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Sustainable Bio-Based Polymers in Action – Diving Deeper into Mechanistic Properties for Cosmetic Formulations

Ashley David¹; Sebastian Hendrickx-Rodriguez²; Kuan Liu²; Annette Mehling³; Markus Dierker³; Thomas Albers³; Reinhold Dauskardt¹

¹Dept. of Materials Science and Engineering, Stanford University, Stanford, CA, USA

²Dept. of Mechanical Engineering, Stanford University, Stanford, CA, USA

³BASF Personal Care and Nutrition GmbH, Dusseldorf, Germany

1. Introduction

Polymers play versatile roles in cosmetic formulations as stabilizers, thickeners, and film-formers [1], [2]. Synthetic options like polyacrylates are favored for tunability and manufacturing. However, environmental interests have driven a shift toward sustainable polysaccharides for their abundance, bio-based chemistry and enhanced biodegradability [3]. To propel this transition, we describe studies of the physical and chemical properties of polysaccharides to promote opportunities and efficacy in cosmetic formulations.

Our work explores how plant-based polysaccharides (Fig 1.) impact film formation in cosmetic oil-in-water (O/W) emulsions containing varying emollients, and how these changes influence the biomechanical properties of the human stratum corneum (SC). O/W emulsions consist of dispersed oil droplets surrounded by a continuous water phase and are commonly used to soften and moisturize the skin, thereby reducing mechanical stresses within the tissue [4],[5]. However, these emulsions can be thermodynamically unstable and are susceptible to phase separation due to several destabilization mechanisms, including creaming, sedimentation, flocculation, and coalescence [6].

Synthetic polymers, such as sodium polyacrylate, and natural polymers, including alginate, xanthan gum, chitosan, and cellulose derivatives, are frequently employed to modify the rheological properties of personal care products. By increasing overall viscosity and enhancing elastic behavior, these polymers play a crucial role in improving the stability of emulsion systems. Beyond stabilization, polymers also form films on the skin surface as water and emollients evaporate or are absorbed. These films contribute to mechanical tension across the skin, inducing sensations of lifting and firming [6].



Figure 1. Structures and classifications of four biopolymers tested for key cosmetic formulation benefits. Polymers included anionic (Xanthan Gum, Konjac Gum), nonionic (Tara Gum), and cationic (Chitosan) types.

It has been shown that polymer-induced films can not only form a tightening/firming film on the skin surface but can also enhance the delivery of emollients into deeper layers of the SC. However, the precise mechanism by which polymers promote enhanced emollient penetration remains unclear. There is a need to better understand how polysaccharides, compared to synthetic polymers, affect both film formation and emollient absorption as these are critical aspects for development of effective moisturizers and for promoting delivery of active molecules in topical formulations [7]. By characterizing key mechanical properties such as viscosity, film behavior, and stress modulation, this work highlights the dual role of polysaccharides in stabilizing formulations and enhancing emollient penetration into the SC and provides a foundation for the rational design of biobased personal care products that balance desirable sensory attributes with skin care functionalities.

2. Materials and Methods

Ex-vivo Substrate Curvature Technique

Full-thickness human skin from Caucasian females aged 40-80 years old were obtained through the National Disease Research Interchange (NDRI). Tissue processing was performed on abdominal samples done as described in Levi et al. [4]. Briefly, the epidermis was separated from the dermis via sequential warm water baths and mechanical lifting. The SC was isolated using a 0.1% trypsin digest in 0.05 M Tris buffer at 35°C for 180 minutes, rinsed then dried, and stored at in a low humidity chamber ~15% relative humidity (RH) and ~18-23°C under ambient conditions. Pieces of hydrated SC were adhered onto a cantilever beam made from borosilicate glass. As the SC dries in a chamber with controllable humidity (<5% RH), the cantilever bends. The resulting SC mechanical stress, σ_{SC} , as a function of the dehydration time can be computed from a variation of the well-known Stoney's equation.

Samples were dried for ~20 hours without application of any formulation as a control. Specimens were then rehydrated at 100% RH for 2 hours to return stresses to zero. Either polymers in aqueous solution or O/W emulsions were applied (approximately 2 mg/cm²) and the specimen was once again left to dry for ~20 hours in the substrate curvature instrument.

Polysaccharide Chemistry

In this study, Xanthan Gum (XG; an anionic polymer derived from the bacteria *Xanthomonas campestris*), Sodium Alginate (SA; an anionic polymer derived from algae), Tara Gum (TG; a nonionic polymer derived from the shrub *Tara spinosa*), and Konjac Gum (KG; a nonionic polymer derived from the vegetable *Amorphophallus konjac*) were tested. A blend (BL) of half XG, half SA was also tested. All these polymers are linear and have similar molecular weights. In addition, a linseed extract (LE) composed of a complex mixture of branched and linear nonionic chains, as well as Sodium Polyacrylate (SPA) as a synthetic alternative were tested. 1% polymer in water was directly applied onto the skin following the substrate curvature procedure described above.

O/W Emulsions Composition

The following emollients were used in O/W emulsions (INCI names): Coco-Caprylate/Caprate, Oleyl Erucate, Dibutyl Adipate, Dibutyl Adipate + Glycerin, Propylheptyl Caprylate, and Caprylic/Capric Triglyceride. The emulsions consisted of 83% water, 15% emollient, 1% Phenoxyethanol and Ethylhexylglycerin as a preservative, 0.05% Sodium Stearoyl Glutamate as an emulsifier, and 1% polymer. The same formulations without a polymer were also tested. Before testing the unstable emulsions (no polymers), the formulations were sonicated for 2 minutes.

X-Ray Diffraction Measurements

X-ray diffraction measurements of polymer films were performed to assess their crystallinity. X-rays were produced from a Cu source with an energy of 8.04 keV (wavelength $\lambda \approx 0.15$ nm), and a scattering vector range, or q-range, from 3 nm⁻¹ to 40 nm⁻¹ was examined using a reflection geometry. Peaks in the spectra correspond to repeated distances in the polysaccharide crystalline structure; humps correspond to more amorphous regimes. The ratio between the integrated crystalline peak area and the total area gives a measure of polymer crystallinity [9].

Synchrotron X-Ray Diffraction Measurements

Small-angle X-ray scattering (SAXS) and wide-angle X-ray scattering (WAXS) experiments were conducted at the Stanford Synchrotron Radiation Lightsource (SSRL). The incident X-ray energy was set to 15 keV, calibrated using the Pb L₃ absorption edge. The beam was focused at the SAXS detector and the calculated photon flux at the sample position was approximately 3.46×10^9 photons/s.

For WAXS, SC samples were mounted on silicon wafers in a humidity-controlled chamber, and time-resolved scans were acquired every 2 minutes. The data was processed using Igor Pro with the Nika package for image reduction and azimuthal integration. Peak parameters including position (q), intensity, and FWHM were analyzed to monitor structural changes in the

stratum corneum over time. Two sets of experiments were conducted. *Set 1*: hydration and emulsion on pre-hydrated skin: SC samples were pre-hydrated at ~100% RH for 2 hours, then scanned for 8 hours during drying. After rehydration, 2 mg of the emulsion was applied, followed by another 8 hours of scanning. *Set 2*: dry skin with emulsion: 2 mg/cm² of deionized (DI) water was applied to dry SC samples which were then scanned for 5 hours observing diffusion into the SC. The samples were removed from the beamline, then the emulsion was applied (2 mg/cm²) and samples were scanned for another 5 hours to track similar emulsion diffusion effects.

Fourier Transform Infrared Spectroscopy (FTIR-ATR)

FTIR spectra were collected with an attenuated total reflectance (ATR) accessory. Samples included 6 mg emulsion droplets alone and droplets applied to human stratum corneum (1 cm × 1 cm). Spectra were acquired in ATR mode with a resolution of 2 cm⁻¹, a data spacing of 0.241 cm⁻¹, and 16 scans averaged per sample.

Penetration Volume

To measure penetration volumes, a square SC piece (2 x 2 cm²) was weighed using a mass balance, before being submerged in a petri dish containing the cosmetic formulation. After 1 h, excess formulation was removed by blotting the SC surface with filter paper and the new mass of the SC was recorded. Mass increase was associated with the presence of formulation components including water within the SC. By using the measured density of each emollient, the increase in mass was converted into an estimate of formulation volume that penetrated the SC. Previous work has shown larger stress decreases correspond with increased penetration volumes, as the SC is prevented from drying when more emollient is present [10].

Rheometry

Dynamic viscosities of 1% (wt/wt) polymer solutions were measured with a 25 mm parallel plate geometry and a 0.5 mm gap. About 3 mL of solution was loaded and trimmed to prevent overfilling. Samples were pre-sheared at 100 s⁻¹ for 1 minute to remove shear history effects, then equilibrated for 1 minute. A logarithmic shear rate sweep from 2.5×10⁻⁵ to 2500 s⁻¹ was performed, with 5 measurements per decade using steady-state sensing (torque stabilization before recording). Dynamic viscosity (η) was calculated as the ratio of shear stress to shear rate. Polymer solutions exhibited yield stress behavior at low shear rates (<0.001 s⁻¹), Newtonian plateaus at intermediate shear rates (~0.001–1 s⁻¹), and shear thinning at high shear rates (>1 s⁻¹).

Nanoindentation

Solid polymer films were prepared by spin-coating 1% (wt/wt) aqueous polymer solutions onto glass substrates and allowing them to dry in ambient air. Young's modulus was measured using a nanoindenter with a standard Berkovich tip. A continuous stiffness measurement (CSM) technique was employed at a strain rate of 0.2 s⁻¹, with a maximum load of 20 mN, indentation depth of 5000 nm, and dynamic frequency of 100 Hz. Poisson's ratio of 0.49 was assumed. At least 10 indentations per sample were performed, spaced >50 μ m apart to avoid

overlap. Due to surface roughness, only indentations showing a stable modulus plateau over ≥ 1000 nm were included. For each valid test, the modulus was averaged over this range. Final values were reported as the mean \pm standard deviation across valid measurements.

Differential Scanning Calorimetry (DSC)

DSC was used to investigate the polymer film glass transition temperatures after drying in ambient air. Between 5 to 10 mg of solid sample was measured, and hermetic DSC pans were used to prevent solvent evaporation events from overlapping with key polymer transitions. A 5°C per minute heating ramp from -50°C to 100°C was used, with a modulation of 1°C with a period of 60 seconds. This modulated DSC technique separates out reversing heat flow events such as the glass transition from non-reversing heat flow events like curing exotherms, enthalpy relaxation endotherms, and solvent evaporation. We analyzed the temperature range at which there is an inflection in the specific heat capacity, characteristic of a glass transition event. The temperature at the midpoint of the transition was reported.

3. Results

Biomechanical Characterization of Individual Polymers in Solution. Drying curves following application of polymers in an aqueous solution show that all polymers increased stresses. The synthetic polymer Sodium Polyacrylate increased stresses by 7%, one of the smallest increases out of all polymers tested. For the polysaccharides TG increased stresses by 6%, XG increased stresses by 12%, BL increased stresses by 13%, LE increased stresses by 13%, SA increased stresses by 18%, and KG increased stresses by 26%. Two factors determine the stress increase from polymer film formation: 1) stiffness of the polymer film, and 2) amount of shrinkage during film formation. The microstructure of the polysaccharide will determine its stiffness, with crystalline polymers generally having higher stiffnesses. In fact, we found a linear relationship between crystallinity measured using XRD and stress increase. The only outlier is KG with low crystallinity, but a high stress increase. This may be because the polysaccharide film contracts a greater amount than others.

Biomechanical Characterization of Full Formulations with and without Polymer Stabilizer.

Compared to pure emollients and full formulations, full formulations containing the SPA and SA stabilizers caused the emollient to penetrate in greater amounts through the SC and correspondingly decreased stresses more (Fig. 2). The stress difference between the previously established linear relationship of the pure emollients, and the measured emollient/SPA and emollient/SA formulations was equal to the stress increase caused by the individual SPA and SA films measured separately. The formulations with SPA reduced the peak stress in the skin more than formulations with SA, but for each emollient, they still had similar penetration volumes.

FTIR results indicate that with the polymer present in the emulsion the emollient is observed immediately and increases as the water peak decreases indicating water evaporation (Fig. 3). On the other hand, without the polymer, we observe a water layer that exists at the ATR crystal surface that must first evaporate before the emollient is observed. We hypothesize that this instability affects the penetration volume of the emollient when applied to the SC. This reduced

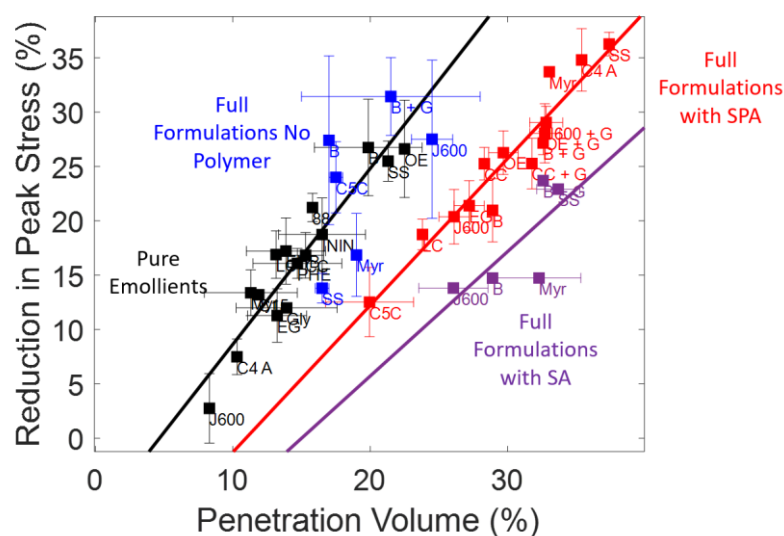


Figure 2: Stress reduction versus penetration volume for pure emollients and full formulations with and without the polymer stabilizers.

stability limits the penetration of emollients into the SC as the oil droplets coalesce and separate. Emollients with lower stability, estimated by the time it took for an emulsion to phase separate following mixing, were most affected by polymer removal.

The diffusion of emollients into the SC was investigated using time-resolved FTIR and high-resolution synchrotron SAXS to determine how structural changes in the SC influence emollient penetration and the observed reduction in mechanical stress. Synchrotron X-ray diffraction enabled precise tracking of keratin interfilament and interchain spacing, as well as the

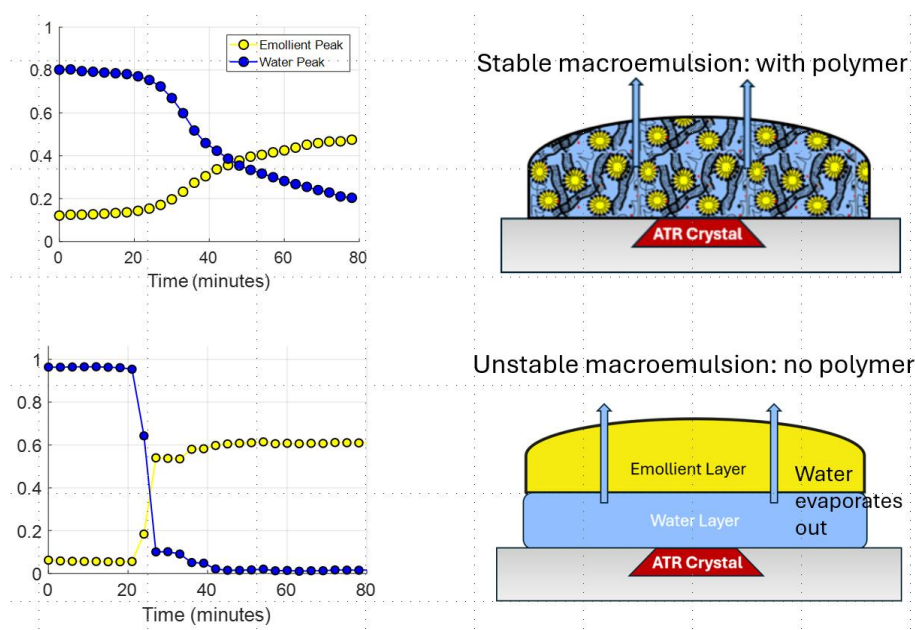


Figure 3. FTIR-ATR Spectra tracking the O-H peak, corresponding to water content in the SC and the emollient peak, $\nu(\text{OH})$, corresponding to the emollient peak Caprylic/Capric Triglyceride, over an 80-minute period.

periodicity of the long-period (LPP) and short-period (SPP) lipid phases over time as formulations diffused into the SC.

Our SAXS results indicate that as the emollients penetrate the SC, the lipid layers reorganize, moving closer together and effectively "filling in the gaps" within the barrier structure. This reorganization is hypothesized to occur more rapidly in the presence of plant-based polymers, which may facilitate faster and more efficient emollient diffusion. FTIR complements these findings by monitoring changes in the lateral lipid ordering. With the formulations initially creating lipid disorder or fluidization, followed by a gradual reordering phase, which is consistent with barrier restoration.

The evolution of specific spectral peaks, particularly those associated with lipid packing, provided insight into the dynamic interplay between disruption and reinforcement of the SC structure. Additionally, time-resolved FTIR enabled estimation of the emollient diffusion coefficient by tracking the increase in absorbance of characteristic emollient peaks. These data allowed us to compare the effects of different polymers on the rate of emollient penetration, revealing that certain polysaccharides promote more rapid diffusion into the SC.

Measurement of Polymer Properties: Film Glass Transition Temperatures and Elastic Moduli.

To understand the observed differences in the SC drying stress experiments on emulsions with and without polymer additives, the thermos-mechanical properties of each polymer were analyzed. The glass transition temperatures, T_g , of dried polymer films were measured with modulated DSC, and the elastic moduli were measured using nanoindentation at room temperature (Fig 4). Sodium polyacrylate (SPA) exhibited the highest T_g (~61 °C), making it more rigid and glassy at skin temperature (~37 °C), while the polysaccharides had lower T_g values closer to or below body temperature (such as the blend and linseed extract films). The glassy polymers relax stress more slowly and tend to retain mechanical tension over longer time scales. In contrast, rubbery polymers are more flexible and release stress more quickly. While SPA may not generate the highest peak stress during film formation, it likely maintains that stress for a longer period, leading to more persistent tension on the SC.

The elastic moduli of polymer films are between ~2 to ~8 GPa (Fig 4B), measured with nanoindentation at room temperature, below the films' glass transition temperatures. The polysaccharide films' elastic moduli were linearly correlated with their degrees of crystallinity. In the crystalline regions, polymer chains are tightly packed together in a regular arrangement and experience stronger Van der Waals forces and hydrogen bonding, restricting their mobility and making the polymer more resistant to deformation. More crystalline regions (higher degree of crystallinity) would correspond to a higher stiffness (higher elastic modulus). The SPA, despite being an amorphous polymer, also has a high elastic modulus comparable to that of the polysaccharides. This could be due to its high glass transition temperature (~61°C). At room temperature (~40°C below the T_g), the SPA chains are very immobile, forming an amorphous

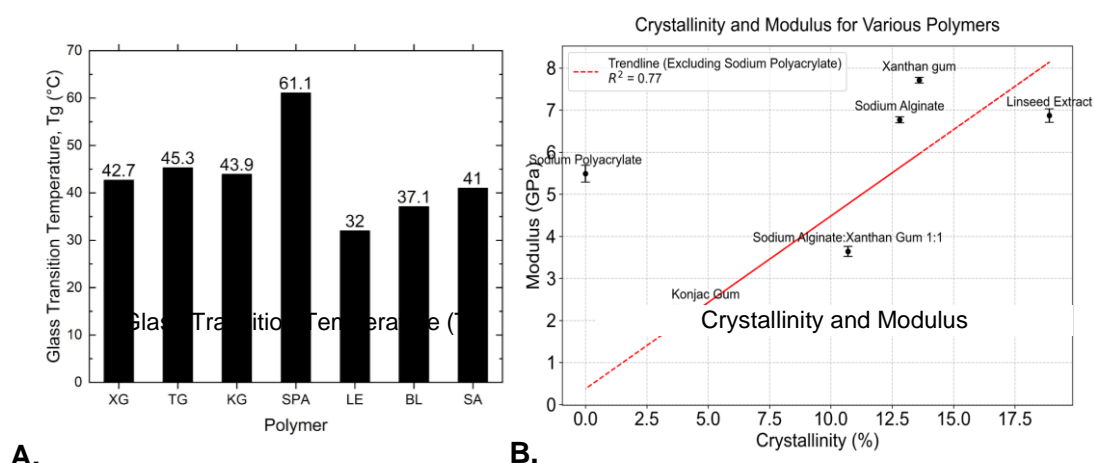


Figure 4. (A) Glass transition temperatures and **(B)** elastic moduli of polymer films measured with modulated DSC and nanoindentation, respectively. The synthetic SPA has a higher glass transition temperature when compared with that of the biopolymers.

structure that requires a high stress to deform, therefore raising its elastic modulus. The blend (BL) sample of XG and SA has a depressed glass transition temperature, potentially due to interactions between the two biopolymers such as complexation or miscibility effects.

4. Discussion

Polysaccharides included in this work can be classified according to their origin (e.g., plant, microbe, animal, algae), charge distribution (e.g., anionic, cationic, nonionic), molecular weight, or branching structure. All these characteristics can have a large impact on polymer-polymer interactions and resulting formulation properties. For example, a charged polymer is more likely to be outstretched in an aqueous solution than its nonionic counterpart due to electrostatic repulsion between like-charged residues [8]. The addition of salt modifiers can neutralize a charged polymer resulting in structural collapse. Including even more ingredients, such as emollients and surfactants, quickly complicates our understanding of the formulation's structure-property relationships.

This study reveals a direct correlation between the nano- and microstructural properties of polysaccharides and their biomechanical effects on human skin. We identify promising polysaccharide candidates for use in cosmetic emulsions. These polysaccharides serve dual functions: they form surface films that enhance stratum corneum (SC) surface stress and stabilize emulsions, thereby influencing emollient diffusion significantly. By fine-tuning the polymer structure, it becomes possible to tailor the mechanical and sensory profiles of formulations, aligning them with individual consumer needs. For instance, to achieve moisturization and reduce sensations of tightness or discomfort, the ideal polysaccharide would both stabilize the emulsion and form a flexible film on the skin surface. Polymers with a glass transition temperature (Tg) near or below body temperature ($\sim 37^\circ\text{C}$) are preferred and conform well to the skin's surface topography, improving spreadability and sensory comfort through their softness and low resistance to flow.

Finally, the stabilizing effects of the polysaccharide also has implications as to how each formulation will interact with the skin's surface. In this study, we found that the stability provided by the polymer additive enhances emollient penetration into the SC compared to the emollient alone. This observation led us to investigate the entry pathways and diffusion rates of the emollients in both stable and unstable formulations. Using unprecedented time-resolved synchrotron XRD experiments, complemented by FTIR-ATR measurements of diffusion coefficients, we obtained a comprehensive view of how each SC structure evolves over time. We examined diffusion behavior on both dry and pre-hydrated skin, revealing how stable formulations not only improve penetration but also slow SC drying and the development of mechanical SC stress, both of which are factors directly linked to consumer perception and comfort.

Conclusion.

Polysaccharides in formulations can form films and can also be engineered to achieve beneficial sensory perceptions and anti-wrinkling properties. These formulations exhibit lower dynamic viscosities than those with polyacrylates, at all shear rates, indicating enhanced spreadability. The glass transition temperatures and elastic moduli of polysaccharide films, influenced by their crystallinity, can be rationalized through film gel concentration and resulting film stress. Removing polysaccharides from formulations destabilized the macroemulsions, significantly reducing their SC penetration and efficacy. This study also investigates how SC structure responds to emollient penetration from both stable and unstable formulations, providing insights into changes in lipid packing and keratin swelling within corneocytes.

This work underscores the impact of plant-based polysaccharides on fundamental film formation principles and demonstrates how stabilized formulations enhance moisturizing efficacy through improved emollient SC penetration. A deeper understanding of the relationship between polysaccharides, skin biomechanics, and formulation chemistry is pivotal for designing sustainable, bio-based cosmetics, further advancing the transition to more eco-conscious cosmetic formulations.

Conflict of Interest Statement.

AM, MD, and TA are employees of BASF Personal Care and Nutrition GmbH, Dusseldorf, Germany.

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