

SELF-AGGREGATION OF ACACIA GUMS IN SOLUTION PROBED AT MOLECULAR, MESOSCOPIC AND MACROMOLECULAR LENGTH SCALES

I.C. Riegel-Vidotti and A. Grein-Iankovski.
 Chemistry Department, Federal University of Paraná, Brazil

Acacia gum, also called gum Arabic (GA), is a tree exudate widely used in the food, pharmaceutical and cosmetic industries due to its good emulsification, encapsulation, stabilization and adhesion properties. These technologically-important features are related to the structural characteristics of both the acacia gum and its components.

Previously, we fully investigated the chemical and structural characteristics of two acacia gum samples.¹ Herein we report a study connecting the nanoscale and macroscale structure and dynamics of the gum as probed by small-angle X-ray scattering (SAXS), X-ray photon correlation spectroscopy (XPCS) and rheology.²

The gum exhibited a steadily increasing elastic modulus with increasing time after they were prepared and also the emergence of shear thickening events within the shear thinning behavior, characteristic of associative polymers. XPCS measurements using gold nanoparticles as tracers were used to explore the microscopic dynamics within the biopolymer gels and revealed a two-step relaxation process with a partial decay at inaccessibly short times, suggesting caged motion of the nanoparticles, followed by a slow decay at later delay times.³

Surprisingly, we have determined that the nanometer-scale mean square displacement of the nanoparticles showed a close relationship to the values predicted from the macroscopic elastic properties of the material, obtained through the rheology experiments (Fig.1).

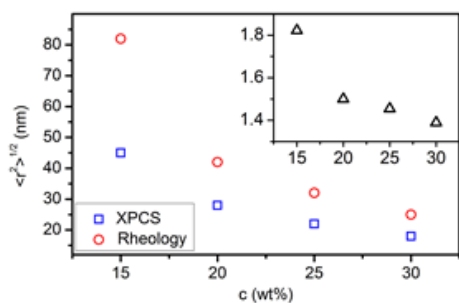


Figure 1. Root mean square displacement $\langle \bar{r}^2 \rangle^{1/2}$ obtained from XPCS (blue squares) and rheology (red circles) for 15, 20, 25 and 30 wt% GN dispersions. Inset: ratio of $\langle \bar{r}^2 \rangle^{1/2}$ determined by rheology over that obtained by XPCS as a function of GN concentration.

In addition, we carried out a full investigations of the gums' physical chemical properties using complementary techniques such as fluorescence spectroscopy, potentiometric titration, viscometry and SAXS, and correlated to the gums' structural and self-association particularities.

Since acacia gums are widely used in many food products, our aim was to elucidate the origin of the *Acacia mearnsii* gum (GN) properties in comparison with a commercial Acacia gum (GA). *A. mearnsii* (GN) macromolecules present a higher intrinsic viscosity indicating a larger hydrodynamic volume despite its lower average molar mass and higher degree of branching, suggesting a less compact conformation. The higher protein content in GN may explain the achieved conformation since it reflects in a higher associative behavior,

forming more hydrophobic microdomains in the gum structure. The uronic acid groups in GN are stronger acids (lower pK_{a1}) than the ones in GA and the pK_{a1} variation as a function of concentration can be related to the gums' self-associative process (Fig.2). The SAXS measurements revealed that the GA scattering profile is consistent with an ellipsoid morphology, as has been described in the literature recently. Nevertheless, GN presents a less defined profile due to its higher structural dispersity and propensity to self-association.

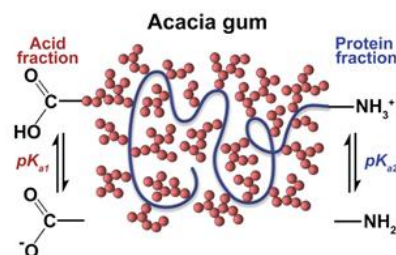
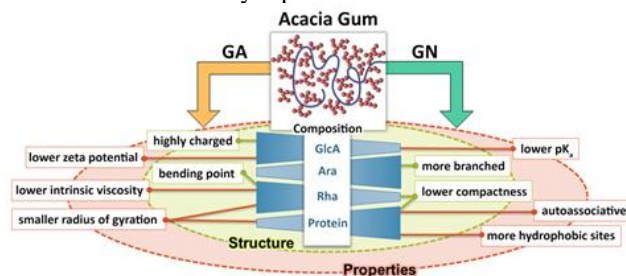


Figure 2. Representation of the dissociation processes occurring in acid and protein fractions of acacia gums corresponding to pK_{a1} and pK_{a2} , respectively.

In summary, several relationships between the chemical structure of each gum and its characteristic properties could be drawn as schematically represented in Scheme 1.



Scheme 1. Summary of the main findings of GA and GN properties based on gums composition and primary structural characterization.

It is noteworthy that the self-association behavior could be verified on the gums properties at the molecular, mesoscopic and macromolecular length scales.

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