Polyelectrolyte Multilayer under Mechanical Stress: How the Internal Structure Follows External Load

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Polyelectrolyte Multilayers (PEM) are composite materials consisting of alternating layers of organic polyions of opposite charge. Due to the good adjustability of the physico-chemical parameters of the PEM (e.g. thickness, surface roughness, or particle incorporation) [1], they are promising materials for technical applications (e.g. coatings, and function-alization). Hereby the mechanical properties of PEM such as stiffness, resistance, and fatigue are crucial. Thus, studying the response of PEM to mechanical stress is an important topic. Several studies on the mechanics of free-standing PEM build as micro-capsules [2] and supported PEM films [3] mainly address the macroscopic properties of the layers such as elastic module and its change under different ambient conditions (e.g. humidity). Our study aims to correlate the (molecular) changes of the internal structure of mechanically loaded PEM with the applied mechanical stress.

The PEM were build-up in LbL-spraying technique on solid support. The polyanion was poly-styrene sulphonate (PSS), and poly-diallyldimethyl ammonium chloride (PDADMAC) was used as the polycation. For studying small elongations (ε ≤ 0.25%) glass slides coated with PEM (partially labelled with deuterated PSS) were deformed, the change in the film thickness and density of the PEM was followed with scattering techniques (e.g. neutron and X-ray reflectivity). Larger deformations (up to ε = 10%) were investigated on Pyrene-labelled PEM coated atop of poly-dimethylsiloxane sheets. The stress-induced change of the characteristic Pyrene-excimer peak is followed using fluorescence spectroscopy.

The first result is that the transition from elastic to plastic behaviour of PEM occurs at the very low value of ε~0.2%. Here an irreversible thickening of the PEM-film is observed. But the inner structure of stratified PE layers changes already below this point. Bragg peaks yielding from the PEM-superstructure vanish upon elongation. This indicates a forced intermixing of the PE layers. Investigations at higher mechanical stress (with Pyrene-labelled PSS) show an irreversible decrease in the excimer to monomer fluorescence intensity of Pyrene. Additionally, an increase in the polarity of the PEM was observed upon stretching which indicates an irreversible molecular decoiling. The molecular decoiling also yields to an increase in the polarity of the PEM, which was found to be irreversible after 10% elongation. When the limit of plastic deformation is exceeded, i.e. the molecules are almost fully decoiled, macroscopic cracks are observed indicating the destruction limit of the PEM. The detailed study on the response of the PEM on external mechanical stress opens a new possibility to manipulate the properties of the PEM on molecular level.