Electrospun Nanowebs Incorporating Essential Oil/Cyclodextrin Inclusion Complexes

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OBJECTIVE

In this study, we aimed to produce functional polyvinyl alcohol (PVA) electrospun nanowebs containing essential oil; eugenol (EG), that have long-term durability and high temperature stability due to cyclodextrin (CD) inclusion complexation.

INTRODUCTION

Cyclodextrins (CDs) which are cyclic oligosaccharides have truncated cone-shaped molecular structures. The most commonly used CDs are α-CD, β-CD and γ-CD having 6, 7 and 8 glucopyranose units in the cyclic structure, respectively [1-3]. The size of the cavity for α-CD, β-CD and γ-CD are ~ 6, 8 and 10 Å, respectively; although the depth of the cavity is same (~ 8 Å) for these CDs (Figure 1) [1]. Relatively hydrophobic cavities of CDs have ability to form inclusion complexes with a variety of guest molecules. Cyclodextrin inclusion complexes (CD-IC) are widely used in many areas such as pharmaceuticals, functional foods, cosmetics, textiles etc. in order to achieve the stabilization/protection and controlled/sustained release of volatile or unstable drugs, fragrances, flavors, essential oils and other functional additives [1-6].

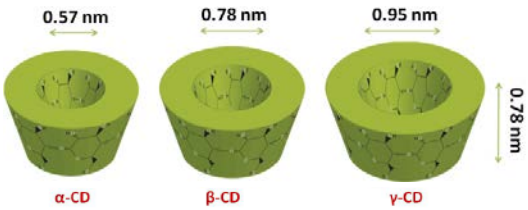

Fig. 1. Approximate dimensions of α-CD, β-CD, γ-CD.

Electrospinning is a quite versatile and cost-effective technique for producing nanofibers/nanowebs from a variety of materials such as polymers, polymer blends, sol–gels, composites, etc. [6-9]. Electrospun nanofibers can be quite applicable in biotechnology, membranes/ filters, textiles, food packaging and sensors due to their large surface-to-volume ratio, highly porous structure and high encapsulation efficiency [6-11].
Eugenol (EG), a phenolic major compound of clove oil, is widely used essential oil as a fragrant and flavoring agent in food and cosmetic industries [12]. This compound is also known as an anesthetic agent in dentistry. Moreover, EG has several biological activities such as antibacterial, antioxidant, antitumor, anti-inflammatory and antifungal properties [12,13].
CDs can eliminate pungent taste, low solubility, irritation effect to the skin of EG due to inclusion complexation and CD-IC could supply prolonged functionality of EG by improving its stability.
In this study, PVA, a biodegradable and non-toxic synthetic polymer, was chosen as the nanofiber matrix and the encapsulation of EG/CD-IC in electrospun PVA nanowebs was carried out. It was observed that the high temperature stability of EG was facilitated by cyclodextrin inclusion complexation.

APPROACH

Aqueous solution mixture of PVA and EG/CD-IC were electrospun in order to obtain functional PVA nanowebs containing EG/CD-IC (PVA/EG/CD-IC). Figure 2 indicates the schematic representation of the formation of EG/CD/IC and PVA/EG/CD-IC nanofibers.

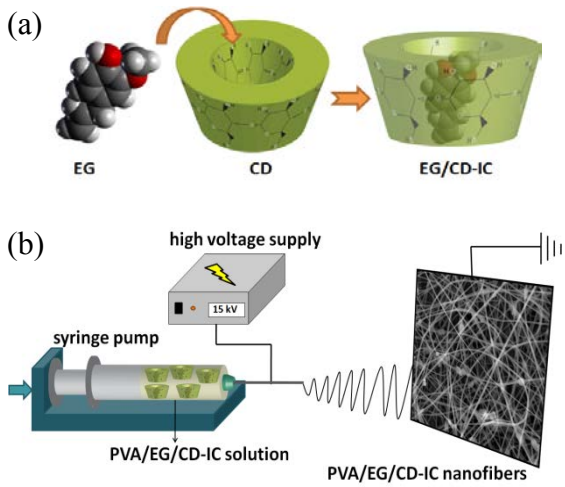

Fig. 2. Schematic representation of the (a) formation of the EG/CD/IC, (b) electrospinning of the PVA/EG/CD-IC nanofibers.

In order to find out the most favorable CD type for the stabilization of EG, the EG/CD-IC was formed by using three types of CDs: α-CD, β-CD and γ-CD. PVA and PVA/EG nanofibers without CD were also produced for comparison. Characterizations of these functional electrospun nanofibers were done by using scanning electron microscope (SEM), X-ray diffraction (XRD),

differential scanning calorimeter (DSC), thermogravimetric analyzer (TGA) and proton nuclear magnetic resonance (^{1}H-NMR).

RESULTS AND DISCUSSION

PVA/EG/CD-IC nanofibers having fiber diameters around 550 nm were successfully obtained via electrospinning technique. For PVA, PVA/EG and PVA/EG/α-CD-IC systems uniform and bead-free nanofibers were obtained. In the case of PVA/EG/β-CD-IC and PVA/EG/γ-CD-IC systems, mostly uniform nanofibers with aggregates of CD-IC crystals were observed.

The XRD diffraction patterns of PVA/EG/β-CD-IC and PVA/EG/γ-CD-IC nanowebs revealed channel-type packing structures of CDs confirming incorporation of EG/CD-IC in PVA nanofiber matrix for these samples. However, the XRD data of PVA/EG/α-CD-IC nanoweb did not show any type of α-CD crystal aggregates and this result correlated with the SEM image of this sample. Therefore, we could not confirm the presence of EG/α-CD-IC in PVA nanowebs.

Previously, we observed that the evaporation of the volatile guest molecules shifted to higher temperatures due to cyclodextrin inclusion complexation [14,15]. As anticipated, the thermal stability of EG was also enhanced for PVA/EG/β-CD-IC and PVA/EG/γ-CD-IC when compared to pure EG due to interactions between EG and the CD cavities. However the loss of EG was observed at almost same temperatures for PVA/EG/α-CD-IC sample with pure EG indicating that inclusion complexation could not form between EG with α-CD. This might be originated from the small cavity size of α-CD that is not suitable for the encapsulation of EG molecule. On the other hand, the cavity size of β- and γ-CD is large enough to form the inclusion complex with EG [16].

In addition, NMR results showed that the amount of EG was the highest for PVA/EG/γ-CD-IC that is possibly due to the bigger cavity size of γ-CD resulting better size fit between the EG and the host γ-CD cavity.

CONCLUSIONS

In this study, the encapsulation of EG/CD-IC in PVA nanowebs was achieved via electrospinning. We observed that the stability of EG is significantly dependent on the CD type. PVA/EG/α-CD-IC nanoweb could not effectively stabilize EG, since α-CD is not proper host for EG guest owing to its small cavity size. PVA/EG/β-CD-IC and PVA/EG/γ-CD-IC nanowebs show high temperature stability of EG so these functional nanofibers/nanowebs may have practical applications in food packaging, biomedical, textile and personal care industries.

FUTURE WORK

The durability of EG in PVA/EG and PVA/EG/CD-IC nanowebs will also be studied at different temperatures by using headspace GC-MS in order to find out the most favorable CD type (β-CD or γ-CD) for the stabilization of EG. As a future work, we will also produce CD-IC functionalized nanowebs by using various essential oils.

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