

# Encapsulation of Vanillin/Cyclodextrin Inclusion Complexes in Electrospun Nanowebs: High-temperature Stability and Slow Release of Vanillin

Fatma Kayaci, Tamer Uyar  
Bilkent University, Ankara, Turkey  
uyar@unam.bilkent.edu.tr, kayaci@unam.bilkent.edu.tr

## OBJECTIVE

Our purpose was to produce functional polyvinyl alcohol (PVA) electrospun nanowebs containing vanillin having prolonged shelf-life and high temperature stability facilitated by cyclodextrin inclusion complexation.

## INTRODUCTION

Cyclodextrins (CDs) are cyclic oligosaccharides having a truncated cone shaped molecular structure, and CDs can form non-covalent host-guest inclusion complexes with a variety of molecules [1-3]. Cyclodextrin inclusion complexes (CD-IC) are widely used in food industry in order to achieve stabilization/protection and controlled/sustained release of volatile or unstable flavors and other food additives [1-5].

Recently, electrospinning has received great attention, since this technique is quite versatile and cost-effective for producing nanofibers/nanowebs [6,7]. Electrospun nanofibers can be quite applicable in active food packaging [8,9] due to their large surface-to-volume ratio. Moreover, high encapsulation efficiency of electrospun nanofibrous matrix supplies the stabilization of active food additives such as flavors and antioxidants. Incorporation of CD-IC into electrospun nanofibrous matrix would improve the shelf-life, stability and slow release of these food additives.

Vanillin is widely used as flavor and fragrance and it is also used as a food preservative due to its antioxidant property [10]. However, vanillin has a short shelf-life because of its volatile nature, therefore, the stabilization of vanillin is very important for its prolonged functionality.

In this study, we have produced functional PVA electrospun nanofibers including vanillin having long-lasting durability and high temperature stability facilitated by cyclodextrin inclusion complexation [11]. PVA nanofiber matrix was chosen, since PVA is a biodegradable and non-toxic synthetic polymer and applicable in food packaging [12-14].

## APPROACH

PVA nanowebs incorporating vanillin/cyclodextrin inclusion complex (vanillin/CD-IC) were produced

via electrospinning technique [11]. The schematic representations of the vanillin/CD/IC formation and the electrospun PVA/vanillin/CD-IC nanofibers were indicated in Figure 1. The vanillin/CD-IC was prepared with three types of CDs;  $\alpha$ -CD,  $\beta$ -CD and  $\gamma$ -CD to find out the most favorable CD type for the stabilization of vanillin. For a comparison study, PVA and PVA/vanillin nanofibers without CD were also electrospun [11].

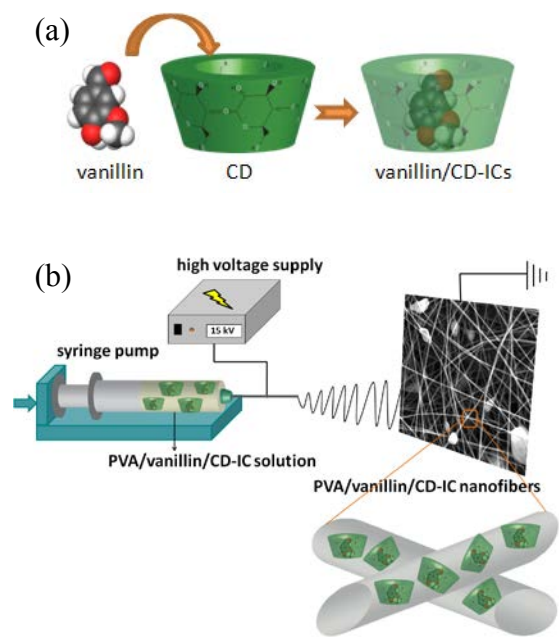


Fig. 1. Schematic representations of the (a) formation of the vanillin/CD/IC, (b) electrospinning of the PVA/vanillin/CD-IC nanofibers.

The morphology and the fiber diameter of the electrospun nanofibers were analyzed by scanning electron microscope (SEM). Other characterizations of these functional electrospun nanofibers were done by using X-ray diffraction (XRD), differential scanning calorimeter (DSC), thermogravimetric analyzer (TGA) and the proton nuclear magnetic resonance ( $^1\text{H-NMR}$ ). The durability of vanillin in PVA/vanillin and

PVA/vanillin/CD-IC nanowebs was also studied at different storage time periods [11].

## RESULTS AND DISCUSSION

PVA/vanillin/CD-IC nanofibers having fiber diameters around 200 nm were successfully electrospun from aqueous solution mixture of PVA and vanillin/CD-IC [11]. Our results indicated that the thermal stability of vanillin in PVA/vanillin/CD-IC nanowebs increased to higher temperature when compared to PVA/vanillin nanoweb, since in CD-IC, the thermal evaporation of the volatile guest molecules shifts to higher temperatures due to their interactions with the CD cavity [15,16]. For PVA/vanillin/ $\gamma$ -CD-IC nanoweb, the loss of vanillin was observed at higher temperature range than PVA/vanillin/ $\alpha$ -CD-IC and PVA/vanillin/ $\beta$ -CD-IC indicating that the interaction between vanillin and  $\gamma$ -CD was much stronger compared to  $\alpha$ -CD and  $\beta$ -CD. Moreover, according to the durability test, PVA/vanillin/CD-IC nanowebs, the preservation of vanillin was very effective compared to PVA/vanillin nanoweb. In addition, we also observed that PVA/vanillin/ $\gamma$ -CD-IC nanoweb was more effective for the slow release of vanillin when compared to PVA/vanillin/ $\alpha$ -CD-IC and PVA/vanillin/ $\beta$ -CD-IC [11]. The reason for forming more stable inclusion complex between vanillin and  $\gamma$ -CD is possibly due to the bigger cavity size of  $\gamma$ -CD resulting better fit in size match between the guest molecule and the host CD cavity. This also correlates with our recent findings where  $\gamma$ -CD forms more stable inclusion complex with vanillin in the solid state [15].

## CONCLUSIONS

Encapsulation of vanillin/CD-IC in PVA nanowebs was achieved via electrospinning. PVA/vanillin/CD-IC nanowebs show prolonged shelf life and high temperature stability. The stability of vanillin was significantly dependent on the CD type. PVA/vanillin/ $\gamma$ -CD-IC nanoweb effectively stabilized vanillin compared to  $\alpha$ -CD and  $\beta$ -CD.

## FUTURE WORK

As a future work, we will produce CD-IC functionalized nanowebs by using different guests such as flavors, antimicrobials, antioxidants, drugs, and bioactive agents, etc. These functional nanofibers/nanowebs may have practical applications in food, biomedical, textile and personal care industries, depending on the type of the guest molecules.

## ACKNOWLEDGEMENTS

State Planning Organization (DPT) of Turkey is acknowledged for the support of UNAM-Institute of Materials Science & Nanotechnology. Dr. T. Uyar acknowledges EU FP7-PEOPLE-2009-RG Marie Curie-IRG (project#PIRG06-GA-2009-256428) and TUBITAK-COST Action (project#111M459) for funding this work. F. Kayaci acknowledges TUBITAK-BIDEB for the national graduate study scholarship.

## REFERENCES

- [1] Hedges, A. (1998), *Chemical Reviews*, 98(5), 2035-2044.
- [2] Del Valle, E. (2004), *Process Biochemistry*, 39(9), 1033-1046.
- [3] Marques, H. M. C. (2010), *Flavour and Fragrance Journal*, 25(5), 313-326.
- [4] Koontz, J. L., Marcy, J. E., O'Keefe, S. F., & Duncan, S. E. (2009), *Journal of Agricultural and Food Chemistry*, 57(4), 1162-1171.
- [5] Wang, J., Cao, Y., Sun, B., & Wang, C. (2011), *Food Chemistry*.
- [6] Li, D., & Xia, Y. (2004). *Advanced Materials*, 16(14), 1151-1170.
- [7] Greiner, A., & Wendorff, J. (2007), *Angewandte Chemie-International Edition*, 46(30), 5670-5703.
- [8] Kriegel, C., Arrechi, A., Kit, K., McClements, D., & Weiss, J. (2008), *Critical reviews in food science and nutrition*, 48(8), 775-797.
- [9] Vega-Lugo, A. C., & Lim, L. T. (2009), *Food Research International*, 42(8), 933-940.
- [10] Karathanos, V. T., Mourtzinou, I., Yannakopoulou, K., & Andrikopoulos, N. K. (2007), *Food Chemistry*, 101(2), 652-658.
- [11] Kayaci, F., Uyar T. (2012), *Food Chemistry*, DOI: 10.1016/j.foodchem.2012.01.040.
- [12] Chiellini, E., Cinelli, P., Chiellini, F., & Imam, S. H. (2004), *Macromolecular bioscience*, 4(3), 218-231.
- [13] Tripathi, S., Mehrotra, G., & Dutta, P. (2009), *International journal of biological macromolecules*, 45(4), 372-376.
- [14] Wu, J. I. H. G., Wang, P. E. I. J. I. N., & Chen, S. C. (2010), *Journal of Food Quality*, 33(6), 780-801.
- [15] Kayaci, F., & Uyar, T. (2011), *Journal of Agricultural and Food Chemistry*, 59, 11772-11778.
- [16] Tsai, Y., Tsai, H. H., Wu, C. P., & Tsai, F. J. (2010), *Food Chemistry*, 120(3), 837-841.