JANUS PARTICLES AS SOLID SURFACTANTS

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Key Words: Emulsions, particles, interface, surfactants, Janus

Janus particles are asymmetric colloids with polar and apolar sides. Their amphiphilicity makes this new class of colloids exhibit behaviors that are similar to those of surfactant molecules. The major goal of our work is to address the following intellectual questions: are Janus particles efficient “solid surfactants” for the stabilization of multiphasic fluid mixtures such as emulsions and foams? We are inspired by how the chemical composition and shape of molecules influence the surfactant properties of molecular amphiphiles. In this talk, I will discuss our recent work on the thermodynamics of emulsion stabilization using Janus particles, the emulsion stabilization and phase inversion emulsification using shape-changing/amphiphilicity-reversing Janus particles. Because the attachment energy of Janus particles to fluid-fluid interfaces is significantly larger than that of homogenous particles, it is possible to generate Pickering emulsions that are thermodynamically stable when Janus particles are used as emulsifiers. I will also describe recently developed Janus particles that undergo significant changes in their shape and amphiphilicity in response to changes in the solution pH. We show that it is possible to stabilize different types of emulsions and also induce the phase inversion of emulsions using these stimuli-responsive Janus particles. New synthetic routes that enable the lage-scale production of Janus particles of various shape and chemistry will be presented.

FORMULATION OPPORTUNITIES DUE TO GELLING AND JAMMING IN COLLOIDAL MULTIPHASE SYSTEMS

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Key Words: colloids, foams, gels, jamming, multi-phase

Colloidal particles can mediate a kinetic arrest of the thermodynamically favored phase separation between immiscible fluids, and the resulting arrested multiphase structures can play a central role in addressing formulation challenges. The kinetic arrest often proceeds via jamming of particles adsorbed at a fluid interface, and sometimes via the formation of a gel network, with different implications for the system's mechanics and transport properties. Gelling and jamming appear to occur in parallel when an aqueous solution and a small amount of oil are combined and frothed in the presence of particles with somewhat similar wettability for both liquids. The resulting structure is that of the recently discovered "capillary foams": water-continuous four-phase systems, in which gas bubbles are coated by a particle-stabilized layer of oil and embedded in a network of oil-bridged particles. I will discuss material properties and formulation opportunities afforded by the complex multi-phase architecture of these new foams.

MULTI-NANOEMULSIONS: NANODROPLETS IN NANODROPLETS FOR FORMULATION DESIGN

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Key Words: Nanoemulsions, multiple emulsions, nanoparticles, microgels

In recent years, multiple emulsions – i.e., droplets with internal structure – have generated great research interest due to their potential applications in materials, foods, cosmetics, pharmaceuticals, and chemical separations. Microfluidic methods have already demonstrated the ability to create micron- and larger scale complex emulsions with breathtaking sophistication and control, as well as compartmentalize encapsulation of molecules within them. However, scaling the size of such droplets to the nanoscale has been extremely challenging due to limitations on the devices and energies required to produce nanoscale droplets, i.e. nanoemulsions.[1] Here, we will review new methodologies we have developed to fabricate scalable quantities of multiple nanoemulsions of various morphologies (Figure 1).[2-4] These methods combine high-energy emulsification with co-surfactants possessing highly asymmetric molecular geometry. The former aids the generation of nanoscale droplets, whereas the latter influences their morphology through ultra-low surface tension and control over frustrated spontaneous curvature, resulting in the reproducible generation of droplets with a range of controlled complex morphologies. The size, stability, internal morphology and chemical compartmentalization of these complex nanoemulsions have been quantified using a combination of scattering, optical microscopy and cryogenic-transmission electron microscopy techniques. Importantly, we show that the preferred droplet morphology is selected by the composition of the fluid alone,[2,4] providing a wide new design space for tailoring the structure and properties of multi-nanoemulsions. These complex droplet morphologies are retained upon the addition of various material pre-cursors, and the droplets are stable over the time scales required for material chemistry, thereby enabling their use as templates for complex nanoparticles.[4] As a detailed demonstration, we show how oil-in-water-in-oil double nanoemulsions can be used to template the synthesis of oil-filled nanogels for encapsulation and controlled delivery of hydrophobic active ingredients.[5]

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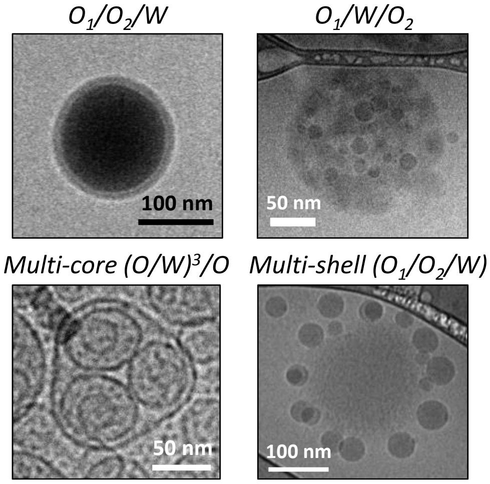

Figure 1 – Cryo-TEM micrographs of various multi-nanoemulsion morphologies.

BIJELS FORMED BY MIXING: ESCAPING FROM PHASE SEPARATING LIQUIDS

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Key Words: Bicontinuity, Pickering emulsion, wettability

The liquid-liquid phase separation of binary fluids, induced by a temperature quench, can be arrested by colloidal particles trapped at the interface. The arrested structure, a novel soft solid known as a bicontinuous interfacially-jammed emulsion gel (bijel), is a variant of a Pickering emulsion [1]. The mechanical properties are controlled by the interfacial tension between the two fluid domains (e.g. a deeper quench yields a stronger bijel) and the volume fraction of particles. Similar structures have also been created using the biopolymer phase separation (e.g. of gelatin and starch) and also using phase separation driven by the transfer of a solvent out of a pre-mix [2].

In spite of this success, the use of the phase-separation behavior of partially miscible liquids greatly constrains the choice of starting ingredients. We have recently found that, by combining interfacial nanoparticles and molecular surfactants together with immiscible liquids of high viscosity, we can avoid the need for a phase separation transition. Others have achieved the same result using closer control of the molecular surfactant together with low viscosity liquids [3]. In both cases the tortuous structure is created via the mixing protocol. We will present these approaches and show how they open the way to creating bijels using a wider spectrum of ingredients.

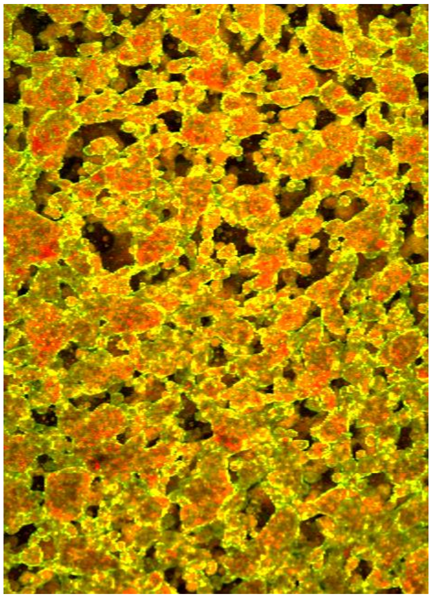

Figure 2 – Glycerol / silicone oil composite stabilized with silica and CTAB

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NEW MODES OF SOLUTE RELEASE FROM CAPSULES AND CAPSULE-LOADED GELS

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Key Words: Directed Assembly, Biopolymers, Microcapsules, Microgels

Several challenges are known to arise in the context of formulations used in cosmetics, and these also extend to formulations in pharmaceutical or agrochemical applications. In all these cases, there is generally a need to deliver an active ingredient to the external environment in a pre-determined profile or mode.

One such mode is where the active remains contained within the formulation (not delivered) for a certain period of time; then a trigger is applied such as a specific temperature or solution pH, whereupon the active is rapidly delivered to the external medium. This mode is termed a step-release mode.

A second mode is a variation of the above. Here, a certain fraction of the active in the formulation is delivered rapidly over the initial time period. Then, when the trigger is applied, the remaining fraction is also delivered to the external medium. This mode is then a multistep-release mode.

A third mode is of a different character, where the delivery of the active occurs at a steady, but slow rate, over an extended period of time. This is termed an extended-release mode. If the release rate is nearly constant, the concentration of the active in the external medium will increase linearly with time, which is termed zero-order release. Ideally, the time period for such release should be tunable from minutes to hours to even months.

This talk will describe the design of formulations in our lab that enable release of actives in line with the above modes. The key to our design is the synthesis of new polymeric capsule structures. In particular, we have made multilayer capsules that have multiple concentric layers, much like an onion. We can control the composition and thickness of each polymeric layer in such capsules. For instance, a specific layer can be made responsive to a stimulus such as temperature or pH whereas the other layer(s) can be unresponsive to the same stimulus. These capsules can also be embedded in viscoelastic polymer gels (giving an overall consistency akin to a cream or lotion) for cosmetic applications.

ELUCIDATING THE MECHANISM OF POLYMER/SURFACTANT COACERVATE DELIVERY/CONDITIONING SYSTEMS

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Key Words: coacervate, delivery, conditioning, Polyquaternium, surfactant.

For almost half a century, stimuli-responsive complexes formed by dilution of anionic surfactant/cationic polymer compositions have dominated conditioning shampoos and dilution-deposition delivery systems. There are a plethora of cationic polymers available but only a few are present in successful commercial products. Moreover, conditioning and delivery attributes are strongly dependent on compositional details and use conditions. In order to explore the reasons for the dominance of few polymers and the variability of performance with composition, we studied the effects on complex coacervate formation of polymer charge density and distribution, polymer backbone rigidity and hydrophilicity, and concentration relative to polymer overlap and entanglement concentrations and surfactant CMC by surface tensiometry, shear rheometry, and fluorescence spectroscopy. Our results show that, above the critical entanglement concentration, complex coacervates separate as shear-thinning gel networks that desorb anionic surfactant from the interface. Such networks are favored by polymers having relatively rigid hydrophilic backbones. Alternatively, systems below the critical overlap concentration separate as unconnected phase droplets which enhance interfacial adsorption. The importance of critical polymer concentrations on these delivery systems helps to provide a mechanistic scientific basis for better tailoring of compositions to confer optimal delivery of attributes.

FROM COACERVATION OF OPPOSITELY CHARGED POLYELECTROLYTES TO SUPRAMOLECULAR BOTTLEBRUSHES AND GELS

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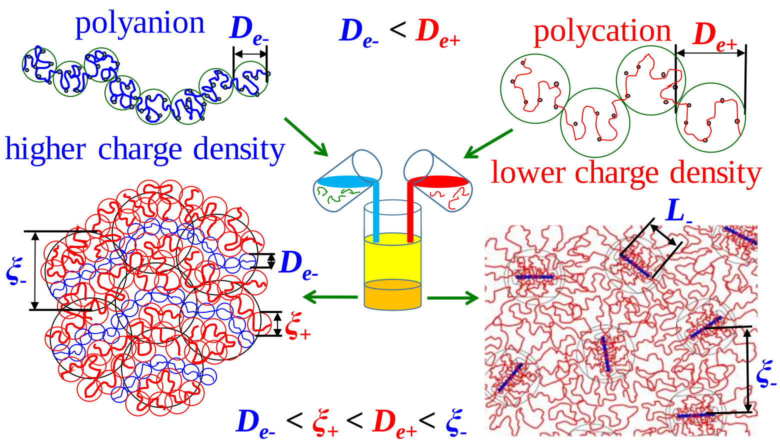
Key Words: coacervation, polyelectrolytes, gels, supramolecular, solutions

We develop a scaling model of coacervates formed by oppositely charged polyelectrolytes. The intramolecular electrostatic interactions in dilute polyanion or polycation solutions are characterized by the so-called electrostatic blobs, D_- or D_+ respectively. Polyelectrolyte sections of electrostatic blob size repel neighboring sections of the same chain with electrostatic energy on the order of thermal energy *kT*. Conformations of polyanion or polycation chains in their respective dilute solutions with no added salt can be described as stretched arrays of their corresponding electrostatic blobs of size D_- or D_+. The structure of a coacervate formed upon mixing polyanion and polycation solutions depends on the electrostatic attraction between oppositely charged polyelectrolytes balanced by the short-range repulsion. In the symmetric case with $D_- = D_+ = D_e$ the coacervate is a dense packing of these electrostatic blobs with neighboring oppositely charged blobs of size D_e attracting each other with energy on order *kT*. This attraction is stabilized by short-range non-electrostatic repulsion with energy on the same order *kT* between all chain sections of size D_e. In the asymmetric case with stronger polyanion intramolecular repulsion $D_- < D_+$ the structure of coacervate is more complex. The highest energy in the coacervate is intramolecular repulsion within polyanions that on scales smaller than inter-polyanion distance $\xi_- \approx D_-^{v/2} D_+^{1-v/2}$ keeps their conformation of stretched arrays of electrostatic blobs of size D_-. Here *v* is the scaling exponent describing interactions of uncharged chain section with solvent (v=1/2 in theta solvent and v=3/5 in good solvent). Conformation of polyanions in coacervate is similar to their conformation in semidilute polyanion solutions with the same correlation length ξ_- – stretched array of electrostatic blobs D_- on length scales smaller that correlation length ξ_- and a random walk of chain sections on larger length scales. Weaker charged polycation adsorbs on stronger charged polyanion forming a screening "coat" around it analogous to a semidilute solution of uncharged polymers. The electrostatic attraction of polycations to polyanions is the second largest energy in coacervate and is balances by the short-range repulsion between sections of polycations of size ξ_+ with energy on the order of thermal energy *kT*. This attraction slowly decreases in strength with increasing distance from polyanion within the polycation "coat" resulting in a slow (logarithmic) decrease of coat concentration. The inter-polyanion correlation length ξ_- is determine by the length scale at which the polycation "coat" compensates the polyanion charge. This compensating polycation coat of coacervates plays the role of counterions of semidilute polyanion solution with the essential difference of negligible translational entropy and important short-range inter-polycation repulsion balancing electrostatic attraction and reducing osmotic pressure of coacervates to zero. The order of interactions from strongest to weakest corresponding from the order of length scales from the smallest to the largest is $D_-<\xi_+<D_+<\xi_-$. Opposite charges form bound pairs and larger ionic clusters at higher strength of electrostatic interactions resulting in a formation of first mixed ionic/screening coat coacervate and eventually at the highest electrostatic strength – ionic network of comb/bottlebrush-like polyanion backbones with polycation loops and bridges. We describe how supramolecular assemblies of oppositely charged molecules can form similar bottlebrushes and networks.



SURFACTANT-ACTIVATED MICRO-GELS IN MICELLAR SYSTEMS

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Personal Care products such as shampoos and body washes are composed of a network of self-assembled surfactant micelles that provide both cleansing and rheology. In many cases it is necessary to modify the rheology of the network to achieve a yield stress suitable for suspension while maintaining high optical clarity. This is commonly done by adding a polyelectrolyte microgel such as a lightly crosslinked copolymer of ethyl acrylate and methacrylic acid. However, incorporation of alkali-swelling (ASE) microgels results in non-uniform performance as a function of pH restricting the useful applications space. More recently we have developed a new class of non-ionic (non-polyelectrolyte) surfactant-activated microgels (SAM) comprising crosslinked amphiphilic copolymers of alkyl acrylates and hydroxy alkyl esters that display uniform properties versus pH in micellar surfactant systems. We discuss the mechanism of action of these materials as a combination of swelling of individual polymer particles by surfactant micelles and surfactant-mediated interaction of the swollen microgels. We also discuss a novel crosslinking approach (reactive surfactant crosslinking) to maximize swelling and interaction of the microgels in micellar media to achieve higher yield stress and optical clarity compared to core-shell architectures with conventional crosslinking as well as microgel compositional variations to improve fragrance and preservative compatibility.

FUNCTIONAL MATERIALS VIA INTERFACIAL ASSEMBLY: STRIPS BIJELS, NICE, & AWESOME STRUCTURES

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Key Words: capsules, polyelectrolytes, complexation, coacervates, nanoparticles

Fluid interfaces are versatile sites for materials assembly; molecules and particles alike adsorb at interfaces to produce novel functional structures via processes suitable for scalable production. Here, three types of structures of interest to this community are described. First, hierarchical bijel structures are discussed, formed by *S*olvent *I*nduced *P*hase *S*eparation (STRIPS). Bijels, *bi*continuous *i*nterfacially *j*ammed *e*mulsion ge*l*s, feature bicontinuous networks with oil-continuous and water-continuous channels. In STRIPS, asymmetric bijel structures are formed via phase separation of a ternary mixture of oil, water and co-solvent. Phase separation, induced by solvent extraction, is arrested to form a bicontinuous structure by the interfacial attachment and jamming of nanoparticles. These structures feature dense populations of nanoparticles on their interfaces that provide additional functionality, and are ideal for loading with hydrophilic or hydrophobic molecules for delivery. Furthermore STRIPS bijels can be crosslinked to a polymeric structure with high continuous tortuous channels suitable for diverse applications. Second, polyelectrolyte (PE) capsules formed by *n*anoscale *i*nterfacial *c*omplexation in *e*mulsions (NICE) are described. Using microfluidics, single emulsions or water-oil-water emulsions are formed. PEs in the oil and aqueous phases complex at the interface to form a membrane. Important similarities and differences from related structures formed by layer-by-layer (LbL) assembly are discussed. In particular, interfacial complexation process is a one step process that is far less laborious than its LbL counterpart. Finally, capsule formation is explored via complexation at the fluid interface formed between droplets in an external phase from an aqueous two phase system. This avoids potentially deleterious oil phases. We study complexation of pairs of PEs, one in the drop phase, the other in the external phase. By balancing the fluxes, capsules are formed. Extensions to complex charged nanoparticles (NPs) with an oppositely charged PE lead to an unexpected structure: multiple emulsions form, with internal droplets that are free of adsorbed materials encased within an external PE/NP shell. These All Water Emulsion Bodies, or AWEsomes, are discussed as means to encapsulate entities ranging from molecules to microbes.

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BIO-INSPIRED METAL-COORDINATION: USING MORE OF NATURE'S TRICKS TO ASSEMBLE HYDROGEL MATERIALS WITH MULTI-FUNCTIONAL PROPERTIES

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Key Words: Bio-Inspired Materials, Hydrogels, Stimuli-responsive, Metal-coordination.

A variety of dynamic bonds have been employed as reversible crosslinks in polymer materials in efforts to obtain desirable properties such as stimuli-response, self-healing and shape-memory. Many dynamic bonds utilized so far however, have poor compatibility with aqueous solvents, thereby limiting their use in polymer materials intended for environmental, medical and personal care applications. Inspired by marine biological materials, we have been exploring metal-coordinate dynamic crosslinks that allow unique control over metal-binding polymer network properties in aqueous conditions. These early bio-mimetic explorations revealed that certain metal-ligand coordination complexes allow aqueous polymer solutions to be finely tuned between fluids and strong viscoelastic gels, simply by the choice of the coordinating metal ion. More recently we have begun exploring stimuli-responsive properties of metal-coordinate polymer networks and have found that temperature, pH, magnetic and mechanical stimuli all can induce strong responses in metal-ligand coordinate crosslink dynamics. These demonstrations open the door to design of multi-stimuli-response controlled polymer hydrogel materials. Early lessons from this pursuit will be presented.

SKIN REGENERATION WITH A SYNTHETIC BIOMATERIAL THAT REPLACES THE EXTRACELLULAR MATRIX

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Our extracellular matrix replacement (EMR) is a photopolymerized, polysaccharide-PEG hydrogel scaffold that promotes functional skin regeneration and stimulates wound closure with reduced scarring. The advanced wound care market is dominated by collagen-based products isolated from animal and human tissues, and these products are often costly, show only modest efficacy, and cannot be extensively modified to provide customized devices. Preclinical data indicates that the EMR provides the optimal mechanical and chemical properties to stimulate an effective and efficient inflammatory response, followed by regeneration of a robust vascular network and restoration of a complete reticulated epithelium, hair follicles, and sebaceous glands. The EMR is a biodegradable synthetic biomaterial, and its properties can be rationally modified by adjusting the reaction conditions under which it is produced. Therefore, future generations of EMR products can be tailored to specific wound types and/or loaded with growth factors and small molecules.

We will review EMR discovery and development, covering its synthesis and chemical and biochemical characterization. We will present data from our preclinical animal studies in murine and porcine third degree burn and excisional wound models. Finally, we will discuss efforts to develop scalable EMR manufacturing processes and highlight some future directions to develop next generation EMR-based products.

NEW CORE-SHELL MICROGEL OFFERS CREATIVE TEXTURE AND WATER-FRESH SENSORY QUALITIES TO SKIN CARE PRODUCTS

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Key Words: core-shell, microgel, sensory, silicone, texture

Sensorial attributes such as texture are essential to designing skin care products that satisfy growing consumer trends. Momentive’s patented, silicone-grafted polyacrylate microgel is an innovative, multifunctional structuring/texturing agent that can deliver a wide range of new, creative textures with a water-fresh feel. The swelling and emulsification properties of this multifunctional hydrophilic/hydrophobic particle demonstrate the microgel’s versatility and array of achievable textures. Core-shell microgel can emulsify a large volume of oil and provide excellent dispersion power for solid particles, and an enhanced, lightweight feel to sunscreen formulations. Silicone copolymer grafting can allow the development of skin care formulations that achieve more with less—more functionality, fewer ingredients.

EMULSIONS, FOAMS AND FRAGRANCE DESIGN IN SKIN CLEANSING FORMULATIONS: REVIEW AND INNOVATIONS

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Keywords: Polymer, surfactants, natural oils, rheology, thickening, yield, suspension, bio actives delivery, barrier protection

This presentation will review oil based emulsions and micro emulsions developed for personal care applications and highlight key trends and innovations in this field. The main function of emulsions is to provide moisturization, occlusion or conditioning benefits to substrates such as skin or hair. A key challenge has been understanding and optimizing the factors effecting the stability of emulsion droplets from destabilization mechanisms such as sedimentation/creaming, flocculation, coalescence, and tolerance to temperature and freeze thaw cycles under equilibrium and kinetic conditions.

The presentation focuses on suspension stability of ester or petrolatum based emulsion droplets achieved by an acrylates copolymer, namely SurfaThix-N, in combination with vegetal amphiphilic molecules called ProLipids carefully selected to form lamellar gels that mimic the skin’s natural ordered lamellar lipid bilayer. The key functionality of enhancing the benefits of cosmetic bio actives delivered to skin and providing skin barrier protection during use will be discussed.

LIGHT SCATTERING AND COLOR ADAPTATION THAT ORIGINATE FROM A NATURAL NANOMATERIAL

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Key Words: Color, pigments, color-change, optics, light-scattering.

Color is ubiquitous in nature; however, the ability to rapidly change color in response to environmental cues is unique to few biological systems. Cephalopods, including squid, octopus, and cuttlefish, are one such system; they use sophisticated optical organs that assist in color adaptation in different environments. While several attempts have been made to explore, understand, and exploit the adaptive coloration of cephalopods for materials applications, much of the progress to date has relied on modeling with assumptions that all light not reflected or transmitted is absorbed, which ignores the contribution of light scattering in the skin. We believe that scattering plays a significant role in color perception and should be included in discussions of new colors and color-changing materials. We argue that both forward and backward scattering must be accounted for in the optical analysis of a sample; otherwise, an incorrect absorption spectrum and resulting color analysis may be deduced from the experimental data.

To test these hypotheses, we fabricated films comprising a distribution of bio-derived pigmented nanoparticles with multiple thicknesses. To achieve these different thicknesses, we casted a suspension (0.16 - 2.45 mg/ml) of nanoparticles which were first isolated and purified from squid *Doryteuthis pealeii* skin onto functionalized surfaces. We chose squid particles in our model system due to their unique refractive index (n =1.92) and ability to potentiate color change via translocation in the skin. The color quality and consistency of the films were measured using the International Commission on Illumination (CIE) tristimulus values. We observed that that both color and brightness in mimetic films could be controlled by varying particle layer thicknesses and by combining a back-reflector with a specific band pass, illustrating new materials applications for these biological nanostructures. Diffuse and specular scattering of the granules was also measured using experimental and theoretical approaches. We observed that the squid-derived pigments not only provide rich color but they can also scatter attenuated light. Combined, these characteristics make such bio-derived materials interesting candidates for future topical materials such as cosmetics and coatings designed to provide color or color-matching to a specific environment.

POLYGLYCERYL ESTER BASED SURFACTANTS – AN ATTRACTIVE GREEN ALTERNATIVE TO THE CURRENT NON-IONIC SURFACTANTS OFFERING

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The consumer demand in personal care for “natural” non-ionic surfactants is growing. The current offerings are mainly based on petrol derived non-ionics and the alkyl polyglucoside based surfactants are one of the few exceptions. In this paper we will present results on relatively new and little known surfactants entirely based on natural renewable sources – polyglyceryl esters. The lack of enough data on their functionality in the literature and their full characterisation has delayed their penetration in a crowded cosmetics market and this presentation will try address this gap. The provided data will manifest the surfactants’ ability to reduce the surface/interfacial tension to very low values. Their mildness combined with an excellent foamability profile make them the surfactant of choice for formulations aimed at sensitive skin consumers.

NATSURFACT: PROGRESS IN COMMERCIALIZING RHAMNOLIPIDS

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NatSurFact is a rhamnolipid-based biosurfactant ingredient for the cosmetics industry developed by Logos Technologies. Rhamnolipids are a member of the glycolipid class of biosurfactants. They are made up of a rhamnose sugar head group and medium chain length 3-hydroxy fatty acid tails. Their structure was first elucidated in 1949 and they have been studied for myriad applications both academically and commercially since. While their properties as an anionic surfactant in the salt form are attractive – natural, mild, high foaming, high cleansing – they are not sold yet in appreciable commercial quantities. To bring rhamnolipids to market, Logos has focused on efficient and cost effective manufacturing. We will present some interesting characteristics of NatSurFact rhamnolipids product grades and discuss our process of production. We are working with a variety of downstream partners and academics to develop personal care formulations, including cosmetics, and our efforts will be detailed. Finally, we will talk about the future of rhamnolipids and NatSurFact as the market for biosurfactants begins to mature.

NOVEL HIGH-PERFORMANCE INGREDIENTS BASED ON FUNCTIONALIZED POLYSACCHARIDES - THE ROLE OF ENZYMATIC CATALYSIS

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Key Words: Enzymatic catalysis, alkylglycosides, carbohydrates, polysaccharides.

Polysaccharides are interesting starting materials in the design of high-performance cosmetic ingredients, not only because of their generally low toxicity and “green” profile, but also because of their wide and exciting propensity to form complex self-aggregated structures. These structures have direct relevance for formulation science, since they provide us with the means to tailor and optimize rheological characteristics, solubilization efficiency, emulsification and other critical attributes of a formulation. However, in order to fully exploit this potential of polysaccharide-based materials we need not only the ability to extract, purify and refine them on an industrial scale. We also need cost-efficient tools that allow us to optimize their performance and enable new functionalities. The present talk will focus on the role of industrial enzymatic catalysis in this context. Because of their natural origin, polysaccharides obviously lend themselves to enzymatic modification, and many carbohydrate-specific enzymes are available in bulk quantities, including well-known examples from the amylase and cellulase families. In the presentation, sugar-based surfactants will be used as the prime example of how enzymes can help us create tomorrow’s polysaccharide-based ingredients. Today, sugar-based surfactants are used in manifold cosmetic and personal care products, in the form of “alkylpolyglucosides” (or “APGs” for short). However, this term is a misnomer in the sense that the hydrophilic head-groups in these surfactants are by no means polymeric. Rather, APGs consist of a mixture of species, in which the head-groups comprise merely one to three repeating hexose units. This constraint severely inhibits the full exploitation of alkylglycoside functionality, and many attempts to increase the head-group size have therefore been performed over the years. However, synthesis of alkylglycosides with longer head-groups by conventional means has proved prohibitively difficult, for reasons of physical incompatibility of the starting materials (glucose and fatty alcohols). Over the last couple of years, Enza Biotech AB has developed an enzymatic technology that allows us to circumvent the limitations of conventional APG synthesis. This technology allows for synthesis of alkylglycosides with longer head-groups, which are truly oligomeric, or even polymeric. As will be discussed in the talk, this opens up vast new possibilities for sugar-based surfactants, in areas that have so far been reserved for ethoxylated non-ionic surfactants. In the talk, the novel alkylglycosides will also be used to illustrate the more general observation that new materials based on sustainable starting materials not only allow us to mimic existing functionalities, but also to identify entirely new ones. For polysaccharides these opportunities generally have their origins in their complex self-aggregation behavior, which involves both the carbohydrate backbone and its substituents.

PROTEIN NANOCAGES AS NOVEL BIOSURFACTANT IN THE FORMULATION OF PICKERING EMULSION AND GEL

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Key Words: nanoparticles, delivery, carrier, oil-water interface, consumer care.

Protein nanocages have been shown to be versatile for multitude of applications in biomedicine [1]. Our group has recently reported that the self-assembling protein nanocages localize at oil-water interface and stabilize 200-400 nm nanoemulsions [2]. The protein nanocages are produced using microbial fermentation and purified using conventional chromatography technique. The protein nanocage-stabilized Pickering emulsion are produced by facile sonication technique. The emulsion has been shown to be pH responsive when the pH is switched between 4 and 8. The switch is reversible up to 6 times. The emulsion is stable for more than 2 years. Varying the mass fraction of the protein nanocages/oil results in a shift in rheology from emulsion to gel. The unique properties of the protein nanocages emulsions have attracted industrial interests and we are currently working with our industry collaborators to encapsulate their cosmetic ingredients. We have shown the potential of protein nanocages as a novel biosurfactant that are of interests to the cosmetic industry.

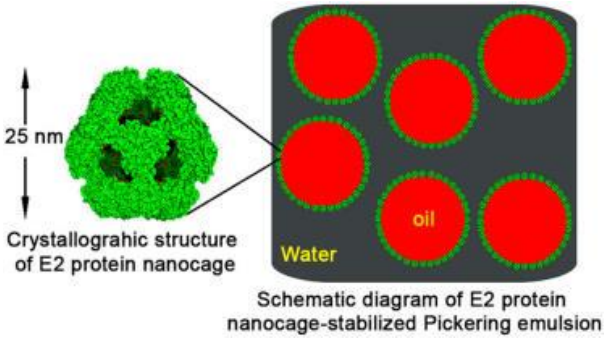

Figure 1. E2 protein nanocages organize around oil droplets in aqueous environment showing its potential as a novel biosurfactant.

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SULFATE FREE SOLUTIONS FOR PERSONAL CARE APPLICATIONS

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The personal care market is driven by consumer needs, where natural ingredients, safety awareness and free-from claims are main drivers. Free-from claims are continuing to grow and sulfate-free is a leading claim for this trend, particularly in the shampoo and body wash market. Sulfate-free cleansers are growing more than 8% CAGR. Sulfate- free surfactants present many challenges in product performance in comparison to sulfates, mainly in providing efficient thickening and desirable sensory and lather performance. Another challenge is to meet the crucial needs of the formulator by providing ingredients that are sustainable, able to be cold processed and delivered to the market in a short amount of time. In this presentation, we will share design rules to overcome these challenges and solutions that can be used to guide formulation development that meets consumer needs, matches new trends.The presentation will further demonstrate the benefits from glucamides, a novel surfactant platform that meets both consumers' core values and formulators' needs and opens new dimension for consumer products innovation.

BIO-BASED NANOPARTICLES FOR BROADBAND UV PROTECTION WITH PHOTO-STABILISED UV-FILTERS

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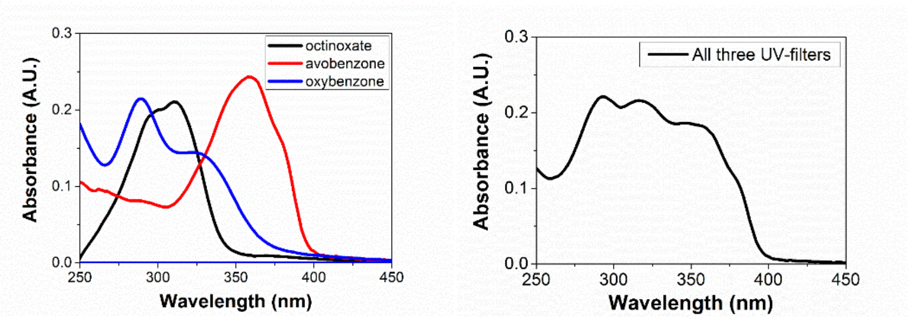
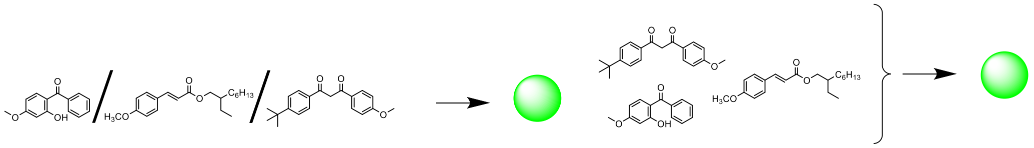
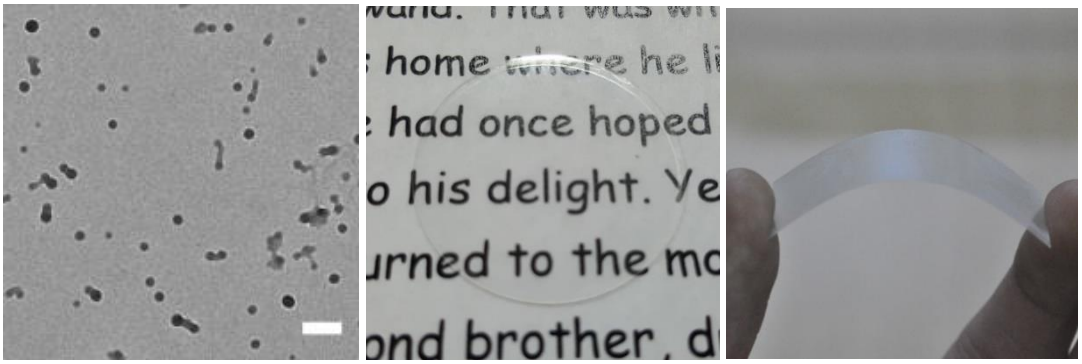
Sunscreen formulations rely on a multitude of compounds to provide effective and safe protection against UV radiation. UV-filters have been strongly linked to the generation of carcinogenic reactive oxygen species upon irradiation by sunlight. Herein, we demonstrate a significant reduction in reactive oxygen species upon irradiation by sunlight by co-localisation of an antioxidant photo-stabiliser with multiple UV-filters into bio-based nanoparticles designed from ethyl cellulose. These nanoparticles display broadband UV-protection and can form transparent and flexible films.







FRAGRANCE SOLUBILIZING PROPERTIES OF BIO-BASED ALKYL POLYGLUCOSIDES AND THEIR IMPACT ON THE AESTHETIC AND FUNCTIONAL CHARACTERISTICS OF A MODEL CLEANSING COMPOSITION

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Consumer demand for cosmetic products that are more natural and safe for the environment has recently triggered the development of bio-based ingredients for skincare. In cleansing products for hair and skin, the choices for bio-based ingredients are limited and information is not readily available to predict their ability to solubilize fragrances oils compared to surfactants typically used for such products. Fragrance hedonics could be affected by the surfactant system due to changes in vapor phase composition and concentration. The objective of this study was to investigate the fragrance solubilizing property of ECOCERT-listed alkyl polyglucosides (APGs) in a model sulfate-free cleansing formulation, which may impact the aesthetic and functional characteristics of the product. The experimental design included fragrance accords with different average cLogP and chemical class, APG chain length (C8/C10, C7, C10) vs. sodium lauroyl sacrosinate, and ratio of fragrance accord to surfactant. The effects of these variables on several properties were measured (product clarity, phase separation, foam quality, bloom, vapor phase properties) and will be discussed during the conference.

BIO-BASED SURFACTANTS FOR BENIGN COSMETIC PRODUCTS: PRINCIPLES AND APPLICATIONS

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Bio-based surfactants offer a unique opportunity alone as well as mixed with traditional surfactants to meet the increasing demand for benign cosmetic actives in this era of concern for toxicity of chemicals. Our overall aim is to understand interactions of typical bio-based surfactants with biosurfaces. Sugar based alkyl glucosides, sophorolipids and protein based surfactants show high surface activity and salt tolerance. Importantly, when mixed with conventional surfactants the systems exhibited synergistic interactions that are useful for reducing the dosage requirements and thus the resultant chemical foot print. The unique surface activity and biodegradability make this group of surfactants potential candidates for future cosmetic agents. The interfacial and colloidal properties of these reagents play critical role in determining their performance in many other industrial applications, such as detergency, enhanced oil recovery and water treatment. We are now exploring the next generation greener and microbial (genetically engineered) and plant-derived based surfactants which show robust emulsification properties and self-assembly behavior of systems involving oil. We also explore role of these surface active agents in the design of novel nano-systems as active drug carriers and disease diagnosis.

STRUCTURAL, NANOMECHANICAL, AND NANOTRIBOLOGICAL CHARACTERIZATION OF HUMAN HAIR AND CONDITIONER USING ATOMIC FORCE MICROSCOPY AND NANOINDENTATION

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Human hair is a nanocomposite biological fiber. Maintaining the health, feel, shine, color, softness, and overall aesthetics of the hair is highly desired. Hair care products such as shampoos and conditioners, along with damaging processes such as chemical dyeing and permanent wave treatments, affect the maintenance and grooming process and are important to study because they alter many hair properties. Nanoscale characterization of the cellular structure, mechanical properties, and morphological, frictional, and adhesive properties (tribological properties) of hair are essential to evaluate and develop better cosmetic products, and to advance the understanding of biological and cosmetic science. The tensile response of hair is of considerable interest. Another property of interest is the surface charge of hair, which has a significant effect on manageability, feel, and appearance. For this reason, controlling charge buildup to improve these factors is an important issue in the commercial hair care industry. The atomic/friction force microscope (AFM/FFM) and nanoindenter have recently become important tools for studying the micro/nanoscale properties of human hair. In this talk, we present a comprehensive review of the cellular structural, nanomechanical, and nanotribological properties of various hair and skin as a function of ethnicity, damage, conditioning treatment, and various environments[1-2]. Various cellular structures of human hair and fine sublamellar structures of the cuticle are identified and studied. Nanomechanical properties such as hardness, elastic modulus, creep and scratch resistance are discussed. Nanotribological properties such as roughness, friction, and adhesion are presented, as well as investigations of conditioner distribution, thickness, and binding interactions.

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RHEOLOGICAL PREDICTION OF SENSORY ATTRIBUTES FOR LOTIONS – LEARNING FROM TOOTHPASTES

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Lotions and toothpastes are rheologically similar in that most of them are thixotropic yield stress materials, semi-solid under static conditions, but flowing when shaken or agitated . Some of their relevant sensory attributes are also similar although methods of their assessment are somewhat different. This presentation demonstrates what formulators of these seemingly different products may learn from each other. To this end, complex rheological behavior of commercial lotions from European and Latin American markets were investigated and compared to panelist assessment of their sensory attributes. Similar studies were performed on some commercial as well as prototype toothpastes. Various rheological procedures, such as stress ramps, creep-recovery, stepped-shear rates, dynamic oscillatory strain sweeps and extensional viscosity measurements are discussed in this presentation. Tribological measurements and some visualization techniques on custom-built instruments are also discussed. The main goal of this work was to identify correlations between such laboratory measurements and consumer perceived properties of these products. For toothpastes, squeezability, shape retention and stringiness are the main sensory properties of interest and can be successfully predicted based on rheological measurements. For lotions, the variety of sensory attributes is much wider, although shape retention and stringiness are also relevant and can be assessed by similar methods. In addition to that, it is shown that firmness, peaking, wetness and oiliness of lotions correlate with yield stress and instantaneous viscosity. For toothpaste, rheological analysis allowed to establish basic structure-property relationships and optimize many formulations in terms of their main structure-forming elements, i.e., optimization can occur through adjusting levels of polymers, thickeners and abrasives. For lotions, similar analysis is possible although appears to be more complicated due to larger variability of formulas.

PHYSICAL CHARACTERIZATION OF LONG WEAR FOUNDATIONS

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Key Words: Long wear, Contact angle, Silicone resin, Rheology, sensory.

The current long wear face make-up products typically comprise of silicone resin or silicone film former and fillers to provide excellent attributes in sebum and sweat resistance to maintain the evenness of make-up for all day long. In order to evaluating the sebum and sweat resistance performance of the current marketed products such as Estee Lauder Double Wear (ELDW), Revlon ColorStay (RCS), and Lancôme Teint Idole Ultra (LTIU), we utilized the contact angle measurement to study the surface energy of the selected foundation films deposited on bio skin as well as the spreading and wetting of artificial sebum/sweat and water droplets on these films as shown in Fig 1. In addition, the tolerance of these foundations under sweat and sebum was evaluated by optical effect and the integrity of the films after exposing to sebum/sweat solutions directly for 8 hrs. The results from these measurements were found to be either dependent of the film former/resin structure and concentration or of the filler types which have strong influence to the performance of the foundations under sebum and sweat condition. In addition, the texture and sensory performance mapping of these long wear foundations were evaluated by rheology and tribology (**Fig.2**). The rheological behavior of these foundations will be discussed in term of the effect of solid contents and type of fillers used in the foundation formulations.

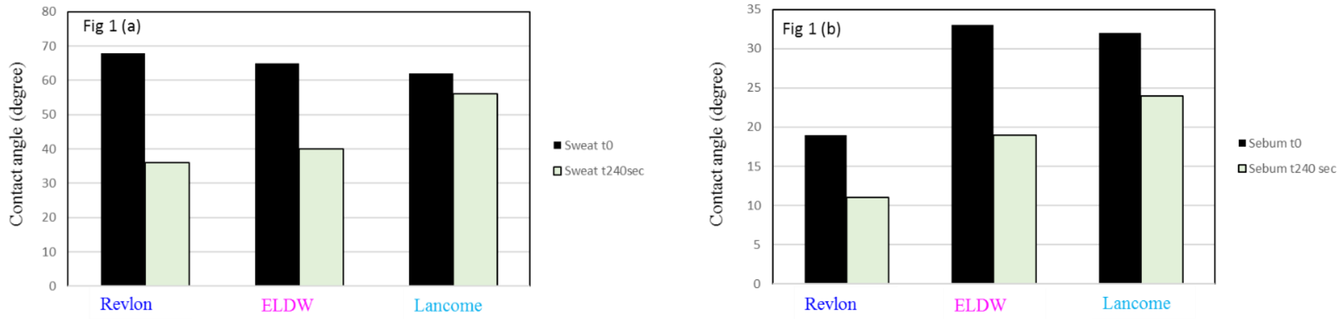

Figure 1 – Contact angle measurement of sweat (a) and sebum (b) on each foundation.

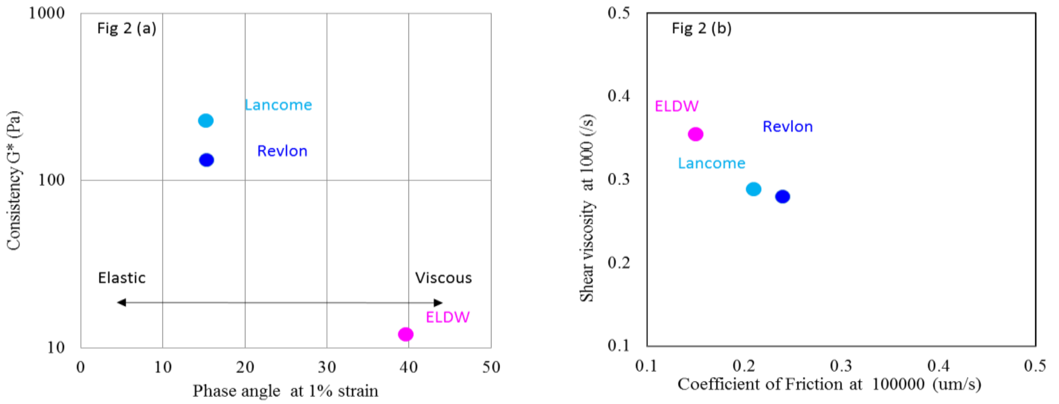

Figure 2 – Rheological mapping of three foundation products: ELDW, RCS and LTIU. Consistency against phase angle at 1% strain (a). Shear viscosity against coefficient of friction from Tribology (b)

EFFECT OF INTERACTIONS BETWEEN A HYDROPHOBICALLY MODIFIED POLYMER AND PHOSPHOLIPIDS IN THE RHEOLOGICAL AND FRICTIONAL PROPERTIES OF COMPLEX GELS

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Key Words: hydrophobically modified polymer, tribology, rheology, isothermal titration calorimetry, interactions.

O/w emulsions with polymers and phospholipids are widely used for personal care products due to their thickening and emulsifying properties. However, the underlying mechanism through which the emulsion components affect rheological and tribological characteristics is not well understood. We investigate simplified systems containing a hydrophobically modified polymer and phospholipids and find that bulk rheology and interaction between components of the studied systems play a role in frictional behavior. We characterize the tribological behavior using a soft model contact consisting of polydimethylsiloxane (PDMS) on a ball-on-disk tribometer. In addition, we investigate the bulk rheology using dynamic and steady shear experiments. Rheological behavior of systems containing the hydrophobically modified polymer is consistent with concentrated microgel systems. For systems containing phospholipids and polymer, the elastic modulus shows to a two-fold increase when compared to systems without phospholipids, leading us to hypothesize that hydrophobic interactions are occurring between these two components. To further investigate these interactions, we performed Isothermal Titration Calorimetry (ITC) experiments. The results are compared to experiments with a similar polymer that does not contain the hydrophobic moiety. No interactions are observed in the latter lending credence to our notion that interactions occur only between the hydrophobically modified polymer and the phospholipids when they are present in the same system. Tribological experiments show that in the elastohydrodynamic lubrication regime, which occurs at higher speeds where the contacts are fully separated by a lubricating film, the friction coefficients increase with increasing sample viscosity. Systems containing the polymer and phospholipids show a lower friction coefficient than Newtonian fluids at the boundary regime, where the contacting asperities dictate the frictional behavior. In order to understand this behavior, friction measurements over time at a fixed low speed and adsorption studies with quartz crystal microbalance (QCM) were performed. The tribological measurements show that the friction coefficient decreases as the concentration of hydrophobically modified polymer increases. The same behavior is observed with phospholipids. In addition, QCM results show that phospholipids are being adsorbed onto the PDMS surface and their hydrated heads are causing a decrease in the friction coefficients at low entrainment speeds due to a hydration-lubrication mechanism. These results indicate that the type of polymer used and their interactions with other components present in the system strongly affect their frictional and rheological behavior, and thus, the final performance of a personal care product containing these components.

SENSORY KALEIDOSCOPE – TAKING SKIN FEEL TO THE NEXT LEVEL TAKING SENSORY FROM NATURE

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The skin feel of a cosmetic formulation is one of the drives for consumers' purchase decision and loyalty to care products. Traditionally, skin sensory evaluations on various attributes are often conducted in comparison among prototypes to predict/screen winning formulations with high probability of consumers' acceptance. However, due to the large number of sensory attributes, it is a challenge to compare several products/formulations of interests with all attributes in one chart. A new interactive tool, developed by Evonik, using a scientific approach to describe and understand the skin sensory profiles, allows simple comparison of formulations in one chart. It also visualizes how changing certain formulation components affect the skin feel in various ways and can therefore help formulators with future product development to achieve a desired skin feel. An example will be shown using a natural cellulose fiber comparing against well-known natural particles and synthetic particles in oil-in-water and water-in-oil systems, and how that supports an optimized design of overall sensory performance of cosmetic formulations.

ADVANCED RHEOLOGICAL AND TRIBOLOGICAL METHODS FOR COSMETIC PRODUCTS

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Key Words: Rheology, Stability, Tribology, Stribeck Curve

Many different rheological procedures can used to tailor cosmetic products in a way that they meet the desired properties. Simple flow curve measurements reveal the viscosity at shear rates prevailing at processing conditions. Strain sweep give information on the strength of the rest structure and the amount of elasticity. The end of the linear visco-elastic range which is measured in a strain sweep is in a direct correlation to with the yield stress and flow point which need to be overcome in order that a gel like material starts to flow. A frequency sweep can help to gain information on the time dependence of relaxation processes. The higher frequency for example correspond to the application of a cream and lower shear moduli relate to a smoother, creamier less solid consumer experience. Difference at lower frequencies might indicate if a sample in a container flows back to a smooth surface after removing part of the sample or not and how fast such a process is.

Indications on long time stability of cosmetic samples can be gained by a so-called temperature swing test in which the temperature is frequently varied between to values and the rheology response over time is followed.

While rheology provides information on stability, flowability, temperature behavior, and sensory attributes like volume, smoothness, and firmness of a cosmetic product, tribology simulates more directly the application process of, for example, a cream on the skin. Since the forces and sliding speeds are rather small in cosmetic applications a tribology setup based on a rotational rheometer with its capability of applying small rotational speeds and normal loads as well as measuring small torques is well suited to perform friction measurements of cosmetic materials. A ball on three pins setup was used with a glass ball and pins made of PDMS to mimic the skin. Stribeck curves, i.e. friction factor measurements over an extended range of sliding speeds, have been performed on various cosmetic materials such as skin creams and sun creams. Differences between different samples are identified and discussed. An alternative approach is the use of a bottom layer of artificial skin and rounded pins which slide on top of the skin layer.

Various rheological and tribological methods are presented and discussed for different cosmetic applications. Rheology and tribology are shown to be helpful tools to assist the formulation of cosmetic products.

FORMULATION DESIGN OF COMPLEX FLUIDS BASED PRODUCTS THROUGH DIFFUSING WAVE SPECTROSCOPY (DWS)

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Complex fluids and soft matter systems are ubiquitous in consumer and cosmetic products and also in products found across many other industrial sectors encompassing foods, paints, coatings, biopharmaceutiucals etc. A critical aspect in the formulation design and optimization of these complex fluids based products is the maintenance of stability and enhancement of the sensory and functional performance. This requires establishing and optimizing the microstructure-property-performance linkages in these complex fluids. Since complex fluids are structured on multiple length scales and undergo dynamics over a wide range of timescales, the establishment of such linkages requires experimental tools that allow access to these length and time scales.

Diffusing Wave Spectroscopy has emerged as a versatile experimental technique that allows unique insights into the microstructure/dynamics/rheology of complex fluid based products, allowing the design and optimization of formulations for enhanced performance benefits. This talk reviews a number of different examples and applications of DWS that are relevant for formulation design. This will include sizing, rheology and stability monitoring in emulsions, rheology of polymers to understand short time dynamics and monitoring the effect active/drug release has on the evolution of a micellar system.

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THE MATERIAL SCIENCE OF COSMETICS

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Cosmetic are products that are designed to maintain or improve visual appearance when applied to skin. Skin is a substrate that is mechanically flexible and changes occur in physio-chemical during the course of the day. Sebum, perspiration, as well as environmental insults work counter to the desired benefits of cosmetics on physical appearance. This review will discuss material science aspects of skin focusing on biomechanical properties, surface and optical properties on skin and design criteria to optimize optical properties of make-up for flawless natural appearance. This review will also provide examples of material science considerations for designing sunscreen and anti-aging solutions. Recent advances on bioinspired materials in designing solutions for unmet cosmetic needs will also be highlighted.

INTERACTIONS OF CATIONIC FORMULATIONS ON HUMAN HAIR: EFFECTS ON CUTICLE TEXTURE AND CORTEX POROSITY

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During the daily care as cleansing, bleaching, ironing and others the hair fiber becomes damaged due to alterations in superficial charges, cuticle breakage and the protein loss from cuticle and cortex (1,2). Cationic formulations are used to treat damaged hair fiber. Cuticle and cortex properties change by the adsorption and diffusion of formulation ingredients (1,2).

The adsorption of cationic surfactants containing quaternary ammonium on hair surface has been majority attributed to electrostatic interactions between the negatively charged cuticle after shampooing and the positive charge of these compounds (1). The uniformity of the adsorbed layer has direct influence on damaged hair texture (3,4). Recent advances in computational image analyses and very low angle illumination on light microscope allow us to develop a new approach of hair texture evaluation (5). On the other hand, the diffusion of ingredients into cortex has been attributed mainly to size, concentration and affinity between the molecule and hair. Cationic surfactants play an important role in the diffusion process due to the deposition and charge-charge interactions on hair surface (1).

The aim of this study was to obtain quantitative data on hair cuticle texture and hair cortex porosity for healthy and damaged hair. The images of surface hair (texture) obtained by light microscope were categorized using by (GTSDM) grey-tone spatial dependence matrices. Bleached hair samples were treated with different conditioning formulations applied as leave on and rinse off processes. After bleaching treatment, the hair texture is significantly different from the control healthy hair. When a cationic formulation and rinsing off process were used, the bleached hair texture improvement by lowering energy beyond the measured to control healthy hair. Cationic formulation using leave on process does not allow the same results, however still improves the texture condition of bleached hair.

The quantitative data and images from cortex porosity were analyzed using X-ray micro–computed tomography (micro-CT) that is a fast-growing method in scientific research applications that allows the obtaining of non-destructive imaging of morphological structures (6,7). The influence of cationic compounds on cortex porosity after treatments was observed. We used two types of leave on formulation on bleached hair, the first formula containing cationic ingredients and the second formula without cationic. The formulation without cationic showed a significant reduction of cortex porosity, about 70% compared to the bleached hair only. Meanwhile another formulation, did not show the same performance.

The data obtained indicate that the conditioner formulation can improve hair texture and decrease cortex porosity. The charge-charge interaction allows the adsorption or diffusion of the formulation ingredients into the hair.

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EFFECT OF CITY POLLUTION AND ITS CLEANSING TREATMENTS ON HAIR

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Key Words: Hair pollution, particulate matter (PM), hair cleansing, pollution prevention, claim substantiation.

With the increasing pollution in urban areas, so has the demand for anti-pollution hair care products. Hair care manufacturers are introducing formularies to fight particulate matter pollution by prevention and treatment/cleansing. The claims are often written in the product descriptions on the webpage, and not boldly displayed on the container. This opens the door for claims substantiation testing. This paper will outline the TRI Princeton test protocol designed to study the effect of city air-borne pollutants on hair and their resultant effects on quality of hair.

A refined selection of commercially available hair pollution cleaning systems has been examined. They consisted of shampoo as basic treatment, and shampoo, conditioner and leave-in as an advanced treatment method. Tested anti-pollution systems were distinguishable by particle repulsion, by cleansing properties, or both. The treated hair was polluted in the TRI Chamber and then cleaned again up to ten times to evaluate (a) the pollution levels and (b) the cleansing efficacies. Effectiveness of different hair treatments were demonstrated by means of color, dry combing and scanning electron microscopy (SEM). The role of hair sebum and oxidative hair damage was also evaluated along with the treatments.

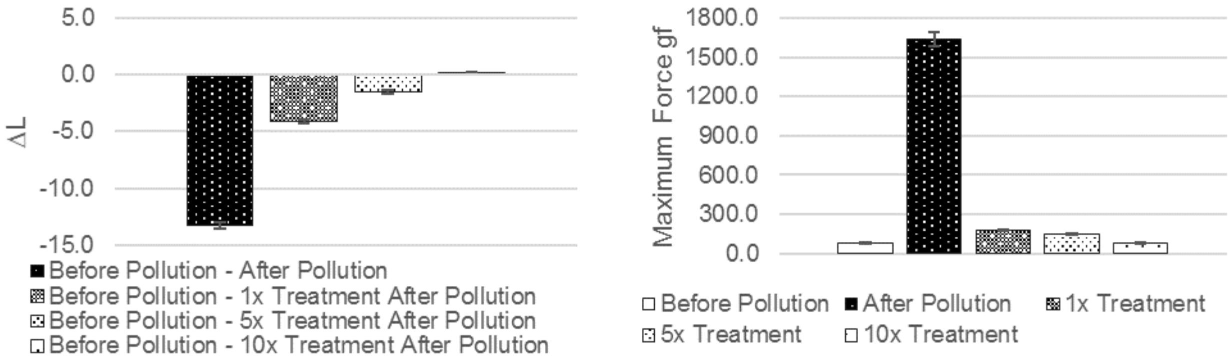

Figure 3 – Hair color lightness (ΔL) and dry combing force using one of anti-pollution treatments on PM polluted hair

ANISOTROPIC ASSEMBLY OF NANOPARTICLES WITHIN POLYMERS

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The introduction of nanoparticles into polymers constitutes a powerful strategy for enhancing their thermomechanical properties and for introducing new optical, electrical, and magnetic functionalities into the polymers. For many applications, such as plasmonics, the nanoparticles are required to be assembled into specific higher-order arrangements or structures. In this talk, I will discuss the crucial role played by molecular simulations in developing new strategies for assembling nanoparticles into anisotropic structures within polymers. I will first discuss our work on the assembly of polymer-grafted shaped nanoparticles that led to a simple strategy for creating tunable face-to-face or edge-to-edge plasmonic nanojunctions within a polymer film [1,2]. Next, I will discuss how 3-body effects arising from the deformability of polymer grafts lead to anisotropic interactions between uniformly-grafted spherical nanoparticle, which could under certain conditions stabilize a novel dimer phase [3]. Finally, I will discuss how one could exploit the surface tension between immiscible polymer layers to assemble nanoparticles into unique configurations, such as dimers with tunable tilt angle or ribbons with planar or zigzag topography.

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A NEW CLASS OF DENDRIMERIC “GECKO LEGS” POLYMER PARTICLES WITH EXTRAORDINARY STRUCTURE-BUILDING, GELATION AND ADHESIVE CAPABILITIES

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Particulate rheology modifiers are important component of many cosmetics, food, and pharmaceutical formulations. The efficiency of rheology modifiers is usually determined by the interplay between surface area and shape of suspended particles. We will present a new class of nanofibrilated dendrimeric polymer particles (DPPs) with very high surface area and morphology engineered for applications in rheology modifiers and adhesives. The DPPs are fabricated in a novel efficient and scalable process for liquid-based synthesis of nanomaterials by antisolvent precipitation in turbulently sheared medium. The process allows for a variety of polymers to be readily made into DPPs which are hierarchically structured, with a big branched corona of nanofibers spreading out in all directions. The hierarchical structure endows DPPs with high excluded volume. They build a stable three-dimensional network leading to gel-like behavior at fractions as low as 1-2 vol.% of DPPs in various liquids. In addition, the biomimetic similarity of their structure to the gecko lizards’ setae endows the DPPs with excellent adhesion and cohesion properties. Our results demonstrate that this strong adhesion and cohesion are attributed to the contact splitting and van der Waals interactions of their nanofibrous structures. This new class of polymeric particles opens new ways to make strong non-covalent binding coatings, new types of dry adhesives, nonwovens and fluid-gels. They could have a transformative role as rheology modifiers and nano-adhesives to hair and skin in many cosmetics formulations.

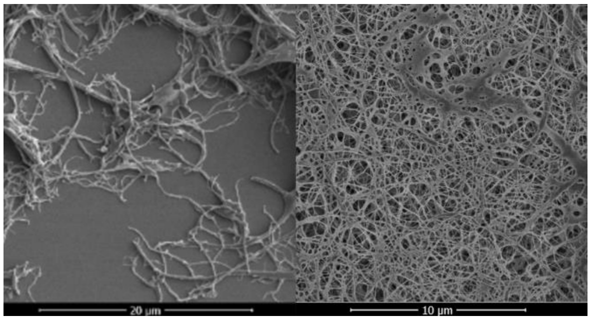

Figure 4 – SEM images of individual dendrimeric particles strongly adhering to a surface and after building up of a strongly adhesive and cohesive superhydrophobic porous layer.