UNIVERSITY OF BIRMINGHAM

Stabilisation of water-in-oil emulsions to improve the emollient properties of Lipstick

A dissertation submitted in partial fulfilment of the requirement for the degree of MRes Chemical Engineering Science at the University of Birmingham

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Abstract

The stabilisation of water-in-oil (W/O) emulsion lipstick with up to 40% aqueous phase has been investigated. The intention is to use these emulsions to deliver moisture, active hydrophilic ingredients and humectants to the lips.

Three lipophilic non-ionic emulsifiers were used to stabilise the water droplets, PGPR (HLB 1.5 ± 0.5), Span 80 (HLB 4.3) and a blend of Span 80 with Tween 80 (HLB 5). These were investigated with or without crystalline particles of microcrystalline and carnauba wax. Emulsification was carried out using high shear (high energy/ short time via a Silverson L4 RT High shear laboratory mixer). The emulsions were produced at 95 to 100 °C to ensure that no crystals were present during droplet formation. This was then followed by rapid cooling to -20 °C over a period of 20 minutes using refrigeration. Emulsion stability and droplet size distribution were determined using pNMR in conjunction with optical microscopy and cryo-SEM. A comparison of the physical and viscoelastic properties of the emulsion lipstick formulations was made with a conventional lipstick. Penetrometer, compression and rheological non-destructive oscillation testing were used for this comparison.

Emulsions prepared with PGPR were shown to be more stable and had smaller droplet sizes and droplet size distributions than those prepared with Span 80 and the blend of Span 80 with Tween 80. As the water content increased the 'lipsticks' softened and became less elastic. This trend could be removed using additional crystalline solids in the continuous phase.

Keywords: Cosmetic; Crystalline; HLB; Lipstick; Non-ionic Emulsifiers; PGPR; pNMR; Span 80; Stabilisation; Tween 80; Water-in-oil (W/O) emulsions; Waxes.

Acknowledgements

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Abbreviations

a_w	Water activity
BHT	Butylated Hydroxytoluene
CMC	Critical Micelle Concentration
cryo-SEM	Cryogenic Scanning Electron Microscopy
$D_{1.0}$	Number-length mean droplet diameter
$D_{3.2}$	Surface-weighted mean droplet diameter
$D_{3.3}$	Volume-weighted mean droplet diameter
Ds	Self-diffusion coefficient
DSC	Differential Scanning Colorimetry
Endo	Endothermic
Exo	Exothermic
F	Force (on the balance)
G’	Storage (elastic) modulus
G’’	Loss (viscous) modulus
HLB	Hydrophile-Lipophile Balance
L	Length of Kruss Standard Plate
N_A	Avagadro’s constant
O/W	Oil-in-water
O/W/O	Oil-in-water-in-oil
PGPR	Polyglycerol polyricinoleate
pNMR	Pulsed Nuclear Magnetic Resonance
Span 80	Sorbitan monooleate
TAG	Triacylglycerols
Tween 80	Polyoxyethylene sorbitan monooleate
W/O	Water-in-oil
W/O/W	Water-in-oil-in-water
wt% & w/w %	Weight percent

Symbols

α	Alpha
β	Beta
β’	Beta prime
θ	Contact angle
Γ	Surface excess concentration
A	Acid number & Area per molecule
C	Bulk concentration
R	Universal gas constant
S	Saponification number
T	Temperature
σ	Interfacial/ Surface tension

1 Introduction

The cosmetic industry is a huge global economy worth approximate £26 billion (Barton, 2008) of which lipstick together with decorative cosmetics occupies 13% of the market (see Figure 1.1). The top 10 global players as illustrated in Figure 1.2 hold 60% of a very competitive market share (Weber & de Villebonne, 2002). There is a direct link between the function and quality of the lipstick and the ingredients used during formulation.

Moisture along with oils, are two of the principal components required to minimise the onset of dry unsightly wrinkled chapped lips (Cannon, 2008). Avoidance of overexposure to UV sunlight along with any infectious pathogens are also paramount along with increasing the lips antioxidant status to neutralize any free radicals activity (Halliwell, 1994; Bagchi and Puri, 1998).

What has prompted this research is to provide a medium in the form of a cosmetic lipstick capable of providing all or most of these properties for the purpose of mainly appearance, health and beauty.

With so much emphasis being placed on aesthetic appearance and youth, together with anti-aging products, any innovative product which promotes the bodies' resistance to aging, looking healthier and younger is of great benefit to the cosmetics industry. Within the cosmetics industry the combination of product quality, backed up with scientific data followed by good marketing must be compelling to gain shelf space and consumer attention.

Although there are a large number of lip products available to the consumer including Lip balm, gloss, plumpers, stain, treatment and pencils, none provide all of the aforementioned properties. The supposition is, by adding water to typical conventional lipstick products, in the form of a water-in-oil emulsion will not only

provide additional moisture for the lips but will also provide a medium through which any additional active healing ingredients including humectants could then be added and therefore delivered to the lips by way of microencapsulation (Cannon, 2008). Microencapsulation provides an ideal sheath medium enabling the isolation of any active healing ingredients, thus providing ideal protection from evaporation; maintaining potency and guarding against deterioration (Guiqin et al., 1997).

As cosmetic emulsions have been predominantly the best delivery system for conditioners to the skin (Rawlings, Canestrari, & Dobkowski, 2004; Kumar 2005; Teo et al., 2010), the initial part of this research is to formulate water-in-oil (W/O) emulsion lipsticks, with a view to deliver not only moisture but also hydrophilic ingredients to the lips, producing stable products with up to 40% water content. Whilst this may appear to be practicable, the predicament is to achieve this with emulsifiers that are ingestible and dermatologically safe to use on the lips, in addition to producing a product that not only resembles a typical conventional lipstick in terms of its physicochemistry, organoleptic qualities, specifically texture and feel, but also has a stable shelf life.

The final challenge is to ensure the active water soluble ingredients in the emulsion products are delivered effectively to the surface of the lips by way of the emulsion droplets breaking after application. Assuming the emulsion was to break during application due to the delivery mechanical stress, this would look and feel unpleasant, however if it was to break too slowly again the product is of minimal use.

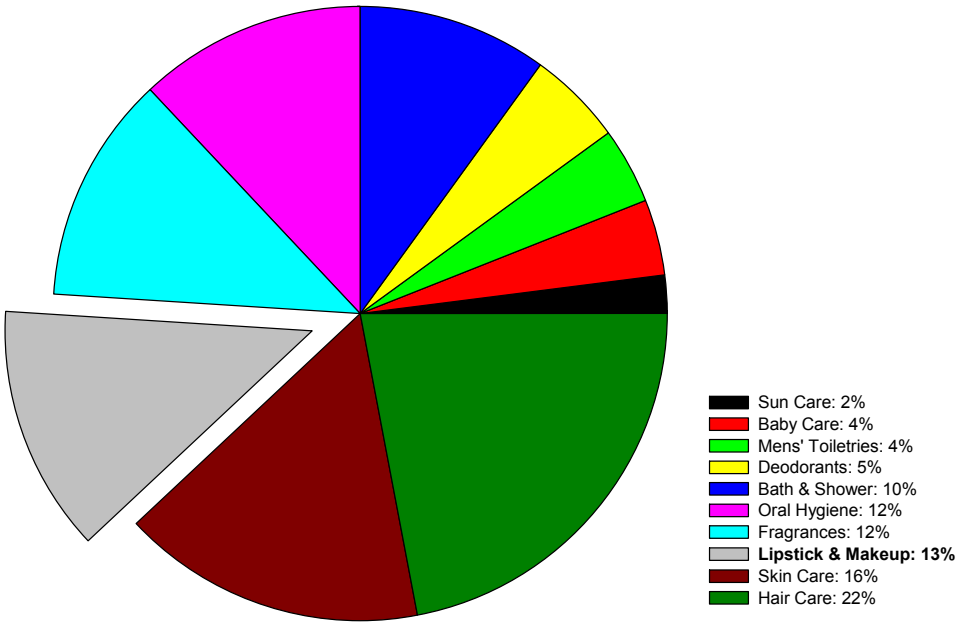


Fig. 1.1. The global cosmetics industry segmented market. (Adapted: Weber & de Villebonne, 2002).

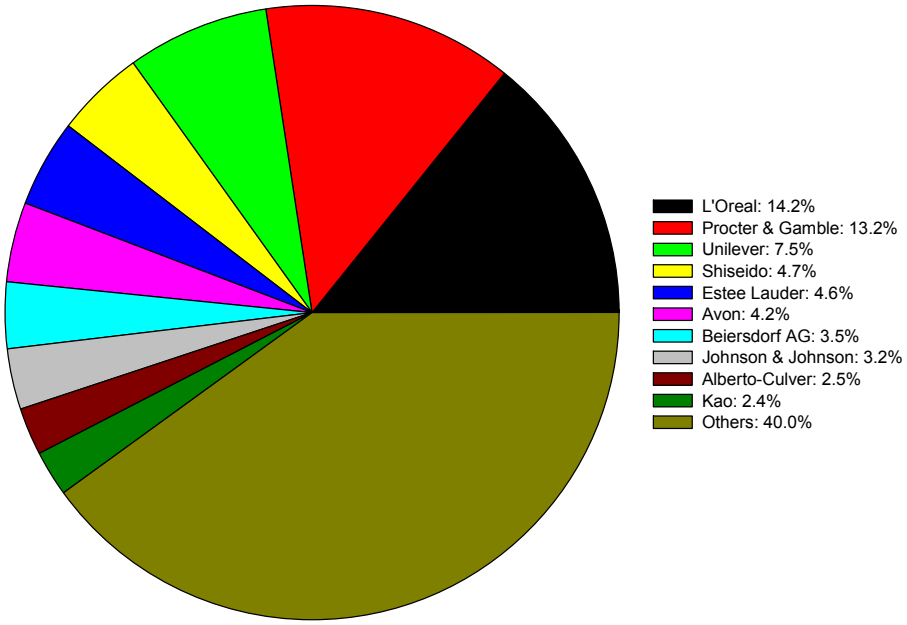


Fig. 1.2. The Top 10 Global Players in the cosmetics industry. (Adapted: Weber & de Villebonne, 2002; Groves, 2008).

1.1 Layout of the Thesis

This Thesis consists of seven chapters. This chapter, **Chapter 1**, gives a brief introduction to the cosmetic industry and introduces the research topic. **Chapter 2** gives a thorough methodical literature review of the research topic. **Chapter 3** outlines the materials used in the experiments followed by **Chapter 4** which outlines the research methodology. A breakdown of the results, data analysis and discussion are detailed in **Chapter 5**. **Chapter 6** summarises, evaluates and reemphasizes the significance of the findings followed by **Chapter 7** which suggests an outline of any future research.

2 Literature Review

2.1 Lipstick

2.1.1 Brief History

Cosmetics including lipstick, although originally developed by the Egyptians as ointments and ritual oils for the dead, eventually came to be used to soothe, adorn, accentuate and treat the skin of the living and are currently used by over 90% of the female population. This association of cosmetics and medicines has continued to the present where beauty products are frequently advertised as having healing properties (Donsky, 1985; Brumberg, 1986; Mulhern et al., 2003). Lipsticks have emerged from a jumble of primitive ingredients such as vermilion - a naturally occurring ore of mercury (red mercury (II) sulphide HgS), seaweed and mulberry, into the sophisticated products used today, containing mainly oils, fats and waxes (Cohen & Kozlowski, 1998).

2.1.2 Ingredients & Product Composition

Lipstick is a solid fatty based cosmetic product made up of waxes and oils, with dissolved or suspended coloured pigments and emollients that apply colour and texture to the lips (Ryu et al., 2005). A good lipstick must possess an ideal minimum and maximum thixotropy. Its viscosity must be high enough in order to produce a moulded stick product, however being thixotropic it must undergo a reduction in viscosity when mechanically disturbed via spreading on application at 32°C (lip temperature) to produce a smooth even layer on the lips with minimum pressure (Salvador & Chisvert, 2007). The applied film must also be impervious to the mild abrasions encountered during eating, drinking and smoking and should ideally last for at least 4 – 6hrs, a period considered reasonably permanent and not requiring

more than 2 to 3 applications daily (Harry & Wilkinson 1973; McKetta Jr., 1993). It should be of such composition as to cover only the portion of the lips up to the vermilion border and not bleed into the surrounding skin regions. Softening temperature should not be confused with melting point temperature. Whilst it should soften at 32°C, the actual melting point range should be between 55 to 75°C (McKetta Jr., 1993).

When producing a lip product with emollient properties not only should the product possess many if not all of the physicochemical organoleptic characteristics of a typical standard lipstick product, but in addition any additions to the formula must be safe to use on the lips and must not be unpleasant to taste.

Lipsticks usually contain three basic ingredients (Harry & Wilkinson 1973; Rajin, Bono & Mun, 2007):

- Oil (30-80%)
- Wax (5-25%)
- Colouring, pigment & Dyes (1-10%)

Oil (refined) is one of the main ingredients used when formulating a lipstick. The oil is required to blend with the waxes to provide a suitable film when applied to the lips. It also acts as a dispersing agent for insoluble pigments. The most common types of oils used in lipstick production are castor, mineral, lanolin, jojoba and vegetable oil. Oils in general are treated with BHT - Butylated Hydroxytoluene, an anti-oxidant used to extend the shelf life and delay rancidity of oils and fats in foods and cosmetics. Castor oil (Figure 2.1), being unusually polar compared to other natural oils is traditionally used for its ability to dissolve bromoacid dyes (Figure 2.2). This is

due to the high content of ricinoleic acid (Figure 2.3) which contains a hydroxyl functional group unique among similar natural triglycerides. In addition other properties include a high viscosity, even when warm, which delays pigment settling and a degree of oiliness which helps with gloss and emollience (Harry & Wilkinson, 1973).

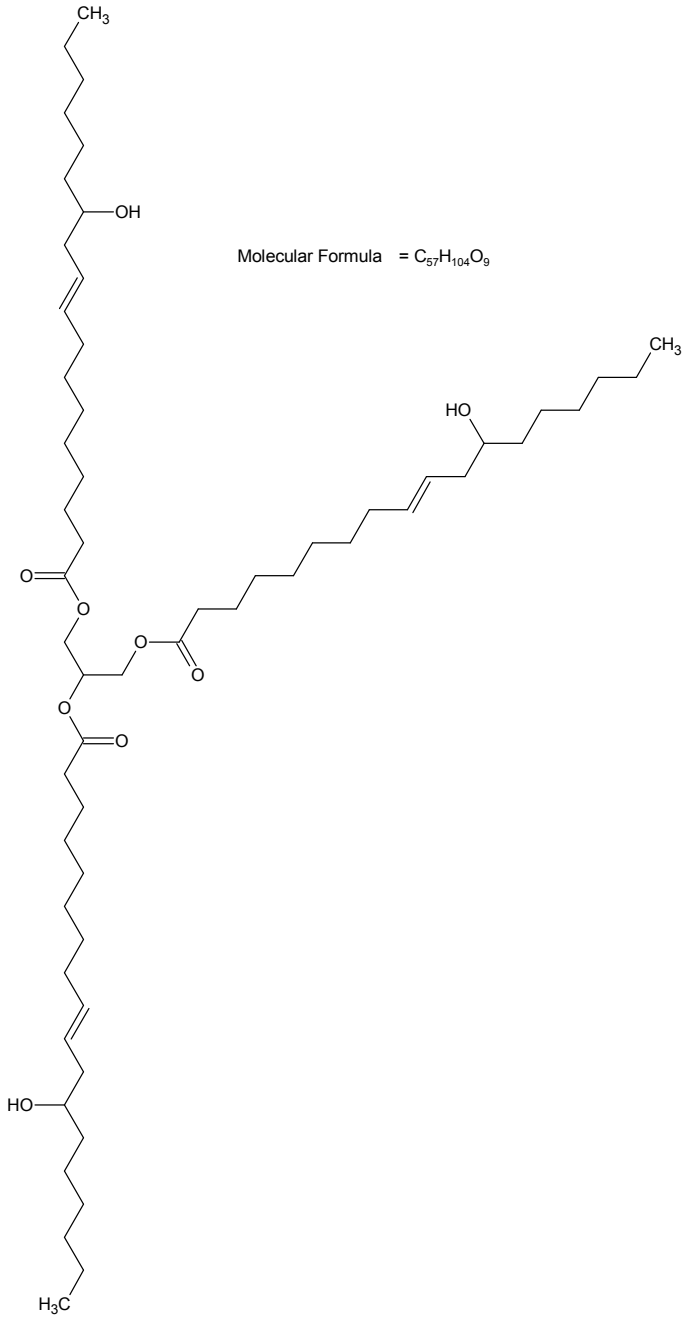
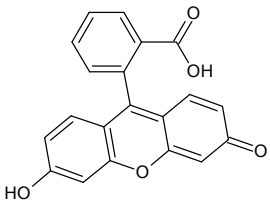
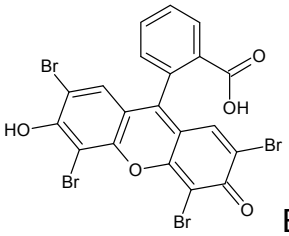


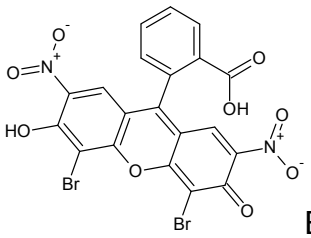
Fig. 2.1. Castor Oil – main triglyceride polar structure with Ricinoleic acid. (Source Structure: Drawn – Advanced Chemistry Development ACD/ChemSketch Product Version 12.01)



Fluorescein (a)



Eosin Y (b)



Eosin B (c)

Fig. 2.2. Pigments & Dyes. (Source Structure: Drawn – Advanced Chemistry Development ACD/ChemSketch Product Version 12.01)

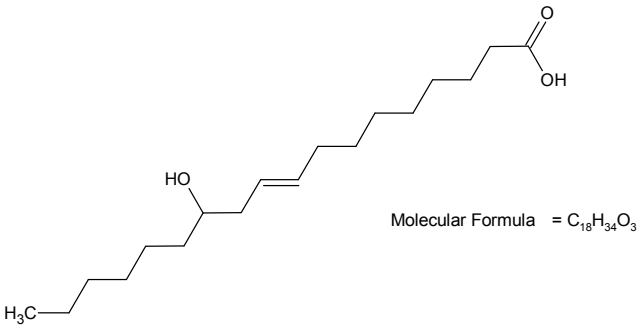


Fig. 2.3. Ricinoleic acid; the main fatty acid in Castor Oil (85%). Hydroxyl fuctional group gives Castor oil its unusual polar qualities. (Source Structure: Drawn – Advanced Chemistry Development ACD/ChemSketch Product Version 12.01)

Dyes in the form of bromo acids - bromo derivatives of fluorescein (Figure 2.2a), are the main common additives used as pigments in lipsticks. Eosin is a fluorescent dye produced by reacting bromine with fluorescein. There are two types used as pigments, Eosin Y (Figure 2.2b) and Eosin B (Figure 2.2c). Eosin Y is a tetrabromo derivate of fluorescein which produces a purple stain while Eosin B is a dibromo dinitro derivate which produced a yellow-red stain. The two are normally used in combination with each other. Whilst Eosin forms the red pigment in lipstick products its intensity increases when it reacts with the NH_2 groups in proteins on the surface of the skin.

In recent years, ingredients such as jojoba oil, sunflower oil, chamomile oil, shea butter vitamin E, aloe vera, collagen, amino acids, and sunscreen have been added

to lipstick. These extra components are used to keep lips soft, moist, and to provide added protection from the sun and dryness.

2.2 Waxes

Waxes are used to give and impart gloss and hardness to the product, to stabilise the stick and allow it to be moulded into shape and enable application. The ideal characteristics are obtained by using a mixture of waxes of different melting points and adjusting the final melting point by incorporating a sufficient amount of high melting point wax e.g. carnauba wax, beeswax and candelilla wax (Harry & Wilkinson 1973; Salvador & Chisvert, 2007).

Waxes are water-resistant materials made up of various substances including hydrocarbons (alkanes and alkenes, branched or normal), ketones, alcohols, aldehydes, sterol esters, alkanoic acids, terpenes, and monoesters with molecular chain length ranging from C_{12} to C_{38}. More commonly waxes are esters of a long chain alcohol other than glycerol and a long chain acid as illustrated in Figure 2.4 with the wax ester of Carnauba.

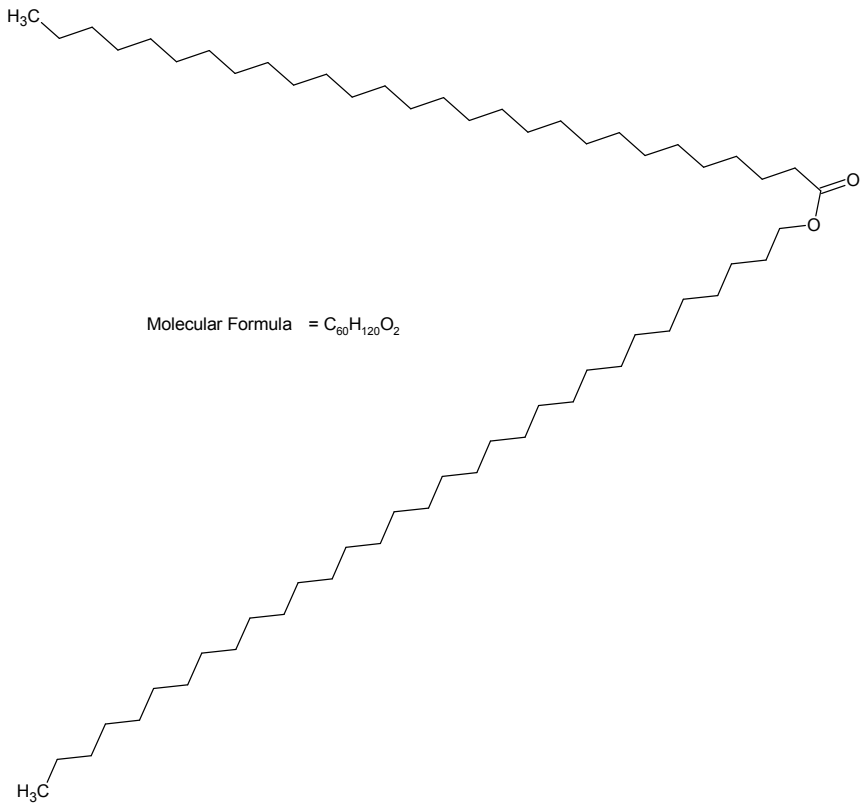


Fig. 2.4. Carnauba Wax main ester structure. (Source Structure: Drawn – Advanced Chemistry Development ACD/ChemSketch Product Version 12.01)

2.2.1 Beeswax

Beeswax (*Cera alba*), with its unique biologically active characteristics, is one of Natures' oldest ingredients. It can be used as a thickening agent, emollient, emulsifier and humectant. Its antiseptic and wound healing properties makes it an ideal ingredient to use in cosmetics such as lipsticks. It is secreted by the honeybee (*Apis Mellifera*), to build the walls of the honeycomb. When secreted it is initially a transparent colourless liquid, which turns into a semi-solid substance on contact with the atmosphere (Peters Rit et al., 1990; Adamczyk et al., 2010).

2.2.2 Berry Wax

Berry wax obtained from its namesake the female wax berry plant (*Morella cordifolia)*. The process of obtaining the wax was first noted by Thunberg in 1772; where the wax was and still is obtain by means of boiling the berries in water and skimming off the wax, followed by sun bleaching. It's primarily used in polish, ointments for wound dressing, candles and soaps. Like beeswax it has antiseptic and wound healing properties making it ideal for cosmetics.

2.2.3 Carnauba Wax

Carnauba wax is obtained from the leaves of the Brazilian palm tree (*Copernicia cerifera*), also referred to as the "Tree of Life". Due to the regional equatorial climate, the palm tree secretes the wax through the petioles of the leaves to protect against dehydration. This wax is obtained from the leaves by either scrapping or mechanical thrashing. Being one of the hardest naturally occurring waxes, when applied to vehicles and floors and tables it is able to create a durable, lasting, glossy finish. It is also used in lipsticks to prevent the oil from separating and to add structure to the final product. Being a plant based substance and safe for human consumption it is also used in a variety of foods as a coating candy and an anti-caking agent (Kelly, 1948; Melo et al., 1998; Milanovic et al., 2010).

2.2.4 Hard Paraffin

Hard Paraffin otherwise known as paraffin wax is essentially a mixture of long chain high molecular weight alkanes of the order $C_{20}H_{42}$ to $C_{40}H_{82}$ inclusively, obtained from crude petroleum. Whilst short chain low molecular weight alkanes are liquids at room temperatures, paraffin wax is a solid due to the cross-linked arrangement of

the long chains. Due to its structure and physicochemistry it is used extensively in pharmaceutical and cosmetic industries. Other applications include water proofing, cork, paper, floor polishes, electric insulators, and leather finishing (Nhlapo, Luyt, & Vosloo, 1998).

2.2.5 Microcrystalline Waxes and Multiwax

Microcrystalline (*Cera Microcristallina*) waxes differ from refined paraffin wax in that the molecular structure is more branched and the hydrocarbon chains are longer (higher molecular weight). Therefore the crystal structure is much finer than paraffin wax, and this directly impacts many of the physical properties. The wax is a refined mixture of solid, saturated aliphatic hydrocarbons, and is produced by de-oiling certain fractions from the petroleum refining process. They are tougher, more flexible and generally higher in melting point than paraffin waxes. Having a finer crystalline structure also enables the wax to bind solvents or oil, and thus prevent the sweating-out of compositions. These characteristic properties would make it an ideal base material for cosmetics such as lipsticks (Crowley & Laefer, 2008).

2.3 Emollients

Emollients have been part of human life for centuries. The Greeks used wool fat on their skin as early as 700 BC (Ersser et al., 2009). Medical grade lanolin is also used in the formulation of many lip products, used to prevent chapped lips due to its hypoallergenic and bacteriostatic properties.

The terms emollient and moisturiser have a tendency to be used synonymously. However technically an emollient is a product that smoothes and softens the skin via

occlusion, whereby a moisturisers is a product that adds moisture to the skin (Choi et al., 2005; Ersser et al., 2009).

Emollients have three basic properties (Rawlings et al., 2004):

- Occlusion – traps water in the skin via a layer of oil on the surface preventing transepidermal water loss, thus increase the moisture content of the stratum corneum (outer layer of skin).
- Humectants – substances with water-attracting properties that increase the water holding capacity of the stratum corneum (outer layer of skin). By either attracting moisture from the dermis to the epidermis or attracting moisture from the environment to the epidermis.
- Lubrication - adding slip or glide across the skin.

2.4 Lip Physiology & Emollient Therapy

The outer layer of the lips (stratified squamous epithelium), as shown in Figure. 2.5, is devoid of the horny stratum corneum layer according to Harry and Wilkinson, (1973); whilst Ryu et al., (2005) state that the stratum corneum is relatively thin in comparison to facial skin. Either way, as a result the lips appear translucent and red due to underlying blood vessels and a lack of keratin (Kobayashi & Tagami, 2004). As a consequence of this deficiency in keratin (partially-keratinised), these outer cells known as corneocytes must be kept moist in order to prevent drying, wrinkling

and subsequent infections. This can however give rise to problems when selecting active substances in an attempt to improve quality and appearance (Ryu et al., 2005) due to its relatively thin outer layer and close proximity of blood vessels and nerve endings.

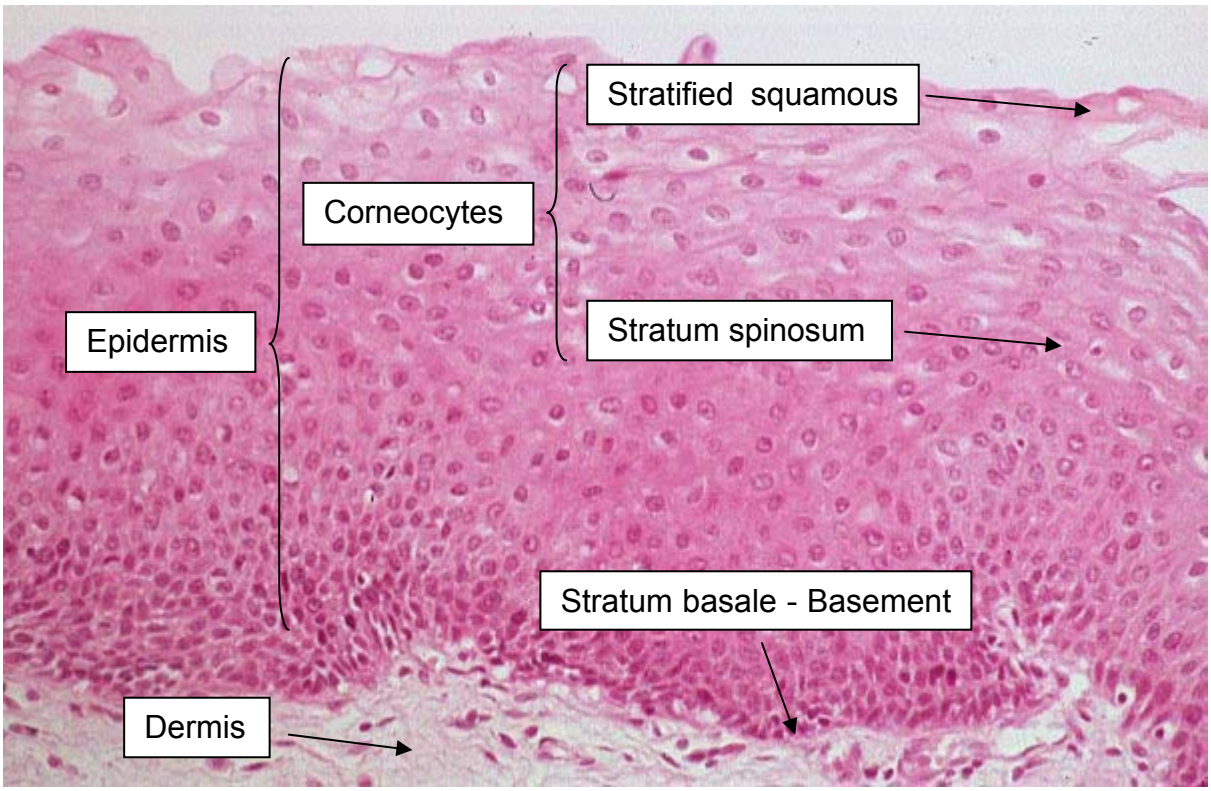


Fig. 2.5. Structural physiology of the Lips, showing the cells of the epidermis and dermis. (Source: Dermatology Nursing, 2005; www.pathguy.com accessed 28/11/2010).

Furthermore the lips do not have any sweat or sebaceous glands to provide the moisture and oils necessary for protection, although this is disputed in research carried out by Kobayashi and Tagami (2004), on transepidermal water loss (TEWL), where it is alleged that approximately 50% of individuals were found to have

sebaceous glands after adolescence at the vermilion border. Additionally, whereby in the case of skin occlusive materials, e.g. barrier creams, which work by physically trapping transepidermal water loss (TEWL) from the dermal layer of the skin (Wolf, Orion & Davidovici, 2007). To facilitate similar additional protection to the lips; to prevent or decrease cracking which could possibly lead to bacterial infections via bacterial colonisation (Brown & Butcher, 2005), moisturisers and humectants are essential. Humectants have an additional value, drawing moisture into the lips from the environment. An additional point made by Kobayashi & Tagami (2004) is that the transepidermal water loss (TEWL) on the lips is much higher than that compared with the skin, to put it simply, its water-holding capacity is much less, in which case moisturisers and humectants along with occlusive protection is necessary. In spite of this, research conducted by Wolf et al (2007) state that reducing the transepidermal water loss brings with it the disadvantage of slowing down tissue repair. This however can be counteracted according to Rawling et al., (2004) as some oils reduce transepidermal water loss by 98% whilst other only reduce it by 20-30%. The formulation of an emollient, water-in-oil emulsion in lipstick form with the correct amount of added humectants forms the basis of this research.

2.5 Emulsions, Emulsifiers & Interfacial Tension

An emulsion is traditionally defined as a dispersion of droplets of one liquid in another, when the two liquids are immiscible. Many products can exist as emulsions, including cosmetics, insecticides, crude oil and some pharmaceuticals (Rousseau, 2000).

In order to attain a state of minimum energy the surface of any liquid will always orientate itself to the smallest possible area. In order to increase this surface area work documented as free surface or free interfacial surface energy must be expended, this energy, numerically is equal to the surface or interfacial tension. Surface tension refers to liquids in contact with air or their saturated vapour, whereas interfacial tension refers to two immiscible liquids in contact with each other. Interfacial tensions are less than surface tensions, because the adhesive forces between the molecules of the two phases forming the interface are greater than the adhesive forces between molecules in a liquid phase interacting with molecules in a gaseous phase. Increasing the adhesive force will give rise to a decrease in the surface tension.

As emulsions are thermodynamically unstable systems (Krog, 1977), they tend to phase separate quickly. Stabilisation is usually achieved by the addition of a protein or an emulsifier or surfactant (**surf**ace **act**ive **a**ge**nt**) (Wolf et al., 2007), however the coexistence of both proteins and emulsifiers could lead to destabilisation and partial coalescence as the proteins and emulsifiers will compete for space at the interface, which can be beneficial in the production complex food colloids like ice cream (Dickinson, Ritzoulis & Povey, 1999). Small molecular surfactants/ emulsifiers are preferentially adsorbed at the interface displacing proteins and in the process weakening the membrane causing destabilisation and partial coalescence. This partial coalescence is essential to enable the fat globules to produce a structured network in the frozen product to entrap the air bubbles (Goff, 1997).

A surfactant lowers the interfacial tension between the two immiscible phases via adsorption at the interface (Everett, 1988) thus forming a mechanically cohesive interfacial film around the droplets after emulsification, preventing coalescence

(Rousseau, 2000). It is important to stress that cohesive forces are the forces that exist between molecules of one phase, whilst adhesive forces are the forces that exist between molecules of two different phases. As the interfacial tension can be defined as the work required in producing or creating a unit area of surface; by reducing the interfacial tension, stable droplets of higher overall surface area can be produced. The nature of the interface established through the adsorption of emulsifiers, influences the two immiscible liquids to such an extent that one breaks up during the emulsification process to form droplets (disperse phase) while the other retains its continuity (continuous phase). How and why this occurs is due to the fact that the emulsifiers at the interface are wetted by both liquids which individually have different surface tensions on either side. As a result of this the interface will always bend so that the side with the higher surface tension becomes concave, thus producing droplets giving rise to either a water-in-oil (W/O) or an oil-in-water (O/W) emulsion (Bancroft, 1913; Griffin, 1949). In order to maintain stability, the interfacial film should be firm and permanent. Likewise, the electric charge produced on the surface of the droplets is important, as its presence will produce repulsion between any approaching droplets thus increasing stability. These two factors are predominantly important during emulsification in order to reduce droplet flocculation, film drainage and subsequent rupture of the interface as droplets formed during the emulsification process will inevitably collide with one another giving rise to incessant coalescence. With regards to solid water-in-oil (W/O) emulsions they carry less significance after the crystallisation/ solidification of the continuous phase as the solid matrix will inevitably help to stabilise the lipstick emulsion. In oil-in-water (O/W) emulsions where the interfacial film is electrically charged this produces an overall charge on the oil droplets balanced by the total charge in the double layer within

which there is an excess of oppositely charged ions (counter-ions). This is known as the electric diffuse double layer or ionising atmosphere, produced by the ionised water continuous phase. If however the oil were the continuous phase the dispersed water droplets would be susceptible to flocculation and coalescence due to the oil being a non-ionising medium absent of any electric diffuse double layer or ionising atmosphere (Schulman & Cockbain, 1939; Pink, 1940).

The most common emulsions are oil-in-water (O/W), where the water constitutes the continuous phase and the oil the dispersed phase; and the reverse, water-in-oil (W/O), where the oil constitutes the continuous phase and the water the dispersed phase. It is also possible to stabilize multiple (double) water-in-oil-in-water (W/O/W) emulsions using a 2-step method and a combination of hydrophilic and hydrophobic surfactants (Jiao & Burgess, 2003), and similarly oil-in-water-in-oil (O/W/O) emulsions (Jahaniaval, Kakuda & Abraham, 2003). The latter (O/W/O) could be beneficial for the delivery of fat-soluble active ingredients in cosmetic lipsticks. However for the purpose of this research and the production of cosmetic emulsion lipsticks only water-in-oil (W/O) emulsions will be investigated.

Emulsifiers and surfactants vary widely and can be classified as anionic (negatively charged), cationic (positively charged), amphoteric or zwitterionic (both positively and negatively charged) or non-ionic (no charge). Additionally they are all amphiphilic molecules, meaning they have a distinct hydrophobic (oil-soluble water-hating) part and a distinct hydrophilic (water-soluble water-loving) part. The charged substances usually contain a polar group attached to a hydrocarbon chain, thus exhibiting both hydrophobic (hydrocarbon chain portion) and hydrophilic (polar group) characteristics (Holmberg, 2002). An additional important point to mention with regards to anionic and cationic surfactants is their ability to form these specific

charges in aqueous solution. Amphoteric surfactants behave like cationic surfactants at low pH, and like anionic surfactants at high pH. At medium pH, they carry both positive and negative charges and they have the structure of a bipolar ion. Non-ionic emulsifiers tend to be condensation products of long chain alcohols with ethylene oxide for example, where the ethylene oxide is hydrophilic and the hydrocarbon chain hydrophobic. With regards to formulation the choice is heavily dependent on the type of emulsion required, the ingredients in the product and its intended use (Rawlings et al., 2004).

2.6 HLB System

Whilst there are hundreds of emulsifiers to choose from the HLB (Hydrophile-Lipophile Balance) system enables one to assign a number to the emulsifier or emulsifier blend. This number indicates or expresses the relative simultaneous attraction of the emulsifier or emulsifier blend for water (hydrophilic), oil (lipophilic) or the two phases to be emulsified. While the theory of the system sounds simple, in practice the task unfortunately is not so clear-cut, as emulsifier classification via HLB only permits some prediction of behaviour (Griffin, 1949).

Prior to making use of the HLB system for selecting a satisfactory emulsifier or blend of emulsifiers, it is imperative to evaluate exactly what is required. Issues such as; is the required emulsion water-in-oil or oil-in-water? How stable does one require the emulsion to be during storage and in use? Must it be non-toxic or non-irritant to the skin? These are some of the factors that will help to eliminate certain types and groups of emulsifiers and aid one in selecting others.

By applying the HLB system, one will be able to obtain an indication of what the emulsifier will do. That is, produce a water-in-oil (W/O) or oil-in-water (O/W) emulsion or behave as a detergent or solubilizing agent. It is important to note that the correct chemical type is just as important when selecting emulsifiers. As detailed in Table 2.1 an emulsifier that is hydrophilic in character and water soluble is assigned a high HLB number (above 11.0) and will produce an O/W emulsion. One that is lipophilic and oil soluble is assigned a low HLB number (below 9.0) and will produce a W/O emulsion. Two or more emulsifiers can also be blended to achieve an ideal HLB; these blends usually work best in achieving stable emulsions (ICI Americas Inc; Pasquali, Sacco & Bregni, 2009). For the purpose of this research and the production of cosmetic emulsion lipsticks, emulsifiers with HLB values below 9.0 will be utilised to produce W/O emulsions.

Table. 2.1. HLB Correlations.

HLB Correlations	
HLB Range	**Use**
4-6	W/O Emulsifiers
7-9	Wetting agents
8-18	O/W emulsifiers
13-15	Detergents
10-18	Solubilizers

Source: ICI Americas Inc., *The HLB System: A Time-saving Guide to Emulsifier Selection* (1980) (Wilmington, DE 19897, USA)

HLB Theoretical and Analytical Calculation for each Emulsifier

For the majority of non-ionic emulsifiers the HLB is purely an indication of the percentage weight of the hydrophilic portion of the emulsifier molecule multiplied by 1/5 for the purpose of convenience as indicated in Equation 2.1 (Pasquali, Taurozzi & Bregni, 2008).

$$HLB = \frac{Weight\ percent\ of\ Hydrophilic\ Group}{5} \tag{2.1}$$

Where the Hydrophilic Group is defined as hydroxyl, sorbitan or polyoxyethylene.

Although this formula works for most non-ionic emulsifiers, for those where the molecular formula is an approximation of the actual composition the method leads to considerable errors. In these cases values are best obtained by means of analytical data using Equation 2.2 (Pasquali, Taurozzi & Bregni, 2008):

$$HLB = 20\left(1 - \frac{S}{A}\right) \tag{2.2}$$

Where S = Saponification number of the ester and A = Acid number of the recovered acid.

2.7 Emulsion stability & instability

Whilst it is well documented that the role of an emulsifier is to lower the interfacial tension between the oil and the water phase by forming a mechanically cohesive interfacial film around the droplets thus aiding in the droplet fragmentation during emulsification and preventing subsequent coalescence, very little is mentioned about (the need for) stabilisation, both transient (during emulsion formation) and long-term (shelf-life). During emulsification, transient droplet stability is of paramount importance in order to reduce re-coalescence during processing (Darling & Birkett, 1987), which in turn determines the final droplet size distribution.

The stability of an emulsion is important in understanding its formation, as its stability is the endpoint or measurement of the entire process (Fingas & Fieldhouse, 2004). There are five main mechanisms that can contribute to emulsion instability: (1) creaming and sedimentation (Binks, 1995); (2) flocculation (Binks, 1995; Dickinson, Ritzoulis & Povey, 1999); (3) Ostwald ripening (Dickinson, Ritzoulis & Povey, 1999); (4) coalescence (Boode & Walstra, 1993; Goff, 1997); and (5) phase inversion (Dickinson, Ritzoulis & Povey, 1999; Rousseau, 2000). Ideally all of the factors need to be minimised or prevented in order to produce a stable emulsion cosmetic lipstick.

Creaming and sedimentation (Binks, 1995) is separation due to the differences in density between the two phases under the influence of gravity, leading to phase separation where either a cream or a sediment layer is produced. The creaming and sedimentation rate is proportional to the difference in density of the two phases and can therefore be minimised by using phases with similar densities (relative $\rho \approx 1$). This would be impossible to achieve as the wax and oil phase would always have a lower density than the aqueous phase. However the high viscosity crystalline wax within the continuous phase would form a solid matrix around the dispersed water

droplets, minimising the chances of any creaming or sedimentation. Additionally as the rate is also proportional to the square of the droplet radius; reducing the droplet size would also help minimize this effect.

Flocculation is the aggregation of particles without destruction of their individuality (producing flocs which may or may not separate out) due to their interaction energy (Binks 1995; Dickinson, Ritzoulis & Povey, 1999). This energy is the balance between the weak attractive (London-van der Waals) forces between the colloidal droplets and the electrostatic repulsion due to charged surfactants present at the emulsion interface as described by Derjaguin, Landau, Verwey and Overbeek (DLVO theory). Whilst the DLVO theory for predicting behaviour of charged particles in an ionic environment is well recognised, very few colloids rely exclusively on electrostatic repulsion forces for stability. Likewise these emulsion systems will rely more on the crystalline wax matrix for stability as opposed to droplet repulsion. There are two main types of flocculation; bridging and depletion. An example of bridging flocculation is where the ends of separate segments of a high-molecular weight polymer in a good solvent adsorbs to different particles drawing them together (Everett, 1988). Depletion flocculation occurs when a non or weakly adsorbed polymer in dispersion is excluded or displaced from the space between two approaching particles resulting in a polymer depleted zone and subsequent flocculation (Everett, 1988; Jenkins & Snowden, 1996).

When the interfacial area of a colloidal droplet is reduced via a diffusional mass transfer process from regions of high interfacial curvature to regions of low interfacial curvature, this interfacial area reduction process is commonly called coarsening, or Ostwald ripening. This is due to the smaller droplets having a higher solubility or vapour pressure, causing them to dissolve or evaporate on the larger ones

(Voorhees, 1992; Dickinson, Ritzoulis & Povey, 1999; Zeng, 2007). Coalescence involve the approach of two droplets, the thinning of the disperse medium between the two and finally the bursting of the film where the droplets combine to form a larger droplet of lower surface area (Everett, 1988; Boode & Walstra, 1993; Goff, 1997). Coalescence can be complete in systems where the droplets are liquid or partial where the droplets contain crystals. Partial coalescence can lead to phase inversion as in butter production from milk, where the oil-in-water (O/W) milk emulsion inverts to the water-in-oil (W/O) butter emulsion. Again these factors can be minimised by the proposed crystalline wax matrix and the strength of the interfacial film. Unfortunately increasing the concentration of the dispersed phase does bring with it proportionately an increase in these factors occurring, a fact that should be considered when looking at producing high water content cosmetic emulsions.

Whereby O/W emulsions (mayonnaise, dressings etc.) tend to be fluid substances containing a partial crystalline phase, food-related W/O emulsions (butter, margarine etc.) tend to be solid like. As mentioned earlier and endorsed by Darling and Birkett (1987), particle stability is based on the viscosity of the continuous matrix in many food systems like margarine and butter, immobilizing the water droplets. Again according to research conducted by Fingas & Fieldhouse (2004), whilst interfacial forces are principal in the formation of water-in-oil emulsions, the viscosity of the oil also plays a major role in stability. This theory was also backed up by Garti, Binyamin & Aserin (1998) citing research carried out by Johansson & Bergenståhl. This notion is important as the concept could be applied in producing W/O cosmetics like lipstick where the crystalline structure of the waxes in conjunction with the oils viscosity would create a rigid matrix (Clermont-Gallerande, Chavardes & Zastrow,

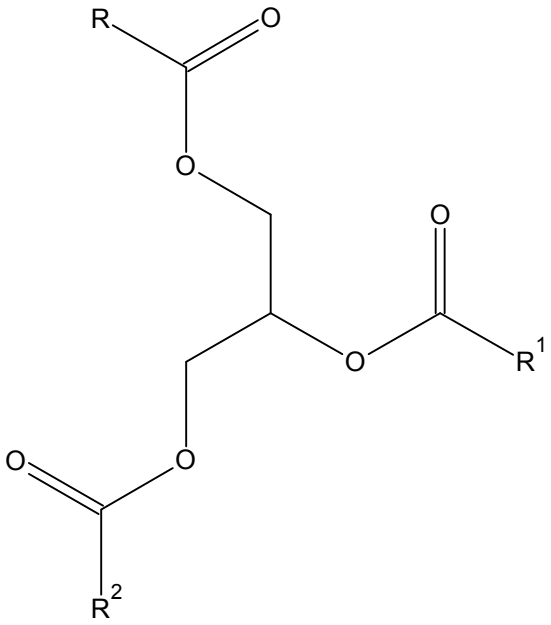
1999) in the continuous phase. Conversely as stated via citation by Hodge & Rousseau (2003), whilst wax crystals can impart stability to water-in-oil emulsions, this stability is not based on an increase in the viscosity or density of the continuous phase. This stability is based on surface-active interaction as opposed to the bulk properties of the system. Either way both of these concepts could prove to be beneficial by way of stabilising water-in-oil cosmetic emulsions.

2.8 Crystal Stabilisation

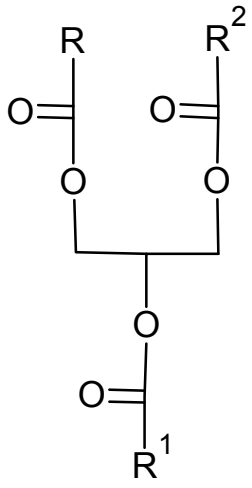
The presence of fat crystals can stabilize or destabilize an emulsion. In order to stabilize an emulsion, the crystals must collect at the emulsion interface, in doing so provide a physical barrier to coalescence (Rousseau, 2000; Hodge & Rousseau, 2003). The study of colloidal particles such as fat crystals in food systems is a relatively recent phenomenon. Whilst it is well known that many emulsified foods rely on solid particles for stability such as ice crystals in ice cream and eggs yolk particles in mayonnaise. The key factors determining the influence of fat crystals on emulsion stability are: (1) the wettability of the crystals at the interface; (2) interfacial film rheology; (3) particle microstructure, polymorphism and morphology; and (4) location of fat crystals – in the dispersed (O/W) or continuous phase (W/O) emulsion (Rousseau, 2000).

The microstructure of the fat crystals, are determined by polymorphism and morphology, which in turn is dictated by processing conditions and composition. Crystallized triacylglycerols (TAG) as shown in Figure 2.6(a) can exist in one of three main polymorphs - alpha (α), beta prime (β') or beta (β). Of these, the alpha form is the least stable of the three, similar to the melted state where the hydrocarbon

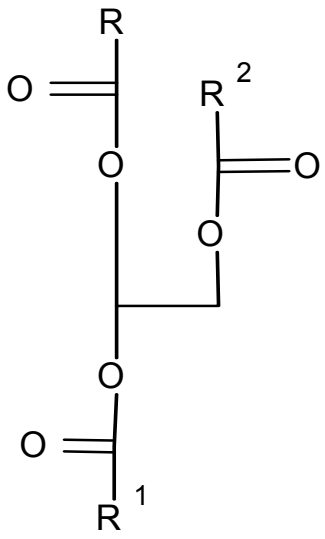
chains are in free rotation and present a tuning fork conformation (Figure 2.6(b)) with the beta form being the most stable forming the chair conformation (Figure 2.6(c)). These triacylglycerols pack in different longitudinal arrangements namely double chain length (Figure 2.7) and triple chain length (Figure 2.8) (Paul et al., 1991; Culot et al., 1994). Whist this is the case as stated by Persson (2008), not all triacylglycerols are able to form the beta polymorph. In many cases the beta prime polymorph is formed in preference due to asymmetry of the triacylglycerols and crystal growth occurring over extended periods. Moreover, Coupland (2002) found that fats tended to nucleate initially in the alpha-form and later partly converting to the beta prime. The reverse was observed with the bulk sample where the beta-prime form would initially be formed followed by the alpha form.



(a)



(b)



(c)

Fig. 2.6. Crystallized triacylglycerols (TAG), (a) molecular structure, (b) tuning fork conformation and (c) chair conformation. (Source Structure: Drawn – Advanced Chemistry Development ACD/ChemSketch Product Version 12.01)

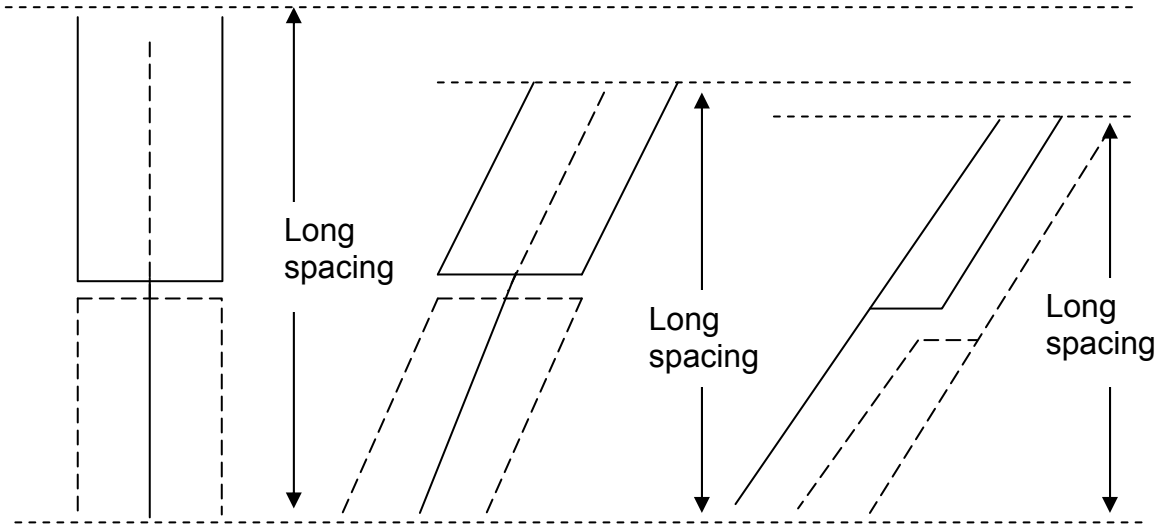


Fig. 2.7. Double chain length structures, (a) alpha (α) tuning fork, (b) beta prime (β') tilted tuning fork and (c) beta (β) stacked chair. (Adapted: Culot et al., (1994))

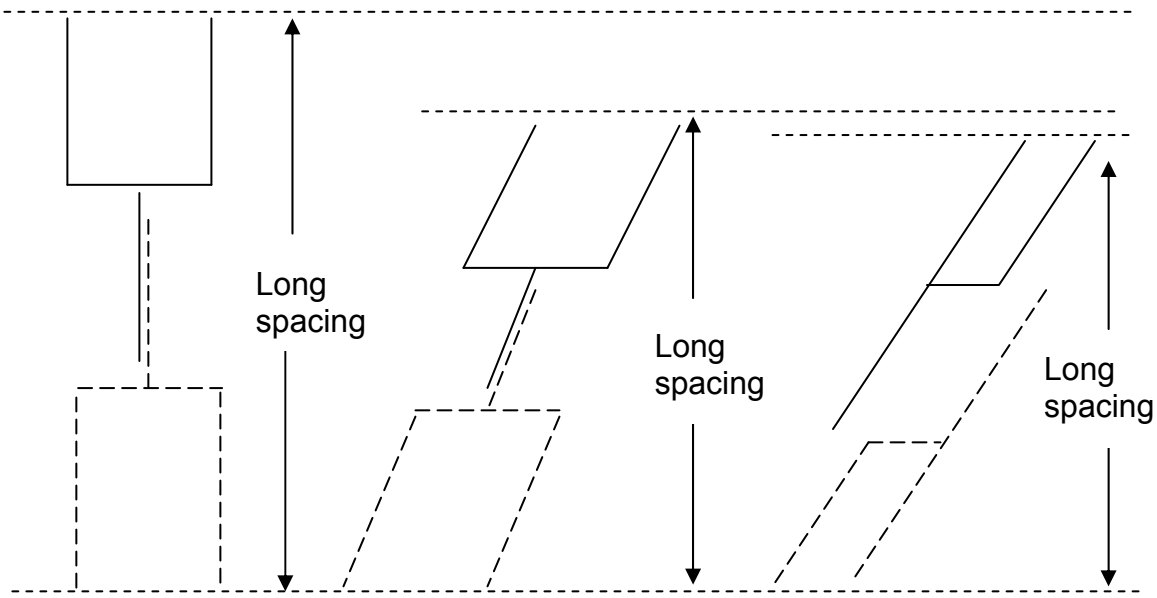


Fig. 2.8. Triple chain length structures, (a) alpha (α) tuning fork, (b) beta prime (β') tilted tuning fork and (c) beta (β) stacked chair. (Adapted: Culot et al., (1994))

Garti, Binyamin and Aserin (1998) have demonstrated that it is possible to stabilise W/O emulsions by α-form polymorphs in conjunction with polyglycerol polyricinoleate (PGPR) which is used as a non ionic lipophilic emulsifier. However in order to achieve a large amount of α-form polymorphs in the continuous phase, flash cooling of the triglycerides (tristearin) was required prior to emulsification. These emulsions were not stable, however, for sufficiently long periods. Applying the hypothesis could be useful in producing water-in-oil cosmetics like lipstick. However as stated crystalline polymorphs transitions over time could result in undesirable and unstable products. This dilemma of polymorphic changes occurring during storage could be

prevented by the addition of crystal modifying emulsifying agents according to research conducted by Krog (1977) where sorbitan esters were used to stabilize the intermediate beta prime (β') crystal form.

Whilst fat crystallisation can help to stabilise W/O emulsions, fat crystallisation within O/W emulsions has a tendency to reduce emulsion stability, causing partial coalescence. This is due to the crystals (those that are rigid enough to overcome the Laplace pressure) penetrating the interfacial layer between the two droplets. This produces a bridge which in turn leads to coalescence between the two drops. Whilst crystal penetration (leading to partial coalescence) of oil droplets in typical oil-in-water emulsions may be undesirable, fat crystallisation is important in supporting the structure of the air cells in typical foams like ice cream and whipped cream (Coupland, 2002). Penetration of the interfacial layer is less likely if the crystals are able to conform to the shape of the droplet. As mentioned earlier alpha (α) polymorphs have a more liquid malleable character and are therefore more likely to follow the contours of the droplets. Also fats containing a broad mixture of triglycerides will tend to form a mixed crystalline structure, giving rise to a softer mechanical structure hence a more stable emulsion. Other factors such as interfacial film thickness along with environmental factors have been found to affect whether or not the crystals are able to penetrate and hence destabilize an emulsion; of course interfacial film thickness is dependent on the choice and quantity of emulsifier used. Protein stabilised emulsions have been found to be more stable than small-molecule surfactants due to the formation of a thicker interface (Darling and Birkett, 1987). Whilst crystallisation may be required to stabilise W/O emulsions, which appropriately would be the case in stabilising W/O cosmetics, this could lead to an increase in the hardness of the final emulsion. Although this is important, in

producing a stable solid stick product, the lipstick must also be pliable to achieve a smooth layer when applied.

Wang & Lee (1997) found that the hardness of emulsion lipstick with two lipophilic emulsifiers was less than that of a conventional lipstick with an accompanying lower degree of crystalllinity. This may have been due to the good compatibility between the lipophilic emulsifiers (Span 60 and Span 80) used with the waxes and oils hence reducing the degree of crystallinity. They also found that an increase in the emulsion droplets also produced a harder product which is unusual, as one would have expected an increase to reduce the hardness.

Whilst it is well documented that to form a stable W/O emulsion one requires the addition of an emulsifier to prevent coalescence between the water droplets, stabilisation can also be achieved via electrostatic droplet-droplet repulsion (Leunissen, 2007). This hypothesis has been backed up by Zwanikken et al., (2008) where W/O emulsions (in fairly polar oils) were stabilized for periods in excess of 18 months. These electrostatic droplet-droplet repulsions occur as a result of ion uptake from the oil. This observed stability and crystallisation can be explained qualitatively via calculations based on the Poisson-Boltzmann theory for monovalent cations and anions in the geometry of a planar water-oil interface (Zwanikken & Rene van Roij, 2007). Whether or not this would be an ideal, practical or realistic approach to take in the preparation of cosmetics is doubtful, as the number of additional additives in the formula would in all probability complicate this method of stabilisation.

2.9 Microbial stability & Origin of Contamination

In order for microbial activity to take place within cosmetics and foods, not only must there be water present, this water must also be available. In addition water used in product manufacture can be an obvious source of contamination.

Water activity (a_w) is an index of the availability of water for chemical reactions and microbial growth (Banwart, 1981). The stability is mainly a consequence of the relationship between the equilibrium moisture content (EMC) and its corresponding water activity (a_w) (Myhara et al., 1998). A potentially hazardous food could become hazardous at a pH greater than 4.6 and a water activity greater than 0.85 (but less than 1.00 as microorganisms cannot grow in pure water), as these conditions provide the right conditions for pathogenic organisms to grow. Therefore in order to reduce the potential hazard, storage at or below 5-7 °C is recommended to retard microbial activity. This would however prove impractical for cosmetics with large quantities of free water where the water activity could exceed 0.85.

Whilst in general, O/W emulsions are more susceptible to bacterial attack for obvious reasons with water being the continuous phase as opposed to W/O emulsions; W/O emulsions do still present a complex system whose implications for microbial growth and survival are not fully understood. Guentert and Linton (2003) found that the dispersion of water droplets in the oil (W/O emulsion) produces an effective barrier to prevent microbial activity taking place. This was backed up by Verrips & Zaalberg (1980), who go on to state that this intrinsic stability is based not only on the size of the droplet, but also on the fact that only a small portion of the droplets within the emulsion is occupied by microorganisms originating from the water phase. Furthermore the production of finer water droplets will consequently limit the number of generations the bacteria can produce (Delamarre & Batt, 1999; Kilcast &

Subramaniam, 2000). All of these theories however are based on emulsions with very little free water where one would assume microbial activity will take place. As substantiated by Brown and Butcher (2005) despite the addition of preservatives, water rich cosmetics are an ideal environment for bacterial and fungal growth. Therefore keeping the free water content to a minimum is of paramount importance alongside producing fine droplets on the micro scale or smaller. Additionally there is still a possibility that organisms may migrate from the continuous oil phase to the dispersed water droplets, plus if the oil phase is not entirely anhydrous migration in the opposite direction cannot be entirely ruled out. Research conducted by Bennet (1962) on preservation of emulsions showed that the oil-to-water ratio had a significant effect upon the magnitude of microbial growth (Harry and Wilkinson, 1973). In view of these findings, producing high water content emulsion (above 20% aqueous phase) lipsticks may carry with it a higher risk of microbial propagation and survival.

2.10 Emulsion Processing

Emulsion formation via the break-up of droplets is based predominantly on turbulence. This can be achieved by the use of devices ranging from high-energy short-time (high-pressure homogenizers), to low-energy long-time (paddle stirrer).

Processing can be dependent on a number of factors including equipment available to the individual choice of the manufacturer. However choice normally comes down to the flow properties of the product and what exactly is required of the final product.

There are a number of important factors involved in the initial emulsification of a product, namely temperature, intensity and duration of mixing, along with the order and rate of addition of phases. For the purpose of this research and the production of emulsion lipstick products the temperature would have to be elevated to around 80-95˚C to ensure melting and subsequent blending of the raw waxes. As mentioned, emulsification can be achieved by high-energy short-time (high-pressure homogenizers), or low-energy long-time (paddle stirrer), where it is important to add that the practical aspects of mixing are both shear and flow. Whilst a high degree of shear is required for the emulsification and dispersion process, a high degree of flow is also required for heating and cooling and blending. Although both processes give both shear and flow the relative balance is very important depending on the product ingredients and what type of emulsion is required. High-energy short-time (high-pressure homogenizers) tend to give more shear whereas low-energy long-time (paddle stirrer) tend to give more flow. With regards to the production of emulsion lipsticks, high-energy short time would be advantageous as opposed to low-energy long-time, due to the viscosity of the oil and waxes and in order to produce a finer water dispersed phase.

A high degree of shear is generally produced by the action of rotating an impeller at high speed in a stationary liquid or by passing the liquid at high speed past stationary baffles or through narrow orifices. High shear mixers combine both processes with a high speed turbine revolving in a mesh stator chamber containing various constrictions and baffles (Harry and Wilkinson, 1973).

There are numerous alternative methods that can be used for emulsifications, namely colloid mills, high pressure homogenizers, ultrasonic homogenizers,

membranes and micro-capillary. None of these processes would be an ideal choice for this type of emulsification due to the temperatures involved and the viscosity of the oil phase.

2.11 Characterisation & Analysis of microcrystalline structure

2.11.1 Rheology & Texture

One of the most significant aspects of any cosmetic lipstick is its rheological properties. Rheological or viscoelastic measurements are generally carried out in order to quantify qualitatively the flow of the material for purpose of quality i.e. spreadability on the skin (Adeyeye et al., 2002). Spreadability, texture, hardness and feel are just a few of the properties that are vital in terms producing a successful marketable product. The term spreadability has been used by consumers for many years to explain the ease of distribution of a product. Like many other common terms, spreadability is not a single physical property. According to Blair (1938), the two principal physical factors involved are brittleness and hardness. By way of endorsement to this, most researchers have studied physical properties using methods such as the penetrometer, extrusion and crushing-strength (Huebner & Thomsen, 1957). As a cosmetic lipstick product is applied by compression to the lips, by far the best method would be crushing-strength. This is backed up by Wang & Lee (1997), even though their choice of method was the penetrometer. Whist the penetrometer test is useful as a hardness indicator; it is mainly related to the yield stress of the test material. However it is an ideal method along with interfacial rheology for comparing the interfacial film strengths formed by specific emulsifiers,

which of course is an important contributor to emulsion stability. It is also useful in determining the presence of undesirable air pockets under the surface.

Although Rheology is measured macroscopically, these measurements depend on what's occurring on a microscopic level, thus revealing valuable important information about the microstructure of the emulsion with regards to particle-particle interaction and consequently stability. Rheological properties of emulsions associated with stability are determined by many factors including the concentration of the dispersed phase along with droplet size distribution, the emulsifiers and associated interfacial film strength. The viscosity and composition of the continuous phase particularly at low dispersed phase concentration and also the temperature are additional factors.

By means of manipulation of the aforementioned parameters the rheological characteristics of the product can be altered (Dickinson & Golding, 1997). With regards to stability, according to work conducted by Fingas & Fieldhouse (2004) the stability can be grouped into three categories; stable, mesostable (intermediate) and unstable, with each having distinct physical properties. For a stable emulsion, the zero shear rate viscosity is at least six orders of magnitude higher than that of the starting oil. For an unstable one, the zero shear rate viscosity is usually less than two to three orders of magnitude greater. Additionally, a stable emulsion will exhibit elasticity whereas an unstable one will not. These viscoelastic properties could be assessed by means of non-destructive oscillatory rheometry (Gaperlin et al., 1998), which would also indicate the physical stability of the emulsion as backed up by Jiao & Burgess (2003) and Adeyeye et al (2002) where one would expect the value for the storage G' modulus (a measure of the solid/ elastic behaviour) to predominate

over that of the loss G'' modulus (a measure of the liquid/ viscous behaviour) whilst the emulsion maintained stability. In addition with the dynamic parameter loss tangent (tan δ) this would provide valuable information with regards to forming a model to assess the point of destabilisation of the systems. One would normally associate a drop in viscosity to be a sign of destabilising coalescence occurring within the dispersed phase, however in research conducted by Dickinson, Ritzoulis & Povey (1999) where destabilisation occurred as a result of bridging flocculation; a stable emulsion appears as a viscous Newtonian liquid, whereas an unstable one appears to be elastic and non-Newtonian. Here the viscoelastic properties during destabilisation (viscous to elastic) are determined predominantly by the nature and chemistry of emulsifier-emulsifier interaction.

2.11.2 Differential Scanning Colorimetry - DSC

It is well documented that thermal analysis is an important tool for material characterisation (Burmester, 1992). Differential Scanning Colorimetry – DSC, has accordingly been found to be an ideal method for the analysis of the microcrystalline structure of emulsions and the polymorphic structure of fats crystals, (Garti, Binyamin & Aserin, 1998; Clermont-Gallerande et al., 1999).

While subjecting the sample to a closely controlled well-defined temperature-change programme any transitional changes in the physical and chemical properties can be measured as a function of temperature or time. This thermal energy can therefore be monitored and recorded as it is proportional to the energy absorbed or evolved during the transition (Willard et al., 1981). Generally the degree of crystallisation is proportional to the heat of transition of the melting point peak, measured by DSC. Due to its sensitivity to thermal changes in materials, DSC has been found to be

ideal for assessing not only the degree of crystallisation, but also any polymorphic structure within the materials namely waxes (Matas, Sanz, & Heredia, 2003) a technique used also by Wang & Lee (1997) in their research on lipsticks. This is also an ideal way of assessing any changes in the crystalline polymorphs of the lipstick during storage and hence a useful method in determining the softening point and melting point range of the lipstick prior to and after extended storage periods.

2.11.3 Pulsed Nuclear Magnetic Resonance – pNMR

Droplet size can be determined by low-field pulsed Nuclear Magnetic Resonance – pNMR, microscopy, laser diffraction and electric sensing (Duynhoven et al., 2002). Pulsed Nuclear Magnetic Resonance has a number of distinct advantages over the other methods as the sample preparation is non-perturbing as stated by Duynhoven et al (2002). This method is well suited for solid emulsions, such as butter (Fourel, Guillement, & Le Botlan, 1995) as the presence of solid components in the continuous phase does not affect the assessment. This would therefore be a useful method to use on harder samples such as lipsticks. Furthermore being a non destructive technique, samples can be analysed repeatedly over time for changes in droplet movement, coalescence, flocculation etc. In addition pNMR will also analyse flocculated droplets (Fourel et al., 1995; Hodge & Rousseau, 2003). This method is useful in terms of emulsion stability and would be useful in assessing the stability and therefore shelf life of the lipstick after production. As pNMR can also measure the amount of free water in the W/O emulsion this would provide a good indication in terms of microbiological storage.

2.11.4 Cryogenic Scanning Electron Microscopy - Cryo-SEM

The droplet size distribution of the dispersed water phase, the nature and stabilisation of the water-oil interface are important factors in determining the stability of the emulsion. Cryogenic Scanning Electron Microscopy – cryo SEM is ideal to elucidate the morphology and the fundamental interactions that ultimately determine the bulk behaviour of emulsions and suspensions (Mikula & Munoz, 2000; John, Bhattacharya, & Raynor, 2004). By way of freeze fracture, followed by image analysis it is possible to obtain three-dimensional compositional information of the dispersed and continuous phase and to a lesser extent the interface.

This method is ideal for water-in-oil emulsions such as lipstick emulsions, where visualisation of particles at the interface is required. Alternatively with water as the continuous phase it would not be possible due to the formation of large chunks of ice via the cryogenic cooling. Furthermore it is particularly useful for opaque emulsions that cannot be visualised in great detail using an optical microscope (Madivala et al., 2009), which would also be the case when attempting to view cosmetic lipstick emulsions. Unfortunately the method does have a number of drawbacks. Because the sample size is very small, it may not be entirely representative of the entire emulsion. Additionally one is relying on a clean fracture of the sampled portion in order to observe the morphology in detail. As a result, in order achieve high-quality micrographs that are representative of the emulsion it would more often than not, require several attempts. In view of this, alternative methods should be used in conjunction with cryo SEM as backup.

3 Materials

3.1 Waxes & Emulsifiers

All the waxes, namely Carnauba, Microcrystalline and Hard Paraffin plus the Castor oil used in the formulations were provided by Boots Group plc (Nottingham, UK).

Three safe food grade non-ionic emulsifiers were selected for the research; namely Sorbitan monooleate - Span 80 (S6760, HLB = 4.3) supplied by Sigma-Aldrich (Sigma Life Science); Polyglycerol polyricinoleate – PGPR (ADMUL WOL 1408K, HLB = 1.5 ± 0.5) supplied by Kerry Bio-Science and Polyoxyethylene sorbitan monooleate - Tween 80 (P8074, HLB = 15) supplied by Sigma-Aldrich (Sigma Ultra).

3.2 Emulsifier Selection

The initial part of the research was to select the correct emulsifier or blend of emulsifiers capable of producing stable W/O emulsions. This was done initially with the aid of the HLB index, which for W/O emulsions is 4-6. Whilst all emulsions are thermodynamically unstable, albeit time dependent, they will therefore eventually destabilise given time. Producing water-in-oil emulsions with a crystalline wax matrix will invariably result in a more stable emulsion system due to steric stabilisation. It would have been far too time consuming to screen emulsifiers over the entire hydrophile-lipophile range. Therefore two food grade non-ionic lipiphilic emulsifiers and a food grade non-ionic emulsifier blend were selected for the research.

1 Sorbitan monooleate - Span 80, HLB = 4.3.
Used mainly as a non-ionic emulsifier in cosmetic and pharmaceutical ointments and creams, and also as a stabilizer in food products (Dziezak, 1988).

2 Polyglycerol polyricinoleate – PGPR, HLB = 1.5 ± 0.5.
Used as a non-ionic water-in-oil emulsifier in low fat margarines and spreads. Used also in chocolates to reduce the yield stress and therefore its viscosity, thickness and flow properties allowing it to melt better in the mouth (Wilson & Smith, 1998).

3 Polyoxyethylene sorbitan monooleate - Tween 80, (HLB = 15) blended with Sorbitan monooleate - Span 80 (S6760), (HLB = 4.3) to give HLB = 5.
Tween 80 alone is normally used as a non-ionic oil-in-water emulsifier (Feng et al., 2006) and stabilizer in medication ice cream, milk products, lotions and creams (Pourreza & Rastegarzadeh, 2004).

Both Sorbitan monooleate - Span 80 and Polyglycerol polyricinoleate – PGPR were selected for lipophilicity and having low HLB values. Span 80 within the 4-6 HLB range at 4.3 is ideal for producing W/O emulsions whilst PGPR, highly lipophilic at 1.5 ± 0.5 may not be ideal.

It been well documented that blending emulsifiers will always produce a more stable emulsion (ICI Americas Inc.) as opposed to using a single emulsifier by the fact that combining a water soluble hydrophilic one with an oil soluble lipophilic one will produce a denser interfacial film due to the hydrophilic and lipophilic portions of the molecules sitting on different sides of the interface (Rieger & Rhein, 1997), hence Polyoxyethylene sorbitan monooleate - Tween 80 (being water soluble hydrophilic) was blended with Sorbitan monooleate - Span 80, (oil soluble hydrophobic/lipophilic). In addition to this Tween 80 also has an analogous chemical type with Span 80, both being of the '-oleate' family.

With chemical composition playing a major role when producing stable emulsions; selecting emulsifiers with similar hydrocarbon chain length and type to that of the oil has been shown to produce emulsions with maximum stability (Korhonen et al., 2004). For this reason PGPR was selected due to its polyricinoleate hydrophobic chain which complements the ricinoleic acid in the castor oil.

With the continuous phase being oil and wax and therefore a non-ionising medium, selecting ionic emulsifiers would have been no benefit with stabilisation depending on the crystalline oil matrix to a greater extent as opposed to charged droplet repulsion. Additionally non-ionic surfactants have traditionally been used in creams and lotions due to a number of reasons. They are generally low in toxicity, neutral, stable to electrolytes (hence additives in the formula) and ideal for solubilising colorants, perfumes and fats (Harry and Wilkinson, 1973).

3.2.1 Emulsifier Blend Calculations

Equations (3.1) & (3.2) were used to calculate the ratio (%) of Polyoxyethylene sorbitan monooleate - Tween 80 to Sorbitan monooleate - Span 80:

$$\%\,(A) = \frac{100(X - HLB_{(B)})}{HLB_{(A)} - HLB_{(B)}} \qquad (3.1)$$

$$\%\,(B) = 100 - \%\,(A) \qquad (3.2)$$

Where;

(A) = Polyoxyethylene sorbitan monooleate - Tween 80

(B) = Sorbitan monooleate - Span 80

X = Required HLB = 5

$$\%\,(A) = \frac{100(5 - 4.3)}{15 - 4.3} = \frac{70}{10.7} = 6.5\%$$

$$\%\,(B) = 100 - 6.5 = 93.5\%$$

4 Research Methodology

4.1 Differential Scanning Colourimetry – DSC & Enthalpy calclations

Prior to attempting to produce an emulsion formulation it was imperative to reduce the number of components in the base formula to produce an actual basic lipstick of oil and wax to build on. Additionally many of the normal ingredients used in a conventional lipstick such as preservatives are surface active and could therefore interfere with the study adversely. As emulsion stabilisation along with the entire structure of an emulsion lipstick is dependent upon the microstructure and crystalline matrix formed by the waxes within the formula by way of interstitial and steric stabilisation, a preliminary assessment was carried out on all of the waxes by DSC to assess their thermal characteristics (Buchwald, Breed & Greenberg, 2008; Nikolova et al., 2009), namely melting point, melting point range, polymorphism and crystalline purity (crystallisation points). This data was necessary in order to select the waxes to be used as components to produce a simplified basic lipstick formula. It was important that the formulations physicochemistry was comparable to that of conventional lipstick upon which an emulsion formula could then be developed. It was later also used to assess the degree of crystallinity and melting point range in the lipstick formulations. This was significant with regards to establishing the correct softening point and organoleptic skin feel.

One of the most important determinants for texture, spreadability and skin feel is the amount and type of waxes present in the formulation along with the degree of crystallisation. Furthermore, the melting profiles of these waxes, determines the consistency of the formulation. The more solid at a given temperature the harder the product is perceived at that temperature. Products should therefore be formulated to have a softening point at skin temperature but should also have a fairly broad

melting point range in order to maintain a degree of consistency over the melting point range. By this, the product has an acceptable yield stress but remains resistant to mild abrasions and does not bleed beyond the vermilion border.

DSC analysis was performed using a Perkin Elmer DSC7 Colourimeter where sample masses ranged from 5-10mg for the raw waxes and 5-20mg for the formulations. An overview of the DSC program settings is detailed in Table 4.1. Aluminium sample cups were used, volume ≈ 40 µL.

Table. 4.1. DSC Program settings (Software used - Pyris for Windows, Version 3.04.)

Program Settings:-	
Initial state:	10 °C at 0 mW, Nitrogen flow 20 $mLmin^{-1}$. Equilibrate within 0.100 °C, (Temperature ±), 0.100 mW (Heat flow ±) & 2.0 min (Max wait time)
Program:	Hold for 1.0 min at 10 °C. Heat ramp, from 10 °C up to 120 °C at 2 $°Cmin^{-1}$. (Run time 56 min)

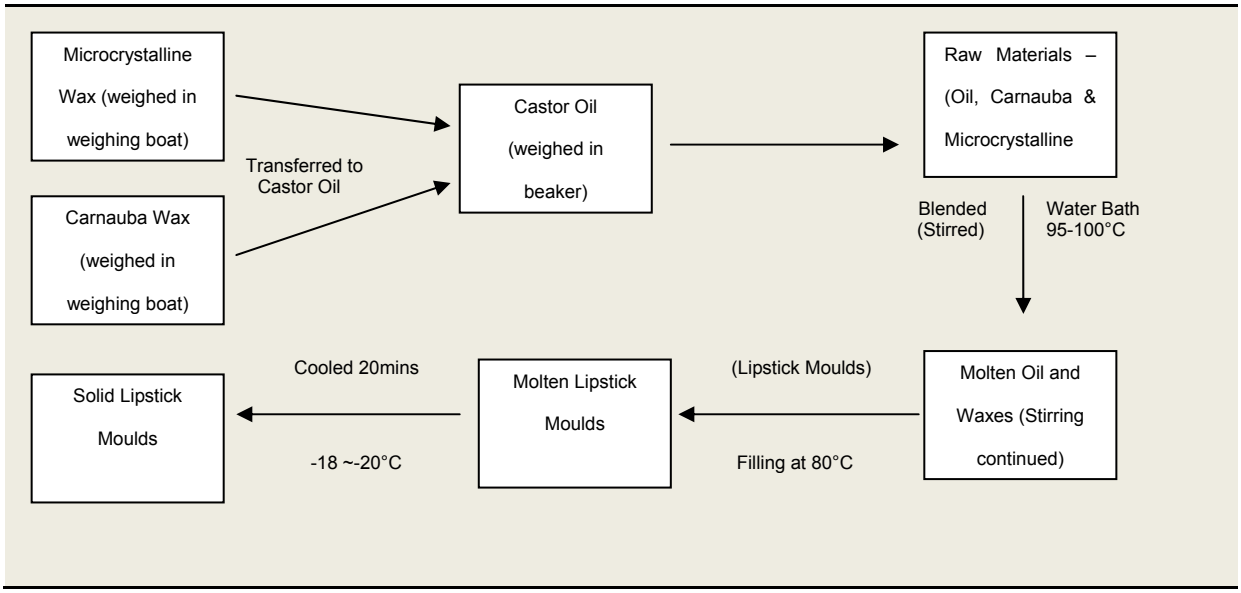
Enthalpy calculations (degree of crystallinity) based on the area under the thermogram peaks were conducted using the Trapezoid method (Equation 4.3);

$$A = \sum_{i=1}^{n=1} \frac{y_i + y_{i+1}}{2}(x_{i+1} - x_i) \qquad (4.3)$$

Where A = Area under the thermogram peaks, y = Heat Flow Endo/Exo (mW) and x = Temperature (°C).

4.2 Basic Lipstick Preparation

Fig. 4.1. Flow Chart for the Preparation of Basic Lipstick.



The constrained basic lipstick formula design was chosen where the sum of all three components was equal to 100 wt% (all components weight-weight percentage w/w%). The contents of the components for basic formula 1 were: Carnauba wax (7.1 wt%), Microcrystalline wax (15.98 wt%) and Castor oil (76.92 wt%).

The Basic lipstick formula was prepared as detailed in Figure 4.1, the waxes were weighed separately; these were then transferred to the castor oil that was weighed separately in a beaker large enough to accommodate the waxes.

After adding of the waxes (to the castor oil), the beaker was placed in a water bath at 95 to 100 °C and stirred continuously to prevent the waxes from separating and creaming to the surface.

The wax/oil mixture was allowed to cool with continuous stirring to approximately 80°C and then transferred to the lipstick moulds (Dweck & Burnham, 1980). It was essential that the moulds were filled to excess to avoid any depression in the centre due to contraction after cooling.

The moulds were then placed in a freezer at -18 to -20 °C for 20 min. This rapid cooling was carried out in order to produce a considerable amount of crystalline nuclei (Garti, Binyamin & Aserin, 1998). In doing this, the potential for crystal growth was reduced significantly, resulting in smaller crystals and a smoother glossier product. Uncontrolled growth, will usually give rise to grainy products with bloom on the surface (Dweck & Burnham, 1980). Whist rapid cooling could lock the particles in an unstable crystalline polymorph slowly transforming into a more stable form on storage, this step was vital in the preparation of these emulsions. In order to assess for this, the emulsions would have to analysed via DSC over extended periods longer than the period allowed for duration of this project. Samples were removed manually and kept for analysis.

4.3 Interfacial Tension and Surface Excess Concentration

Equilibrium Interfacial Tension was carried out in order to assess the surface active properties of each of the emulsifiers and emulsifier blends at various concentrations. In addition the emulsifier molecular packing was assessed and related to the HLB values, the interfacial structure and the overall stability & texture of the final product. Furthermore there is a limit to the lowering of the interfacial tension by an emulsifier (Santos et al., 2009), which is normally when surfactant molecules start to self aggregate and form micelles in the bulk solution. This concentration is commonly known as the critical micelle concentration (CMC) relating to the surface concentration reaching its' critical saturation point. It is important to note that the Equilibrium Interfacial Tension was carried out initially as an indication of the emulsifiers surface active properties and to judge their suitability. The only

conclusive way is to include them in the formulation and characterize the final emulsion product.

The Equilibrium Interfacial Tension between the main continuous oil phase and water was assessed using a Kruss K100 Tensiometer. Measurements were carried out using the Wilhelmy plate (Kruss Standard Plate – roughened platinum, width 19.900 mm, height 10.000 mm & depth 0.200 mm) method with the temperature elevated and maintained at 31.0 ± 0.2 °C using an external circulating water bath. This temperature was used to accommodate the conditions (unusually high temperature) in the laboratory at the time. Procedure settings are detailed in Table 4.2.

Sample vessel (121.5 mL with diameter 70 mm) was used for the measurements, with 20.0 g (20 mL) of de-ionised water and 45 g of castor oil with the emulsifiers dissolved in the oil phase. The system was not stirred as this would have given rise to a degree of emulsification. Whilst both liquids were measured using an analytical balance, a small portion of the oil always remained in the initial vessel after transfer

Measurement involved two stages:

i. The plate was initially tared by means of immersion via the automated height-adjustable sample carrier, in 45.0 g of the light low density oil phase.
ii. Secondly 20.0 g of the higher density water phase was introduced to the tensiometer in a separate vessel. After allowing the plate to touch the surface, again via the automated height-adjustable sample carrier, the light low density oil phase was then transferred carefully on top via the use of a syringe.

Time-dependent changes in the interfacial tension were detected automatically.

Table. 4.2. IFT Procedure settings

IFT Procedure settings;	
Immersion Depth (Plate):	2.0 mm
Maximum Time:	50,000 s
Values (Plot):	5,000
Values for Mean:	20
Surface detection sensitivity:	0.005 g
Surface detection speed:	6 mm/min
Plot:	Surface Tension (mN/m) vs Time (s)

After stabilisation, twenty stable consecutive readings were taken and used to create isotherms of equilibrium Interfacial Tension (mN/m) vs Concentration of Emulsifier (mg/L). Values were also taken to create isotherms of equilibrium Interfacial Tension vs natural logarithm concentration - ln Conc. in order to calculate the surface excess concentration and area per molecule. The Gibbs' adsorption equation (Equation 4.4) was used in order to determine the number of moles of emulsifier per square meter (mol/m^2) - surface excess;

$$\Gamma = -\frac{1}{RT}\frac{d\sigma}{dlnC} \tag{4.4}$$

Where Γ = surface excess per unit area of emulsifier, R = the universal gas constant, T = the temperature (Kelvin), σ = interfacial tension and lnC= natural log of the bulk concentration.

With the surface excess Γ, the area per molecule of adsorbed surfactant was calculated using equation 4.5;

$$A = \frac{1}{N_A\Gamma} \tag{4.5}$$

Where A = Area per molecule and N_A = Avagadro's constant.

4.3.1 IFT Plate Measurement principle

Using the Kruss Standard Plate method, the liquid was raised as detailed via the automated height-adjustable sample carrier, until contact on the surface or interface is registered. At this point the tension acting on the balance is at its maximum which means the sample carrier is not moved again during measurement.

The Interfacial/Surface Tension is calculated from equation (4.6) below:

$$\sigma = \frac{\mathrm{F}}{(\mathrm{L}.\cos\theta)} \qquad (4.6)$$

Where σ is the Interfacial/Surface Tension, F is the Force acting on the balance, L is the wetted Length of the plate and θ is the contact angle.

The Kruss Standard Plate being made of roughened platinum is wetted so that the contact angle is virtually zero. Therefore $\cos\theta \approx 1$, and therefore only the Force F and the Length L need to be taken into consideration (Tensiometer K100).

4.4 Emulsion Lipstick Preparation

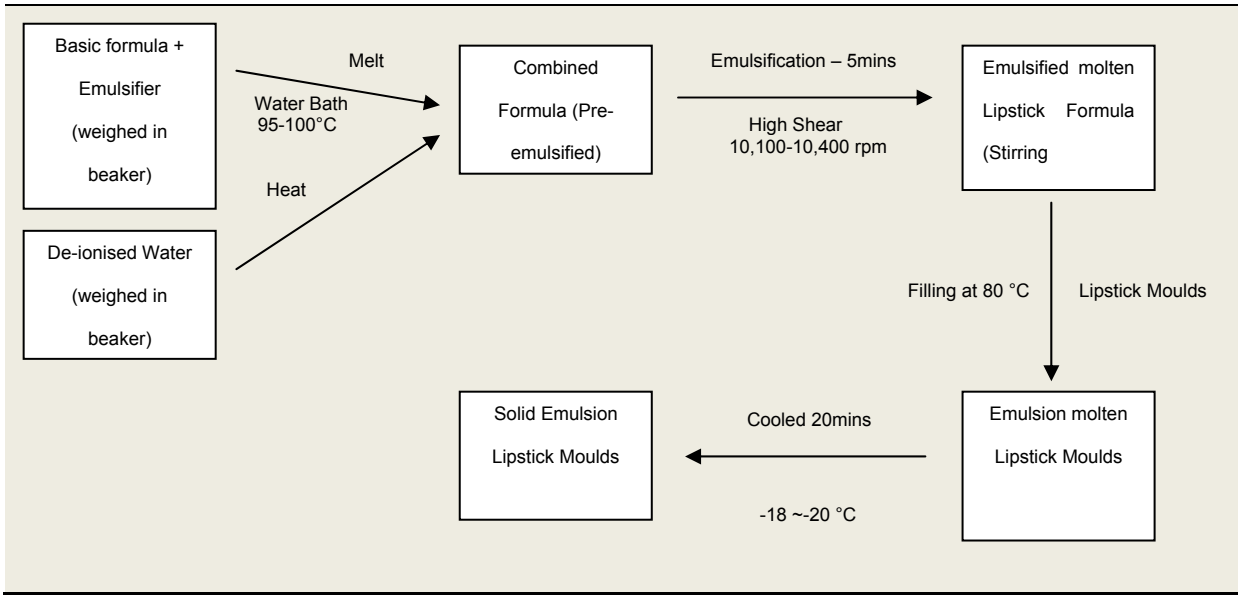
Table. 4.3. Lipstick Formulations

	Ingredients						
Formulations	Carnauba Wax (w/w %)	Micro-crystalline Wax (w/w %)	Castor Oil (w/w %)	Hard Paraffin (w/w %)	Water (w/w %)	Emulsifier (w/w %)	Total (w/w %)
Basic Lipstick	7.10	15.98	76.92	0.00	0.00	0.00	100
Emulsion 1 (10% water, 1% Emulsifier)	7.10	15.98	65.92	0.00	10.00	1.00	100
Emulsion 1 (20% water, 1% Emulsifier)	7.10	15.98	55.92	0.00	20.00	1.00	100
Emulsion 2 (10% water, 1% Emulsifier)	6.32	14.22	68.46	0.00	10.00	1.00	100
Emulsion 2 (20% water, 1% Emulsifier)	5.61	12.62	60.77	0.00	20.00	1.00	100
Emulsion 2 (30% water, 1% Emulsifier)	4.90	11.03	53.07	0.00	30.00	1.00	100
Emulsion 2 (40% water, 1% Emulsifier)	4.19	9.43	45.38	0.00	40.00	1.00	100
Emulsion 2 (10% water, 2% Emulsifier)	6.25	14.06	67.69	0.00	10.00	2.00	100
Emulsion 2 (20% water, 2% Emulsifier)	5.54	12.46	60.00	0.00	20.00	2.00	100
Emulsion 2 (30% water, 2% Emulsifier)	4.83	10.87	52.30	0.00	30.00	2.00	100
Emulsion 2 (40% water, 2% Emulsifier)	4.12	9.27	44.61	0.00	40.00	2.00	100
Emulsion 3 (40% water, 1% Emulsifier)	4.19	9.43	40.38	5.00	40.00	1.00	100
Emulsion 3 (40% water, 4% Emulsifier)	3.98	8.95	38.33	4.74	40.00	4.00	100

Three approaches were taken with regards to preparing the emulsion based lipsticks (Table 4.3). Emulsions based on the Basic lipstick formula were prepared by initially varying the amount of castor oil in the formula and keeping the amount of waxes and emulsifiers constant and secondly by varying the entire wax/oil content and again keeping the amount of emulsifier constant. The third approach was identical to the second with the addition of Hard Paraffin to produce a more rigid formula only at 40 wt% water content. The constrained emulsion lipstick formula design was again

chosen where the sum of all of the components was equal to 100 wt% (all components weight-weight percentage w/w%) and sample batch size in total was kept at 60 ml each time. The content of emulsion components was varied: aqueous phase (10-40 wt%), oil phase (56-89 wt%) and emulsifier (1-4 wt%). The emulsifiers used were Span 80 (HLB = 4.3), PGPR (HLB = 1.5 ± 0.5) and a blend of Span 80 (93.5%) and Tween 80 (6.5%); (HLB = 5).

Fig. 4.2. Flow Chart for the Preparation of Emulsion Lipstick



The Emulsion based Lipstick formulations were prepared as detailed in Figure 4.2. The Basic Lipstick as detailed in section 4.3 (which was essentially the continuous oil phase) and the emulsifiers were weighed separately in a beaker large enough to accommodate the de-ionised water (the dispersed phase), which was weighed separately in another beaker. Both beakers were placed in a water bath at 95 to 100 °C, to melt the basic oil phase and to heat the de-ionised water up to matching temperature.

The water was transferred directly to the molten oil phase and emulsifiers then emulsified using a Silverson L4 RT High Shear laboratory mixer for exactly 5 mins at 10,100 – 10,400 rpm.

The emulsified formulation was allowed to cool (with continuous stirring) to approximately 80 °C and then transferred to the lipstick moulds. For the high water content emulsions (30-40 wt%) the emulsion had to be transferred with a syringe as pouring became impossible due to shear thickening of the emulsion. This was due to the increase in interfacial area and resultant increase in the possibility of droplet interactions.

Once again the moulds were placed in a freezer at -18 to -20 °C for 20 min. In addition, according to research conducted by Hodge and Rousseau (2003), rapid crystallisation of wax in the continuous phase of a W/O emulsion following emulsification is an effective way of enhancing long-term stability. Samples were removed manually and kept for analysis.

4.5 Pulsed Nuclear Magnetic Resonance – pNMR; Emulsion stability & Droplet size distribution

The emulsion stability was assessed in terms of droplet coalescence. Each of the emulsions containing 40 wt% water content and 1 wt% emulsifier were analysed by means of the volume-weighted droplet diameter $D_{3.3}$ over a period of 127 days (4.5 months). Ideally a longer period (up to 6 months) would have been better, however the time allocated to the project would not allow this. Only the samples containing 40 wt% water content and 1 wt% emulsifier were assessed as the aim of the research was to produce stable products with up to 40% water content with the minimum

amount of potentially unfavourable additives. Any significant statistical increase in the volume-weighted droplet diameter $D_{3.3}$ over this period was used to determine the overall kinetic stability of each system.

The droplet size distribution achieved in any emulsification process is a result of the competition between two opposite processes; namely the breaking of droplets and the droplet-droplet coalescence (Tcholakova, Denkov & Danner, 2004). Both of these processes are promoted by the intensity of the emulsification process; here the hydrodynamic power density (energy) dissipated from the high shear mixer on the two immiscible liquids during emulsification. The rate of adsorption (diffusion coefficient) of the emulsifier to the droplet surface interface is dependent on type and concentration, the viscosity ratio between the two immiscible liquids and the volume fractions of the oil, wax and water.

Droplet size determinations by NMR were carried out with a low-resolution NMR spectrometer Bruker minispec, mq20, permanent magnetic strength 0.47 T, instrument settings (Table 4.4) and acquisition parameters (Table 4.5). The instrument was equipped with a variable temperature gradient probe head mq-PGU2, with operating range -10 up to 70 °C and a pulse gradient unit, field gradient strength 2 T/m. The calibrated pulsed gradient strength was determined measuring echo amplitudes without and with gradient using a sample of 0.5 mM $CuSO_4 \cdot 5 \cdot H_2O$ with a self-diffusion coefficient (Ds = 1.38 10^{-9} m^2/s) at 5 °C. Therefore all analyses, being W/O emulsions had to be conducted at 5 °C ± 2.5 °C via the use of external circulation cooling unit, cooled with water/ethylene glycol (circulating fluid). A thermometer was used to check the inside of the probe chamber prior to analysis. Approximately 0.5 to 0.6 ml sections (up to 1 cm height in NMR tube) of each of the

emulsions were taken in triplicate and analysed both for droplet size and at regular intervals over a period of 130 days in order to assess for emulsion stability to coalescence. These stability samples were all stored at room temperature in order to replicate the conditions comparable to storing typical cosmetics.

Table. 4.4. pNMR Instrument settings (software version V2.2)

Instrument settings	
90° Pulse Length:	8.5 µs
180° Pulse Lenth:	17.32 µs
Det. Angle broad:	351 °
Det. Angle narrow:	355 °
Gain:	59 dB
Recycle delay:	2 sec
Magnetic Field steps:	-59
Rec. Dead time:	0.0173 ms
Field Homog. Limit:	0.2 ms
NMR Base Frequency:	19.95 MHz
NMR Frequency offset:	+8.00 kHz

Table. 4.5. Acquisition parameters for W/O droplet size analysis

Acquisition parameters	
Gradient Pulse separator – Ldelta (Δ):	210 ms
Gradient Pulse width – delta (δ):	19 ms
Oil Suppression delay – Tau_null (T_0):	28.84 ms
Diffusion coefficient:	1.38 10^{-9} m^2/s
Analysis Temperature:	5 °C ± 2.5 °C

4.5.1 Droplet Size Distribution measurement

Log-normal droplet (particle) size distributions are mathematically described as follows:

$$q_i(d) = \frac{1}{d \times \sigma \times \sqrt{2\pi}} \times e^{\left(-\frac{(\ln(d)-\ln(d_{50,i}))^2}{2\sigma^2}\right)} \quad (4.7)$$

Where $q_i(d)$ is the relative frequency of a droplet with a specific diameter, d is the droplet diameter, σ is standard deviation of the normal distribution plot,

Geometric median (mean) diameter $d_{50,i}$; 50 % of droplets are smaller and 50 % larger than this diameter, e is the natural exponential function.

Note:

$d_{50,0}$; 50% of the total number of droplets, have diameter at this size.

$d_{50,3}$; 50% of the total volume of droplets, have diameter at this size.

$d_{1,0}$; number-length mean (e.g. droplets measured via microscopy)

$d_{2,0}$; number-surface area mean (based on surface area of droplets)

$d_{3,0}$; number-volume or number-weight mean

$d_{2,1}$; length-area mean

$d_{3,1}$; length-volume mean

$d_{3,2}$; surface area-volume mean or surface area moment mean – Sauter Mean Diameter

$d_{4,3}$; volume-mass mean or volume/mass moment mean – De Broukere Mean Diameter

$d_{0,0}$; number-weighted mean (e.g. NMR)

$d_{3,3}$; volume-weighted mean (e.g. NMR)

The surface-weighted mean $d_{3.2}$ was calculated from the volume-weighted mean $d_{3.3}$ using the following equation (4.8) :

$$d_{3.2} = d_{3.3} \times e^{-0.5\sigma^2} \qquad (4.8)$$

Where σ is the standard deviation of the logarithm of the droplet diameter and e is the natural exponential function (Duynhoven ey al., 2002).

4.6 Microscopy

Optical (Light) Microscopy and cryo-Scanning Electron Microscopy were used to observe, evaluate and classify the size of the droplets individually. This was also used to assess visually the degree of emulsion instability, in terms of droplet flocculation, partial coalescence etc. An association was then made between the results obtained here and those obtained using the NMR.

4.6.1 Optical Microscopy

A Reichert-Jung Polyvar Met Optical Microscope was used for the analysis, capable of a wide range of incident and transmitted light techniques. The Illumination system was made up of a 100 Watt halogen low voltage lamp with a colour temperature of 3200 K.

This system was capable of producing accurate images of extremely large object fields with the absence of chromatic and spherical aberration. The objectives were plan achromates and plan fluorites for infinite tube lengths and had a high brilliance, resolution and flatness of field. Standard, long working distance (LWD) and extra-long working distance (XLWD) objectives were available. Objective magnification were 10x, 25x, 40x and 100x (with Oil).

Microscope slides used were from Thermo Scientific size 76 x 26mm, thickness 1.0-1.2mm. Cover glass (borosilicate) slides used were from VWR International, 22 x 50mm, thickness no. 1.5.

4.6.2 Cryo-Scanning Electron Microscopy – Cryo-SEM

A Philips XL-30ESEM Cryo-Scanning Electron Microscope was used for the analysis. Cryogenic temperatures were used to preserve the structure of the sample in the original chemically unmodified state.

A small amount of the sample (approximately 3 x 2 x 6 mm) was fixed onto the sample holder, the holder having a layer of carbon-rich conductive glue (conductive to allow discharge of electrons). The sample was then frozen (cryo-fixed) rapidly in a bath of boiling-liquid nitrogen at -196 to -210 °C for about 2 min. The sample was then transferred to the high vacuum cryo-unit chamber and freeze fractured. Any surface water was sublimated and a thin layer (approximately 10 nm) of gold sputtered onto the surface. This was done to aid conductance with electrons. The sample was then inserted into the observation chamber and observations were carried out at 3-5 kV at temperatures between -100 and -175 °C.

4.7 Texture Profile Analysis - TA

The Texture Profile analysis on the formulated products was conducted with a Stable Micro Systems TA.XTPlus Texture analyser. With the cosmetic samples being temperature sensitive, it was imperative that the temperature was carefully monitored with all tests being conducted at the same temperature throughout.

4.7.1 Penetrometer Test

The initial method used, was based on that which uses a penetrometer to determine the extent of penetration of a standard needle. This was carried out mainly as an indicator for hardness, yield stress and interfacial film strength of the different emulsifiers. A standard (SMS P/2N) 2 mm needle was selected, using a 5 kg load cell. Due to the absence of a temperature controlled chamber, all of the tests were conducted at room temperature 24.5 ± 0.5 °C according to the settings as detailed in Table 4.6, using sections of sample measuring 25 mm in length, with the standard lipstick diameter of 11.80 mm. With a chamber it would have been ideal to conduct the tests at 32 °C lip temperature.

Table. 4.6. TA settings Exponent Stable Micro Systems version 4,0,13,0

TA Penetrometer Settings	
Test Mode:	Compression
Pre-Test Speed:	0.50 mm/sec
Test Speed:	0.50 mm/sec
Post-Test speed:	10.00 mm/sec
Force:	15.0 g
Hold Time:	3.0 sec
Trigger Type:	Auto (Force)
Trigger Force:	5.0 g
Advanced Options:	Off

The sample cuts were placed centrally under the needle probe and the needle adjusted until it was just above the sample (approximately 1-1.5 mm) and the probe tared (zero) prior to analysis.

Once the trigger force of 5.0 g was attained this triggered the start of the test where the needle proceeded to penetrate the sample at 0.50 mm/sec until a force of 15 g was achieved, at which point the probe head maintained a 3.0 sec hold time prior to extracting the needle at 10 mm/sec. After each test, the needle tip was wiped clean towards the point. Plots of needle penetration Distance (mm) vs Time (sec) were obtained as shown in Figure 4.3, and these values compared against those of standard conventional lipstick samples.

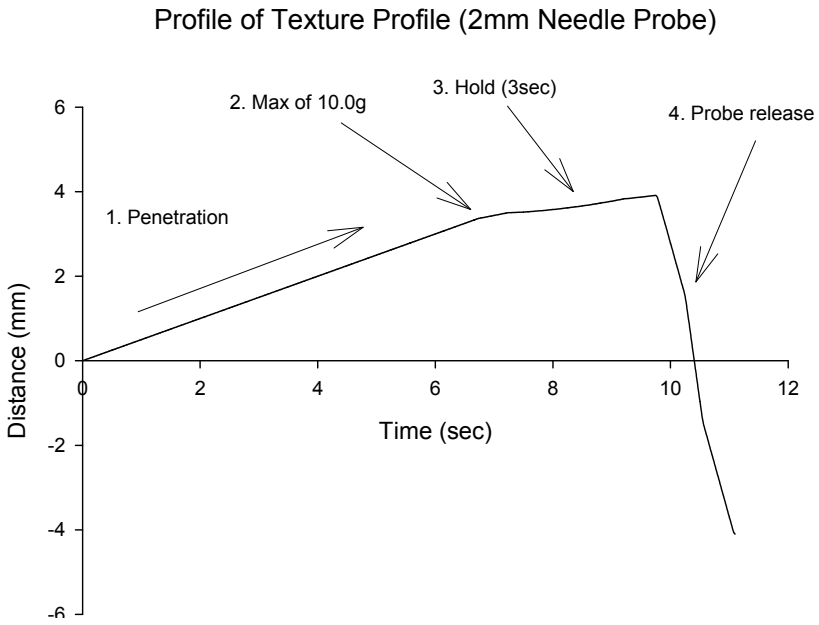


Fig. 4.3. Profile of Penetrometer Test

4.7.2 Compression Test

The second method used, was based on the compression test (crushing) to determine specifically the brittleness and hardness of the samples.

This involved the use of a standard compression plate (SMS P/40) with a 40 mm diameter and again a 5 kg load cell. All tests again were conducted at room temperature 24.5 ± 0.5 °C according to the settings as detailed in Table 4.7 with sections of samples measuring 10 mm.

Table. 4.7. TA settings Exponent Stable Micro Systems version 4,0,13,0

TA Compression Settings	
Test Mode:	Compression
Pre-Test Speed:	0.50 mm/sec
Test Speed:	0.50 mm/sec
Post-Test Speed:	0.50 mm/sec
Target Mode:	Distance
Distance:	4.000 mm
Trigger Type:	Automatic (force) g
Trigger Force:	0.5 g
Break Mode:	Off
Stop Plot at:	Start Position (20mm above base plate)
Tare Mode:	Auto

The sample cuts were again placed centrally, this time under the compression plate and the plate adjusted and set to 20 mm above the sample base plate and the probe tared (zero) prior to analysis.

Once a trigger force of 0.5 g was attained this triggered the start of the test where the compression plate proceeded to compress the sample at 0.5 mm/sec to a target distance of 4.000 mm. After compression the system being automated returned to its start position. Between each test the compression plate was cleaned prior to the

start of the subsequently test. Plots of Compression force (g) vs Time (sec) were obtained as shown in Figure 4.4, and these values compared against those of standard conventional lipstick samples.

The peak (plot maximum) value obtained for the compression force determined the firmness of the sample. The lower the value obtained the softer the samples, the higher the firmer the sample. The area of the curve up to this maximum point is taken as a measure of consistency. The higher this value is, the thicker the consistency. The negative region of the plot (produced on plate return) was used also to determine the cohesive (adhesive) properties of the lipstick. This gives an indication of the consistency/resistance to spread. The more negative the value the more cohesive the sample. The area of the negative region of the curve may be referred to as the 'work of cohesion'. The higher this value is, the more resistant the lipstick has to breaking down, the higher the adhesive properties and viscosity (Smewing, 1998).

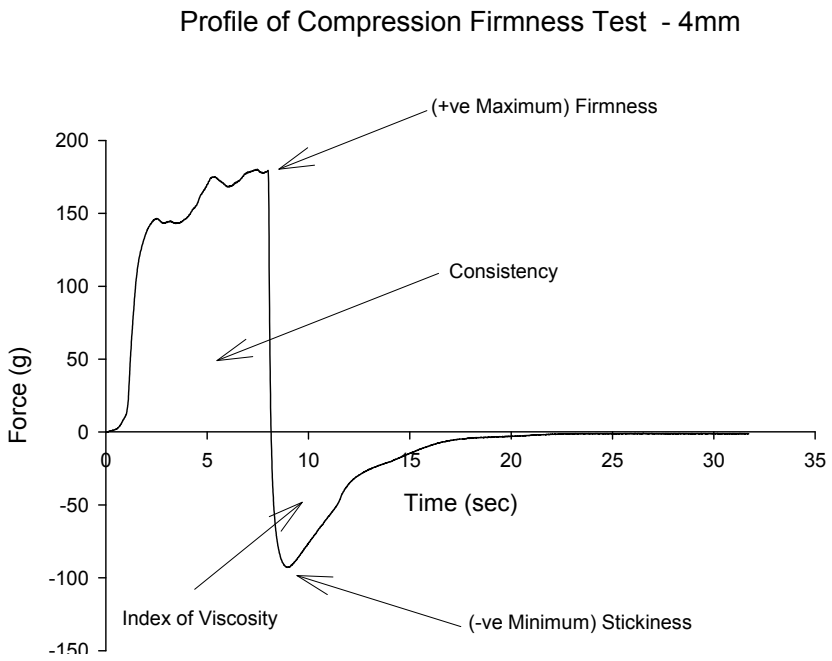


Fig. 4.4. Profile of Compression Firmness Test conducted

4.7.3 Rheology

Rheological non-destructive oscillation testing was conducted in order to predict and quantify the samples' properties under deformation, before flow i.e. without destroying the structure. This will give an indication of specifically the viscoelasticity profile, structure, toughness, flow and emulsion stability with varying water and emulsifier content.

Rheological analysis was conducted on a Bohlin CVO 120 Rheometer (Malvern Instruments Range) according to settings detailed in Table 4.8, using Bohlin Software version 6. 50. 5. 8. All Viscoelastic property measurements were conducted using a serrated 25 mm parallel plate geometry (PP25) with corresponding base plate to eliminate plate slip due to the high oil and wax content of the samples involved. All tests were conducted at 32 °C (Lip temperature) controlled by means of a circulating water bath.

Table. 4.8. Viscoelastic – Dynamic oscillation sweep settings (Stress controlled)

Oscillation sweep settings			
Temp Mode :		ISOTHERMAL 32.0 °C	
Thermal Equilibrium Time :		0.00 s	
Pre-Shear :		OFF	
Auto-Tension :		OFF	
Shear mode :		Controlled Stress	
Sweep Type :	AMP SWEEP	Range :	LOG
Frequency :	1 Hz	No. Samples :	31
Strain Control :	OFF		
Steady Shear Stress :		0 Pa	
Minimum Stress :	0.512 Pa	Maximum Stress :	512.000 Pa
Ramp Direction :	Up		
Periods :	8.00	Points :	8192

5 Results, Data Analysis & Discussion

5.1 Introduction

The aim of this thesis was to formulate stable W/O emulsion lipsticks with up to 40 wt% water content, concurrent with all of the skin feel organoleptic qualities of a conventional lipstick. These qualities along with overall stability were subsequently characterised using the following techniques: DSC for thermo-physical characterisation of microcrystalline structure along with melting point and melting point range, Oscillation Rheology and Texture profiling to assess spreadability, viscoelasticity, texture and emulsion stability, and pNMR in conjunction with Microscopy to determine droplet size, droplet size distribution and long term emulsion stability.

5.2 Interfacial tension

Figures 5.1 & 5.2 shows interfacial tension measurements of castor oil against a water phase containing Span 80, PGPR and a blend of Span 80 with Tween vs Concentration of Emulsifier (mg/L) and concentration Natural logarithm - ln Conc. respectively. From Figure 5.1, it is evident that all of the emulsifiers and blends possess surface active properties, reducing the initial interfacial tension from 10.65mN/m with increasing concentrations. A greater reduction in the interfacial tension was observed for both PGPR and the blend of Span 80 with Tween 80 than for Span 80 alone with the blend proving to be extremely effective at reducing interfacial tension at much lower concentrations than both of the others due to interfacial tensions being reduced on both sides of the interface. In addition the

critical micelle concentration (CMC) of the blend is significantly lower than that of Span 80 and PGPR as observed by the equilibrium interfacial tension isotherm (Figure 5.1) and the surface excess concentration value of 0.19 x 10^{-6} mol/m^2 compared with 0.90 x 10^{-6} and 1.02 x 10^{-6} mol/m^2 for PGPR and Span 80 alone respectively (Table. 5.1). As expected, the average packing area per molecule was much higher; 887 $Å^2$ compared to 185 and 163 $Å^2$ for PGPR and Span 80 alone respectively.

Very hydrophilic emulsifiers such as Tween 80 will when adsorbed at the interface only form expanded monolayers (Krog, 1977; Lu & Rhodes, 2000) which would explain the excessive large packing area value of 887 $Å^2$ (Table 5.1). In addition to this, the expanded polyoxyethylene sorbitan head (increasing ethene oxide EO groups) (Figure 5.7 and 5.8) will reduce the CMC value, favouring micellisation (Santos et al., 2009) which would explain the lower CMC value compared to PGPR and Span 80 alone. In order to achieve optimum stability a strong closely packed cohesive monolayer film is essential to prevent droplet coalescence. This would suggest that the blend of Tween 80 with Span 80 based on the values obtained (Table 5.1) may not be as strong as that produced using Span 80 alone or PGPR even though it appears to have better surface active properties than Span 80 alone.

Although the CMC, surface excess concentration and the packing area for both PGPR and Span 80 appear to be similar, Span 80 showed a slightly higher surface excess concentration, showing tighter packing. Admittedly both emulsifiers contain different hydrophilic and hydrophobic groups making it difficult to make a direct comparison, however the polyglycerol group (Figures 5.3 and 5.4) has a molar volume almost twice that of the sorbitan group (Figures 5.5 and 5.6), which could be a contributing factor to the aforementioned differences. Nonetheless PGPR was

found to be better at reducing the interfacial tension as increasing chain length has a tendency to promote enhanced chain-chain interactions leading to lower interfacial tension (Chattopadhyay, Shah and Ghaicha, 1992). Generally it has been noticed that for a homologous series of non-ionic emulsifiers, the increase in the hydrophobic chain length increases the apparent CMC at the oil-water interface (Peltonen & Yliruusi, 2000; Zhang and Yin, 2005). Again with the emulsifiers being non-homologous it was not possible to model a direct comparison.

Note that the average packing of the area for the blend is a mixture of both the Span 80 (93.5%) and Tween 80 (6.5%) expanded monolayer molecules.

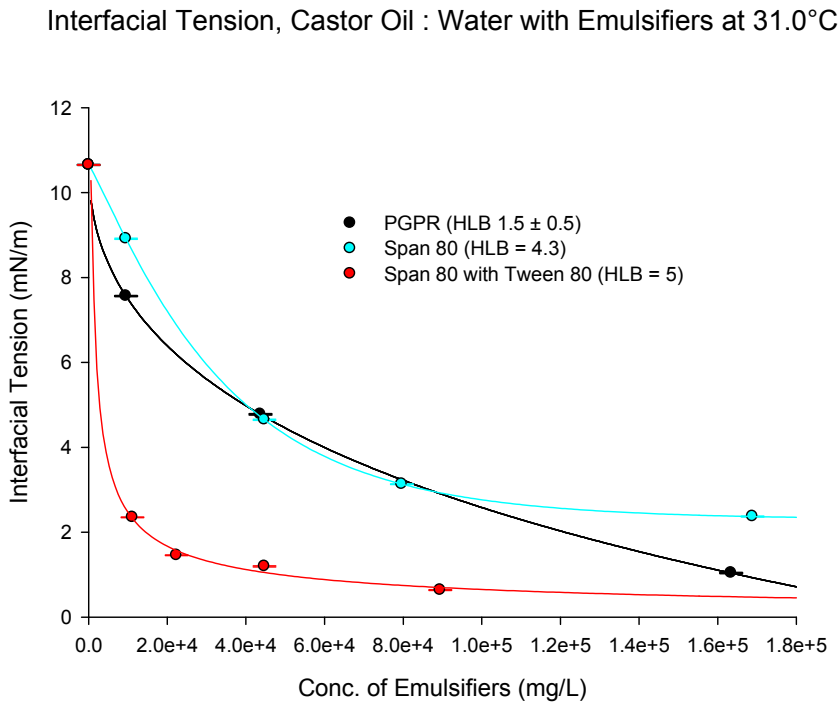


Fig. 5.1. Isotherms of equilibrium Interfacial Tension (mN/m) vs Concentration of Emulsifier (mg/L), between Castor oil and water (de-ionised), measured by Kruss Standard Plate (Pt). Emulsifiers tested: Span 80 (HLB = 4.3), PGPR (HLB = 1.5 ± 0.5) and a blend of Span 80 with Tween 80 (HLB = 5).

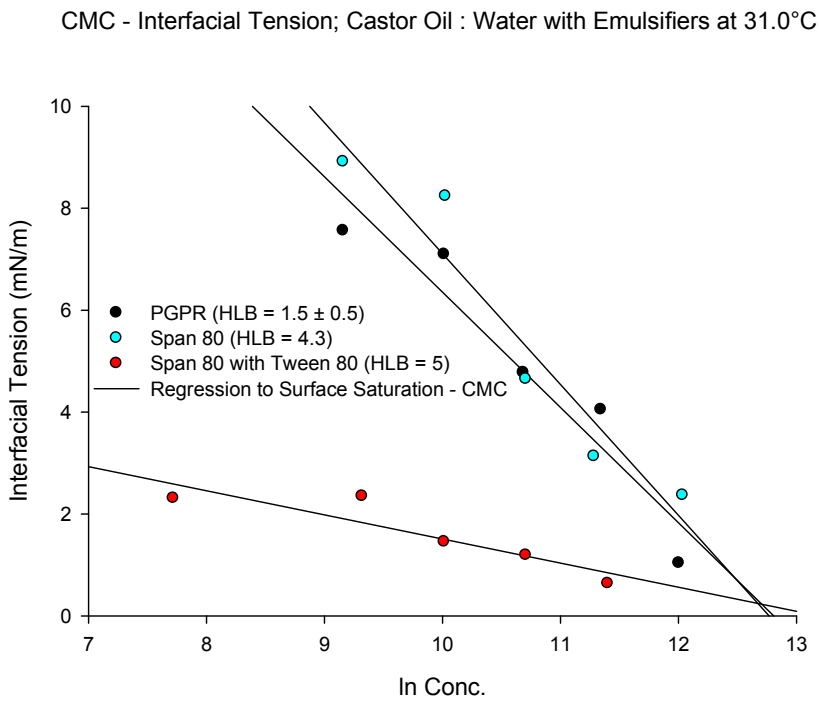


Fig. 5.2. Isotherms of equilibrium Interfacial Tension vs concentration natural logarithm - ln Conc. (mg/L) between Castor oil and water (de-ionised), measured by Kruss Standard Plate (Pt). Emulsifiers tested: Span 80 (HLB = 4.3), PGPR (HLB = 1.5 ± 0.5) and a blend of Span 80 with Tween 80 (HLB = 5). ***Showing only the linear regression portion approaching the surface saturation critical micelle concentration points.***

Table. 5.1. Surface activity of Emulsifiers and blend at 31.0°C.

Emulsifier	$\frac{d\sigma}{dlnC}$	R^2	Γ (mol/m^2)	Area (Å^2)
PGPR (HLB = 1.5 ± 0.5)	-2.26	0.92	0.90 x 10^{-6}	185
Span 80 (HLB = 4.3)	-2.57	0.92	1.02 x 10^{-6}	163
Span 80 with Tween 80 (HLB = 5)	-0.47	0.82	0.19 x 10^{-6}	887

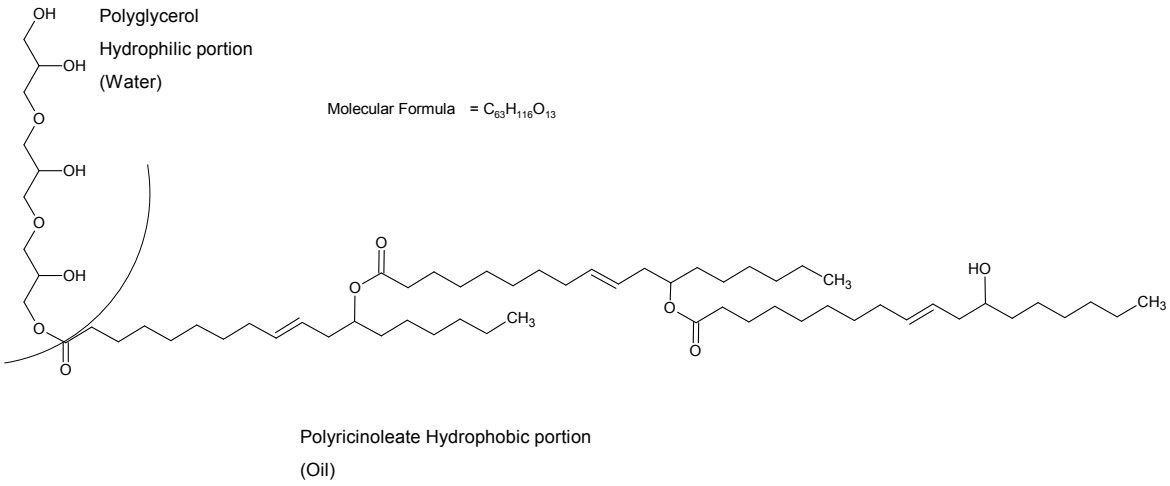


Fig. 5.3. Molecular structure of Polyglycerol polyricinoleate – PGPR.

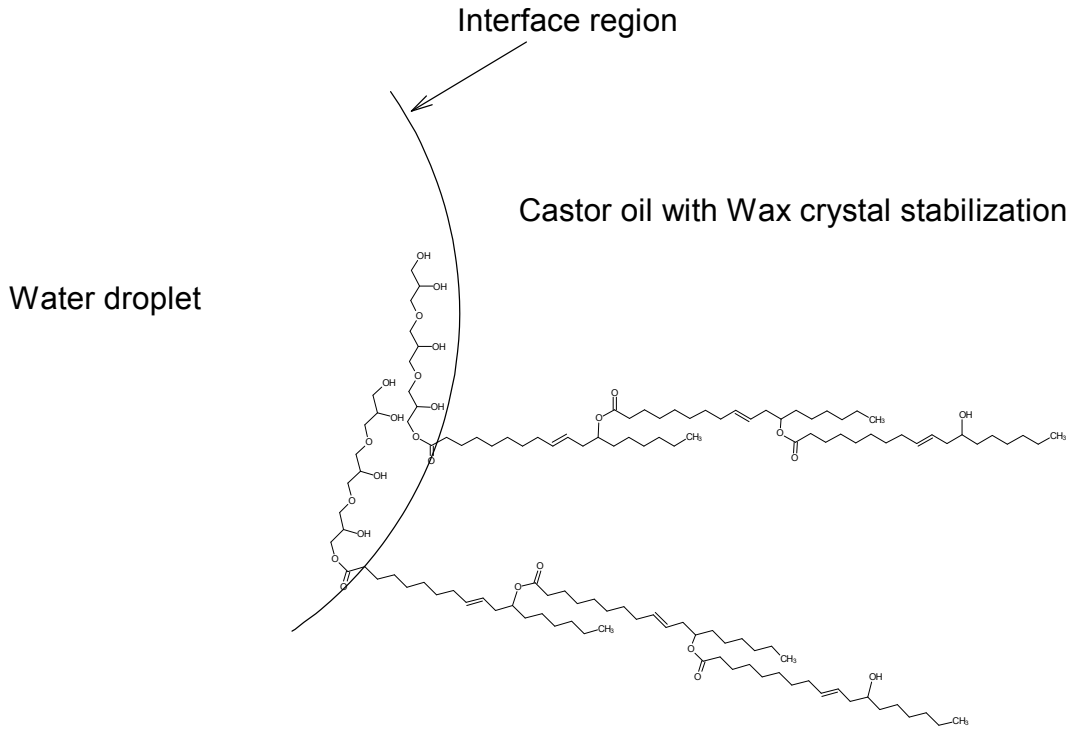


Fig. 5.4. Schematic orientation of two PGPR molecules in a W/O emulsion adsorbed at the oil-water interface.

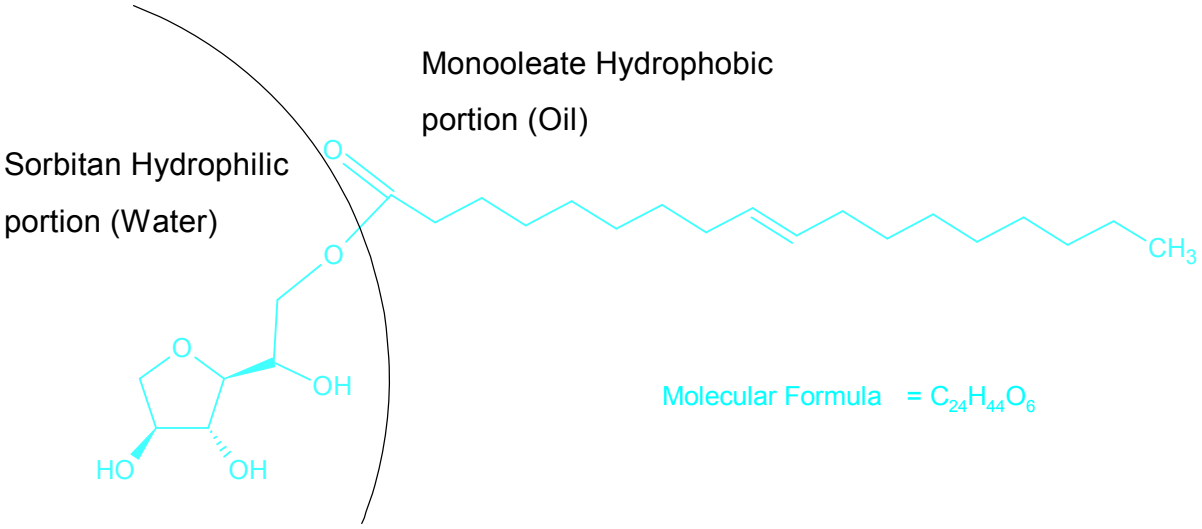


Fig. 5.5. Molecular structure of Sorbitan monooleate – Span 80.

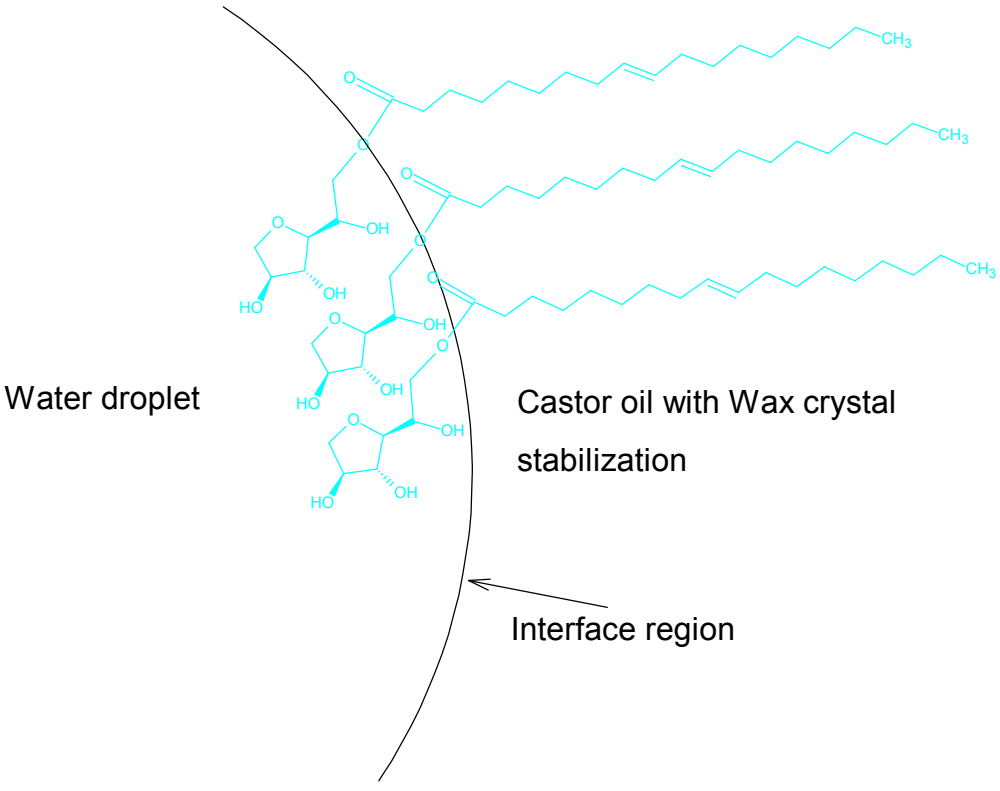


Fig. 5.6. Schematic orientation of two Span 80 molecules in a W/O emulsion adsorbed at the oil-water interface.

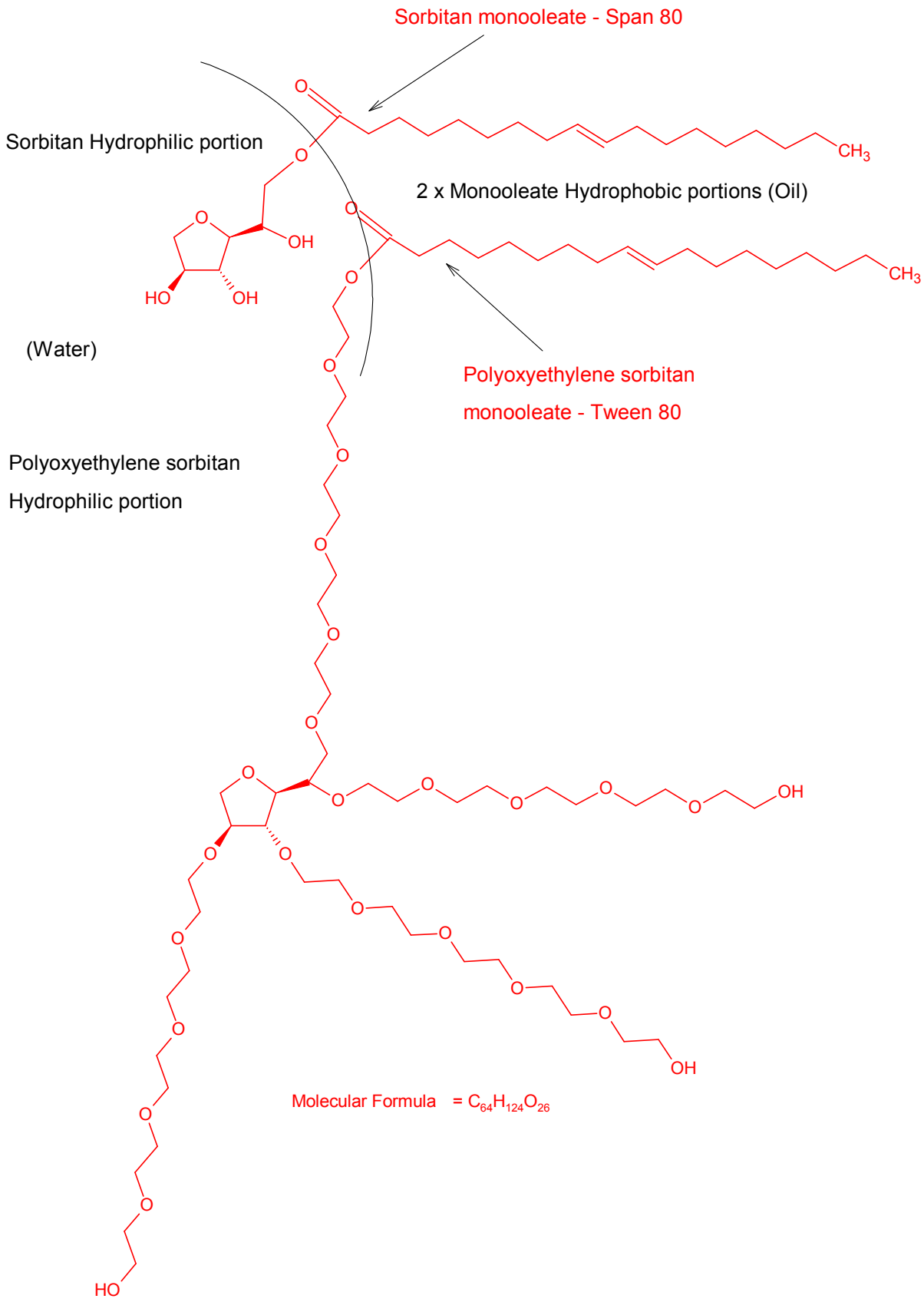


Fig. 5.7. Molecular structure of Polyoxyethylene sorbitan monooleate – Tween 80 and Sorbitan monooleate – Span 80.

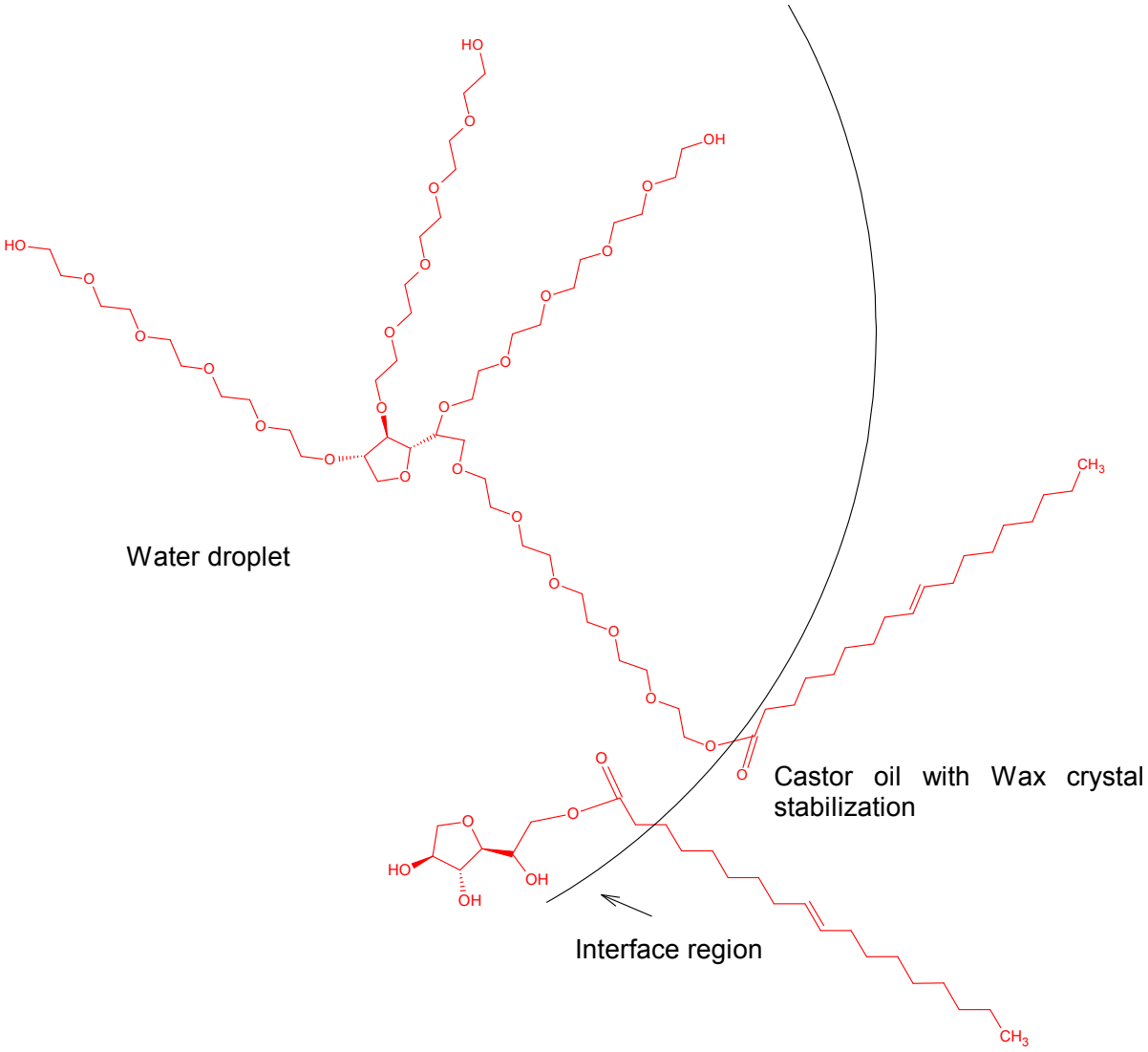


Fig. 5.8. Schematic orientation of Span 80 and Tween 80 molecules in a W/O emulsion adsorbed at the oil-water interface.

5.3 Thermo-physical Characteristics using Differential Scanning Colorimetry – DSC on Raw Waxes & Basic Lipstick Formula

5.3.1 Thermo-physical Characteristics – DSC on Waxes

Table 5.2 present a summary of the thermo-physical values obtained with onset temperatures (start of melting or hardening process), the peak maxima (melting point) and enthalpies of a selection of waxes used in a conventional lipstick. The corresponding thermograms, Figures 5.9 to 5.14 are presented in the Appendix with accompanying chemistry of their thermo-physical characteristics. It is important to note that both Beeswax and Carnauba wax produced three endothermic events. This was due to either lack of purity and other admixtures being present or a mixture of hydrocarbons. It could also be due to polymorphism where one would expect to see two (dimorphism) or three (trimorphism) endothermic events due to differences densities and as a result subsequent differences in melting points.

Table. 5.2. Thermo-physical Characteristics of Waxes using Differential Scanning Colorimetry.

Wax	No. of DSC endothermic events	Temperature °C (Onset) & Maximum	Enthalpy J/g
Beeswax	3	(17.2) 29.3,41.1 & 49.1	169.7
Berry wax	2	(27.1) 42.8 & 47.6	104.6
Carnauba wax	3	(44.7) 54.0, 72.0 & 78.3	193.2
Hard Paraffin	2	(21.4) 32.6 & 51.2	195.2
Microcrystalline	2 (combined)	(27.1) 47.9 & 62.0	140.1
Multiwax	2 (combined)	(18.2) 47.8 & 58.3	121.9

5.3.2 Wax selection for Simplified Basic Lipstick Formula & Thermo-physical Characteristics – DSC Basic Lipstick Formula

Both Carnauba and Microcrystalline wax were selected in order to produce the Basic Lipstick formula whose DSC thermogram is presented in Figure 5.15 based on a number of factors.

Carnauba wax possess the highest degree of crystallinity (193.2 J/g) and the highest melting point along with the firmest rigid structure – due to long chain fatty acids esterified with long chain alcohols. This was therefore chosen to form the basis of the structure which is required for satisfactory moulding. Only Hard Paraffin wax which was subsequently used in the final formula at 40 wt% water content only for firmness, had a higher degree of crystallinity (195.19 J/g), however its melting point was not high enough to achieve a melting point range of 55 to 75 °C in the basic formula. The content of carnauba wax was kept to the minimum as excessive amounts would have produced a product too rigid, with too high a yield stress making application extremely difficult. With the selection of non-ionic emulsifiers and a non-existent electric diffuse layer, the carnauba wax also formed the stabilizing rigid crystalline wax matrix (continuous phase bulk viscosity) required to prevent flocculation of the water droplets (dispersed phase) in the emulsion formulation.

Microcrystalline wax which was interchangeable with multiwax was selected for its characteristic flexible, tacky, elastic properties which is required for a conventional lipstick. In addition it was the only wax, which when formulated was able to produce a product with a softening point of 32 °C (skin temperature) and a melting point range of 55 to 75°C, a fundamental prerequisite for a good quality lipstick (McKetta, 1993). Additionally, the wax possessed a microscopic crystalline structure (140.1 J/g), facilitated by means of flash cooling which was required, not only in the basic

and conventional formula for quality and to bind the oil to prevent sweating, but also proved ideal for surface-active stabilisation in the subsequent W/O emulsion product. The microcrystalline structure given its smaller size and hence higher surface area should lead to increased particle interactions (droplet coverage) via interacting with the hydrocarbon (hydrophobic/lipophilic) chain of the non-ionizing emulsifier and should potentially increase the interfacial viscosity and therefore the overall stability of the emulsion (Lee, 1999; Rousseau, 2000).

In order to achieve the correct chemical and physical characteristics, 7.1 wt% Carnauba wax was combined with 15.98 wt% Microcrystalline wax and 76.92 wt% Castor oil to produce a product (Basic Lipstick) with an enthalpy of 44.04 J/g and a softening point and melting point range characteristic to that of a conventional lipstick.

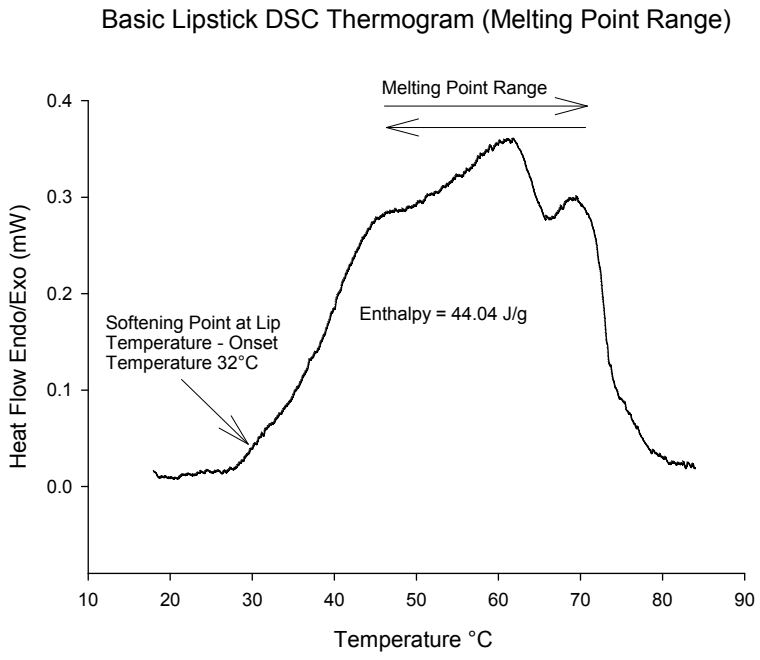


Fig. 5.15. DSC Thermogram for the Basic Lipstick formula (Melting Point Range) containing 7.1 wt% Carnauba wax, 15.98 wt% Microcrystalline wax and 76.92 wt% Castor oil.

5.3.3 Thermo-physical Characteristics – DSC on Emulsions

The degree of crystallisation for each of the emulsion lipstick samples was compared with that of the basic sample by assessment of the thermo-physical changes within the samples by DSC as indicated by the thermograms (Figures 5.16 to 5.23). Whilst all of the thermograms are plotted on the same heat flow scale (mW), due to the fact that slightly different samples weights were used throughout for each test, a breakdown of the endothermic events per unit mass (J/g), are detailed in Table 5.3.

On observation one can see that all of the emulsion samples have the same characteristic melting profile to that obtained for the basic sample. The emulsion samples containing hard paraffin also show the same characteristic profile with an additional endothermic event mid way (47 to 55 °C) along the melting point range (Figure 5.23), which naturally ties in with that for the hard paraffin (Figure 5.12).

Surprisingly although there is a drop in enthalpy compared to the basic sample, there is no significant consistent reduction in enthalpy throughout with increasing water content as would be expected with changes in the volume and weight fraction. A reduction was however observed with the 40 wt% samples, which was amended with the addition of hard paraffin, which was expected with hard paraffin having the highest degree of crystallinity of all the waxes. Increasing the emulsifier content from 1 % to 2 % and subsequently 4 % for the hard paraffin samples did not make any significant difference to the degree of crystallisation. This would in all probability indicate that a content of 1 wt% emulsifier throughout, even at the highest water content is sufficient (or in excess) in production of emulsion lipstick products as increasing the concentration would give rise to a smaller drop size distribution and a

higher degree of surface active crystallinity. With this being the case it may not be a significant enough change to see a change in the overall enthalpy value.

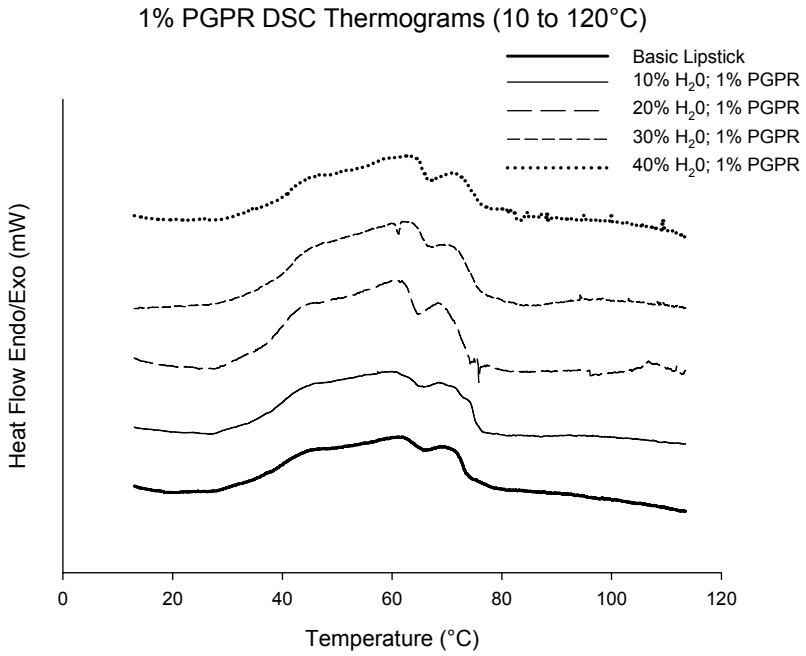


Fig. 5.16. DSC Thermograms for the Basic Lipstick formula and Emulsion Lipstick Formulas 10, 20, 30 and 40 wt% water content with 1 wt% PGPR.

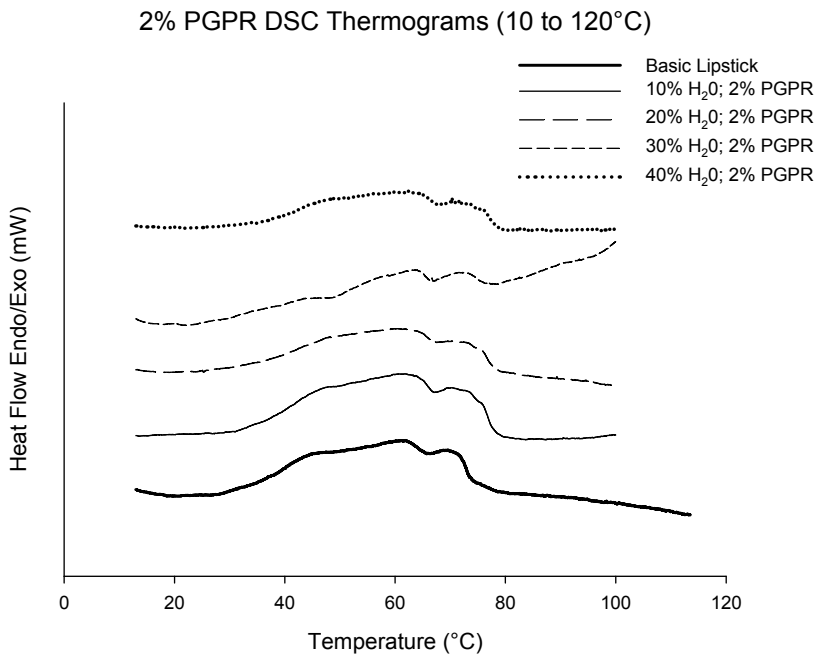


Fig. 5.17. DSC Thermograms for the Basic Lipstick formula and Emulsion Lipstick Formulas 10, 20, 30 and 40 wt% water content with 2 wt% PGPR.

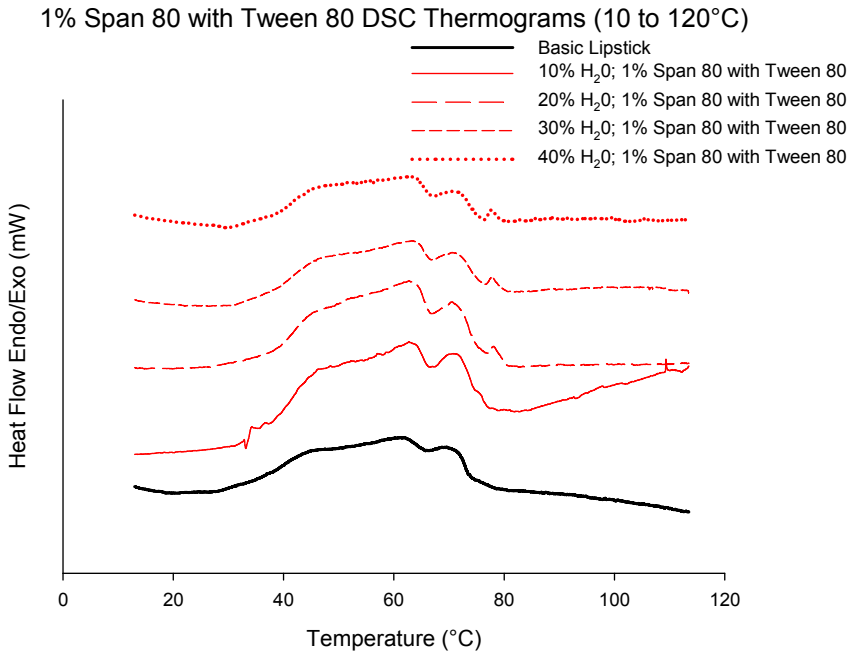


Fig. 5.18. DSC Thermograms for the Basic Lipstick formula and Emulsion Lipstick Formulas 10, 20, 30 and 40 wt% water content with 1 wt% Span 80 with Tween 80.

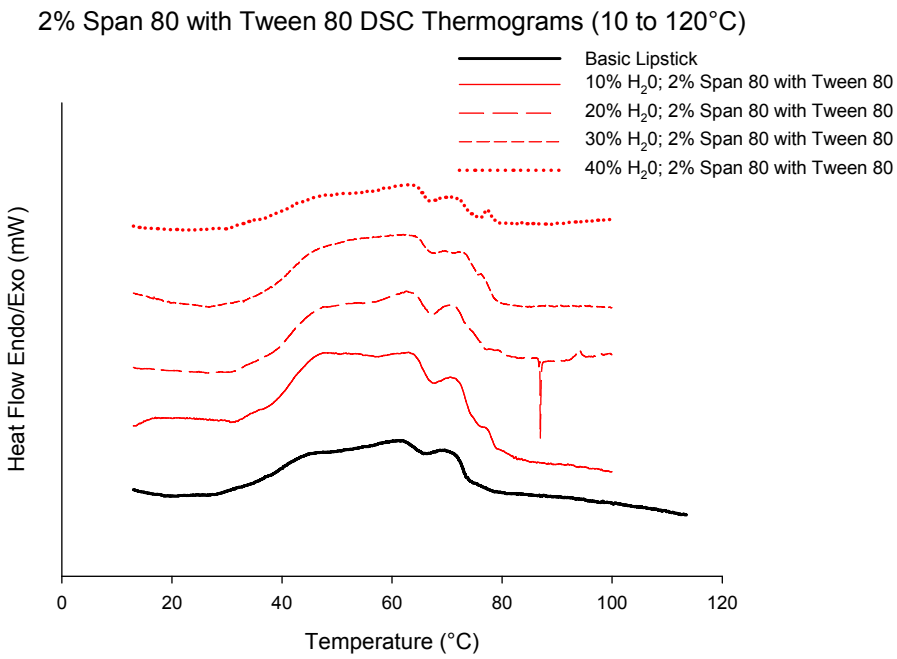


Fig. 5.19. DSC Thermograms for the Basic Lipstick formula and Emulsion Lipstick Formulas 10, 20, 30 and 40 wt% water content with 2 wt% Span 80 with Tween 80.

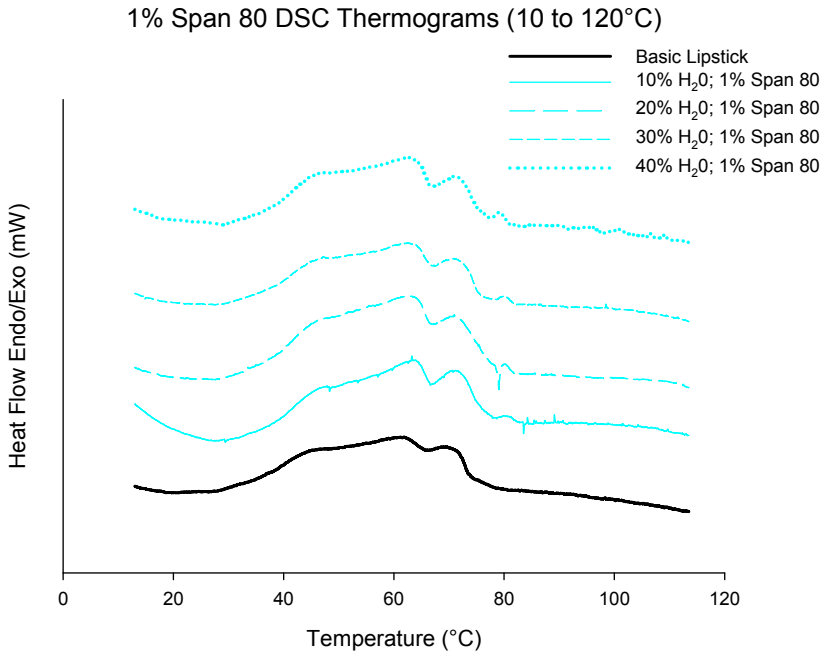


Fig. 5.20. DSC Thermograms for the Basic Lipstick formula and Emulsion Lipstick Formulas 10, 20, 30 and 40 wt% water content with 1 wt% Span 80.

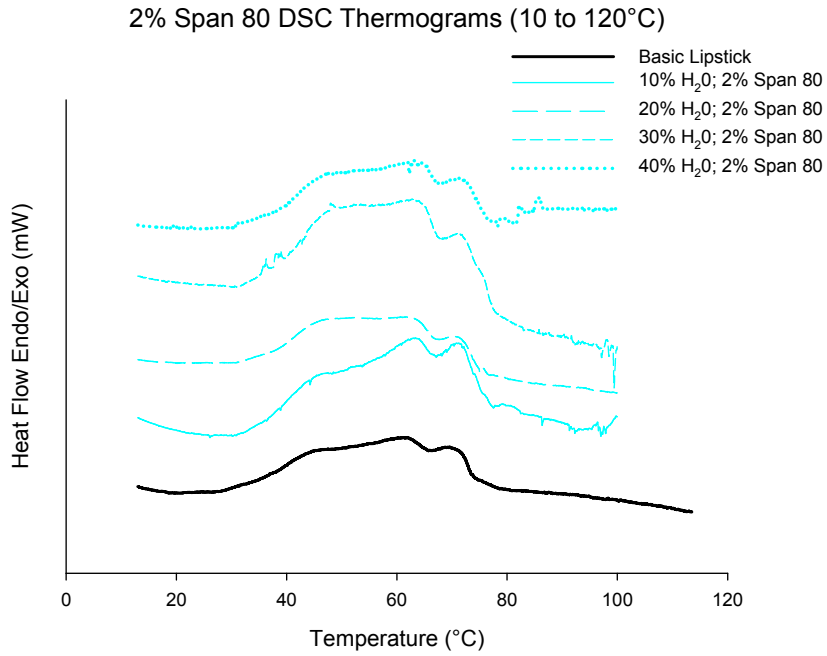


Fig. 5.21. DSC Thermograms for the Basic Lipstick formula and Emulsion Lipstick Formulas 10, 20, 30 and 40 wt% water content with 2 wt% Span 80.

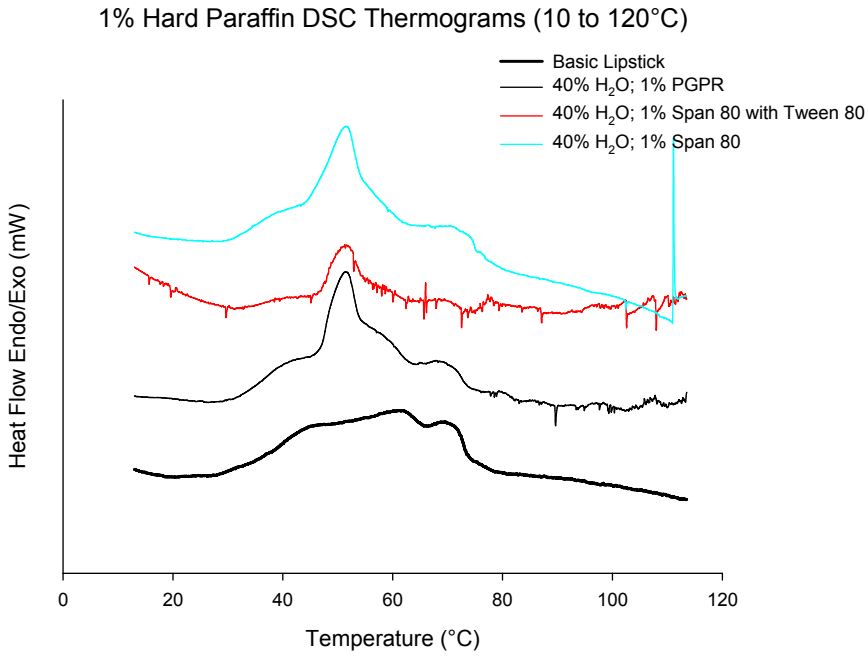


Fig. 5.22. DSC Thermograms for the Basic Lipstick formula and Hard Paraffin Emulsion Lipstick Formulas containing 40 wt% water content with 1 wt% Emulsifiers PGPR, Blend of Span 80 with Tween 80 and Span 80.

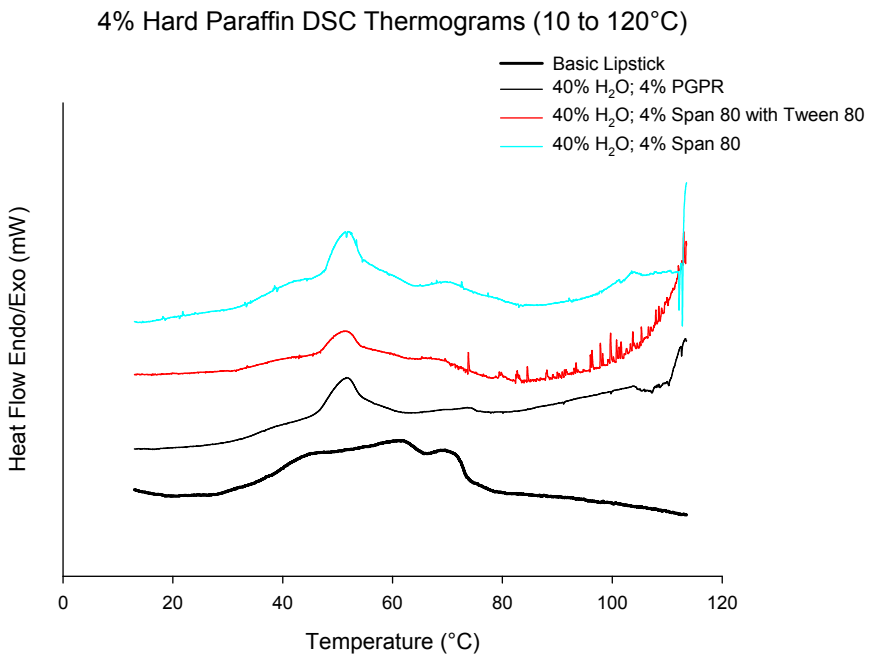


Fig. 5.23. DSC Thermograms for the Basic Lipstick formula and Hard Paraffin Emulsion Lipstick Formulas containing 40 wt% water content with 4 wt% Emulsifiers PGPR, Blend of Span 80 with Tween 80 and Span 80.

Table. 5.3. Thermo-physical characteristics comparisons for Basic Lipstick and Emulsion samples

Lipstick Sample	Enthalpy J/g
Basic Sample	44.04
10% H_2O; 1% PGPR	27.33
10% H_2O; 1% Span 80 with Tween 80	29.34
10 % H_2O; 1% Span 80	26.59
10% H_2O; 2% PGPR	27.52
10% H_2O; 2% Span 80 with Tween 80	28.40
10 % H_2O; 2% Span 80	27.29
20% H_2O; 1% PGPR	27.18
20% H_2O; 1% Span 80 with Tween 80	27.35
20 % H_2O; 1% Span 80	27.00
20% H_2O; 2% PGPR	30.88
20% H_2O; 2% Span 80 with Tween 80	30.77
20 % H_2O; 2% Span 80	26.28
30% H_2O; 1% PGPR	33.89
30% H_2O; 1% Span 80 with Tween 80	28.55
30 % H_2O; 1% Span 80	25.65
30% H_2O; 2% PGPR	24.49
30% H_2O; 2% Span 80 with Tween 80	27.63
30 % H_2O; 2% Span 80	27.46
40% H_2O; 1% PGPR	30.19
40% H_2O; 1% Span 80 with Tween 80	21.33
40 % H_2O; 1% Span 80	21.21
40% H_2O; 2% PGPR	18.76
40% H_2O; 2% Span 80 with Tween 80	20.51
40 % H_2O; 2% Span 80	23.13
Hard Paraffin 40% H_2O; 1% PGPR	31.77
Hard Paraffin 40% H_2O; 1% Span 80 with Tween 80	25.18
Hard Paraffin 40% H_2O; 1% Span 80	27.44
Hard Paraffin 40% H_2O; 4% PGPR	28.93
Hard Paraffin 40% H_2O; 4% Span 80 with Tween 80	29.06
Hard Paraffin 40% H_2O; 4% Span 80	28.97

5.4 Emulsion Stability

5.4.1 Coalescence and Droplet Evolution

All of the samples showed some degree of droplet coalescence over the entire 127 day period, albeit initially after the first 30 days (Figure 5.4), with PGPR showing the highest degree of stability overall with an increase of 11% for volume-weighted mean droplet diameter $D_{3.3}$ compared to the blends of Span 80 with Tween 80 which showed an increase of 19%, with Span 80 being the least stable showing a 45% increase. Not only did PGPR exhibit greater stability by way of droplet size, but also, the breadth of the distribution remained much smaller throughout compared to the blend of Span 80 with Tween 80 and Span 80 alone (Figures 5.25, 5.26 & 5.27), indicating less coalescence throughout for both the smaller and larger droplets.

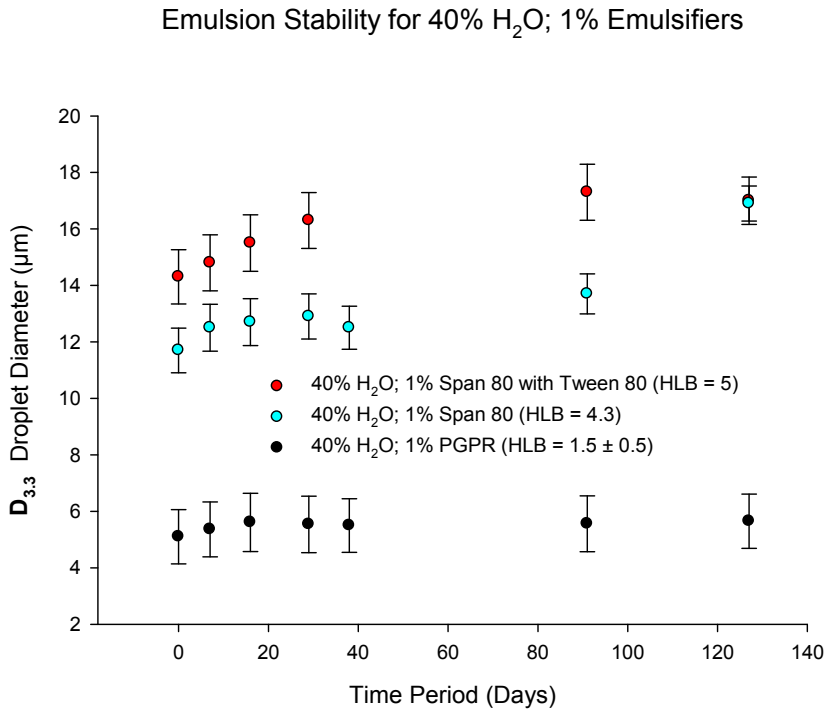


Fig. 5.24. Stability (evolution) of the volume-weighted mean droplet diameter $D_{3.3}$, for 40 wt% water content and 1 wt% emulsifier over a period of 127 days.

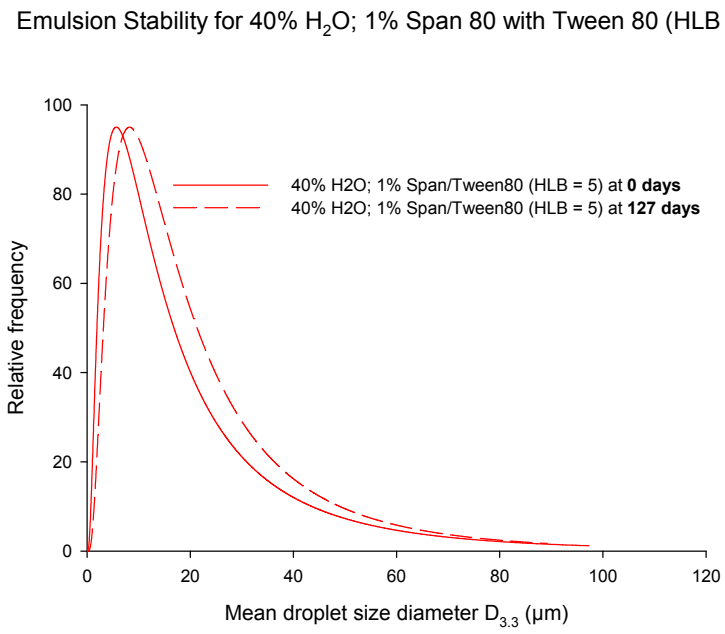


Fig. 5.25. Stability (evolution) of the volume-weighted mean droplet diameter $D_{3.3}$ frequency distributions for 40 wt% water content, 1 wt% Span 80 with Tween 80 (HLB = 5) at 0 and 127days.

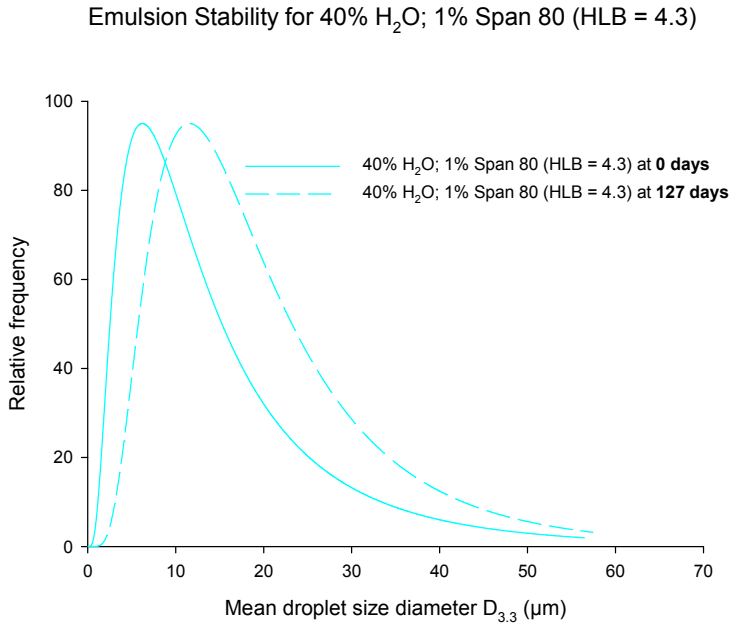


Fig. 5.26. Stability (evolution) of the volume-weighted mean droplet diameter $D_{3.3}$ frequency distributions for 40 wt% water content, 1 wt% Span 80 (HLB = 4.3) at 0 and 127days.

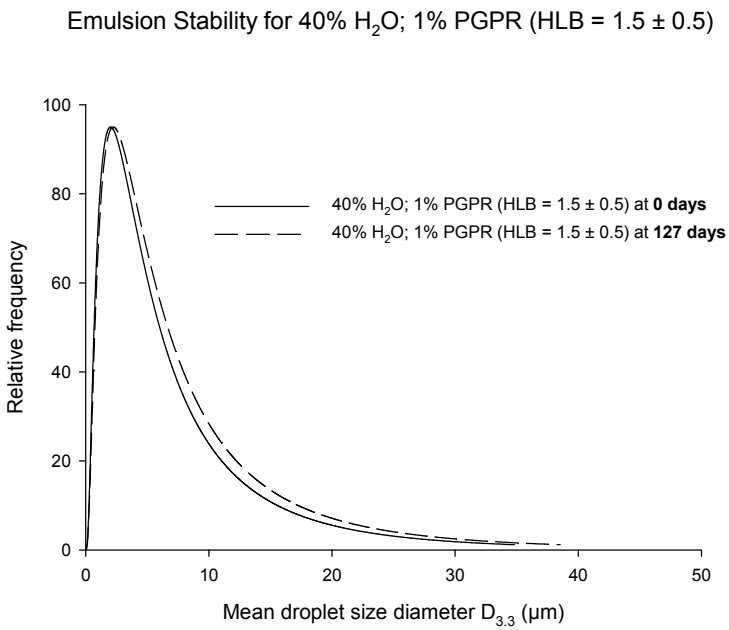


Fig. 5.27. Stability (evolution) of the volume-weighted mean droplet diameter $D_{3.3}$ frequency distributions for 40 wt% water content, 1 wt% PGPR (HLB = 1.5 ± 0.5) at 0 and 127days.

Coalescence follows four main steps, namely flocculation, thin film drainage, film rupture and coalescence (Johansson, Bergenståhl & Lundgren, 1995). PGPR exhibited the greatest degree of stability, indicating less flocculation and coalescence. It is in all probability that there is a much higher degree of interstitial crystallisation at the interface keeping the droplets separate compared to the crystallisation at the interface when using either Span 80 alone or a blend of Span 80 with Tween 80. This could be attributed to the chemistry, the length and type of the lipophilic polyricinoleate chain (Figure 5.4) having a much greater affinity towards forming a tight crystal network with the wax crystals as opposed to that produced via the lipophilic monooleate chain in the other two systems (Figures 5.6 and 5.8). Additionally if or when flocculation does occur, any coalescence will again be inhibited or reduced if a rigid tightly packed interfacial film is present preventing film

drainage and rupture. In spite of the fact that both PGPR and Span 80 were found to have similar surface excess concentration values, it is most likely, based on the time stability (evolution) data over the entire 127 day period that the cohesive forces existing between molecules at the interface are much stronger for PGPR than Span 80. Span 80 produced a more stable emulsion when blended with Tween 80 with much better surface active properties. This backs up the theory that blending emulsifiers will give rise to a more stable emulsion than using a single emulsifier of the same group.

Whilst none of the three emulsifier systems can be described as being exactly monodispersed, there is however a degree of difference between not only the actual droplet size, but also the droplet size distribution throughout for the PGPR emulsions compared to the droplet size and droplet size distribution for both Span 80 and the blend of Span 80 with Tween 80. As a consequence the emulsions stabilised with PGPR are less likely to encounter Ostwald ripening. In general and more specifically to the emulsion stability observed with these three systems the coalescence along with sedimentation is influenced as stated by the initial droplet size. Coalescence will always increase with the breadth of the droplet size distribution and additionally sedimentation velocity will inevitably be proportional to droplet size.

5.5 Emulsifier, Droplet Size Distribution & Microscopy

5.5.1 Size Distribution and Mophology

Table 5.4 shows the droplet size diameter $D_{3.3}$ with calculated $D_{3.2}$ for the initial formulation attempt, where the amount of castor oil in the formula was reduced by 10 wt% and the amount of water increased by the same amount. Unfortunately this

method was only useful in preparing low water content emulsions up 20 wt%. Tables 5.5 to 5.7 show the second formulation, where the entire oil content (carnauba wax, microcrystalline wax and castor oil) was altered by 10 wt% and the water content changed by the same amount. This allowed the preparation of emulsions up to 40 wt% water content. However the final emulsion products containing 40 wt% water content were much softer than a conventional lipstick product, so in order to produce a more rigid product hard paraffin was added as shown in Table 5.8. Please note that the calculated $D_{3.2}$ does not have a standard deviation as these values are based on the mean (single) $D_{3.3}$ value.

Table. 5.4. Emulsion based Lipsticks, initial approach with 10 & 20 wt% water content and 1 wt% Emulsifiers. Volume-weighted mean droplet diameter $D_{3.3}$ and the calculated surface-weighted mean droplet diameter $D_{3.2}$.

	Emulsion Lipstick Formula					Droplet size Diameter		
Emulsifier System	Carnauba Wax (w/w %)	Micro-crystalline Wax (w/w %)	Castor Oil (w/w %)	Water (w/w %)	Emulsifier (w/w %)	D3.3 (μm) ± σ	D3.2 (μm)	Free Water (%/100)
PGPR (HLB = 1.5 ± 0.5)	7.10	15.98	65.92	10.00	1.00	5.30 ± 0.48	4.73	0.02
	7.10	15.98	55.92	20.00	1.00	4.57 ± 0.53	3.97	0.02
Span 80 (HLB = 4.3)	7.10	15.98	65.92	10.00	1.00	28.91 ± 0.39	26.57	0.25
	7.10	15.98	55.92	20.00	1.00	26.20 ± 0.55	22.97	0.16
Span 80 with Tween 80 (HLB = 5)	7.10	15.98	65.92	10.00	1.00	13.39 ± 0.53	11.62	0.04
	7.10	15.98	55.92	20.00	1.00	8.89 ± 0.74	6.78	0.02

Table. 5.5. Emulsion based Lipsticks, second approach with 10, 20, 30 & 40 wt% water content and 1 & 2 wt% PGPR (HLB = 1.5 ± 0.5). Volume-weighted mean droplet diameter $D_{3.3}$ and calculated surface-weighted mean droplet diameter $D_{3.2}$.

	Emulsion Lipstick Formula					Droplet size Diameter		
Emulsifier System	Carnauba Wax (w/w %)	Micro-crystalline Wax (w/w %)	Castor Oil (w/w %)	Water (w/w %)	Emulsifier (w/w %)	D3.3 (μm ± σ)	D3.2 (μm)	Free Water (%/100)
PGPR (HLB = 1.5 ± 0.5)	6.32	14.22	68.46	10.00	1.00	5.63 ± 0.54	4.85	0.07
	5.61	12.62	60.77	20.00	1.00	4.74 ± 0.56	4.05	0.03
	4.90	11.03	53.07	30.00	1.00	5.30 ± 0.77	3.93	0.09
	4.19	9.43	45.38	40.00	1.00	5.26 ± 0.98	3.26	0.14
	6.25	14.06	67.69	10.00	2.00	2.65 ±0.36	2.48	0.08
	5.54	12.46	60.00	20.00	2.00	3.26 ± 0.46	2.93	0.04
	4.83	10.87	52.30	30.00	2.00	3.30 ± 0.60	2.76	0.06
	4.12	9.27	44.61	40.00	2.00	4.10 ± 0.91	2.71	0.10

Table. 5.6. Emulsion based Lipsticks, second approach with 10, 20, 30 & 40 wt% water content and 1 & 2 wt% Span 80 (HLB = 4.3). Volume-weighted mean droplet diameter $D_{3.3}$ and calculated surface-weighted mean droplet diameter $D_{3.2}$.

	Emulsion Lipstick Formula					Droplet size Diameter		
Emulsifier System	Carnauba Wax (w/w %)	Micro-crystalline Wax (w/w %)	Castor Oil (w/w %)	Water (w/w %)	Emulsifier (w/w %)	D3.3 (μm ± σ)	D3.2 (μm)	Free Water (%/100)
Span 80 (HLB = 4.3)	6.32	14.22	68.46	10.00	1.00	14.92 ± 0.67	12.02	0.14
	5.61	12.62	60.77	20.00	1.00	16.46 ± 0.76	12.36	0.09
	4.90	11.03	53.07	30.00	1.00	17.26 ± 0.67	13.76	0.13
	4.19	9.43	45.38	40.00	1.00	14.93 ± 0.76	11.20	0.29
	6.25	14.06	67.69	10.00	2.00	25.80 ± 0.57	21.93	0.10
	5.54	12.46	60.00	20.00	2.00	29.60 ± 0.20	29.01	0.45
	4.83	10.87	52.30	30.00	2.00	26.40 ± 0.20	25.88	0.56
	4.12	9.27	44.61	40.00	2.00	16.45 ± 0.70	12.91	0.33

Table. 5.7. Emulsion based Lipsticks, second approach with 10, 20, 30 & 40 wt% water content and 1 & 2 wt% Span 80 with Tween 80 (HLB = 5). Volume-weighted mean droplet diameter $D_{3.3}$ and calculated surface-weighted mean droplet diameter $D_{3.2}$.

	Emulsion Lipstick Formula					Droplet size Diameter		
Emulsifier System	Carnauba Wax (w/w %)	Micro-crystalline Wax (w/w %)	Castor Oil (w/w %)	Water (w/w %)	Emulsifier (w/w %)	D3.3 (μm ± σ)	D3.2 (μm)	Free Water (%/100)
Span 80 with Tween 80 (HLB = 5)	6.32	14.22	68.46	10.00	1.00	4.16 ± 0.51	3.64	0.03
	5.61	12.62	60.77	20.00	1.00	5.47 ± 0.79	4.01	0.03
	4.90	11.03	53.07	30.00	1.00	12.30 ± 0.88	8.32	0.17
	4.19	9.43	45.38	40.00	1.00	13.48 ± 0.87	9.29	0.27
	6.25	14.06	67.69	10.00	2.00	25.80 ± 0.87	19.01	0.11
	5.54	12.46	60.00	20.00	2.00	19.35 ± 0.71	15.10	0.03
	4.83	10.87	52.30	30.00	2.00	21.73 ± 0.68	17.29	0.13
	4.12	9.27	44.61	40.00	2.00	14.83 ± 0.84	10.40	0.24

Table. 5.8. Emulsion based Lipsticks containing Hard Paraffin, final approach with 40 wt% water content and 1 & 4 wt% Emulsifiers. Volume-weighted mean droplet diameter $D_{3.3}$ and calculated surface-weighted mean droplet diameter $D_{3.2}$.

	Emulsion Lipstick Formula						Droplet size Diameter		
Emulsifier System	Carnauba Wax (w/w %)	Micro-crystalline Wax (w/w %)	Castor Oil (w/w %)	Hard Paraffin (w/w %)	Water (w/w %)	Emulsifier (w/w %)	D3.3 (μm) ± σ	D3.2 (μm)	Free Water (%/100)
PGPR (HLB = 1.5 ± 0.5)	4.19	9.43	40.38	5.00	40.00	1.00	4.76 ± 0.96	3.00	0.20
	3.98	8.95	38.33	4.74	40.00	4.00	3.95 ± 0.71	3.06	0.06
Span 80 (HLB = 4.3)	4.19	9.43	40.38	5.00	40.00	1.00	17.13 ± 0.57	14.52	0.24
	3.98	8.95	38.33	4.74	40.00	4.00	13.13 ± 0.90	8.79	0.15
Span 80 with Tween 80 (HLB = 5)	4.19	9.43	40.38	5.00	40.00	1.00	22.38 ± 0.77	16.64	0.20
	3.98	8.95	38.33	4.74	40.00	4.00	18.22 ± 0.61	15.15	0.52

For the initial preparation the emulsifiers were kept at 1 wt% throughout, for the second preparation emulsifiers were tried at both 1 and 2 wt%, and finally in the hard paraffin formula emulsifiers were tried at both 1 and 4 wt%. These changes in the emulsifier contents were necessary in order to assess any changes in the droplet size and other characteristics.

Due to the fact that three different non-ionic emulsifiers with different hydrophobic and hydrophilic groups were used in the preparation it would be almost impossible to model exactly the differences in droplet sizes and droplet size distribution in relation to their chemistry. However an evaluation can be made based on an assessment of their individual distinctive characteristics.

On observation of the results one can see throughout that the volume-weighted mean droplet diameter $D_{3.3}$ and the calculated surface-weighted mean droplet diameter $D_{3.2}$ achieved throughout with the use of PGPR was much smaller than what was achieved with the use of Span 80 and the blend of Span 80 with Tween 80. This was verified by optical microscopy and cryogenic Scanning Electron Microscopy (SEM) Figures 5.28 to 5.33.

Using the high shear mixer will always produce droplets, however due to the Laplace pressure within the droplets, which will inevitably increases as the droplets decrease in size makes it harder to produce smaller droplets as they resist deformation. Decreasing the interfacial tension with the addition of an emulsifier will also decrease the Laplace pressure allowing the production of smaller droplets. Although all of the emulsifier systems have been found to have good surface properties the reason why smaller droplets are produced using PGPR could be down to the fact that it produces better surface coverage, in conjunction with a higher surface adsorption rate during

the emulsification process along with a stronger interfacial film. This is significant because during emulsification there will always be frequent encounters between droplets which could lead to coalescence if there is insufficient droplet coverage or a tenuous interfacial film. One could infer that the extended structure of the ricinoleate chain and the orientation of the molecules produce a much stronger interface than that of the oleate chain. Of course even though the blend of Span 80 with Tween 80 has better surface properties than Span 80 by way of producing a lower interfacial tension, the surface excess concentration value of 0.19×10^{-6} mol/m^2 is very low compared with 0.90×10^{-6} and 1.02×10^{-6} mol/m^2 for PGPR and Span 80 alone respectively. Less surface coverage means a weaker (expanded) interfacial film and therefore a higher probability of droplet coalescence during emulsification. In addition, droplet formation occurs as a result of a higher interfacial tension on the concave side. Therefore using a blend of emulsifiers will reduce the likelihood of this due to reductions on both sides of the interface, thus producing larger droplets in the process as opposed to PGPR which reduces the interfacial tension significantly on the side of the oil continuous phase. Span 80 has a surface excess concentration value comparable with that of PGPR however its surface active properties by way of reducing the surface tension are not as good; therefore the droplets Laplace pressure throughout emulsification will remain higher.

The mean droplet size during the emulsification process is heavily dependent on emulsifier concentration. At very low emulsifier concentrations, below the surface excess concentration one would expect much larger droplets due to a lack of surface coverage giving rise to coalescence, as opposed to smaller droplets with increasing concentrations due to better surface coverage and less coalescence. There will inevitably be a plateau after the surface excess concentration. In addition one would

expect to see larger droplets with increasing water content if the increase in water content pushes the surface concentration below the surface excess concentration. Whist this trend is partially evident in the final formulation (Table 5.8), it is not obvious throughout the other formulations. This could have been due to the fact that a change of 1 wt% was not enough to see a significant change or could have been down to other factors like insufficient emulsification or inconsistencies in the high shear mixing process. It could also suggest that a concentration of 1 wt% is sufficient to produce emulsions at all of the relevant water contents.

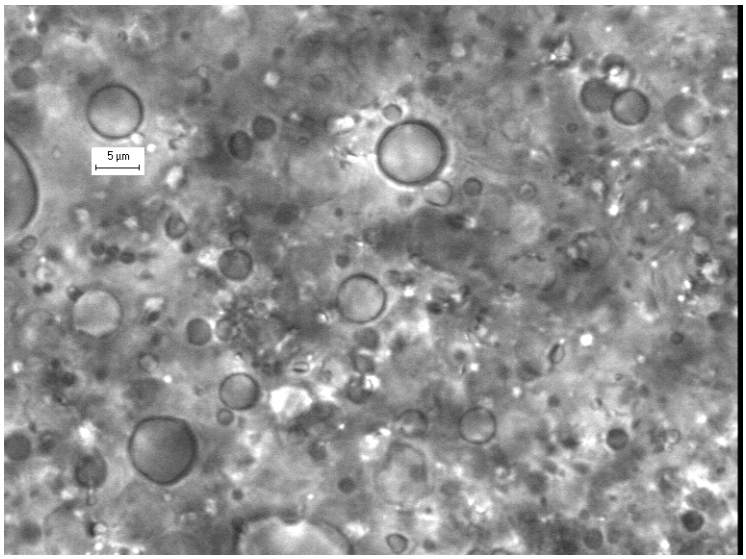


Fig. 5.28. Photomicrographs of 20 wt% water content with 1 wt% PGPR, showing droplets with diameter $D_{1,0}$ 5 µm and smaller.

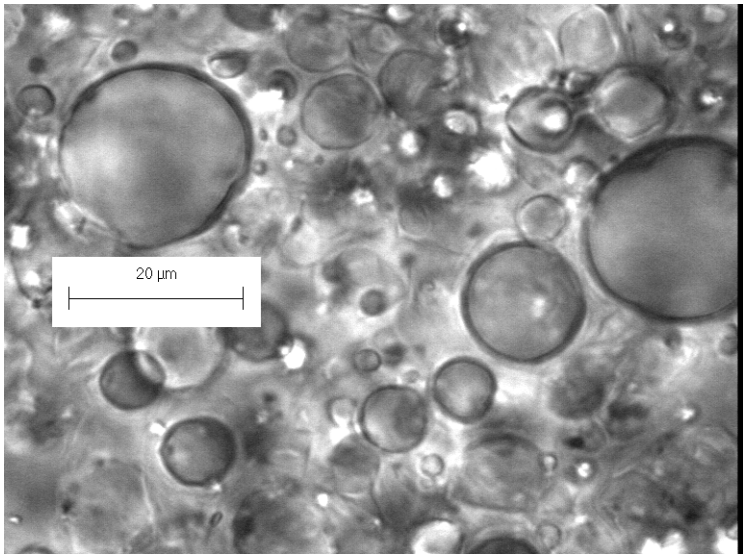


Fig. 5.29. 30 wt% water content with 1 wt% Span 80, showing droplets with diameter $D_{1,0}$ 20 µm and smaller. Droplet coalescence can also be observed for droplets around 5 µm.

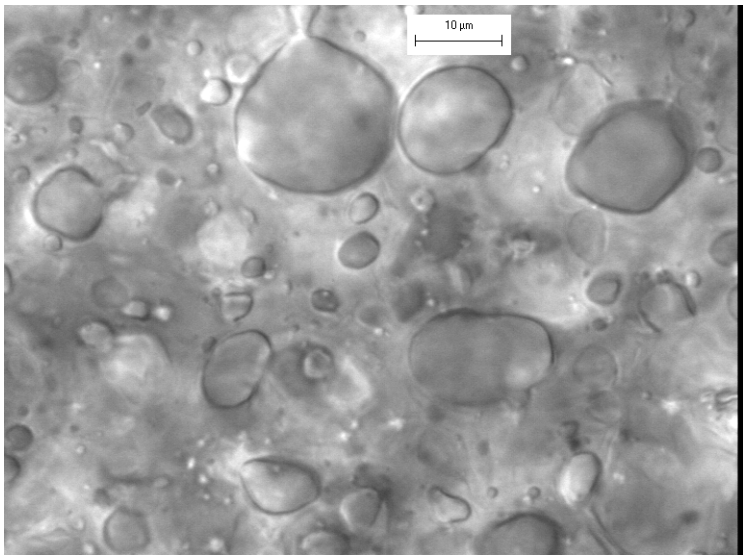


Fig. 5.30. 40 wt% water content with 1 wt% Span 80 with Tween 80, showing droplets with a droplet diameter $D_{1,0}$ spread above 10 µm and smaller than 5 µm.

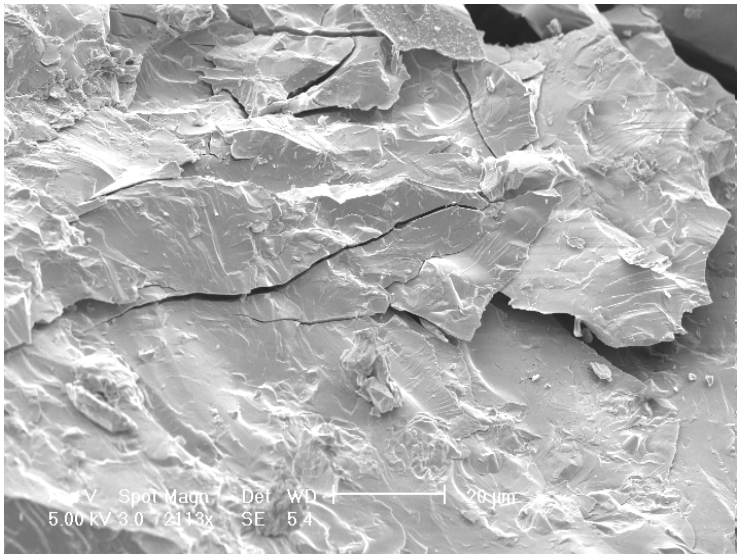


Fig. 5.31. Cryo-SEM micrograph of Basic Sample (7.1 wt% Carnauba, 15.98 wt% Microcrystalline wax and 76.92 wt% Castor oil) with a pure crystalline structure.

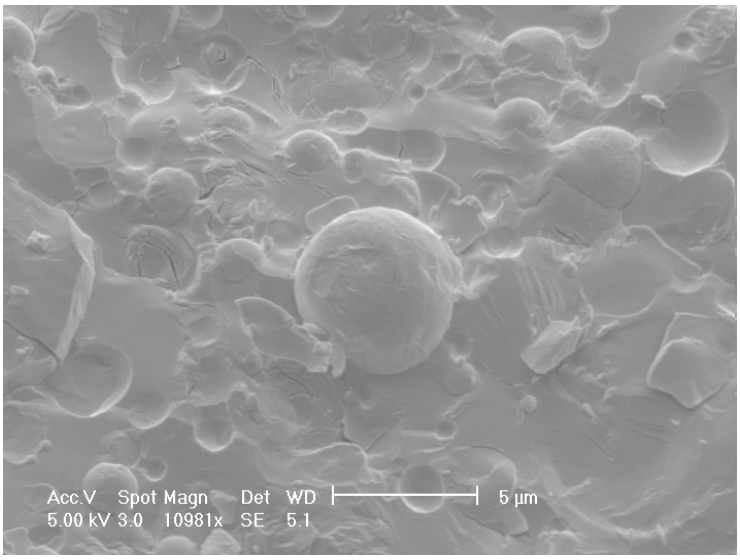


Fig. 5.32. Cryo-SEM micrograph of 40 wt % water content with 1 wt% PGPR showing a droplet $D_{1,0}$ of 5 µm surrounded by smaller droplets at pits. Continuous oil and crystalline phase can be seen encasing the droplets.

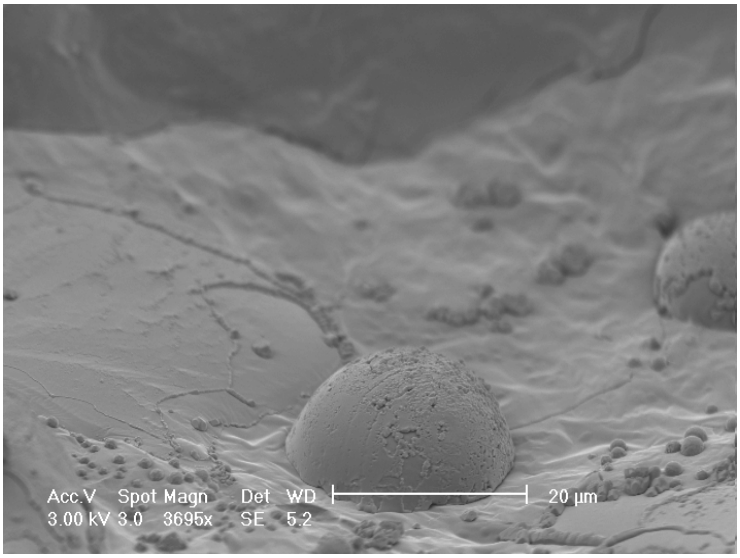


Fig. 5.33. Cryo-SEM micrograph of Hard paraffin formula containing 40 wt% water content with 1 wt% Span 80 with Tween 80. A couple of water droplets can be seen around $D_{1,0}$ = 20 µm in diameter encased in surface active wax crystals.

5.6 Texture Profile Analysis - TA

5.6.1 Introduction

Hardness is important in determining the physical characteristic properties of any product. Consequently lipstick hardness assessment based on mainly the wax, oil and water composition together with albeit to a lesser extent the emulsifier content, is a useful tool in determining objectively the effects of changing the formulation has on the product.

5.6.2 Penetration and Compression

Texture profile analysis as illustrated in Figures 5.34, (penetration; indication of hardness, yield stress and interfacial film strength) and Figures 5.35, (compression; brittleness and hardness) was conducted on the basic lipstick sample and all of the emulsion samples containing 1 wt% of emulsifier plus the hard paraffin samples containing 40wt% water content with 1 & 4% emulsifiers. The test was also carried out on a conventional shelf sample (Tables 5.9 & 5.10) for comparison (values not plotted). An important point to mention is that the values obtained via compression were attributed mainly to the overall macrostructure as opposed to the microstructure properties via the penetration test.

One can observe there is an increase in penetration distance with increasing water content throughout for all samples which would indicate a corresponding softening with the increasing water content. Although all of the samples show a degree of softening throughout, the emulsion samples containing PGPR do not appear to yield as much as those containing both Span 80 and the blend of Span 80 with Tween 80, which could be attributed to a number of factors. Not only did PGPR produce a much smaller droplet size distribution, the free water content was much lower, which would

no doubt give rise to a much denser compact product exhibiting less yielding. In addition this could verify that the interfacial film produced by PGPR is much stronger than that produced with both Span 80 alone and the blend of Span 80 with Tween 80. In addition the specific surface area of the interface produced by PGPR based on the average droplet size distribution was approximately five times that produced by Span 80 and the blend of Span 80 with Tween 80 which again would give rise to less yielding. With the addition of hard paraffin the overall texture profile was brought in line with that of the basic sample. However differences with regards to emulsifier type, emulsifier concentration and interfacial film strengths were not detected. In order to detect these differences one can postulate that a penetration test at a higher sensitivity would be necessary.

Significant differences in hardness/ brittleness between sample types were detected at low water content as shown (Figure 5.35), via the compression firmness test, where the addition of span 80 appeared to have considerable effect on the overall crystalline hardness of the sample. The blend of Span 80 with Tween 80 produced a harder product with PGPR being intermediate. These differences were overridden by the subsequent addition of water, where particularly at 30 to 40 wt% any difference in hardness was indistinguishable. Whilst the addition of hard paraffin produced a harder product the compression results did not appear to be comparable with those obtained via the penetration test. Here the hard paraffin crystalline hardness was affected much more with PGPR than Span 80 and the blend of Span 80 with Tween 80.

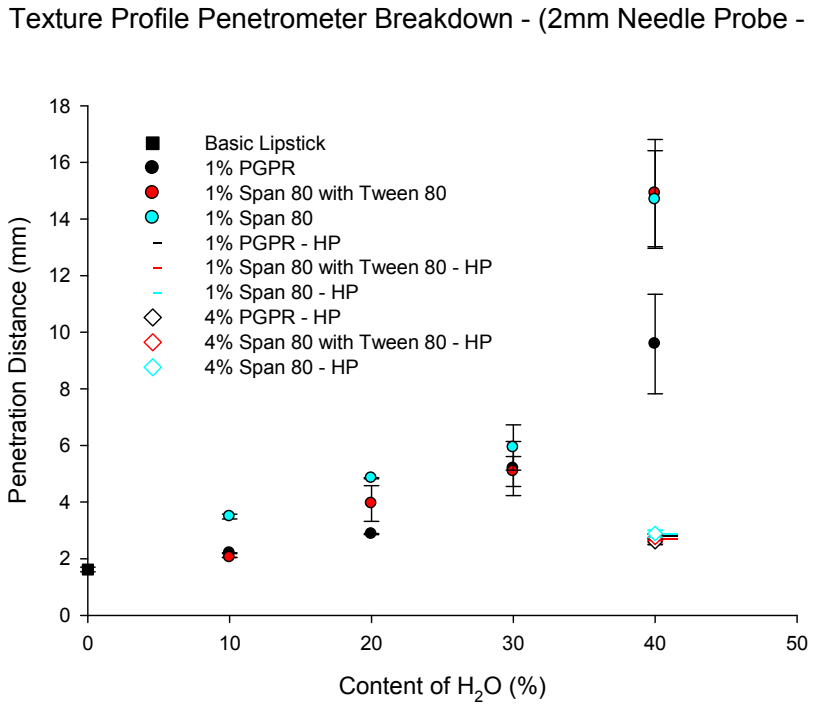


Fig. 5.34. Texture profile penetrometer test on Basic Lipstick, Emulsions samples containing 10, 20, 30 & 40 wt% water content with 1 wt% Emulsifiers and 40% wt% water content, 1 & 4% Emulsifiers with Hard Paraffin.

Table. 5.9. Texture profile penetrometer data for all samples.

Lipstick Sample	Mean Distance (mm)	SD (mm)
Conventional Shelf Lipstick	1.90	0.05
Basic Lipstick	1.62	0.09
10% H_2O; 1% PGPR	2.20	0.02
20% H_2O; 1% PGPR	2.87	0.02
30% H_2O; 1% PGPR	5.18	0.97
40% H_2O; 1% PGPR	9.58	1.79
10% H_2O; 1% Span 80 with Tween 80	2.04	0.004
20% H_2O; 1% Span 80 with Tween 80	3.95	0.64
30% H_2O; 1% Span 80 with Tween 80	5.08	0.54
40% H_2O; 1% Span 80 with Tween 80	14.91	1.93
10% H_2O; 1% Span 80	3.49	0.09
20% H_2O; 1% Span 80	4.85	0.02
30% H_2O; 1% Span 80	5.93	0.82
40% H_2O; 1% Span 80	14.69	1.76
Hard Paraffin 40% H_2O; 1% PGPR	2.79	0.10
Hard Paraffin 40% H_2O; 1% Span 80 with Tween 80	2.69	0.18
Hard Paraffin 40% H_2O; 1% Span 80	2.86	0.14
Hard Paraffin 40% H_2O; 4% PGPR	2.60	0.11
Hard Paraffin 40% H_2O; 4% Span 80 with Tween 80	2.75	0.11
Hard Paraffin 40% H_2O; 4% Span 80	2.89	0.13

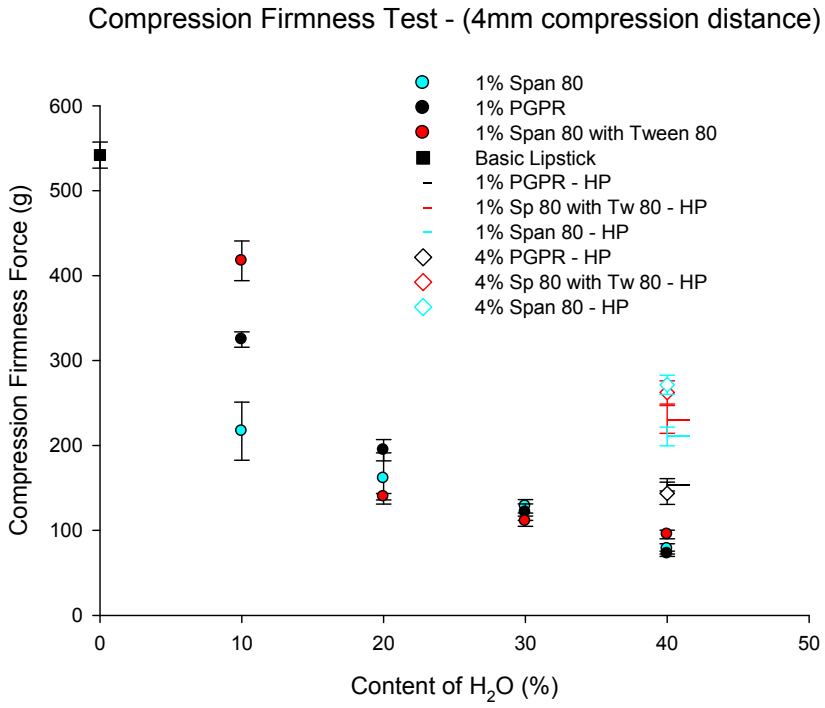


Fig. 5.35. Compression firmness test on Basic Lipstick, Emulsions samples containing 10, 20, 30 & 40 wt% water content with 1 wt% Emulsifiers and 40% wt% water content, 1 & 4% Emulsifiers with Hard Paraffin.

Table. 5.10. Compression firmness data for all samples.

Lipstick Sample	Mean Compression Force (g)	SD (g)
Conventional Shelf Lipstick	609.7	29.0
Basic Lipstick	541.9	15.3
10% H_2O; 1% PGPR	324.7	8.9
20% H_2O; 1% PGPR	194.4	12.5
30% H_2O; 1% PGPR	121.4	9.7
40% H_2O; 1% PGPR	72.5	3.1
10% H_2O; 1% Span 80 with Tween 80	417.3	23.4
20% H_2O; 1% Span 80 with Tween 80	139.7	3.7
30% H_2O; 1% Span 80 with Tween 80	110.8	6.1
40% H_2O; 1% Span 80 with Tween 80	95.3	5.2
10% H_2O; 1% Span 80	216.9	34.2
20% H_2O; 1% Span 80	161.1	30.1
30% H_2O; 1% Span 80	128.4	7.9
40% H_2O; 1% Span 80	78.3	6.0
Hard Paraffin 40% H_2O; 1% PGPR	153.7	7.2
Hard Paraffin 40% H_2O; 1% Span 80 with Tween 80	230.6	16.3
Hard Paraffin 40% H_2O; 1% Span 80	210.5	11.0
Hard Paraffin 40% H_2O; 4% PGPR	143.8	13.2
Hard Paraffin 40% H_2O; 4% Span 80 with Tween 80	262.4	13.7
Hard Paraffin 40% H_2O; 4% Span 80	271.4	11.4

5.7 Rheology

5.7.1 Introduction

The majority of materials including lipsticks are not completely solid or liquid like, they are viscoelastic. During storage lipstick clearly needs to behave like a solid; however during application it should behave like a fluid and flow just enough to enable even spreading on the lips.

5.7.2 Viscoelasticity

The structural characteristics of each of the lipstick emulsion samples were measured via non-destructive oscillations at 32 °C to replicate lip conditions. The viscoelastic moduli, Storage (elastic) G' and Loss (viscous) G'', being direct measurements of the particle-particle interactions within the samples were assessed in order to determine the emulsions' stability and how they compared against the conventional and basic lipstick samples.

Throughout all the tests as illustrated in Figures 5.36 to 5.38 and Table 5.11, the storage modulus G' was greater than the loss modulus G'', indicating that all of the samples were more solid-like (elastic). Although there was a characteristic increase in the elasticity throughout all of the three systems, where the emulsions at 10 wt% water content showed a higher degree of solidity than the basic lipstick; an increase in water content was accompanied by a loss in elasticity, indicative of G' approaching G'' together with a drop in the dynamic viscosity, showing characteristic emulsion instability with increasing water content, indicating samples becoming more liquid-like (viscous).

Although no emulsions were prepared above 40 wt% water content, based on these results any further increase in water content would probably result in subsequent phase inversion destabilisation and an obvious changeover in the viscoelastic moduli. Why all of the three emulsion systems at 10 wt% water content showed a higher degree of solidity in comparison with the basic sample was in all probability due to the additional interfacial film rheology. However by increasing the volume fraction of the dispersed phase in the system the overall solidity and dynamic viscosity would therefore decline and approach that of the dispersed water phase.

This loss in elasticity at 40 wt% water content was re-established by the addition of both hard paraffin and by increasing the emulsifier content from 1 to 4% (Table 5.11), where the flow/ viscoelasticty of the samples were reverted back to those of the basic lipstick. These values are acceptable although they do not correspond exactly with the conventional samples; again this is due to the extreme sensitivity of these rheological measurements.

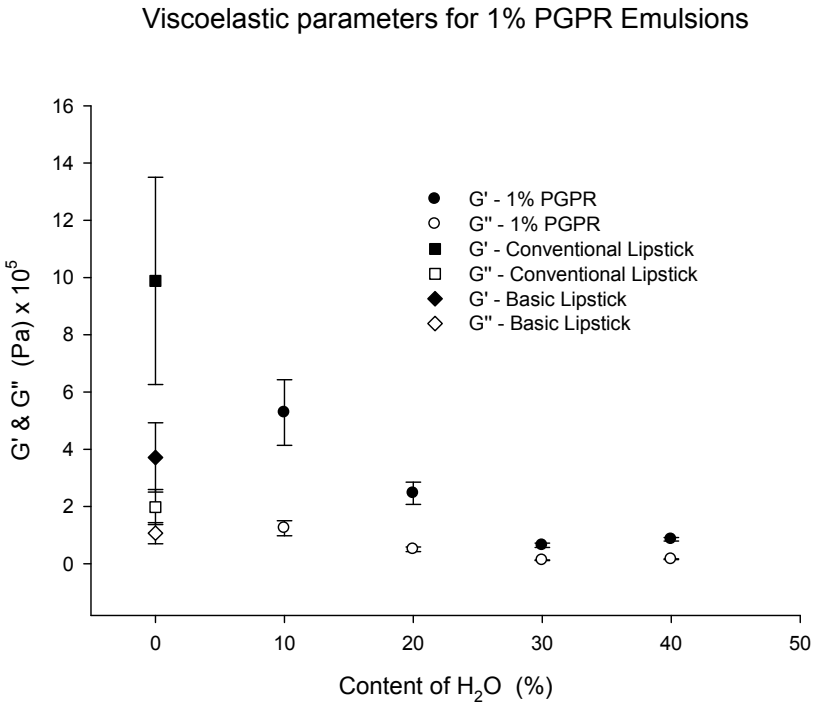


Fig. 5.36. Changes in the viscoelastic Storage (elastic) G' and Loss (viscous) G'' moduli vs. changes in the emulsion water content for 1 wt% PGPR, comparisons with a conventional lipstick and the basic lipstick.

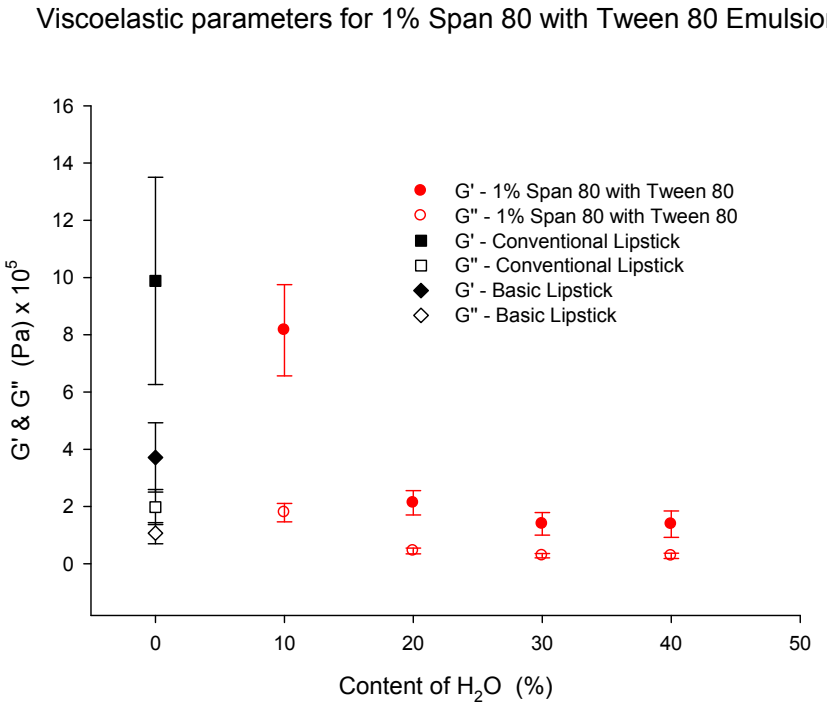


Fig. 5.37. Changes in the viscoelastic Storage (elastic) G' and Loss (viscous) G'' moduli vs. changes in the emulsion water content for 1 wt% Span 80 with Tween 80, comparisons with a conventional lipstick and the basic lipstick.

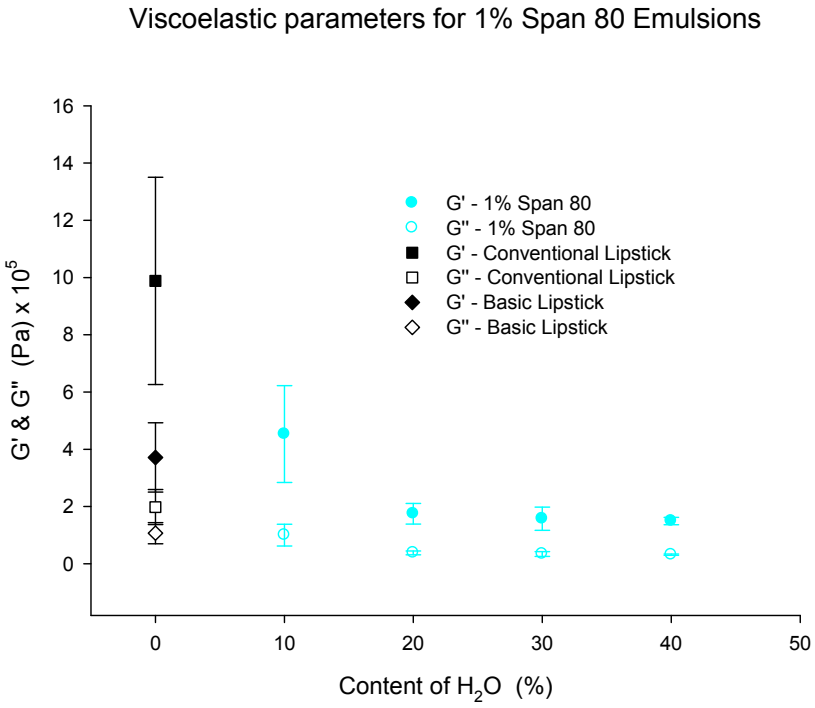


Fig. 5.38. Changes in the viscoelastic Storage (elastic) G' and Loss (viscous) G'' moduli vs. changes in the emulsion water content for 1 wt% Span 80, comparisons with a conventional lipstick and the basic lipstick.

Table. 5.11. Viscoelastic moduli, G' (Storage) & G'' (Loss) data for all samples.

Lipstick Sample	G' Storage (Pa) x 10^5	SD (Pa) x 10^5	G'' Loss (Pa) x 10^5	SD (Pa) x 10^5
Conventional Shelf Lipstick	9.89	3.62	1.98	0.61
Basic Lipstick	3.71	1.21	1.07	0.37
10% H_2O; 1% PGPR	5.28	1.15	1.24	0.26
20% H_2O; 1% PGPR	2.46	0.39	0.51	0.08
30% H_2O; 1% PGPR	0.64	0.08	0.12	0.01
40% H_2O; 1% PGPR	0.85	0.06	0.16	0.01
10% H_2O; 1% Span 80 with Tween 80	8.16	1.60	1.79	0.32
20% H_2O; 1% Span 80 with Tween 80	2.13	0.43	0.45	0.10
30% H_2O; 1% Span 80 with Tween 80	1.39	0.39	0.28	0.08
40% H_2O; 1% Span 80 with Tween 80	1.38	0.46	0.28	0.09
10% H_2O; 1% Span 80	4.53	1.69	1.00	0.38
20% H_2O; 1% Span 80	1.75	0.36	0.38	0.07
30% H_2O; 1% Span 80	1.58	0.40	0.34	0.08
40% H_2O; 1% Span 80	1.49	0.13	0.32	0.02
Hard Paraffin 40% H_2O; 1% PGPR	1.68	1.09	0.33	0.20
Hard Paraffin 40% H_2O; 1% Span 80 with Tween 80	3.51	1.11	0.78	0.21
Hard Paraffin 40% H_2O; 1% Span 80	1.62	0.27	0.38	0.06
Hard Paraffin 40% H_2O; 4% PGPR	3.47	0.04	0.08	0.01
Hard Paraffin 40% H_2O; 4% Span 80 with Tween 80	4.08	0.71	0.94	0.14
Hard Paraffin 40% H_2O; 4% Span 80	1.97	0.62	0.46	0.14

6 Conclusions

By using non-ionic emulsifiers it has been possible to formulate W/O emulsion lipsticks with up to a 40 wt% aqueous phase content. The emulsions were stabilised interstitially with microcrystalline wax with carnauba wax and hard paraffin playing a central role in the stabilisation by thickening the continuous phase. The hard paraffin was required specifically to restore the hardness to the samples with 40 wt% water content. Although the emulsifier blend proved to be superior at reducing the interfacial tension at lower concentrations, due to the hydrophilicity of the Tween 80, this resulted in the formation of expanded monolayers hence a weaker interface and larger droplets due to coalescence during emulsification. It did however show a higher degree of evolution stability than Span 80 alone. Both Span 80 and particularly PGPR produced condensed monolayers giving rise to smaller droplets due to less coalescence during emulsification. In addition, lowering the interfacial tension on the oil continuous phase side of the interface did as expected produce much smaller droplets as opposed to lowering it to the same degree on both sides of the interface, as the interface would always bend towards the side with the higher interfacial tension. Although the duration of the project would not allow it, a shelf life in excess of 6 months, up to a year would be ideal. Based on the stability results, this would be best achieved using PGPR.

As producing fine monodispersed macroemulsions would be the ultimatel formulation to aim for; this would be best produced by selecting a highly lipophilic non-water dispersing emulsifier with an extremely low HLB value of 0 and 2 as established using PGPR together with chemical compatibility with the oil phase. Fine monodispersed macroemulsion droplets would be ideal for a number of reasons including; increased stability (less Ostwald ripening), a firmer product and could

potentially reduce microbial spoilage. Increasing the concentration of the emulsifiers from 1 to 4 % did as expected produce a reduction in droplet size, however equally as important it showed a significant reduction in the amount of free water which again is important as it could reduce the potential for microbial spoilage.

7 Further Work

With it being possible to formulate course W/O macroemulsions using Span 80 and a Span 80 with Tween 80 blend and fine W/O macroemulsion using PGPR, to formulate W/O microemulsions alternative more effective high energy processing methods should be investigated in combination with alternative chemically compatible highly lipophilic non-water dispersing polymeric emulsifier at HLBs in the region 0 to 2. Emulsifier blends of similar chemical type should also be looked at in this HLB region for stability.

As the objective of the research was to produce W/O emulsions to deliver moisture and active water soluble ingredients to the lips; the effectively breaking of the emulsion droplets after application should inevitably be looked at.

Additionally the production of O/W/O emulsions should be investigated with a view to delivering fat-soluble active ingredients to the lips, plus a more detailed analysis of the polymorphic changes occurring in the crystalline structure over typical shelf life times as changes could produce undesirable products.

Emulsion formulations with preservatives, colouring, pigments and dyes should be attempted, characterised and compared with formulations without, in an attempt to assess for any adverse effects by these normal ingredients.

Appendix

The following Figures; 5.9 to 5.14 present the DSC thermograms obtained in order to select the waxes for the basic lipstick formula and subsequent emulsion formulations.

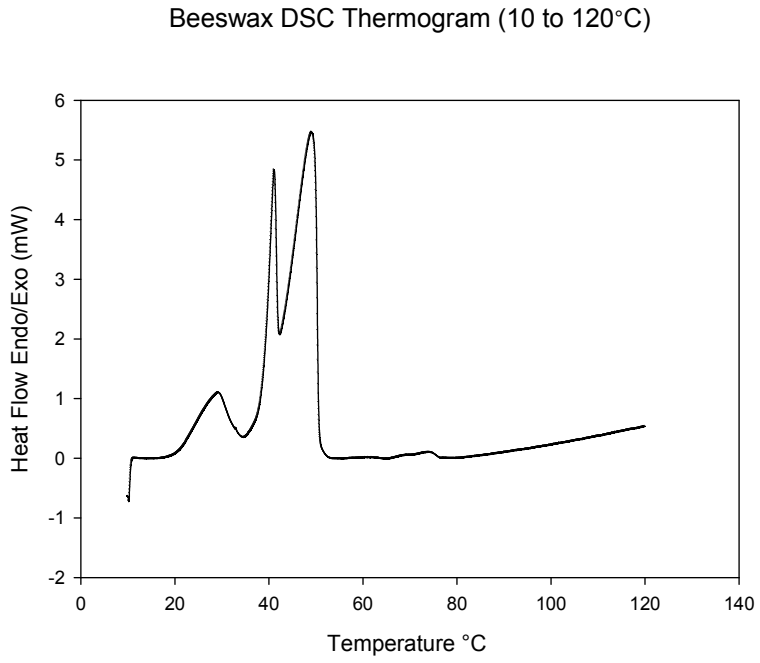


Fig. 5.9. Differential Scanning Colorimetric Thermogram for Beeswax (10 to 120°C).

Figure 5.9 presents a thermogram for Beeswax showing a triple endothermic event at 29.3, 41.4 and 49.1 °C. This could be due to the fact that beeswax is made up of a number of long-chain hydrocarbons including alkanes (C_{21} to C_{33}), alcohols, free acids (C_{22} to C_{30}), long-chain diesters, esters of long chain alcohols (C_{40} to C_{52}) along with other materials. (Kameda, 2004; Talens & Krochta, 2005).

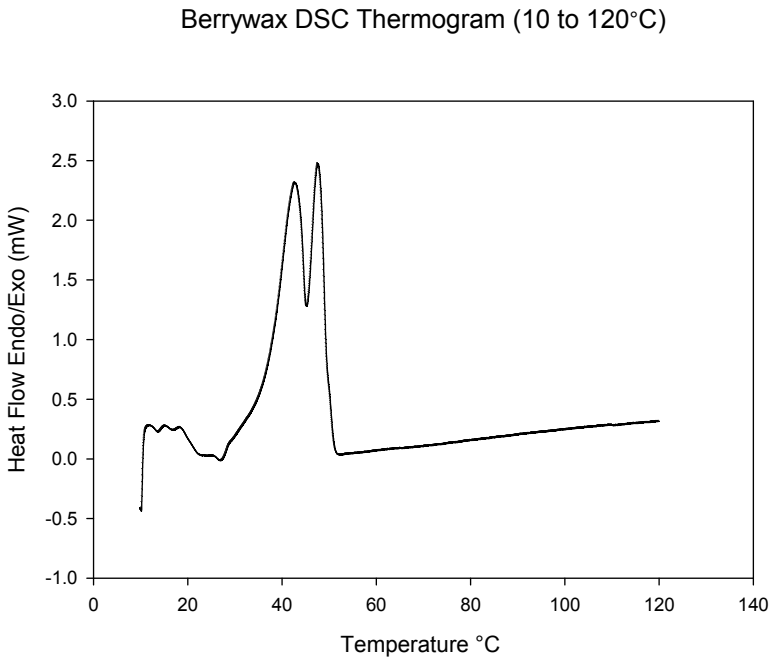


Fig. 5.10. Differential Scanning Colorimetric Thermogram for Berry wax (10 to 120°C).

Figure 5.10 presents a thermogram for berry wax which has a double endothermic event observed at 42.8 and 47.6 °C. Though made up of mainly oleanolic acid (60%), it also contains glycerides of stearic, palmitic and myristic acids, lauric acid, unsaturated fatty acids, esters, primary alcohols and other aliphatic compounds (Casado & Heredia, 1999).

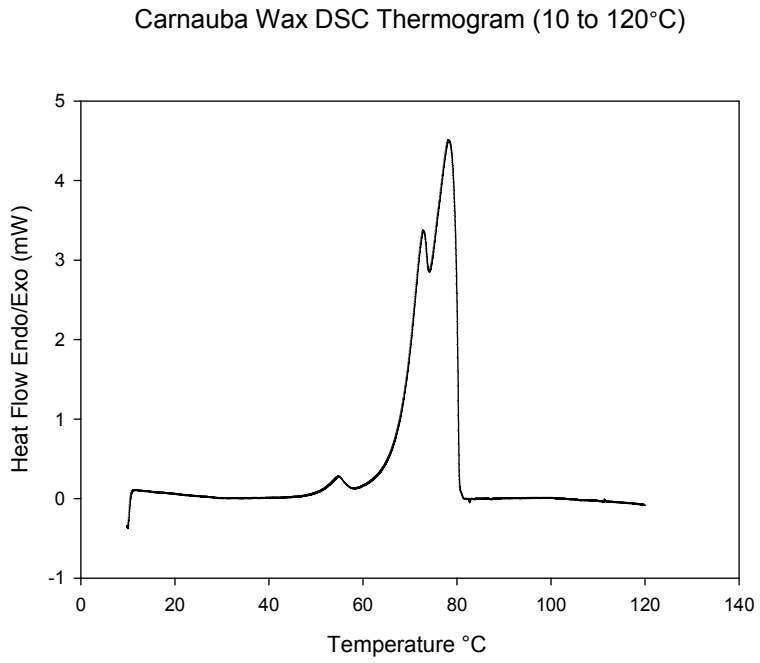


Fig. 5.11. Differential Scanning Colorimetric Thermogram for Carnauba wax (10 to 120°C).

Figure 5.11 presents a thermogram for Carnauba wax which shows a triple endothermic event observed at 54.0, 72.0 and 78.3 °C. The main composition is wax esters (80 to 85%), and small amounts of free acids and alcohols (10 to 20%), with hydrocarbons and resins (1 to 3%). These acids include the even carbon n-aliphatic acids (C_{18} to C_{34} inclusive), carnaubic acid (C_{24}), cerotic acid (C_{26}), heptacosanoic acid (C_{27}), and arachidic acid (C_{20}) (Koonce & Brown 1945). The alcohols are straight chains of even carbon number (C_{26} to C_{34}) with the higher alcohols dominating (Murray & Schoefeld, 1951; Milanovic et al., 2010).

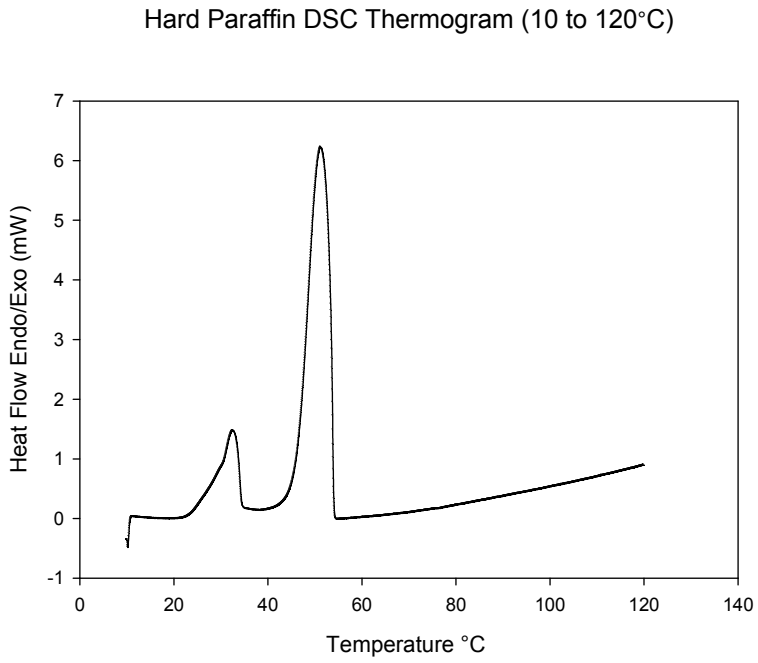


Fig. 5.12. Differential Scanning Colorimetric Thermogram for Hard Paraffin (10 to 120°C).

Figure 5.12 presents a thermogram for hard paraffin which has a double endothermic event at temperatures 32.6 and 51.2 °C. It consists of a mixture of straight chain high molecular weight hydrocarbons (C_{28} to C_{90}) (Nhlapo, Luyt & Vosloo, 1998).

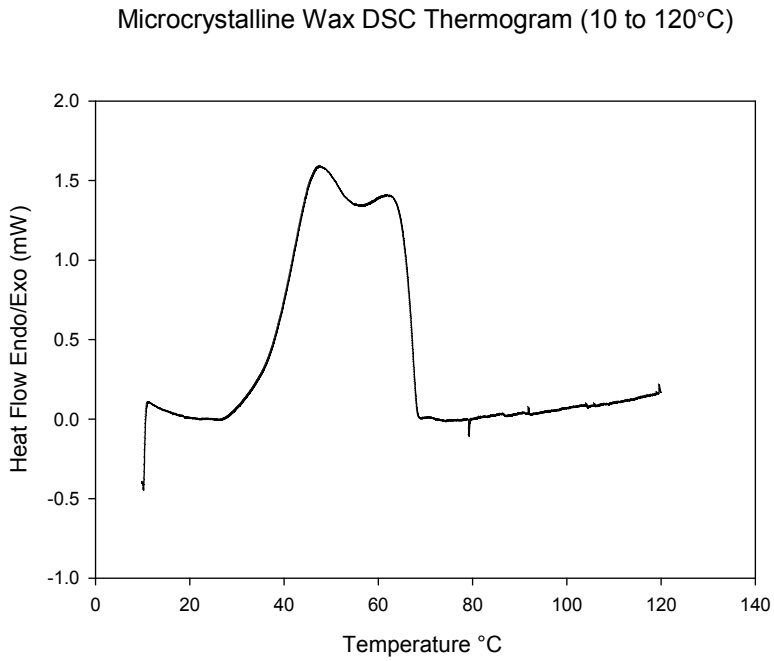


Fig. 5.13. Differential Scanning Colorimetric Thermogram for Microcrystalline Wax (10 to 120°C).

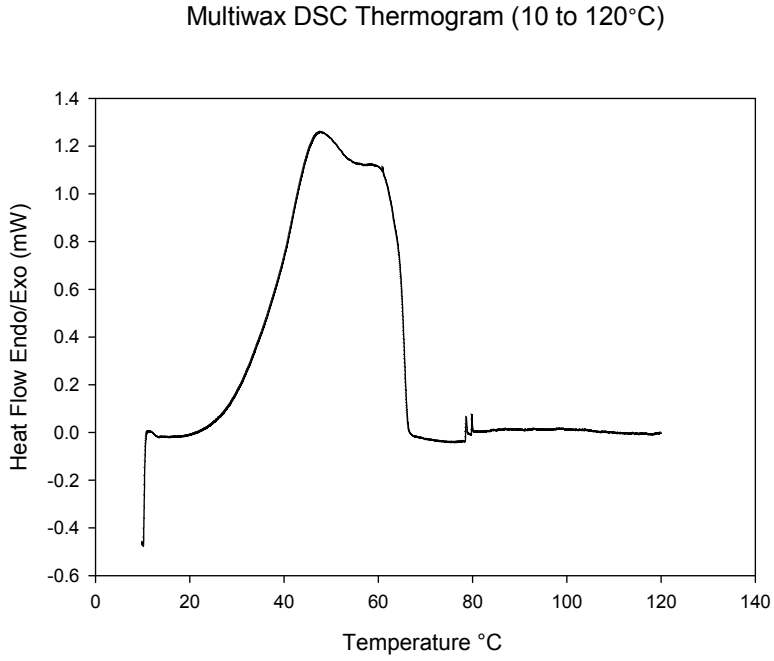


Fig. 5.14. Differential Scanning Colorimetric Thermogram for Multiwax (10 to 120°C).

The thermograms for Microcrystalline (Figure 5.13) wax and Multiwax (Figure 5.14) are almost identical confirming similar crystalline structures with melting point ranges of 30 to 69 °C and 25 to 67 °C respectively. There are two merged double endothermic events at 47.9 and 62.0 °C for the microcrystalline wax and for the multiwax 47.8 and 58.3 °C. This is due to the mixture of high molecular weight branched (iso-paraffinic) alkanes hydrocarbons and naphthenic hydrocarbons (Crowley & Laefer, 2008).

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