

Layer-by-layer deposition of PAMAM dendritic material onto polylactide nonwoven

Supervisor and co-supervisor:

Prof. Dawid Stawski, TUL, Poland

Dr. Somaye Akbari, AUT, Iran

Produced by:

Sima Shakooryavan

ID No.: 801455

September 2024, Poland

Abstract

Multilayer self-assemblies build up through layer-by-layer (LBL) deposition of polyelectrolytes has been recognized as a straightforward, adaptable, and bottom-up surface modification approach which can be applied on various substrates, regardless of their shape, size, and surface chemistry, under mild conditions. The growth profile and structure of polyelectrolyte (PE) multilayer assemblies constructed through LBL technique on fully smooth, flat, and non-porous inorganic surfaces including quartz slides or silica wafers have extensively investigated in literature. However, there is a significant gap in the understanding of the fundamental mechanism governing the LBL deposition and PE multilayer assemblies on rough, uneven, and porous surfaces, particularly those found in textile materials, including nonwoven fabric. Therefore, the aim of this study is to monitor the construction of multilayer assemblies consisting of dendritic amine-terminated poly(amidoamine) (PAMAM) and poly(acrylic acid) (PAA) on pre-treated polylactide (PLA) nonwoven fabric using the layer-by-layer technique via the dipping method.

In order to functionalize PLA substrate with positively charged surface, aminolysis reaction at different time interval and two temperature was designed. According to characterization tests, optimum conditions to provide the highest amine content with acceptable mechanical properties were obtained.

After finding the optimum condition of pre-treatment, the experiments and characterization tests have been engineered to understanding the multilayer growth on the PLA nonwoven. Three key parameters including polyelectrolytes solution pH, their concentration ratio, and intermediate drying was consider in LBL deposition. Since PAMAM and PAA are both weak polyelectrolytes, can possess different surface charge and conformational structure based on the PE pH, which can directly influence PE complex formation. Therefore, the study was conduct in two phases: liquid-liquid phase to study polyelectrolytes complex formation and liquid-solid phase to monitor multilayer growth with hydrated and dry LBL (intermediate drying effect).

According to liquid-liquid phase, the optimal pH and concentration ratio of PAMAM: PAA complex to form stable and irreversible turbid colloidal PEC dispersion were determined through turbidimetry measurements. Acid-base titration and DLS analysis revealed that PAMAM: PAA at their partially charged state (PAMAM/pH=8 and PAA/pH=4) where both have compact and globular conformation (not fully compact), provide the stable higher concentration of aggregated PECs (highest turbidity~1668 NTU). UV-visible spectroscopy were employed to characterized PECs interaction and confirmed PAA penetration into PAMAM structure, along with electrostatic interaction of primary amines and carboxylate groups of PAA.

Three different concentration ratios of PAMAM: PAA, corresponding to the obtained highest turbidity at each series of titration in liquid-liquid phase, were selected to study the PEC multilayer growth on the substrate in liquid-solid phase. Based on the K/S value of the colored substrate, a concentration ratio of 7:7 ($10^{-4}\times\text{g/mL}$), at the obtained optimal pH, provided the highest PE multilayer growth on the substrate in liquid-solid phase. Ninhydrin assay was conducted to quantify amine density after each deposition step. It was revealed that PAMAM/PAA PE multilayer assemblies till the 7 layers have the converging profile growth, while applying one step intermediate drying between LBL caused the stability of the PAA layers and final divergent profile growth with more NH_2 density at the even top layer of the material. In addition, according to air permeability analysis, it was found that PE multilayered assembled on the substrate with dry LBL have less compact structure than those assembled hydrated LBL. In addition, based on the staining test as a function of layer number, it was revealed that highest NH_2 density on the top even layer did not always lead to higher accessible amine site to interact with other molecule. Indeed, the highest NH_2 density does not lead to higher dye adsorption; there is a thresholds and limitation of the substrate layering to achieved the desirable application such as dye adsorption or drug delivery.

In conclusion, knowledge of the PE multilayer growth profile and controlling their density to tailor surface properties with optimal accessible functional groups is crucial for designing nonwoven substrates with developed multilayer assemblies for applications like drug delivery where microbial contamination is crucial.