CHAPTER II
THEORITICAL BACKGROUND AND LITERATURE REVIEW

Many studies have been done in order to understand the factors influencing flocculation, the corresponding mechanisms of flocculation and also to identify the most appropriate methods for floc characterization. These studies will be reviewed in this section. However, no studies of the influence of deposited flocs on surface properties have been reported. For shampoos, one of the key attributes consumers use to evaluate overall product performance is the smoothness of hair. Generally, consumers evaluate product performance by finger through along the hair length or how the hair feels whilst it is being rubbed by the fingers or palm. This can be instrumentally measured as frictional properties. Therefore, understanding the impact of flocs composition and characteristics on the surface properties will be the focus of this work, in particular the impact on friction.

This chapter will be broken into two sections: i) the theory of flocculation and floc characterisation and ii) the theory of tribology and friction measurement

I) The Theory of Flocculation and Floc Characterisation

The majority of polymer- surfactant studies have been directed to understand dilute solutions and tend to focus on the thermodynamics of the interactions in term of binding isotherms and the structure of the formed polymer-surfactant complexes (or flocculation). The proposed models regarding the mode of surfactant binding to polymers were divided into three main groups; a) where the surfactant molecules bind individually, b) where the surfactant molecule bind in the form of micelles or c) the binding occurs as a combination of a) and b) in such a way that the monomers form "nuclei" for further binding of micelles.

Surface tension measurement is a simple and informative method of studying mixtures of two components, one of which is highly surface active and the other is relatively inactive at the air/water interface. Figure 1.1(Goddard E.D. 1992) represents the progressive uptake of surfactant (sodium dodecyl sulphate, SDS) by polymer JR (hydroxyethyl cellulose reacted with a lauryl dimethylammonium substitued epoxide). There were three regions observed: 1) lowering surface tension

at very low surfactant concentration, 2) the persistence of a low surface tension zone even in the presence of high precipitation where most of the original SDS is removed through precipitation and 3) eventual coincidence with the surface tension curve of polymer-free surfactant system which is in the micellar phase.
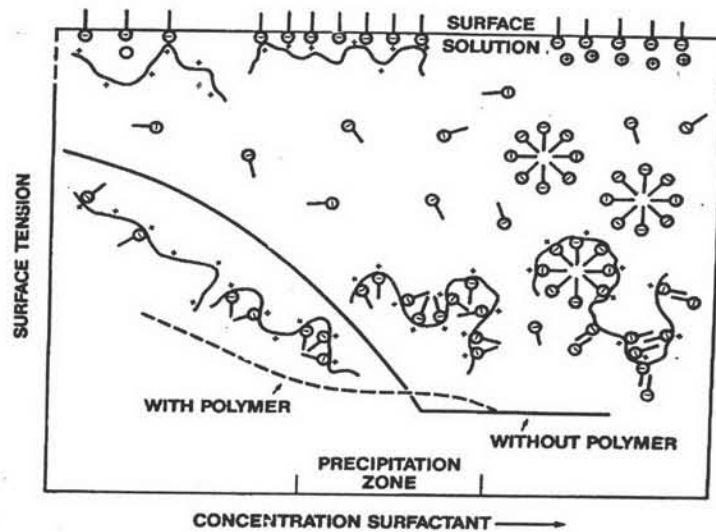

Figure 1.1 conditions in bulk and surface of solution containing a polycation (fixed concentration) and ionic surfactant; ref : Goddard, E.D.(1992).

Goddard and Hannan (1975) studied the interaction of a water-soluble cationic polymer substituted cellulosed ether, Polymer JR400 with sodium dodecyl sulfate (SDS) through a study of precipitate pattern and measurement of surface tension and electrophoretic mobility. The results showed that the addition of SDS to a polymer solution resulted in a progressive reduction of both solubility and electrophoretic mobility, with maximum precipitation being close to the point of zero mobility. Increasing further the surfactant concentration resulted in resolubilization. Whilst theoretically interesting, such studies which progress from a dilute regime to a more concentrated regime are not indicative of the experience that the consumers undergoes. It would be of interest to identify if similar results would be obtained when starting from the more concentrated regime.

A surface tension study using a Wilhelmy plate method showed addition of cationic polymer to a surfactant solution results in a large reduction in the surface

tension of SDS solutions. They interpreted the results in terms of the formation of a highly surface-active polymer/surfactant complex resulting from "head to head" adsorption of surfactant onto polymer. Resolubilization occurs by "tail to tail" adsorption of a second layer of surfactant ions to form a polyanion. This result was also observed by Guerrini, M.M. *et al*(1997) where they studied the interaction of aminoalkylcarbomoyl cellulosics and sodium dodecyl. They found that the reduction of surface tension was greater with increased polymer concentration. Moreover, this reduction in surface tension continued despite precipitation of the polymer surfactant complex and ultimately coincided with the surface tension curve of surfactant alone above the CMC (critical micelle concentration). This lowering of surface tension has been attributed to the modification of the polymer by adsorption of anionic surfactant at the cationic sites. In addition, the surface tension technique was also used in the study of the interaction of cationic surfactant, cetylpyridium chloride (CPC) and anionic polymer, polystyrenesuifonate (PSS) by Komesvarakul, N., Scamehon, J.F. (2003). The result was similar to that of other workers; synergistic lowering of surface tension with increasing polymer concentration was observed below the surfactant concentration at which the surface tension reach a plateau. Moreover, there were two breakpoints found in the diagram plot of surface tension as a function of surfactant concentration. This is in agreement with an ideal schematic of oppositely charged polymer-surfactant interactions reported by Goddard, E.D. (1992)

Gilanyi and Wolfram (1980) proposed a quantitative model based on a hydrophobic interaction concept for oppositely charged polymer-surfactant complex formation. This study involved the use of potentiometric measurements using $Au/Hg/Hg_1Ds$ and sodium ion selective glass electrodes. They reported that the main driving force for polymer-surfactant formation is the micelle-like aggregation of the surfactant ions. They also indicated that the binding of the surfactant to the polymer with increasing amount of surfactant is interrupted by free micelle formation, this is because surfactant monomer concentration has reaches its upper limit and hence additional biding would be independent on additional surfactant.

Leung, P.S. *et al.*(1985) investigate the interaction of anionic surfactant (SDS) with 2 cationic polymers with different backbone structures a) cationic cellulose ether, Polymer JR and b) synthetic vinyl copolymer, Reten by using a

variety of techniques, especially small angle neutron scattering, viscosity and dye-solubilization measurements. The results indicated that the cationic polymer/anionic surfactant associated complex structure is dependent on polymer backbone structure and configuration. At low surfactant concentration, intermolecular interaction was favoured for the more rigid Polymer JR, whereas, intramolecular interaction was favoured for the more flexible Reten polymer. In the resolubilization zone, Polymer JR favoured a polymer micellar association while Reten seem to stabilize a structure involving association of surfactant into smaller units, perhaps a surfactant pair. However, both polymers showed similar results of micellar structure in the large excess surfactant concentration region.

Magdassi (1996) studied the possibility of obtaining effective flocculation as a result of the interaction of ionic monomeric surfactants with oppositely charged polymers that pre-adsorb on negatively charged clay particle. The formation of insoluble particle have been studied by measuring the turbidity and zeta potential in order to identify the optimum flocculation process. Light scattering experiment were also used to obtain the size of the aggregates. The result showed the process consisted of 2 steps a) adsorption of a cationic polymer on to the negatively charged clay particle resulting in charge reversed and suitable for b) further binding of anionic surfactant to form an insoluble surfactant-polymer complex. The result showed that at about 1 : 1 molar ratio (SDS : cationic monomer) the highest turbidity was obtained, presumably due to all charges of polymer being neutralized. As a consequence, the resulting hydrophobic species is formed through the hydrophobic group of the surfactant molecules binding to the polymer molecules. The result was also confirmed by elementary analysis showing that sulphur and nitrogen exist in the precipitate in a weight ratio of 2.07:1. The implication of which is that the insoluble complex is composed of a cationic polymer in which all its charged groups are neutralized by the anionic surfactant. Moreover, it was found that the aggregate size and flocculation rate are larger when flocculation was obtained with surfactant-polymer complex compared to polymer alone, thereby indicating the significant role of the hydrophobic interactions. It was concluded that this flocculation process is based on polymer-surfactant interactions and is expected to occur for any combination of particle-polymer-surfactant which fulfils the interaction requirement.

Potentially, this would be relevant information for shampoo formulation containing other hydrophobic ingredients such as silicone or pearlizers which are typically emulsified with anionic surfactants

Goddraich *et al.* (1996) studied the resulting microstructures in a mixed solution of SDS and the oppositely charged quaternary ammonium polymer (polymer JR-400) throughout the interaction zone. This study used two complimentary methods; cryo-transmission electron microscopy to provide imaging of the dispersed microstructures formed in the mixed systems without staining, while maintaining their original state and light microscopy extended the length-scale of the structure observed from one to hundreds of micrometers. The results indicate that both techniques clearly showed the structure formed in the solution. At low SDS concentration, bilayer fragments, small vesicles and disc like aggregates form. Increasing the SDS concentration further resulted in the solution becoming turbid as the charge neutralization point was reached. The image indicated microphase separation and flocs were clearly apparent. Such flocs were mainly globular in structure with no microstructures observed in the supernatant in the precipitation zone. At this precipitation point, particles of many different sizes could be observed using light microscopy. Further additions of SDS produced a turbid solution, indicating microphase separation with well developed flocs of spherical aggregates. Resolubilization occurred at higher SDS concentration and a variety of microstructures, including vesicle, disc-like, and thread-like structures appeared. Ultimately at excess surfactant, resolubilization was completed with the formation of spheroidal micelles.

Fielden, M.L. *et al.*(1998) studied the effect of polyelectrolyte charge density on the polyelectrolyte/surfactant interaction at the negatively charged solid surface. Measurement of flocculation and electrophoretic mobility in bulk solution at intermediate surfactant concentration clearly showed a phase separation with a maximum turbidity corresponding approximately to charge neutralization of the polyelectrolyte/surfactant complex. Adsorption of intermediately charged polyelectrolyte onto mica left the surface slightly charged, resulting in a weak electrostatic repulsion between the surfaces. Addition of a small amount of SDS (0.005x cmc) did not affect the surface charge. Increasing SDS concentration by ten

times caused a massive increase in repulsive forces and layer thickness. This is due to the formation of an associative complex between surfactant molecules and the adsorbed polyelectrolyte.

Bigg, S. *et al.* (2000) studied the aggregated structure of a high molecular weight cationic polymer flocculated with a colloidal dispersion of anionic polystyrene latex particles via a bridging flocculation mechanism. They used low angle laser light scattering (LALLS) to follow the flocculation process as a function of time to determine aggregate size, size distributions and aggregate mass fractal dimension. The light scattering confirmed the flocs formed had a mass fractal character. They defined LALLS as a tool to generate some useful information about aggregate structures formed through a bridging flocculation mechanism

Glover, S.M *et al.* (2000) studied the structure of the aggregates formed by comparing two techniques, the static light scattering and settling. Several parameters have been investigated, ie. electrophoretic mobility for charge identification, intramolecular interaction was favoured intramolecular interaction was favoured mass fractal dimension to observe mass density together with the information of aggregate shape and size. They concluded that both techniques are excellent for investigating the structural compactness of particle aggregates and they complement each other in their validity for a certain range of aggregation. The author proposed that the use of light scattering is most applicable for small, open aggregates, whereas settling is most suitable for large and/or dense aggregates.

Voison, D., Vincent, B. (2003) have recently studied the phase behaviour of a cationic polyelectrolyte (Jaguar) and an ionic surfactant (either sodium dodecylsulfate , SDS or sodium lauryl ether sulfate, SLES). Various characterization techniques were used in order to obtain robust data. The phase diagram and surface tension were studied. Three phase regions were identified with increasing surfactant concentration. Similar results as other studies were obtained. The surface tension decreased significantly at very low SDS concentrations when jaguar was presented. Electrophoretic mobility of the aggregates as a function of SLES concentration was also measured in the one phase region below and above the phase separation region. Each separate phase was analysed in order to assess the factors affecting the flocculation and phase separation. Elemental analysis was used to investigate the

molar ratio the average molar ratio of surfactant molecules bound to cationic sites. In addition, dynamic light scattering was proposed to obtain hydrodynamic radius of two different salt concentration and the result showed flocculation rate is faster at the higher salt concentration. Moreover, the rate of flocculation was studied by stopped-flow turbidity experiment. The result showed that at some concentration above the critical aggregation concentration of a given anionic surfactant with a cationic polyelectrolyte stable, open-network 'particles' form, typically ~100 nm in size that were positively charged. As the surfactant concentration is increased further, these particles aggregate and form a separate gel phase, which contained a high percentage of water. At higher surfactant concentrations, the particles become sufficiently negatively charged that they restabilise. An iso-electric point for the particles has been observed at a surfactant concentration corresponding to the aggregated region. Within this aggregated, gel-phase region there appears to be typically ~ 2 to 4 surfactant molecules associated with each cationic site of the polymer chains. It is postulated that association of the anionic surfactant molecules occurs within the polyelectrolyte chains, binding them together, to form the discussed particles. These associated surfactant structures were referred to here as 'internal 'micelles. A crude estimate has been made, based on turbidity / time measurements, that there may be up to ~1000 polymer chains in each primary particle, bound together by the internal surfactant micelles. Small-angle light scattering studies of the aggregating particles indicates a fractal dimension for the aggregates that would correspond to a diffusion-limited aggregation process.

Rattakawin, C. (2003) studied the aggregate (floc) size distribution resulting from hydrophobic flocculation of a hematite suspension with sodium oleate by using a laser light scattering technique. The author concluded that by measuring floc size distribution it is possible to distinguish clearly among floc formation, growth and breakages. By adding sodium oleate in a pre-coagulated suspension, the particle progressed further to a larger size. The median floc size, derived from size distribution, was used as a performance criterion and found to increase rapidly at the initial stage of the flocculation process, and decreased with extended agitation time and intensity.

Zhang, J.J and Li, Z.Y.(2003) modeled the particle size distribution dynamics in a flocculation system using a modified sectional modeling technique. The effect of shear rate, collision efficiency and initial concentration were studied. They proposed that an increase in a shear rate resulted in increasing the rate of particle coagulation but also decreased the rate of aggregate breakage. A higher initial particle concentration produced more large aggregates with a higher peak concentration when the dynamic steady state was achieved.

Flocculation or precipitation is a crystallization process. Such a crystalization process occurs firstly through the formation of crystal nuclei, followed by the growth of the crystal through additional microscopic precipitation. Before the crystals can grow, there must be an exist in the solution a number of solid bodies known as centres of crystallisation, seeds, embryos or nuclei. Nucleation may occur spontaneously or it may be induced artificially; these two cases are frequently referred to as homogeneous and heterogeneous nucleation, respectively. It is not always possible, however to decide whether a system has nucleated of its own accord or whether it has done so under the influence of some external stimuli (Mullin. 1993).

The kinetic of flocculation can be considered as a two stage process of i) the formation of aggregate nuclei and ii) growth of those nuclei through hydrophobic precipitation.

II) The Principle of Friction & Its measurement
Friction

The study of friction is known as "tribology". It describes the study of the interacting surface in relative motion. Tribology (Greek) derived from Tribos has the meaning of rubbing. The basic law of friction between two unlubricated surfaces, is Amontons' law. In this law the coefficient of friction μ between two solids is defined as

$$\mu = F/W$$

where :   F denotes the frictional force and

W is the load or force normal to the surface

It has been determined that the coefficient of friction is independent of the apparent area of contact. Even very smooth-appearing surfaces are highly irregular on a microscopic scale. As a result, the two contacting surfaces will touch only in isolated regions. Hence ultimately the friction is confined to a real area that is much smaller than the apparent area.

In the case where a lubricant is included, the Stribeck curve should be applied, deposited floc could be considered as one such case. There are two limiting cases. In the first case the lubricant layer fills the space between the two. As such the two surfaces are independent of each other and the coefficient of friction depends on hydrodynamic properties of the separating lubricant. As such the coefficient of friction will depend on the applied force and velocity of the contacts. In addition it will depend on the bulk viscosity of the hydrodynamic lubricant. In the second limiting case the lubricant forms a thin layer over each surface. In this instance the friction coefficient will be largely independent of the applied force, bulk viscosity and velocity. This is primarily because friction is a governed by a number of isolated contacts rather than the bulk. This is referred to as boundary lubrication. In reality it is anticipated that most boundary lubricants will not behave entirely as a pure lubricant but would display some hydrodynamic lubricant properties. This is to be expected as at the point of contact the two surfaces would be kept apart by a thin but contiguous layer of lubricant i.e. reminiscent of a hydrodynamic lubricant. As such some dependency on applied force and lubricant viscosity is to be expected.

The Stribeck curve is illustrated in figure 1.2; the abscissa quantity, $(\eta.v)/P$ is know as the generalized Sommerfifeld number where

η is represented viscosity

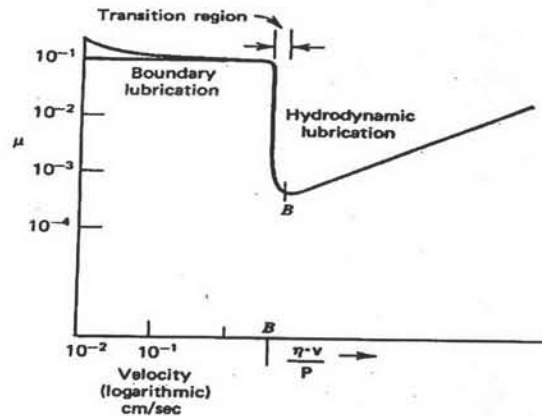v is represented speed

P is represented load.

Figure 1.2 Region of hydrodynamic and boundary lubrications (Adaman, A.W., 1990).

For hair care products, the term 'conditioning hair' is very important and as such it can be instrumentally measured as a frictional property. Friction is a consequence of the contact between the two surfaces, in the context of this study the two surfaces of interest are human hair and skin (from hand or fingers). Therefore, it would be useful to start with the summary of current concepts of the structure and properties of human hair fibres. Figure 1.3 shows a schematic of a human hair fiber with its various layers of cellular structure. The hair fiber consists of cortex and cuticle cells which run longitudinally along the hair fiber axis. The cortex takes up the majority of the hair fiber composition and plays a large role in the mechanical properties of the hair. Of more interest to tribologists, however, is the cuticle, the outermost region that protects the cortex. This multi-layered region is important to the hair's frictional characteristics because it is this structure which comes in contact with other hair, skin or combing devices. The cuticle is composed of keratin and consists of an A-layer, exocuticle, endocuticle, and cell membrane complex. The cuticle consists of flat, overlapping cells (scales) that are attached at the root end and point toward the tip end of the hair fiber, like shingles on a roof. Each cuticle cell is approximately 0.3–0.5 micron thick and the visible length of each cuticle cell is approximately 5–10 micron. The cuticle in human hair is generally 5–10 scales thick. The diameter and shape of hair fibers vary considerably from consumer to consumer but most noticeably from ethnic race to ethnic race. For example the diameter may

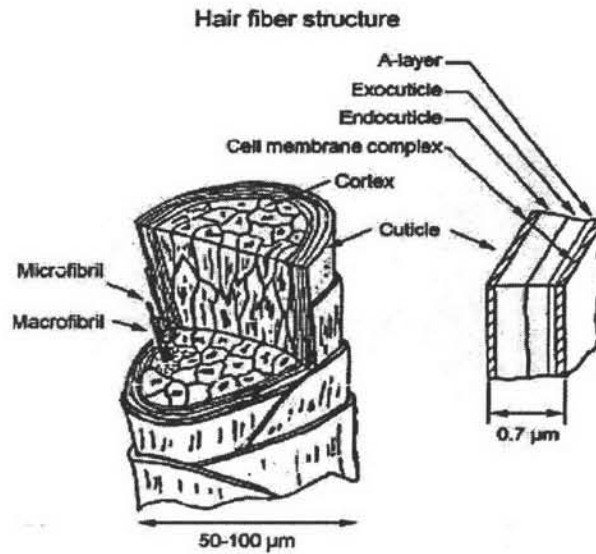vary from approximately 50 to 100 micron but the shape may also change from round to highly elliptical.

Figure 1.3 Cross-sectional schematic of a human hair fiber. The tribological properties of hair are attributed to the cuticle, which is the outermost surface (Robbins 1994).

Schwartz, A., Knowles, D. (1963) used the fibre-capstan method to study the frictional property of hair fibre with and without polymer treatment. They concluded that the frictional forces and coefficients of friction depend considerably on relative humidity, or in an extreme case on the presence of water. Moreover, the nature of the capstan material is also significantly important i.e. hard rubber produced higher coefficient of friction than aluminium and the different is more pronounced in wet stage. Similarly, the surface of the hair, especially its hydrophilicity, affects its friction behavior. Bleaching and permanent wave treatments increase hydrophilicity of hair due to removal of outer lipid. In these cases, scission of disulfide bonds in the outer layer of the cuticle leads to a softening of the surface, resulting in an increase in the area of real contact.

The deposition of polymeric materials on fibre surface lowers the coefficient of friction, especially for bleached hair. Goddard, E.D. (1999) made an interesting observation that after treatment the hair with Cationic Polymer JR-400 a

pronounced stick-slip phenomenon on the against-scale-sliding direction was observed which was not observed in the with-scale direction as shown in Figure 1.4. A "ploughing" effect of scale edges into the water-swollen polymer film on the capstan may be involved. This seems to indicate that while polymer deposits on the fibre surface does lower friction against a hard surface this may not necessarily be the case against soft surfaces, this has implications for consumer perceived combability.
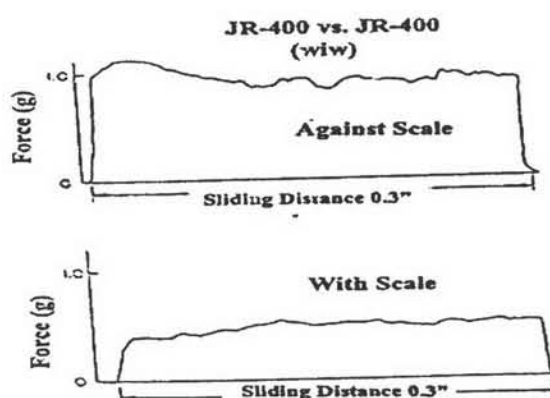

Figure 1.4 Frictional curve of human hair treated with Polymer JR-400 against a capstan at wet in water (Godard, E.D. 1999).

Mcmullen, R. L and Kelly, S.P. (2001) used atomic force microscopy (AFM) and lateral force microscopy (LFM) to investigate the morphology and surface changes associated with various surface modification to human hair. The results showed that topographic morphology can be investigated from both techniques. Lateral force measurement in combination with AFM can provide fundamental information about physical and chemical properties of the surface. Furthermore, study of surface modified and native surfaces indicated that when investigated as a function of tip loading force the different hair modification resulted in change of friction coefficient. The friction coefficient increased in the order of native, bleached, solvent extracted and polymer treated hair. These results are reported to be consistent with dry combing values obtained experimentally with a

Dia-stron Minature Tensile tester which measure the force require to comb through a bulk of hair fibers, in essence providing information with regard to interfiber friction.

Bhushan, B, K. *et al.* (2005) investigated a new technique to mount hair and measure the coefficient of friction by using the flat-on-flat tribometer under reciprocating motion. There were three types of hair used in this study, Caucasian, Asian and African hair with varied types of treatment, i.e. virgin, chemo-mechanically damaged and conditioner treated. The effect of temperature and humidity on hair friction were also studied. They concluded that the coefficient of friction of treated hair increased with increasing temperature while no effect was obtained on virgin hair. Moreover, the coefficient of friction was determined to be a strong function of humidity and it increased as the relative humidity increased. An even greater effect could be observed on virgin hair than on treated hair.

One of the techniques used internally in Unilever for friction measurement is the texture analyser (TA). The friction is defined as the resisting force that arises when a surface of one substance slides, or tends to slide, over an adjoining surface of itself or another substance. Between surfaces of solids in contact there may be two kinds of friction: 1) the resistance opposing the force required to start to move one surface over another (static friction) and 2) the resistance opposing the force required to move one surface over another at a variable, fixed, or predetermined speed (dynamic friction). It should be noted here that TA was recently discovered to be sensitive for silicone differentiation. Hence, it is a challenge to investigate whether or not this technique would be able to use in this study.

The technique is based upon the commercially available Texture Analyser (ex Stable MicroSystems) and uses a load cell with a 5Kg full-scale deflection. The apparatus is shown below in Figure 1.5.
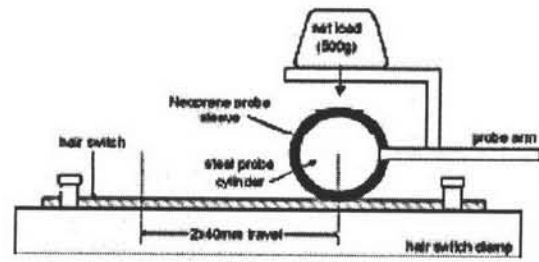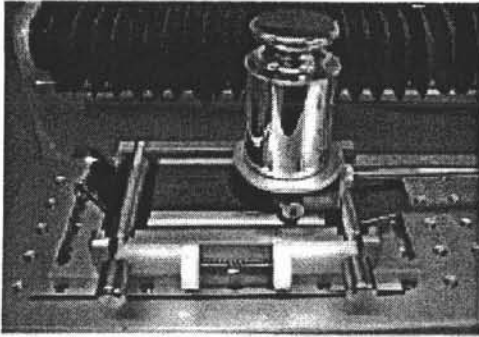
Figure 1.5 photograph and schematic of frictional hysteresis apparatus based upon Texture analyzer.