POLYELECTROLYTE ASSEMBLIES: FUNDAMENTALS AND APPLICATIONS

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Charged assemblies bearing opposite or complementary charges span natural (proteins, enzymes, DNA) to synthetic materials (surfactants, synthetic polyelectrolytes). Assembly is facilitated by electrostatic attraction and entropic release of counterions, and most often occurs in aqueous media. Notably decades ago, Michaels described synthetic polyelectrolyte complexes as brittle when dry but “leathery or rubberlike” when wet, which points to the strong effect of water on the mobility of a charged assembly. Here, the molecular origin of the glass transition is quantified for several charged macromolecular systems is investigated using calorimetry and molecular modeling as a function of water content. A general relationship is revealed as it holds for two completely different types of charged systems (pH- and salt-sensitive) and for both polyelectrolyte complexes and polyelectrolyte multilayers, which are made by different paths. This suggests that water facilitates the relaxation of charged assemblies by reducing attractions between oppositely charged intrinsic ion pairs. We further demonstrate the dual role of water and temperature in the dynamics of polyelectrolyte complexes by showing time-temperature and time-water superpositioning in a single polyelectrolyte complex system for the first time. With regard to applications, charged polymers can assemble with functional nanomaterials such as reduced graphene oxide or MXene sheets. These 2D nanomaterials are conductive, facilitating their application as sensors or electrodes for energy storage. Here, the nature of polyelectrolyte-2D nanomaterial assemblies is investigated as thin films. A reversibly stretchable MXene/polyelectrolyte strain sensor and humidity sensor is demonstrated, and the origin of this response is discussed. Also, mechanically robust graphene-based electrodes are presented as assemblies with nanoscale Kevlar.

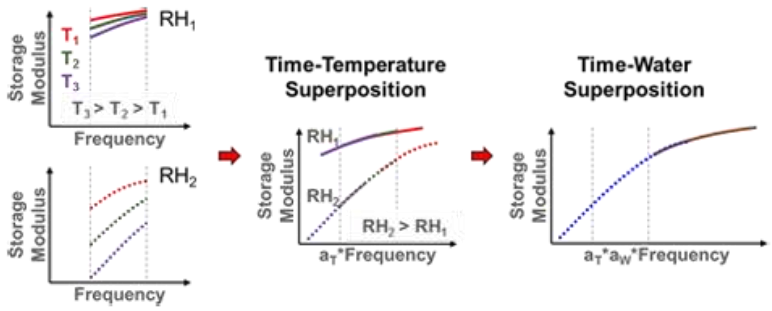

Figure 1 – We report the time-temperature-water superposition principle for polyelectrolyte complexes. (Accepted to Macromolecules 2019).