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1 Introduction

In conventional packaging concepts multilayer structures often use to provide the required functionality tailored to the packaging goods. These are generally not biodegradable and difficult to recycle. Therefore, the development of more sustainable and bio-based multilayer composite materials are required in following projects: BiOnTop, Preserve and BioSupPack.

The coating with whey protein as an oxygen barrier is a bio-based alternative to the conventionally used ethylene-vinyl alcohol co-polymers (EVOH). However, the barrier properties decrease with increasing humidity due to the hydrophilic character of the whey protein coating. Therefore, functionalization of the coating is required.

One method of a nanoscale surface hydrophobization of hydrophilic substrates is the chemical fatty acid grafting technique. In this process, fatty acids are covalently bonded onto the surface of the substrate, improving the water vapour barrier and water repellent properties.

2 Materials and Methods

In the project BiOnTop the fatty acid grafting of the WPI (Whey protein isolate) films with the transfer method was conducted using different fatty acid chlorides (myristoyl chloride (C14), palmitoyl chloride (C16), stearoyl chloride (C18)) and anhydride (palmitic anhydride). The grafting temperature was tested between 60°C - 160°C and the grafting time was set constantly to 10 min based on previous investigations.^{1), 2), 3), 4)}

Therefore, the fatty acid chlorides and the anhydride are dissolved into a solvent. A transmitter paper is wetted in the fatty acid solution after which the solvent evaporates from transmitter. Then, the transmitter paper is placed on the top of the whey protein based film and put into an oven for a set temperature and time. In this process step the esterification of the fatty acids onto the surface of the substrate occurs.^{1), 2), 3), 4)}

The method of fatty acid grafting via transmitter paper is schematically illustrated in figure 1. The fatty acid grafting was analyzed by measuring the water vapour permeation (WVTR at 23°C, 50% 0% r. h.) and the contact angle against water.

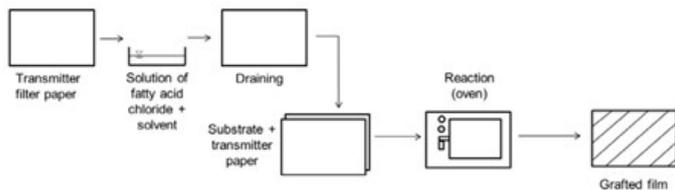


Figure 1: Chemical grafting process via transmitter paper (adapted from¹⁾)

4 Further results on the topic of nanoscale surface functionalization are available in the following recently launched EU projects:



For more information go to our website: www.hs-albsig.de/spi

References

- 1) Gernsek, E., Schmid, M. and Lindner, M. (2020) 'Grafting of Fatty Acids on Poly(vinyl Alcohol): Effects on Surface Energy and Adhesion Strength of Acrylic Pressure Sensitive Adhesives', *Frontiers in Materials*, vol. 6, p. 335.
- 2) Haas, A., Schlemmer, D., Grupa, U. and Schmid, M. (2017) 'Effect of Chemical Grafting Parameters on the Manufacture of Functionalized PVOH Films Having Controlled Water Solubility', *Frontiers in Chemistry*, vol. 5, p. 38.
- 3) Schmid, M., Benz, A., Stinga, C., Samain, D. and Zeyer, K. P. (2012) 'Fundamental Investigations Regarding Barrier Properties of Grafted PVOH Layers', *International Journal of Polymer Science*, vol. 2012, pp. 1–6.
- 4) Stinga, N. C. (2008) Utilisation de la chimie chromatogénique pour la conception et la réalisation de matériaux celluloseux barrières à l'eau, aux graisses et aux gaz, Phd thesis, Grenoble, France, Université Joseph Fourier - Grenoble 1.

3 Results and Discussion

The results of grafting of the WPI based films with fatty acid chlorides indicate an improvement in the water vapour barrier. In figure 2 the results of the WVTR are illustrated. The WVTR values of the WPI films grafted with fatty acid anhydrides indicate a small improvement in the barrier values (Barrier improvement factor 1.4 (BIF)). However, due to the high standard deviation, no significance can be determined. This is due to the low reactivity of the palmitic anhydride.⁴⁾ The results of the WVTR of the samples grafted with the three fatty acid chlorides consistently show an improvement of the WVTR with increasing temperature. The highest barrier improvement was measured for the films grafted with stearoyl chloride (C18) (BIF 4.8). This indicates that the water vapour barrier could be increased by both factors using fatty acids with a higher chain length and using increased grafting temperatures.

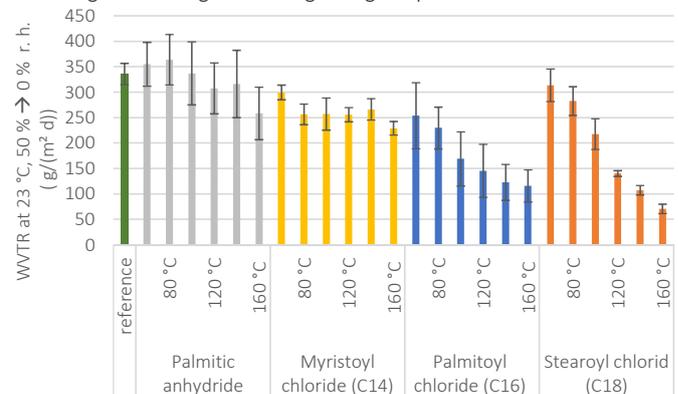


Figure 2: WVTR of grafted WPI castfilms (transfer method)

The water contact angle of palmitoyl chloride (C16) grafted samples was measured. The reference and the WPI based films grafted with the anhydride could not be measured based on the rapid spreading of the water drop into the WPI based films. The contact angles of the grafted WPI based films ranged between 92° and 102°. The results of the contact angle of the grafted WPI films are comparable with contact angle measurements of paper coated with PVOH and grafted with the transfer method (90°-106°)³⁾. In contrast to the samples grafted with palmitoyl anhydride and the reference (a), the WPI films grafted with palmitoyl chloride (b) showed a clear hydrophobic effect (Figure 3).



Figure 3: Water drop on the surface of a non grafted WPI film (a) and a grafted WPI film (160°C, 10 min) (b)