The title of the thesis suggests that, it is well and good to introduce Surface Coatings.

1.1 Introductory about Polymer

The word Polymer is commonly understood to mean a large molecule composed of repeating units, or mers (from the Greek word meros-part), connected by covalent bonds. 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 processbility. 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 versatile properties.

To the general public, consumer products like plastics, fibres, rubber, adhesives, paints and varnishes, and surface coating that all are based on polymers, and that often the same polymer is used for more than one application. Until the 1920s and 1930s the several industries that depend on polymeric materials grew rather independently of one another and were based on natural or modified natural materials. These industries can be identified in the broad sense as, Plastics, Rubber, Fibres, Coatings, and adhesives [1].

1.2 Surface Coatings

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.

Surface 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) [2].

1.3 Surface coatings based on renewable resources

The utilization of renewable raw materials, can meet principles of green chemistry, such as a built-in design for degradation or an expected lower toxicity of the resulting products [3].

Presently for the production of surface coatings and polymeric resin synthesis, industry 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 [4] in synthesis of resins for coating and thus to overcome the limited availability of fossils products (Petroleum Source).

The non-conventional or non-traditional oils derived from oil seeds of trees of forest origin are increasingly becoming favourite 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. [5]. 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. [6,7]. 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 [8]. In addition to these cross-linked systems, linear, processible polymers can also be obtained from plant oils.

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 [9]. The oils are frequently used as a binder in paints and coatings [10] and also used for the synthesis of polymers such as alkyd [11], polyepoxides [12] and polyurethane [13].

### 1.4 Synthetic resins for Surface Coating

A wide range of resins (also known as binders) are commercially available for surface coating industries now a days. However earlier chemist had to depend on natural product. Very first synthetic resin suitable for coating material and which is still in use today was phenolic resin, developed by Leo Backeland in earlier 1900s [14]. After this, there came the new resin called alkyd (Alkyd which is made from Alcohol + Acid) in 1923 which is used till date. After the industrial revolution, extensive research in the field of polymer chemistry resulted in the availability of numbers of different resins for suitable for surface coating.

Resin is the continuous phase in a paint films and is largely responsible for the protective and the general mechanical
properties of the films. A large numbers of resins with different chemical composition, solubility, nature of film formation, application characteristics and performance properties of their films are available for surface coating industries. It is generally found that the performance properties of a coating systems are best at higher molecular weight of resin, but it will be difficult to process high molecular weight during paint manufacturing or even at the time of paint application whereas at low molecular weight polymer will facilitate of processing during manufacturing of a coating system but at the loss of performance properties.

1.4.1 Alkyd Resins

Alkyd resins [15-17] form the largest group of the synthetic resins available to the paint industries and consumption is greater than that of the any other resin for wide variety of application due to their low cost and versatility [18-20]. Alkyds are formed by polycondensation of a dibasic acid and a fatty acid and in a strict manner alkyds can be defined as oil modified polyester resin [21]. Most commonly used dibasic acid in alkyd synthesis is phthalic anhydride while glycerol, pentaerythritol, trimethylol propane, glcols etc. are used as polyols and unsaturated fatty acid determines the drying characteristics of the alkyd resin. Saturated fatty acid yields non-drying or plasticizing resin while drying properties are conferred by unsaturated acids. Alkyds are compatible with most of the resins used in paint industries like rosin, epoxy, phenolic resin, amino resin, polyurethanes etc. so they can be easily modified to achieve specific properties [22].

Thus alkyd is the most popular in coating industries which find applications in printing inks, decorative as well as industrial coating and water soluble and electro deposition systems.
1.4.2 Phenol Formaldehyde Resins

The formation of resinous materials by the reaction of phenol and formaldehyde has been known for many years [23,24]. Phenolic resin finds application in protective coatings [25,26]. The reaction of phenol and formaldehyde alone is slow but in presence of acid or base different products: Novolacs (acid catalyst) and Resoles (base catalyst).
Novolacs are produced when molar ratio of formaldehyde to phenol is less than one and acid catalyst is used. Since they are insoluble in oils and hydrocarbon solvents, they are not used in surface coating industries but widely used in plastic industries as a thermoplastic material. Resoles are produced when the molar ratio of formaldehyde to phenol is greater than one and alkali catalyst like sodium hydroxide or lime is used. Resoles are thermo-setting and soluble in oils so they are used widely in varnish making but if they are further heated, they react to produce insoluble and infusible products and result in little application in surface coating industries.
It is found that resoles react with rosin to give products which could be esterified with polyhydric alcohols and the resulting resins are soluble in oils and these resins are known as rosin modified phenolics which find extensive application in decorative undercoats, primers, marine paints and in certain types of printings inks.

1.4.3 Polyester Resins

The product obtained from the condensation polymerization of a polyhydric alcohol and polyfunctional acid is known as polyester resin [27] and widely used in surface coating industries. The most commonly used polyfunctional acids are maleic anhydride, phthalic anhydride, adipic acid, sebasic acid etc. whereas ethylene glycol, propylene glycol, diethylene glycols are used as polyhydric alcohols. Depending upon the raw material used, Polyester can be either saturated polyester or unsaturated polyester. Both find extensive use in surface coatings [28-32]. Unsaturated polyester is cured by many different ways but the basic reaction of curing is free radical initiated addition reaction. Free radical initiation can be achieved either at elevated temperature by use of an electron beam or UV beam or certain metal ions as a catalyst by decomposition of peroxides. Unsaturated polyesters are generally dissolved in reactive solvent such as styrene to produce final resin and then curing is carried out. Saturated polyesters are such formulated so that they produce high hydroxyl contents as they are mainly used in production of polyurethanes. They also react with some amino resins.
1.4.4 Epoxy Resins

Epoxy resins [33] are the products of condensation of epichlorohydrin and diphenylol propane derivative is 2,2′-bis (4-hydroxyphenyl) propane also known as its trivial name Bisphenol-A. They are formed by condensing the reactants in presence of alkali and resulting product is known as diglycidyl ether of bisphenol-A (DGEBA).

Epoxy resins contain hydroxyl and epoxy groups. They can be cured by cold curing or stoving with a wide range of materials which includes amino and phenolic resin, amines, anhydrides, polyamides and isocynates etc.

The resulting films of epoxy resins are high abrasion resistant, resistant to chemical attack and show a high degree of adhesion to metal and other surfaces and thus used for industrial maintenance [34-36].
1.4.5 Amino Resins

These [37] are derived by reaction between formaldehyde and either urea or melamine to produce urea formaldehyde or melamine-formaldehyde respectively. They are not used on their own as a coating material as they give very brittle films but widely used in combination with alkyd resins mainly and also with other resins in co-cure systems.
Amino resins used in surface coating industries are generally modified with butanol. The modification of amino resins with butanol provides solubility in normal coating solvents and better compatibility with order resins in co-cure systems. Melamine-formaldehyde shows better properties than urea-formaldehyde in terms of color retention and exterior durability.

Amino resins and alkyd resin are widely used in staving finishes of all types. Amino resins are also used with many other resins like saturated polyester, epoxies, acrylics etc.

One of the resin say Polyurethane (PU) is received much attention industrially for the technological development of surface coating. Thus the detail review about polyurethane is given here.

1.4.6 Polyurethane Resins

The basis of formation of these polymers [38] is reaction of a diisocyanate with compounds containing an active hydrogen atom to produce urethane linkages. There are many compounds that contain active hydrogen like water, alcohol, amines hydroxyl group etc. Thus a polyurethane film may contain ester, ether, amide, urea or other groups. The hydroxyl component may be polymeric polyols like polyesters, polyether etc. Diisocyanates generally used are tolylene diisocyanates (TDI), isophorone diisocyanate (IPDI), hexamethylene diisocyanate (HMDI) etc. Polyurethanes can be either single pack or two pack system.

Polyurethane coating facilities low temperature curing. They provide wide range of flexibility and hardness. They also process good adhesion [39] and exhibit excellent weather resistance [40]. Other film properties are good resistance to moisture [41]. Chemical attack [39,42,43] and many solvents [39].
The versatility of this material can be demonstrated by looking at the applications in five major areas.

- **Automotive**

  The use of polyurethanes in this area is now well established to the benefit of both the manufacturer and the end consumer. Applications include seating, interior padding, such as steering wheels and dashboards, complete soft frontends, components for instrument assemblies and accessories such as mirror surrounds and spoilers. Door panels, parcel shelves, sun roofs, truck beds, headliners, components mounted in the engine space and even structural chassis components are now made from polyurethanes.

- **Furniture**

  The market for cushioning materials is mainly supplied by polyurethane flexible foam, which competes with rubber latex foam, cotton, horse hair, polyester fibre, metal springs, wood, expanded polystyrene, propylene and PVC. Polyurethanes are also ideal where strong, tough, but decorative integral-skinned flexible or rigid foam structures are needed.


- **Construction**

  When sandwiched between metal, paper, plastics or wood, polyurethane rigid foam plays an important role in the construction industry. Such composites can replace conventional structures of brick, concrete, wood or metal, particularly when these later materials are used in combination with other insulating materials such as polystyrene foam, glass fibre or mineral wool. Technically advanced wood composites can be produced for use in load-bearing applications and wood construction boards for flooring and roofing.

- **Thermal insulation**

  Rigid polyurethane foam offers unrivalled technical advantages in the thermal insulation of buildings, refrigerators and other domestic appliances and refrigerated transport. Competitive materials include cork, glass fibre, mineral wool, foamed expanded and extruded polystyrene and phenol formaldehyde.

- **Footwear**

  Soles, some synthetic uppers and high performance components for many types of footwear are produced from polyurethanes. These compete with traditional leather and rubber, PVC, thermoplastic rubber and EVA. Polyurethane adhesives are widely used in shoe manufacture and coatings are used to improve the appearance and wear resistance of shoe uppers made from both real and synthetic leather.
1.5 General remarks about polyurethane coatings

1.5.1 Urethane chemistry

The polyurethane chemistry is centred on the reactivity of isocyante groups with compounds carrying labile hydrogen atoms like hydroxyl or amine functions. The reactions of isocyantes can be divided into two categories: (1) reactions on reactive hydrogen to give addition products, for example the reaction between an isocyante and an alcohol that leads to the formation of the so-called urethane function, and (2) polymerization of isocyantes, i.e., self-addition reactions analog to the formation of dimers (uretdiones) or trimers (isocyanurates). An overview of basic isocyante reactions is given in Scheme 1.

Aromatic isocyanates are more reactive than aliphatic ones with decreasing reactivity from primary through secondary to tertiary isocyanate groups unless steric or catalytic influences result in reversal reactivity. Primary and secondary alcohols will react easily at 50-100 °C while tertiary alcohols and phenols will be slower. The reaction of primary and secondary aliphatic amines or primary aromatic amines with isocyanates at 0-25 °C will proceed rapidly. Isocyanates are also very sensitive to water to yield amine groups. Therefore, PU paint films possess a complex polymeric structure with urethane groups but also urea, biuret or allophanate coupling groups.

The formation of an organic coating usually involves a liquid phase and generally speaking, two drying mechanisms can be identified during the formation of the coating paint film: physical and chemical drying. Physical drying is the evaporation of the medium where the coating is dissolved or dispersed. Chemical drying is the formation of the film by means of chemical reaction. Usually both mechanisms overlap during the formation
of the film. However, a chemical drying which involves the polyaddition of high and/or small molecular weights starting products is the most interesting. Two important components can be identified: oligoisocyanates and co-reactants, usually polyols.

Scheme 1: Basic reactions of isocyanates with different reactants [44].
1.5.2 Isocyanates

The common PU coating formulations are based on few diisocyanates with aliphatic, cycloaliphatic or aromatic isocyanate groups. Toluene diisocyanate (TDI), hexamethylene diisocyanate (HDI), isophorone diisocyanate (IPDI), methylene diphenyl diisocyanate (MDI) and 1,1-methylenebis(4-isocyanato)cyclohexane (HMDI) are those of commercial importance (see Scheme 2). Except MDI and its derivatives, all monomeric diisocyanates are classified as highly toxic substances and cannot be used into PU formulations. They have to be converted into higher molar mass products or prepolymers, physiologically benign polyisocyanates. For this, urethane chemistry is used in the production of oligomeric polysiocyanates and permits to obtain oligoisocyanates with functionalities greater than two, necessary for spatial cross-linking. Derivatization from diisocyanates is usually performed by reaction with polyols forming isocyanate-functionalized urethanes, with water (biurets), with alcohol under catalytic influence (allophanates) or by catalytic dimerization or trimerization of diisocyanates (isocyanurates, uretdiones). The properties of the derivated prepolymers can vary as a function of molecular weight, type and functionality. For example, aromatic isocyanates are more reactive than aliphatic ones but their oxidative and ultraviolet stabilities are lower. They give more rigid PU but with limited suitability for exterior applications.
Polyols (coreactants) can be hydroxyl terminated polyester, polyether, polycarbonate or acrylic polymers (Scheme 3). The simplest are glycols like ethylene glycol, 1,4- butanediol, 1,6-hexanediol, and various grade of polyethylene glycols (PEG). The polyol component of the PU formulation is usually a mixture of those different polymers and includes sometimes castor oil. The choice of suitable polyols (architecture, molecular weight...) and oligoisocyanates allows us to control key characteristics of the paint film like solids content, gloss, drying, elasticity, hardness or resistance to chemicals. The ratio of isocyanate to hydroxyl functions (NCO:OH) plays therefore an important role in the

Scheme 2: Common diisocyanates used in polyurethane formulations.

1.5.3 Polyols

Polyols (coreactants) can be hydroxyl terminated polyester, polyether, polycarbonate or acrylic polymers (Scheme 3). The simplest are glycols like ethylene glycol, 1,4- butanediol, 1,6-hexanediol, and various grade of polyethylene glycols (PEG). The polyol component of the PU formulation is usually a mixture of those different polymers and includes sometimes castor oil. The choice of suitable polyols (architecture, molecular weight...) and oligoisocyanates allows us to control key characteristics of the paint film like solids content, gloss, drying, elasticity, hardness or resistance to chemicals. The ratio of isocyanate to hydroxyl functions (NCO:OH) plays therefore an important role in the
design of the coating film properties. The use of low molecular weight polyols, for instance, will result in stiff and hard PU because of the high concentration of urethane groups (hard segments). High molecular weight polyols, on the other hand, will produce more flexible films due to fewer urethane groups. Polyether polyols are obtained by a catalyzed addition of ethylene oxide or propylene oxide on small polyhydroxyl molecules such as ethylene glycol or trimethylolpropane. Polyester polyols are the result of the condensation of polyfunctional carboxylic acids (or anhydrides) with polyfunctional alcohols. Acrylic polyols are produced by free radical polymerization of 2-hydroxyethyl acrylate or methacrylate with other alkyl acrylates precursors.

![Chemical structures](image)

**Scheme 3: Typical polyols for PU coating formulations. (a) polyether, (b) polyester, and (c) acrylic polymer**

### 1.5.4 Catalysts

The rates of the different reactions occurring during hardening of the PU coating film vary and depend on the type of oligoisocyanates and polyols used but also on the temperature, on the humidity level, on the catalyst and its nature if one is
used. Most popular catalysts are tertiary amines[45] such as triethylamine (TEA), 1,4- diazabicyclo[2.2.2]octane (DABCO), organotin compounds[46] especially dibutyltin dilaurate (DBTDL) or stannous octoate (Scheme 4). The catalytic effect of organometallic compounds is due to their ability to form complexes with both isocyanates and hydroxyl groups [47, 48] (Scheme 5). Tertiary amines form a complex with isocyanate groups which further react with alcohol to form urethane product [49]. In the absence of a strong catalyst, allophanate and biuret formation does not take place for aliphatic isocyanates.

\[ \text{DABCO} \]

\[ \text{DBTDL} \]

**Scheme 4: Catalysts for 2K PUR formulation.**
Scheme 5: Catalytic reaction with (a) an organometallic compound and (b) a tertiary amine
1.6 Polyurethane Coatings

Organic coatings or paints on a substrate give aesthetic desired appearance such as gloss and colour, but also provide protection against environmental influences like mechanical or chemical damages, corrosion or radiation.

Discovered in 1937 by Otto Bayer [50], polyurethane (PU or PUR) raw materials (polyols and polyisocyanates) corresponded, in 2005, to 1 million tons of the world production of coatings in industrial applications which totalled 13 million tons. In the original equipment manufacturer (OEM) automotive coatings branch, the two-component PUR coating systems almost completely replaced the traditional alkyd resins especially in large vehicles production (planes, buses...) where baking of the coating is not always possible. Indeed, the quality of the PU films dried under mild conditions matches the performances of the baked coatings which make PU the ideal system for such application. PU provide demanded high gloss, colour retention, scratch, corrosion resistance and the presence of cross-links leads to tensile strength, good abrasion and mar resistance as well as acid, alkali and solvent resistance. However, the constant increase in demands for improved technical performances has motivated research in both industrial and academic organizations in building new PU materials with innovative properties. The wide applicability of PU coatings is due to their versatility in selection of monomeric materials. Recently, plastic coatings have also become a further domain for PU among wood furnishing, corrosion protection or textile coating. The chemistry involved in the synthesis of PU is centred on the isocyanate reactions.
➢ **Thermoplastic polyurethane coatings**

Thermoplastic PU coatings can be qualified as linear copolymers made up of “soft” and “hard” segments. Hard segments are composed of polar materials that can form hydrogen bonds and thus tend to aggregate into hard domains. Opposite to hard segments, soft segments constitute the amorphous domains. Such structure was first discovered in 1966 by Cooper et al. [51] where the hard segments play the role of physical cross-linker to inhibit the motion of soft segments [52]. Hard domains present high glass transition temperature ($T_g$) and provide high modulus, tensile strength and dimension stability while the soft domains with lower $T_g$ impart elastomeric properties to the material. Therefore, the length of the hard and soft segments, the sequence of length distribution, the chemical nature of the units composing the polymer and its molecular weight are as many parameters that can influence hydrogen bonding and the subsequent properties of the thermoplastic PU coating.

➢ **Thermoset polyurethane coatings**

In thermoset coatings, the presence of high chemical cross-linking points provides high tensile strength, abrasion resistance and chemical resistance which are lacking in thermoplastic PU coatings and are essential for most industrial coatings. Thermoset polyurethane coatings may contain polyether or polyester as soft segments with high functionality [53-57], isocyanates with the functionality greater than two [58, 59], NCO/OH ratios greater than one [55-57, 60]. The increase in functionality increases cross-linking concentration which promotes phase mixing [61-64]. And at the other hand, reduces the mobility of the hard segments [54, 65]. For high performance applications, a calculated amount of cross-linker is needed to adjust the properties of the PU
coating. At last, the material, obtained with cross-links deliberately added or created in-situ, exhibits both phase-separated and phase-mixed structures, depending on the concentration of cross-links.

- **Moisture cured polyurethane coatings**

  Moisture-cured PU coating contains isocyanate-terminated prepolymer and lead to highly cross-linked coatings. The diffusion and reaction of moisture produces primary amines that further react into urea groups. The drawback of such coating is their storage instability. Several side-products such as allophanate or isocyanurate are usually generated while stored. The introduction of those additional hard segments changes their volume fraction within the coating and ultimately alters adhesion or thermal properties [66-68]. However, moisture scavengers can be used to improve shelf life and pot stability. On the other hand, moisture-cured PU coatings produce with superior hardness, strength and stiffness. Since moisture is consumed, the risk of blisters or the formation of a weak boundary layer caused by water trapped under the coating is also greatly reduced.

1.7 Recent Scenario of Coating Technology

Now a day, the trend of using solvent-based paints has been greatly shifted to the more environmentally friendly alternatives due to the more severe 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. 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\[77\], 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 [69-75].

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 [76].

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 [77].

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 [77].

In modern age technology and globalization 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.

1.8 Environmental 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 severe damage to our environment and destroying the ecological balance [78]. Green chemistry initiatives must be commercially feasible and provide products or services that have enhanced performance qualities and/or cost savings in addition to reducing the environmental pollution [79].

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.

Reduction of volatile organic compounds (VOCs) has been a major focus of the Paint & Coatings industry as regulations have become increasingly inflexible. 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. Now a day, “The market for low VOC latexes is growing at an exponential pace, and is significantly larger than earlier” [80-81].

1.9 Alternative techniques 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 and demerits has been well described in the literatures [82, 83, 84].

Control of VOC by eco-friendly technologies [85]

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Type of Coatings</th>
<th>%Reduction of solvent</th>
<th>Remark</th>
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<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>High Cost, Limited for flat surfaces</td>
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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 [86]. Since the present work is about Radiation curable coatings, a brief introduction about Radiation curable coatings is in order.

1.10 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 [87].

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 cures 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) cures 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. 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.

**Figure 1**: Radiation cure technology.

- **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 emits radiation over a broad spectrum of wavelengths, the peak wavelengths varying with the temperature of the hot body.
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.

➢ **Radio- Frequency**

Radio-frequency drying is also 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.

➢ **Electron-Beam Curing**

High-energy electron beams (EB) can be used to polymerize acrylates coating. 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. The principal advantages of EB curing are that no photoinitiator is needed and that pigments do not interfere with the curing. 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.
1.11 Ultra Violate (UV) curing coating technology

UV-radiation curable coatings are reactive, having 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, rolling 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 [88].

UV curing has found an increasing number of industrial applications over the past decade due to their unique benefits, like solvent-free formulations, high-curing 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.

1.11.1 Components of the UV cured coatings

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 majority of UV curable coatings are based on radical producing photoinitiators. Radiation curing coatings cure through unsaturation sites on oligomer and reactive diluents. Practically, radiation curable formulations consist of the following:

- Oligomers
- Reactive monomers (Diluents)
- Photoinitiators
- Additives
1.11.2 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 [89]. 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 [90]. 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 Acrylate Oligomer**

  These groups comprise of melamine acrylates, silicone acrylate, and radiation curable unsaturated polyester resins dissolved in styrene or acrylic monomers [91]. 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 [92]. 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 [93] 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 [94]. 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 [95].

- **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 [96].

### 1.11.3 Reactive monomers (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 odors, 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 odors.

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 [97] etc.

To understand more clearly a somewhat more extensive listing of monomers and their primary function in the formulation is presented in Table: 1.1[97].

**Table 1.1 Monomers Commonly Used in Radiation Cured Coating Formulation**

<table>
<thead>
<tr>
<th>REACTIVE MONOMERS</th>
<th>CHARACTERISTICS</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>Ethoxylatedneopentylglycoldi acrylate</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>Tripropyleneglycol diacrylate</td>
<td>General purpose reactive dilluent (P.T.O)</td>
</tr>
</tbody>
</table>
Table 1.1 Continue....

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Dipropylene glycol diacrylate</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 trimethylolpropane triacrylate</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>Pentaerithretol triacrylate</td>
<td>High reactivity, excellent scratch resistance, High irritancy and skin sensitizer</td>
</tr>
<tr>
<td>Ethoxylated pentaerithretol tetraacrylate</td>
<td>Low viscosity, low irritancy, high reactivity</td>
</tr>
</tbody>
</table>

1.11.4 Photoinitiators

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: [98]

(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 [99]. The choice of photoinitiator 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 [100]. 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 [101].

Photo fragmentation type photoinitiators are:

- Alkyl ethers of benzoin
- Benzildimethylketal
- 2-benzyl-2-N,N-dimethylamino-1-(morpholinophenyl)butanone
- 2, 2-diethoxy- acetophenoe [102] etc.

Electron transfer type photo initiators are:

- Benzophenone
- Diphenoxybenzophenone
- Anthraquinon derivatives
- Fluorenone derivatives
- Halogenated and amino functional benzophenone derivatives
- Thioxanthone derivatives benzil and camphorquinone [103] etc.

1.11.5 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, rehology modifiers, stabilizers and oxygen scavengers [104]. 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 [105]. Hindered amine light stabilizers are also used to provide good colour retention, weather ability and non-yellowing properties [106].

1.12 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 bean generators to be shielded.

The UV curable coatings can be cured by two fundamental mechanisms

- Free radical polymerization
- Cationic polymerization

The free radical polymerization [107] 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**

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

**Propagation**

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

**Termination**

\[ \begin{align*}
\text{Couplin} & : R - M - (\text{Oligomer}) - M- R \\
\cdot(\text{Oligomer}) M - R + RM^\cdot & \rightarrow \\
\text{Dis-proportionation} & : RM(\text{Oligomer})H + RM(\text{Oligomer})
\end{align*} \]

Where, \( R^\cdot \) 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 [108] 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.

1.13 Advantages and Disadvantages of UV-curing coatings

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 [109].

- **Economical advantages are:**
  - Energy saving (commonly rapid cure at room temperature)
  - High production speed
  - Small space requirements
  - Immediate post cure processing possible
Ecological advantages are:
- In general solvent free formulations (VOC-reduction)
- Possibility of easy recycling (waste reduction)
- Energy saving

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

Drawbacks are:
- Material costs are higher than 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 photoinitiators (cost, migration, volatility)
- Direct food contact packaging approval
- UV curing equipment requires high capital investment and Material costs.

1.14 Research Question

Looking to the review of surface coating the renewable resources are much more utilized commercially. One of the resins, Alkyd resin is key component for any other oil paint formulation. One of the alkyd resin derived from the coconut oil received good attention for its properties like good film formation, excellent adhesion, easily compatible to the other resins, etc. The resin has good number of hydroxyl groups to have capacity to form polyurethane and that can be easily modified with different acrylates which have received much more attention for radiation curable surface coating technically. So the thought of the research is to explain the study on UV curable surface coating derived from coconut oil based alkyd resin.

1.15 Objectives

In view of above review and research question, the objective of work is: to study the UV-curable poly(urethane acrylate)s surface coating formulated from coconut oil based alkyd resin.
1.16 Present Work

The coconut oil modified hydroxyl terminated Alkyd resin was reacted with different diisocyanates (aliphatic and aromatic) in four different NCO/OH mole ratios (1.25, 1.50, 1.75, and 2.00). The resultant isocyanate terminated prepolymers were then reacted with hydroxyl functionalised acrylates (2-hydroxyethyl methacrylate) to yield urethane acrylate oligomers. The synthetic details and characterization details are presented in Chapter 2.

The above polyurethane acrylate oligomers blended with reactive monomers like methyl methacrylate, styrene, and butyl acrylates, Benzophenone act as photoinitiator, and two different reactive diluents like Ethylene glycol dimethacrylate and Trimethylol propane tri-methacrylate separately at the room temperature and another one is without reactive diluents. One more composition also prepared by blending of nano silica in two different weight percentages (5% and 10%) separately with the mixer of 1.50 NCO/OH mole ratio having polyurethane acrylates oligomers, monomers, reactive diluents, and photoinitiator at the room temperature. The resultant materials, designated as UV curable coating compositions are discussed in Chapter 3.

The UV curable coatings on MS Panels were evaluated for effect of cross-linking density, different reactive diluents, and nano silica on glass transition temperature, the storage and loss modulus were analysis by Dynamic mechanical properties of the UV cured films. The results of all these characterization are discussed in Chapter 4.

These all compositions are applied on MS (Mild Steel) panel and cured by Ultra Violute radiation [Medium Pressure Mercury Vapour Lamp (200 Watt/inch) (280-360nm)]. These all UV cured
panels were characterized by mechanical properties i.e. (Scratch hardness, Pencil hardness, Impact strength, Flexibility, and X-hatch adhesion tests), by Chemical resistance properties and by IR spectroscopy. And the details are described in Chapter 5.

The whole work represents in to the reaction scheme 1.1.
Scheme 1.1: UV-curable poly(urethane acrylate)s coatings.

\[
\begin{align*}
CH_2=CH₂ + OCN-R'-NCO & \rightarrow OCN-R'-NH-C-O-R\cdot-C\cdot-NH-R'-NCO \\
& \text{Polyurethane prepolymer} \\
& \text{Polyurethane acrylates oligomer} \\
& \text{UV-cured polyurethane acrylates coating}
\end{align*}
\]

Where \( R' \) =

1. TDI
2. IPDI
3. TIMDI
4. MDI

Other vinyl monomers used are,

- EA = ethyl acrylate
- BA = butyl acrylate

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REFERENCES


21. S Rengasamy, V Mannar; Prog.Org. Coat; 76(1); 78; (2012).


25. A. Krishnakar, Ind. Pat. IN 178,262, *(1997).*

26. Baitao Gan, Chain.Pat. CN 1,392,211, *(2003).*

27. S. Paul, *Surface Coating Science and Technology*, John Wiley & Sons p.70, *(1986).*


99. Rengasamy S, Mannar V; Prog.Org. Coat; 76(1); 78; (2012).


