1.0 Introduction to Coating

Polymers are indispensible for modern mechanized civilization because of the versatility of the application. These materials can be tailored as per desire. However polymer science as a coherent subject is barely few decades old. The importance of polymers had increased because of lightweight, low cost, excellent chemical resistance, anti corrosive nature and easy processability. It deals with the chemistry the molecular structure, physical properties, the application and processing in to useful forms and biological significance of materials consisting of large macromolecules. Polymers have versatility of properties. In Polymer a part of Surface coatings have been used for thousands of years in gradually increasing quantities as civilization developed. In the prehistoric period painting was limited almost entirely to the decoration of caves and other dwellings. The ancients applied coatings to their ships, utensils, musical instruments, weapons, mummies, temples and palaces. For centuries, surface coatings were used only for decorative purpose and their preparation and applications remained more of an art than a science. The materials used were derived from nature. After the industrial revolution, the need for protection of metal objects arose. This in turn slowly transformed the art of paint-making and its application, into science which gave an impetus to scientists for making efforts for better understanding of coating compositions, their constituents, applications and testing. Besides, the discoveries of new materials and their various applications constantly pose a challenge for surface coating research in terms of satisfying increasingly stringent requirements of protection coupled with decoration in certain instances under diverse service conditions.

1.0.1 Definitions and Scope

Coatings may be described by their appearance (e.g., clear, pigmented, metallic, or glossy) and by their function (e.g., corrosion protective, abrasion protective, skid resistant,
decorative, or photosensitive). Coatings may be distinguished as organic or inorganic, although there is overlap. For example, many coatings consist of inorganic pigment particles dispersed in an organic matrix (binder). A confusing situation results from multiple meanings of the term coating. It is used to describe the material (usually, a liquid) that is applied to a substrate, the resulting “dry” film, is termed as coating. Usually, the intended meaning of the word coating can be inferred from the context [1].

Surface coatings have been a part of man’s environment for many years, the caveman was probably the first to use paint for his cave paintings. For centuries, surface coatings were used only for decorative purpose and their preparation and applications, remained more of an art than a science. The materials used were derived from nature. After the industrial revolution, the need for protection of metal objects arose. This in turn slowly transferred the art of paint making and its applications into science which gave an impetus to scientist for making efforts for better understanding of coating composition, their constituents, applications and testing. Besides the discoveries of new materials and their various applications constantly pose a challenge for surface coating research in terms of protection coupled with decoration in certain instances under diverse service conditions [2].

1.1 Present Scenario of Surface Coating

The increasing legislative restrictions on VOC emission and awareness among the surface coatings users force the technologists to develop the Eco friendly coatings which are
safer in production, storage and applications. The Eco friendly methods of surface coatings viz. High solid coatings, Powder coatings, Radiation cured coatings and Water borne coatings are very well described in various literatures[3] presently majority of the research work is going towards the above mentioned areas.

Since the present work is about the development of newer raw material for surface coatings. The various types of the surface coatings which are commonly used in the market are briefly introduce. Before we go for the classification or the types of surface coatings, the brief introduction about the composition of the surface coatings are as under

Organic coatings are complex mixtures of chemical substances that can be grouped into four broad categories:

(1) Binders,

(2) Volatile components, (Solvent)

(3) Pigments, and

(4) Additives.

1.1.1 Binders or Resins

Binders are the materials that form the continuous film which adheres to the substrate (the surface being coated), bind together the other substances in the coating to form an adequately hard film on the surface [4]. The binder is the most important one of the components. Many of the properties of coatings, such as their mode of drying and adhesive. Mechanical properties of the films are determined by the nature of the binder. Resins can be divided into two as natural resins and synthetic resins. Both natural resins and synthetic resins are organic compounds, often with complicated chemical structure and in many cases of high molecular weight.
Today, synthetic resins have mostly replaced natural resins because of their advantages. They may be produced to fairly close technical tolerances. Most important advantage of the synthetic resins is that they can be varied in relation to the end use for which they are required; in other words, they can be ‘tailor’. Some examples of natural resins are rosin, amber, mastic etc. and some examples of synthetic resins are alkyd, amino, epoxy, acrylic etc. [5].

The primary functions of coatings are:

1. To form a continuous film that adheres to the substrate.
2. To prevent corrosion of metal substrate.
3. To prevent moisture absorption on substrate.
4. To bind the pigments and
5. To give good aesthetic look to the substrate.

1.1.2 Volatile Components (Solvent)

Solvents are used in paints to reduce the viscosity or consistency of the material and so facilitate the application of a uniform coating. After application, the solvent is no longer needed and it should evaporate completely from the film.

Coating solvents, with the exception of water, are volatile organic liquids. The classes of materials used as solvents include aliphatic hydrocarbons, aromatic hydrocarbons, alcohols, esters, ketones and ethers. Water is the solvent in water-borne and emulsion paints [7].

1.1.3 Pigments

Pigments are finely divided insoluble solids that are dispersed in the vehicle and remain suspended in the binder
after film formation. Generally, the primary purpose of pigments is to provide color and opacity to the coating film [4]. However, there are many other reasons for the incorporation of pigments into the system. Pigments have a considerable influence on the consistency of the paint and hence on its application properties. Pigments are also of importance for the resistance of the film to external attack, in that they are partially responsible for such properties as resistance to abrasion and weathering. They are also added for the durability characteristics and to inhibit the corrosion [5, 6].

Pigments can be inorganic or organic. Inorganic ones are usually metallic oxides, such as lead oxide, chromium oxide, cobalt blue etc. Organic ones are generally not found in nature, and they are synthesized from the coal tar and petroleum distillates.

1.1.4 Additives

In addition to these three components, modern paints may contain additives of various kinds, such as plasticizers, driers, emulsifiers or other stabilizers. Additives are the chemical compounds incorporated in paint in small amounts to improve and to modify certain desired properties of paint during processing, storage or during performance of the paint films. They play a decisive role in the formulation and functioning of a coating [7].

1.2 Type of Surface Coating based on their Function

Surface coatings can be classified into two general types, convertible (thermosetting) and non-convertible (thermoplastic).
Further classification is possible—particularly with convertible coatings based on their curing mechanism (air-dry, stoving etc.) and also based on their performance characteristics (heat resisting, corrosion resisting, etc.)

A further, very general classification is based on the order of application, i.e. Based on the methods familiar to professional decorators, industrial finishers and the general public. In brief the types are followings.

1.2.1 High-solids coating

High-solids coatings meet the requirements for environmentally friendlier coatings, with lower emissions of organic solvents compared to the conventional alkyd varnishes.

The composition of the binder in oxidatively drying high-solids alkyd coating systems is partially similar to that of the binders used in conventional alkyd paints with low solids, the cross linking process is accelerated by driers. There are, however, a few characteristic differences that are important for the drying performance. A part from the higher solids content, the molecular mass of the binder is also lower and the reactivity for auto-oxidation cross linking is much higher.

Therefore, to formulate paints with high-solids contents, low viscosity and acceptable application properties are required. The high solids content result in thicker applied films, making the through-drying properties more critical than in low-solids systems [8].

1.2.2 Water borne coating

Waterborne coatings contain some organic solvent. The solvents play a variety of important roles in resin manufacture, coating production, application, and film formation. The two largest classes of waterborne coatings are water-reducible
coatings and latex coatings, smaller amounts of emulsion coatings are also used. We use the term water-reducible for resins made in solvent and reduced with water to form a dispersion of resin in water. Other resins as aqueous dispersion resins or water-soluble resins. Some Latex resins are prepared by emulsion polymerization. Polyurethane latexes are called aqueous dispersion resins. There is growing use of blends of different types, for example, combinations of latex and water-reducible resins.

Water is also used as a co-solvent in solvent borne coatings, which we call water thinning. In relation to organic solvents, water has both advantages and disadvantages. Water is non toxic, non hazardous and odor free, and is not flammable. Non flammability reduces risks and insurance costs and permits use of less make up air in baking ovens, reducing energy consumption. There are no emission or disposal problems directly attributable to use of water. With some formulations, cleanup of personnel and equipment is easier with waterborne coatings; however, in other cases, cleanup is more difficult. The cost of water is low; but it does not necessarily follow that the cost of waterborne coatings is low. The surface tension of water is higher than that of any organic solvent. In water reducible coatings, pigments can be dispersed in solvent solutions of the resins before addition of water, and the surface tension can be reduced with solvents such as butyl alcohol or a butyl glycol ether. Water increases corrosion of storage tanks, coating lines, ovens, and so on. This requires that corrosion resistant equipment be used in applying waterborne coatings, increasing capital cost [9].

1.2.3 High build coating

High build coatings are meant for protection by giving a high dry film thickness in the minimum number of coats. This is achieved by the incorporation of a gelling agent in the coating
composition, which allows application of thick coats without the risk of sagging on vertical surface [10].

**1.2.4 Solvent less coating**

Solvent less coating is based on liquid resins of low viscosity and is used where the presence of solvent is undesirable e.g. Coatings applied in the interior of tanks. These coatings are applied on submerged parts of steel and concrete structures. These paints of high dry film thickness are formulated to cure either by chemical reaction (two pack types such as epoxy and polyurethane) or non-convertible types (e.g. High build chlorinated rubber) which dry slowly by solvent evaporation [11].

There are several reasons for developing solvent-free and low-solvent paints: [12]

1. Reduction of atmospheric pollution
2. Savings in materials and transportation costs
3. Savings in energy costs involved in paint production and use
4. Time savings due to higher layer thicknesses per application cycle
5. Improvement in safety due to low-solvent content.

**1.2.5 Primers**

The first consideration in formulating a primer is to achieve adequate adhesion to the substrate. The substrate should be clean and preferably have a uniformly rough surface. The surface tension of the primer must be lower than that of the substrate. The viscosity of the continuous phase of the primer should be as low as possible to promote penetration of the vehicle into pores and crevices in the surface of the substrate. Penetration is also promoted by use of slow evaporating solvents, use of slow cross-linking systems, and whenever feasible, use of baking primers. The primer binder should have polar groups scattered along the backbone of the resin that can interact with the substrate surface. The presence of salts within the film
should be minimal. Interaction between the binder and the substrate should be such that the coating will resist displacement by water when water molecules permeate through the coating to the interface. For primers over metal substrates, as well as wood and cement substrates [13].

1.2.6 Sealers

Sealers are used to eliminate the suction of coating when applied on the substrates that are porous and where the absorption of medium can upset the pigment/binder ratio of the coating applied. In some cases the formulation of primer can be modified to enable it to function as a sealer also [14].

1.2.7 Putty or Fillers

When substrates contain holes or deep indentations they are treated with putty after application and drying of the primer. Putties or paste fillers are very highly pigmented so that they dry without shrinkage and can be rubbed down to a smooth substrate before application of further coat of coating. The putty is an underbound pigmented coating composition and thus it is porous when dry and require treatment with sealer before further coating [15].

1.2.8 Under coats

They are applied over the primers. Undercoats are fairly highly pigmented to give good opacity and adequate dry film thickness to the paint film. They usually dry to an eggshell finish. They serve as a base coat for finishing coat (usually enamel) to be applied on it [15].

1.2.9 Finishing coats

Finishing coats are the coatings which after drying produces films that exhibit a high gloss (enamel), semi – gloss
eggshell or matt finish. These are the topcoats and directly exposed to the environment [15].

1.3 Methods of Application for the Surface Coating

A surface coating system is useful in practical sense only if it forms a film with considerable physical integrity fulfilling several property demands. The conversion of liquid composition into an adherent and durable coating is termed as the process of film formation. It comprises three main steps viz., application, fixation and cure [16].

Many methods for painting different substrates under various conditions and Constraints have been developed. And the choice of application method depends on many factors some one are listed below [17].

(1) The geometry of the articles to be painted, their weight, dimensions and Compositions

(2) The type of paints (liquid or powder)

(3) The rate at which the parts are to be painted. The coat of the painting Process

(4) Safety and pollution considerations

1.3.1 Brushes, Pads and Rollers

Brushes, pads, and hand rollers are frequently used for the application of architectural coatings. Although the same paints can usually be applied by spray gun, few do-it-yourselfers use spray guns on the other hand, to save time, professional painters use spray guns whenever possible.

A variety of brushes is available: narrow and wide, long handled and short handled, nylon, polyester, and hog bristle. Hog bristles are appropriate for solvent borne paints but not for waterborne paints. Nylon bristles are appropriate for waterborne paints but are swollen by some solvents. Polyester bristle brushes can be used with either.
The most common type of pad consists of a sheet of nylon pile fabric attached to a foam pad that is attached to a flat plastic plate with a handle. For low-viscosity coatings such as stains and varnishes, a lamb’s-wool pad is used.

Hand rollers are the fastest method of hand application and are widely used in applying architectural paints to walls and ceilings. A variety of rollers and roll coverings is available [18].

1.3.2 Spraying

Spraying is widely used method for applying paints and coatings in architectural and especially in industrial applications because it is faster than application by brush or hand roller. Different types of spraying technology and guns used are compressed air spray guns, electrostatic spray guns, airless spray gun, air assisted spray guns, dual feed spray guns, rotary disc gun etc. The main disadvantage associated with the spraying technique is wastage of paint due to overspray which also leads to pollution problem [19].

1.3.3 Roller coating

Roller coating is a process to coat coils and sheets by passing them through two Preset rollers. The quantity of paint consumed is reduced by approximately 50% of that used in other coating methods. The thickness of paint film is controlled by adjusting the rollers. One-side or both-side coatings are possible [20].

It is high speed technique of applying the surface coatings to uniform flat or cylindrical surfaces. It is generally used for coil coatings, plywood and hardboard, paperboard for packaging and printing processes [21].

1.3.4 Dip and Flow coating
Dip coating can be an efficient method for applying coatings. It offers both relatively low capital cost equipment and low labor requirements. The object is dipped into a tank of coating and pulled out, excess coating drains back into the dip tank. An advantage of dip coating is that all surfaces are coated, not just the outer surfaces accessible to spray.

Flow coating and dip coating are related methods. Objects to be flow coated is carried hung on a conveyor through an enclosure in which streams of coating are squirted on the object from all sides [22].

1.3.5 **Curtain coating**

Curtain coating is widely used for coating flat sheets of substrate material such as wall panels and metal doors. Coating is pumped through a slot in the coating head so that it flows out as a continuous curtain. The sheet to be coated is carried through the curtain on a conveyor. The curtain must be wider than the substrate being coated, to avoid edge effects on the film thickness [23].

1.3.6 **Electrodeposition coating**

Electro deposition is very similar operation to electroplating as there is an anode & cathode is immersed in the aqueous medium through which current is passed. The electrodeposition coating may be anodic electrode deposition or cathodic electro deposition depending upon whether the object to be coated is made anode or cathode respectively. Today most significant use of electro deposition coating is for application of automotive primers. The significant advantages of electro coat over other application methods include film uniformity, improved appearance and quality, complete coverage of complex
geometries, high throughputs due to automation, reduced air and waste water emissions and reduced fire hazards, high transfer efficiencies [24].

Some advantage and disadvantages are shown below [25]

**ADVANTAGES:**

- Ideally suited for automation on a production line
- Uniform film weight applied
- Consistent film weight applied to every article coated, which gives good control
- Excellence penetration of hard to reach parts of a complex shaped article
- Fast rate production
- Excellence corrosion resistance possible

**DISADVANTAGES:**

- Article to the coated must be electrical conductors
- High capacity investment required
- Potential effluent problems due to low solids
- Limited Colour changes
- Need high throughput of article of the same type
- Changing the article to be coated may require the bath setting to be altered.
### Application efficiency (%) of various application methods: [26]

<table>
<thead>
<tr>
<th>APPLICATION METHOD</th>
<th>% EFFICIENCY</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Conventional Spray:</strong></td>
<td></td>
</tr>
<tr>
<td>Air atomized</td>
<td>35-50</td>
</tr>
<tr>
<td>Airless atomized</td>
<td>40-65</td>
</tr>
<tr>
<td><strong>Electrostatic Spray:</strong></td>
<td></td>
</tr>
<tr>
<td>Air atomized</td>
<td>60-70</td>
</tr>
<tr>
<td>Airless atomized</td>
<td>45-80</td>
</tr>
<tr>
<td>Centrifugal atomized</td>
<td>80-90</td>
</tr>
<tr>
<td>Dip, flow &amp; curtain coating</td>
<td>70–80</td>
</tr>
<tr>
<td>Roller coating</td>
<td>85–90</td>
</tr>
<tr>
<td>Electro deposition</td>
<td>90–98</td>
</tr>
</tbody>
</table>

#### 1.3.7 Knife coating

Knife coating can be used for the coating of flat and usually continuous sheet material e.g. Paper, Plastic Film. Excess coating is applied by any suitable technique, e.g. Roller coating and the coating thickness is then reduced by passing the web under a doctor knife or an air knife. This technique is particularly suitable where very thin coatings indeed are required. Viscosity of coating can be relatively high, since the pressures of the knife determine film thickness [27].
1.4 Method for Film Formation

Most coatings are liquids with a viscosity appropriate for the application method, generally in the range 0.05 to 1 Pa.s at high shear rates. After application, the liquid is converted to a dry (solid) film. In powder coatings, the powder is liquefied after application and then converted to a solid film. The chemical and physical changes that occur in this process are called film formation, a process that is critical to the ultimate appearance and performance of the coating. If the applied coating were crystalline, there would be no difficulty in defining a solid film. The film would be solid if the temperature were below its freezing point; however, binders of coatings are almost always amorphous, with no melting point and no sharp demarcation between a liquid and a solid [28].

The quality of the dry coating depends on the composition of the coating, the nature and pretreatment of the substrate, and the processing conditions. Four routes of film formation are implemented either alone or in combination: [29]

(a) Evaporation of organic solvents from polymer solutions or dispersions

(b) Evaporation of water from polymer solutions or dispersions

(c) Cooling of polymer melts

(d) Reaction of low molecular weight substances and or polymers to form

Macromolecules by polymerization and cross-linking.

Drying processes depending on the nature of resin and solvent which can be divided into two main categories:

(1) Physical drying

(2) Chemical drying

Physical drying

Physical drying mainly involves solvent evaporation and the film integrity is usually obtained by chain entanglements since the chain entanglement is the main criteria on for such
systems. The resin used should have very high molecular weight to give durable coatings. This type of drying is generally involved in thermoplastic systems such as nitrocellulose lacquers, chlorinated rubber paint, thermoplastic acrylic lacquers etc.

(2) Chemical drying

Chemical drying always involves some type of chemical reactions at room temperature or at elevated temperature in order to obtain durable film. These chemical reactions cause the formation of high molecular weight three-dimensional networks and are often termed cross-linking reactions. These cross-linking reactions can either be due to auto-oxidation of unsaturated groups present in the resins or due to condensation reaction between the functional groups present in the same polymer or between the functional groups present in curing agents and the resin [30].

1.4.1 Drying due to Inter and Intra molecular condensation

Drying involving intermolecular or intramolecular condensation reaction of the functional groups is often called chemical drying. When functional groups undergoing condensation reactions are present on the same polymer molecules, it is termed intra molecular whereas it is termed intermolecular if condensation reactions involve functional group present on the polymer and on added curing agent. These condensation reactions result in the formation of high molecular weight polymers, which, in turn, impart filmsetting. Functional groups most frequently used to bring about these condensation reactions are hydroxyl, carboxyl, isocyanate, epoxy, amides, amines etc. The curing agents commonly used for this purpose are melamine resins, phenolic resins, di and polyisocyanates, amines, amides etc. the condensation reaction for film formation may occur at room temperatures or at elevated temperatures[30].
1.5 **Properties of Surface coating**

Evaluation of mechanical and chemical properties of coatings is of paramount importance in maintaining the protective and decorative properties of the coatings during their service life. Surface coatings are subjected to a great variety of mechanical forces or deformations. They may suffer large forces concentrated on a small surface area for very short time (as in the impact of stones, gravels etc. on car body paints) or they may suffer a succession of slow cycles of deformation in response to change in atmospheric moisture or temperature. Not only do the films suffer a wide variety of mechanical stresses and strains during their service life, but also their mechanical properties of the film. Chemical properties of the films in general, depend upon the chemical composition of the film former, the presence or absence of free functional groups and, in case of thermosetting resins, the cross link density of the film. The evaluation of resistance to variety of chemicals, water and solvents by coating is generally dictated by the end use application of the coating. It is, therefore, imperative that the evaluation of mechanical and chemical properties of the film is conducted since these properties determine how long a coating film can preserve its physical integrity and can fulfill its protective role satisfactorily for given application. The most commonly measured properties viz. mechanical and chemical are discussed below [31].

Properties of surface coatings can be broadly classified into three categories.

(1) Physical properties

(2) Performance properties: Mechanical and Chemical properties

(3) Optical properties

All the coating materials prior to being tested are observed for their appearance in container. Coating in the container may apparently exhibit the appearance like consistency (thick or thin), skinning, flocculation, settling, floating etc.
1.5.1 Physical properties

General physical properties of coatings include viscosity, weight per liter, fineness grind of pigment particles in resin vehicle, nonvolatile content by volume (NVV), nonvolatile matter by mass (NVM), shelf life (package stability), wet and dry film thickness, drying time.

1.5.1.1 Viscosity

Rheology is the science of flow and deformation. A liquid exerts resistance to flow called viscosity, $\eta$ defined as the ratio of shear stress, $\varsigma$ to shear rate, $r^*$. This type of viscosity is correctly called simple shear viscosity.

Paint brush ability, leveling and sagging are highly dependent on viscosity. To evaluate the force required for brushing the viscosity should be measured at a high shear rate of about 10,000 s$^{-1}$. Sagging is the downward movement of a coating film that occurs between the time of application and setting. The viscosity should be measured at a shear rate of at most 1 s$^{-1}$ in order to assess sagging on vertical walls. Leveling is the ability of a coating to flow out after application (e.g. to obliterate brush marks).

The viscosity of organic solvent based coating is determined by Ford cup No.4 and the viscosity of the water based coatings is determined by Stormer viscometer or Brookfield viscometer [32].

A wide variety of instruments are used in measuring the viscosity of coatings. e.g. capillary viscometers, rheometers, rotating disk viscometers, bubble viscometers, efflux cups, and paddle viscometers [33-34].

1.5.1.2 Weight per liter

Many of the coatings are sold on volume basis hence all the coatings should be evaluated for their weight per liter. It can be measured by standard weight per liter cup expressed in terms of kg/lit or lb/gal.
1.5.1.3 Fineness Grind of Pigment particles

The fineness of grind test is carried out with a fineness grind gauge. Which is made of a polished metal plate with 2 grooves whose depth varies uniformly from nothing to a set depth. By depositing a little paint spread over the entire surface, one can determine during the first five seconds of the measurement the fineness of grind of the paint. This is the point at which surface imperfection can be first observed. The gauge is marked and the point at which the bits are first seen is read from the gauge. This will give an indication of die gloss and the surface, appearance of the applied and dry paint film, and the resistance to settlement of the liquid paint prior to application [35].

The fineness of grind is reported in microns and is checked by the Hegmann gauge, which has scale reading from 0 to 8 corresponding to 100 to 0 micron size respectively [36].

1.5.1.4 Wet and Dry Film thickness

Coatings are applied at adequate film thickness so that uniform curing and leveling of the film is achieved. This applied film thickness is referred as wet film thickness (WFT) and the thickness that is obtained after the coating has dried or cured is referred as dry film thickness (DFT). Different instruments are available to measure the film thicknesses [37].

1.5.1.5 Non volatile content by volume (NVV$_T$)

Non–volatile by volume (NVV$_T$) is calculated from the relationship.

\[
\text{DFT} = \text{WFT} \times \frac{\% \text{NVV}_T}{100}
\]

Non-volatile by volume is the parameter which gives the coating the desired film builds. Non-volatiles by volume are also assessed by the American Standard of Testing and Materials (ASTM) specification D2697–86(1998) and the WFT and DFT are checked by their respective gauges [38].
1.5.1.6 **Shelf life (Package stability)**

The shelf life of coatings is defined as the period for which coatings may be stored in a sealed unopened container without the coating showing any significant deterioration in quality.

One method for assessing the shelf life is to test the coating for accelerated storage comprising five cycles. One cycle means the coating is stored at room temperature for 48 hrs followed by storing at 45°C for another 48 hrs and then assessing for any sign of deterioration. This resembles the duration of storage of six months [39].

1.5.2 **Performance properties: Mechanical and Chemical properties**

Evaluation of mechanical and chemical properties of coatings is paramount importance in maintaining the protective and decorative properties of the coatings during their service life. Surface coatings are subjected to a great variety of mechanical forces or deformations. They may suffer large forces concentrated on a small surface area for very short time (as in the impact of stones, gravels etc. on car body paints) or they may suffer a succession of slow cycles of deformation in response to change in atmospheric moisture or temperature. Not only do the films suffer a wide variety of mechanical stresses and strains during their service life, but also their mechanical properties of the film.

Chemical properties of the film in general depend upon the chemical composition of the film former, the presence or absence of free functional groups and in case of thermosetting resins the crosslink density of the film [40]. The evaluation of resistance to variety of chemicals, water and solvent by coating is generally dictated by the end use applications of the coating. Therefore the evaluation of mechanical and chemical resistance properties of the film is conducted because these properties determine how
long a coating film can preserve its physical integrity and can fulfill its protective role satisfactorily for a given application.

Some of the mechanical properties and resistance to water, chemicals and solvents are described below.

1.5.2 Evaluation of Mechanical properties

1.5.2.1 Adhesion

Adhesion is the state in which force, which may consist of valence attractions, or interfacial forces or a combination of both holds two surfaces together. Interfacial forces are physical bonds whereas valence attractions are chemical in nature. The interfacial forces are too small to be measurable by any mechanical device.

There are two major factors, which affect the adhesion of organic coatings to various substrates like,

- The affinity of the solvent and the resin in the coating for the substrate.
- The profile or the roughness of the substrate.

The first is referred to as the specific adhesion and the second is the mechanical adhesion.

In order for a specific adhesion to be formed, there must be an initial interaction between the solvent system and the substrate, followed by an adsorption of the polymeric phase on to the substrate.

The cleanliness of the substrate is a major factor for proper adhesion of any organic coatings. The surface must be free from oils, greases and other foreign materials, which can reduce the wetability of the substrate. The coating must be applied to oxide-free surfaces (in the case of metallic substrates) since their presence would prevent the formation of any chemical bond between the metal and the coating.
As adhesion is defined as interfacial forces between coating and substrate, their magnitude cannot be measured by mechanical means. Since adhesion cannot be measured, as such, it is necessary to determine the forces needed for the removal of the coating from the substrate.

Among the methods for measurement of adhesion, organic coatings are removed by empirical scratching with a sharp blade, by a mechanically operated knife, by exposure to high-speed vibration or by high-speed centrifugal force. The amount of force necessary is then measured and a value for adhesion is ascribed to the coating. Another method is to apply a given force, using a definite instrument or device. The resulting delamination, in quantitative terms, is directly proportional to the adhesion of the coating. Forces necessary for the coating’s removal under controlled conditions to measure adhesion, wide range of methods and devices for the purpose has been employed over the years. Adhesion test of coated materials was observed by cross hatch, according to ASTM D 3359 method to determine unacceptable adhesion. The test coatings were cut through the substrate using a sharp razor blade to give parallel lines 2mm apart, forming a 10x10-block grid. The test surface was then brushed lightly to remove loose particles. Adhesive tape (Scotch Brand = 810 magic tape or 3M adhesive tape) was pressed on to the scribed area and then pulled off rapidly at 180° angles within 60 seconds. The scribed area was inspected visually with an illuminated magnifier to determine percentage of coating removed [41].

1.5.2.2 Hardness

The hardness of organic coatings [42] cannot be expressed in absolute or intrinsic terms and cannot be expressed quantitatively. The measurement of hardness of organic coatings is based on practical concepts. A material is considered to be hard when it can resist indentation and scratching. Hardness determination by the use of tests is most widely used. When resistance to indentations is used as measure of hardness, then
it is related to rigidity of the material or its elastic modulus. The Four widely used tests are:

- **Pencil Hardness**

  The organic coatings are rated according to their resistance to be scratched or marked by various pencils having different hardness [43]. A coated panel placed on a flat horizontal surface and pencil is held at an angle 45° to the film. The pencil is pushed away from the operator in 1/4” stroke. This process is started with the hardest level pencil and is repeated with progressively softer pencil until the pencil did not cut the film. The pencil, which does not cut the film, denotes its hardness. The coating of test formulations, pencil hardness is measured at 27 °C.

- **Scratch hardness**

  In this method, resistance to scratching by hemispherical hardened steel point under specified load on a dried film of coating is tested by a mechanized or hand operated apparatus [44].

- **Pendulum or Rocker type hardness**

  This hardness is measured by a pendulum or rocker, the mechanism being the dampening of the oscillations of pendulum, rested on the test sample, due to the mechanical losses, rolling friction, shear modulus, and in case of coatings the hardness of the substrate [45].

- **Indentation test**

  In this test an indentor with diamond shaped tip is pressed into the film with fixed weight over a fixed time period. The indentation made in the film is measured by calibrated microscope. Results are expressed in knoop hardness number (KHN) that is related to the weight divided by the area of indentation [45].
1.5.2.3 Flexibility and Formability

The term flexibility refers to the characteristics of a coating film to have sufficient elasticity so that it will not split or crack following the shrinkage of the film due to weather or service conditions.

The Indian Standard Institution [46] defines the term flexibility as the degree to which a film after drying is able to conform the movement or deformation of its supporting surface without cracking, the flexibility depends not only on the elasticity of the applied film but also on the adhesion of the film to the substrate. It has been shown that the well adhering films have better flexibility than those which adhere poorly. The factors affecting the flexibility of any coatings are humidity, temperature and the strain rate [47].

Flexibility tests are of two basic types.

(1) The bend test, in which coated panels are bent around mandrels

(2) The Erichsen test in which the panel metal is deformed by a large hemispherical ended indenter.

Among the most commonly used test is conical mandrel apparatus and a bending apparatus as described in IS: 101–1989 [48].

In many cases a coated metal object is subjected to mechanical forces either to make a product, as in forming bottle caps. To avoid film cracking during such distensions, the elongation at break must be greater than the extension of the film under the conditions of fabrication or distortion. Cross-linked coatings have low elongations-at-break well below Tg. Properties are affected by the extent to which cross-linking has been carried to completion. If the cross-linking reaction was not complete, the reaction may continue decreasing flexibility.
Another possible factor with baked films is densification. If a coating is heated above its Tg and then cooled rapidly, the density is commonly found to be lower than if the sample had been cooled slowly. During rapid cooling, more and/or larger free volume holes are frozen into the matrix. On storage, the molecules slowly move and free volume decreases, causing densification; it is also called physical aging [49].

1.5.2.4 Impact resistance

From the viscoelastic properties of the coatings it is difficult to present and predict impact resistance due to complicated stress-strain profiles. Timoshenko and Goodier [50] have derived a theory of impact, which allows the magnitude of the most significant impact parameters to be estimated. Impact test evaluates the ability of coating to withstand extension without cracking when the deformation is applied rapidly [51]. In the measurement of impact resistance, an indenter of low mass is forced against the panel at a specified velocity. The minimum velocity at which damage becomes visible at the point of impact is measured.

In another method determination of impact resistance involves indentation by an object of specified weight on to a panel from the varying height. If the coated side is up, the test is called direct impact test. If the back of the panel is up, the test is called a reverse impact test. The weight is dropped from greater and greater height until the coating on panel cracks. Generally reverse impact tests where coating is extended as a result of impact are more severe than direct impact test where coating is compressed. The results are generally reported in inch-lb that is the number of inches from which the weight falls times its weight. The thickness, mechanical properties and surface of the substrate substantially affect the results.
1.5.2.5 Abrasion resistance

Abrasion resistance may be defined generally as the ability of a material to withstand mechanical action such as rubbing, scarping or erosion that tends progressively to remove material from its surface [52]. Abrasion resistance of a coating is related to other properties of the coating such as hardness, toughness, tensile strength, and elasticity. The measurement of abrasion resistance is a complex interrelationship of several properties of the coatings and many devices have been derived and developed to indicate the maximum correlation between the laboratory testing and actual service performance.

The devices used for determination of abrasion resistance fall into three basic categories: [53]

1. Those using loose or falling abrasive particles.
2. Those using abrasive blast, where the abrasive particles are forced onto the coatings by compressed air.
3. Those using rotating disc or wheels.

Abrasion is the wearing away of a substance. The assumption that hard materials are less likely to fail by abrasion than soft materials is true in some cases but in many other cases softer materials are more abrasion resistant. Energy to break values of films can be related to abrasion resistance of films. The coefficient of friction of the coating can be an important variable in abrasion resistance. As the energy to break values increase and coefficient of friction decreases abrasion resistance increases [54].

The widely used test is the Taber abraser in which two rotating abrasive wheels rolls on a panel creating a circular wear path. Another commonly used abrasion test is the falling sand
test. Other than these many more methods are there to evaluate abrasion resistance in which one of above mentioned three mechanism is used [52, 53, 55].

1.5.3 Evaluation of Chemical Properties

1.5.3.1 Water and Moisture resistance

Surface coatings are invariably designed to control the action of water. They basically function as barriers between substrate and the aqueous environment. The effect of water on paint films & substrate has been extensively studied and reported in the literature [56].

Three basic tests are employed to measure the resistance of coatings to water, viz.:

(a) Measurement of the water-vapors permeability of the film.

(b) Measurement of effect of water that condenses or is splashed on to the film.

(c) Determination of the effect of the water vapors being transmitted through a Permeable substrate.

Coatings, which are applied to nonporous substrate and are exposed to the atmosphere, must be able to repel and resist the deteriorating effect of water. The laboratory tests designed to determine these effects use water that has been condensed on the substrate, water that has been mechanically sprayed on the substrate or water as the medium for immersion.

Another category of test is based on the transmission of water vapors through substrate to the paint film.

1.5.3.2 Alkalis and Acids resistance

Alkali and acid [57] solution can have detrimental effect upon wooden and metal substrates. The test involves immersion of coated panels at room temperature into an alkali solution of sufficient concentration. After the immersion for 24 hours, specimen are rinsed under running water, allowed to dry for 30
minutes at room temperature and examined for various parameters. The resistance of coating to acids or alkalis, among other factors, mainly depends upon the chemical composition of polymer backbone and the degree of cross-linking in thermosetting films.

### 1.5.3.3 Chemical resistance

A coating is often formulated to exhibit certain degree of chemical resistance [58]. It is necessary to express the resistivity of a coating to varying chemicals. The tests to determine chemical resistance of coating range from the simple spot test to the complicated method requiring sophisticated equipment. The exposure of paint film to various chemicals can reduce its gloss, change color and produce a swelling and softening of the paint film. In the extreme case the film can be stripped from the substrate or completely destroyed by solvent action.

### 1.5.3.4 Solvent resistance

Solvent resistance property is one of the properties that must be balanced with mechanical properties for many applications. Solvent resistance of the thermoplastics resin film is poor than the films of thermosetting resin. In thermosetting resin films, solvent resistance generally improves with increase in crosslink density of the film. The resistance to swelling by solvent is directly related to crosslink density of the film, which also affects many mechanical properties [59].

Solvent resistance may be tested for many different reasons, depending upon the intended use of the coating. The immersion test is commonly performed to assess solvent resistance of the film. The panels are immersed in a bath of appropriate solvent at ambient temperature for certain period of time and are assessed for blistering, hardness, adhesion and discoloration of film. Such a test is useful in assessing the performance of a particular system in use. Alternatively the test may serve to give indication of the degree of cure in which case
it is common to use the solvent that carried the original coating system [60]. In addition to immersion testing, solvent resistance may be assessed by a solvent rub test. In this test the surface of a panel is rubbed with a piece of cloth or cotton moistened with the solvent. Solvent resistance may be measured by number of rubs necessary to disintegrate the films. Alternatively, a specified number of rubs may be carried out and the appearance of the film be assessed.

1.5.4 Optical properties

Aesthetic look and obliteration is the most important function of the coatings. Some of the important optical properties are described below:

1.5.4.1 Hiding power

Hiding is a complex phenomenon and is affected by many factors. Hiding increases as film thickness increases. Low hiding coatings require thicker films that are coverage decreases, the area covered (hidden) by a liter of coating is less and the cost is higher. Hiding increases as the efficiency of light scattering increases; that is, hiding is affected by the refractive index differences, particle sizes, and concentrations of scattering pigments present. Hiding increases as absorption increases.

Carbon black pigments, which have high absorption coefficients for all wavelengths, are particularly effective. Colorants also increase hiding but not as much as black. Surface roughness increases hiding; a larger part of the light is reflected at the top surface, reducing the differences of reflection resulting from differences in the substrate to which a coating is applied.

An important factor affecting hiding, sometimes forgotten in testing coatings is uniformity of film thickness. Application of coatings commonly results in nonuniform thickness. Coatings are generally formulated to level, that is, to flow after application to make the film thickness more uniform. Leveling is
often incomplete, however, and there can be effects on hiding. Consider a poor leveling coating where an average film thickness of 50 mm of dry coating has been applied, but there are brush marks remaining, so adjacent to each other are lines with film thicknesses of 65 and 35 mm. If the hiding at 50 mm is just adequate, hiding will be inferior at 35 mm. The difference in color is emphasized by the thin layers of coating being right next to the thick layers. The contrast results in a poorer rating in hiding by the uneven film than by a uniform 35-mm film of the same coating. Further complicating hiding is the variation of substrates over which the coating is applied. Hiding of a white coating applied over a white surface might be rated as excellent, but hiding of the same coating over a black surface might be rated poor [61].

There are quality control tests that compare hiding of batches of the same or similar coatings, but no test is available that can provide an absolute measure of hiding [62].

1.5.4.2 **Color and Gloss properties**

The color and gloss are the two important properties of paints and coatings. The color matching of the coating is done visually or by the color computer in which the color is specified by tristimulus values (ASTM method E–1347-97). The gloss of the coating is often described as giving the lustrous or shiny appearance and referred as secular reflection of the incident light. It is checked by the method prescribed in ASTM method E-430-97 [63].

All the testing methods have also been described in detail in the Indian standard specification IS: 101-1989.

Gloss and gloss retention are properties which are of great importance for most surface coatings. This importance is not only confined to aesthetic considerations, in many cases technical considerations are of equal weight. For instance the
property of a surface to collect dirt is to a large extent bound up with its gloss, being reduced by an increase in gloss. In judging the resistance of a film to the effects of destructive agents, loss of gloss is one of the most important criteria [64].

Gloss is a complex phenomenon associated with the physical nature of a surface and the way in which the nature of the surface affects the reflection of incident light. Two extreme cases of reflectivity of a surface may be distinguished, ideal mirror reflection, and an ideal diffuse or matt reflection. The perfect mirror surface is a plane surface reflecting all the incident light flux unidirectionally according to the angles of incidence. As primary surfaces for gloss standards, optically plane highly polished black glass surfaces are often used. They are ascribed an arbitrary value of 100 for all angles of incident and reflected light. From Fresnel's formula it is clear that the amount of light reflected increases with increasing angle of incidence. Therefore, in the measurement of specular gloss 20° is recommended for glossy surfaces and 85° for matt surfaces. A perfectly matt surface is one which spreads the reflected light equally in all directions. Perfectly matt surfaces are extremely rare in practice. In almost all cases differences in brightness will be apparent if the surface is viewed from different directions. Such a surface having luster will show a greater intensity of reflected light in the direction of specular reflection.

1.6 Recent Scenario of Coating Technology

Newly developed objects are nowadays designed with different shapes and are made from various materials that demand new ways of protection and application techniques with the desired performance. In addition, the trend of using solvent-based paints has been greatly shifted to the more environmentally friendly alternatives due to the more stringent legislations on environmental aspects, especially on the emission
of volatile organic compounds (VOC). Because of these concerns and demands, new paint systems such as water-based coatings, UV and EB radiation curable coatings, high solids coatings, and powder coatings have been developed in the last few decades. As fundamental understanding of the roles of the materials played in paint systems increases, control over the ingredients of the paints has been much more sophisticated. In order to obtain the desired performance and to meet legislation requirements, new proprietary binders, additives and cross-linking technologies such as hybrid binders (alkyd-acrylic latexes), organic-inorganic hybrid systems, tailor made binders[73], telechelic polymers, novel hyperbranced resins, low surface energy films, new chemistries for UV-curing systems, chromate free paints for metal substrates, tin-free antifouling coatings, and low temperature curing for powder coatings have been extensively investigated [65-71].

The coating industry has only occasionally been presented with the challenges and opportunities that either bring about, or proceed from, radical change – the advent of latex house paints, powder coatings and electrodeposition coating have been among the very few. Today, however, large variety of potential technology approaches like solid paint, solvent less liquids, energy curing systems (UV & EB Curable coatings) use of nanotechnology or combinational chemistry etc might lead to shifting products and processes. It is easy to envision a future in which painted metal might replace asphalt shingles, clay tiles, and other common roofing materials widely used on residential roofing, and the automotives industry [72].

In early 1980s, the late Dr.Marco Wismer, one of the coatings industry’s more visionary members, enunciated “Six Strategic goals for the coatings industry” as follows which have
never been far from our collective thought in the years since [73].

1. Corrosion Protection
2. Elimination of Solvents.
3. Conservation of Energy
4. Reduction of Toxic Wastes
5. Cost Reduction
6. Improved durability

Although stated over about almost 2 decade ago, these six goals are more valid than ever today, and it is clear that the various global coatings market places, both industrial and consumer, are seeking (in some cases struggling) to provide positive, proactive and economically viable realizations for each of these goals [73]. So in all over the world the efforts of coatings industry are targeted towards these six goals.

Along with the reduction in paint cost, there has been tremendous concentration on reduction in paint application cost by innovative technologies like new pretreatment processes at low temperature; advanced application technologies like electrodeposition, airless spraying, robotic paint application; recycling of the excess paint from the paint booth; increased productivity by automation of painting processes and low waste generation [74].

In modern age technology and globalization there has been see through changes in mind set of the industry. Now there has been more emphasis on the painting process and both Aesthetics and protection qualities.

Along with the high productivity at low cost, protection of our environment, health & safety is also the biggest task ahead for the coating technologist.
1.6.1 Environment factor need for Green Coating Technology

Our environment is under attack and there is a potential threat ahead for earth's water, air, land, animals and human beings. Every year lots of toxic gases, chemicals and effluents are being pumped into the environment. This uncontrolled emission is causing irreparable damage to our environment and destroying the ecological balance [75].

For the entire chemical industry, operating sustainable businesses that provide value-added products and services with minimal or no environmental impact continues to be a top priority. The adoption of a “Green” approach to the manufacturing and marketing of chemical products, including paints and coatings, clearly assists companies in attaining this goal. Green chemistry initiatives must be commercially viable and provide products or services that have enhanced performance qualities and/or cost savings in addition to reducing the environmental pollution [76].

In Europe, the regulations to control VOC emissions took place in the decade 1970-80. Currently the main bodies that concern with the effect of VOCs are the UN, EC, and CONCAWE [77].

Reduction of VOCs has been a major focus of the Paint & Coatings industry as regulations have become increasingly stringent. The green chemistry initiatives of many companies have centered on developing products and processes that reduce or eliminate the use of VOCs and the emissions associated with them. “The market for low VOC latexes is growing at an exponential pace, and is significantly larger than earlier” [78-79].
1.6.2 Volatile Organic Compound need for Environmental

One of the major pollutants emitted by the usage of surface coatings is organic solvents used during their processing and application. In the surface coating terminology such compounds are called Volatile Organic Compound (VOCs). It is reported that coating industry contributes 47.2% of total VOC emissions [80].

The detrimental effect of VOC on the environment via chemical / photo-chemical reactions is well described in the literatures [81, 82, 83, 84].

Staying abreast of the many regulations is one of the difficulties faced by the paint & coating industry. Developing cost effective technologies & alternative formulations that meet the regulatory requirements while still providing the level of performance expected by customers is the main challenge for resins & paints manufacturers. The pace of new product development necessary for meeting continually reduced VOC levels has been a hurdle for some companies as well. Thus Environment protection without affecting the quality of coatings rather increased performance of coating is one of the biggest challenges for the coating industry [85].

1.7 Alternative Technologies for Controlling VOCs:

In efforts to lower the VOC emission to reduce risk to human health, many possibilities in the field of resin chemistry are being explored by the researchers to develop eco-friendly organic coating and paint systems.

They are:

1. Waterborne Coatings
2. High Solid Coatings
3. Powder Coatings
4. Radiation Curable Coatings.
The basic technology involved in these eco-friendly coating technologies along with their relative merits & demerits has been well described in the literatures [82, 86, 87].

### Control of VOC by eco-friendly technologies [88]

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Type of Coatings</th>
<th>% Reduction of solvent</th>
<th>Remark</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Waterborne coatings</td>
<td>60-90</td>
<td>Adapted to most equipment</td>
</tr>
<tr>
<td>2.</td>
<td>High Solid Coatings</td>
<td>60-90</td>
<td>Viscosity problem, limited systems</td>
</tr>
<tr>
<td>3.</td>
<td>Powder coatings</td>
<td>100</td>
<td>High cost, need new equipments</td>
</tr>
<tr>
<td>4.</td>
<td>Radiation Curable coatings</td>
<td>Up to 100</td>
<td>Limited for flat surfaces</td>
</tr>
</tbody>
</table>

Among these, Radiation Curable coatings in particular have succeeded in producing excellent replacements for solvent borne industrial coatings. This is due to their very fast rate of cure, near complete conversion of coating, uniformity of application and better rate of transfer [89]. Since the present work is about Radiation curable coatings, a brief introduction about Radiation curable coatings is in order.

### 1.8 Radiation Cure Coating Technology

Radiation curing is a technology which uses electromagnetic (mainly UV) or ionizing (mainly accelerated electrons) radiation to initiate a chain reaction in which mixtures of polyfunctional compounds are transformed into a cross-linked polymer network [90].

Radiation cure coatings cross-link by reactions initiated by radiation, rather than heat. Such coatings have the potential
advantage of being indefinitely stable when stored in the absence of radiation, following application, cross-linking occurs rapidly at ambient temperature on exposure to radiation. Rapid cure at ambient temperature is particularly significant for heat sensitive substrates, including paper, some plastics, and wood.

Two classes of radiation cure coatings

1. UV cure coatings, in which the initial step is excitation of a photoinitiator (or Photosensitizer) by absorption of photons of UV–visible electromagnetic radiation.

2. EB (electron beam) cure coatings, in which the initial step is ionization and excitation of the coating resins by high energy electrons. Cross-linking is initiated by reactive intermediates that are generated from the photoexcited Photoinitiator in UV curing and from excited and ionized resins in EB curing.

Infrared and microwave radiation are also used to cure coatings, but these systems are not included here, since the radiation is converted to heat, which initiates thermal curing. While the physical volume of radiation cure materials used in the United States is relatively small, perhaps 50,000 metric tons per year, their economic importance is disproportionate to their volume. They are essential to the production of computer chips, optical fibers, printed circuit boards, and printing plates and they are used in a variety of other economically important applications, including dental and medical applications.

Most types of electromagnetic radiation have been employed to cure or dry industrial coatings. The high frequency oscillations of an electric field are employed in radio-frequency drying and radiations varying in wavelength from long wave infrared to the ultra short wavelength β-radiation have been used.
Radio-Frequency

In radio-frequency drying, otherwise known as ‘dielectric heating’, two electrodes (rods or platens) of opposite polarity are arranged parallel to one another and to the conveyor, but at right angles to the flow of work pieces. The work pieces should be flat boards or sheets e.g. hardboard sheets, since the coating should pass within about 5 cm of the electrodes. The electrodes are connected to a high frequency generator so that the polarity of each electrode oscillates at about 20 MHz. The method is used for board and paper coatings based on water.

Infrared heating

In this method IR heat is emitted by the radiation source and directed at the coating, which uses the energy efficiently if it absorbs most of it.

IR sources are hot bodies which emit radiation over a broad spectrum of wavelengths, the peak wavelengths varying with the temperature of the hot body. White-hot sources at 1200°C-2200°C emit with peak wavelengths in the short wavelength region (1-2 µm), red-hot sources at 500°C-1200°C in the medium wave-length region (2-3.6 µm), and dull emitters 90°C-500°C in the long wave-length region (3.6-8 µm). Emitters may be heated by gas or electricity. Since the high temperature sources emit more energy, they seem the natural choice of all uses. Most polymers contain groups which absorb in the IR. These groups absorb strongly around 2.9-3.7 µm and above 5.5 µm. Thus medium and long wave length IR is better for heating clear coatings; because short wave heats the substrate.

Infrared heating is good for substrates such as chipboard, hardboard and plastic where substrate heating is to be avoided and where an article is in sheet form or of simple shape.
Electron-Beam Curing

High-energy electron beams (EB) can be used to polymerize acrylate coatings. In an electron accelerator, electrons are generated at a heated wire or rod within a vacuum-chamber and are directed through a thin titanium window as a narrow beam this scans rapidly backwards and forwards across a conveyor or as a curtain beam covering the full width of the conveyor. The electrons are highly energetic (Voltages of 150-600kV are used), penetrating the coating and creating free radicals on impact with molecules therein. Photo-initiators are not needed; otherwise coatings compositions are similar to UV curing. Thick coatings of any color can be cured, though the depth of penetration is directly related to voltage. At 150 kV penetration to a depth of 120 µm is possible in a coating of density 1.0. The very high capital cost of this process limits its use to high volume production outlets. EB curing is used on wood panels and doors, car fascia panels, car wheels and in certain reel to reel processes e.g. silicone release papers and magnetic tapes.

The principal advantages of EB curing are that no photoinitiator is needed and that pigments do not interfere with the curing. These advantages are often offset by the higher capital cost of the electron beam or curtain generating equipment, the need to use inert atmospheres, and the need for shielding to protect workers from the electron beam. The advantage of being able to cure pigmented systems is real but is of limited importance in coatings, since the flow problem is not alleviated by EB curing [91].

UV curable coating

UV-radiation curable coatings are reactive, low viscosity and usually solvent free, coating compositions that can be applied to a substrate by any of the conventional application methods such as spray, roller coating etc. and then polymerized or cured by exposure to a UV radiation. Each UV curable
formulation requires a certain threshold amount of UV energy to initiate the polymerization reaction. Nowadays various energy-sources for UV-cure are available in the market such as medium pressure mercury lamps, pulsed xenon lamps, electrode less vapor lamps or laser. The UV radiations are focused on the substrate by reflectors in the lamp [92].

UV curing has found an increasing number of industrial applications over the past decade due to its unique benefits, for example solvent-free formulations, high-cure speed and low-temperature processing. In addition to these benefits, two additional properties of UV-cured coatings are of increasing interest: scratch resistance and resistance against chemicals. One major field where UV curing has been unable to compete with existing coating technologies is the area of outdoor applications [93]. Coatings for outdoor use are subject to especially harsh weathering conditions, for example UV light, oxygen, moisture and air pollutants. The absorption of UV light by the polymer backbone or impurities leads to primary photochemical reactions resulting in a photo-oxidative degradation of the polymer [94].

1.8.1 Advantage, Disadvantage and Drawback of UV curable coating

The advantages and good performance characteristics of this technology are very obvious, the reasons for the limited penetration into large volume coating applications must lie in some substantial disadvantages. Major reasons are the limited availability of three-dimensional curing equipment, the very limited use of UV cured coatings in exterior applications, due to the existing paradigm that UV curing would not be possible in the presence of UV exterior durability stabilizers, and higher material costs compared to conventional coatings [95].
- **Economical advantages are:**
  - Energy saving (commonly rapid cure at room temperature)
  - High production speed
  - Small space requirements
  - Immediate post cure processing possible

- **Ecological advantages**
  - In general solvent free formulations (VOC reduction)
  - Possibility of easy recycling (waste reduction)
  - Energy saving

- **Performance advantages**
  - Low substrate heating
  - High product durability
  - Application versatility
  - High scratch resistance and chemical resistance
  - Exceptional abrasion, stain and solvent resistance
  - Superior toughness

- **Drawbacks**
  - Material costs are higher than, e.g., alkyds, polyesters or epoxies
  - 3D curing equipment development is in its infancy
  - UV curing in the presence of UV stabilizers decelerated
  - Oxygen inhibition at the surface (in many radical curing systems)
  - Sensitivity to moisture (cationic curing system)
  - Difficult through-cure of pigmented coatings (at thicknesses >5 µm)

- **Topics to eliminate weaknesses**
  - Improving adhesion to metal, plastics
  - Minimizing skin irritation caused by some reactive diluents
  - Reducing odor (of the formulations)
  - Reducing extractable of cured coatings
Improving photo initiators (cost, migration, volatility)
Direct food contact packaging approval
UV curing equipment requires high capital investment and Material costs.

1.8.2 Components of UV cure formulation

The UV curing technology is based on the photoinitiated rapid transformation of a reactive liquid formulation into a solid coating film. The initiating species may be a cation, an anion or a radical. The vast majority of UV curable coatings are based on radical producing photoinitiators. As with any coating formulation, variables are critical to the processing and performance characteristics. Radiation curing coatings cure through unsaturation sites on oligomer and reactive diluents. Practically, radiation curable formulations consist of the following:

- **Photoinitiator**: it absorb UV light, form free radicals and start the polymerization reaction, as well as cross linking reaction with oligomer

- **Reactive Monomers (Diluents)**: low molecular weight acrylates. This component contributes physical characteristics such as hardness, flexibility, elasticity, etc. to the coating.

- **Oligomers**: a base resin reactive material generally high molecular weight acrylates of urethanes, polyesters, silicones, etc responsible for physical properties of coating.

- **Additives**: control and impart color, adhesion, surface properties such as gloss, slip, marring, filling properties of porous substrates and so on.
**Photoinitiator**

Photoinitiators are molecules that absorb photons upon irradiation with light and form reactive species from their excited state, which initiate consecutive reactions. The initiating species may be radicals, cations or anions.

A photoinitiator for radical polymerization should exhibit properties, from which the following are the most important: [96]

- (a) High absorption at the exposure wavelength and high molar extinction coefficient
- (b) High quantum yield of formation of initiating species
- (c) High reactivity of the radical to the monomer

UV light alone will not usually have sufficient energy to interact with reactive groups in a molecule and generate free radicals. Hence a photoinitiator is used in the formulation which when exposed to UV light of specific wavelength, absorbs the UV light and produces free radical polymerization system or cations [97]. The choice of photo initiator depends on resin system used in the formulation, radiation source and the coating film thickness. To be effective the absorption band of a photo initiator should overlap the emission spectra of the light source [98]. There are two general classes of photo initiators: those that undergo direct photo fragmentation on exposure to UV light irradiation and produce active free radical and those that undergo electron transfer by proton transfer to generate free radicals. Benzophenone is one of the most commonly used photo initiator [99].

Photo fragmentation type photoinitiators are alkyl ethers of benzoin, benzildimethylketal, 2-benzyl-2-N,N-dimethylamino-1-(morpholinophenyl) butanone, 2, 2-diethoxy- acetophenoe [100] etc.

Electron transfer type photo initiators are benzophenone, diphenoxybenzophenone, anthraquinon derivatives, fluorenone derivatives, halogenated and amino functional benzophenone derivatives, thioxanthone derivatives benzil and camphorquinone [101] etc.
Reactive monomer (Reactive Diluents)

As reactive diluents monomers and oligomeric acrylates or vinyl ethers are used in order to adjust the application viscosity. Belong to the best diluents, their use is decreasing due to their high volatility, strong odour, skin irritation and flammability. Since their mono-functionality provides a higher molecular weight between crosslink's or lower crosslink density, which results in a better flexibility, monomers with lower volatility and odour.

The primary function of monomers, in a radiation cure coating formulation is to provide crossing sites and act as reactive diluents to reduce viscosity to facilitate application. They are also used to enhance a range of properties such as adhesion, reactivity, chemical resistance and scratch resistance [102] etc.

To understand more clearly a somewhat more extensive listing of monomers and their primary function in the formulation is presented in Table: 1[102].
# Table: - 1 Monomers Commonly Used in Radiation Cured Coating Formulation

<table>
<thead>
<tr>
<th>MONOMER</th>
<th>CHARACTERISTIC</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-(2-Ethoxyethoxy) ethylacrylate</td>
<td>Very low viscosity, Highest reactivity of monofunctional monomer, good adhesion to plastic substrate</td>
</tr>
<tr>
<td>Lauryl acrylate</td>
<td>Low polarity, hydrophobic monomer gives highly flexible coating</td>
</tr>
<tr>
<td>2-Phenoxy ethyl acrylate</td>
<td>Excellent reactive diluents, good adhesion on several substrates</td>
</tr>
<tr>
<td>Tetrahydrofurfuryl acrylate</td>
<td>Slightly swells plastic substrates and hence show good adhesion</td>
</tr>
<tr>
<td>Isoboronyl acrylate</td>
<td>Gives coating with high Tg, Flexible, Low Viscosity, has an odour problem</td>
</tr>
<tr>
<td>Polyethyleneglycol(600) diacrylate</td>
<td>Highly flexible used in water dillutable coating formulation.</td>
</tr>
<tr>
<td>Ethoxylated neopentylglycoldiacrylate</td>
<td>Low shrinkage, Low irritancy, Highly flexible coatings</td>
</tr>
<tr>
<td>Tetraethylene glycol diacrylate</td>
<td>High reactivity, Low viscosity, High irritancy</td>
</tr>
<tr>
<td>Tripropyleneglycoldiacrylate</td>
<td>General purpose reactive diluent</td>
</tr>
<tr>
<td>Dipropylene glycoldiacrylate</td>
<td>High reactivity, High irritancy, Low viscosity</td>
</tr>
<tr>
<td>Ethoxylated bisphenol A diacrylate</td>
<td>Low viscosity oligomer, Low irritancy, good hardness</td>
</tr>
<tr>
<td>Ethoxylate trimethylolpropanetriacrylate</td>
<td>Lowest viscosity among all triacrylates, High reactivity, Low irritancy</td>
</tr>
<tr>
<td>Propoxylated glyceryl triacrylate</td>
<td>Low surface tension, Low irritancy</td>
</tr>
<tr>
<td>Pentaerythretol triacrylate</td>
<td>High reactivity, excellent scratch resistance, High irritancy and skin sensitizer</td>
</tr>
<tr>
<td>Ethoxylated pentaerythrol tetraacrylate</td>
<td>Low viscosity, low irritancy, high reactivity</td>
</tr>
</tbody>
</table>
Because there are so many monomers available, it is important to keep in mind some general guidelines. There are four major parameters responsible for the monomer's characteristics: functionality, chemical backbone, chemical structure and molecular weight. These are defined and related coating performance in Table: 2[102].

**Table:- 2 Parameters of Monomer Chemistry**

<table>
<thead>
<tr>
<th>PARAMETER</th>
<th>CHARACTERISTIC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Functionality</td>
<td>Higher functionality higher reactivity, lower functionality lower viscosity lower shrinkage on polymerization</td>
</tr>
<tr>
<td>Chemical backbone</td>
<td>Hydrocarbon type Low surface tension, good flexibility, low yellowing and good weathering properties, excellent water resistance.</td>
</tr>
<tr>
<td>Chemical backbone</td>
<td>Ether type Have higher polarity then hydrocarbons, so better reactive diluents, more reactive then hydrocarbon but poor in non yellowing and weather resistance</td>
</tr>
<tr>
<td>Chemical backbone</td>
<td>Alkoxylated Low irritancy, higher polarity then hydrocarbons, higher reactivity despite higher molecular weight</td>
</tr>
<tr>
<td>Chemical backbone</td>
<td>Propoxylated Low surface tension, lower viscosity, good wetting and adhesion property to difficult substrates</td>
</tr>
<tr>
<td>Chemical structure</td>
<td>Can be cyclic, branched or linear mainly affect Tg in order of Cyclic &gt; Branched &gt; Linear</td>
</tr>
<tr>
<td>Molecular weight</td>
<td>Lower the molecular weights lower the viscosity and Higher reactivity and higher Tg. By changing structure and chemical backbone of the monomer the effect of molecular weight is also changed.</td>
</tr>
</tbody>
</table>
**Oligomers**

Oligomers are raw material that can be compared with the “Resin” in classical coating. The oligomer is or an even the most important component in the formulation by weight. Because of this, its choice has a major impact on the final performance of the system. UV curable oligomers carry unsaturation at the end or it may be an end group of chain. While selecting the oligomers following factors are considered, nature of substrate, desired reactivity of the Composition, Gloss, Adhesion, Chemical resistance, Scratch resistance, Non-yellowing and Abrasion resistance of the film. Often a combination of oligomers is used to achieve desired properties and selection is made based on the functionality, molecular weight and the chemical family of the oligomer. On the basis of chemical families UV curable oligomer are classified as:

- Polyester acrylate
- Polyether acrylate
- Acrylic and acrylate oligomers
- Miscellaneous acrylate oligomers
- Epoxy acrylate
- Urethane acrylate
- Silicon based oligomer

**Polyester acrylate**

The performance properties of polyesters are generally between urethane acrylate and epoxy acrylates. Polyester acrylate is varying in functionality, chemical backbone and molecular weight [103]. The influence of functionality is similar to urethane acrylate, higher the functionality higher the reactivity and lower the flexibility. Polyesters are comparatively darker in colour and some of the low molecular weight and highly reactive polyester acrylates may give skin irritation.
Polyether Acrylate

They generally have high flexibility and low viscosity but relatively poor water and chemical resistance [104]. Their low viscosity makes them suitable for use with very small quantity of monomers or reactive diluents. The water resistance and chemical resistance of polyether acrylates can be improved to certain extent by adding amine groups. The main application of these oligomers is in paper coatings and coatings for wood furniture.

Miscellaneous oligomer

These groups comprise of melamine acrylates, silicone acrylate, and radiation curable unsaturated polyester resins dissolved in styrene or acrylic monomers [105]. They are used for spatiality applications. Silicone acrylates provide excellent release properties, flexibility and heat and moisture resistance. Epoxy and Glycidyl ethers are used in cationic polymerization coating system.

Epoxy acrylate

Epoxy acrylates are the dominant oligomers used in radiation curable coatings [106]. They react through unsaturation and generally; they do not have any free epoxy group. Wide range of epoxy acrylates are available in the market and used in varieties of applications such as overprint varnishes for paper and paper board, wood coatings for furniture and flooring, and coatings for compact discs and optical fibers. Acrylated oil epoxy acrylate shows good pigment wetting properties [107] etc.

Urethane Acrylate

Urethane-acrylates as resins for UV-curable coatings have the best mechanical and chemical properties among all UV curable resins, but suffer from the high viscosities [108]. Urethane acrylate is produced by the reaction of a
polyisocyanate with a hydroxyl alkyl acrylate and other hydroxy compounds. Urethane-acrylate oligomers are commercially available with molecular weights ranging from 600 to 6000 g/mol and with functionalities ranging from 2 to 6. They provide either hard or flexible coatings depending on molecular weight, functionality and chemical structure [109].

♡ **Silicon based oligomer**

Silicon based oligomeric (Metha)acrylates are used in so-called hybrid polymers based on sol–gel reactions, where an inorganic network is obtained via the siloxane condensation and an organic network via the UV or thermal polymerization of reactive groups like acrylates or methacrylates. Such systems can also be classified as dual cure systems. Oligomers of this type can be synthesized by the reaction of functional (trialkoxy)siloxanes(–OH,–NH₂,epoxy) with functional (Metha) acrylates [110].

♡ **Additives:**

The wide ranges of additives are used in radiation curable coating formulations. These include pigments, antioxidants, defoamers, flow and wetting agents, slip aids, adhesion promoters, rheology modifiers, stabilizers and oxygen scavengers [111]. Oxygen scavengers and stabilizers are specific to radiation cure coatings. Oxygen inhibits the curing of acrylates by scavenging the free radicals or by quenching the photo initiator. This may lead to slower cure rate and may also deteriorate the performance properties of cured films. Other way to prevent oxygen inhibition is to provide an inert atmosphere [112]. Hindered amine light stabilizers are also used to provide good colour retention, weather ability and non-yellowing properties [113].
1.8.3 **Principle of UV curing Mechanism**

In UV curing, Photons electronically excite molecules in a coating, which then generate free radicals or cations. The energies of electron beams are far higher than the energies of photons in UV radiations. This can lead to the generation of X-rays that require electron beam generators to be shielded.

The UV curable coatings can be cured by two fundamental mechanisms

⇒ Free radical polymerization
⇒ Cationic polymerization

The free radical polymerization [114] is more common and the curing reaction takes place through unsaturation sites between oligomers and monomers. The basic reaction consists of a chain reaction with three distinct steps,

⇒ Initiation
⇒ Propagation
⇒ Termination

These can be illustrated as follows,

**Initiation**

\[ R^* + \text{(Oligomer)} \rightarrow R \text{(Oligomer)}^* \]

**Propagation**

\[ R \text{(Oligomer)}^* + M \rightarrow R \text{(Oligomer)} M^* \]

**Termination**

\[ \text{Couplin} \quad \begin{array}{c}
R - M - \text{(Oligomer)} \\
\text{Dis-proportionation}
\end{array} \\
\text{R} - M - \text{(Oligomer)} + \text{RM}^* \rightarrow \]

Where, \( R^* \) is free radical from photoinitiator

\( M \) is reactive diluent
In case of free radical cure, the photoinitiators on exposure to UV light decompose into free radical with unpaired electrons \((R^\cdot)\) and start a chain reaction with monomers (reactive diluents). For better photo initiation, the emission spectra of UV lamp should overlap with absorption spectra of UV-photoinitiator in a given UV curable formulation.

During the propagation step, the active sites react with more monomer molecules and the oligomers to buildup the desired network structure. This reaction stops by termination steps. Free radicals and oligomer polymer chains can interact with oxygen, which will also terminate the reaction leading to lower number of cross-links.

Termination may also occur by absorption of the growing chain without further reactions, such as the reactions for the free radical Photoinitiator.

Cationic polymerization [115] involves highly reactive positively charged polymeric centers. The cationic photoinitiators are activated by UV light to generate a super acid that initiate the polymerization process. Cationic polymerization is not affected by oxygen inhibition but affected by high ambient humidity, amines and other basic materials and pigments present in the formulation.

### 1.9 Scarcity of Raw Materials and Utilization of Renewable Resources

The use of renewable raw materials can significantly contribute to a sustainable development, [116] usually interpreted as “acting responsibly to meet the needs of the present without compromising the ability of future generations to meet their own needs” [117]. In ages of depleting fossil oil reserves and an increasing emission of green house gases it is obvious that the utilization of renewable raw materials wherever and whenever possible is one necessary step towards a sustainable development.
In particular, this can perennially provide a raw material basis for daily life products and avoid further contribution to greenhouse effects due to CO$_2$ emission minimization. Furthermore, the utilization of renewable raw materials, taking advantage of the synthetic potential of nature, can (in some cases) meet other principles of green chemistry, such as a built-in design for degradation or an expected lower toxicity of the resulting products [116].

Some of the most widely applied renewable raw materials in the chemical industry for non-fuel applications include plant oils, polysaccharides (mainly cellulose and starch), sugars, wood, and others. Products obtained from these renewables are as diverse as pharmaceuticals, coatings, packaging materials or fine chemicals, to only name a few. Moreover, recent discussions focus on the gasification of biomass (e.g. wood, wood wastes, corn stover, switch grass, agricultural waste, straw or others) with temperature, pressure and oxygen to obtain syngas [118] (mainly consisting of CO and H$_2$) and subsequent Fischer–Tropsch synthesis to obtain higher hydrocarbons. Alternatively, the obtained syngas can be converted to methanol and the thus obtained alcohol could contribute to the “methanol economy” as discussed by Nobel laureate George A. Olah and co-authors [119]. In both approaches biomass can be used as fuel but can also serve as renewable feedstock for the chemical industry.

Presently for the production of surface coatings and polymeric resin synthesis, industry relies heavily on synthetic polymeric resins produced from petrochemical resources. Petrochemicals are depleting resource and ever increasing demand for petroleum based products has adversely affected their cost and availability in recent times. Hence, an important goal in polymer science is to creating new pathways which allow a more extensive use of non-traditional vegetable oils [120] in synthesis of resins for coating and thus to overcome the limited availability of fossils products.(Petroleum Source)
Rising imports and drift from self sufficiency of edible oils has been a matter of acute concern. The supply of vegetable oils is increasing at the rate of 2.25% per annum at an optimistic level. Oil consumption being price sensitive is growing at the rate of 3.4%. If we forecast the demand and supply gap through 2010 AD at the same level of demand and supply growth rates, we may come to the conclusion that India would likely be deficit by around 28 lakh tones. At a very pessimistic level the deficit is expected to be around 40 lakh tones.

The non-food uses of edible oils constitute almost one third of the total oils and fats marketed in the world. The search and chase for oils and fats of non-food applications is becoming more and more relentless. The necessity of exploring newer sources of oils useful for industrial utilization has been drawing major concern and attention among the fraternity of scientists and technologists, not only in India but also in various parts of the world, who look to practical applications for oils that are not presently produced at commercial level. The main objective is to make available equal quantities of oils for human consumption.

The non-conventional or non-traditional oils derived from oil seeds of trees of forest origin are increasingly becoming favorite objectives of research, development and investigative activities.

Therefore, in line with need and requirements of oil and allied industries ‘untried’ non-traditional oils have been explored as sources for coating materials with the following objectives in mind:

⇒ Their low cost and local availability in abundance.
⇒ Their suitable inherent structure and composition favoring utilization for the purpose for which they are intended to be used.
⇒ Imparting possible value addition by exploiting them as objects for new avenues against their present low value applications.
Today plant oils are the most important renewable raw material for the chemical industry (e.g., in Germany 30% of the 2.7 million tons of renewable raw materials in 2005 were plant oils, in total approximately 10% of all resources were renewable) and are heavily used as raw materials for surfactants, cosmetic products, and lubricants. [121]. In addition, plant oils have been used for decades in paint formulations, as flooring materials and for coating and resin applications. The probably best known application example is Linoleum, which was already industrially produced in 1864 and developed by F. Walton in London, UK. [122-123]. Its main component is linseed oil and it provides a durable and environmentally friendly alternative.

Recently, the application of triglycerides in polymer science was reviewed with a focal point on cross-linked systems for coating and resin applications with the conclusion that triglycerides are expected to play a key role during the 21st century to synthesize polymers from renewable sources [124]. In addition to these cross-linked systems, linear, processible polymers can also be obtained from plant oils. Within this contribution, we want to provide an overview of the field by highlighting and discussing the current state-of-the-art as well as selected perspectives of the utilization of plant oil renewable resources in polymer science. We will thereby only consider triglycerides and their derivatives and will not discuss other chemicals that can be derived from plants, such as limonene, even if these chemicals have also been shown to have an application potential in polymer science.

The use of oils for the synthesis of value added polymeric resins provide an opportunity to utilize ecofriendly and sustainable resource, which ultimately benefits to the farmers and industry [125]. The oils are frequently used as a binder in paints and coatings [126] and also used for the synthesis of polymers such as alkyd [127], polyepoxides [128] and polyurethane [129].
The acute shortage coupled with tremendous increase in cost of various solvents used by surface coating industry and pollution becoming serious concern has resulted in intensive study of the radiation curable coating systems based on modified polyols which are derived from the non-traditional oil as a renewable resource.

The newer Modified polyols based on non-traditional oils (Dehydrated Castor oil, Jathropha oil and Sesame oil) were reacted with polyol (ethylene glycol, dipropylene glycol, glycerine and trimethylol propane) separately in presence of catalyst in different Oil: Polyol ratio and the various characteristics of novel modified polyols have also been studied in Chapter 2.

The Modified polyols prepared in chapter: 2 were reacted with polyisocyanates (isophorone diisocyanate & toluene diisocyanate) in stoichiometrically excess proportion to give isocyanate terminated prepolymer which are reacted with hydroxyl functional acrylic monomer to give urethane acrylate oligomer which generate the unsaturation (reactive site) at the polymer ends. The resultant oligomers containing unsaturation in the backbone due to oil portion and at the ends are characterized in Chapter 3. For its physico-chemical properties according to standard methods.

The UV curable coating formulations were derived from Urethane acrylate oligomers by blending with reactive diluents, photoinitiator and certain additives. These formulations were used as coating composition for Mild Steel Panels. Subsequently were cured by Ultra Violet radiation (Medium Pressure Mercury Lamp (200 Watt/inch) (280-360nm). These coated MS-panels were characterized by Mechanical Properties (Scratch resistance,
Impact resistance, Pencil Hardness, Chemical Properties (Acid Resistance & Alkali Resistance) are described in Chapter 4. The application, performance and related work concerning evaluation of film properties of each of these UV curable compositions are described in **Chapter 4**.

The UV curable coating on MS Panel was evaluated to effect of the cross link density, effect of the type and amount of modified polyols and effect of glass transition temperature were analysis by Dynamic mechanical properties of the UV cured films. And thermal behavior of UV cured films were analysis by Thermogravimetry analysis method in **Chapter 5**.
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