

## ABSTRACT

Polymeric materials with gas barrier equivalent to metalized plastics have become increasingly important for food packaging, electronic device encapsulation, and vacuum insulation. Metalized plastics offer excellent barrier behavior, but they suffer from poor opacity, lack of microwavability, and poor recyclability. Early attempts to develop alternative gas barrier materials have focused on thick ( $>10\ \mu\text{m}$ ) polymer/clay composites produced using physical mixing, but only limited improvement was achieved due to aggregation and random orientation of clay platelets. Metal-oxide thin films have excellent gas and water vapor barrier, but these films need to be deposited under vacuum, making the deposition process expensive and complicated. Layer-by-layer (LbL) assembly is a simple yet powerful bottom-up fabrication technique, which allows assembly of thin films with designed microstructure under ambient conditions. These multilayer thin films have many desirable properties: mechanical flexibility, transparency, and impermeability. This dissertation sought to further improve the processing and properties of high gas barrier thin films produced using LbL assembly.

The influence of deposition time on gas barrier of polymer/clay multilayer thin films composed of polyethylenimine (PEI), poly(acrylic acid) (PAA), and clay was investigated. Multiple PEI/PAA bilayers (BL) were deposited between clay layers to construct multilayer assemblies with quadlayer (QL), hexalayer (HL), and octalayer (OL) sequences. Regardless of film structure, polymer/clay multilayer thin films prepared using shorter dipping time were thicker and exhibited better gas barrier than samples prepared using longer dipping time in the first few layers. This seemingly counterintuitive result was explained by considering desorption

of previously deposited polymers between clay layers. Reduced deposition time helped to retain more polymer between clay sheets, leading to larger clay spacing and better gas barrier.

In an effort to expand the applications and improve the throughput of layer-by-layer assembly, spray-assisted deposition of PEI/PAA bilayers was investigated. The influences of spraying time, spraying pressure, and flow rate on thickness, roughness, and gas barrier were evaluated. Spraying time was determined to be the most important parameter. A 7-bilayer PEI/PAA thin film assembled using optimized spraying parameters exhibited better gas barrier than a dip-coated multilayer prepared using the same deposition time for each layer. These findings pave the way for using the LbL technique commercially, where fast and continuous deposition of high performance thin films on large substrates is needed.

Finally, the first example of super stretchy, super gas barrier was developed by combining polyacrylic acid and poly(ethylene oxide) (PEO). Despite being weaker than electrostatic bonding, the hydrogen bonding between H-bond donating PAA and H-bond accepting PEO managed to impart relatively high gas barrier to the final assembly. Oxygen transmission rate (OTR) of 1.58 mm thick natural rubber was reduced by an order of magnitude after deposition of a 20 BL PAA/PEO assembly. More importantly, no cracking was observed on the PAA/PEO coating after 100% strain. A 5X improvement in gas barrier was retained after this extreme stretching. Additionally, the effect of assembling condition on the permeability of PAA/PEO multilayer thin films was investigated. By setting the assembling pH at 2.75, the negative impacts of PAA ionization and COOH dimer formation could be minimized, leading to a 50% reduction in oxygen permeability. This unique combination of elasticity and gas barrier makes the PAA/PEO assembly an ideal candidate for improving the barrier of elastomeric materials.