Abstract **2019 Materials Research Society Conference**
December 1-6, 2019, Boston, MA

Static and Dynamic Properties of Aggrecan Assemblies

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Aggrecan is a bottlebrush shaped high molecular weight proteoglycan. It consists of an extended protein core to which many chondroitin sulfate and keratan sulfate (linear sulfated polysaccharide) chains are attached. This array forms a bottlebrush structure. Aggrecan's primary biological role is to provide the osmotic properties for cartilage. In the presence of hyaluronic acid (HA) aggrecan molecules self-assemble into a supramolecular structure with as many as 100 macromonomers bound to a HA molecule. The aggrecan-HA complexes govern the load bearing properties of cartilage.

Small angle neutron scattering (SANS), dynamic light scattering (DLS) and osmotic pressure measurements were made on near physiological solutions of aggrecan and aggrecan-HA complexes. SANS reveals that the supramolecular structure of aggrecan assemblies is only marginally affected by the HA molecules. DLS indicates that the dynamic response of the aggrecan-HA complex is slower than that of the corresponding aggrecan solution. The relaxation rates measured by dynamic light scattering is proportional to q^3, which is the signature of internal modes in large loosely connected assemblies of smaller units, such as individual aggrecan molecules. This is reflected in the hydrodynamic radius, R_H, whose apparent value varies inversely with q. With increasing aggrecan concentration R_H increases, which is a consequence of the steric hindrance due to densification of the aggrecan aggregates. HA slows the relaxation rate in agreement with an increase of the friction coefficient owing to the rearrangement of the aggrecan molecules along the HA chain. However, addition of calcium chloride slightly increases the relaxation rate of the correlation function. Osmotic pressure measurements quantify the effects of HA and calcium chloride on the osmotic modulus, which defines the compressive resistance of aggrecan assemblies.