

# Development and Characterisation of HPMC Films Containing PLA Nanoparticles Loaded with Green Tea Extract for Food Packaging Applications

Magdalena Wrona, Marlene J. Cran, Cristina Nerín and Stephen W. Bigger

## 1 Nanoparticle Size Optimization

### 1.1 Method

There are numerous synthesis variables that can influence the resulting properties of nanoparticles and that are primarily related to particle size (Patra & Baek, 2014; Petkova, Francesko, & Tzanov, 2015). Therefore, a computer-aided experimental design of PLA nanoparticle synthesis was performed using the software program Modde 6.0 from Umetrics (Umeå, Sweden). A face-centred central composite design (FCCCD) fitted with multiple linear regression (MLR) was applied with the following experimental factors: concentration of green tea extract (GTE), concentration of emulsifier (PVA) and vortex speed (VS). The two independent responses analysed were the size of nanoparticles and the polydispersity index (PDI). Finally, 15 different experiments were performed with two additional repetitions of the central point. Table S1 shows the applied conditions for the experimental matrix. All experiments were performed randomly.

### 1.2 Results

The effects and the interactions between each parameter were studied using effects plots with the results showing that the strongest negative effect on nanoparticle size was the PVA concentration followed by the GTE concentration. An insignificant effect (when the confidence interval includes zero) was observed in the case of the vortex velocity. Moreover, interactions between the concentration of GTE and other parameters (GTE\*PVA and GTE\*SV) were considered to be positive and significant. All factors were insignificant in the case of the PDI of the resulting particles.

Table S1. FCCCD experimental design matrix for nanoparticle optimization.

Experiment number	Factors		
	GTE (%)	PVA (%)	VS (rpm)
1	0.2	0.0	700
2	0.2	0.0	1400
3	1.0	0.0	700
4	1.0	0.0	1400
5	0.2	1.0	700
6	0.2	1.0	1400
7	1.0	1.0	700
8	1.0	1.0	1400
9	0.6	0.5	700
10	0.6	0.5	1400
11	0.2	0.5	1050
12	1.0	0.5	1050
13	0.6	0.0	1050
14	0.6	1.0	1050
15	0.6	0.5	1050
16	0.6	0.5	1050
17	0.6	0.5	1050

The variation of the response ( $Q^2$ ) predicted by the model according to cross-validation was also determined. Values of  $Q^2$  were 0.75 and -0.89 for size and PDI respectively and the poor value of  $Q^2$  in the case of PDI is probably due to insignificant terms in the model. In the case of nanoparticle size, the proposed model adequately predicts the data and subsequent effective control over experimental data was considered to be confirmed by a reproducibility value equal to 0.999. Similar to the  $Q^2$  value, poor reproducibility was obtained in the case of the PDI with a value of -0.2. The percentage of the variation of the response explained by the model ( $R^2$ ) was 0.970, and 0.613 for size and PDI factors respectively. This again confirms a better fit of the size data compared to the PDI.

The surface contour plots from the optimization experimental set-up as shown in Figure S1 indicate that the synthesis of different sizes and PDIs of GTE-loaded PLA nanoparticles can be described by a non-linear mathematical model. The smallest nanoparticles were obtained when using 0.5% (w/w) of PVA in the emulsion with the largest obtained without using PVA. Different size distributions of nanoparticles were subsequently obtained by the use of different concentrations of PVA and different vortex speeds (see Table S1). For preparation of HPMC films with GTE-loaded PLA nanoparticles, a fixed concentration of 1% (w/w) GTE was used to enable a comparison of migration from and antioxidant (AO) capacity of the HPMC films. Optimum conditions using this GTE loading at 0% PVA and 1400 rpm were applied for the synthesis of small nanoparticles whereas 0.5% PVA and 700 rpm were applied for the synthesis of larger nanoparticles. The PDI response was excluded from further experiments as in this case, the mathematical model obtained was deemed inadequate.

## **2 Infrared Spectra of Nanoparticles and HPMC Film**

The infrared spectra of the prepared PLA nanoparticles, neat PLA, and the green tea powder are shown in Figure S2. The region highlighted in this figure shows the peak that may indicate some interaction between the PLA and GTE. The infrared spectra of the HPMC films loaded with PLA and GTE/PLA nanoparticles are shown in Figure S3. The region highlighted in these spectra indicate the peak that may suggest some interaction between the PLA nanoparticles and the HPMC film.

## **References**

- Patra, J. K., & Baek, K.-H. (2014). Green Nanobiotechnology: Factors Affecting Synthesis and Characterization Techniques. *Journal of Nanomaterials*, 2014, 12.
- Petkova, P., Francesko, A., & Tzanov, T. (2015). Enzyme-assisted formation of hybrid biopolymer hydrogels incorporating active phenolic nanospheres. *Engineering in Life Sciences*, 15(4), 416-424.

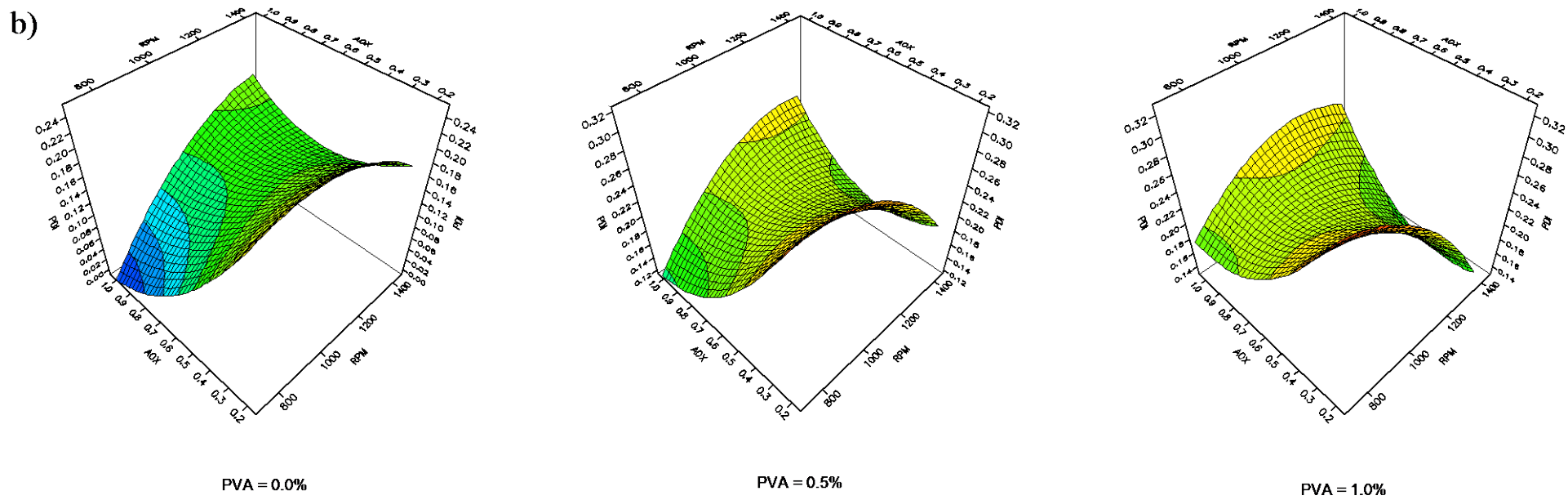
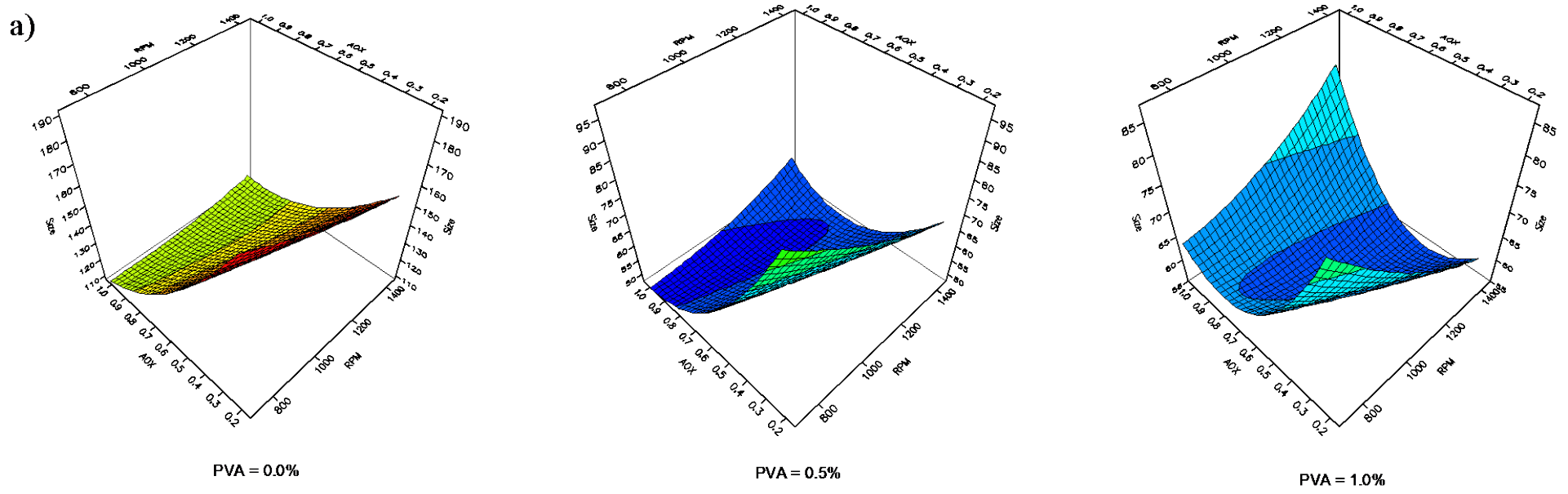


Figure S1. Contour plots for experimental optimization: 4D surface response of (a) nanoparticle size and (b) PDI.

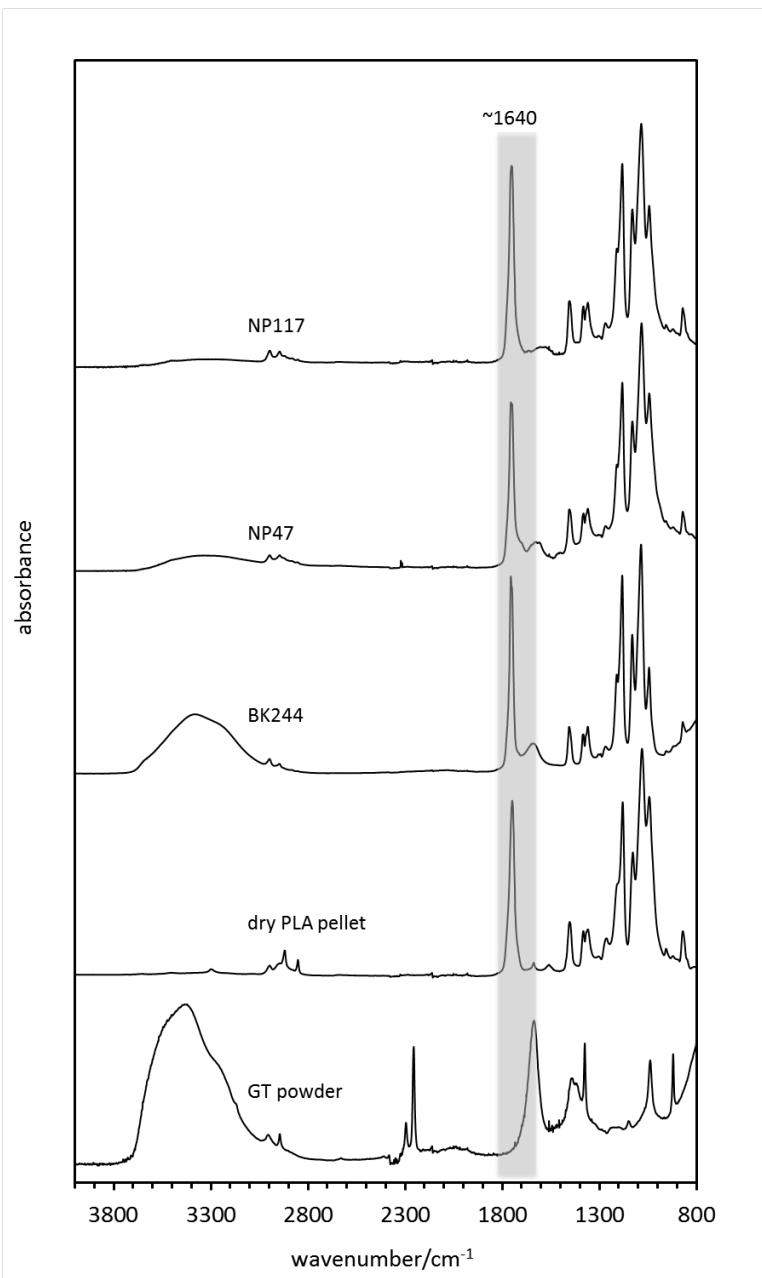


Figure S2. ATR-FTIR spectra of nanoparticles and base materials.

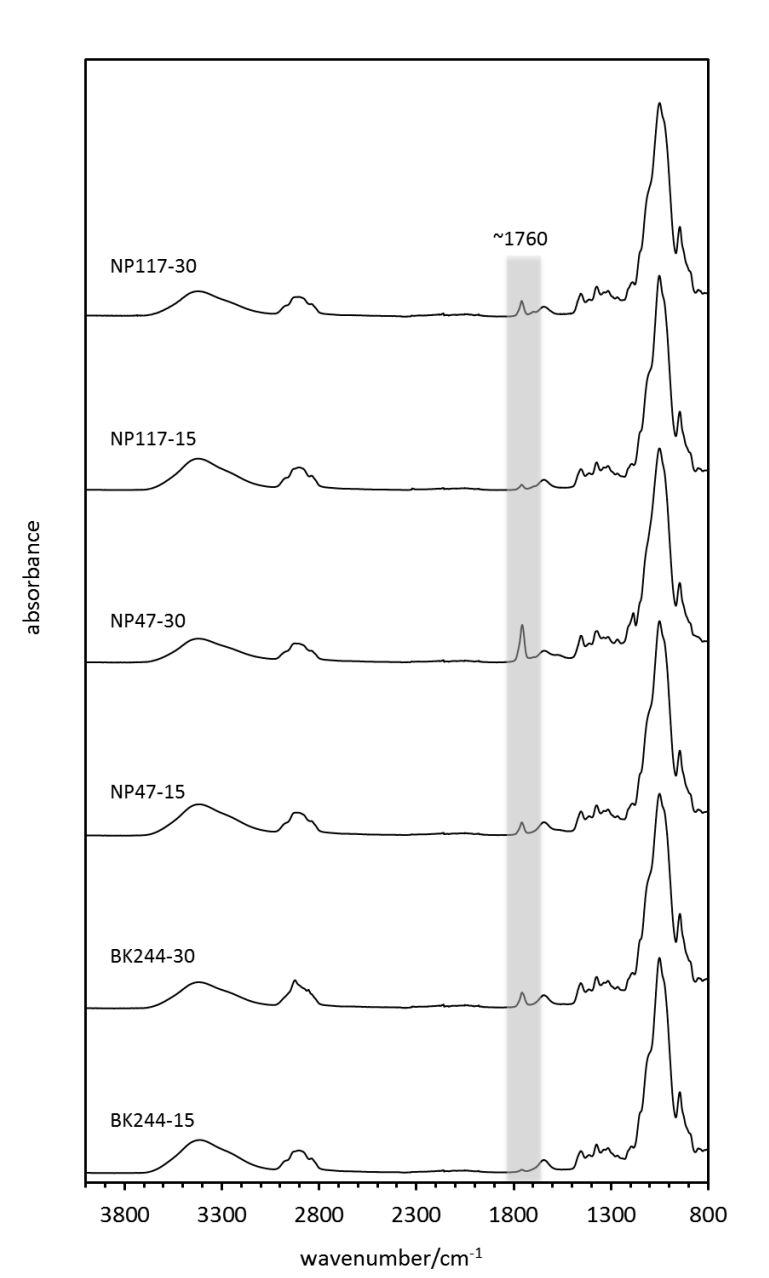


Figure S3. ATR-FTIR spectra of HPMC films containing PLA and PLA/GTE nanoparticle.