Electrospun polystyrene fibers containing high temperature stable volatile fragrance/flavor facilitated by cyclodextrin inclusion complexes

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\textbf{A B S T R A C T}

In this study, we report on electrospinning of functional polystyrene (PS) fibers containing cyclodextrin-menthol inclusion complexes (CD-menthol-ICs). Our goal is to develop functional electrospun fibers containing fragrances/flavors with enhanced durability and stability assisted by cyclodextrin inclusion complexation. We have used menthol as a model fragrance/flavor material and CD-menthol-ICs were incorporated in electrospun PS fiber by using three types of CDs: α-CD, β-CD and γ-CD. Due to complexation of menthol with CDs, we observed that the stabilization of menthol was achieved up to 350 °C for all the PS/CD-menthol-IC webs whereas the PS fibers without the CD complex could not preserve volatile menthol molecules. In addition, γ-CD was more effective for the stabilization and release of menthol at a broad temperature range (100–350 °C) when compared to α-CD and β-CD. This study suggested that the electrospun fibers functionalized with CD-ICs are very effective for enhancing the temperature stability of volatile fragrances/flavors and therefore show potentials for the development of functional fibrous materials.

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1. Introduction

Electrospinning of fibers with cyclodextrins (CD) is of our particular interest, since nanofibers with specific functions can be produced. Electrospinning is a versatile and cost-effective technique for producing multi-functional nanofibers from various polymers, polymer blends and composites, etc. [1,2]. Electrospun nanofibers/nanowebs have several distinctive characteristics such as a large surface-to-volume ratio, pore sizes in the nano range and moreover, it is fairly easy to improve the functionality of the nanofibers by incorporating additives into the nanofibers during the electrospinning process [1–4].

Cyclodextrins (CDs) are cyclic oligosaccharides having a toroid-shaped molecular structure and they are able to form noncovalent host–guest inclusion complexes (IC) with various molecules [5,6]. The most common CDs have either 6, 7, and 8 glucopyranose units in the cycle and are referred to as α-, β- and γ-CD, respectively (Fig. 1). The formation and the stability of the CD-ICs depend on many factors such as the size/shape match and the binding forces between the host CD and the guest molecules, and the chemical environment [7,8]. When the CD-ICs are formed, CD cavity assists to stabilize/protect the guest molecules and control/sustain their delivery. CDs are natural, nontoxic and slowly biodegradable molecules, and consequently the CDs are used in variety of areas such as pharmaceuticals (e.g., enhancement of drug solubility and stability, bioavailability, controlled drug delivery, reduction of drug toxicity, etc.), food science (stabilization of volatile or unstable flavors, masking/removal of unwanted tastes and odor), cosmetics and home/personal care products (releasing fragrances and masking unpleasant odor), textiles (stabilization and control release of textile additives), membranes/filters (removal of waste molecules), etc. [5,6,9–12].

The stabilization of fragrances/flavors at high temperatures is an important issue, since significant problems such as short shelf-life may arise due to the high volatility nature of these fragrance/flavor constituents. Studies showed that cyclodextrins are very effective for the stabilization and sustained release of fragrances/flavors [5,6,13–16]. Therefore, the incorporation of CD-ICs of fragrances/flavors in electrospun fibers would be extremely interesting since such functional fibers can have fragrances/flavors with enhanced stability, and these fibers can be very handy for the development of multi-functional fibrous materials. In this study, by means of the electrospinning technique we successfully produced functional polystyrene (PS) fibers containing CD-menthol-ICs and we investigated the stability and temperature release of this volatile fragrance/flavor material; menthol. To find the optimal CD type, three types of CDs; α-CD, β-CD and γ-CD were investigated. We found that the stabilization and temperature release of...
menthol was sustained up to a very high temperature range (100–350 °C) for the PS webs containing CD-menthol-IC.

2. Experimental

2.1. Materials

Polystyrene (PS) (M_n ~280,000, Aldrich), N,N-dimethylformamide (DMF) (98%, Fluka), and menthol (99%, Aldrich) were purchased and used without any additional purification. α-, β- and γ-cyclodextrins (CD) were gift from Wacker Chemie AG, Germany and used as-received.

2.2. Preparation of solutions and electrospinning

The menthol and cyclodextrin (α-, β- and γ-CD) were dissolved in DMF and stirred for 3 h at room temperature (RT), and then PS was added to CD-menthol solutions and stirred for additional 20 h. PS/CD-menthol-IC fibers were subsequently electrospun from the resultant solutions. For comparison, we also have electrospun fibers from the solution of PS/menthol without CD and PS/α-CD without menthol. In the solutions, the menthol content was 3.3% (w/w) with respect to the PS content and the CD content was adjusted to 20% (w/w) for α-CD, 24% (w/w) for β-CD and 27% (w/w) for γ-CD, respectively, with respect to PS, which corresponds with the assumption that each type of CD forms 1:1 (molar ratio) complex with menthol [17].

The prepared solutions were loaded individually in a 1 ml syringe. The syringe (needle inner diameter = 0.4 mm) was fixed horizontally on the syringe pump (Model: KDS 101, KD Scientific) and the solutions were electrospun by using high voltage power supply (Spellman High Voltage Elec. Corp., MP Series). For the electrospinning process a feed rate = 1 ml/h, applied voltage = 15 kV and tip-to-collector distance = 10 cm were employed. A grounded stationary rectangular metal collector covered by a piece of aluminum foil was used for the fiber deposition. The complete electrospinning apparatus was enclosed in a glass box and the electrospinning of the fibers was carried out at RT. The fibrous webs were dried at RT in the suction hood for 24 h to let the uncomplexed menthol evaporate and to remove the residual solvent if any present.

2.3. Measurements and characterization

The viscosity of the solutions was measured at 24 °C using the Brookfield DV-III Ultra Rheometer equipped with a cone/plate accessory of spindle type CPE-41. The viscosity measurements were repeated three times. The conductivity of the solutions was measured with Multiparameter meter InoLab Multi 720 (WTW) at RT. The morphologies of the fibers were investigated by scanning electron microscopy (SEM) (FEI, Nova 600 NanoSEM). The fiber diameter distributions were determined from the obtained SEM images and around 50 fibers were measured. 2D X-ray diffraction (XRD) data were collected using a Stoe Stadi P diffractometer applying Cu Kα radiation at a range of 2θ = 5–30°. Some of the webs were shipped to Turkey, Middle East Technical University for the direct pyrolysis mass spectrometry (DP-MS) analyses, and in all cases the samples were analyzed after five days of their production. DP-MS system consisting of a Waters Quattro Micro GC tandem MS with an EI ion source and a mass range of 10–1500 Da, was coupled with a direct insertion probe (T_max = 650 °C), and 0.010 mg samples were pyrolyzed in the quartz sample vials at a heating rate of 10 °C/min.

Table 1

The properties of PS/menthol and PS/CD-menthol-ICs solutions and the morphology of the resulting electrospun fibers.

<table>
<thead>
<tr>
<th>Solutions</th>
<th>% PS (w/w)</th>
<th>% CD type (w/w)</th>
<th>Menthol (w/w)</th>
<th>Viscosity (cP)</th>
<th>Conductivity (μS/cm)</th>
<th>Fiber diameter range (μm)</th>
<th>Fiber morphology</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS/menthol</td>
<td>25</td>
<td>-</td>
<td>3.3</td>
<td>384.8 ± 1.5</td>
<td>0.5</td>
<td>0.63–4.24</td>
<td>Bead-free, mostly microfibers</td>
</tr>
<tr>
<td>PS/α-CD-menthol-IC</td>
<td>15</td>
<td>α-CD, 20%</td>
<td>3.3</td>
<td>698 ± 0.3</td>
<td>1.8</td>
<td>0.30–2.27</td>
<td>Bead-free, mostly nanofibers</td>
</tr>
<tr>
<td>PS/β-CD-menthol-IC</td>
<td>15</td>
<td>β-CD, 24%</td>
<td>3.3</td>
<td>731 ± 0.6</td>
<td>3.1</td>
<td>0.72–3.77</td>
<td>Bead-free, mostly microfibers</td>
</tr>
<tr>
<td>PS/γ-CD-menthol-IC</td>
<td>15</td>
<td>γ-CD, 27%</td>
<td>3.3</td>
<td>742 ± 0.4</td>
<td>1.5</td>
<td>0.53–3.38</td>
<td>Bead-free, mostly microfibers</td>
</tr>
</tbody>
</table>

a With respect to solvent (DMF).
b With respect to polymer (PS).
3. Results and discussion

Table 1 summarizes the properties of the solutions used in the electrospinning and the morphologies of the resulting electrospun fibers. We first optimized the polymer concentration to produce bead-free fibers. The polystyrene (PS) concentration of 25% and 15% (w/v) was optimal for producing bead-free fibers from PS/menthol and PS/CD-menthol-ICs solutions, respectively. The positive effect of CD on electrospinning of bead-free PS fibers from low concentrations is mostly related to higher conductivity of the polymers.

![SEM images and fiber diameter distribution of the electrospun webs of (a) PS/menthol, (b) PS/α-CD-menthol-IC, (c) PS/β-CD-menthol-IC and (d) PS/γ-CD-menthol-IC.](image)

Fig. 2. SEM images and fiber diameter distribution of the electrospun webs of (a) PS/menthol, (b) PS/α-CD-menthol-IC, (c) PS/β-CD-menthol-IC and (d) PS/γ-CD-menthol-IC.
solutions. This observation correlates with the literature findings where the higher solution conductivity facilitated the electrospinning [18,19] and the effect of CD on electrospinning of PS fibers was discussed in detail elsewhere [20].

Fig. 2 shows the SEM images of the PS/menthol and PS/CD-menthol-IC webs as well as the measured fiber diameter distributions. For the PS/menthol, PS/β-CD-menthol-IC and PS/γ-CD-menthol-IC webs, the fiber diameter distribution was very broad resulting mainly micro fibers. Conversely, PS/α-CD-menthol-IC web have a smaller diameter distribution resulting mostly in nanofibers. The variation of fiber diameter for the resulting electrospun fibers is owing to differences in conductivity and viscosity of the solutions.

Cyclodextrins (CDs) are crystalline and have crystal structures referred to as either a “cage” or “channel” type (Fig. 1c and d) [21,22]. The 2D X-ray diffraction (XRD) spectra of PS/menthol, PS/CD-menthol-ICs and PS/α-CD webs are depicted in Fig. 3. PS is an amorphous polymer and the PS/menthol web showed a broad halo-like XRD pattern. For PS/β-CD-menthol-IC and PS/γ-CD-menthol-IC webs, similar broad halo diffraction patterns were observed, which suggest that CD-menthol-ICs were present as an amorphous state. On the other hand, characteristic peaks of α-CD channel-type packing [23] at 2θ = ~20° and ~13° were observed for the PS/α-CD-menthol-IC web. We initially attributed the presence of channel-type for the α-CD-menthol-IC crystal aggregates, but a control sample of PS/α-CD web without menthol revealed the same XRD pattern, which indicated that the α-CD crystals aggregated also as channel-type packing in the electrospun PS fibers by itself. The possibility of a complexation between CD and PS can be ruled out, as our previous studies have shown that atactic PS does not form inclusion complexes with CDs, since the cavity of PS can be ruled out, as our previous studies have shown that atactic aggregates also as channel-type packing in the electrospun PS fibers.

We performed the direct pyrolysis mass spectrometry (DP-MS) study to confirm the complexation of menthol with CDs and to study the stability and temperature release profiles of menthol for the electrospun fibers. For a multi-component system, DP-MS allows separation of the components as a function of their volatilities and/or thermal stabilities. Once included in the host CD cavities, the thermal evaporation of the volatile guest molecules shifts to higher temperatures due to the interactions with the CD cavity [26-28], and thus the DP-MS technique is a very versatile technique to characterize the CD-host-guest inclusion complexes [27].

In general, by means of the DP-MS technique we can analyze the thermal characteristics such as volatility, thermal stability and degradation products of the materials. However, pyrolysis mass spectra of a multi-component system, especially the ones involving polymers, are usually very complex due to dissociative ionization processes and due to the fact that all fragments with the same mass to charge ratio contributes to the intensity of the same peak in the mass spectrum. Thus, in pyrolysis MS analysis, not only the detection of the product, but also the variation of its yield as a function of temperature, i.e. the thermal evolution profile is very important to determine the source of the product or the mechanism of thermal degradation [29].

To investigate the interactions of menthol with CDs in the electrospun webs, we first carried out DP-MS analyses of each pure component present in the webs. Under the high vacuum conditions of the MS, pure menthol was released immediately below 50 °C in accordance with its high volatility. The product yield was maximized in 0.70 min (around room temperature) and decreased steadily and then totally disappeared. In Fig. 4, the total ion current (variation of total ion yield as a function of temperature) (TIC) curve and the pyrolysis mass spectrum recorded at 0.70 min are depicted. The recorded pyrolysis mass spectrum, involving intense peaks at m/z = 71, 81, 123 and 138 Da and a very weak molecular ion peak at m/z = 156 Da, is identical to the mass spectrum of menthol given in mass libraries confirming the evaporation of menthol. For PS fiber, mainly the styrene monomer (m/z = 104 Da) was produced by the depolymerization process showing a maximum at around 440 °C. The pyrolysis mass spectra of CDs were quite complex and the diagnostic peaks of CDs appeared above 300 °C and reached maximum intensity at around 355 °C.

The thermal release profiles of the characteristic fragment ions of each component are illustrated in Fig. 5. The 138, 60 and 104 Da ions due to fragment ions generated by loss of H₂O from menthol,
the C\textsubscript{2}H\textsubscript{4}O\textsubscript{2} ions of CD and the styrene monomer ions of PS, respectively, are depicted for the pure materials and the electrospun fibers. Note that PS-based products followed identical evolution profiles for all the samples under investigation, which indicated that the presence of menthol and/or CDs has no detectable effect on thermal behavior of PS (Fig. 5a). As for CD, thermal release profiles of α-CD base products depicted two distinct peaks with maxima at around 290 and 355 °C indicating that the α-CD units have different thermal stabilities than β-CD and γ-CD in the PS fibers. This behavior was possible due to the presence of two types α-CD units; amorphous units and the channel-type crystal units which was identified by the XRD studies. This observation correlates with the literature findings at which α-CD channel-type crystals have low thermal stability when compared to the parent α-CD crystals [23]. We also observed that the main thermal decomposition temperature of the CDs in PS/CD-menthol-ICs was slightly shifted to lower temperatures when compared to pure CDs. This finding indicated that the presence of PS and menthol seems to have some effect on the thermal stability of CDs.

In the case of menthol, we observed that the thermal release profile of menthol was strongly affected by the matrix. The lack of characteristic peaks of menthol in the pyrolysis mass spectra of PS/menthol fibers indicated that menthol was evaporated from the web after the production of the fibers. On the other hand, the thermal release of menthol was detected over a broad temperature range during the heating process of all the PS/CD-menthol-IC fibers. This finding shows that electrospun PS fibers could not preserve volatile menthol molecules without the cyclodextrins inclusion complexes.

In the pyrolysis of PS/CD-menthol-IC fibers, the thermal release profile of menthol started around 100 °C and continued up to 350 °C which confirmed the complexation of menthol with CDs. The fact that the thermal release of menthol occurred in a broad temperature range (100–350 °C) suggested that various types of interactions with different strength exist in the CD-menthol com-

**Fig. 4.** (a) The DP-MS total ion current (TIC) curve and (b) the pyrolysis mass spectrum recorded for pure menthol.

**Fig. 5.** TIC evolution profiles of some characteristic fragment ions of each component detected by direct pyrolysis mass spectrometry (DP-MS) during the pyrolysis of the materials. The 138, 60 and 104 Da ions are due to loss of H\textsubscript{2}O from menthol, C\textsubscript{3}H\textsubscript{4}O\textsubscript{2} ion from CD and molecular ion for styrene, respectively.
plex. The low temperature releases might be associated with weak interactions while the thermal release at higher temperatures is related to the presence of stronger interactions between the menthol and the CD cavity. The presence of possible hydrogen-bonded CD-menthol complex was also considered and the release of menthol at very high temperatures (above 300 °C) may be attributed to this type of strongly bounded menthol. When PS/CD-menthol-IC fibers were compared with each other, the release of menthol around 100 °C was lowest for the PS/α-CD-menthol-IC fibers and highest for the PS/γ-CD-menthol-IC fibers. Additionally, the thermal release of menthol occurred over a much broader temperature range (100–350 °C) for PS/γ-CD-menthol-IC fibers and this behavior may be attributed to the presence of interactions with different strength due to wider γ-CD cavity as compared to α-CD and β-CD cavities.

4. Conclusions

Polystyrene (PS) fibers containing cyclodextrin-menthol inclusion complexes (CD-menthol-ICs) were successfully produced by the electrospinning technique with the goal to obtain functional fibrous webs. Despite the high volatility of menthol, the presence and the stability of menthol at higher temperatures was observed for PS/CD-menthol-IC webs whereas PS fibers without CD complex could not preserve volatile menthol molecules after the fiber production. The DP-MS findings suggest the existence of strong interactions between menthol and CD molecules due to the complexion and CD-menthol inclusion complexation ultimately determines the durability and temperature stability of menthol in the fibers. Three types of CDs: α-CD, β-CD and γ-CD were explored in our studies of CD-menthol-ICs. For the PS/γ-CD-menthol-IC web, the thermal release of menthol occurred at fairly broad temperature ranges (100–350 °C) suggesting that γ-CD is a better candidate over α-CD, β-CD for the stabilization and temperature release of menthol. In summary, we have shown that the CD-ICs can be incorporated in fibers by electrospinning and these CD-IC functionalized webs may have practical applications for the development of multi-functional fibrous materials in general.

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References