

COLLOIDAL STABILITY OF NATURAL RUBBER LATEX

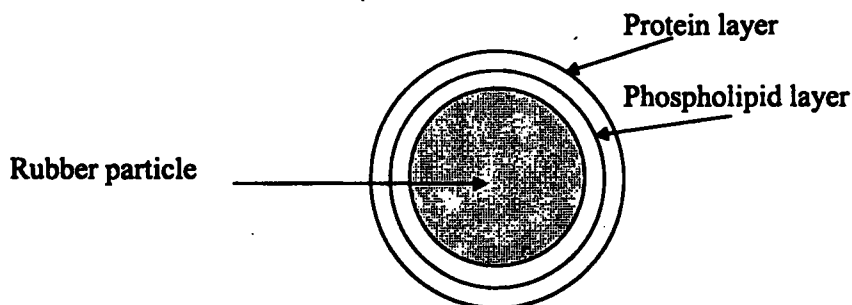
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INTRODUCTION

Natural rubber latex is basically a colloidal dispersion of rubber hydrocarbon in an aqueous medium. The chemical composition of rubber hydrocarbon has been identified as linear *cis*-1,4-polyisoprene of high molecular weight, and it is present in latex as molecular aggregates in the form of discrete particles which are usually spherical in shape with diameters ranging from 15nm to 3 μ m (Lucas, 1938). In addition to the rubber hydrocarbon fresh NR latex contains proteins, lipids, sugars, carotenoids, mineral salts, enzymes and numerous other nitrogenous substances in addition to water & rubber hydrocarbon. Most of these non-rubber constituents are dissolved in the aqueous phase of the latex, some are adsorbed at the surface of the rubber particles and the others are suspended in the latex. It has been established that in fresh NR latex the non rubber constituents which are adsorbed on the rubber particles are mainly proteins and lipid materials, possibly in the form of a complex. At least some of these proteins are phosphoproteins (Tunncliffe, 1954) and at least some of the lipids are phospholipids (Smith, 1954).

Structure of Natural Rubber particle

Based on the reactions of NR latex towards various chemical treatments and physical techniques the following structure has been proposed for the structure of natural rubber particle.



Outline of structure of natural rubber particle

The principal phospholipids of the NR latex are of the lecithin type and they are strongly adsorbed on to the surfaces of the rubber particles. They are thought to be intermediaries by which the proteins are anchored on to the rubber particles. The adhesion between the proteins and the adsorbed lecithin has been accounted for the fact that at the pH of fresh latex the lipid layer carries a slight overall positive charge, whereas the proteins, being on the alkaline side of their iso electric point are negatively charged, so that ionic interaction between the two layers is possible (Blackley, 1966).

Chemical composition of fresh NR Latex

Being a natural product the composition of NR latex would vary depending on various factors such as clone, season, soil conditions, fertilizer application techniques and tapping frequencies etc. As such it is not possible to give an exact composition for the NR latex. However a typical composition can always be suggested as given below;

	<u>% by weight of latex</u>
Dry rubber content	30-35
Proteinous substances	1-1.5
Lipids	1-2.5
Sugars	1
Inorganic ions	1
Water	60-65

All these non-rubber substances are distributed between three principal phases. The average percentage of each of these three phases is given below:

	<u>% by weight of latex</u>
Rubber phase	35
Aqueous phase	55
Lutoid phase	10

Lutoid phase can only be seen in fresh NR latex since the lutoid particles which constitute the lutoid phase are very sensitive to various factors such as dilution, ammoniation and heat. Lutoid particles are slightly larger than the rubber particles and are irregular in shape. Chemically, they appear to be mainly water. In addition to that they contain various other substances such as carotenoids, acids, mineral salts, proteins and even rubber particles. The boundary of a lutoid particle is a semipermeable membrane and hence they are osmotically sensitive. As a result if a

fresh latex is diluted the luteoid particles absorb water and become larger in size and eventually they burst releasing the inside materials into the serum.

Spontaneous coagulation of fresh NR latex

NR latex is a very good source for microbial growth since it contains various nutritious substances such as proteins, sugars, amino acids etc. As a result NR latex gets contaminated by micro-organisms on tapping as well as during the collection. Under tropical conditions these micro-organisms multiply rapidly by utilising some of the non rubber constituents in the latex with the production of certain acids. This is followed by the neutralisation of the negative charge of the protective protein-lipid layer surrounding the latex particles leading to the destabilisation of latex. Thus it is necessary to add a preservative in order to keep the latex as a fluid until it is ready for processing.

Preservation of NR latex

Preservation of NR latex is normally achieved by adding up to 1.0%(w/w on the aqueous phase) of ammonia. Ammonia being a good biocide has several advantages; it

- controls the proliferation of bacteria
- neutralises the free acids formed in the latex
- helps in the precipitation of heavy metals such as Mg
- hydrolyses the interfacial proteins and phospholipids, thereby making the latex more stable.

The hydrolysis of phospholipids has been found to occur more rapidly than that of the proteins, and as a consequence, by the time the latex reaches the latex reception point of the industrial user, the phospholipids of ammoniated and concentrated latex have been converted to fatty-acid soaps (Blackley, 1966). Among other products, much of the proteins remain unhydrolysed. The interfacial film at this stage consists of a soap/protein mixture, and the composition of this interfacial film changes as the latex ages.

Colloidal instability of latices:

The simplest type of colloid system is a dispersion of one phase in a second phase, in which the disperse phase is in a state of dispersion such that at least one dimension is in the range between 1nm and 1000nm. Colloids are generally classified lyophobic (there is no tendency for the disperse phase to mix with the dispersion

medium) or lyophillic (there is a strong tendency for the disperse phase to mix with the dispersion medium). The most important property of a lyophobic colloid is its colloid stability. Rubber latices are examples of lyophobic colloids. The factors which determine the colloid stability of a rubber latex are essentially those which determine the colloid stability of any lyophobic colloid .

In latices, as in colloidal dispersions in general, frequent encounters between particles occur due to Brownian movement, to gravity (creaming and sedimentation), and to convection. Whether such encounters results in permanent contact, or whether the particles rebound and remain free, is determined by the forces which are operative between the particles. If the attractive forces, which are assumed to be of London Van der Waals type, are larger than the repulsive forces, interaction between two or more particles may first cohere to give a loose aggregate and then subsequently to give a little larger particle.

Nature of stability of lyophobic colloids

A lyophobic colloid is said to be stable if it persists as a colloidal dispersion over a period of time. However, all lyophobic colloids are thermodynamically unstable because of their high interfacial free energy which is a result of the high ratio of interfacial area to volume of the disperse phase. Aggregation or the flocculation of the dispersed particles, which brings about a reduction of the interfacial area and free energy is therefore thermodynamically favourable. As mentioned earlier the stability/flocculation behavior of a lyophobic colloid is governed by the various attractive and repulsive forces between the particles. Amongst the possible basic interparticle forces involved in colloidal systems of all types, the following can be considered as the important forces which are operative between the rubber particles in NR latex;

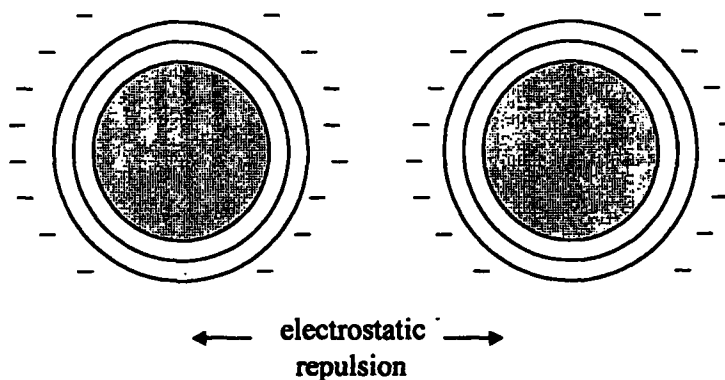
1. Van der Waals attractive forces : these originate from the quantum-wave mechanical interactions between all the atoms in one particle and all the atoms in a neighbouring particle.
2. Electrostatic repulsive forces: these arise from the presence of a counterion cloud which surrounds the particles in the dispersion medium. The counterion cloud is brought into existence by the presence of electric charges of opposite polarity attached to the particle surfaces.
3. Steric repulsive forces: these arise from the presence of lyophillic macromolecules that are attached to the particle surfaces.

4. Solvation forces : these arise from the presence of solvent molecules which are tightly bound in the interfacial region.
5. Depletion or exclusion forces : these arise from the presence of lyophilic macromolecules dissolved in the dispersion medium.

Amongst these interparticle forces, at least four types of repulsive forces namely, electrostatic, steric, solvation and depletion (exclusion) are believed to contribute to the stability of lyophobic colloids. The types of stabilisation conferred by these four types of repulsive forces are known, respectively, as electrostatic, steric, solvation & depletion (exclusion) stabilisation. It is reasonable to assume that the stability of NR latex is conferred by the above stabilisation forces and will be discussed in following sections.

Electrostatic stabilisation

Electrostatic stabilisation of lyophobic colloids is a consequence of the presence of bound electric charges at the surface of the particles. The origin of the surface charge can be either ionisation of chemical groups at the surface of the particles or the adsorption of charged species from the dispersion medium at the particle surface. In the case of NR latex the lyoprotein layers surrounding the rubber particles confer the negative electric charge on the particle surfaces thereby making the latex electrostatically stabilised. Electrostatic stabilisation of two NR latex particles can be represented schematically as given below;

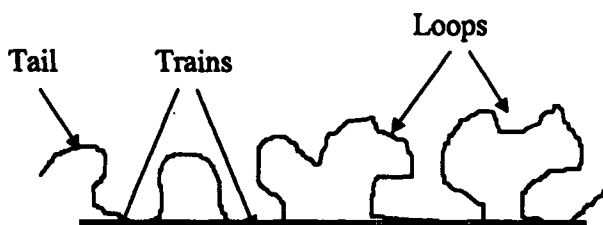


Schematic representation of electrostatic stabilisation of two NR latex particles

Steric stabilisation

Steric stabilisation of lyophobic colloids is a consequence of the presence of adsorbed macromolecules at the surfaces of particles. The practical use of hydrophilic macromolecules for the stabilisation of aqueous hydrophobic colloidal dispersions is not new. The ancient Egyptians and Chinese used naturally-occurring polymers, such as gum arabic, casein, egg albumin, etc. to make stable dispersions of carbon black and other pigments (Encyclopaedia Britannica, 1968). Traditionally, colloid scientists have referred to stabilisation by macromolecules as "protection". Heller and Pugh appear to have been the first to use the term "steric stabilisation", and this term is now generally used to describe the stabilising action of attached non-ionic polymers.

It has long been known that best steric stabilisers are block or graft copolymers. One of the comonomers should form a polymer which is immiscible with the dispersion medium but miscible in the disperse phase, whereas the other monomer should form a polymer which is miscible with the dispersion medium. Accordingly the theories of polymer adsorption assume that the configuration of an adsorbed polymer on a solid surface can be represented as a flexible chain of segments, some of which are in direct contact with the surface, whilst others extend into the dispersion medium. A schematic representation of the conformation of an adsorbed polymer molecule at a plane interface is shown below;



Schematic representation of conformation of an adsorbed polymer molecule at a plane interface

Those segments which are in direct contact with the surface are referred to as "trains", and those in between and extending into the dispersion medium are referred to as "loops". The free ends of the adsorbed polymer also extending into the dispersion medium are referred to as "tails". The interaction forces between sterically stabilised colloidal particles which tend to keep the particles dispersed in solution are of two major kinds:

1. Entropic interactions (Mackor, 1951) (Van Der Waarden, 1951) : these result from the loss in configurational entropy of a polymer molecule on the approach

of a second particle. The reduction in configurational entropy of the adsorbed polymer molecule is a result of the compression of the adsorbed polymer chains which reduces the total volume available for each polymer chain. This effect is also called the "volume restriction" or "elastic" effect.

2. **Mixing interactions** (Fisher & Kolloid, 1958): these result from the interpenetration of the polymer molecules adsorbed on colloidal particles. When the layers of adsorbed polymer chains on two particles interpenetrate, the higher polymer segment concentration between the particles leads to an increase in the local osmotic pressure and free energy.

Solvation stabilisation

The presence of a solvation layer surrounding the particles can also enhance the colloidal stability of a lyophobic colloid. There is evidence in the literature to show the presence of solvation layer near the solid surface (Thomas & Cremers, 1970) (Faucett *et al.*, 1964). The extent of solvation depends to a considerable extent upon the chemical nature of the stabiliser. The solvation layer arises from the presence of nonionic hydrophilic materials adsorbed on the particle surfaces. In NR latex based products manufacturing industry nonionic hydrophilic polymeric materials are often used as secondary stabilisers. They enhance the stability of NR latex simply through a mechanism of hydration stabilisation.

Depletion stabilisation

It has been shown that colloid stability can also be imparted by the presence of free polymer dissolved in the dispersion medium (Feigin & Napper, 1980). This type of stabilisation is referred to as "depletion" or "exclusion" stabilisation. It has been suggested that the stability arises from the depletion of the concentration of free polymer between the surfaces of the particles when they are in close proximity. Closer approach of the particles can only be achieved by a further depletion of the segment concentration between the particles. At much closer approach between the particles, almost complete exclusion of polymer molecules from between the surfaces of the particles occurs. In a good solvent this is energetically unfavorable. This type of stabilisation mechanism may also be operative in NR latex since it contains some macromolecules dissolved in the aqueous phase.

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