Liquid Crystals: New Frontiers in Cosmecueticals

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Abstract

The speedy growth of the life sciences industry is likely to drive dynamic delivery vehicles into broader market places such as personal care and consumer products. No matter what ultra-modern actives or atypical botanicals a skin treatment product may contain, the delivery system is still a central key to the product's effectiveness. The assertion underlying cosmeceuticals is that active ingredients will irrefutably penetrate and maintain or repair the deeper layers of the skin. The need for skin care products with consumer-perceivable benefits and sensory attributes has made it essential to resort to nanotechnology. Self-assembling lipid-based liquid crystalline (LC) systems are a broad and an active area of research. A brief market application of LC structures pertaining to nail lacquer, hair dyes, lipstick, creams, gels and emulsions formulations has been reviewed here.

Keywords - liquid crystal, nail lacquer, hair dyes, lipstick, creams, gels, emulsions.

Introduction

Cosmeceuticals are cosmetic products that include biologically active ingredients and assert to have medicinal benefits that influence the biological function of the skin (1). A cosmetic delivery system is a composition or a process that can improve perceptual or measured performance of cosmetic product. Developments in delivery systems have drifted formulation targets from organoleptic to expertly blending organoleptics and therapeutics to boost the efficacy and provide cost effective therapy. The goal of a cosmetic scientist is to facilitate a formulation that can effectively reach cutaneous cell whilst at the same time restraining the passage into the blood circulation. Intercellular lipids of the stratum corneum have a vital role in retaining a healthy skin by a three step mechanism of hydration, cell adhesion and reduction of transepidermal water loss. These functions are owed to the self-alignment of the amphiphilic molecules of the stratum corneum lipids. High water content in these lipids leads to creation of liquid crystalline (LC) structures which is a transparent vehicle similar in consistency to soft butter. This fact clarifies why skin in high relative humidity looks elastic, glossy and pleasing while under dry conditions it has a dry and scaly appearance. Higher water content results in a LC organization of the lipids. Certain surfactants/co-surfactants in combination or alone, depending on the variables of concentration/ temperature instead of micelles orient themselves in different mesomeric forms like lamellar, hexagonal, inverted hexagonal, cubic and inverted cubic structures.

Spontaneous conversion of lamellar liquid crystals to liposomes is achieved by diluting lamellar LC phase with water. Formulation of liposomes by this method is low-cost as compared with current technologies and improves stability of liposomes. Pro lipid lamellar gels that mimic the native lipid structure in the skin have been shown to form a wide variety of stable o/w emulsion products that effectively deliver themselves into upper levels of stratum corneum. Combination of non conventional emulsifiers like sodium stearyl phthalamate with low HLB emulsifier and a polymeric emulsifier, results in the formation of multiple phase, oil in water emulsions that have lamellar gel network structure. A three dimensional lyotropic liquid crystal matrix with the aim of suspending solid particles is formulated using structured surfactant system. Thermotropic liquid crystals were introduced in the cosmetic product for the first time by the Estee Lauder Company, with the introduction of Eyxon. At present microcapsules incorporating liquid crystals made of gelatine are available for topical application. Lyotropic liquid crystals exhibit excellent hydrating properties (Liphaderm). Furthermore, with Chanel's limited edition Duo Platinum.

Holographic nail polish, that took brainwave from NASA's satellite technology and Givenchy's Rouge Interdit, incorporates a similar liquid-crystal technology used to create a 3-D effect in plasma TVs, thus giving an impetus to a new generation of makeup in quest of benchmarking products (2). The global cosmeceutical market offers huge potential among the Asian countries, such as Japan, China, and India which are set to draw major players in the future. Japan has by now made a remarkable position in the global cosmetics market and its mark in the cosmeceutical segment is effectively improving (3). It has been forecasted that the global cosmeceuticals market has reached $72.7 billion by 2022 (4).

Thermochromic liquid crystal for Nail Lacquers, Hair dyes and Lipsticks

Thermochromism based color-changing nail lacquers utilize either temperature activation, or photochromism as an outside stimulus to initiate the color change [5]. It can be achieved by the aid of liquid crystals or leuco dyes. Liquid crystals display a variety of colors attributed to selective reflection of certain wavelengths by the crystalline structure as it transforms from the low-temperature anisotropic LC phase to the high-temperature isotropic LC phase. The nematic mesophases are unique and demonstrate thermochromic properties. These are incorporated in the form of microcapsules to shield their thermochromic properties. Thermochromic LC nail paints accentuate nail design, alike mood rings. The liquid changes color according to temperature, creating a beautiful effect. For nails, the transition temperature should be in a temperature range at which nails would be exposed to (including changes in body temperature). As can be seen that temperature change occurs in discontinuous manner across the nail, different effects are visible as the color changes (spots, gradations, etc). Thus making thermochromic nail lacquers to stand apart. The commercial examples of thermochromic nail polish are LILYCUTE Thermochromic liquid crystal gel (6) and Mood Ring Nails Thermochromic Liquid Crystal Nail Polish (7). Patents have been granted wherein cholesteric liquid crystals have been added to nail paint formulations to achieve color shades by reflecting light in the visible region of the spectrum (8).

A patent on the efficacy of liquid crystals to provide a temporary hair color effect with vibrant color has been reported (9). The coloring effect is achieved without lightening the hair by combining color dyes (encapsulated liquid crystal) and a coating medium (thickening agent/rheology modifier). The liquid crystal provides either a single static color or color change, i.e., a thermochromic effect due to external stimulus (increase or decrease of temperature), or a combination of both. The formulation may be designed with a unique set of liquid crystals triggering a different color profile at varied temperatures thus multi-stranded hair color effect can be visualized. A color gradient effect is possible on long hairs due to variation in temperature at the roots and hair tips giving an ombre effect.

To give a mermaid look, Handaiyan brand has explored Liquid crystal technology by launching Mermaid® lip gloss which gives an iridescent sheer glow with added plump like look to the lips (10). Lumi® crystal a liquid crystal lip hydrator on the market has excellent feature in treating dry lip skin (11). Liquid crystal forming oils are softer than film forming agents previously used in lipsticks at the same time these oils provide proper hardness to lipsticks. These lipsticks on application to lips causes the clear oil part to seep out by forming a layer leading to long-lasting color, ample moisture, and gloss by way of a single lipstick. MAQuillAGE Perfect Gloss marketed in 2009, and MAQuillAGE Lasting Perfect Rouge marketed in 2010 are based on above technology, further advancement has lead to long-lasting three-layer products (12).

Liquid crystals as emulsions, creams and gels

The skin exhibits natural LC structure which is a bi-continuous composition of water and amphiphilic lipids (13). Emulsionswith LC structure at theo/w interface exhibit better moisturization, greaterphysical stability, and better penetrability of pharmaceutical actives in contrast to usual emulsions (14).Moreover studies have pointed out LC gels ability to generate signals to the skin stimulating its own natural self-repair and regeneration functions without damaging it (15). Other product on the market is liquid crystal cleansers. These are surfactant systems with low water content. The bicontinuous nature of these cleansers is also beneficial as an oil-based cosmetic remover for dissolving and dispersing dirt/make-up easily by rubbing it onto the skin. The phase transition of LC structures during the rubbing process enhances the dissolution of the oily impurities while the rinsing process leads to self emulsification and its removal (16). A patent on multi lamellar liquid crystal emulsion formulated with sucrose esters in combination with solid fatty alcohol has been reported with excellent moisturizing, protective action, and as a vehicle for delivery of active ingredients to the skin (17). MONTANOV®202 an o/w emulsifier of the alkylpolyglucoside type also favors formation of LC creams with finer restructuring and moisturizing effect (18). OLEAMULS® WO emulsifier forms a network of liquid crystals inside the emulsion giving a smooth and glossy touch with excellent moisturizing ability (19).

Over the market products such as Matmarine® a light BB cream that enhances shine control with a more mattified complexion, and Argireline® a peptide solution for anti-aging have a robust LC structure formed by using a combination of Glucamate®SSE-20 and Glucate®SS emulsifiers with Carbopol® Ultrez 20 polymer (20).

Moreover the combination of Glucamate® SSE-20 and Glucate®SS emulsifiers structure a LC matrix well-suited to incorporate UV filters, ethanol and electrolytes, and thus an excellent sun screening coat on the skin. The molecular complex structure posed by LC system is beneficial in stabilizing the aerosol emulsions and foam as it is insoluble in either the propellant or aqueous phase it concentrates at the interface by outlining effectively a solid interfacial film (21) . A newer type of UV-A screen system demonstrating selective reflection of UV using cholesteric liquid crystal (CLC) has also been reported (22). On the market Morpho Designer Contouring Crystal Emulsion introduced by Phytomer is formulated with liquid crystals with loaded marine algae extracts of Halopteris scoparia and Palmaria palmate with potential application to restore firmness, contouring and skin quality (23). LC have also attracted the hair care sector including shampoos, conditioners, and serum due to their unique ability to settle over the intact length of the capillary stem, thus doing away with frizz, split ends, make hair shiny, strong, nourish and enrich them.

Pantene Pro-V Blonde, BioPharma Bio Oil Liquid Crystals Shampoo are some examples of products on the market (24, 25). Table 1 highlights about the recent research in LC technology with respect to LC cream, emulsions and gels.

Conclusion

Thus, looking at the numerous benefits offered by LC technology, the potential of these formulations over usual emulsifiers makes them better skin and hair care products for replenishing the intercellular matrix structure of skin and hair. Moreover, the current research trends point out LC systems to be excellent vesicles for delivering bioactives. The camouflaging ability of thermochromic liquid crystals in response to external stimulus make them finer grooming aids that are useful in nail art, hair dyeing and for face makeup. Overall, the LC technology has revolutionized the current market space for consumers worldwide focusing primarily on personal care products with manifold benefits.

Table 1. Recent research in liquid crystalline technology with respect to LC cream emulsions and gels.

Formulation type	Active ingredients incorporated in liquid crystalline system	Purpose/use	Reference
Liquid crystalline emulsion composed of cetearyl alcohol, dicetyl phosphate, and ceteth-phosphate	Glycolic extracts from Centella asiatica leaves, Aesculus hippocastanum seeds, and Hamamelis virginiana leaves and nano-actives from safflower, coconut, and clove oils.	Treatment of cellulite	[26]
Lyotropic liquid crystalline emulsion prepared using Transcutol®, FagPlus°Cristal	Resveratrol	Antiaging	[27]
Liquid crystal gel formulated with Emulgen 2020HA®, glycerol, squalene, water	----	Antiaging	[28]
Liquid crystalline emulsion cream using Montanov 202®	Helianthus annuus oil	Sun protection and moisturizing	[29]
Sepigel 305®, Lanette N®, Uniox C ®, Tinogard TT®, and Lecithin were used to develop LC system	Retinoic acid	Photoaging, rosacea, actinic keratosis	[30]
LC emulsion- Nonionic surfactant, liquid paraffin, and water	Urea	Moisturizing	[31]
LC emulsion-PEG-100 stearate, potassium cetyl phosphate, cetearyl alcohol, behenyl alcohol and glyceryl stearate citrate	Inorganic particles	Sun protection	[32]
LC gel- n-dodecane, tridecyl salicylate, propylene glycol and PEG-7 glyceryl cocoate/ PEG-40 hydrogenated castor oil/ glyceryl monooleate	Mulberry stem extract	Antiaging	[33]
LC α-gel-Cetearyl Glucoside, Cetearyl alcohol, Isohexadecane and Caprylic capric glycerides	--------	Moisturizing	[34]
LC emulsion- Cetylethylhexanoate, Phenoxy-ethanol, Stearyl glucoside/ polyglyceryl-3methyl glucose distearate Ceteareth-22, palmeth-2, Sodium polyacrylate, demineralized water	Wild Yam root extract	Moisturizing	[35]
LC emulsion-PEG-12, dimethicone, Crodafos® CES and water	Andiroba oil	Anti-inflammatory	[36]
LC α-gel-cetyltrimethylammonium chloride, docosyltrimethyl-ammonium Chloride, cetyl alcohol, water	-----	Hair conditioner	[37]
LC β-gel- SLE1S, stearyl alcohol, cetyl alcohol and deionized water	------	Cleansing of hair	[38]
LC emulsion- Sepineo SE® 68, isopropylmiristate, caprylic-capric triglycerides, decyl oleate, mineral oil, dimethicone, glycerol, water.	Lactobionic acid	Improves signs of photoaged skin and actinic keratoses	[39]
LC cream- EmulgadeSE, Isopropyl myristate, Myritol®318, Lanette O, glycerol, water	Malus sylvestris fruit extract	Antioxidant, moisturizing and lightening of hyperpigmented skin	[40]
LC microemulsion -Cithrol GMO HP, squalane, water	Nicotinamide	Atopic dermatitis, photocarcinogenesis, anti-skin ageing.	[41]
LC emulsion- Crodamol® IPP, Crodafos ®CES, Transcutol P, white petrolatum, and water	Inorganic particles	Moisturizing, and sunscreening	[42]
LC emulsion- Ceteth-2, Steareth-2, Steareth-20, Ceteareth-20, Ceteareth-5, Ceteth-10, and water	Marigold oil (Calendula officinalis L)	Moisturizer	[43]
LC emulsion- Cetearyl alcohol, Ceteareth–20, Ethylhexyl stearate, propylene glycol and water	Ascorbic acid	Skin lightening and antiageing	[44]
LC emulsion-Oleth 3, Oleth 20, Ceteareth 5, Steareth 2 and water	Annatto oil, Melaleuca oil and coffee oil	Sunscreen agent and antiseptic, anti- inflammatory, and antimicrobial	[45]

Table 1. Recent research in liquid crystalline technology with respect to LC cream emulsions and gels (cont...).

Formulation type	Active ingredients incorporated in liquid crystalline system	Purpose/use	Reference
Cetostearyl alcohol, sorbitan monostearate ethoxilated 20OE, glycerol, propylene glycol, sorbitol, and water	Peach oil	Emollient and antioxidant	[46]
LC emulsion- cetyltrimethyl-ammonium chloride, water, mineral oil/vegetable oil	Avocado, wheat germ and grape seed oils	Hair conditioner	[47]
LC nanoemulsion- olive oil, sunflower oil, Span 80: Brij L23 and water	Elaeis guineensis leaves extract	Antioxidant and antiageing	[48]
LC system- Polyalkoxylated fatty alcohol, Alkyl sulfonate, cocamidopropyl betaine, Alkyl polyglucosides,water	Rapeseed oil methyl esters	Emollient and antioxidant	[49]
LC system- Silicone glycol copolymer-DC193, Polycarbophil, PPG-5-CETETH-20	octyl methoxycinnamate	Sunscreen	[50]
LC cream- Emulium® Delta, Schercemol®DISM Ester, and stearyl alcohol	3-O-Ethyl-Ascorbic Acid and Potassium 4-Methoxysalicylate	Sunscreen	[51]
LC cream- Isopropyl isosterate, Sorbitan oleate, Polysorbate 80, propylene glycol, xanthan gum, water, propanediol	Alkenones from marine Isochrysis algae	Sunscreen	[52]

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