

DYNAMICS OF DOUBLE-SEMIDILUTE LIQUID COACERVATES FORMED BY OPPOSITELY CHARGED POLYELECTROLYTES

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Dynamics. Coacervates. Polyelectrolytes. Dynamics.

Mixtures of oppositely charged polyelectrolytes can undergo a phase separation to form a polymer rich phase, typically called a coacervate, and a polymer depleted phase¹. The polymer rich phase can be a soft, viscous liquid, or a solid like complex. Both types have drawn much attention in the literature due to their applications in the food², pharmaceutical^{3,4}, and other industries as well as their role in many biological systems¹. Studies have focused on the formation of the coacervate phase⁵, and models have been developed to predict phase separation and static properties⁶. However, much less attention has been given to the dynamic properties of coacervates, and how these can be predicted and controlled through the experimentally controllable parameters of the system. In this work, we develop a scaling theory for the dynamic behavior of asymmetric liquid-like coacervates formed from oppositely charged polyelectrolyte solutions. We consider asymmetric coacervates, characterized by having a different number density of charges in the polyanion and polycation. Depending on the degree of polymerization, the asymmetric liquid coacervate can form either an interpenetrating double-semidilute structure, wherein both polyanion and polycation are found above their overlap concentration, or a dilute-semidilute structure, where only one of the polyelectrolytes is found above their overlap concentration⁶. We will discuss a scaling theory for the unentangled dynamics of double-semidilute and dilute-semidilute coacervates, providing scaling predictions for the relaxation modulus and steady state shear viscosity of the coacervate, and the diffusivity of the polyelectrolyte chains. The scaling theory will highlight the different dynamical regimes of the system, and how the dynamic properties depend on experimentally controllable parameters such as the degree of polymerization, the number density of charges of the polyanion and polycation, and the strength of electrostatic interactions throughout different regimes. This scaling theory should provide useful guidelines for the tuning of dynamic and rheological properties for future application in the cosmetics, food, and other industries.

1. Srivastava S, Tirrell M V. 2016. Polyelectrolyte complexation. In *Advances in Chemical Physics*, ed SA Rice, AR Dinner. 161:499–544. John Wiley & Sons. First Edit ed.
2. De Kruif CG, Weinbreck F, De Vries R. 2004. Complex coacervation of proteins and anionic polysaccharides. *Curr. Opin. Colloid Interface Sci.* 9(5):340–49
3. Black KA, Priftis D, Perry SL, Yip J, Byun WY, Tirrell M. 2014. Protein encapsulation via polypeptide complex coacervation. *ACS Macro Lett.* 3(10):1088–91
4. Davis ME. 2009. The first targeted delivery of sirna in humans via a nanoparticle : from concept to clinic. *Mol. Pharm.* 6(3):659–68
5. Sing CE. 2017. Development of the modern theory of polymeric complex coacervation. *Adv. Colloid Interface Sci.* 239:2–16
6. Rubinstein, Liao, Panyukov 2018. In preparation.

LARGE SCALE FABRICATION OF ENVIRONMENTALLY BENIGN NANOPARTICLES FROM LIGNIN FOR USE AS DELIVERY VEHICLES OF ACTIVE INGREDIENTS

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Key Words: nanoparticles, benign, delivery, green synthesis, biopolymers

Our group previously introduced a new class of environmentally-benign nanoparticles (EbNPs) with cores made of biodegradable lignin (*Nature Nanotech.*, 10, 817, 2015). Unlike traditional inorganic nanoparticles, the environmentally benign nanoparticles made of lignin can degrade after they have been used, so there is no potential for toxic impact on the environment or humans. The lignin core nanoparticles are synthesized through flash precipitation, but until recently they were only produced in mL-scale batches. We have developed a semi-continuous system featuring a recycle loop, making it possible to produce such nanoparticles in practical quantities for industrial applications. We investigated the role of each variable in our process to determine how we can control the size of our EbNPs and the final concentration of the EbNP suspensions. Because of the turbulent flow in the system, we found that the range of possible flow rates did not have any impact on our final size. The amount of anti-solvent added to the medium also had no effect on our final EbNP size distribution, revealing that we have continuous nucleation throughout each run instead of the LaMer mechanism, which would result in growth of existing particles with the addition of more lignin. This allows effective control of the resulting nanoparticle size through the starting concentration of lignin in acetone. Then, by altering our anti-solvent volume, we can control the final NP concentration of our solution. Using our system, we are now able to make liters of more concentrated nanoparticle suspensions at a time. We will discuss a few applications of our EbNPs, including their role as highly efficient antimicrobials and antifungals. For making EbNPs that serve as antimicrobials, silver ions were infused into the lignin core and the nanoparticles were coated with a polyelectrolyte layer that enabled them to stick to bacteria. This formulation can dramatically decrease the use of silver in consumer products. We are also investigating the application of the EbNPs to other biological surfaces, such as leaves and hairs. We can coat the nanoparticles with a cationic biopolymer, chitosan, to make them adhere to these surfaces, and in some cases we have observed antifungal action even with unfunctionalized lignin nanoparticles alone.

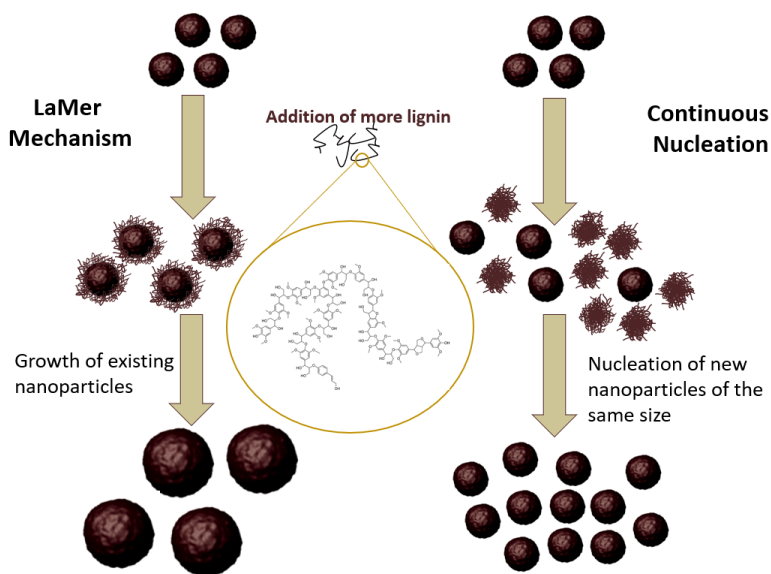


Figure 1- Possible mechanisms of organic nanoparticle formation resulting from addition of lignin to a solution of existing lignin nanoparticles.

COMPOUND DESIGN PROCESS - TO A BETTER START

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Molecule and formulation design is an information demanding activity, since all relevant knowledge is to be accessible within a single space and requires synchronized application of computational models to assist decision making on synthesis candidates. Our study aims to evaluate a software platform coping with this complexity (Marvin Live). The tool provides central management of innovative ideas and helps triage them based on predicted properties and available knowledge collected from a variety of sources. The calculated properties span physico-chemical descriptors, combined metrics, 3D overlay and modelling results, with the ability to check if they are compliant with local and international regulations. Use cases of rapid freedom to operate analysis by ultra-fast searching (MadFast Similarity Search) of exemplified structures from patents (SureChEMBL, ~17M entries) and opened access documents and databases in real time will be shown to ensure that designers can seamlessly exploit the chemical space around their ideas. The poster will walk through an example compound design cycle to obtain statistical results regarding performance as well as to demonstrate the suitability of the calculations.

UNDERSTANDING TRIBOLOGICAL BEHAVIOR OF COMPLEX GEL SYSTEMS FOR PERSONAL CARE APPLICATIONS USING *SURROGATE SKIN* AND THEIR BULK RHEOLOGY

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Key Words: tribology, rheology, phospholipids, hydrophobically modified polymers, sensory.

Creams and lotions based on oil-in-water emulsions with polymers are commonly used to treat dry skin conditions. Since the accumulation of traditional surfactants on the skin can promote irritation, an alternative is the use of hydrogenated phosphatidylcholine (HPC), a type of phospholipid that can form a lipid lamellar structure similar to the *stratum corneum*, the outermost layer of the epidermis which acts as a skin barrier. This research aims to investigate the effect of composition on the rheological and tribological characteristics in systems with HPC as surfactant and to find relationships between rheological and tribological properties to help predicting sensory perception of emulsions for skincare applications. For tribology experiments we used a ball-on-disk configuration to obtain friction curves *using different disk materials to mimic the skin surface* (PDMS and artificial skin, Bioskin™), while for bulk rheology studies we used dynamic and steady shear experiments. We examine how the addition of different amounts of HPC and polymers with different hydrophobicity affects friction and lubrication regimes from the tribological standpoint and the viscoelasticity, yield stress, and gel formation from the rheological standpoint. The bulk rheology shows that the studied systems are shear thinning and have gel-like behavior. The effect of each component was investigated by going from a simple system (polymer and water) to the more complex system. Systems containing a hydrophobically modified polyacrylic acid lightly crosslinked showed lower yield stresses and lower moduli than systems with carbomer type polymer. Analogous experiments were carried out in tribology. In the range of entrainment speed investigated, the friction coefficients in the boundary regime were lower for diluted systems containing the hydrophobically modified polymer than for systems containing the carbomer type polymer. The Stribeck curves obtained for each of the systems are compared for different polymer types and related to the bulk rheology results to obtain physical insights into these complex systems.

DERIVATIZATION OF THE LOW-PRICED COMMERCIAL RETINOL FOR THE ANTI-AGING COSMETICS

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Key Words: Anti-aging cosmetics, Low-priced Retinol, Derivatization, Esterification, Retinyl acetate

A retinol is a well-known source material for the anti-aging cosmetics due to its superior effects on the anti-wrinkle and anti-skin aging, and lots of cosmetic manufacturers have used it for the high-priced anti-aging products. However it is easily oxidized in the air and the oxidation causes the side effects like the skin irritation and a poor delivery of the active ingredients into the skin. Thus the stability improvement of the retinol must be required to minimize the side effects and enhance the absorbability and moisturizing property of the final products.

In this study, the derivatization of the retinol was performed to enhance the stability and the low-priced commercial retinol was used as the material to strengthen the competitiveness of the retinol based anti-aging products.

A commercial Retinol 50C (BASF) was separated from the additives by the column chromatography for the purification and the retinol purified would be applied to the derivatization. The retinyl acetate would be synthesized through the esterification with the acetyl chloride (Figure 1) and the derivatives were finally recovered as the crystal through the crystallizing purification. Their structural and physicochemical properties were analyzed by $^1\text{H-NMR}$ and FT-IR and it was confirmed that the purification of the low-priced retinol and the derivatization of the retinol purified were performed successfully (Figure 2).

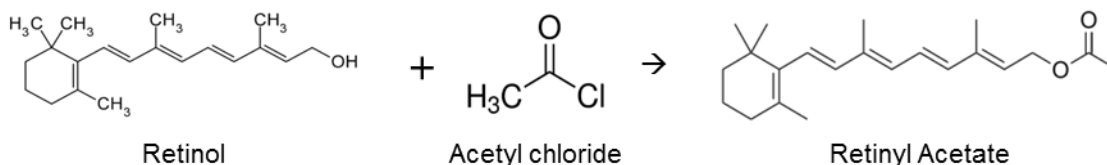


Figure 2. Derivatization of the retinol through the esterification

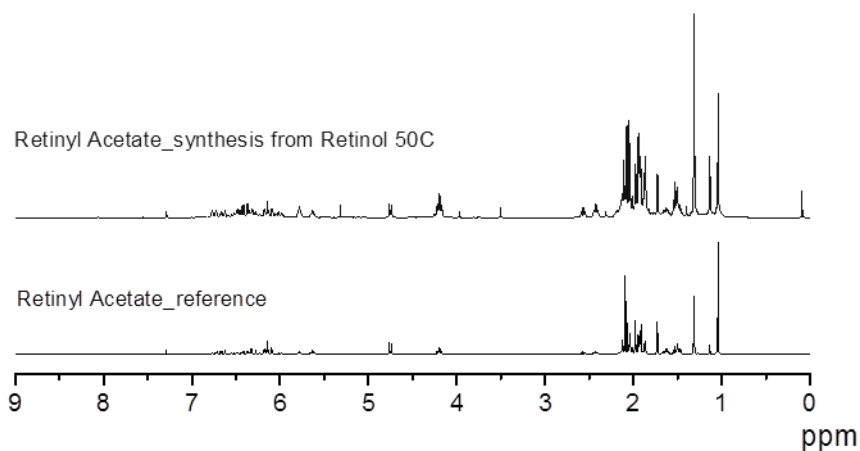


Figure 3. Retinyl acetate syntheses from the low-priced retinol

MULTI-METHOD IN-VITRO AND IN-VIVO EVALUATION OF COACERVATION AND DEPOSITION BEHAVIOR IN CLEANSING FORMULATIONS

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Key Words: cleansing, deposition, coacervation, Lochhead effect, polyquaternium

The inclusion of cationic polymers in cleansing formulations is a commonly utilized practice to provide conditioned after-feel to skin and hair and increase the efficiency of insoluble benefit agent deposition. However, predicting the efficiency of polymer-surfactant complexation (coacervation) and the resulting deposition efficacy of polymer complexes and insoluble actives purely from formulation components remains a challenge, due to the complex interactions of polymer, surfactant and solution properties. In this work, we validate and implement multiple methods for rapidly screening and quantifying dilution-induced polymer precipitation and deposition in cleansing formulations. We then utilize these methods to verify and compare deposition behavior in several well-utilized polymer-surfactant systems and commercial cleansing products.

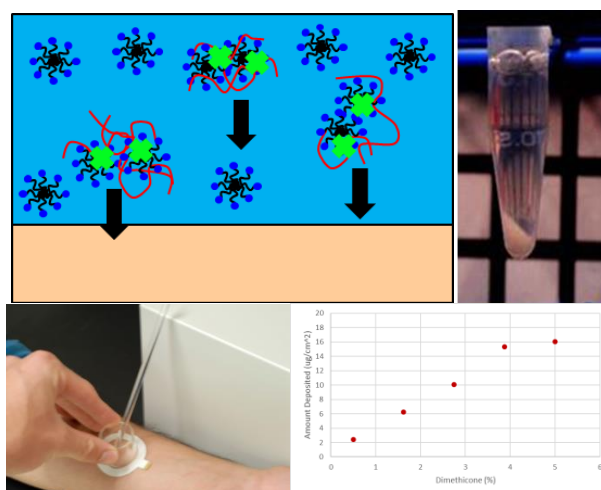


Figure 1: (Top left) Qualitative illustration of polymer-surfactant micelle complexation and deposition of insoluble actives to skin in a dilute cleanser formulation; (top right) Polymer-surfactant coacervate centrifuged down from a dilute cleanser; (bottom left) Cup-scrub method for extracting water-insoluble actives from surface of the skin after cleansing; (bottom right) Dimethicone measured on skin after cleansing as a function of dimethicone incorporated into original undiluted cleansing formulation.

CHARACTERIZATION OF OZONE EFFECT ON HUMAN HAIR

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Key Words: Hair pollution, ozone.

Ozone is a toxic, oxidizing agent formed in nature by lightning or UV radiation. In the modern world, exposure to ozone rises due to outdoor environmental pollution as well as various indoor appliances and consumer products, including those marketed for air “purifying” purposes.

The effect of ozone on human hair is not well studied consequently, we provide a brief study in this poster. Virgin, 6% and 9% bleached hair was exposed to ozone in a chamber for 1, 3 and 6 hours. Hair oxidation by the ozone revealed different behavior to oxidation as a result of liquid (bleach) or radiation (UV, IR). We observed changes of the hair both inside and outside the fiber.

We observed significant increase in hair roughness (dry combing force) as well as properties characterizing alpha-helix and matrix interaction (as observed by denaturation temperatures and post-yield tensile properties). The highest changes in properties were observed with virgin hair. The insult mechanisms of ozone action will be discussed.

QUANTIFICATION AND VISUALIZATION OF TAURINE DELIVERY AND PENETRATION INTO SKIN

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Key Words: Taurine, Penetration, Skin, Serum, Enhancer

Taurine is used in many personal care products to help deliver skin repair and anti-irritation benefits. Enhancing the deposition and penetration of taurine in skin is likely to boost the performance of these products. In this study, we demonstrated the deposition of taurine onto skin surfaces through a serum formulation, as well as enhanced penetration of taurine into deeper skin layers, aided by permeation enhancers such as glycerin and dimethyl isosorbide. We used a tape stripping method to collect samples from porcine skin and, coupled with HPLC analysis, to quantify the deposition and penetration of taurine. Serum formulations containing different levels of the permeation enhancers were tested. Glycerin and dimethyl isosorbide were found particularly effective and showed a dose-response manner to enhance the taurine penetration. We also employed two spectroscopic techniques, ATR-FTIR and confocal Raman to visualize the taurine distribution in the skin. The hyperspectral images of both IR and Raman clearly demonstrated the increased penetration of taurine into the deeper layers of the skin, beyond stratum corneum and into the epidermis, through the use of these permeation enhancers. These observations are consistent with the results from the tape stripping-HPLC analyses.

TRANSPARENT AND SOFT ELASTOMERIC COMPOSITES AND OIL/WATER BIPHASIC SYSTEMS WITH STIMULI-TRIGGERED RELEASE OF “INVISIBLE” LIQUID

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Key Words: Soft material, refractive index, stimuli-responsive material, emulsion, silicone.

The synthesis, principles, and properties of a new class of stimuli-responsive soft matter biphasic composites will be introduced. The soft composite consists of more than 30% of aqueous solution emulsion (of micron-sized droplets) optically hidden in a matrix of silicone or hydrocarbon gel. Through delicate adjustment of the refractive index (RI) of the internal aqueous phase, the composite is completely transparent to visible light and the internally dispersed aqueous droplet phase is invisible to the naked eye. Multiple phases can be included in the form of gelled multiple emulsion. The composite exhibits unique stimuli-response capabilities, such as changing its optical transmittance upon mechanical, thermal, osmotic and other stresses. Intrusion damage causes the composite to release the RI matched aqueous phase, which causes change in transparency of color. In addition, when the composite is present in an aqueous medium where salinity is different from the dispersed phase, the osmotic pressure in the droplets causes instantaneous transparency change triggered by osmotic pressure. This enables us to measure osmotic pressure of the aqueous medium quickly. The new composites and gels could find many applications including a number of cosmetics and other consumer products with attractive and unusual appearance and stimulus-triggered active ingredients delivery.

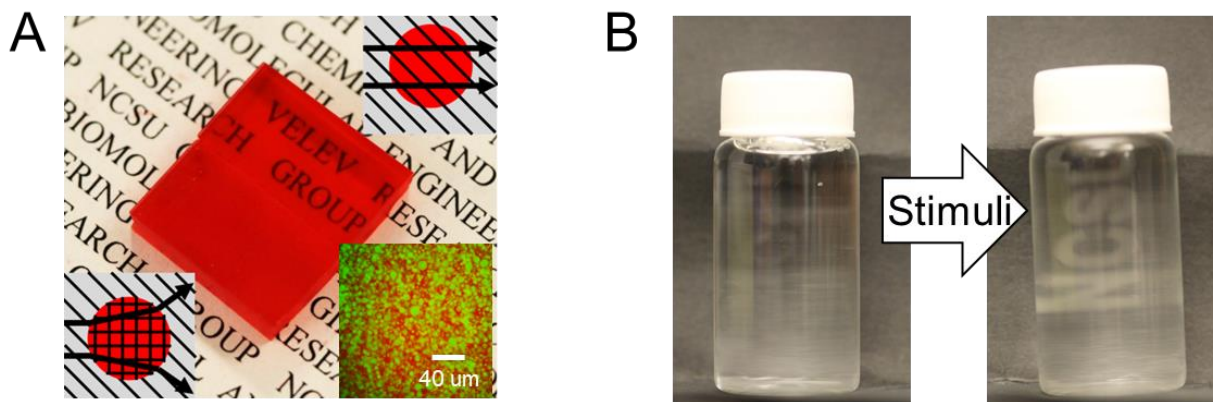


Figure 4 – (A) Example of a block of the multiphasic material after partial internal liquid release. (B) Images of the multiphasic material in a vial exhibiting optical property change (transparent → opaque) with osmotic pressure difference.

EFFECT OF RHAMNOLIPIDS BIOSURFACTANT ON TRADITIONAL SURFACTANTS: A MACRO- AND MICRORHEOLOGICAL STUDY

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Key Words: Biosurfactant, Rhamnolipids, Rheology, Microrheology,

The global surfactant market is expected to reach \$44.9 billion by 2022, of which 67% of the demand is from the personal care and detergents market [1]. Due to consumers' increasing awareness on product sustainability, the microbially produced biosurfactants are increasingly gaining the interest of the personal care industry as potential alternatives for traditional petroleum derived and chemically synthesized surfactants [2]. The future of personal care and detergent products is the elimination of non-biodegradable, environmentally toxic surfactants. However, prior to that, an understanding of how performance criteria such as rheology is affected by substitution of traditional surfactants with biosurfactants is required. In this study, the affect of rhamnolipid biosurfactant on the rheological response of traditional surfactants such as sodium laureth sulfate and cocamidopropyl betaine is explored utilizing mechanical rheometry, microrheometry, microfluidic rheometry and Raman spectroscopy. The study provides unique insights into microstructure-rheology linkages in complex biosurfactant-surfactant mixtures.

Reference

[1] News & Views - Market Reports: Global Markets for Surfactant Chemicals and Materials. Chemical Industry Digest. 2018. ISSN: 0971-5266.

[2] Fakruddin Md (2012) Biosurfactant: Production and Application. J Pet Environ Biotechnol 3:124.
doi:10.4172/2157-7463.1000124

*L.Xu and Y.Zhou contributed equally to this work.

EFFECT OF RHAMNOLIPIDS ON SURFACE TENSION AND INTERFACIAL BEHAVIORS ON TRADITIONAL SURFACTANTS

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Key Words: Rhamnolipid, biosurfactant, surface tension, interfacial tension, rheology.

The global surfactant market is expected to reach \$44.9 billion by 2022, of which 67% of the demand is from the personal care and detergents market [1]. Due to consumers' increasing awareness on product sustainability, the microbial-produced biosurfactants are increasingly gaining the interest of the personal care industry as potential alternatives for traditional petroleum-derived and chemically synthesized surfactants [2]. The future of personal care and detergent products is the elimination of non-biodegradable, environmentally toxic surfactants. However, prior to that, an understanding of performance criteria such as surface tension is affected by substitution of traditional surfactants with biosurfactants is required. This study mainly focuses on the influences of rhamnolipid biosurfactant on surface tensions and CMC behavior of sodium laureth sulfate and cocamidopropyl betaine. In addition, the effect of rhamnolipids on the interfacial tensions of surfactants mixture and dimethicone have also been evaluated.

Reference

[1] News & Views - Market Reports: Global Markets for Surfactant Chemicals and Materials. Chemical Industry Digest. 2018. ISSN: 0971-5266.

[2] Fakruddin Md (2012) Biosurfactant: Production and Application. J Pet Environ Biotechnol 3:124.
doi:10.4172/2157-7463.1000124

* Y.Zhou and L.Xu contributed equally to this work.

PROTEIN NANOCAGES FOR CUTANEOUS DELIVERY

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Key Words: Hyperpigmentation, Protein nanocages, Skin penetration, Targeted delivery, skin lightening actives

The skin protects the body from UV-induced DNA damage by the sun exposure through the pigment, melanin produced by the melanocytes. This pigment is sometimes over-expressed leading to pigmentation disorders such as melasma. Current treatment involves using tyrosinase inhibitors and lasers, leads to complications such as depigmentation, irritation, and dermatitis, with only 50% patient response. This is mainly due the inability of the delivery system to penetrate the stratum corneum layer of the skin and its non-specificity to the melanocytes. This project is aimed at engineering E2 protein nanocage for enhanced penetration into the stratum corneum layer of the epidermis and targeting/penetrating the melanocytes for the delivery of therapeutics. Genetic fusion of SPACE (Skin Penetrating And Cell Entering) peptide to the E2 nanocage helps its transduction through the stratum corneum layer, in vivo and to the interior of the melanocytes in vitro. Further modification of the E2 protein cage with targeting ligands can facilitate its uptake in melanocytes through the corresponding cell membrane receptors. Multiple modifications could also be imparted to the E2 protein cages without affecting its self-assembly, thereby aiding both penetration and targeting functions for drug delivery. Successful delivery of the engineered protein cages can aid the formulation of novel protein-based drug releasing molecules to be applied to the skin, which can be biocompatible with efficient pharmacokinetics.

NEW CUSTOMIZED SOLUTIONS FOR HAIR CONDITIONING APPLICATIONS

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Market research shows that far more than 50% consumers globally consider their hair damaged, dry, or limp and lifeless. Analysis of consumers from key countries globally (TNS and Clariant, 2016) concluded that there are clearly differentiated segments of dry and damaged hair: heavily damaged hair due to chemical treatments, naturally dry hair due to everyday elements, and thin, limp and lifeless hair, either due to stressful lifestyle, or genetics, or ageing.

To better target those consumer needs, we have developed three new hair conditioning ingredients (Genadvance® range), with very specific performance profiles. Genadvance® is the new generation of conditioning ingredients, allowing for performance premium in consumer needs segments for hair that is very damaged, dry, or lifeless.

We will show that a careful design of the chemical structure leads to different mechanism of deposition on hair and thus providing better performance. Considerably different benefits areas can be accessed, resulting in that the formulation and conditioning space of conventional ingredients (quats) can be expanded to achieve new formulation formats and well substantiated claims for specific consumer needs.