

Super Stretchy Polymer Multilayer Thin Film with High Gas Barrier

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EXPERIMENTAL SECTION

Polyethylenimine (PEI) ($M_w = 25,000$ g/mol), PAA ($M_w = 100,000$ g/mol), and n-propanol were purchased from Sigma-Aldrich. PEO ($M_w = 4,000,000$ g/mol) was purchased from Polysciences. All solutions were prepared by simply rolling for 24 h to achieve homogeneity. Prior to deposition, the pH of each PEO solution (0.1 wt%), PAA solution (0.1 wt%), and deionized (DI) rinsing water was altered to the same value using 1 M HCl.

Natural rubber films with a thickness of 1.58 cm were purchased from McMaster-Carr and used as the substrate for SEM imaging and OTR testing. Every natural rubber film was rinsed with DI water, soaked in n-propanol at 40 °C for 10 min, and rinsed again with n-propanol and DI water before being dried with compressed air. Cleaned natural rubber was treated with an ATTO plasma cleaner (Diener, Germany) at 25 W for 5 min prior to deposition. Polished silicon wafers were used as substrates for ellipsometry and profilometry. Silicon wafers were cut to 10 × 1 cm strips and then cleaned with piranha solution for 30 min, rinsed with acetone and DI water prior to deposition. **Caution!** Piranha solution reacts violently with organic materials and needs to be handled properly. Polypropylene sheets were used as substrates for making free-standing

Supporting information

films that were used in differential scanning calorimeter (DSC) testing. Polypropylene sheets were cut to 10×3 cm strips, and then rinsed with methanol and DI water before deposition.

All cleaned substrates were initially dipped into a 0.1 wt% PEI solution (at natural pH around 10.5) for 10 min and then rinsed with DI water to lay down a primer layer. Substrates were then dipped in the PAA solution for 5 min, rinsed with DI water of the same pH three times (20 sec each time), and dried with filtered air. This procedure was followed by an identical dipping, rinsing, and drying procedure in the PEO solution. After this initial bilayer was deposited, different numbers of layers were added using 1 min dipping with the same rinsing and drying conditions. This procedure was repeated until the desired number of layers was achieved. All thin films were prepared using a home-built robotic dipping system.¹

Film thickness was measured (on silicon wafers) using an alpha-SE ellipsometer (J.A. Woollam Co., Inc., Lincoln, NE). Films that are too hazy for the ellipsometer were measured with a P-6 profilometer (KLA-Tencor, Milpitas, CA). Regardless of the measurement method used, reported film thickness was the average of three measurements. Glass transition temperature was measured by a Q20 DSC (TA Instruments, New Castle, DE). 5-10 mg of 100 BL PAA/PEO thin film were placed in aluminum pans and scanned from -40 to 80 °C at a heating and cooling rate of 5 °C/min. OTR measurements were performed by MOCON (Minneapolis, MN) using an Oxtran 2/21 ML oxygen permeability instrument (in accordance with ASTM Standard D-3985) at 23 °C and at 0% RH. An Instron 4411 tensile tester was used to stretch samples at ambient conditions (23 °C, 45% RH) to different strain levels (25, 50, and 100%). Strain rate was set at 20 inch/min, and each sample was held at a given strain level for 2 min before being released. Surface morphology of 20 BL PAA₃/PEO₃ coated natural rubber films, before and after stretching, was imaged using a JSM-7500F FESEM (JEOL, Tokyo,

Japan). Prior to imaging, each film was coated with 3 nm of platinum/palladium to reduce surface charging. A Bruker Dimension Icon AFM was used to determine the elastic modulus of the thin films. All quantitative nanomechanical property mapping measurements were conducted at ambient conditions (24 °C, 45% RH). The half angle, tip radius, and spring constant of the AFM tip (Tap150A, Bruker) are 18°, 8 nm, and 5 N/m, respectively. The ramp size used for all tests was set at 397.2 nm. 40 BL PAA/PEO thin films assembled at different pH were used to prevent the influence of silicon substrate on test results. The reported modulus of each sample was the average of 20 measurements.

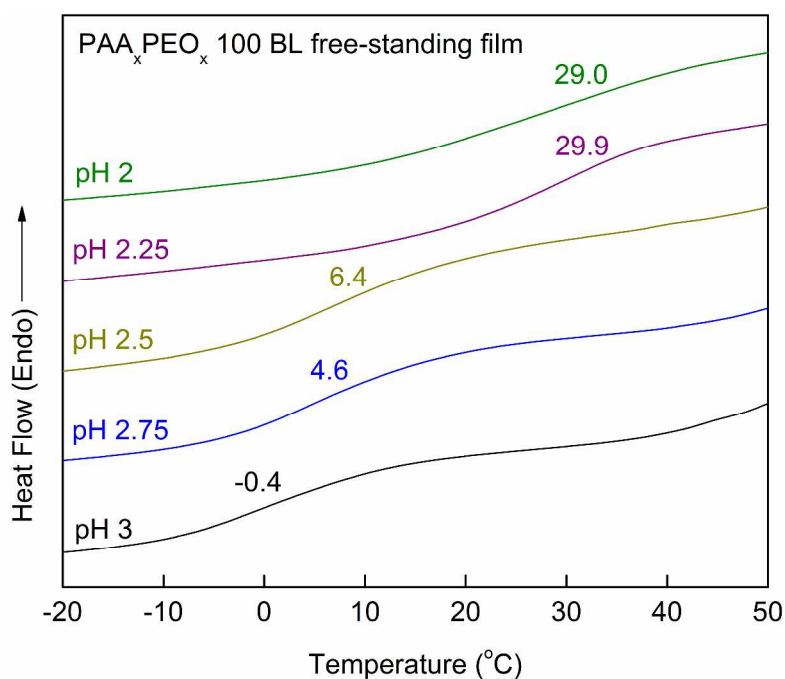


Figure S1. DSC curves of 100 BL PAA₃/PEO₃ free-standing films assembled at different deposition pH.

Reference

1. Gamboa, D.; Priolo, M. A.; Ham, A.; Grunlan, J. C. *Rev. Sci. Instrum.*, **2010**, *81*, 036103-036103-3.