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Polymer/surfactant interactions and nanostructures: Current development for cleansing, release, and deposition of actives

P. SOMASUNDARAN and P. PUROHIT, *Center for Particulate and Surfactant Systems and Langmuir Center for Colloids and Interfaces, Columbia University, New York, NY 10027.*

Synopsis

Nature exhibits a variety of remarkable phenomena that are useful but difficult to be imitated in real life. Examples are a "touch me not" plant folding up upon being attacked or microbes depositing on ocean vessels even under hostile conditions. Understanding of mechanisms governing these phenomena can prove powerful for developing new classes of cosmetic products. Systems based on polymer/surfactant colloid chemistry are being developed for achieving transport and release of cosmetic and pharmaceutical molecules at desired rates and desired sites. Modifications of the surfactants and polymers provide cleansing properties such as scavenging of odor and sebaceous body excretions and controlled delivery and deposition of sensory/hygienic attributes. New surfactants (sugar based and bio surfactants), hybrid polymers (silicone based and hydrophobically modified) and nanogels have been recently synthesized which may have applications in fields of cosmetics/fragrances/drugs etc. Due to the associative nature of the hydrophobic groups, hybrid polymers can form intramolecular nanodomains at all concentrations of the polymer and inter-molecular aggregates at high concentrations. New hybrid polymers and nano-gel particles can be developed with ability to extract and deliver actives by varying such properties as swelling/shrinking capacity and sensitivity to temperature, shear and dilution. Control of such properties as size, shape and cross linking of nanohybrid particles offer maximum opportunity for producing families of nanovehicles in personal and homecare industry. This review article provides an insight into current developments in field of nano-surfactant science, comprising discussions on nanogel particles, hybrid polymer and liposomes.

INTRODUCTION

Nano-sized systems are currently finding increasing applications in personal care (1-4) and pharmaceutics (5,6). Potential advantages of these nano systems include homogeneous distribution in the formulation, better encapsulation and the ability to release encapsulates at targets in a controlled fashion. The delivering agents as nanogel particles/emulsions, hybrid polymers, and liposomes are discussed in this paper. Innumerable active nanostructures exist in nature in different forms, exhibiting a variety of sensory phenomena. A most intriguing example is that of the nodes of plant 'Mimosa pudica' that is responsive to the stimulus of touch (7). When the plant is touched, the liquid in the nano and microgels in the nodes apparently get squeezed out leading to the folding of the leaves and dropping of the braches. This principle can conceivably be used in designing

nanogel materials for the controlled delivery of flavors (8), fragrances (4), drugs (9), vitamins (10), steroids (10), proteins (11), or enzymes (12). Ideally these materials should be capable of prolonged activity, protect actives against adverse conditions and release them at desired site with desired stimulus. The polymers can be modified with functionalized groups that are responsive to external stimuli. Such nanoparticles, owing to their submicron size, can also be well dispersed in the cosmetic and personal care products

Hybrid polymers are another nano-sized system which can be employed for effective delivery of cosmetic ingredients. In hybrid polymers, the polymeric chains are associated with hydrophobic and hydrophilic moieties. In order to avoid unfavorable contacts between the solvent and moieties of different polarity, they form nano-domains. These domains can grow and shrink depending on the enviromental conditions and hence can be utilized to encapsulate and release actives. Also hybrid polymers such as modified silicones can be used as an oil phase for oil-in-water nanoemulsions where the nanodroplets can act as carriers of actives. Liposomes can be used for encapsulation and release of cosmetic attributes. Liposomes are nanocapsules with hydrophobic domains, but with different permeation properties. Correspondingly the cleansing agents such as conventional surfactants are produced from petroleum, or from seed oils such as palm or coconut oil. Production from petroleum contributes to the release of atmospheric CO_2 while there is a limit to the amount of palm and coconut oil that can be manufactured responsibly, while preserving the rainforest. Hence there is a need for sustainable manufacturing of surfactants and development of greener surfactants is necessary for cosmetic industry for moving forward. Developement and use of the above systems for cleansing, controlled extraction and release of fragrance, flavors and other attributes are explored in the following:

NANOGEL PARTICLES

Nanoparticles can be organic, inorganic or hybrid type. The organic nanoparticles include particles made out of organic polymers, e.g. poly(acrylic acid) and poly(acrylamide) (32). Inorganic nanoparticles are particles of inorganic elements and their compounds, e.g. gold nanoparticles. The third and a very novel class of nanoparticles are hybrid - organic/inorganic nanoparticles, e.g. silicone nanoparticles. There is very little work done on such hybrid nanoparticles. Somasundaran's group had initiated the synthesis and characterization of functionalized silicone nanoparticles using the reactions between amino silicones and acid modified silicones in a microemulsion system. It was observed that cyclic silicones can solubilize skatole, an odor molecule, an order of magnitude higher than water. Clearly these hybrid silicone nanoparticles can be very effective for odor control (13,14). Currently mostly organic nanoparticles are employed as nano-delivery systems for cosmetic applications.

EXTRACTION AND RELEASE OF ATTRIBUTES

Controlled extraction and release of attributes can be achieved by using nanoparticles systems based on selective interaction. Use of nanoparticles as carriers of fragrance was tested by monitoring extraction of linalyl acetate from methanol solution by poly(acrylic acid) (PAA) and hydrophobically modified poly(acrylic acid) nanoparticles. It was found

that modification of nanoparticles with hexylamine enhanced the extraction of linalyl acetate due to hydrophobic interactions (Figure 1a).

Release of fragrances in aqueous medium from these modified and unmodified PAA nanoparticles were tested at various pH values. In the case of modified as well as unmodified nanoparticles, release of the attribute was more pronounced in the neutral and alkaline pH range than in the acidic range due to better swelling of nanoparticles (Figure 1b).

Similarly, the performance of poly(acrylamide) nanoparticles in extraction and release of vanillin flavor was also studied (4).

Similar to the cosmetic attributes, nanoparticles can also be very effective for controlled delivery of other hydrocarbon actives including drugs. The potential of the polyacrylamide (PAM) nanogels to scavenge amitriptyline, an antidepressant, from aqueous dispersion was found to be marked (Figure 2). Nanogel particles modified with hexyl and carboxylic acid groups showed enhanced binding to the drug due to ionic exchange combined with hydrophobic interactions. Similar studies can be undertaken for applications in cosmetic technology by using actives such a fragrance molecules.

HYBRID POLYMERS

Hybrid polymers with both hydrophilic and hydrophobic characteristics when dissolved in a solvent can form coiled structures in such a way that the functional groups that are compatible with the solvent protrude outwards and those that are incompatible are

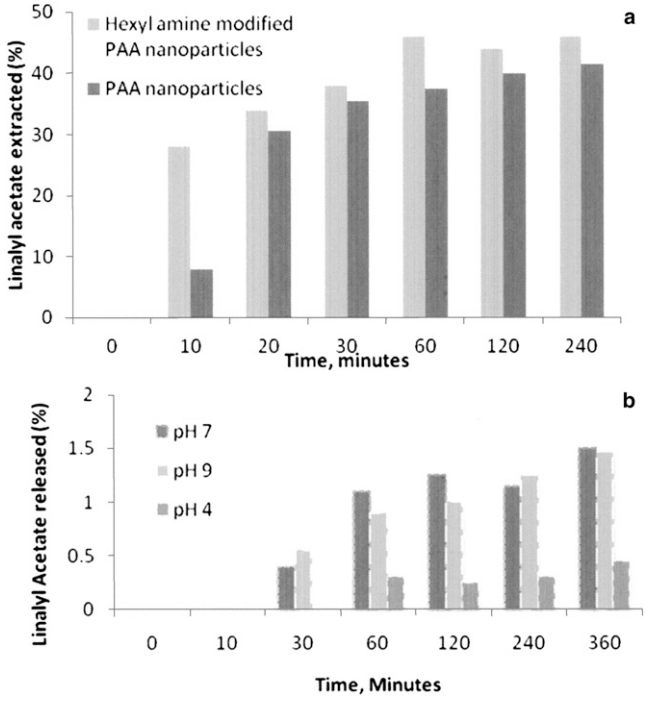

Figure 1. (a) Extraction of linalyl acetate by poly(acrylic acid) and hexylamine modified poly(acrylic acid) nanoparticles. (b) Release of linalyl acetate by poly(acrylic acid) nanoparticles and hexylamine modified poly(acrylic acid) nanoparticles as the function of pH of the dispersion medium.

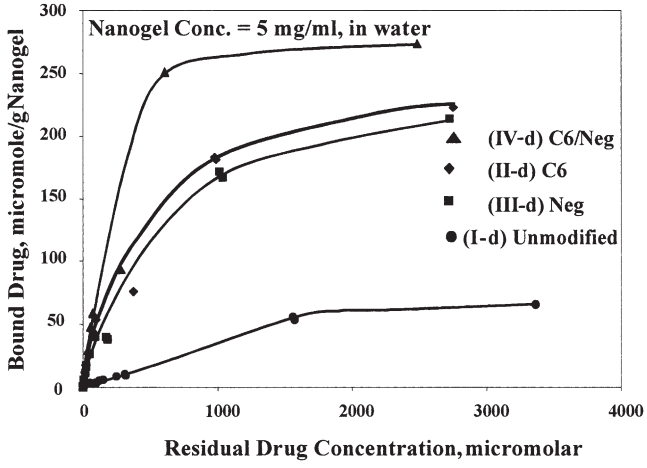

Figure 2. Drug binding ability of PAM and modified PAM as a function of residual drug concentration.

packed to form nanodomains, which are either hydrophilic or hydrophobic depending on the nature of the solvent. Ability of the hydrophobically modified hydrophilic polymers to from oleophilic nanodomains can be utilized for the encapsulation and release of organic sensory attributes (16).

The potential use of hybrid polymers for formulation of cosmetic products is illustrated in Figure 3. It shows that in polar solvents the hybrid polymers can form hydrophobic domains, where hydrophobic attributes can be incorporated and released as desired.

Hybrid silicones are also useful in cosmetic industry not only due to their selective hydrophobic/oleophobic character but also due to their structure they can be used as agents to

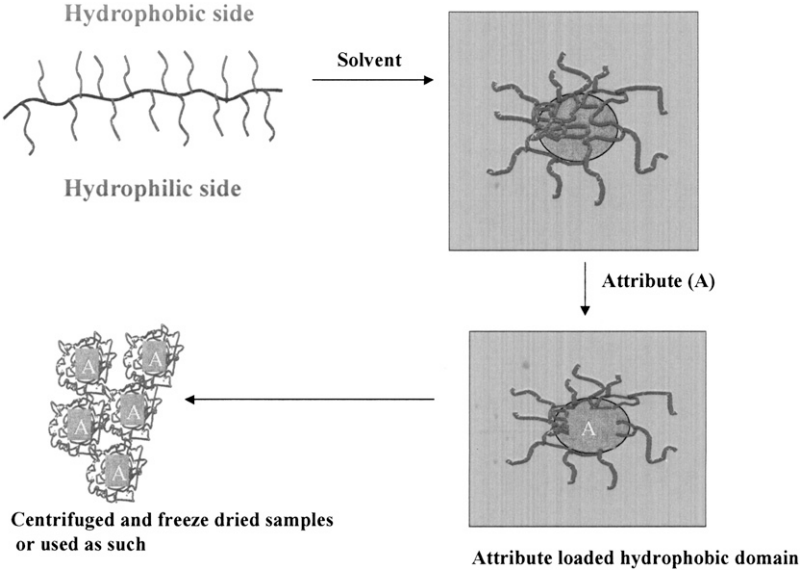

Figure 3. Use of a hybrid polymer for encapsulation of cosmetic attributes.

impart shine, gloss, smoothness and silkiness to substrates such as a skin, fibers (33) and hair nails. One requirement for handling/delivering these polymers is necessity of transporting them in form of micro/nano emulsion droplets (42) to the given substrates. Silicone emulsions for personal care appears either in the form of antiperspirant formulations or creams and lotions for skin care and sun protection[34]. These are mostly water-in-silicone-oil emulsions that possess the special properties of silicones: excellent spreading and film-forming properties, gloss, dry nonsticky feel (35). Polish formulations in the form of water-in-silicone emulsions are obtained in a way similar to those described for antiperspirants. Silicones in these applications create easily spreading films and also facilitate the transport of other polishing oils and waxes.

LIPOSOMES

Liposomes are similar to nanogels but with different permeation properties, and are made up of phospholipids building blocks. Each phospholipid molecule has three major parts, one hydrophilic head and two hydrophobic tails. Liposomes, are self-assembled spherical colloidal vehicles of phospholipids bilayers with an aqueous cavity, which engulfs the water-soluble actives. They are proven to be very good carriers for cosmetics and drug attributes (18).

Use of liposome in cosmetics can improve the permeation and availability of skin active components (19). The liposome particles have means for binding to microorganisms responsible for skin disorders, scalp irritation, and underarm and foot odor and hence can be used to selectively treat these disorders (20). Though they are highly biocompatible, they suffer from the disadvantages of being leaky and of limited loading capacity (18).

When a surfactant such as dodecyl sulfonate is added to a liposome made up of phosphatidyl choline and phosphatidic acid, initially the size of the liposome increases and subsequently it is solubilized (21). Electron spin resonance studies have shown the polarity and viscosity of liposomes change to that of micelles of dodecyl sulfonate at sufficiently high concentrations of the surfactant. While the actual processes by which such disintegration takes place are not known, the process is very important from the release point of view. Recent experiments suggest that phosphatidic acid exits first, leading to the weakening of the liposome structure and hence its dissolution. Furthermore, while the addition of cholesterol stabilizes liposomes, proteins destabilize them (22).

GREENER SURFACTANTS FOR CLEANSING

As discussed earlier, surfactant production from petroleum resources contributes to the release of atmospheric CO_2 while there is a limit to the amount of palm and coconut oil that can be manufactured responsibly for natural derived surface active agents. There is a need for sustainable manufacturing of surfactants and development of greener surfactants will be important in cosmetic and personal care applications.

Generally, the surface active reagents that are produced from renewable resources or bioprocesses are considered to be green surfactants. For instance, sugar based polyglucosides and amino acid based lipopeptides, which have been studied toward many applications in industries. These green surfactants have many advantages, such as biodegradability, low

toxicity and environmental compatibility. For further understanding on green surfactants, their interfacial properties have to be investigated in the comparison with conventional petroleum based surfactants. More importantly, the synergistic effect when mixed with other green surfactants or conventional ones is the key property towards higher efficiency at lower dosage. For e.g., acyl glutamate surfactants have shown unique interfacial properties such as high surface activity when mixed with conventional surfactants such as dodecyl maltoside (36).

Acyl amino acid surfactants, such as myristoyl glutamate, are popular with consumers because these surfactants interact favorably with skin and hair (37), are hypoallergenic (38), do not cause eye irritation (39), and are readily biodegradable (40). In collaboration with modular genetics a new green surfactant was synthesized by using an engineered *Bacillus* strain. The engineered synthetase produces an acyl amino acid composed of a beta-hydroxy fatty acid linked to glutamate, referred to as FA-Glu (fatty acid-glutamate) (41). Due to the similarity in structure of FA-Glu to myristoyl glutamate, the water solubility and CMC of these surfactants were measured (Figure 4). It was found that FA-Glu is more water soluble than myristoyl glutamate. In addition, FA-Glu has higher surface activity, as reflected by its lower CMC (41) (1.3 mM for FA-Glu versus 14.1 mM for myristoyl glutamate). A lower relative CMC indicates that less FA-Glu should be required in a formulation to achieve a particular desired reduction in surface tension. In addition, a lower CMC is correlated with an increased effectiveness in removing soils in cleaning formulation (39).

CONCLUDING REMARKS

Nanomaterials, such as nanogel particles, hybrid polymer nanodomains, nanoemulsions and liposomes have shown good applications in cosmetic science. The present article discusses the mechanisms of development and understanding of these the nano-sized systems. Hybrid polymers and their nanoemulsions can be used a delivery systems as well as for cosmetic effect (shine, glossiness, softness) on a given substrate.

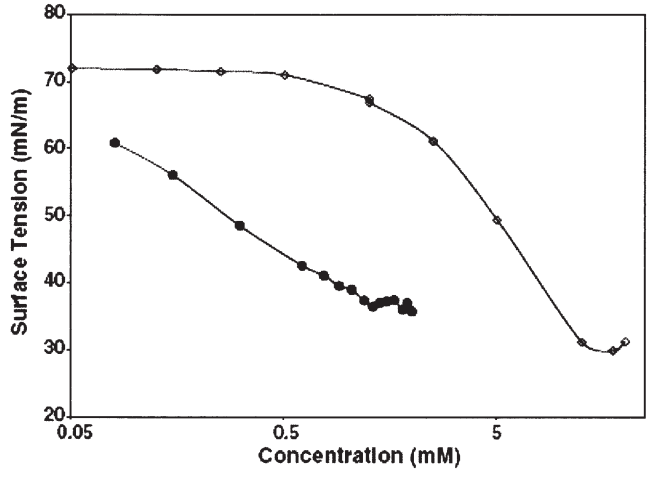

Figure 4. Comparison of critical micelle concentration for Fa-GLU (filled circle) and myristoyl glutamate (empty diamond), adapted from Gabriel O. Reznik *et.al.*

Nanoparticles are discussed as delivery systems while bilayers of liposomes can be related to skin membranes. Also modification of the nanogel particles with functional groups has a significant impact on its interaction with the active molecules. The observed interaction of attributes with the liposomes can be correlated to the penetration of attributes through skin. The emergence of "greener" surface active agents and its applications in cosmetic industry has opened new avenues for research. Though there are considerable advantages of nanomaterials for cosmetics delivery, some of the emerging nanomaterials need to be further studied for their toxicity.

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