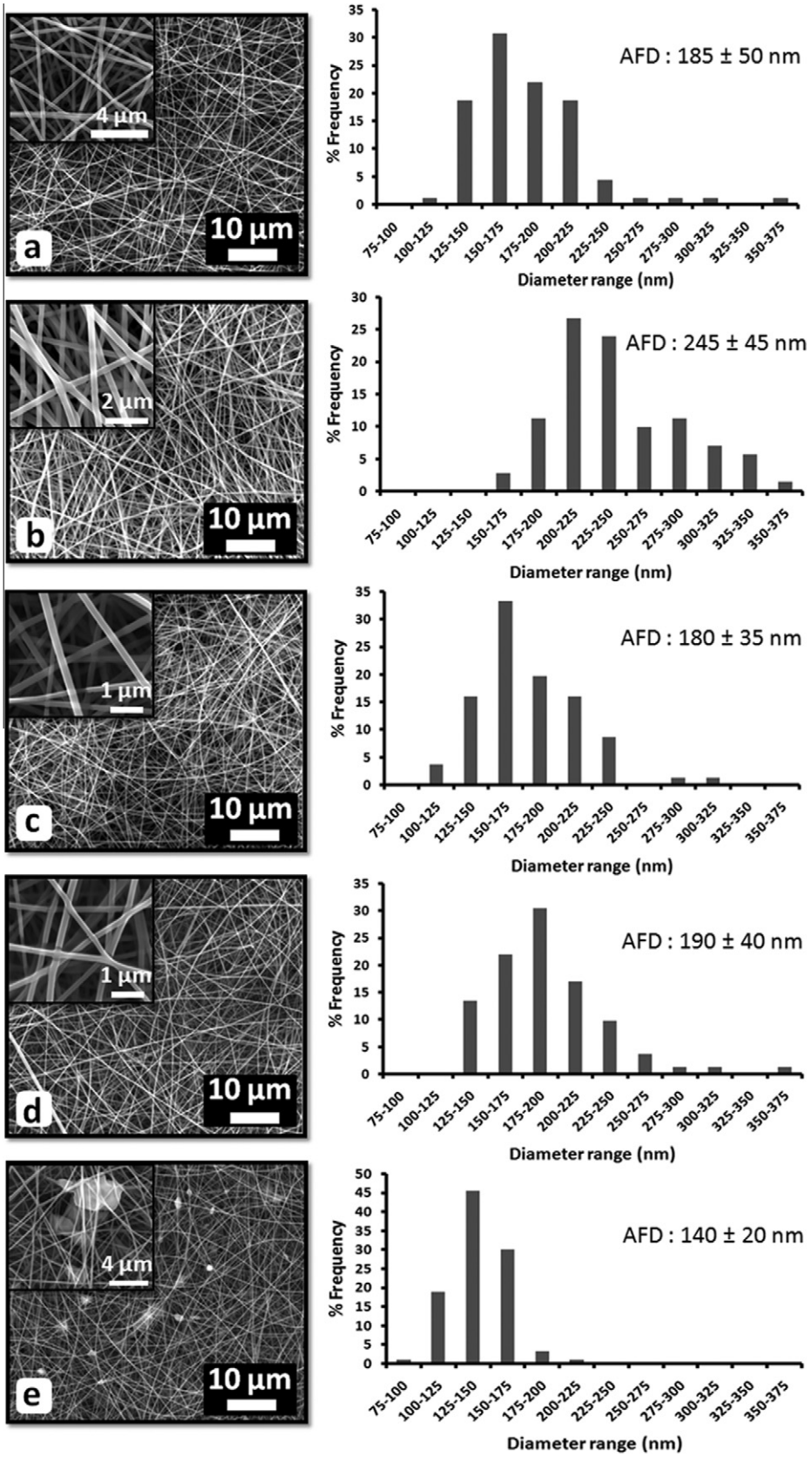

Fig. 2. SEM images and fibre diameter distribution of the electrospun nanowebs obtained from solutions of (a) PVA, (b) PVA/vanillin, (c) PVA/vanillin/α-CD-IC (d) PVA/vanillin/β-CD-IC and (e) PVA/vanillin/γ-CD-IC. The insets show the high magnification images.

all the samples, yet, small variations were observed among the samples. The variations of the fibre diameters observed for the nanofibres are possibly owing to differences in viscosity and conductivity of the solutions, hence, we have investigated the rheological behaviour and conductivity of the solutions (Table 1). PVA/vanillin/CD-IC solutions have shown higher viscosity when compared to pure PVA solution, which was possibly due to the interactions between the PVA polymer chains and the CD molecules. Similarly, the viscosity of the PVA/vanillin was higher than pure PVA solution. The conductivity of PVA/vanillin/CD-IC and PVA/vanillin solutions was lower than the PVA solution. In general, higher solution viscosity and lower solution conductivity resulted in less stretching of the electrified jet and therefore thicker nanofibres were obtained in electrospinning (Bhardwaj & Kundu, 2010; Uyar & Besenbacher, 2008). For PVA/vanillin system, slightly thicker fibres were obtained when compared to pure PVA system because of the higher solution viscosity and lower solution conductivity. In the case of PVA/vanillin/CD-IC systems, the solutions have higher viscosity and lower conductivity compared to pure PVA solution, yet, fibre diameters of PVA, PVA/vanillin/α-CD-IC and PVA/vanillin/β-CD-IC were very similar to each other and thinner fibres were obtained from PVA/vanillin/γ-CD-IC. This result seems to contradict with the general observation for the electrospinning, but, PVA/vanillin/CD-IC solutions were rather unhomogeneous and complex when compared to PVA homopolymer solution. We observed that the electrospinning of these solutions did not follow the general trend observed in electrospinning in terms of fibre diameter thickness.

The X-ray diffraction (XRD) patterns of as-received CDs, pure vanillin powder and the nanowebs of PVA, PVA/vanillin and PVA/vanillin/CD-IC are depicted in Fig 3a and b. Vanillin is a crystalline material having a sharp diffraction peak centred at $2\theta \cong 13^{o}$. The electrospun PVA nanoweb has a semi-crystalline nature showing a broad diffraction pattern centred at $2\theta \cong 20^{o}$. The XRD pattern of PVA/vanillin nanoweb is very similar to PVA nanoweb having a broad diffraction pattern and no diffraction peak for crystalline vanillin was observed, suggesting that vanillin molecules were distributed in the fibre matrix without any crystalline aggregates.

The XRD patterns of PVA/vanillin/CD-IC nanowebs have broad diffraction centred at $2\theta \cong 20^{o}$ due to the PVA indicating that the presence of CD-IC did not significantly affect the semi-crystalline nature of the PVA matrix. In the XRD patterns of CD-IC, the diffraction peaks for the guest molecules would be absent since the guest molecules would reside in the CD cavity and they are separated from each other by the CD molecules and therefore, they cannot form crystals (Harata, 1998). For PVA/vanillin/CD-IC nanowebs, no diffraction peak for crystalline vanillin was observed in the XRD patterns suggesting that vanillin was complexed with CDs or even there may be some free vanillin present in the nanowebs, the uncomplexed vanillin should be present without crystalline aggregates as in the case of PVA/vanillin nanoweb.

The as-received CDs (α-CD, β-CD, and γ-CD) are crystalline materials having cage-type packing structure (Harata, 1998) and have characteristic diffraction peaks in the range of $2\theta = 5–30°$ (Fig 3a). However, PVA/vanillin/α-CD-IC and PVA/vanillin/β-CD-IC nanowebs have shown no diffraction peaks for CDs, suggesting that vanillin/CD-IC were dispersed in the PVA nanofibre matrix without forming any crystalline aggregates. The SEM images of PVA/vanillin/α-CD-IC and PVA/vanillin/β-CD-IC nanofibres were also smooth, showing no sign of CD-IC aggregates, and consequently, the SEM findings correlates with the XRD data. In the case of PVA/vanillin/γ-CD-IC nanoweb, the diffraction peaks at $2\theta \cong 7.5°$, 11°, 12°, 14°, 17° and 22° were observed elucidating that channel-type packing structure (Uyar, Hunt, Gracz, & Tonelli, 2006) of vanillin/γ-CD-IC was present in the PVA nanofibre matrix. The inclusion complexation is generally confirmed by the formation

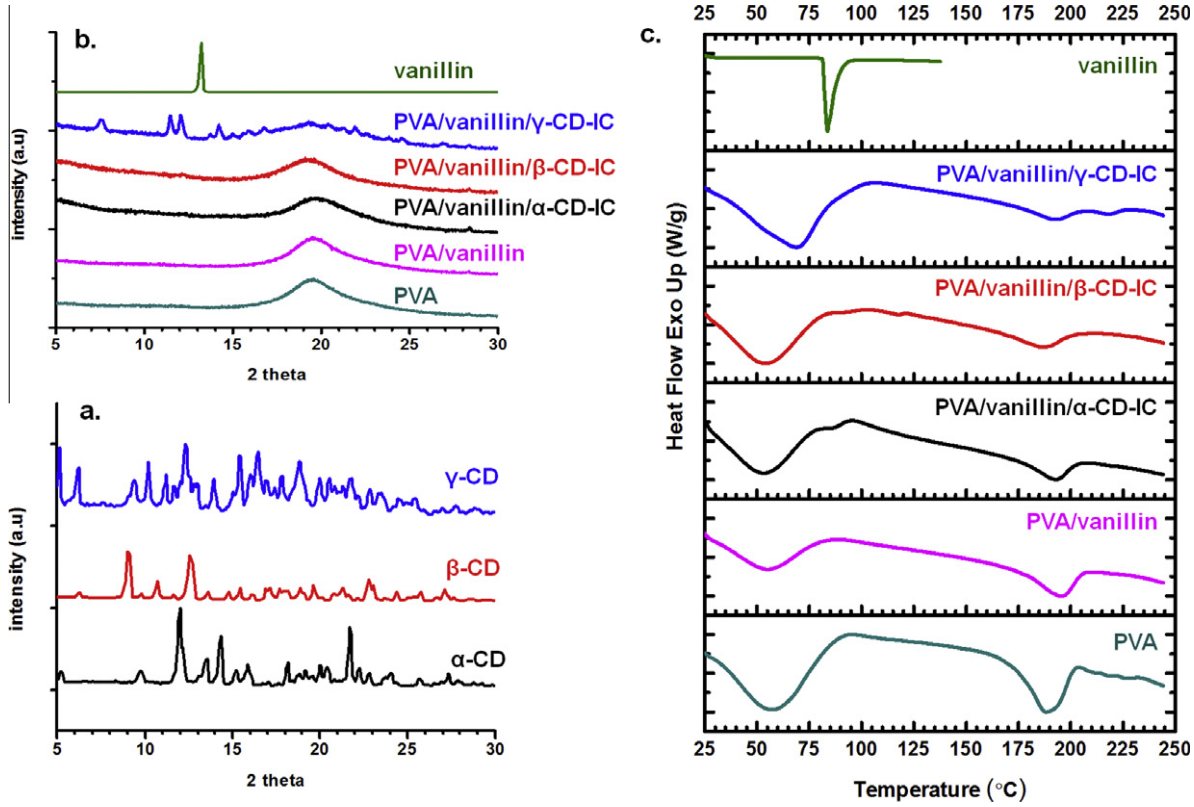

Fig. 3. X-ray diffraction patterns of (a) as-received CDs, (b) vanillin and the electrospun nanowebs, (c) DSC thermograms of vanillin and the electrospun nanowebs.

of channel-type arrangement of the CD molecules, in which CD molecules are aligned and stacked on top of each other by forming cylindrical channels (Harata, 1998). As discussed above, these crystalline vanillin/γ-CD-IC aggregates were also clearly observed in the SEM images of the nanoweb. In brief, the XRD studies of PVA/vanillin/CD-IC nanowebs reveal the incorporation of vanillin/CD-IC in PVA nanofibre matrix for γ-CD since CD molecules adopt channel-type packing structures. However, in the case of α-CD and β-CD no distinct XRD diffraction patterns were observed for any type of CD crystal aggregates, for that reason, XRD did not give any valid information for the presence of vanillin/CD-IC in these samples. However, as discussed below, the thermal characterisations of these nanowebs revealed the presence of vanillin/CD-IC in PVA nanofibre matrix.

The thermal properties of the PVA/vanillin and PVA/vanillin/CD-IC nanowebs were investigated by the differential scanning calorimeter (DSC) studies (Fig 3c). The DSC studies for pure vanillin and PVA nanoweb were also performed for comparison. The DSC thermogram of pure vanillin has shown a main endothermic peak at around 82 °C, which corresponds to the melting point of vanillin. PVA nanoweb has shown a broad endothermic peak between 30 and 100 °C due to loss of water and an endothermic peak, at around 188 °C, corresponding to the melting temperature (T_m) of PVA itself. The DSC thermograms of PVA/vanillin and PVA/vanillin/CD-IC nanowebs are similar to PVA nanowebs showing water loss between 30 and 100 °C and a melting peak of polymer matrix at around 192 °C. There is a slight shift of T_m to higher temperature for PVA/vanillin/CD-IC and PVA/vanillin nanowebs and this is possibly because of the interactions between the polymer matrix and CDs and vanillin.

Typically, for CD-IC, the thermal transitions such as the melting point for guest molecule, could not be observed when they are included inside the CD cavity (Giordano, Novak, & Moyano, 2001; Kayaci & Uyar, 2011; Paramera, Konteles, & Karathanos, 2010). The DSC thermograms of the PVA/vanillin/CD-IC nanowebs did not show any significant melting peak for vanillin, except, DSC thermogram of PVA/vanillin/α-CD-IC has shown small endothermic peak at around 80 °C, which maybe due to presence of some free vanillin in this sample. So, the absence of vanillin melting peak in DSC of PVA/vanillin/β-CD-IC and PVA/vanillin/γ-CD-IC nanowebs could be because the vanillin was fully complexed with the CDs. In the case of PVA/vanillin nanoweb, the DSC thermogram also did not show any melting peak for vanillin suggesting that the vanillin molecules were dispersed in the fibre matrix without any crystalline aggregation. In short, the DSC data correlates with the XRD data as discussed in the previous section where the vanillin was mostly present in the PVA fibre matrix without any crystal aggregates for PVA/vanillin and PVA/vanillin/CD-IC nanowebs.

Thermogravimetric analysis (TGA) is a useful technique in order to investigate the volatility and thermal stability of fragrances/flavours. Here, we have investigated the thermal characteristics of vanillin present in PVA/vanillin and PVA/vanillin/CD-IC nanowebs (Fig 4a). The TGA studies were also performed for pure vanillin and PVA nanoweb for comparison. In the TGA thermogram of pure vanillin, the weight loss was started at around 80 °C, showing an onset point at around 150 °C, indicating that vanillin has a volatile nature. The main thermal degradation of PVA nanoweb started at around 250 °C. TGA thermogram of PVA/vanillin showed three weight losses; the initial weight loss below 100 °C is due to water loss, the second weight loss between 80 and 175 °C is due to the evaporation of vanillin, and the major weight loss started at around 250 °C corresponds to the main thermal degradation of PVA. For PVA/vanillin/α-CD-IC nanoweb, water loss below 100 °C, weight loss between 100 and 190 °C due to vanillin evaporation and the major weight loss started around 270 °C corresponding to the main degradation of PVA and CDs were observed. In the TGA thermogram of PVA/vanillin/β-CD-IC nanoweb, the weight loss due to the vanillin evaporation was observed between 100 and 180 °C. In the case of PVA/vanillin/γ-CD-IC nanoweb, the weight loss was continuous between 125 and 250 °C indicating that the release of vanillin occurred at much higher temperature range. It was noted that the main degradation temperature of PVA shifted to slightly higher temperature with the presence of CDs, which may be because of the hydrogen bonding interaction between the hydroxyl groups of CDs and PVA; this may resulted in higher thermal stability for PVA. More importantly, the thermal stability of vanillin in PVA/vanillin/CD-IC nanowebs was shifted to higher temperature when compared to PVA/vanillin nanoweb. In CD-IC, the thermal evaporation of the volatile guest molecules shifts to higher temperatures due to the interactions with the CD cavity (Kayaci & Uyar, 2011; Tsai, Tsai, Wu, & Tsai, 2010), and as anticipated, enhanced thermal stability for vanillin was observed for PVA/vanillin/CD-IC nanowebs due to the complexation between vanillin and CDs. The loss of vanillin was observed at slightly higher temperature for PVA/vanillin/α-CD-IC and PVA/vanillin/β-CD-IC nanowebs when compared to PVA/vanillin nanoweb suggesting that the interaction between vanillin and α-CD or β-CD is not that strong. However, in the case of PVA/vanillin/γ-CD-IC nanoweb, the loss of vanillin was observed at higher temperature range (between 125 and 250 °C), indicating that the interaction between vanillin and γ-CD was much stronger compared to α-CD and β-CD.

The durability of vanillin in PVA/vanillin and PVA/vanillin/CD-IC nanowebs was also studied. At different storage time periods; after 1, 8 and 50 days of storage of the nanowebs at room temperature, the TGA and NMR studies were performed in order to determine the remaining amount of the vanillin in the nanowebs. Table 2 summarises the initial amount of vanillin in the PVA solutions before the electrospinning and remaining amount of vanillin in the nanowebs after certain days. For PVA/vanillin, around ~45% of the vanillin was evaporated after the first day of nanoweb production. The loss of vanillin could take place both during the electrospinning of PVA/vanillin solution and during the storage of the nanoweb. After the 8 days of storage, only about ~20% of the vanillin was left in PVA/vanillin nanoweb indicating that PVA nanoweb without CD-IC could not preserve volatile vanillin.

In the case of PVA/vanillin/CD-IC nanowebs, the preservation of vanillin was very effective compared to PVA/vanillin nanoweb. For PVA/vanillin/α-CD-IC nanoweb, the loss of vanillin (with respect to initial amount of vanillin) was ~25% and ~60% after 1 and 8 days of storage, respectively. For PVA/vanillin/β-CD-IC nanoweb, the loss of vanillin amount was ~30% and ~65% after 1 and 8 days of storage, respectively. In the case of PVA/vanillin/γ-CD-IC nanoweb, the loss of vanillin amount was minimal when compared to PVA/vanillin/α-CD-IC and PVA/vanillin/β-CD-IC nanowebs which was ~10% and ~20% after 1 and 8 days of storage, respectively. TGA results indicated that γ-CD was more effective for stabilization of vanillin when compared to α-CD and β-CD. The reason for forming more stable inclusion complex between vanillin and γ-CD is possibly because of the bigger cavity size of γ-CD, resulting better fit and size match between the guest molecule and the host CD cavity. This also correlates with our recent findings where γ-CD forms more stable inclusion complex with vanillin in the solid state (Kayaci & Uyar, 2011).

We have also analysed the nanowebs by TGA after 50 days of their storage, but, the weight loss between 80 and 225 °C was insignificant and the analyses of the TGA data was rather difficult. Therefore, we performed ^{1}H-NMR studies to check the presence of vanillin in the nanowebs after 50 days of their storage (Fig 4b). Vanillin was not detected for PVA/vanillin nanoweb indicating that the all the vanillin was evaporated from the sample after 50 days of storage. For PVA/vanillin/α-CD-IC and PVA/vanillin/β-CD-IC nanowebs, trace amount of vanillin was detected, but since the intensity

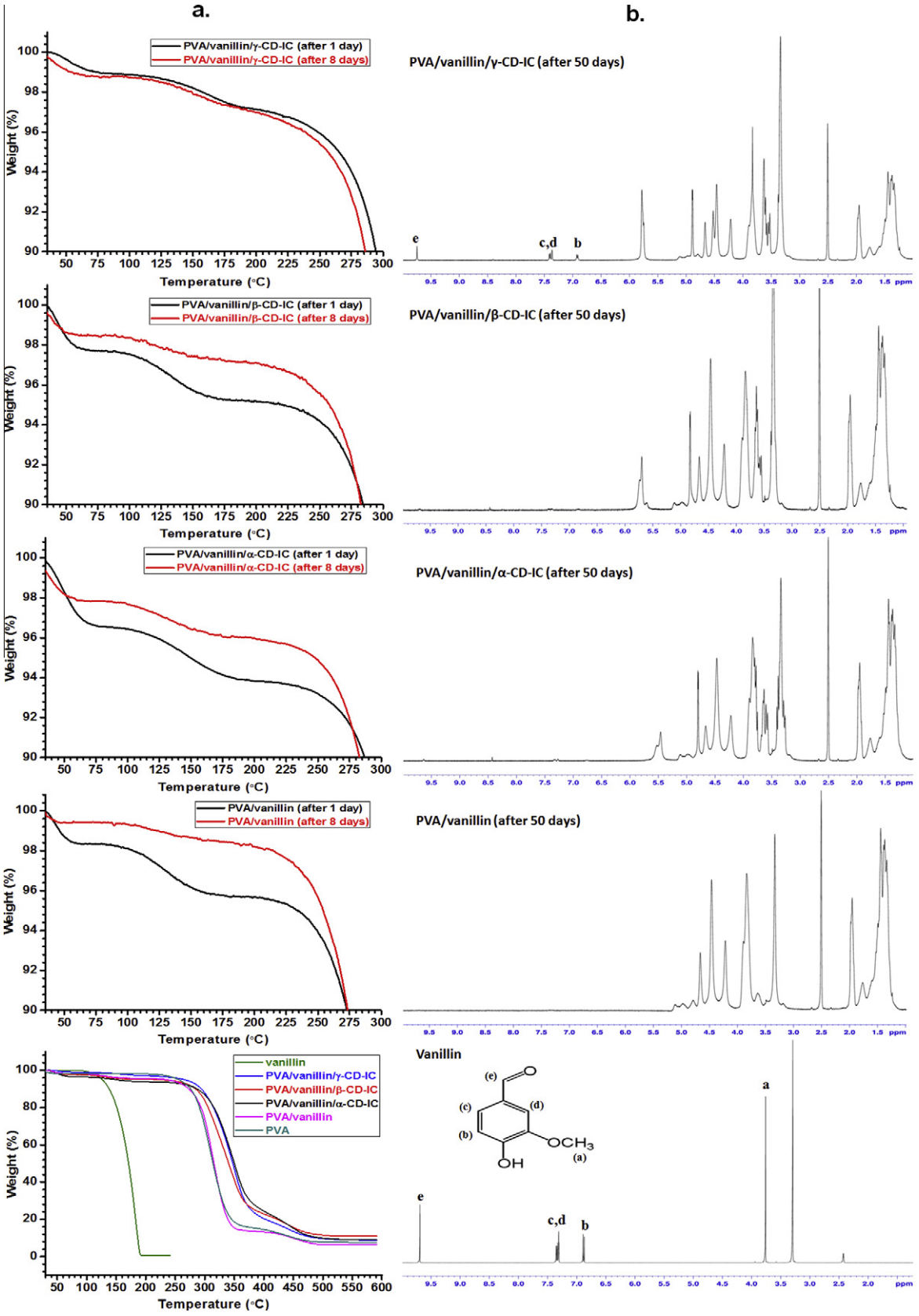

Fig. 4. (a) TGA thermograms of the electrospun nanowebs after 1 and 8 days of storage period, (b) ^{1}H-NMR solution spectra of vanillin and the electrospun nanoweb samples dissolved in DMSO-d6 after 50 days of storage.

Table 2
Initial amount of vanillin in the solutions and the remaining amount of vanillin in the nanowebs after certain days obtained by TGA and NMR.

Samples	% Weight of vanillin (% weight loss of vanillin)			
	Initial	After 1 day[a]	After 8 days[a]	After 50 days[b]
PVA/vanillin	4.76 (0%)	2.65 (44%)	0.92 (81%)	–
PVA/vanillin/α-CD-IC	3.65 (0%)	2.65 (27%)	1.48 (60%)	–
PVA/vanillin/β-CD-IC	3.52 (0%)	2.41 (32%)	1.19 (66%)	–
PVA/vanillin/γ-CD-IC	3.39 (0%)	2.97 (12%)	2.71 (20%)	1.98 (42%)

[a] Measured by TGA.
[b] Measured by NMR.

of the vanillin peaks were very weak, we were unable to integrate the peaks and therefore could not able to calculate the amount of vanillin in the sample. In the case of PVA/vanillin/γ-CD-IC nanoweb, the vanillin peak was present and the molar ratio of vanillin to γ-CD was calculated as 1:1.7 which corresponds that the amount of vanillin was around 1.98% weight of the total sample. This corresponds to ~40% loss of vanillin from PVA/vanillin/γ-CD-IC nanoweb after 50 days of its storage. The initial amount of vanillin was about ~3.4% and ~60% of the vanillin was remaining in the nanoweb after 50 days of its storage. This finding elucidates that PVA/vanillin/γ-CD-IC nanoweb is quite effective for the prolonged durability of vanillin. In short, our studies showed that high temperature stability and prolonged shelf-life of vanillin was achieved PVA/vanillin/CD-IC nanowebs, whereas vanillin in PVA nanoweb without CD-IC could not be preserved effectively. In addition, we observed that the prolonged shelf-life of vanillin was highly dependent on the type of CDs; γ-CD was more effective for stabilization of vanillin over longer time period when compared to α-CD and β-CD.

4. Conclusions

Polyvinyl alcohol (PVA) nanowebs incorporating vanillin/cyclodextrin inclusion complex (vanillin/CD-IC) were successfully produced via electrospinning technique with the goal to obtain functional nanowebs containing flavour/fragrance molecules with enhanced thermal stability and durability. Three types of CDs; α-CD, β-CD and γ-CD were used for the formation of vanillin/CD-IC, and these vanillin/CD-IC were encapsulated in electrospun PVA nanowebs. Vanillin has a volatile nature; however, higher thermal stability and prolonged shelf-life for vanillin were attained for PVA/vanillin/CD-IC nanowebs, whereas PVA nanoweb without the CD-IC could not efficiently preserve the vanillin. The thermal evaporation/degradation of vanillin shifted to higher temperature for PVA/vanillin/CD-IC nanowebs when compared to PVA/vanillin. In addition, we observed that the PVA/vanillin/CD-IC nanowebs are quite effective for the prolonged shelf-life of vanillin. For PVA/vanillin/γ-CD-IC nanoweb, the loss of vanillin amount was minimal when compared to PVA/vanillin/α-CD-IC and PVA/vanillin/β-CD-IC nanowebs and about 60% of the initial amount of vanillin was preserved after 50 days of storage. This reveals that the durability of vanillin was significantly dependent on the CD type, that is, γ-CD was much more effective for stabilization of vanillin over longer time period when compared to α-CD and β-CD.

In brief, vanillin/CD-IC was encapsulated in electrospun PVA nanofibres and higher thermal stability and prolonged shelf-life was achieved for vanillin. Vanillin is a widely-used flavour/fragrance; therefore, PVA/vanillin/CD-IC nanowebs can be quite applicable in food industry, active food packaging and textile industry, etc. Our study shows that the electrospinning of nanowebs incorporating cyclodextrin inclusion complexes would be very effective for achieving long-term shelf-life and high temperature stability for volatile flavours/fragrances. Our results should be of interest to food, biomedical, textile and personal care industries, since CD-IC functionalized nanowebs may have practical applications depending on the type the functional components used such as flavours, antimicrobials, antioxidants, drugs, and bioactive agents, etc.

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