INVESTIGATION ON THE EFFECT OF VARIOUS CROSS-LINKING AGENTS IN ACRYLIC EMULSION POLYMER & ITS APPLICATION PERFORMANCE

A Major Project Report Submitted for the Award of the Degree of

MASTER OF TECHNOLOGY
IN
POLYMER TECHNOLOGY

Submitted by

NAVNEET KUMAR
(Roll No. 2K15/PTE/13)

TO

DEPARTMENT OF APPLIED CHEMISTRY AND POLYMER TECHNOLOGY
DELHI TECHNOLOGICAL UNIVERSITY, DELHI- 110042

July 2017

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UNDER THE ESTEEMED GUIDANCE OF

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CERTIFICATE

This is to certify that the project report titled **“*INVESTIGATION ON THE EFFECT OF VARIOUS CROSS-LINKING AGENTS IN ACRYLIC EMULSION POLYMER & ITS APPLICATION PERFORMANCE*”** submitted by **Mr. Navneet Kumar (Roll No. 2K15/PTE/13)** in partial fulfilment for the award of degree of “**Master of Technology in Polymer Technology**” to Delhi Technological University, Delhi, is a bonafide record of the work carried out by him in the Department of Applied Chemistry, Delhi Technological University, Delhi, and Research and Development Centre, Uflex Limited {Chemicals Division}, Noida, under our supervision. The project embodies the original work by him to the best of our knowledge and has not been submitted to any other degree of this or any other university. The matter embodied in this project report is original and not copied from any source without proper citation.

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ACKNOWLEDGEMENTS

I am heartily thankful to my project supervisor **Dr. S.G. Warkar**, whose encouragement, guidance and support from initial to the final stages of my major project work enabled me to develop an understanding of the project work and subject. In spite of his busy schedule he was always there to meet, discuss, refine and resolve my worries, thoughts and ideas. He has been a great source of inspiration throughout my project work endeavor.

I also wish to express my gratitude to **Dr. Archna Rani**, Head of the Department, Department of Applied Chemistry & Polymer Technology, for her kind hearted support. I am also grateful to all teachers for their constant support and guidance.

I am highly grateful to **Dr. N.K.S. Raghav** (DGM; Adhesive, R&D) Uflex Limited, Chemicals Division, Sector-57, Noida for granting me the permission to carry out my project work in the research and development center.

I am thankful to Mr. Amit Garg for their great contribution and advice on laboratory works and equipment to make my project work easier.

Finally, I offer my blessings and love to all those who supported me in any aspect during the completion of my project work.

Thank You Very Much!!

Sincerely,

Navneet Kumar

DECLARATION

I, Navneet Kumar certify that,

- The work contained in this project report is original and has been done by me under the guidance of our project mentors.
- The work has not been submitted to any other University or Institute for the award of any degree, diploma, or certificate.
- I have followed the guidelines of the University and Industry in preparing the project report.
- I have conformed to the norms and guidelines given in the Ethical Code of Conduct of the University and Industry.
- Whenever I have used materials (data, theoretical analyses, figures, text, etc.) from other sources, I have given due credit to them by citing them in the text of the project report and giving their details in the references.

Signature

Navneet Kumar

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Symbols	**Abbreviations**
Tg	Glass transition temperature
hrs.	Hours
DMW	De-mineralized Water
SFT	Surfactants
BFR	Buffer
BA	Butyl Acrylate
STY	Styrene Monomer
AAEM	Acetoacetoxyethyl Methacrylate
MMA	Methyl Methacrylate
2-eHA	2-Ethyl Hexyl Acrylate
AA	Acrylic Acid
2-HEA	2-Hydroxy ethyl Acrylate
HPA	Hydroxy Propyl Acrylate
ITR	Initiators
CT	Catalyst
NZR	Neutralizer
%NVC	Non Volatile Contents (%Solid)
Qty.	Quantity
PET	Polyethylene terephthalate
m-PET	Metalized Polyethylene terephthalate
m-BOPP	Metalized Biaxial oriented Polypropylene
ST	Slight tack
NMT	No metal transfer
Adh.	Adhesive

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Chapter 1 **Introduction**

Chapter 1: Introduction

1.1 Introduction

Emulsion and emulsion technology is also considered as the most suitable and valuable topic for academic and industrial research due to wide range applications and their complex nature. If the natural emulsions are taken into considerations the emulsions are in the use for thousands of years.

As definition given by Paul Becher[1] the emulsion is ***"A heterogeneous system consisting of at least one immiscible liquid dispersed in the form of droplets, whose diameter, in general exceeds 0.1 mm. Such systems possesses minimal stability, which may be accentuated by the additives such as surface active agents, finely divided solids, etc."***

In simple words emulsion is defined as, ***"Emulsion is a two phase system consisting of two immiscible liquids, the one being dispersed as finite globules in the other".***

The discontinuous or internal, dispersed phase of liquid which is broken up into globules. The surrounding liquid of globules is known as continuous or external phase.[2] the industry has define the definition of emulsion to include colloidal solubilisation or dispersions as well as solid dispersions. Where at least one phase either continuous or dispersed is liquid as shown in following table

Table 1.1 – Types of Emulsions

Type	Continuous Phase	Dispersed Phase
Foam	Liquid	Gas
Aerosol	Gas	Liquid
Emulsion	Liquid	Liquid

Solid Suspension	Liquid	Solid

Emulsions are broadly used in various industrial applications due to following reasons-

1. To introduce an insoluble ingredient into the system with help of surface active agents.
2. To dilute vital and an expensive ingredient by an inexpensive and immiscible diluents.
3. To control physical and application parameters such as taste, odor, dose, reactivity or toxicity of material.
4. To obtain an equal distribution of active ingredients.
5. To control the aesthetic and physical properties of emulsion formulation.

The economical as well as commercial value of emulsion has been recognized in terms of milk. Which is the most natural emulsion. The other examples are natural rubber latex, crude oil, etc.

1.2 Emulsions

Emulsions are the metastable colloids virtually prepared from two immiscible liquids. Amongst the two immiscible liquids one liquid is dispersed in the other liquid with the help of surface active compounds. The dispersed droplets of emulsion possess all classical characteristics of metastable colloids such as, reversible phase transitions due to droplet interactions, Brownian motion and irreversible transitions that generally involve droplet destruction.[3] The metastability of emulsion is mainly dependent upon the concentration and properties of surface active species at the interface.[4, 5]

1.3 Types of Emulsions

1.3.1 Coarse Emulsions

Depending upon the type of external and internal phases involved, they are subdivided into four classes such as,

1. Water in oil (W/O) - water droplets are being suspended into oil matrix.

2. Water in water (W/W) – consists of aqueous solutions of mixture of incompatible polymers systems such as, polysaccharides, proteins, etc.

3. Oil in water (O/W) – oil droplets are suspended in aqueous matrix

4. Oil in oil (O/O) – consists of incompatible organic solvents stabilized by copolymers with residues of different solubility in the solvents used.

1.3.2 Multiple Emulsions

In multiple emulsions the globules of dispersed phase encapsulate smaller droplets, which in most of the cases are similar or identical with continuous phase. The two major types of multiple emulsions are O/W/O in which water separates the two oil phases and W/O/W in which internal and external aqueous phases are separated by an oil layer. Multiple emulsions are unstable thermodynamically systems. Principal modes of emulsion breakdown involve coalescence of external or internal droplets, expulsion of internal droplets, and osmotic swelling or shrinking.[6]

Stability of multiple systems may be improved by forming the polymeric gel either in the external or internal aqueous phase.[7]

1.3.3 Micro Emulsions

Micro-emulsions are transparent (or translucent), stable, dispersions of oil and water stabilized by an interfacial film of surfactant molecules and having diameter <100 nm.

Micro-emulsion formation involves a combination of three to four components- water, oil, surfactant/s and co-surfactant/s. The surfactants are generally selected in the non-ionic group because of their good cutaneous tolerance and balanced lipophilic and hydrophilic property. The most important effect of co-surfactant in the formation of micro-emulsions are to increase interfacial fluidity and to modify the Hydrophilic-Lipophilic Balance (HLB) of surfactant to optimal value.[8] Thus, their combination of surfactants are more effective than a single surfactant.

Factors affecting stability of micro-emulsions include interfacial curvature, interfacial tension, entropy and fluidity.

Micro-emulsions containing di-decanoyl glycerol are used to increase melanin content of melanocytes thereby increasing pigmentation of skin. Micro-emulsion containing ascorbyl palmitate effectively prevents UV-A-induced lipid peroxidation.[9]

1.3.4 Nano Emulsions

Nano Emulsions are consist of very fine oil-in-water (o/w) dispersions, having smaller diameter droplet than 100 nm.

They are prepared by spontaneous emulsification such as phase inversion composition or phase inversion temperature (PIT) emulsification, or by using a high shear equipment, which allows to control of the droplet size and large choice of compositions.

The Nano-emulsions are easily used in skin care because of their good sensorial properties (merging textures, rapid penetration) and their biophysical properties (especially, hydrating power). They lead to generate a large variety of products from water-like fluids to ringing gels, transparent milks, lotions, crystal-clear gels with different rheological behaviors, visual aspects, richness and skin feel are blended with nanoemulsions.[10]

1.3.5 Liquid crystals

Liquid crystalline phase are thermodynamically stable and represents a state of incomplete melting. Liquid crystals are mainly of two classes- lyotropic liquid crystals and thermotropic liquid crystals (smetic and nematic type). Liquid crystals enhance the product appeal because of the colored appearance of preparations. In which they are incorporated. Liquid crystals form multilayer around the emulsion droplets, increasing the viscosity which increases the emulsion stability and decreasing the Vander Waal’s energy. These multilayers are act as rheological barriers to coalescence. Lipophilic materials such as vitamins, are incorporated into liquid crystalline matrix and are protected from both photo and thermal-degradation.

The Emulsions containing liquid crystals; have a rate of active release much slower than those without the stabilizing ingredients. This effect is generated because of multilayer structure of liquid crystalline material around droplet, which reduces effectively the interfacial transport of the dissolved actives from within the droplet e. g. timed release of vitamin A palmitate containing liquid crystals dispersed in water-based gel.[11, 12]

1.4 Methods of Polymerization

This refers to the physical phases of polymerization reactions in which decides whether the monomer is polymerized in its gaseous and condensed states. Monomers is easily polymerized as such or with other inert components such as non-solvents and solvents.[13, 14] Factors such as the nature of the monomer and the type of polymerization mechanism. Depending upon the physical conditions; polymerization techniques are classified into four types.

They are:

1. Solution polymerization
2. Bulk polymerization
3. Emulsion polymerization
4. Suspension polymerization

1. Solution polymerization

In solution polymerization, the monomer is dissolved into a suitable solvent along with the suitable chain transfer agent. The free-radical initiator is dissolved into the solvent medium. The presence of inert solvent medium helps to control viscosity rise and promote a proper heat transfer.

The major disadvantage of the solution polymerization technique, by this technique it is difficult to not get very high molecular weight polymer products. Solution polymerization used in certain coating and adhesives compositions. E.g. industrial production of polyacrylonitrile (PAN) by free-radical polymerization and poly isobutylene by cationic polymerization. Block co-polymers are also made by this technique.

2. Bulk Polymerization

In bulk polymerization, the monomer is taken and the initiator and chain transfer agent are dissolved into the monomer.[15] The chain transfer agent is to control the molecular weight. So the whole system is in a homogeneous phase.

The reaction mass or monomer is heated or exposed to a radiation source for initiating the polymerization and is kept under continuous stirring for proper heat and mass transfers. As the polymerization proceeds, the viscosity of the reaction mass increases and mixing becomes progressively difficult. So that product has high molecular weight distribution. Another disadvantage of bulk polymerization of the growing polymer chains becomes restricted.

Bulk polymerization is simple technique and the product obtained by bulk polymerization has a high purity. By this technique the free-radical polymerization of methyl methacrylate or styrene is used to get transparent moulding powders, cast sheeting and also of vinyl chloride to get PVC resin.

3. Emulsion Polymerization

Emulsion polymerization is a heterogeneous reaction process in which the unstable monomers are dispersed in a continuous phase with the help of surface active agents and polymerized with free radical initiators [2]. The colloidal dispersion of polymer product is called as latex. The surfactant may be anionic, cationic or nonionic. Some of the surfactants commonly used are sodium lauryl sulphate (SLS), Cetyltrimethyl ammonium bromide (CTABr), triton-X etc.

The monomer is dispersed in water containing the surfactant and initiator. The surfactant forms the core of the micelles. This technique is mainly used for the free radical polymerization of vinyl monomers containing water soluble initiators. Monomers polymerized by this emulsion process include butadiene, styrene, acrylics, vinyl chloride and vinyl acetate, etc.

Emulsion polymers have a much broader range of applications especially in water based adhesives and surface coatings.

4. Suspension Polymerization

In suspension polymerization only water-insoluble monomers can be polymerized. The monomer is suspended in water, in the form of fine droplets. The size of the monomer droplets formed depends on the water-to-monomer ratio. In this polymerization system the initiators should be monomer soluble. Each monomer droplet is get isolated and independent of the other droplets; it can be visualized to act as an independent bulk polymerization nucleus.[16] In this polymerization system water is used as the heat transfer medium, the process is also economical as compared to solution polymerization.

In this polymerization proceeds up to 100% conversion of monomer and the product is obtained as spherical beads involves only filtration of the beads and removal of the protective colloids and surface-active agent by water washing. The water washed and dried product can be used for coatings, moulding purpose and adhesives.

1.5 Types of Emulsion Polymerization

It is classified into three types depending upon the method by which the polymerization reaction is carried out.

I. Batch Emulsion polymerization

II. Semi-continuous Emulsion polymerization

III. Continuous Emulsion polymerization

I. Batch Emulsion Polymerization

All the ingredients except initiator are added in single shot. The product formed depends on the reactivity of monomer. The rate of polymerization depends on the reactivity ratio of monomers. In Batch Emulsion co-polymerization, block type polymers are generally formed since the reactivity ratio of two monomers is not same.

II. Semi continuous Emulsion Polymerization

First seed latex is prepared. The seed latex, is having low molecular weight and monomer mixture is added at a constant feed rate throughout the polymerization. The rate of polymerization depends on the feed rate of monomer and it is less when compared to batch emulsion polymerization. The main advantage of this emulsion polymerization is that the polymer can be prepared with desired molecular weight and structure by controlling feed rate. The main disadvantage is that the reactor set up is of high cost.

III. Continuous Emulsion Polymerization

Here the monomer feed rate is maintained through the polymerization reaction. By altering the rate of feeding, the polymer with desired structure and molecular weight can be obtained. The rate of polymerization is very less when compared to both batch and semi continuous polymerization. Reactor set up is of high cost this is the main disadvantage of continuous emulsion polymerization.

1.6 Ingredients of Emulsion Polymerization

A typical emulsion polymerization formulation comprises of four basic ingredients-

i. Dispersion medium
ii. Monomer
iii. Emulsifier and/or protective colloids
iv. Initiator

v. Chain Transfer Agents
vi. Buffer
vii. Seed Latex

Further, auxiliaries, such as coalescing aids, plasticizers, thickening agents, antimicrobial agents, antioxidants, UV-absorbers, antiquing agents, defoamers & other additives.

i. Dispersion medium

In emulsion polymerization, the dispersion medium for monomer droplets and polymer particles are generally water. Water is cheap, inert and environmentally friendly. It provides excellent heat transfer because of low viscosity of water.

Usually deionized water “DM Water” is used; problems in the stability of an emulsion or dispersion can occur if water with high calcium content is used.

ii. Monomer

In emulsion polymerization require polymerisable monomers by free radicals. The main monomers are used in emulsion polymerization include butyl acrylate, ethyl acrylate, styrene, acrylic acid, math acrylic acid acrylonitrile, methacrylate esters, acrylate esters and vinyl acetate.

All monomers have a different chemical, physical properties and structure, monomers can be a considerable influence on the type of emulsion polymerization.

iii. Classification of the typical monomers

According to different solubility’s of monomers, monomers are divided into three groups:

- Monomers that have good solubility in water such as acrylonitrile (solubility in water 8%).
- Monomers having 1-3% solubility in water (methyl methacrylate and other acrylates).

- Monomers that are practically insoluble in water (butadiene, isoprene, styrene, vinyl chloride, etc.).

  Monomers are further divided into two principal groups: ***Soft and Hard monomers***. Soft and hard refer here to the properties of the resulting homopolymers in the latex particle, usually defined through the glass transition temperature (Tg) of the polymer, which in turn is an important property to denote the hardness or mechanical durability of a polymer.

  Hard monomers include styrene, methyl methacrylate, vinyl chloride, vinyl acetate, vinyl propionate and acrylonitrile; while soft monomers include acrylic esters, butadiene, ethylene, versatic acid vinyl ester, maleic and fumaric acid esters.

  Besides this classification often an additional classification into stabilizing and cross-linking monomers is performed.

- ***Stabilizing monomers*** play an important role in preparation, storage and formulation of dispersions by creating a stabilizing, hydrophilic sphere around the particle or by serving as internal protective colloids. The list includes acrylic acid, methacrylic acid, maleic acid, fumaric acid, ethylene sulphonate and ethylene phosphate.

- ***Crosslinking monomers*** have a great influence on the application properties of a dispersion, such as pendulum hardness, blocking or elasticity. Generally, two different crosslinking mechanisms are distinguished: crosslinking during polymerization leading to polymer networks in the particles and crosslinking during film formation. Monomers in this category include polyvinyl and polyallyl compounds, N-methylol compounds and their ester derivatives, and active halogen contacting compounds.

  E.g.

  M.1 - Vinyl esters

  Vinyl acetate is less expensive monomer, but the polymer is easily hydrolyzed (especially for polyvinyl alcohol), and has less UV stability. Its homopolymer has high Tg, and copolymerization with second monomers is necessary. Its low tendency for copolymerize with acrylics, but copolymerize with styrene is impossible commercially, in this styrene monomer acts as ‘stopping agent.’ VeoVa 10 is copolymerized with vinyl acetate; increase the resistance towards hydrolysis & decrease the Tg & UV decomposition of final copolymer. VeoVa 10 has low solubility in water and shows lower tendency to hydrolyze in comparison of the vinyl acetate.

M.2 - Vinylidene chloride

Vinylidene chloride is a colorless liquid with a boiling point near room temperature, and with a characteristic sweet odor. Copolymers of vinylidene chloride have excellent vapor barrier & gas properties, while its homopolymers are highly crystalline and in emulsion polymerization the particles of other monomers are not swollen. The crystallinity of the polymer may be destroyed by incorporation of acrylic monomers up to15-20 wt. %.

M.3 - Ethylene

In emulsion polymerization ethylene monomer is together with vinyl acetate & vinyl chloride to act as an internal plasticizer (when low ethylene contents <30%, otherwise formation of crystallites in the resulting polymers). Pressure vessels are required necessary for performing emulsion polymerization with ethylene.

M.4 - Styrene

Styrene has high boiling liquid & is just liked with acrylic monomers – inhibited to prevent premature polymerization using TBC (t-butyl catechol). Styrene may be copolymerized with other monomers such as acrylonitriles, acrylates & vinylidene chloride, but not with vinyl acetate monomer, in this order to increase high yield Tg polymers.

M.5 - Acrylates & Meth-acrylates

In this family of monomers are easily capable for thermal polymerization, therefore its storage condition is important. These monomers are strong irritants & exposure should be minimum.

Methyl methacrylate monomer yields clear, hard & tough polymers, increases strengthens & Tg of the resulting polymer. n-Butyl acrylate & 2-Ethyl hexyl acrylate are soft monomers, leads to internal flexibility, plasticization, adhesion, tackiness & weather ability of the resulting copolymers. 2-EHA increases tack but not easily homopolymerized.

M.6 - Water-soluble and functional monomers

Water-soluble monomers are generally functional monomers & used to insert hydrophilic centers into hydrophobic polymers. In this order to stabilize the particles & to promote dye acceptance & adhesion.

Monomers having carboxyl group are introduced & to act as for to enhance the colloidal stability of the latex particles or post polymerization crosslinking reactions of the latex. These groups improve the shear, mechanical & freeze thaw stability of the latex; to improve film hardness, the tolerance towards electrolytes & adhesion of a latex to the application substrate. In few cases dicarboxylic acids (E.g. fumaric acid, itaconic acid), which may be introduced & cannot be homo-polymerized.

- **Glass transition temperature of homopolymers**

The glass transition temperature is defined as the temperature where a polymeric material loses its rubber-like features and instead transforms into a glassy state. At this temperature the rotational flexibility of the chain C-C bonds and the concomitant independent segmental mobility is lost, and the material becomes rigid.

The introduction of longer alkyl chains in the acrylic monomer prevents the polymer chains from aggregation and microcrystallisation and therefore acts as an internal softener in the homopolymers; the longer the alkyl-chain, the lower the glass transition temperature.

The same influence of the alkyl chain is observable in the methacrylates, although the level of the Tg is about 100°C higher than for the ‘simple’ acrylics system. This effect can be attributed to the methyl group in the methacrylate. This methyl group is directly attached to the polymer main chain and therefore sterically hinders chain rotation and segment mobility: Substituents at the main chain lead to an increase in Tg. The structure of the esterified alcohol in the side chain also has a considerable effect upon Tg. Bulky substituents in the side chain (in vicinity to the polymer backbone) lead to an increase in Tg.

The glass transition temperature (‘Tg’) of the acrylic emulsion polymer is generally from -40℃ to 50℃ for flexible packaging lamination application. The monomers and amounts of the monomers selected to achieve the desired polymer Tg range are well known. Theoretical Tg of copolymers are calculated by using the Fox equation (T. G. Fox, Bull. Am. Physics Soc., Volume 1, Issue No. 3, page 123 (1956). E.g. calculating the Tg of a copolymer of monomers M1 and M2,

$$1/ Tg\ (calc.) = w\ (M1)/Tg\ (M1) + w\ (M2)\ /Tg\ (M2)$$

Where in

Tg (calc.) is the glass tradition temperature calculated for the copolymer.

w (M1) is the weight fraction of monomer M1 in the copolymer.

w (M2) is the weight fraction of monomer M2 in copolymer.

Tg (M1) is the glass transition temperature of the homopolymers of M1.

Tg (M2) is the glass transition temperature of the homopolymers of M2.

All temperature being in °K.

The glass transition temperature may be determined in the form of what is called the ‘midpoint temperature’ by means of differential scanning calorimetry (ASTM D 3418-08).

iv. Emulsifier/Surfactants

Emulsifiers are also known as “surface active agents”. The low molecular weight compounds having a hydrophobic and a hydrophilic moiety. Emulsifiers stabilize the dispersed polymer particles, it produced by emulsion polymerization technique.

These materials play an important roles in emulsion polymerizations such as

- Reduces interfacial tension between the water phase & monomer phase so that, with agitation the monomer material is dispersed (or emulsified) into the water phase.
- Stabilize, the monomer droplets in an emulsion form; monomer within emulsifier micelles; growing latex particles & the particles of the final latex.
- Acting as retarders or chain transfer agents.

Emulsifiers are consist of a hydrophilic (water-soluble) head group & a long-chain hydrophobic (oil-soluble) group (dodecyl, hexadecyl or alkyl-benzene).

They are mainly classified according to the nature of this head group. This group may be cationic, anionic, nonionic or zwitterionic.

- Cationic emulsifiers having quaternary salts E.g. hexadecyl trimethyl ammonium bromide and acetyl dimethyl benzyl ammonium chloride.
- Anionic emulsifiers mainly having negative charged hydrophilic group are the potassium, sodium & ammonium salts of higher fatty acids, & sulphonated derivatives of arylaliphatic, aliphatic or naphthenic compounds. Sodium dodecyl benzene sulphonate, [C12H25C6H4SO3- Na+], sodium lauryl (dodecyl) sulphate, [C12H25OSO3Na+] and sodium dioctyl sulphosuccinate, [(C18H7COOCH2)2SO3- Na+] are commonly used anionic emulsifiers in emulsion polymerization.
- Non-ionic emulsifiers having no charge. The mainly used this type of emulsifiers; having a head group of the ethylene oxide (EO) units. Polyoxyethylated polyoxypropylene glycols (i.e. the block copolymers of propylene oxide and

ethylene oxide) & polyoxyethylated alkylphenols are the main common types of non-ionic emulsifiers are used.

- Amphoteric (zwitterionic) emulsifiers having anionic or cationic properties, depends on pH of the medium. They are mainly alkylimino or alkylamino propionic acids.

v. Initiators

There are two principal ways in which free radicals may be generate in order to start the polymerization:

By single electron transfer to or from an ion or molecule or by homolytic scission of a single bond.

Homolysis of a single bond is most simply achieved by the heat application & there are many other compounds which undergo thermolysis at the most convenient temperature approx. 50-100°C. The most commonly using initiators are the persulphates. For persulphate initiators the only difference are found in the counter ion. Because of this difference in the counter ion results in difference in the molecular weight. Second reason is the strong difference in solubility of APS, NaPS and KPS; For KPS required more water for solubility, therefore only less concentration initiator solutions are prepared. Third reason initiators are not easily interchangeable is because of half-life time constants.

Peroxodisulphate initiator shows two pH dependent decomposition mechanisms. When in contact with water they are easily decompose into peroxosulphate & a sulphate fragment. The peroxosulphate fragment is unstable condition in an acidic environment and therefore rapidly easily decomposes into hydrogen peroxide and a sulphate fragment. The peroxosulphate fragment is more stable in a basic medium & decomposes easily under the thermal stress.

Hydrogen peroxide initiator decompose at 80°C. But small impurities, such as traces of alkaline & metal salts are catalyse decomposition. In an alkaline medium, the reaction rate may be out of control.

The common peroxide initiators (usually sulphur compounds with high oxidation state) may be combined with other reduction agents; in this way to start the polymerization reaction at lower temperature. But additionally, more catalyst may be used for increase the rate of radical formation.

Generally sulphur compounds with low oxidation state are used as reduction agents. E.g. Sodium meta bisulphite, sodium bisulphite, sodium thiosulphate, sodium sulphite or sodium formaldehyde sulphoxylate.

Iron (II) salts are generally used as catalysts, especially Iron (II) sulphate & Mohr’s salt (Iron (II) ammonium sulphate hexahydrate). These salts are used in low catalytic amounts & to increase the decomposition rate of the redox system. Since the Iron (II) ion are become first oxidized & in a second step reduced again, it will regenerate its activity throughout the reaction.

vi. Chain Transfer Agent

These are generally added in the polymerization reaction to control the average molecular weight of the polymer. Factors affecting the chain transfer agent’s reactivity and transport of chain transfer agent to the reaction site.

vii. Buffer

Buffers are normally added to the polymerization to maintain pH of the Emulsion.

viii. Seed latex

Seed latex is the preform (with very low molecular weight) of the polymer to be prepared. This is normally employed to alter the final properties of polymer.

1.7 Basic Processes in Preparation of Emulsion Polymerization

1.7.1 Droplet formation and development of monomolecular film

The formation of globules of dispersed phase is main objective of the emulsification process. The formation of globules are achieved by high speed agitation. Under the mechanical agitation the interface between two immiscible liquids are first deformed up to certain limit that the droplets are produced.

Initially droplets are too large in size & to maintain free existence in medium and hence these droplets are again broken into the finer and quite stable droplets.

These droplets prevent from reuniting, energy barrier is required to prevent their collision and again fusing to form a layer. Such barrier properties is generated by the monomolecular layer of surfactant surrounding the dispersed droplet & the barrier properties of droplets may be maintained by the addition of emulsion stabilizers.

The surfactant molecules put together at the interface under the influence of agitation and orient themselves in such a way that their hydrophilic groups projections into aqueous phase and hydrophobic groups towards the organic phase. Thus surfactants produce an interfacial film and it adsorbs additional surfactant molecules if the droplets are further broken up mechanically until all the droplets are enveloped by a surfactant film.[18, 19]

The thickness of interfacial surfactant layer depends upon concentration of surfactants, type of system and internal phase. Though a monomolecular layer is needed to the surrounding of droplets in many cases the multiple layers are built up.[20] The dissolution of dispersed phase into fine droplets is accompanied by the terrific rise in globule surface area and interfacial area. This interface determines flow behavior of the emulsion products and hence the action of emulsifiers at the interface acquires conclusive importance.

1.7.2 Work of division

A liquid always reduce its surface area or interface to a minimum. Thus the increase in the interfacial area is possible only by if the external energy is supplied in terms of agitation or ultrasonication.

$$dA = \mu.dI$$

The work diffuse (dA) for droplet formation is proportional to the increase in the interface area (dI). The proportionality factor is the magnitude of interfacial tension (μ) between two phases, which to be emulsified. When the interfacial tension between two phases is higher than considerable mechanical energy is required for emulsification unless the emulsifier is added.[21-23]

1.7.3 Decrease in interfacial tension

The emulsifiers are the effective surface active agent lowers the interfacial tension at lowest possible concentration. This decrease in interfacial tension is due to the accumulation of emulsifier molecules at the interface position between two phases; which is to be emulsified. To obtain above results by emulsifier molecule must possess two effects, [24, 25]

1. Adsorption effect: To be adsorbed at the interface to minimize the interfacial tension to lowest possible value.
2. Diffusion effect: To reach the interfacial region as soon as possible from the one phase in which they are initially dissolved.

The main property of the good emulsifier molecule to occupies the smaller area at the interface & arrange themselves at right angles to the interface by forming stable film but the polar hydrophilic emulsifier groups pull out into aqueous phase & non polar hydrocarbon groups towards the organic phase.

1.7.4 Marangoni Effect

Marangoni effect is the phenomenon of uniform diffusion of emulsifier molecules at the freshly generated interface.[26] In this case the formation of two emulsion droplets from one larger droplet under the mechanical force or by Brownian motion. The rupture point of droplet is generally free from emulsifier molecules. Such shortage of emulsifier molecules at the interface develops an interfacial tension gradient between the unoccupied droplet surface & emulsifier occupied droplet surface.

1.7.5 Initiation Process and Chain Propagation

The starting reaction in radical polymerization is determined by two steps: initiator decomposition i.e. free radical generation & radical addition to the first monomer. The rate of reaction depends upon the decomposition rate (E.g. the activation energy, half life time) of the initiator, which is dependent upon temperature process. This radical is a highly reactive species which easily reacts with the double bond of the first monomer molecule by forming a covalent bond and another radical react at the terminal site of the monomer. Now this terminal radical is able to add another unsaturated monomer unit, leading to polymer chain growth. The polymer chain growth reaction requires a much lower activation energy compared to the initiation reaction, therefore its rate of reaction is less dependent upon temperature than the gross rate of reaction of the starting reaction.

1.8 Emulsion Stability

The stability phenomenon of emulsions, it is important factor for emulsion. By joining of small droplets to form a larger droplet of emulsion is initiated the demolition of emulsion; this process is called as coalescence.

The term “Flocculation” is defined as the natural adhesion of emulsion droplets to form a three dimensional network without coalescence.

The term “Creaming” is the separation of dispersed droplets from the continuous phase under the influence of either external applied force such as, sonication, centrifugation or gravity, etc. If the dispersed medium is less dense than the continuous phase, the upward creaming takes place form the dense dispersed system to the downward creaming occur.

When dilute emulsions then creaming layer occur mainly due to the difference in the specific gravity of the different phases.

In commutable creaming is an insignificant form of emulsion instability hence it is mainly pull off by the addition of thickener. This thickener is changes the rheology of emulsion system.

Figure 3.1 shows the mechanism of emulsion destabilization. In early endeavor of stabilizing emulsions, adsorption of ionic species from electrolyte solution and forming an electrically charged double layer has retarded the coalescence to some limits. In this consideration potassium thiocyanate shows some positive effect to some limit. The adsorption of natural modified gums, starch and protein molecules at the interface stage have shown a better performance in the stabilizing emulsion systems. The use of synthetic polymeric materials such as polyacrylic acid, polyvinyl pyrrolidone, etc. have reduce rate of desorption from the droplet surfaces by their adsorption at many sites. The adsorption of finely divided clays such as bentonite, montmerillonite, etc. was also used to achieve the "Pickering stabilization." [27]

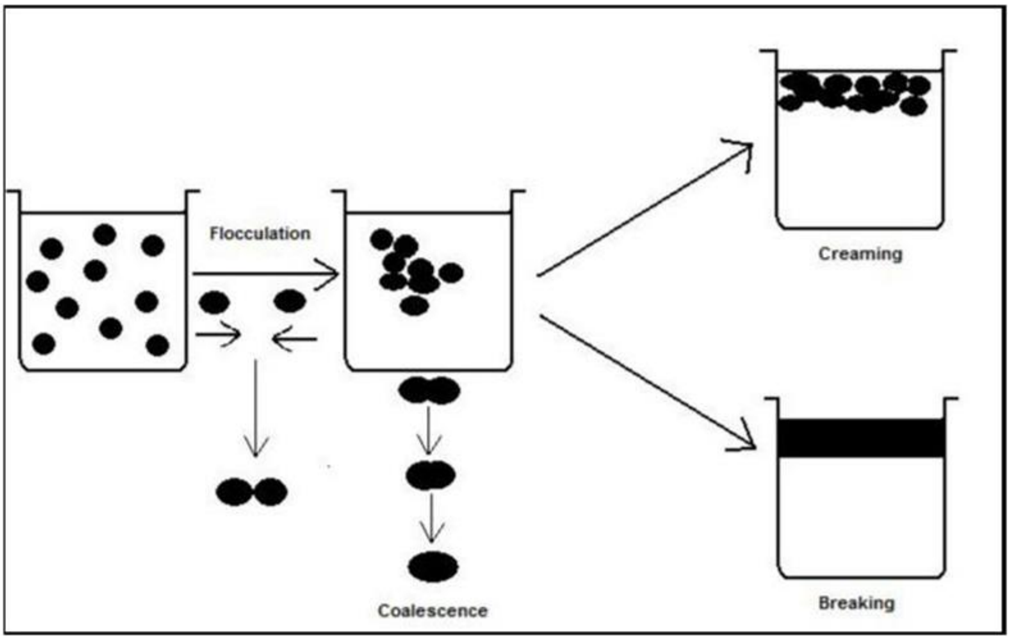

Figure 1.1 - Mechanism of emulsion destabilization.

The shelf life of typical emulsion can be replanted to the phenomenon such as, convection currents, random disturbances and Brownian motion of the droplets. The intensity of above three parameters determines the possibility of coalescence in case of poor stabilized emulsions.

1.9 Factors affecting emulsion stability

1.9.1 Temperature

Increase in temperature is allied with increase in the Kinetic energy of dispersed droplet. Under the coalescence inner droplet collisions occur & under these conditions the protective layer of the droplets are easily penetrated. But the increase in the emulsion temperature favors the stability of sterically stabilized emulsions.[28]

1.9.2 Addition of electrolyte

The electrical charge of the outer layer is very sensitive to the addition of foreign ions; this charge destabilizes the emulsion.[29]

Its effect of electrolyte increases with increase in its valency.

1.9.3 Removal of Surfactant

The addition of external substances which changes the film forming properties by the interface synergistically destabilizes the emulsion. E.g. addition of bases or acids destroys the hydrolysis sensitive surfactants whereas the addition of cationic compound into emulsion; which is stabilized by the anionic surfactant causes precipitating sparingly soluble complexes and rapid breaking by forming.

Addition of adsorption agents such as, silica gel, activated carbon, fuller's earth for the adsorption of surfactants destabilize the emulsion stability. Generation of voluminous precipitate such as aluminum and iron oxide hydrates in the aqueous phase destabilizes emulsions.[30, 31]

1.9.4 Mechanical Stress

External mechanical force in terms of impact or shaking, pressure, disturbs the uniformly formed critical interfacial film thereby destabilizing the emulsion.[32, 33]

Breaking of film protein of fat droplets in milk is mechanically extinct to produce butter at the same time. The foam formation is also removes some of the proteins from the milk.

1.9.5 Freezing, Evaporation and Dilution

All above parameters affect contrarily on the uniform distribution of emulsion ingredients as well as on the optimum composition and hence they suddenly destroy the emulsion network. In addition above parameters promote growth of biological culture such as bacteria and destabilize the emulsion.[34]

1.10 Emulsion Stability Testing Procedures

1.10.1 Freeze Stability

The developed emulsion is compacted either in the form of thin microscopic film & bulk form. In this case o/w emulsions on freezing the external aqueous phase forms long ice crystals & their ice crystal structures change in the solution forces the dispersed oil droplets into a narrow space between the unfrozen fluids.[35]

The ice crystal growth subverts the oil globules to such an extent that they extend into filaments and lastly make contact with each other. The magnitude of coalescence for this case is impacted by several factors such as type of surfactant and its concentration, limit of globule area covered by surfactant and the nature of oil phase unified. In case of o/w emulsion of mixture of paraffin oil and triglyceride or pure triglyceride as an internal phase, the crystallization point of triglyceride in emulsion state is lower in comparison of its normal phase.[36]

The stability of o/w emulsions to coalescence is decreased by the freezing of triglycerides in the dispersed oil globules. The increase in temperature of emulsions following freezing causes intense emulsion break-up.[37]

1.10.2 Elevated Temperature Stability

An increase in temperature is required for the initiation of strong thermal conducting currents in the internal phase leading to destabilization due to the coalescence.

It is believed that the rate of reaction is almost double for each 10°C increase in temperature. Thus testing the physical stability of emulsions at high temperature has received extreme importance in predicting the long term storage stability of emulsion systems. An emulsion system is stable for a period of six months at the 40°C / 75% relative humidity (R. H.). The emulsion is normally found to have shelf life stability for two years.[38]

1.10.3 Centrifugation Stability

The centrifugation stability of emulsion is impressed by several parameters such as, time and speed of centrifugation, purity of surfactant, ratio of dispersed phase to continuous phase and physiochemical nature of rheological additives.[39]

1.10.4 Stability in terms of Turbidity Measurements

The turbidity of emulsion is the function of droplet size and concentration. Therefore, the change in these parameters changes the turbid metric properties of emulsion system.[40, 41] Thus any change in emulsion turbidity may be considered as measure of emulsion destabilization.

1.10.5 Rheological Measurements for Emulsion Stability

Rheological parameters of emulsions such as, consistency index, flow behavior index and apparent viscosity are cumulatively dependent upon the uniformity and physiochemical stability.

A novel technique for the measurement of rheological properties at accelerated storage stability conditions such as high speed centrifugation and elevated temperature, gave a credible picture for the long term storage stability of the emulsion system. This factor shows a very important role in delivering emulsion based products to consumers via transportation, storage and handling procedures.[42 – 45]

1.11 Cross-linker

When cross-linker is used in emulsion polymerization then cross-linker controls the particle morphology & improvement of the mechanical properties of the latexes emulsion used for paints & coatings.[46] In cross-linking process the linking of the polymer chain involves to obtain a polymer cross-linking network. The results of this network is to increase in resistance to chemicals, film hardness, detergents & solvents. Polymeric chains are viscoelastic in nature & the cross-linking will increase the rigidity of polymeric chains. Which will retards the segmental motion of chains.

When polymer materials having lower molecular weight then by cross-linking to obtain the better mechanical properties.

Difference between post-cross-linking and cross-linking, in post-cross-linking the material is again cross linked after the pre-crosslinked materials but in cross-linking the materials is directly cross linked at the time of synthesis.

Crosslinking are of different types depending on the nature of bonds

I.Ionic bonds
II.Covalent cross-linking
III.Physical cross-linking (involves Hydrogen bonds, Vander waal forces & other interaction)

Cross-linking mainly depends on functionality of reagents (Monomers, Oligomers & diluent) and the addition of reactive groups are introduces in polymeric chains for post-cross-linking.

The reaction rate and reactivity of these groups may be controlled by

I. Radiation
II. Temperature
III. Processing method
IV. External reactants (E.g. O_2, H_2o & moisture etc.)

1.12 Post-cross-linking & Cross-linking

The post-cross-linking and cross-linking reactions is categorized by different types of chemical function. As per temperature range different types of reaction are proceed-

1. Reaction at room temperatures
2. Reaction at medium temperature but below 150°C.

1. Room Temperature Cross-linking

Following types of chemicals functions are considered.

i.1 Carboxylic acid Functions

In this types two cross-linking agents are used

I. Carbodiimides - Carbodiimides are best cross-linking agents for emulsion at low temperatures. The acrylic emulsion contains acrylic acid and carbidiimides leads to film formation with excellent tensile & solvent resistance properties.[47-49]

II. Aziridines - Polyaziridines are obtained by the Michael reaction; such as addition of the amine onto unsaturated activated groups (E.g. acrylics).[50] It improves the chemical resistance & mechanical properties (high strength, lower elongation) of multiple coatings E.g. wood varnishes for interior coatings.

Main two lacks were observed:

- In carbodiimides, its poor water stability leads to amino alcohol. This limitation may be taken over by the addition of polyaziridine cross-linker; use prior to processing the oligomers.
- Compounds of aziridine are toxic, irritant, toxic and mutagen.

i.2 Aceto acetyl function

In Cross-linking the aceto acetyl function is the new function. In this function the reactivity due to keto-enol tautomerism. The approachability of aceto acetyl functionality in the polymer reduces the glass transition temperature & viscosity.[51] The other reactivity part arises from the metal chelation (with silver, copper, nickel, aluminium etc.) by bisketores.[52-53]

This reaction is able to enhance adhesion to the metal. Aceto acetyl derivatives may react with various other groups such as

- Activated alkenes - The reactions between methylene group and electron deficient an alkene may occur under the strong basic conditions. The reactions between aceto acetyl derivatives and acrylates are proceed under the various bases.

- Isocyanates - The activated methylene group of aceto acetyl function may react with isocyanates at room temperatures. When lower reaction rate allows to better control of the cross-linking.
- Amines - The amines are react with hydroxyl group of aceto acetyl enolic form.
- Aldehydes mainly formaldehyde- Acetyl acetonate has been used with the formaldehyde to generates the short linkage between two acute acetyl groups.

i.3 Amine Functions

As amines are high nucleophile, because of this reason many reactions may occur at room temperature.

The other reaction of amines involves with epoxides. The epoxy/amine system was developed for latex by Gleurts.[54]

In this case, the material is separated into two different phases; called “two in one system”. The main problem in incorporating amine groups in acrylic latex. First the insertion of the epoxide groups through the addition of glycidyl methacrylate (GMA) monomer. The utilisation of GMA for latex emulsion synthesis having a limitation due to instability of monomer in aqueous medium.

The primary amines or tertiary amines are used for cross-linking of epoxides.

i.4 Acetyl Function

The acetal function shows the protected form of an aldehyde group and its protection to the aldehyde function from amines. At low pH values, the aldehyde is again regenerated and their reaction with amine leads to the corresponding imines.

The development of emulsion for paints, are able to go further reaction for film forming step at room temperatures. Emulsion should be chemically stable during synthesis and its storage. The acetyl functions are stable and inert in basic medium. The balance required in protective chemical groups of emulsion & de-protective groups during the film forming & they become reactive.

The monomers E.g. N-(methoxy methyl acetate) acrylamide (MAGME) is copolymerized with other monomers having the hydroxyl groups, such as 2-hydroxy ethyl acrylate, to obtain self-crosslinking emulsions.

i.5 Acrylamide Functions

Acrylamide are able to self-cross linking at higher temperatures. Monomers having these groups are synthesised for addition in emulsion. E.g. isobutoxymethylacrylamide (IBMA), N-methylolacrylamide (NMA), acrylamidoglycolic acid monohydrate (Highlink® AG) or N-(2, 2’ -hydroxy-1-dimethoxyethyl) acrylamide (Highlink® DMH).

i.6 Other Cross-Linking Moieties

By these moieties the post-crosslinking process are proceed at room temperature.

- Water
- Sol-gel reactions, - Isocyanates
- Oxygen
- Acetylenic coupling, -Reaction generating peroxide, -Acrylamide derivative

2. Reaction at medium temperature but below 150ºC

The medium temperature range are in between 40 to 150ºC, but higher temperatures range between 150 to 300ºC. The chemical functions involves the chemical reactions with others. E.g. the carboxylic acid reacts with other functions, such as azetidines, hydroxyl groups or other key functions involve in Die-Alders reaction.

Harold A. S. Schoonbrood, et al[55] studied the mechanisms of copolymerization of three anionic polymerizable surfactants, crotonic ester, a methacrylic ester & a maleic esters in the emulsion terpolymerization of butyl acrylate/styrene/acrylic acid (BA/S/AA) were investigated. In order to clarify the contribution of each polymerization in the process, polymerization in the aqueous phase in the absence of both micelles and monomer droplets and emulsion polymerizations with different solids contents (55, 50, and 30 wt %) and different particle sizes were carried out.

Enrique Saldi Var et al[56], for evolution of conversion and average particle diameter in batch experiments are compared against experimental data for four emulsion copolymerizations of styrene with the following monomers: (i) butyl acrylate, (ii) methyl methacrylate, (iii) butadiene & (iv) acrylic acid. For each copolymerization system the experiments covered simultaneous variations in five variables: surfactants & initiator concentrations, monomer to monomer ratio, monomer compositions & temperature.

Maria j. Unzue, et al[57] studied the reactive surfactants in heterophase polymerization. Synthesis and screening of polymerizable surfactants with varying reactivity in high nonvolatile contents Butyl acrylate-Styrene-Acrylic Acid by emulsion polymerization.

Yaqiu Zhao et al[58] studied the behaviour of sodium dioctylsulfosuccinate (SDOSS) surfactant molecules in butyl acrylate/styrene (n-BA/Sty) copolymers and blended latexes. Using a combination of Raman & IR spectroscopy and micro analytical techniques, not only stratification of SDOSS surfactant molecules across latex film thickness.

Xiaoguang Liu et al[59] studied the low viscosity, high solids, stable poly(acrylamide-co-acrylic acid) aqueous latex dispersions were prepared by the dispersion polymerization of acrylamide (AM) and acrylic acid (AA) in an aqueous solution of ammonium sulfate (AS) medium using anionic polyelectrolytes as stabilizers. The anionic polyelectrolytes employed include poly (2-acrylamido-2-methylpropanesulfonic acid sodium) (PAMPSNa) homopolymers and random copolymers of 2-acrylamido-2-methylpropanesulfonic acid sodium (AMPSNa) with methacrylic acid sodium (MAANa), acrylic acid sodium (AANa) or acrylamide (AM).

R.F. Storey et al[60] prepared amphiphilic poly (arylicacid-styrene-isobutylene-styrene-acrylic acid) (PAA-PS-PiB-PS-PAA) block copolymers using a combination of quasi living carbocationic and atom transfer radical polymerization (ATRP) techniques.

R.Seda Tigli et al[61] synthesized acrylic resin, homo and copolymers by emulsion polymerization using butyl acrylate (BA), methyl acrylate (MA), & ethyl acrylate (EA) monomers. The film structures of copolymers & homopolymers were investigated and three of them [P (MMA)/BA] 1:1, P (MMA/MA) 1:3 & P (MMA)/EA) 1:1.5] were indicated as appropriate binders for paint production. They suggested from AFM studies that, [P (MMA)/EA) 1:1.5] copolymer was good binder used in the paint industry.

Dr. Karl-Heinz Schunacher[62] studied new water-based adhesives for flexible food packaging chemical design, performance and toxicological safety.

S. Mondal et al[63] synthesized methyl methacrylate and butyl acrylate copolymers with varying percentage of methacrylic acids and 2-hydoxy ethyl methacrylate were synthesized using emulsion polymerization technique for coating application.

Faai Zhang et al[64] synthesized by using butyl acrylate (BA), methyl methacrylate (MMA), acrylic acid (AA), and hydroxyl ethyl methacrylate (HEMA) as commoners, along with ammonium per sulfate as initiator, emulsions with high hydroxyl content (10–35%) and carboxyl groups were synthesized from semi-continuous seed emulsion polymerization methods. Emulsifier types and levels, reaction temperature, level of hydroxyl monomer, and level of monomer carboxyl on stability of the emulsion polymerizations were investigated.

Yuri Reyes-Mercado et al[65] studies the effect of acrylic acid content on the permeability and water uptake of latex films.

Muhammad Abu Taher et al[66] synthesized organic acrylate binder through emulsion polymerization to ensure the best mechanical properties on applicable substrates.

Andrew B. Foster et al[67] studies the control of adhesive properties through structured particle design of water borne pressure sensitive adhesives.

Yasuharu Nakayama[68] reviewed development of novel aqueous coatings which meet the requirements of ecology conscious society: novel cross-linking system based on the carbonyl-hydrazide reaction and its applications.

Richard J. Esser et al[69] synthesized water based cross-linkable surface coatings by using a monomer mixture of methyl methacrylate (MMA), butyl acrylate (BA), AAEM and methacrylic acid (MAA) in a ratio of 21: 37: 30: 12 by weigh.

Dr. Nicola et al[70] studies the waterborne colloidal polymers (i.e. latex) represents a promising alternative to organic solvent based systems in coatings applications by using the diacetone acrylamide cross-linking reaction & its influence on the film formation of an acrylic latex.

Pradip S. Asodekar et al[71] reviewed process parameters of micro gravure coater to improve the quality of wet coating.

2.1 Scope of the Present Work

In the present work different compositions of the acrylic co-polymer emulsions have been synthesized and evaluated for its application performance on flexible packaging substrates (Plain PET, m-PET, m-BOPP). The copolymerization was carried out using three types of base monomers with three different cross-linking agents of 0.5% & 1% concentration respectively (Table 2.1).

These copolymer lamination adhesives were further tested for their applications on performance of peel strength on plain polyester film/metallized polyester film & plain polyester film/metalized BOPP film.

Table 2.1 - Formulation of Acrylic Emulsion

Base Monomers	1.	Butyl acrylate, Methyl methacrylate & Acrylic acid
	2.	Butyl acrylate, Styrene & Acrylic acid
	3.	Butyl acrylate, Methyl methacrylate, 2-Ethyl hexyl acrylate & Acrylic acid
Cross-linking Agents	1.	Acetoacetoxyethyl methacrylate (AAEM)
	2.	2-Hexyl ethyl acrylate (HEA)
	3.	Hydroxy propyl acrylate (HPA)

These acrylic emulsions were used as lamination adhesives for flexible packaging application substrates (Plain Polyester {PET}, metallized Polyester {m-PET}, metallized BOPP {m-BOPP}). These lamination adhesives were coated on flexible packaging substrates by gravure roller. The viscosity of lamination adhesive should be in the range of 14 to 22 second by Ford cup; B-4(ASTM D 1200-10) for effective coating. The % non-volatile contents (% solids) of acrylic lamination adhesive should be in the range of 35% to 50% for uniform distribution of acrylic lamination adhesive on to the application substrates for desired adhesive coating weight.

Chapter 3: Synthesis of Acrylic Emulsions

3.1 Materials

i. Butyl acrylate

Homopolymers and copolymers of butyl acrylate can be prepared. Butyl acrylate can be copolymerised with acrylic acid and its salts, amides and esters, and with methacrylates, acrylonitrile, maleic acid esters, vinyl acetate, vinyl chloride, vinylidene chloride, styrene, butadiene, unsaturated polyesters and drying oils, etc. Butyl acrylate is also a very useful feedstock for chemical syntheses, because it readily undergoes addition reactions with a wide variety of organic and inorganic compounds.

ii. Styrene

Styrene Monomer is most commonly used in the production of valuable styrene homopolymers and copolymers, which are either solid (SPS) or expandable (EPS). Some SPS grades are used for the production of disposable transparent containers and EPS grades are useful in the fabrication of blocks for thermal insulation and boxes for vegetables and fruits. High Impact Polystyrene (HIPS) is polystyrene blended with rubber for better mechanical properties useful in the production of dairy products, packaging materials and sheets. The copolymers of styrene monomer with butadiene and/or acrylonitrile create valuable products combining characteristics of synthetic rubbers and strong plastics.

iii. Methyl methacrylate

MMA is produced for the use as monomer for production of polymers and as intermediate for synthesis of other methacrylate esters. MMA is produced for the use as a building block to make a wide range of polymer based products that we see and use every day from acrylic glass, car paints, toners and inks, oil additives to dental and medical products to name but a few. MMA is of low concern to human health and the environment. It is classified as hazardous (highly flammable and skin irritant and sensitizing) but has been handled safely by industry and professionals for over 60 years. MMA-based polymers are inert in the environment and can be recycled by close-loop recycling.

iv. 2-Ethyl hexyl acrylate

2-Ethylhexyl acrylate forms homopolymers and copolymers. Copolymers of 2-Ethylhexyl acrylate can be prepared with acrylic acid and its salts, amides and esters, and with methacrylates, acrylonitrile, maleic acid esters, vinyl acetate, vinyl chloride, vinylidene chloride, styrene, butadiene, unsaturated polyesters and drying oils, etc. 2-Ethylhexyl acrylate is also a very useful feedstock for chemical syntheses, because it readily undergoes addition reactions with a wide variety of organic and inorganic compounds.

v. Acrylic Acid

Acrylic acid is an unsaturated carboxylic acid. It reacts as a vinyl compound and as a carboxylic acid. It readily undergoes polymerization and addition reactions. It can be used as a carboxylic acid to produce acrylic esters, acrylamide, N-substituted acrylamides and acrylic chloride by common methods.

Copolymers can be produced with acrylic and methacrylic esters, acrylonitrile, maleic acid esters, vinyl acetate, vinyl chloride, vinylidene chloride, styrene, butadiene and ethylene.

Homopolymers of acrylic acid and copolymers which contain a preponderance of acrylic acid have a glassy consistency and are frequently soluble in water. They can be used in the form of their free acids and ammonium and alkali salts in many different applications, such as thickeners, dispersing agents, flocculants, protective colloids for stabilizing emulsions and polymer dispersions, wetting agents, coatings and textile finishes.

Acrylic acid readily undergoes addition reactions with a wide variety of organic and inorganic compounds. This makes it a very useful feedstock for the production of many low molecular compounds. For instance, acrylic acid can be used to produce derivatives of propionic acid with water, alcohols, amines, halogens and chlorinated hydrocarbons. It can also be used with other substances to produce unsaturated fatty acids, heterocyclic compounds and Diels-Alder addition products.

vi. **2-Hydroxy ethyl acrylate**

2-Hydroxyethyl Acrylate (HEA) forms homopolymers and copolymers. Copolymers of 2-Hydroxyethyl Acrylate (HEA) can be prepared with acrylic acid and its salts, amides and esters, and with methacrylates, acrylonitrile, maleic acid esters, vinyl acetate, vinyl chloride, vinylidene chloride, styrene, butadiene, unsaturated polyesters and drying oils, etc. 2-Hydroxyethyl Acrylate (HEA) is also a very useful feedstock for chemical synthesis, because it readily undergoes addition reactions with a wide variety of organic and inorganic compounds.

vii. **Acetoacetoxyethyl methacrylate**

AAEM is a methacrylic monomer used to formulate high-solids solution acrylic resins and acrylic emulsions for lower VOC emission industrial coatings and adhesives. The ability of AAEM to react with amines and hydrazides makes it an ideal monomer for self-cross linkable, room temperature cure acrylic emulsions. It also finds use in acetoacetylated polymers cross-linked through chelation with metal ions and for acetoacetylated polymers for producing colorfast fibers (azo-dye). AAEM readily polymerizes with other acrylic and methacrylic monomers.

viii. **Hydroxy propyl acrylate**

Hydroxypropyl Acrylate (HPA) forms homopolymers and copolymers. Copolymers of Hydroxypropyl Acrylate (HPA) can be prepared with acrylic acid and its salts, amides and esters, and with methacrylates, acrylonitrile, maleic acid esters, vinyl acetate, vinyl chloride, vinylidene chloride, styrene, butadiene, unsaturated polyesters and drying oils, etc. Hydroxypropyl Acrylate (HPA) is also a very useful feedstock for chemical syntheses, because it readily undergoes addition reactions with a wide variety of organic and inorganic compounds.

ix. DM Water

De-mineralized water is taken as dispersion medium. The various organic components are dispersed in it.

x. Emulsifier / Surfactants

The water-monomer emulsion is stabilized by surface active agents (surfactants). These surfactants are mostly ionic or non-ionic in nature. Both types of surfactants are used in the preparation of acrylic emulsion.

xi. Buffer

Carbonate salts are used as buffer in the preparation of acrylic emulsion.

xii. Initiators

Persulphate salts are used as initiator in polymerization reaction.

xiii. Neutralizer

Hydroxide solutions are used as neutralizer in emulsion preparation. Final pH of acrylic emulsion are maintained with help of neutralizer quantity.

xiv. Polyester Film (PET)

PET is a high performance film made from the reaction between terephthalic acid and ethylene glycol. This reaction is called a condensation reaction since the by-product is water. PET is a linear thermoplastic material. Although it is costly, it shows exceptional tensile strength, good impact strength, toughness, stiffness, dimensional stability, chemical resistance, clarity and some barrier properties. Orientation of the film can be done either by blown-bubble or tenter frame process thereby enhancing all of its properties.

Heat treatments can be done on PET to improve the heat resistance. Heat resistance can be further increased by adding some nucleating agents to achieve a higher level of crystallinity.

xv. Polypropylene Film(PP)

Polypropylene is widely used in the field of packaging, both in amorphous (cast PP) and oriented (OPP) forms. PP has higher temperature resistance and also better water vapor barrier properties compared to PE. OPP can either be made by blown film (double bubble) process or by orienting the film on a tenter frame both giving similar physical properties like clarity, high tensile strength, better barrier properties, high tensile strength and adequate impact strength. PP becomes brittle at freezing temperatures, but orientation is proven to reduce this drawback. PP also has a narrow heat seal range and hence close control of temperature is important on a packaging line. The film must be surface treated for oxidizing the surface to achieve printability and application of adhesives.

Coefficient of friction can be lowered by the addition of slip additives. Heat seal range, slip and sparkle can be improved by coating the film with acrylic and other coatings. OPP can be metalized to improve the appearance and a thicker layer of metal will remarkably improve the barrier to moisture, light and gases. Metallization is the process of coating the surface of the film with a thin layer of metal. This process is done under vacuum.

3.2 Methods of Synthesis

The emulsions of different formulations were prepared by thermal initiated free radical polymerization using 0.3 % potassium per sulphate as initiator. The polymerization was carried out in a 2 liter; three necked round bottom flask immersed in a constant temperature water bath at 85-88°C, equipped with a reflux condenser, stirrer, dropping funnel and a nitrogen inlet. DM water, surfactants and buffer were initially added and maintained under a constant agitation of 160 +/- 40 rpm; then 4% monomer premix solution was added for micelle generation followed by half quantity of the initiator solution. During polymerisation it was observed that initially temperature decreased to 77-80°C and then subsequently increased to 82-84°C. The initiation of copolymerisation is marked by the appearance of light blue color. Rest 96% of the monomer premix solution was added drop wise in a polymerisation flask over a period of 3 hrs. and the balance initiator solution was divided into 12 equal parts and added at regular interval of 15 minutes. The polymerisation reaction was carried out for 45 minutes after the addition of last instalment of monomer premix and initiator solution. The residual monomers were polymerised using peroxide catalyst in two instalment ratios (60 and 40) for further 30 minutes and 60 minutes respectively. The product was cooled down to 40ºC by cold water circulation in oil bath followed by addition of ammonium hydroxide to maintain the pH of emulsion up to 7 to 8.

Figure 3.1 - Acrylic emulsion during initiation

Figure 3.2 - Acrylic emulsion preparation

3.3 Formulations

The formulations for the synthesis of a series of acrylic emulsions are given in experiment table no. (1, 2, 3, 4, 5, 6, 7, 8 & 9). The three categories of base monomers were polymerised using 0.5 % and 1 % of three cross linking agents keeping the amounts of surfactants (SFT), buffer (BFR), initiator (ITR), catalyst (CT) & neutralizer (NZR) as constant. The theoretical glass transition temperature of acrylic copolymers were calculated by Fox equation. The theoretical glass transition temperature of the experiments were adjusted in between -18°C to -19°C by changing the quantity of the monomers.

In experiment no. 1P-1, base monomers Butyl acrylate (BA), Methyl methacrylate (MMA) & Acrylic acid (AA) with 0.5% concentration of AAEM as cross-linking agent.

In experiment no. 1P-2, base monomers Butyl acrylate (BA), Methyl methacrylate (MMA) & Acrylic acid (AA) with 1.0% concentration of AAEM as cross-linking agent.

Experiment Table No. 1

Exp. No.	**1P-1**	**1P-2**
Tg(°C)	-18.68°C	-18.70°C
Raw Materials	**Qty. (Parts)**	**Qty. (Parts)**
DMW	56.489	56.489
SFT + BFR	0.505	0.505
BA	28.000	27.800
MMA	12.500	12.200
AAEM	0.500	1.000
AA	1.100	1.100
ITR + CT	0.371	0.371
NZR	0.535	0.535
Total	**100.000**	**100.000**

In experiment no. 1P-3, base monomers Butyl acrylate (BA), Styrene monomer (STY) & Acrylic acid (AA) with 0.5% concentration of AAEM as cross-linking agent.

In experiment no. 1P-4, base monomers Butyl acrylate (BA), Styrene monomer (STY) & Acrylic acid (AA) with 1.0% concentration of AAEM as cross-linking agent.

Experiment Table No. 2

Exp. No.	**1P-3**	**1P-4**
Tg(°C)	-18.64°C	-18.70°C
Raw Materials	**Qty. (Parts)**	**Qty. (Parts)**
DMW	56.489	56.489
SFT + BFR	0.505	0.505
BA	27.750	27.550

STY	12.750	12.450
AAEM	0.500	1.000
AA	1.100	1.100
ITR + CT	0.371	0.371
NZR	0.535	0.535
Total	**100.000**	**100.000**

In experiment no. 1P-5, base monomers Butyl acrylate (BA), Methyl methacrylate (MMA), 2-Ethyl hexyl acrylate (2-EHA) & Acrylic acid (AA) with 0.5% concentration of AAEM as cross-linking agent.

In experiment no. 1P-6, base monomers Butyl acrylate (BA), Methyl methacrylate (MMA), 2-Ethyl hexyl acrylate (2-EHA) & Acrylic acid (AA) with 1.0% concentration of AAEM as cross-linking agent.

Experiment Table No. 3

Exp. No.	**1P-5**	**1P-6**
Tg(°C)	-18.71°C	-18.72°C
Raw Materials	**Qty. (Parts)**	**Qty. (Parts)**
DMW	56.489	56.489
SFT + BFR	0.505	0.505
BA	19.100	18.900
MMA	15.000	14.700
2-EHA	6.400	6.400
AAEM	0.500	1.000
AA	1.100	1.100
ITR + CT	0.371	0.371
NZR	0.535	0.535
Total	**100.000**	**100.000**

In experiment no. 2P-1, base monomers Butyl acrylate (BA), Methyl methacrylate (MMA) & Acrylic acid (AA) with 0.5% concentration of 2-Hydroxyethyl acrylate (HEA) as cross-linking agent.

In experiment no. 2P-2, base monomers Butyl acrylate (BA), Methyl methacrylate (MMA) & Acrylic acid (AA) with 1.0% concentration of 2-Hydroxy ethyl acrylate (HEA) as cross-linking agent.

Experiment Table No. 4

Exp. No.	**2P-1**	**2P-2**
Tg(^oC)	-18.70^{o}C	-18.74^{o}C
Raw Materials	**Qty. (Parts)**	**Qty. (Parts)**
DMW	56.489	56.489
SFT + BFR	0.505	0.505
BA	28.900	29.600
MMA	11.600	10.400
HEA	0.500	1.000
AA	1.100	1.100
ITR + CT	0.371	0.371
NZR	0.535	0.535
Total	**100.000**	**100.000**

In experiment no. 2P-3, base monomers Butyl acrylate (BA), Styrene monomer (STY) & Acrylic acid (AA) with 0.5% concentration of 2-Hydroxy ethyl acrylate (HEA) as cross-linking agent.

In experiment no. 2P-4, base monomers Butyl acrylate (BA), Styrene monomer (STY) & Acrylic acid (AA) with 1.0% concentration of 2-Hydroxy ethyl acrylate (HEA) as cross-linking agent.

Experiment Table No. 5

Exp. No.	**2P-3**	**2P-4**
Tg(°C)	-18.75°C	-18.72°C
Raw Materials	**Qty. (Parts)**	**Qty. (Parts)**
DMW	56.489	56.489
SFT + BFR	0.505	0.505
BA	28.700	29.400
STY	11.800	10.600
HEA	0.500	1.000
AA	1.100	1.100
ITR + CT	0.371	0.371
NZR	0.535	0.535
Total	**100.000**	**100.000**

In experiment no. 2P-5, base monomers Butyl acrylate (BA), Methyl methacrylate (MMA), 2-Ethyl hexyl acrylate (2-EHA) & Acrylic acid (AA) with 0.5% concentration of 2-Hydroxy ethyl acrylate (HEA) as cross-linking agent.

In experiment no. 2P-6, base monomers Butyl acrylate (BA), Methyl methacrylate (MMA), 2-Ethyl hexyl acrylate (2-EHA) & Acrylic acid (AA) with 1.0% concentration of 2-Hydroxy ethyl acrylate (HEA) as cross-linking agent.

Experiment Table No. 6

Exp. No.	**2P-5**	**2P-6**
Tg(°C)	-18.73°C	-18.76°C
Raw Materials	**Qty. (Parts)**	**Qty. (Parts)**
DMW	56.489	56.489
SFT + BFR	0.505	0.505
BA	20.000	20.700

MMA	14.100	12.900
2-EHA	6.400	6.400
HEA	0.500	1.000
AA	1.100	1.100
ITR + CT	0.371	0.371
NZR	0.535	0.535
Total	**100.000**	**100.000**

In experiment no. 3P-1, base monomers Butyl acrylate (BA), Methyl methacrylate (MMA) & Acrylic acid (AA) with 0.5% concentration of Hydroxy propyl acrylate (HPA) as cross-linking agent.

In experiment no. 3P-2, base monomers Butyl acrylate (BA), Methyl methacrylate (MMA) & Acrylic acid (AA) with 1.0% concentration Hydroxy propyl acrylate (HPA) as cross-linking agent.

Experiment Table No. 7		
Exp. No.	**3P-1**	**3P-2**
Tg(°C)	-18.63°C	-18.61°C
Raw Materials	**Qty. (Parts)**	**Qty. (Parts)**
DMW	56.489	56.489
SFT + BFR	0.505	0.505
BA	27.900	27.600
MMA	12.600	12.400
HPA	0.500	1.000
AA	1.100	1.100
ITR + CT	0.371	0.371
NZR	0.535	0.535
Total	**100.000**	**100.000**

In experiment no. 3P-3, base monomers Butyl acrylate (BA), Styrene monomer (STY) & Acrylic acid (AA) with 0.5% concentration of Hydroxy propyl acrylate (HPA) as cross-linking agent.

In experiment no. 3P-4, base monomers Butyl acrylate (BA), Styrene monomer (STY) & Acrylic acid (AA) with 1.0% concentration of Hydroxy propyl acrylate (HPA) as cross-linking agent.

Experiment Table No. 8

Exp. No.	**3P-3**	**3P-4**
Tg(°C)	-18.60°C	-18.70°C
Raw Materials	**Qty. (Parts)**	**Qty. (Parts)**
DMW	56.489	56.489
SFT + BFR	0.505	0.505
BA	27.650	27.400
STY	12.850	12.600
HPA	0.500	1.000
AA	1.100	1.100
ITR + CT	0.371	0.371
NZR	0.535	0.535
Total	**100.000**	**100.000**

In experiment no. 3P-5, base monomers Butyl acrylate (BA), Methyl methacrylate (MMA), 2-Ethyl hexyl acrylate (2-EHA) & Acrylic acid (AA) with 0.5% concentration of Hydroxy propyl acrylate (HPA) as cross-linking agent.

In experiment no. 3P-6, base monomers Butyl acrylate (BA), Methyl methacrylate (MMA), 2-Ethyl hexyl acrylate (2-EHA) & Acrylic acid (AA) with 1.0% concentration of Hydroxy propyl acrylate (HPA) as cross-linking agent.

Experiment Table No. 9

Exp. No.	**3P-5**	**3P-6**
Tg(°C)	-18.66°C	-18.63°C
Raw Materials	**Qty. (Parts)**	**Qty. (Parts)**
DMW	56.489	56.489
SFT + BFR	0.505	0.505
BA	19.000	18.700
MMA	15.100	14.900
2-EHA	6.400	6.400
HPA	0.500	1.000
AA	1.100	1.100
ITR + CT	0.371	0.371
NZR	0.535	0.535
Total	**100.000**	**100.000**

The physical properties of above acrylic emulsion experiments were tested. The following physical parameters were tested:

i. Appearance of acrylic emulsion.
ii. pH of acrylic emulsion.
iii. Viscosity by Ford Cup; B-4 at 30°C.
iv. % Non-volatile content (% Solid) at 120°C / 1 hr.
v. Film appearance (dry 50µ)

4.1 Comparative Physical Properties Analysis of Experiments

	Physical Properties				
Experiment No.	**Appearance**	**pH**	**%NVC at 120°C / 1 hr.**	**Viscosity at 30°C by Ford Cup; B-4**	**Film appearance (dry)**
Exp. 1P-1	Milky White Emulsion	7.08	41.42	14.6	Clear
Exp. 1P-2	Milky White Emulsion	7.04	42.20	15.4	Clear
Exp. 1P-3	Milky White Emulsion	7.22	42.60	14.7	Clear
Exp. 1P-4	Milky White Emulsion	7.26	42.86	14.5	Clear
Exp. 1P-5	Milky White Emulsion	7.28	42.36	19.0	Clear
Exp. 1P-6	Milky White Emulsion	7.24	43.27	20.0	Clear
Exp. 2P-1	Milky White Emulsion	7.70	41.15	18.5	Clear
Exp. 2P-2	Milky White Emulsion	7.65	42.03	20.0	Clear
Exp. 2P-3	Milky White Emulsion	7.50	40.78	16.0	Clear

Exp. 2P-4	Milky White Emulsion	7.46	42.76	16.8	Clear
Exp. 2P-5	Milky White Emulsion	7.25	41.60	20.4	Clear
Exp. 2P-6	Milky White Emulsion	7.30	40.28	19.0	Clear
Exp. 3P-1	Milky White Emulsion	7.02	42.72	17.0	Clear
Exp. 3P-2	Milky White Emulsion	7.40	42.62	20.0	Clear
Exp. 3P-3	Milky White Emulsion	7.06	42.81	16.5	Clear
Exp. 3P-4	Milky White Emulsion	7.80	42.17	17.5	Clear
Exp. 3P-5	Milky White Emulsion	7.40	41.58	18.5	Clear
Exp. 3P-6	Milky White Emulsion	7.45	40.73	19.0	Clear

These water based acrylic emulsion were evaluated for its applications as lamination adhesive for film to film application in place of solvent based polyurethane adhesives which are toxic in nature. Theses acrylic emulsion were coated by gravure roller for flexible packaging applications. For gravure roller application the viscosity of the acrylic emulsion should be in the range of 14 to 22 seconds. In laboratory this application was done manually by bar coater no. 2.

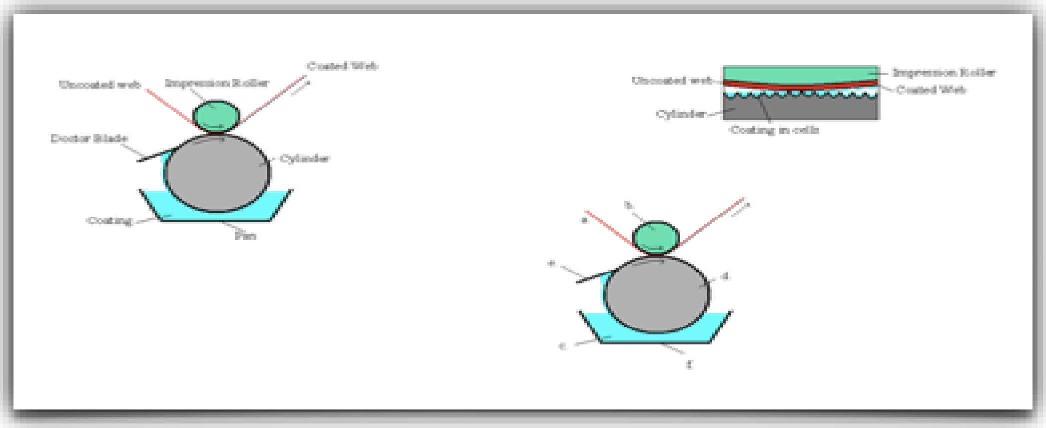

Figure 4.1- Gravure coater (Source: Darby, PKGSC 430)

4.2 Lamination Process

Lamination process are of mainly two types one dry bond lamination & other wet bond lamination. In dry bond lamination process the acrylic lamination adhesive are dried after coating and second layer/film of other substrate are adhere with this dried adhesive surface. In wet bond lamination process the acrylic lamination adhesive are coated on the substrate. In wet condition this second layer/film of other substrate are adhere with wet adhesive coating. In wet lamination process one substrate should be porous. In laboratory dry bond lamination process is used for the lamination of film to film application substrates.

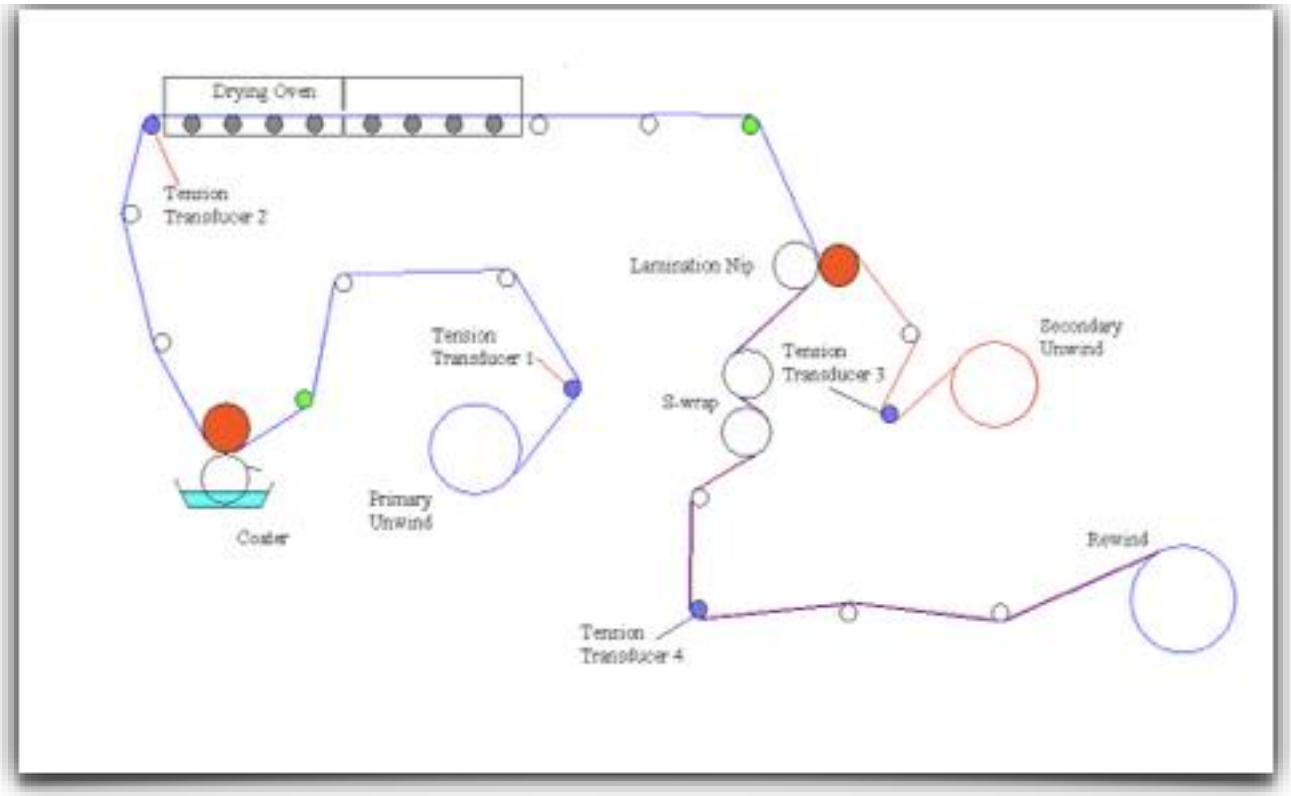

Figure 4.2 - Dry bond lamination (Source: Darby, PKGSC 430)

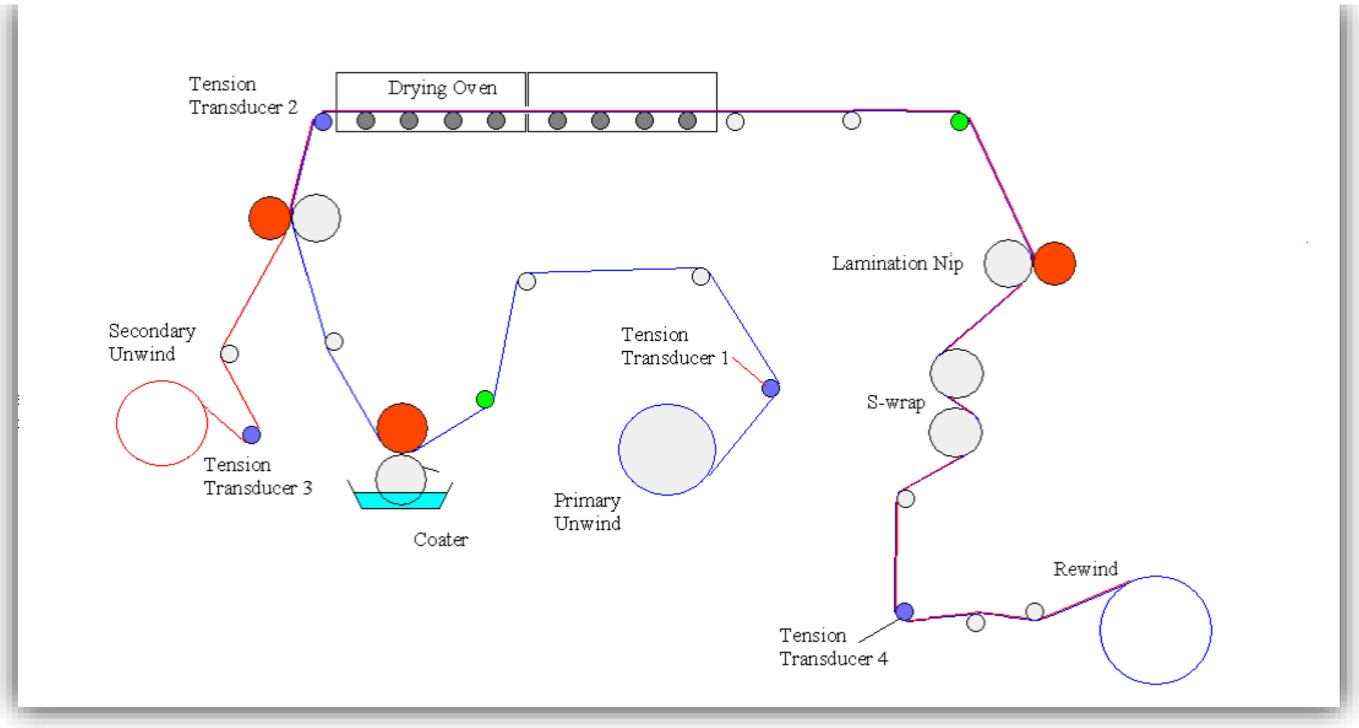

Figure 4.3 - Wet bond lamination (Source: Darby, PKGSC 430)

After 24 hrs. curing checked the bond strength tested by universal tensile strength machine followed by ASTM F 904-98 (2003).

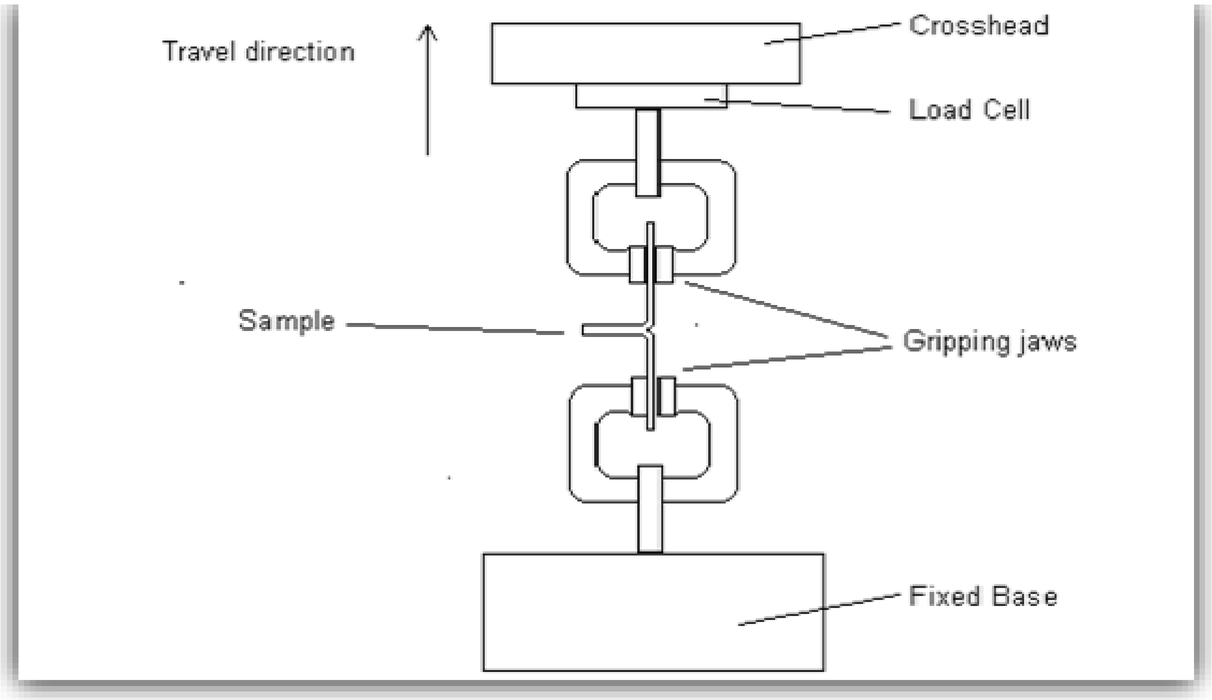

Figure 4.4 - Schematic for Bond Strength testing (Source: Darby, PKGSC 430)

4.3 Comparative Bond Strength

Bond strength (gf/15mm), M/c speed = 50 mm/min.		
Lamination Process	Dry bond	Dry bond
Adh. Coating wt. (dry) (g)	2.3	2.3
Lamination structure	**Plain PET/ m-Pet**	**Plain PET/ m-BOPP**
Exp. 1P-1	55 - 65, ST, NMT	50 - 60, ST, NMT
Exp. 1P-2	65 -75, ST, NMT	55 - 65, ST, NMT
Exp. 1P-3	70 - 80, ST, NMT	80 - 90, ST, NMT
Exp. 1P-4	65 - 75, ST, NMT	70 - 80, ST, NMT
Exp. 1P-5	70 - 80, ST, NMT	70 - 80, ST, NMT
Exp. 1P-6	75 - 85, ST, NMT	70 - 80, ST, NMT
Exp. 2P-1	55 -65, ST, NMT	60 - 65, ST, NMT
Exp. 2P-2	65 -75, ST, NMT	60 -70, ST, NMT
Exp. 2P-3	70 - 80, ST, NMT	65 - 75, ST, NMT
Exp. 2P-4	70 -80, ST, NMT	70 - 80, ST, NMT
Exp. 2P-5	60 - 70, ST, NMT	60 -70, ST, NMT
Exp. 2P-6	65 -75, ST, NMT	70 - 80, ST, NMT
Exp. 3P-1	65 - 75, ST, NMT	60 -70, ST, NMT
Exp. 3P-2	70 - 80, ST, NMT	65 - 75, ST, NMT
Exp. 3P-3	70 - 80, ST, NMT	65 - 75, ST, NMT
Exp. 3P-4	75 - 85, ST, NMT	70 - 80, ST, NMT
Exp. 3P-5	80 - 90, ST, NMT	70 - 80, ST, NMT
Exp. 3P-6	85 - 95, ST, NMT	80 - 90, ST, NMT

Chapter 5: Conclusion

Emulsion polymerization technique is used for manufacturing of water based acrylic lamination adhesives. This technology offers environmental compliance in comparison of solvent borne polyurethane lamination adhesives.

The monomer selection was based on the formation of copolymers with low Tg homopolymers (E.g. BA, 2-EHA) & the addition of the high Tg monomers (E.g. MMA, STY, AA).

In this project work the three cross-linking agents used were - Acetoacetoxyethyl methacrylate (AAEM), 2-Hydroxy ethyl acrylate (HEA) & Hyrdoxy propyl acrylate (HPA) with different three copolymer monomers -

1. Butyl acrylate (BA), Methyl methacrylate (MMA) & Acrylic acid (AA).
2. Butyl acrylate (BA), Styrene (STY) & Acrylic acid (AA).
3. Butyl acrylate (BA), Methyl methacrylate (MMA), 2-Ethyl hexyl acrylate (2-EHA) & Acrylic acid (AA).

Highest bond strength (85 - 95 gf/15mm) between the laminate structure plain PET to m-PET was observed in experiment no. 3P-6 i.e. acrylic emulsion with copolymers of Butyl acrylate (BA), Methyl methacrylate (MMA), 2-Ethyl hexyl acrylate (2-EHA), Acrylic acid (AA) & Hyrdoxy propyl acrylate (HPA).

Highest bond strength (80 - 90 gf/15mm) between the laminate structure plain PET to m-BOPP was observed in two experiments i.e. experiment no. 1P-3 & 3P-6. In the experiment no. 1P-3; acrylic emulsion with copolymers of Butyl acrylate (BA), Styrene (STY), Acrylic acid (AA) & Acetoacetoxyethyl methacrylate (AAEM) & in experiment no. 3P-6; acrylic emulsion with copolymers of Butyl acrylate (BA), Methyl methacrylate (MMA), 2-Ethyl hexyl acrylate (2-EHA), Acrylic acid (AA) & Hyrdoxy propyl acrylate (HPA) was used.

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