CHAPTER 2

LITERATURE SURVEY

2.1. EPOXY RESIN

Epoxy resins are polyether resins containing more than one epoxy group capable of being converted into the thermoset form. These resins, on curing, do not create volatile products in spite of the presence of a volatile solvent. The epoxies may be named as oxides, such as ethylene oxides (epoxy ethane), or 1,2-epoxide. The epoxy group also known as oxirane contains an oxygen atom bonded with two carbon atoms, which in their turn are bound by separate bonds as in Figure 2.1.

![Figure 2.1: Functional oxirane ring in Diglycidal ether bisphenol A epoxy resin](image)

Ethylene oxide is a cyclic ether. The carbon atoms in oxirane are trigonally sp\(^2\) hybridized. One orbital from each carbon atom overlaps with the atomic orbitals of the oxygen atom to form a molecular orbital in the center of the ring. Atomic p orbitals, in the plane of the ring, overlap sideways. This explains the conjugative ability of epoxy ring, and results in a bent bond structure. Since the H-C-H bond is 116° 15’, the carbon will be sp\(^2\) hybridized. But it also shares the triangular ring, so it is possible to give the correct hybridization structure. Very often the epoxy groups deform to keep the area of the ring constant. The ring atoms do not lie along the lines of the greatest electron density of the atomic orbitals from the neighboring atoms. The smaller amount of overlapping is more than offset by a decrease in the strain energy.

Through the ring opening reaction, the active epoxide groups in the uncured epoxy can react with many curing agents or hardeners that contain hydroxyl, carboxyl, amine, and amino groups [2]. Epoxy resins are unique among all the thermoset resins due to several factors: minimum pressure is needed for fabrication of products normally used for thermosetting resins; cure shrinkage is
much lower and hence lower residual stress in the cured product than that encountered in the vinyl polymerisation is used to cure unsaturated polyester resins; use of a wide range of temperatures by judicious selection of curing agents enables good control over the degree of crosslinking; and availability of the resin ranging from low viscous liquid to tack-free solids. Epoxy resins can be produced to have excellent chemical resistance, excellent adhesion, good heat and electrical resistance, and good mechanical properties, such as high strength and toughness. These desirable properties result in epoxy resins having wide markets in industry, packaging, aerospace, construction, etc. They have found remarkable applications as bonding and adhesives, protective coatings, electrical laminates, apparel finishes, fiber-reinforced plastics, flooring and paving, and composite pipes.

The first production of epoxy resin occurred simultaneously in Europe and in the United States in the early 1940s. Today, a wide variety of epoxy resins of varying consistency are available. The three main manufacturers of epoxy resins are Shell Chemical Company, Dow Chemical Company and Ciba-Geigy Plastics Corporation. They produce most of the world’s epoxy resins. The United States and other industrialized countries such as Japan and those in Western Europe are the main producers and consumers of epoxy resins. Tanaka [3] gave a complete list of epoxides and discussed their properties and preparation. The simplest epoxy resin is prepared by the reaction of bisphenol A with epichlorohydrine (Figure 2.2). The value of ‘n’ varies from 0 to 25. This determines the end-use applications of the resin.

![Figure 2.2: Diglycidal ether bisphenol A epoxy resin](image)

Apart from innumerable patents [4-9], several books [10-12], review articles [13-17] and technical bulletins have been published on various aspects of epoxy resins. The chemistry of 1, 2 epoxides has been reviewed by numerous authors, including [18-21].
CHAPTER 2

2.2. EPOXY RESIN IN SURFACE COATING

In any civilized society, the varying forms of surface coatings are used in different areas of everyday life. They are used mainly for two purposes. The first one is the protection of materials from chemical and physical external attacks, and the other one is the decoration of objects for attractive appearance. The protective function includes resistance against weather damage, decay and corrosion, combined with improved superficial mechanical properties, such as greater impact and abrasion resistance. The decorative effect may be obtained through colour, gloss or texture or combinations of these properties.

The chemistry of epoxy resins at the present time is one of the most vigorously developing branches of polymer chemistry [22]. Epoxy resins, since they were introduced to the paint industry in the late 1940’s, have assumed an important place in the spectrum of materials available to the paint chemist. This is because the highly versatile nature of these resins allows the formulation of a wide variety of coating systems. These epoxy coatings range from industrial baking finishes that deliver the maximum performance in solvent and chemical resistance, to maintenance systems for corrosive environments and also include can linings, overprint varnishes, durable laminates, cold solders, lightweight foams, and potting compounds for all varieties of electrical and electronic apparatus and chemically resistant floor and wall coatings [23].

Epoxy polymers contain the epoxide group, also called the epoxy, oxirane or ethoxyline group, which is a three membered oxide ring. The resin can be regarded as compounds, which contain more than one epoxide group per molecule. They are polymerized through these epoxide groups or hydroxyl groups in the resin using a crosslinking agent to form a tough three dimensional network. The crosslinking element is also called curing agent or hardener [24]. In the presence of a suitable catalyst, epoxy resins can be made to link with each other or with other polymers or high molecular weight species. It is the capability of the epoxy resin to react with a variety of reactants that gives these resins great versatility in coating applications [25]. Depending upon the choice of curing agent, these versatile resins can be made to cure, or harden, either slowly (several hours) or very quickly (less than 1 min) at room temperature or at elevated temperatures. Versatility is also achieved in performance. Epoxy resins can be formulated to yield a variety of properties ranging from soft, flexible materials, to hard, tough, chemical resistant products. They
can be modified into low viscosity liquids for easy pouring or converted to solid compositions for laminating and molding applications.

Epoxy resins are comparatively expensive and are only used in coating formulation when their superior properties are required. These properties include outstanding water resistance, good chemical resistance, particularly in alkaline environments, outstanding adhesion to a variety of substrates, excellent toughness, hardness and flexibility. In addition, cured epoxy resins have good mechanical and electrical properties, superior dimensional stability, and good resistance to heat and chemical attack.

Epoxy resins vary in physical form as the molecular weight is increased. They range from a viscous liquid which is essentially a diepoxide and contains only a minor quantity of hydroxyl groups, to solid polyethers which are though epoxy terminated and contain principally hydroxyl groups as reaction sites.

Epoxy resins are characterized by their, Epoxide Equivalent Weight (E.E.W.) which is defined as the weight of resin containing one gram equivalent of epoxide. The E.E.W. is also referred to as, Weight per epoxide. (W.P.E.) or Epoxy molar mass. (E.M.M.). All three terms are interchangeable. Most epoxy resins used in surface coating systems have epoxide equivalent weights (E.E.W.) between 180 and 3200. Epoxy resins with E.E.W.’s of 180 - 475 are used mainly in ‘two-package’ low temperature cure systems. Epoxy resins with E.E.W.’s in the range 700 . 1000 are normally used in epoxy-ester systems. Epoxy resins with E.E.W.’s in the range of 1500 - 3200 are used in stoving finishes.

2.3. WATERBORNE EPOXY RESIN

Before about 1950, almost all coatings were solvent-borne. The introduction of latex paints for architectural uses was the first major step away from solvent-borne coatings. Since 1970, there has been a further trend away from solvent-borne coatings because of higher solvent prices and particularly the need to reduce VOC (volatile organic chemical) emissions to meet air quality standards. Because the solvents play a variety of important roles in resin manufacture, coating production, application, film formation and the properties of water are very different from those of organic solvents; this leads to distinct differences in characteristics of waterborne coatings as compared to solvent-borne coatings. Some of these differences are advantageous. For example, water presents no toxic hazard and it is odor-free. Water is not flammable; this reduces risks and
thus insurance costs. There are no emission or disposal problems directly attributable to the use of water. With some formulations cleanup of personnel and equipment is easy and the cost of waterborne coatings is usually low. On the other hand, there are some disadvantages to the use of water. For example, the heat capacity and heat of vaporization of water are high, resulting in high-energy requirements for evaporation. A further problem with waterborne coatings is that the water tends to increase corrosion of storage tanks, paint lines, ovens, and so forth. This requires that corrosion resistant equipment be used in waterborne coatings, increasing the capital cost.

In recent years with the environmental legislation in various countries becoming stricter, waterborne coating has become more important in the industrial coatings. Epoxy resin has outstanding chemical resistance and protective properties and because of this it is one of the most important materials in coating industry. Nowadays, the properties of water-based epoxy systems can generally match with their solvent-based counterparts in many important application fields including construction industry, building engineering, and corrosion protection [26]. In addition to waterborne coatings, waterborne epoxy systems have some main advantages and disadvantages. They are illustrated in Table 2.1 [27,28].

<table>
<thead>
<tr>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Excellent adhesion on difficult Substrates (e.g., Various metals, Wet concrete)</td>
<td>Shorter pot life</td>
</tr>
<tr>
<td>Excellent interlayer adhesion (Even on Old Coatings)</td>
<td>Gloss stability depending on formulation somewhat lower chemical Resistance, especially to organic acids</td>
</tr>
<tr>
<td>Coating of plastics possible</td>
<td>Poorer protective properties</td>
</tr>
</tbody>
</table>

2.4. EMULSION POLYMERIZATION

Emulsion polymerization, the heterogeneous reaction initiated by free radicals, is a method to prepare dispersions of monomers having a limited solubility in water. Specific architectures, e.g., Grafting, core-shell, can be obtained through emulsion polymerization. The emulsion polymer particles can be designed with respect to the end use. Functional groups are added so particles
are crosslinkable to enhance mechanical properties. Emulsion polymer having different functionality can be formulated for different applications. The glass transition temperature (Tg) can be modified in the acrylic latex. Minimum film forming temperature (MFFT) can be decreased below room temperature by virtue of monomers. Volatile organic content can be eliminated in emulsion polymerization. Thus, environmentally friendly coatings, adhesives, sealants and paints are prepared.

Emulsion polymerization is carried out by stabilizing components (polymers) by virtue of stabilizers into the emulsion. Emulsion refers to a two-phase system. One phase is continuous that is water and the other one is small droplets, which is the dispersed or discontinuous phase. Latex is the final product having fine and stabilized polymer particles by surfactants. Particle sizes are typically sub-micrometer (0.1-0.5 µm). Latexes have $10^{16}$ particles per 10 liter and very high surface area (2000 m$^2$/liter). Aqueous emulsion polymers are now the highest volume resins used in the coatings industry due to easy modification of resins for different applications [29].

Emulsion polymerization has some advantages over other techniques. Advantages can be summarized briefly as:

- Heat, evolved due to free radical polymerization, is easily absorbed by continuous phase.
- Polymer has a higher molecular weight than polymer obtained from bulk polymerization.
- Higher rate of polymerization is obtained in emulsion polymerization than corresponding bulk polymerization.
- Viscosity of dispersion is much lower than that of polymers in organic solvents. Therefore, processing of polymer is easy.
- Volatile organic content (VOC) is reduced, which allows one to decrease costs and environmental hazards.
- Very high conversion is obtained due to the low viscosity of medium.
2.4.1. Components in Emulsion Polymerization

The main components in emulsion polymerization are monomers, dispersing medium (water or solvent), emulsifying agent, and initiator. Monomers used in the industry can be divided into five main categories;

- Butadiene-styrene-acrylonitrile
- Vinyl chloride-vinyl acetate
- Vinylidene chloride
- Acrylate and Methacrylates
- Water-soluble monomers, e.g., (Meth) acrylic acid and acrylamide

The most suitable monomers for emulsion polymerization are the ones that have enough water solubility, but not too much. Monomers such as acrylic acid are used as adhesion promoters and crosslinking sites. Monomers with low glass transition temperature as a polymer form decrease minimum film-forming temperature (MFFT). Lower MFFT of formulation is especially preferred in highly pigmented resins. The dispersing medium of emulsion polymerization is generally water. Emulsifiers are used to stabilize polymer particles after and during polymerization. Emulsifiers (surfactants) also form a locus (swollen micelles with monomers) which is one of the possible nucleation sites. Surfactants are categorized into Ionic (cationic and anionic), nonionic and amphoteric (zwitterionic). Dispersion is stabilized by electrostatic repulsions in anionic surfactants. Nonionic surfactants provide steric stabilization.

Polymerization is initiated by free radicals. Initiators (water or oil soluble) are the source of free radicals. A good initiator should have high free radical efficiency at reasonable temperatures. Dissociation energy of an initiator lies between 100 and 170 KJ/mole. Water-soluble initiators, potassium or sodium persulfates, decompose at 50-90 °C. Oil soluble initiators are peroxides and azo compounds. Persulfate-bisulfite and persulfate-hydrosulfite are two common redox initiators employed at lower temperatures [30]. Water-reducible resins are prepared by reacting carboxylic acid-functionalized resins with amine compounds. After the reaction between carboxylic acids and amines, the stability of resin is increased due to electrostatic repulsions. However,
neutralizing agents have a dramatic effect on the viscosity of resin. Therefore, a neutralizing agent has to be selected carefully.

2.4.2. Emulsion Polymerization Stages

When water-insoluble monomers are employed, most of the monomers take place in micelles, if the surfactant concentration exceeds the critical micelle concentration (CMC). The surface area of micelles is higher than the surface area of droplets, which feeds micelles during polymerization. Therefore, polymerization mostly occurs in micelles due to high surface area and high solubility of monomers. The polymerization in droplets is insignificant (<0.1 wt%).

During the progress of emulsion polymerization, three distinct intervals are observed, according to Harkins [31]. Particle formation, initiation and nucleation take place in the interval I. At low monomer conversion (2–10%) when most of the monomer is located in relatively large (1–10 mm) droplets. Particle nucleation takes place when radicals formed in the aqueous phase grow via propagation and then enter into micelles or become large enough in the continuous phase to precipitate and form primary particles which may undergo limited flocculation until a stable particle population is obtained. Significant nucleation of particles from monomer droplets is discounted because of the small total surface area of the large droplets. Micelles are used up due to growth of particles. Figure 2.3 represents three intervals of a typical emulsion polymerization reaction.

![Figure 2.3: Emulsion polymerization intervals](image-url)
Interval I ends when the maximum number of particles is formed and the highest rate of polymerization is reached. In interval II, the number of particles remains constant while the volume of monomer droplets decreases. At this stage, surfactant concentration decreases below CMC. Monomer droplets supply monomer and surfactant to growing particles. At the beginning of interval III, polymer droplets completely disappear. The polymerization rate increases in interval I since new particles are formed. On the other hand, the rate is constant in interval II. The rate of polymerization decreases in interval III since monomer concentration is low.

2.4.3. Film Formation of Latex

Latexes can be used in two different forms in the industry: coagulated latex films or dispersed form. The film formation of dispersed form of latex follows three main steps [32]:
• Figure 2.4 shows, the schematic representation of the film formation mechanism of latex. It starts with the formation of a closed-packed layer when water evaporates. As water evaporates, particles approach each other. Thus, void-free arrays are formed.

• Deformation of particles from their spherical shapes into polyhedral shapes by virtue of capillary forces that are formed by the spaces between particles. Initial interfaces gradually vanish. To complete deformation of particles, a temperature higher than the minimum film formation temperature (MFFT) is required. Capillary forces have to overcome steric and electrical repulsions. Reduction in free energy of particles due to a decrease in the surface area of particles has to be taken into account in particle deformation. Broader particle distribution is also helpful to attain a rapid film formation.

Inter-diffusion of chains occurs across boundaries. Entanglements between polymer chains form a totally continuous film. The initial granular structure is lost. This step is crucial to strengthen the film. In order to have complete inter-diffusion, temperature has to be higher than the glass transition temperature (Tg) of polymers. If the Tg of polymer is greater than room temperature, baking is needed for a totally continuous film. Rate of inter-diffusion depends on the Tg of polymers, which is a function of free-volume and chain length of polymer chains. Less branched polymers diffuse more rapidly compared to more branched polymer chains. The distance of inter-diffusion is much smaller than the diameter of the particle. The full strength of the film is
CHAPTER 2

achieved if polymer chains near interfaces diffuse a distance equivalent to their root-mean squared radius of gyration ($R_g$) across inter-particle boundary [33].

![Diagram of latex film formation process](image)

**Figure 2.4:** Schematic representation of main steps in latex film formation

Film properties depend on the diffusion rate of chains and crosslinkers. If the reaction rate of crosslinking is higher than the diffusion rate, mainly intracellular cross linking occurs. This kind of pre-crosslinked latex particles results in films having brittle structure and insufficient cohesive strength, especially when the molecular weight between crosslinking points ($M_c$) is smaller than the molecular weight between two entanglements ($M_e$) [34]. Diffusion rates in negatively charged particles, e.g. neutralized acrylic acids, are slower due to electron repulsion [35].

The cohesive strength of the film depends on the friction between polymer chains and the concentration of chain segments cross boundaries during the application of tensile force. The chain breaking-up dominates over chain pullout in glassy polymers [36]. Adhesion strength of particles depends on the diffusion rate of polymer chains. When the crosslinkers are used, polymer diffusion is more complicated. A compromise between diffusion rate and the rate of crosslinking has to be obtained. Inter-diffusion slows down when the molecular weight of chains
and the rate of crosslinking are higher [37]. If the rate of crosslinking is smaller than the diffusion rate, particle interfaces have perfect coalescence. In this case, tear strength of the film is almost equal to cohesive strength. When the rate of crosslinking is almost the same as the diffusion rate, the boundary is crosslinked before reaching equilibrium. If the rate of crosslinking is very fast, no cross linking across boundaries is formed. The concentration of polymer segments passing through the interface is smaller [38].

2.5. SOLUBILITY PARAMETERS

Polymer chemistry related to coatings, hybrids, blends or composites are produced as multicomponent mixtures. Often these mixtures or formulations include polymers and low molecular weight components of high and low boiling points. Basic knowledge of the miscibility of the various components is required to meet environmental, shelf life, and product quality specifications. There have been numerous efforts to correlate polymer solubility. In this regard, Hildebrand and Hansen solubility parameters have played an important role in the development of stable commercial chemical formulations as well as for assessing phase segregation during product synthesis.

It can be argued that, first principles predictions of Hildebrand solubility parameters should be of great practical value in chemical formulation work. The usual approach has been to use the solubility parameter [39], in connection with some other parameter to account for hydrogen bonding.

The solubility behavior of an unknown substance often gives us a clue to its identification, and the change in solubility of a known material can provide essential information about its ageing characteristics. Our choice of solvent in a particular situation involves many factors, including evaporation rate, solution viscosity, or environmental and health concerns, and often the effectiveness of a solvent depends on its ability to adequately dissolve one material while leaving other materials unaffected. The selection of solvents or solvent blends to satisfy such criterion is a fine art, based on experience, trial and error, and intuition guided by such rules of thumb as "like dissolves like" and various definitions of solvent "strength". An organized system is often needed that can facilitate the accurate prediction of complex solubility behavior.
2.5.1. Solubility scales:

The various scales available to determine the solubility parameter are: Kauri-Butanol number, solubility grade, aromatic character, aniline cloud point, wax number, heptane number, and a Hildebrand solubility parameter. The Hildebrand solubility parameter is applicable for almost all systems and hence is the most widely used. It includes variations as the Hildebrand number, hydrogen bonding value, Hansen parameter, and fractional parameter, to name a few. Sometimes only numerical values for these terms are encountered, while at other times values are presented in the form of two or three dimensional graphs, and a triangular graph called a Teas graph. It is used because of its accuracy and clarity. Graphical plots of solvent-polymer interactions allow the fairly precise prediction of solubility behavior, enabling the control of numerous properties in practical applications that would be very difficult without such an organizing system. The systems mentioned here, are actually quite simple and can be used to advantage with little understanding of the chemical principles at work. It should be noted that, these systems relate to non-ionic liquid interactions that are extended to polymer interactions and water based systems.

From the heat of vaporization, in calories per cubic centimeter of liquid, we can derive the cohesive energy density (c) by the following expression

\[ C = \Delta H - RT/V_m \]

Where,

\( C \) = cohesive energy density

\( \Delta H \) = heat of vaporization

\( R \) = gas constant

\( T \) = temperature

\( V_m \) = molar volume

In other words, the cohesive energy density of a liquid is a numerical value, that indicates the energy of vaporization in calories per cubic centimeter, and is a direct reflection of the degree of
van der Waals forces holding the molecules of the liquid together. The Hildebrand solubility parameter can be used to indicate the solvency of solvent.

\[ \delta = (\Delta H - RT/Vm)^{1/2} \]

Solubility behavior can be adequately described using Hildebrand values, although in some cases differences in polar composition give unexpected results. Predictions become more consistent if the Hildebrand value is combined with a polar value, giving two parameters for each liquid. Even greater accuracy is possible if all three polar forces (hydrogen bonding, polar forces, and dispersion forces) are considered at the same time. This approach assigns three values to each liquid and predicts miscibility if all three values are similar.

As long as data are presented in the form of a single list, or even a two dimensional graph, it can be easily understood and applied. With the addition of a third term, however, problems arise in representing and using the information; the manipulation of three separate values presents certain inconveniences in practical application. It is for this reason that the development and the use of three component parameter systems has centered on solubility maps and models.

The most widely accepted three component systems to date is the three parameter system developed by Charles M. Hansen in 1967 [40]. Hansen parameters divide the total Hildebrand value into three parts: Dispersion force component, Hydrogen bonding component, and Polar component. This means that Hansen parameters are additive:

\[ \delta^2 = \delta^2_t + \delta^2_p + \delta^2_h \]

Where,

- \( \delta^2 \) = Total Hildebrand parameter
- \( \delta^2_t \) = dispersion component
- \( \delta^2_p \) = polar component
- \( \delta^2_h \) = hydrogen bonding component
The numerical values for the component parameters are determined in the following way: First, the dispersion force for a particular liquid is calculated using what is called the homomorph method. The homomorph of a polar molecule is the nonpolar molecule most closely resembling it in size and structure (n-butane is the homomorph of n-butyl alcohol). The Hildebrand value for the nonpolar homomorph (being due entirely to dispersion forces) is assigned to the polar molecule as its dispersion component value. This dispersion value (squared) is then subtracted from the Hildebrand value (squared) of the liquid, the remainder designated as a value representing the total polar interaction of the molecule $\xi_a$ (not to be confused with the polar component $\xi_p$). Through trial and error experimentation on numerous solvents and polymers, Hansen separated the polar value into polar and hydrogen bonding component parameters best reflecting empirical evidence.

2.5.2. Hansen model

Charles Hansen also used a three-dimensional model to plot polymer solubilities. He found that, by doubling the dispersion parameter axis, an approximately spherical volume of solubility would be formed for each polymer. This volume, being spherical, can be described in a simple way (Figure 2.5): the coordinates of the center of the solubility sphere are located by means of three component parameters ($\xi_d$, $\xi_p$, $\xi_h$), and the radius of the sphere is indicated, called the interaction radius ($R_o$).

On the other hand, a two-dimensional graph sacrifices some of that accuracy and conciseness in return for a system that clearly illustrates the relative positions of numerous materials, and can be easily used in practical applications. Predicting whether a polymer is soluble in a mixture of two solvents, for example, while possible mathematically, is accomplished on a graph by drawing a line between the two solvents and seeing whether that line passes through the area of solubility for the polymer.
Figure 2.5: Three-dimensional Hansen solubility sphere

The Hansen volume of solubility of a polymer is located within a 3-D model by giving the coordinates of the center of a solubility sphere (\( \xi_d, \xi_p, \xi_h \)) and its radius of interaction (\( R_o \)). Liquids whose parameters lie within the volume are active solvents for that polymer.

A polymer is probably soluble in a solvent (or solvent blend), if the Hansen parameters for the solvent lie within the solubility sphere of the polymer. In order to determine this (without building a model) it must be calculated whether the distance of the solvent from the center of the polymer solubility sphere is less than the radius of interaction for the polymer:

\[
R_{(S-P)} = \sqrt{4(\xi_d S - \xi_d P)^2 + (\xi_p S - \xi_p P)^2 + (\xi_h S - \xi_h P)^2}
\]

Where,

\( R_{(S-P)} \)= Distance between solvent and center of solubility sphere

\( \xi_d S \)= Hansen component parameter for solvent

\( \xi_d P \)= Hansen component parameter for polymer
The figure "4" in the first term of the equation, which doubles the dispersion component scale, is intended to create a spherical volume of solubility. If the distance $R_{(S-P)}$ is less than the radius of interaction for the polymer, the solvent would be expected to dissolve the polymer. This method avoids the reliance on graphic plots of solubility behavior and can be used effectively in a solely numerical form.

The ratio between $R_{(S-P)}$ and $R_o$ is called the relative energy difference (RED) and it is defined by equation.

$$\text{RED} = \frac{R_{(S-P)}}{R_o}$$

The RED, which is calculated from the difference in HSPs between the materials involved, is used as a single parameter to evaluate the compatibility of the two materials. The RED simplifies comparisons because it is 0 for a perfect match in the HSPs of the two materials. The RED is 1.0 at the limit of compatibility. RED less than 1.0 indicates compatibility, while progressively higher RED indicates progressively less compatibility [41].

Hansen C. M., reported the solubility parameters for different solvents in their research work. Some of the solvents with their Hansen parameters are reported in Table 2.2.
Table 2.2: Components of Hansen solubility parameters

<table>
<thead>
<tr>
<th>Solvent</th>
<th>δd</th>
<th>δp</th>
<th>δh</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>7.42</td>
<td>6.0</td>
<td>10.9</td>
</tr>
<tr>
<td>Ethanol</td>
<td>7.73</td>
<td>4.3</td>
<td>9.5</td>
</tr>
<tr>
<td>n-Propanol</td>
<td>7.75</td>
<td>3.3</td>
<td>8.5</td>
</tr>
<tr>
<td>n-Butanol</td>
<td>7.81</td>
<td>2.8</td>
<td>7.7</td>
</tr>
<tr>
<td>Ethylene glycol</td>
<td>8.25</td>
<td>5.4</td>
<td>12.7</td>
</tr>
<tr>
<td>1,3 butanediol</td>
<td>8.10</td>
<td>4.9</td>
<td>10.5</td>
</tr>
<tr>
<td>Ethylene glycol</td>
<td>8.25</td>
<td>5.4</td>
<td>12.7</td>
</tr>
<tr>
<td>Methyl cellosolve</td>
<td>7.90</td>
<td>4.5</td>
<td>8.0</td>
</tr>
<tr>
<td>Diethyl ether</td>
<td>7.05</td>
<td>1.4</td>
<td>2.5</td>
</tr>
<tr>
<td>Dimethyl sulfoxide</td>
<td>9.00</td>
<td>8.0</td>
<td>5.0</td>
</tr>
<tr>
<td>Acetone</td>
<td>7.58</td>
<td>5.1</td>
<td>3.4</td>
</tr>
<tr>
<td>Methyl ethyl ketone</td>
<td>7.77</td>
<td>4.4</td>
<td>2.5</td>
</tr>
<tr>
<td>Cyclohexanone</td>
<td>8.65</td>
<td>4.1</td>
<td>2.5</td>
</tr>
<tr>
<td>Tetrahydrofuran</td>
<td>8.22</td>
<td>2.8</td>
<td>3.9</td>
</tr>
<tr>
<td>Ethyl acetate</td>
<td>7.44</td>
<td>2.6</td>
<td>4.5</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>7.50</td>
<td>8.8</td>
<td>3.0</td>
</tr>
<tr>
<td>Chlo-ro-form</td>
<td>8.65</td>
<td>1.5</td>
<td>2.8</td>
</tr>
<tr>
<td>Chlo-ro-benzene</td>
<td>9.28</td>
<td>2.1</td>
<td>1.0</td>
</tr>
</tbody>
</table>
2.6. HYBRID POLYMER EMULSION

The term hybrid is basically defined as, the combination of more than two compounds to get the third one with properties different than participating compounds. Hybrid polymer can behave as homogeneous phase or can show phase separation within the particle. They are mainly classified as organic-inorganic and organic-organic hybrids based on the material used for modification of polymer. Simplest way to synthesized hybrid is blending of two participants from different families. However, there are some polymers which can’t be prepared by blending technique. In case of acrylic polymer hybrid can be synthesized by radical emulsion copolymerization. Hybrid of polymers from class like alkyd or epoxy resin obtained by polycondensation must be added to the solution before polymerization. Main problems for utilization of these materials for hybrid synthesis are the solubility in solvents. After emulsification solvent must evaporate which will contribute to volatile organic content (VOC). This process is not environment friendly compared to waterborne processes. Such hybrids are, blends of acrylic and polycondensate latexes [42]. Hybrid polymers are mainly applied in field of paint, coatings, adhesives, inks, paper coating industry.

Organic–inorganic hybrid materials have attracted increasing attention from researchers in both academic and industrial areas. These hybrids are combination of the thermally stable, robust inorganic components with flexible organic components possessing various functional groups within a single material. These hybrid materials exhibit novel and excellent properties (e.g. Mechanical, chemical, electrical, rheological, magnetic, optical, and catalytic) by varying the compositions, dimensions, and structures of the components. They have diverse applications in areas such as drug delivery system (DDS), diagnostics, coatings, catalysis, photonic crystals, coatings, adhesives, pharmaceutical, biomedical and cosmetic formulations [43-59]. Compared to organic-inorganic hybrids, the field of organic-organic hybrids is new to researchers,
introduced in literature from late 1990s. Organic-organic hybrid consists of more than two polymers in one particle and had superior performance than participating polymers. The polymers present in single particle may be covalently bonded or incompatible with each other. The organic-organic hybrids can be synthesized by dissolving polycondensates, such as polyester, PU, alkyd resin, or epoxy resin, in radically polymerizable monomer(s). Another route can be used in which the polycondensates, suitably modified, directly form latex in the presence of water, and this latex is used as a seed in an emulsion polymerization of suitable monomers. It is also possible to combine these two routes as some polycondensates can now be prepared via /mini-emulsion and then can be used as seeds for an emulsion polymerization.

Emulsion polymerization can be classified in many heterogeneous polymerization techniques [60], such as conventional emulsion polymerization [61,62], dispersion polymerization [63,64], microemulsion polymerization [65,66], Miniemulsion polymerization [67-72] etc., Have been used to synthesize hybrid polymers. Traditionally, emulsion polymerization has been the main process for making polymer latexes. But restrictions on this method for producing copolymers of monomers with different properties or polymer/monomer solutions lead to an extensive research on miniemulsion polymerization. Miniemulsion polymerization is an ideal method for producing hybrid sub-micron particles [73] because, in this method, each droplet behaves as an independent “nanoreactor” without being seriously disturbed by kinetic events in the aqueous phase [74-78]. The other polymerization technique proved to be used for synthesis of hybrid polymers. The conventional emulsion polymerization and miniemulsion polymerizations have many similarities, but particle nucleation and monomer transport are very different [79,80]. Conventional emulsion polymerization is started with a monomer emulsion comprised of relatively large (in the range of 5-10 microns) monomer droplets and significant free or micellar surfactant. Particle nucleation takes place early in the reaction via homogeneous (water phase) polymerization followed by precipitation, or via free radical entry into monomer-swollen micelles. Radicals can enter the monomer droplets, but this phenomenon is generally discounted because of the relatively small droplet surface area. Nucleation stops or slows significantly after the surface area of the particles becomes sufficient to adsorb all of the surfactant from the micelles. The major locus of polymerization, thereafter, is in the nucleated particles. The monomer must move from the monomer droplets to the reaction sites in the particles by diffusion. The droplets in a miniemulsion are typically in the range of 100-500 nm in diameter.
Smallest droplet size and consequent large droplet surface area results, in most of the surfactant being adsorbed to the droplets with little free surfactant available to form micelles or stabilize aqueous phase particle nucleation. Hence, there may be little or no micellar or homogeneous nucleation. The droplets becomes, the primary locus of particle nucleation. The term, miniemulsion is commonly used to denote systems in which particle nucleation is predominantly from small monomer droplets stabilized against Ostwald ripening [81]. In miniemulsion polymerization, being non-equilibrium systems cannot be formed spontaneously. Consequently, energy input, generally from mechanical devices or from the chemical potential of the components, is required. Miniemulsion formation by the so-called dispersion or high-energy emulsification methods are generally achieved using high shear stirring, high-pressure homogenizers and ultrasound generators [82]. It has been shown that, the apparatus supplying the available energy in the shortest time and having the most homogeneous flow produces the smallest sizes [83]. High-pressure homogenizers meet these requirements. Therefore, they are the most widely used emulsifying machines to prepare miniemulsions. Generally, the conventional high-pressure homogenizers work in a range of pressures between 50 and 100 MPa. Pressures as high as 350 MPa have been achieved in a recently developed instrument [84], although O/W miniemulsions with methylcellulose as emulsifier could only be stabilized by selecting a homogenization pressure lower than 150 MPa, because of the very strong elongational flow produced at higher pressures that promoted the irreversible degradation of long chain molecules. Ultrasonic emulsification is also very efficient in reducing droplet size but it is only appropriate for small batches. A recent study [85], on the preparation of polymerizable miniemulsions has shown that, the efficiency of the dispersion process is strongly dependent on the ultrasonication time at different amplitudes. With increasing hydrophobicity of monomer, longer the sonication time required. An effective surfactant/hydrophobe system is used to stabilize very small monomer droplets. The hydrophobe (also known as a cosurfactant) is a highly monomer-soluble, or high water-insoluble material added to increase diffusion stability of the emulsion. In their original discovery of miniemulsion polymerization, Ugelstad and coworkers [86] used either Cetyl alcohol (CA) or hexadecane (HD) [87] to retard monomer diffusion from submicron monomer droplets. Both CA and HD are volatile organic components and therefore not entirely desirable in the final product. Other researchers have used polymer, chain transfer agents, and comonomers as stabilizers. Because these hydrophobes cannot diffuse readily through the
aqueous phase (due to their extremely low water solubility), removing monomer from a small
monomer droplet will cause an increase in the concentration of the hydrophobe, with a resultant
increase in the free energy. Therefore, the use of a hydrophobe will significantly retard, or even
prevent Ostwald ripening (transfer of monomer from small droplets to large droplets to reduce
the total surface energy of the system), and thus keep the small droplets stable during
polymerization. For an ideal miniemulsion polymerization, there is no mass transport involved.
The large droplet surface area in miniemulsions (because of small droplet size), results in most of
the surfactant being adsorbed to the droplets with little free surfactant available to form micelles
or stabilize aqueous phase polymerization [88]. Therefore, the predominant nucleation
mechanism in miniemulsion polymerization is droplet nucleation. This is exactly what is desired
for the current application, since if there is significant micellar or homogeneous nucleation,
particles will be formed which contain little or no resin. The total water-insolubility of the resin
makes it difficult for the diffusion of the resin from the monomer droplets to the particles, that
are the loci of polymerization. In miniemulsion polymerization, polymerization takes place in the
(very small) droplets in the presence of the resin, and without the need for diffusion of the resin
across the aqueous phase. This advantage of miniemulsion technique makes it a valuable tool for
hybrid polymerization. The miniemulsion polymerization used for preparation of the hybrid
system is termed as hybrid miniemulsion polymerization by some researchers reported grafting
of polycondensate polymers. The hybrid synthesized with this technique is submicron dispersion
of one polymer into the other. Process of polymerization and chemical aspects of reaction varies
with choice of prepolymer and monomer used; for this reason, each system will be discussed
separately.
This review is divided in two parts: (i) Organic–inorganic hybrid (ii) Organic-organic hybrid.
These two groups are subdivided based on materials from which hybrid has been synthesized.
The synthesis of hybrids from both classes mainly with emulsion polymerization techniques has
been discussed. The hybrids from different classes of materials has been studied with different
approaches through emulsion polymerization for there prepration. The hybrids can be
synthesised with different morphological properties with emulsion polymerization using
different approaches. The following discussion disclose emulsion polymerization technique with
various materials for hybrid synthesis, on the basis of which experimental work was planed.
2.6.1. **Organic–inorganic hybrid:**

In the past decade, organic–inorganic hybrid materials have attracted a great deal of interest from material scientists, because of their extraordinary properties deriving from the synergism between each individual component. It has also been recognized that, organic-inorganic hybrids are very important materials in the field of photonic crystals, coatings, adhesives, pharmaceutical, biomedical and cosmetic formulations [89-97].

2.6.1.1. **Hybrid silicon**

Silica is the cheapest material available and its hybrids can be widely used in many industrial areas ranging from paints and drug delivery to composite materials. Research on organic–inorganic hybrid containing silica based materials was widely reported in the literature. The sol–gel process is a powerful method for preparing polymer/silica organic–inorganic hybrids [98-104] in which a nanometer size silica component is dispersed in a polymer matrix. The sol–gel process seems to be applicable to hybrid emulsion coatings, because the condensation of alkoxy silanes occurs under room temperature to produce crosslinking between the polymer particles and silica. In polymer/silica hybrid films it is expected that, the silica component will work as a hard segment in a soft polymer matrix to give rise to excellent performance coatings. Silane coupling agents are commonly used to achieve miscibility of the polymer and silica. Research disclosing hybrid of silica with PU are reported in the literature [105]. Waterborne poly (urethane acrylate) /silica hybrid was synthesized by Dongmei Wu et al [106], using sol-gel process. Epoxy-capped alkoxy silane coupling agent was used as the precursor, which provided two different reactive functionalities. The acrylate monomers were polymerized to obtain waterborne poly (urethane acrylate) dispersion. The organic solution was synthesized by coupling 3-glycidyloxypropyl trimethoxysilane with waterborne poly (urethane acrylate). The hybrid was obtained by the addition of inorganic solution of hydrolyzed tetraethoxysilane. The hybrid shows, improved properties due to network formation between organic and inorganic phases. The effect of tetraethoxysilane content on optical properties of hybrid has also been reported.

Hybrid polymer of silica with PU had improved thermal and performance properties [107]. Lei Wang et al reported, the synthesis of hybrid PU/silica emulsion synthesis followed by sol-gel to obtain the hybrid films [108]. Water based PU with highly crosslinked hybrid polymer networks
has been prepared. The tri-functional trimethylol propane gives three-dimensional chemical bondings between PU prepolymer, leading to the increasing crosslinking density of the polymer. With this understanding, the nanosilica particles (Aerosil 200) were introduced into PU and a silane coupling agent for the preparation of PU hybrid emulsions. It is an organofunctional alkoxy silane monomer, that can undergo both the sol-gel polymerization of the alkoxy groups and the reaction with NCO functionality in the polymer. With this monomer hybrid network containing covalent bonds between organic and inorganic phases can be achieved. Hydrolysis of ethoxy groups in hybrid emulsion gives silanol groups, which can subsequently condense with silanol groups on the nanosilica to form siloxane. Accordingly, crosslinking density of hybrid can be further improved which enhances the thermal stability of the hybrid.

Emulsion polymerization has been proved to be an effective technique for the synthesis of hybrid polymer/silica [109,110]. Hybrids of silica can be classified based on their morphology; the silica particle can act as a shell [111-122] as well as core [123-129]. Hybrid of silica with fluoropolymer was synthesized to obtain high performance coatings with improved hydrophobicity. Emulsion polymerization has been used as an effective route to obtain hybrid of low surface energy fluoropolymer with silica. Ailan Qu [130], prepared hybrid with snowman shape and sandwich shape morphology. The conventional emulsion polymerization was carried out using a combination of nonionic and anionic surfactants. Silica particles move towards the surface and increases micro roughness of the coating during film formation. Xinyan [131], synthesized the hybrid with core shell particle in which silica with fluorine act as a shell. Polyacrylate core emulsion was first synthesized using seed emulsion polymerization to which shell material was added to obtain hybrid. The presence of silica in hybrid shows, improved hydrophobicity while fluorine gives thermal stability due to their presence at film air interface.

Silica-coated hybrid in which silica acts as the shell can be prepared by the following three approaches:

a) Controlled precipitation of inorganic precursors onto the core particles, which are always assisted by a coupling agent or surface functionalization to favor the silica shell depositing on them [132]. For instance, Lu, et al. [133] in 2004 obtained polystyrene/silica (PS/SiO$_2$) colloids by selecting PS beads terminated in the $-$NH$_2$ group and controlling the hydrolysis and condensation of alkoxide precursor within the
pH value in the range of 10–11.6. Tissot et al [134] 2001, described, the synthesis of PS latex with a silica layer by using a silane coupling agent to improve the compatibility of organic core and inorganic shell materials. Graf, C. et al [135] 2003, prepared PS/SiO$_2$ core-shell particles by using poly (N-vinylpyrrolidone) (PVP) as a coupling agent. First, PVP was adsorbed onto PS colloids and then directly transferred into an ammonia/ethanol mixture, in which a sol-gel process of tetraethoxysilane (TEOS) was carried out.

b) Another approach is to deposit nanosilica particles on the core particles by heterocoagulation, which was typically reported by Amos [136-138] and Wu, [139,140] who used 4-vinylpyridine (4-VP) or 1-vinylimidazole (1-VID) as the auxiliary monomers, which copolymerized with methyl methacrylate (MMA) in the presence of aqueous silica sols, and prepared raspberry-like organic inorganic particles, with PMMA as core and nanosilica particles as shell, respectively.

c) The third technique, termed the layer-by-layer (LbL) self-assembly technique has become an attractive topic of investigation. Since, the pioneering works done by Caruso [45]. The basis of this process is the electrostatic association between alternately deposited, oppositely charged species. Multilayered silica particles as shells can be assembled onto submicrometer-sized PS latex by the sequential adsorption of nanosilica and poly (diallyldimethylammonium chloride) from aqueous solutions. Unfortunately, however, the first method based on classical Stober process usually needed surface treatment or functionalization; the latter two approaches, repeated centrifugation/redispersion cycles, made the whole process very energy consuming.

Synthesis of acrylic polymer/silica hybrid emulsions, such as acrylic latex particles containing silica nanoparticles prepared by emulsion or miniemulsion polymerization in the presence of colloidal silica are widely reported in the literature [141-144].
Tamai, T. [145], reported hybrid acrylic/silica prepared with a combination of emulsifier free emulsion polymerization and sol-gel processes. Synthesis was carried out in two steps, first acrylic emulsion was prepared using batch emulsion polymerization, and then to this emulsion TEOS was added at room temperature to obtain hybrid. The films prepared from this hybrid material were transparent and solvent resistant.
In another study of Tamai, T. [146] feasibility of the combination of a silane coupling agent containing acrylic polymer emulsion and a sol–gel process to obtain a solvent-resistant hybrid was reported.

Modification of an epoxy resin by polysiloxane is an effective way to enhance the hydrophobicity, toughness, and heat resistance for a highly crosslinked epoxy resin system. Various research works on polysiloxane modification of epoxy resin have been published [147,148].

Wan, T. [149], prepared and characterized homogeneous transparent epoxy-silica-acrylate coating by combination of radical solution copolymerization and sol-gel process. Methacryloxypropyl trimethoxysilane (KH570) capped acrylic resin was prepared by copolymerization with acrylate monomers. UV absorption of hybrid increases in agreement with TEOS content which decrease the transmittance. The presence of bridging between inorganic/organic phases, increase the compatibility between two phases and retard phase separation. AFM (Atomic Force Microscopy) analysis confirms, homogeneous dispersion of silica in the polymer matrix.

Chen, M. [150], prepared hybrid of silica with polystyrene in which silica was deposited on polystyrene colloid by application of static charge. The hybrid was prepared by deposition of negatively charged silica on the positively charged polystyrene colloids. For synthesis of positively charged polystyrene colloid surfactant free emulsion polymerization technique was used with cationic initiator. This polystyrene colloid was then hydrolyzed with TEOS in acidic aqueous ethanol media to obtain hybrid colloid. The stability of hybrid was strongly depends on the rate of hydrolysis and condensation of TEOS.

Donescu, D. [151], carries out miniemulsion polymerization of acrylate monomers in the presence of methyl triethoxysilane, vinyl triethoxysilane, teraethoxy orthosilicate and 3 (trimethoxysilyl) propyl methacrylate. Comonomers with functional groups which capable of participating in the sol-gel process was used for miniemulsion synthesis. The effect of the presence of the functional copolymers is the growth of the amount of bonded water of latex particles.

Hybrid of silica and polyester having anisotropic particles was synthesized using radiation miniemulsion polymerization [152]. The hybrid was synthesized with several morphologies mushroom-like, hollow egg-like and bowl-like structures. $\gamma$ radiations were used to carry out the
miniemulsion polymerization at lower temperature. Morphology of the hybrid was controlled by monomer/silica weight ratio. Synthesize morphologically-controllable anisotropic hybrid particles, because of the existence of different surface functionalities, could have a wide range of potential applications in bioscience and molecular recognition.

Hybrids based on polyhedral oligomeric silsesquioxane (POSS) are receiving increasing attention because of the unique features derived from their hybrid nanometer-scale architecture. All POSS derivatives consist of an inner chemically inert silica-like cage covalently bonded to an outer organic layer, since each Si atom in the siloxane framework bears either a hydrocarbon or a reactive functional organic substituent [153-158].

A hybrid polymer, poly (vinyl pyrrolidone co isobutylstyryl polyhedral oligomeric silsesquioxanes) (PVP-POSS) were synthesized by one step polymerization, by Hong Yao XU [159]. Acetoxy styrene and isobutylstyryl polyhedral oligosilsesquioxane were polymerized using free radical initiator. Comparative study, of hybrid with pure poly-(acetoxy styrene) (PAS) was carried out. Molecular weight analysis of hybrid shows that, POSS decreases the polymerization activity of the vinyl pyrrolidone possibly due to the steric bulkiness. It was suggested that, presence of POSS may reduce the extent of the PVP carbonyl dipole-dipole interaction, thus decreases its Tg when the POSS content is low. At a higher POSS content, the dipole interaction between the POSS siloxane and the PVP carbonyl, nanosize POSS and the aggregated POSS cluster physically dominates the local polymer chain motion, which is able to provide another contribution to the Tg increase in the hybrid polymer.

Valter Castelvetro [160], had also reported synthesis of hybrid nanocomposites of POSS-acrylic copolymer latexes. Emulsion and miniemulsion free radical polymerization routes are used to carry out the synthesis. POSS nanoparticles linked to the macromolecules causes an increase of both modulus and tensile strength of the hybrid sheets prepared by casting, as well as a net reduction of the elongation at break. However, the solvent resistance of the hybrid film was not satisfactory due to absence of crosslinking.

2.6.1.2. Hybrid clay

Clay is well known for its excellent thermal stability to provide a retarding effect on the thermal degradation of the organic component of the hybrid materials. Especially, at high temperature region. Polymer/clay hybrids have been more widely investigated, probably because the starting
clay materials are easily available and because their intercalation chemistry has been studied for a long time. Comparison between, commercial organically modified clays and MA16 modified montmorillonites showed that, the latter ones were more compatible with the monomer system. Hence, MA16 modified montmorillonites allows some platelets to be encapsulated in contrast with the armored structures found with the less compatible commercial ones. They also discussed by means of Monte Carlo simulations. The most probable location of the clay platelets depending on the interfacial tensions of the clay with the aqueous phase and the monomer phase, length/thickness ratio and the monomer droplet diameter [161,162].

Smectic clay montmorillonite (MMT) had an octahedral aluminum sheet sandwiched between tetrahedral silicate layers which can be used for hybrid synthesis. Lee Jang[163], reported the poly (methylmethacrylate) /clay hybrid by emulsion polymerization. Intercalation of Na+ exchanged montmorillonite with PMMA has been carried out using emulsion polymerization. Free radical emulsion polymerization of methyl methacrylate was carried out in the presence of montmorillonite. Thermal insulation of montmorillonite was not affected by polymer content; all hybrids with different polymer content had a same onset temperature of decomposition. Structural analysis confirms that, the polymer chains are confined between the interlayer of montmorillonite and segmental motion of polymer is restricted.

Lee and Jang [164] in their further study synthesized the hybrid of epoxy/clay by intercalation of resin in the montmorillonite by emulsion polymerization. The hybrid was obtained by heterogeneous reaction between bisphenol A and emulsified epoxy pre polymer in presence of Na+ montmorillonite in a colloidal system of urea. The thermal stability of this hybrid was also found to be unaffected by polymer content. Strong fixation of polymer to inorganic surface was proposed due to the ion-dipole force.

Shao, H. [165] synthesized hybrid of organophilic clay and epoxy. Organophilic clay was first grafted with the protonated 4, 4’-methylene diamine and then hybrid was prepared by acetone clay slurry method. Wide angle X-ray diffraction method and TEM analysis shows, increasing distance between clay platelets is caused by the penetration of a large amount of epoxy and curing agent within acetone. Protonated 4, 4’-methylene diamine was found to compatible with epoxy and clay. Higher thermal stability of hybrid was reported compared to pristine cured epoxy resin.
D. C. Lee [166] synthesized acrylonitrile–butadiene–styrene (ABS) terpolymer/clay hybrid. The terpolymer ABS, having very high resistance to impact, is considered to be ideal for the fabrication of a variety of molded parts and storage for housewares, panels for automotive instruments, an impact-resistant container, industrial applications. The mixture of acrylonitrile–styrene comonomer and 1, 3-polybutadiene rubber latex was copolymerized in the presence of a Na$^+$ type MMT using emulsion polymerization technique. The synthesis procedure involves dispersing of sonicated Na$^+$-MMT in a heterogeneous comonomers/aqueous system, followed by emulsion polymerization. Then hybrid was purified by, a successive hot-solvent extraction to remove styrene acrylonitrile (SAN) copolymers and ABS that simply adhered on the outer surfaces of clay. The hybrid synthesized exhibit nearly the same decomposition temperature in thermal study, regardless of their copolymer contents. One possible implication of this result is that, the thermal-insulation effect of MMT was not significantly affected by the copolymer quantity intercalated. Polymer/clay hybrids prepared via miniemulsion polymerization can be divided based on their structures: irregular dispersion of exfoliative clay in a polymer matrix, clay armored polymer particles and clay encapsulated inside the polymer particles. For example, Leiza and co-workers, successfully synthesized a series of high content waterborne acrylic copolymer/clay nanocomposites using commercial organically modified clays [167,168] or montmorillonite clays exchanged with MA16 [169].

The combination of clay was tried [170] with poly (vinyl chloride) (PVC) via an emulsion polymerization route. PVC is one of the most important commercial plastics owing to its wide applications and low cost. Despite its enormous technical and economic importance, PVC still possesses many problems, such as low thermal stability and brittleness. In order to overcome inherent disadvantages, the hybrid was prepared with MMT clay. The emulsion polymerization was carried out with radical initiator and sodium dodecyl sulfate emulsifier. Due to the very large surface area of inorganic material there is strong interfacial interaction between PVC and Clay, hybrid exhibit improved modulus and strength. Thermal degradation of hybrid was retarded due to the thermal insulation effect of MMT [171].

Coroea [172] synthesize hybrid materials based on polyvinyl acetate (PVAc) and clay by emulsion polymerization. There had reported another route for hybrid synthesis, in which free radical emulsion polymerization of vinyl acetate was carried out in presence of organically modified montmorillonite (OMMT). Incorporation of OMMT offers a good swelling capacity for
organic monomers. It was reported that, OMMT exfoliation is more related to more to PVAc than PVA.

The reversible addition fragmentation chain transfer (RAFT) miniemulsion polymerization can be used for Polymer/clay hybrid spheres synthesis. Use of the attached RAFT agents can minimize the exit problem of the radical group to the aqueous phase, that is, there is little radicals exiting into the aqueous phase. Moreover, there is no phase separation when the RAFT agents attach to clay platelets, due to little or no super swelling effect, thus close to monomodal polymer particle size distribution is achieved.

Hartmann and co-workers [173] first reported that, the RAFT grafted montmorillonite (MMT) clays of various loadings were dispersed in styrene monomer and the resulting mixtures emulsified and sonicated in the presence of hexadecane into miniemulsions. The stable miniemulsions were polymerized to yield encapsulated polystyrene/clay nanocomposites spheres. The nanocomposites were of partially exfoliated morphology at low clay loadings, and changed to intercalated morphology as the clay loading increased.

In comparison with the pure polymers, the hybrid polymer/clay exhibit many excellent properties such as reduced gas permeability, high fire resistance and lower flammability, enhanced mechanical and thermal properties [174-176]. Since, the Nylon 6/clay hybrid was prepared via in situ polymerization of ε-caprolactam by a Toyota research team [177], more and more polymer/clay hybrid have found their applications in cosmetics, pharmaceuticals, catalysis, optics, agriculture, coating and painting areas [178,179].

2.6.1.3. Hybrid titanium dioxide

Titanium dioxide (TiO₂) had many applications in field of coatings, plastics and papers, because it has a high refractive index. TiO₂ also possesses the ability to reflect and refract or scatter light more effectively than any other pigments. El-Asser and co-workers [180-183], prepared the dispersion of modified TiO₂ nanoparticles with polybutylene succinimide diethyltriamine in styrene prior to the miniemulsion process. The polymerization gives about 89 wt% of TiO₂ encapsulated in polystyrene. The average particle size and mean size increased from unencapsulated polystyrene particles to TiO₂ encapsulated polymer. This increase was attributed to the increasing numbers and sizes of the TiO₂ particles encapsulated in each particle [184].
Besides, the encapsulation of TiO₂ inside polymer particles, TiO₂ hybrid nanoparticles can also be coated on the surfaces of polymer particles via miniemulsion polymerization. Incorporation of acrylic acid as a commoner can increase the interaction between TiO₂ and polymer cores, and the addition of a hydrophobic agent effectively prevents monomer diffusing into the aqueous phase [185].

Dong-Guk Yu [186], synthesized inorganic/organic hybrid particles by polymerizing organic monomers in the interface of the titanium dioxide particles. The dispersion stability of TiO₂ in the monomer mixture is crucially dependent on the surface characteristics of TiO₂ in the dispersion state during polymerization. In this contribution, the usefulness of emulsion polymerization in producing carboxylic acid functional group titanium dioxide/poly (methyl methacrylate-co-n-butyl acrylate-co-methacrylic acid) [TiO₂/P(MMA-BA-MAA)] hybrid particles were estimated. Polymerization of monomers was carried out in the presence of TiO₂, ammonium persulfate was used as radical initiator. With an increasing percentage of monomer the encapsulated TiO₂ and density of hybrid goes on decreasing, which was attributed to escaping of inorganic particle into continuous phase. Hybrid samples show nearly the same spectral reflectance as bare TiO₂, which will not cause any problems in their ultimate uses.

Hybrid with multifunctionality was synthesized by Topfer and Schmidt-Naake [187] successfully. Two different inorganic materials were used as cores. Prepared polymer/SiO₂-TiO₂ hybrid spheres by embedding the 3-methacryloxypropyltrimethoxysilane- functioned SiO₂ and TiO₂ nanoparticles into the core, which was composed of styrene as the matrix monomer and 2-hydroxyethyl methacrylate, styrene sulfonic acid and aminoethyl methacrylate hydrochloride as co-monomers and copolymerized under miniemulsion conditions using SDS as a surfactant and radical initiator.

Polystyrene/TiO₂ hybrid nanocomposite spheres by using miniemulsion technique were synthesized by Chen et al [188]. Both organic monomer and inorganic precursor trapped in the miniemulsion droplets was synthesized. First, the O/W miniemulsion with oil composed of acetylacetone chelated tetra-n-butyl titanate (TBT) and styrene were prepared. The oil droplets were positively charged stabilized by adsorption of cationic surfactant on the surface. Then, the polymerization of styrene and the sol–gel reaction of TBT occurred inside the miniemulsion droplets, directly causing polystyrene/TiO₂ spheres. The hydrophilic TBT diffused to the O/W
interface during the polymerization of styrene. TiO$_2$ particles formed via hydrolysis and condensation of TBT were successfully adsorbed onto the surfaces of the polymer particles through electrostatic interaction. A hybrid of TiO$_2$ with PU using in situ RAFT emulsion polymerization has been reported in the literature [189-193].

Some researchers reported that incorporation of nano TiO$_2$ into organic material not only capable of photolytic degradation but also it can also retard photo aging by UV light absorption [194,195]. The tensile strength of hybrid was found to be greater than PU films due to strong adhesion between TiO$_2$ and the polymer matrix. Inorganic material gets wrapped in polymer by formation of a bridge or chelating coordination between titanium and end group of polymer chains.

TiO$_2$ nanoparticles hybrid can form colloidosomes, that may be used as the polymerization vessels [196]. A hybrid of TiO$_2$ with supracolloidal structures are permeable and govern controlled release [197, 198]. The presence of ZnO nanoparticles in the hybrid particles could enhance electron transfer between an electrode surface and electrolyte solution, which would be further used as the small scale of surface electrode in the application of chemical sensors. Moreover, the highly positive charge of composite particles could immobilize negatively charged biomolecules, such as DNA and enzyme, that have high potential in developing biosensors. Panya Sunintaboon [199], report the novel preparation of hybrid materials of ZnO nanoparticles dispersed in poly (methyl methacrylate) –Chitosan core–shell particles (PMMA–CS/ZnO), which was carried out via an emulsifier-free emulsion polymerization. Firstly, the ZnO nanoparticles, after a sol–gel process, were modified with 3-(trimethoxysilyl)propyl methacrylate (TPM), which could result in polymerizable and hydrophobic ZnO nanoparticles. Then, they were incorporated into the core–shell PMMA–Chitosan core–shell particles through the emulsifier-free emulsion polymerization.

TiO$_2$ has good photocatalytic properties even in its amorphous or rutile state, so they could be degraded under UV or sun irradiation. Therefore, how to exert both the photocatalytic and UV blocking or other properties of TiO$_2$ nanoparticles in polymers at the same time still needs to be investigated [200, 201].

Except, the above major hybrids which were frequently investigated, some other functional hybrids were occasionally explored based on type of inorganic particle, e.g., Zinc oxide-based
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CHAPTER 2

[202-210], alumina-based [211, 212], silver-based [213-220], gold-based [221], and so on. Junbai Li et al [222], briefly reviewed the “smart” polymer/gold hybrids from the preparation, property to potential applications. The covalent linkage methods based on the gold–sulfur interaction are described in details, as well as the novel developed physical approaches. Subsequently, the responsive properties were listed in the thermosensitive, pH-responsive and other stimuli-responsive parts. The smart polymer/gold hybrids have various potentials in nanocarriers for catalyst and biosensors due to the “live” outside polymer shells, and thereby the biocompatible hybrids are facing a significant challenge in biology and life science. Moreover, the smart gold hybrid nanocomposites as a fundamental building block to materials on the “bottom-up” process have obvious chances in the hierarchically structured 2D/3D nanomaterials. Nano zinc oxide is not only an important semiconductor material but, also serves widely as catalysts for chemical reactions, photocatalysts, photoelectric conversion, antibacterial and bactericide, UV-shielding material, and Photoluminescent materials [223-226]. The structures of zinc oxide-based hybrid prepared via miniemulsion polymerization can be divided into two types as that of the other organic-inorganic hybrid: (i) Zinc oxide coated hybrid polymer spheres [227] and (ii) Polymer encapsulated zinc oxide hybrid particles [228].

The idea of combining miniemulsion technique with in situ assembly in the fabrication of ZnO nanoparticle-coated polymer hybrid microspheres or polymer-encapsulated ZnO nanoparticle hybrid microspheres has been proposed by FengQi Liu et al. [229]. 3-(trimethoxysilyl) -propyl methacrylate (MPS) was used to modify the surface properties of ZnO nanoparticles and two types of core–shell hybrid microspheres, ZnO-coated PS and PS-encapsulated ZnO with different structural morphologies, were obtained. The two kinds of hybrid microspheres keep either the characteristics of Zn nanoparticles or the flexibility and easy processing of polymers. The aggregation phenomenon among ZnO nanoparticles was effectively avoided and the quenching function of water was suppressed by using MPS as a modified monomer.

Alumina nanoparticles have widely been used as fillers, in polymers for improvement of the mechanical, tribological, barrier, and conductive properties. Meanwhile, polymer/metallic hybrid has shown promise for use in a range of device applications and in medical diagnosis and treatment recent years [230-232].

The incorporation of silver or gold nanoparticles into polymer can be obtained successfully via miniemulsion polymerization. Commonly, the ligands such as thiols and amines were
incorporated during the metal nano particles synthesis or at the surface of preformed nano particles by ligand exchange. However, this method was limited to producing functioned nano structures containing only a single metal nano particles domain.

Berkel and Hawker [233], developed a new synthetic approach combining miniemulsion polymerization with thiol-ene chemistry to prepare composite nanoparticles consisting of multiple inorganic cores. First, metal nanoparticles were prepared and grafted with short, hydrophobic polymer chains, which render the nanoparticles dispersible in organic solvents. The grafted metal particles were then dispersed in a suitable monomer for miniemulsion polymerization, and the nano particle/monomer mixture was emulsified with an aqueous solution of a surfactant and a free radical initiator. Polymerization within the miniemulsion droplets yields composite nano structures comprising metal domains encapsulated with larger polymer nano particles.

A novel and highly versatile synthetic route was presented by Andreas T. et al [234], for the incorporation of inorganic materials within water-based miniemulsions with a complex and adjustable polymer composition. This involved cohomogenization of two inverse miniemulsions constituting precursors of the desired inorganic salt dispersed within a polymerizable continuous phase. This was followed by a transfer to a direct miniemulsion via addition to a surfactant solution with subsequent homogenization and radical polymerization. Zinc phosphate, calcium carbonate, and barium sulfate were all successfully incorporated in the polymer–epoxy matrix. Depending on the pigment type, strongly different results in terms of pigment distribution within the polymer-based particles were observed, indicating complex pigment–soft matter interactions. The choice of the system was based on a typical functional coating system, but was not limited to it. This system can be extended to incorporate various inorganic and further materials, as long as the starting materials are water-soluble or hydrophilic. The fact that, the process was also performed completely organic solvent free and that miniemulsions can be scaled-up using high-pressure homogenizers; this route opens vast opportunities for different industries.
2.7. **Organic-Organic hybrid**

These classes of hybrids composed of mainly two or more types of organic compounds. In these hybrid systems, the two polymers may form a homogeneous blend within the particle, or nanophase–microphase separation may occur. Organic-organic hybrid shows, significant improvement in properties compared to a physical blend of polymers. The improvement in properties is attributed to true homogeneity of polymers within the hybrid particle.

2.7.1. **Epoxy resins**

Epoxy resin is used for several decades and still well liked because of its number of excellent properties, such as high flexibility, good weather resistance, and excellent thermal stability. [235]. Thus, it is an excellent material for the modification in order to enhance its properties and overcome the disadvantages. Internal stress in epoxy resins is produced by the shrinkage occurring in the cooling process for curing at high temperature. This internal stress reduces adhesion strength and occasionally induces cracks in the casting material.

Yoshinobu N. et al [236], reported the hybrid of epoxy with poly (butyl acrylate) / poly (methyl methacrylate) core-shell particle by a simple blending process at room temperature. The core-shell particle was synthesized with seeded emulsion polymerization technique. First the poly butyl acrylate core particle was synthesized and used as seed for polymerization of methyl methacrylate monomer. The core-shell particle obtained contains, poly butyl acrylate rich core and poly methyl methacrylate shell. The hybrid was prepared by mixing core-shell particle with epoxy resin at room temperature. Modified epoxy was found to have lower internal stress without lowering of thermal stability.

Ruckenstein and Li [237], reported crosslinked hybrids of concentrated emulsions prepared from an epoxy resin poly (bisphenol A-coepichlorhydrin) (PBPAE), an amine-ended poly (butadiene-Co acrylonitrile) (PBAn), and a mixture of glycidylmethacrylate (GMA) with a commoner (styrene, MMA, BMA), which was partially polymerized. All three components were prepared as concentrated emulsions. In curing treatment crosslinking of the composites through surface reactions between the boundaries of the concentrated emulsion polyhedral particles takes place. The compatibilization of the different components is obtained through such heterogeneous
crosslinking process. Excellent mechanical properties result from this compatibilization process, depending on the nature of the system, molecular weight of the PBPAE, the extent of the swelling of the insoluble materials and duration of the post curing treatment.

In work described by Aerts et al. [238], core-shell particles of epoxy-MBS (MMA–butadiene–styrene) particles for the reinforcement of poly (amide-6) and other plastics were described. In this work, an MBS-GMA was prepared through the emulsion copolymerization of styrene, MMA and GMA from a seed of polybutadiene, resulting in core-shell morphology with epoxy functions at the particle surface. The extrusion process was used for blending dried emulsion with the thermoplastic materials. When the polymerization process is carried out using a semicontinuous addition profile so that, the epoxy groups are located at the core-shell particle surface. An excellent dispersion in the polyamide matrix has been observed, as compared with blends with MBS, even if a compatibilizer additive has been used.

De Wet-Roos et al. [239, 240], carried out a study of the emulsion polymerization of a mixture of an epoxy resin in the presence of acrylate. In this study, a solution of polyacrylate was first prepared and used as a stabilizer for the emulsion polymerization in the presence of dimethylaminoethanol for neutralization. A study was reported in two parts, it was observed that the amount and type of the neutralizing amine and the addition of salt were important factors for the control of the particle size and particle size distribution, while the type of initiator and the stirring speed were not particularly important. In a further study, the effect of various parameters was studied. It was found that, level of epoxy and also the amount of monomer are important for controlling the viscosity in the initial steps of the polymerization, impacting the nucleation and the growth of the particles. The molecular weight of the polyacrylate stabilizer was also a determinant factor.

H. Kawahara [241] and L. Wu, [242], reported emulsion polymerization of acrylate for modification of epoxy resin. H. Kawahara, study miniemulsion polymerization of acrylate monomers in the presence of epoxy using redox initiator. Dimethylaminoethylmethacrylate (DMAEMA) and MMA were added in order to improve functionality, batch and two stage polymerization were used. The comparison shows, emulsion synthesized using two stage polymerization had good polymerization stability, storage stability, and solvent resistance. L. Wu et al, polymerize acrylate monomer and epoxy pre emulsion to obtain seed latex. To this emulsion pre emulsified acrylate was added to get ungrafted epoxy, grafted epoxy and
polyacrylate. The epoxy resin was modified through hydrogen abstraction and grafting of the polymerizing monomer mixture. The synthesized epoxy acrylate emulsion was compared with epoxy acrylate blend. Analysis by FTIR showed that, the epoxy resin tends to migrate toward the mold side rather than toward the air side. Glass transition temperature and tensile strength of blend polymer seemed to be high due to higher crosslink density. Chengyin M. et al [243], modified epoxy with a 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS) using emulsion polymerization. An AMP was grafted to epoxy backbone using benzoyl peroxide (BPO) and the product obtained was dispersible in water needless of neutralization. The relationship of the acid value and intrinsic viscosity along with reaction time, the whole polymerization included chain extension and graft course. Structural analysis indicates, copolymer AMPS-EP contained hydrophilic sulfonic acid groups. Some epoxy groups remained and the others turned into sulfonic ester.

Corrosion resistant hybrid epoxy acrylate cured with melamine formaldehyde (MF) resin was reported by Zafar, S. et al. [244]. Epoxy acrylate copolymer was synthesized by grafting acrylic acid on epoxy backbone using ammonium persulfate initiator. Curing of this copolymer was performed using water soluble melamine formaldehyde resin. The reins were cured with varying ratios of MF resin (20 wt % MF, 30 wt % MF, and 40 wt % MF) and optimum composition were chosen for the preparation of corrosion-resistant coatings. They were found to cure at ambient temperature and form well adherent coatings on mild steel. The presence of MF in the resin increases the scratch hardness, impact resistance, alkali resistance, and thermal stability of the coatings.

2.7.2. Alkyd resin

Solvent based alkyd coatings commonly are used because of favorable properties such as gloss, hardness, durability, chemical resistance, and low cost. This is due to curing mechanism of oil based coatings in which the oils react with atmospheric oxygen to form very hard crosslinked materials. This mechanism is generally lacking in water-based coatings, which tend to be soft and pliable, due to the fact that the coatings are made soft to allow film formation, and since there is no curing chemistry available, remain soft on drying. Also the challenge with waterborne alkyds is encountered by the hydrophobicity of the materials, which requires organic solvents to reach application viscosities. Over the last 50 years, researchers have developed many ways to
modify alkyd resins as emission regulations have become tightened. The first modification made to alkyd resins was made with styrene over half a century ago [245]. Modified alkyds (Styrene-
modified alkyd, acrylated alkyds) [246-251], and the reaction of monoglycerides with carboxylic acid groups [252] have been used to enhance performance and reduce the need for VOCs. Although modified alkyds provided a way to reduce VOC content, the batch-to-batch reproducibility was poor due to the lack of control of side reactions. One of the first vinyl monomers to modify alkyds was styrene; however, the number of monomers that could be grafted onto alkyd was limited. Styrenated-alkyds afforded reduced viscosity systems and required less amount of solvent.

Wang et al. [253], investigated the miniemulsion technique for polymerizing acrylates in the presence of resins or grafting polyacrylates onto the unsaturated backbone of resins. This work demonstrated that, the miniemulsion technique provides an ability to form a water-based graft copolymer, that is unavailable with most other polymerization systems. Hybrid mini-emulsion polymerization have the advantages of water-based systems (low VOC, etc.), With the drying (air cure) properties of solvent-based systems. X. Q. Wu [249], extents the work of Wang et al and investigates the effects of the recipe and reaction temperature on the polymerization of acrylates in the presence of alkyd resin. The alkyd resin served as both reactant and co surfactant. Hybrid miniemulsion was carried out by dissolving alkyd resin in the mixture of methyl methacrylate and butyl acrylate. Free radical initiator was used to carry out polymerization, the hybrid system synthesized consist of grafted alkyd, ungrafted alkyd and poly acrylate. In this experiment, it was found that the emulsion was stable at high alkyd content this is very different from the conventional cosurfactants, such as long-chain alkane and alcohol.

The latexes obtained from the mini-emulsion polymerization of the alkyd–acrylate mixtures were uniform emulsions, and no coagulation occurred during polymerization. While, in case of macroemulsion polymerization with alkyd resulted in colloidal instability, probably due to the inability of the alkyd to reach the locus of polymerization. The polymerized hybrid latex formed good films with acceptable hardness.

Minari, R. J. [254], had performed molecular characterization of hybrid alkyd synthesized using miniemulsion technique. They had focused on study of gel fraction and developed a method based on conventional size exclusion chromatography (SEC) for measurement using dual [UV and differential refractive index (DR)] detection. This technique is not as rigorous as two-
dimensional chromatography; it allows one to obtain very useful information for either industry or academia in the development of hybrid acrylic/alkyd with just a routine measurement carried out in a conventional SEC.

The properties of alkyd used for preparation of hybrid emulsion depends on participating oils, Saravari O. [255], used to modify palm oil for synthesis of alkyd resin which was then reacted with acrylic copolymer to get water reducible resin. This resin shows, excellent coating properties like adhesion, impact, solvent and chemical resistance.

The miniemulsion polymerization technique has proven its ability to produce hybrid alkyd emulsions by incorporation of acrylate on a backbone of alkyd resin. The hybrid prepared by this method was found to be superior in properties compared to alkyd or acrylate emulsion. Recently, hybrid alkyd-acrylate emulsion has been reported with conventional free radical emulsion polymerization [256].

2.7.3. Polyester resin

In order, to gain the benefits of each system in hybrid polyester was first tried by blending with acrylic resin [257]. It was reported that, the polymer blends exhibited superior properties when compared to either system alone. Also suggested that, this combination of an acrylic system and polyester system could not be prepared without this blend process.

Tsavalas et al., In the year 2000 try to combine these two systems using miniemulsion technique [258]. The polymerization was carried out with acrylic monomers in the presence of a Bayer Roskydal TPLS2190 unsaturated polyester resin. Latexes were obtained in which the polyester resin was grafted to the acrylic polymer, forming a water-based crosslinkable coating. Both emulsions and latexes were shelf stable for over six months, shear stable, and resistant to at least one freeze/thaw cycle. Resin to monomer ratios were studied as high as 1:1 (wt: wt). In this work, the resin used after grafting function as hydrophobe stabilizing the small droplets against Ostwald ripening, virtually eliminating VOCs in the process and product.

Fatemeh J. et al [259], synthesize hybrid of polyester and polystyrene using miniemulsion polymerization. The polymerization was carried out eliminating the use of Cosurfactant and it was found that, the polyester chains and initiator lauroyl peroxide act as Cosurfactants to give the emulsion stability. The effect of various parameters (surfactant level, solid content, sonication time, polyester viscosity) on particle size was studied. The hybrid polyester with polyacrylate has
been also reported [260]. The polyester was synthesized in first step followed by polymerization of acrylate monomers which act as stabilizers. The styrene was added at the last stage and polymerized to reduce particle size of polyester. The hybrid miniemulsion obtained was stable without any flocculation.

2.7.4. Poly Urethane

Aqueous PU dispersions are widely used for applications such as, adhesives and coatings for various materials. For example, textiles, metals, plastics, and wood. PUs are known for their excellent mechanical properties, and depending on their structure, it is possible to have hard or tough systems with flexibility (even at low temperatures). This characteristic is attributed to the combination of hard and soft segments in the polymer and the hydrogen bonding between the urethane linkages of different chains. Latex of PU can be made by direct mini-emulsification of a monomer mixture of diisocyanate and diol in an aqueous surfactant solution, followed by heating [54]. Acrylic (AC) emulsions and PU aqueous dispersions have been used extensively in coatings applications. Both systems have some disadvantages, such as reduced film formation, lower chemical resistance, coarse mechanical properties of acrylic, a high cost, low pH stability, and limited outdoor durability of PU [261]. To improve the properties of an individual polymer system it is common to mix them. Better mechanical stability, solvent and chemical resistance, and toughness are obtained from the PU portion. Outdoor resistance, pigmentability, and lower cost are due to the AC component [262, 263]. Direct blending of AC emulsion and PU dispersion results in films with properties of lower quality to those predicted by the “rule of mixtures,” because of limited compatibility between PU and polyacrylate [264].

Kukanja, D. [265], reported a comparative study of hybrid PU emulsion and physical blends. MMA/BA/AA copolymer was synthesized with semi batch emulsion polymerization and mix with the same amount of PU dispersion to prepare blend. The hybrid was synthesized by polymerizing monomers in the presence of PU with varying ratios of AC to PU. Hybrid system represents, a single tag with improved mechanical strength compared to blend due to inter diffusion of polymer chains.

Lai, J. reported [266], PU hybrid synthesis by blending method. Self-emulsified PU dispersion and water-reducible acrylate copolymer emulsion, which are compatible with each other in the water phase. These two polymers are blended with an equal weight ratio and various dosages of
the latent curing agent. Latent curing agents (HDDA-AZ and TMPTA-AZ) are synthesized from the reaction of aziridine with hexandiol diacrylate (HDDA) and trimethylolpropane triacrylate (TMPTA). The thermal properties of the polymer hybrids are better than any of these original polymers. These improvements show the benefits of new polymer hybrid formation. This polymer hybridization process of self-emulsified PU and water-reducible acrylate copolymer via a postcuring reaction offers an alternative for polymer modification and cost effectiveness of more expensive aqueous-based PU.

The improved mechanical properties of hybrid PU synthesized with emulsion polymerization have been reported [267-270]. Comparative study of hybrid PU synthesized using conventional emulsion and miniemulsion polymerization technique is also present in the literature [271, 272]. Several approaches, to prepare waterborne PU-acrylic hybrid emulsions have been proposed. The most representative approach is to polymerize acrylic monomers in the presence of a PU dispersion, resulting in intimately mixed hybrid particles, that is, both polymers are present in a single latex particle and form core–shell structure. If one of both polymers is a crosslinked structure, the hybrid polymer will form latex interpenetrating polymer networks (IPN) [273]. When both polymers consist of a cross-linked network, an IPN is formed. These IPNs show, a lower amount of phase separation than physical blends. It could reveal “forced miscibility and coordinated effect”, leading to outstanding comprehensive properties. With regard to the IPN PU-acrylic (PUA) hybrid emulsions, most reports are as follows: (1) the PU prepolymer are prepared first by using general method, then the hybrid emulsions are synthesized by using the unsaturated carbon–carbon bond monomers, such as hydroxyethyl methacrylate, hydroxypropyl methacrylate, Maleic anhydride, fumaric acid, methacrylic anhydride as the bridge of the copolymerization reactions [274] (2) The hydrazine group is introduced into the shell part, reacts with the ketone group in diacetone acrylamide which is one of the core monomers, then another crosslinking reaction can take place between core and shell [275]. A more complicated approach involves preparing the new hybrid system by chain extension of the PU in the presence of AC, or the opposite, by emulsion polymerization of AC monomers in the presence of PU. To obtain a storage stable AC-PU dispersion, the emulsification and/or dispersing mechanism of both polymers must be compatible within the desired pH-range, usually of 7-8. The formation of hybrid systems, on the other hand, leads to a better mixing of components with the suitable combination of the properties of both polymers. The polymerization of acrylic monomers in the
presence of preformed PU chains with polymerizable terminal vinyl groups; leads to products known as PU/acrylate or acrylic/PU hybrids [276]. Several trials toward this objective have been described during recent decades, so there are examples of synthesis of polycrylic/PU hybrid emulsions and morphology characterizations of these systems in the existing literature [277-288]. Hirose and Kadowaki [289], found that, it is possible to develop waterborne emulsions with superior performances by producing emulsions with a multi-phase structure in each emulsion particle with different techniques, such as core-shell polymerization type [290, 291], seeded polymerization technology or the formation of interpenetrating network. Javier I. Amalvy [292], had reported the synthesis and the effect of thermal treatment on structural properties of hybrid PU with acrylic part core and PU shell. Polymerization of acrylate monomers was carried out in the presence of preformed PU, glass transition of the acrylic component was adjusted to obtain film-forming systems. Hegedus and Kloiber Hegedus [293, 294], observed that, the formation of the so-called “hybrid” particles is the result of in situ polymerization of the respective monomers and polymers. PU is formed by step growth polymerization, whereas polycrylic is formed by free radical chain-growth polymerization. Therefore AC and PU segments are not directly attached through primary bonds. The presence of hybrid particles is the result of numerous entanglements and secondary intermolecular bonding forces (hydrogen bonding, dipole-dipole interactions, etc.). The process appears to result in the IPN formation of AC and PU chains at the molecular level. The hybrid PU has been reported in the literature, with a combination of glycidyl methacrylate copolymer [295], grafted epoxy resin [296], oil modified PU [297-300]. Emulsion polymerization in combination with other techniques for hybrid synthesis are reported in literature. Guang-Hui, M., reported combination of Shirasu porous glass (SPG) membrane emulsification technique and a subsequent radical suspension polymerization process to obtain hybrid PU. The SPG membrane is a special porous glass membrane with very uniform pores. By applying adequate pressure, an oil phase containing a urethane prepolymer and vinyl monomer permeates through the uniform pores of the membrane into the aqueous phase to form uniform droplets. The stabilizer and surfactant dissolved in the aqueous phase are adsorbed on the surface of the droplets to stabilize them. Then, by elevating the temperature to above the decomposition temperature of the initiator, the suspension polymerization proceeds to form uniform particles. During the polymerization, the monodispersity is maintained, if the emulsification and
polymerization conditions are adequate. PU urea-vinyl polymer (PUU-VP) was synthesized with SPG emulsification technique with interpenetrating networks (IPN). Disadvantages of the system, like phase separation between PUU and VP, low monomer conversion and unstable dispersion can be overcome by addition of crosslinker and the trifunctional chain extender. Hybrid particle obtained has smooth surface and high destructive strength.

The properties of hybrid materials depend on, the molecular characteristics and morphology at both the micro and macro scales. Molecular parameters such as, the molecular weight (averages and distributions), molecular architecture (linear, branched, crosslinked, blocks or grafts, and tacticity), copolymer composition and distribution (block copolymers, grafting and branches), and residual concentrations of low-molecular-weight materials are significantly influenced and can be (to some extent) controlled in the polymerization process.

M. krajnc et al, study the hybrid PU with different molecular weight of PU and varying the ratio of acrylate monomers [301]. The hybrid emulsions were prepared by a semi batch process with particles of the higher average particle size than PU dispersions. PU part of the hybrid was preferentially located in the shell region of hybrid particle. Soft PUs were modified with acrylate; the hybrid obtained had improved performance properties.

Jiang, X. [302], synthesizes hybrid of PU and acrylate monomers with grafting mechanism, hydroxyl ethyl acrylate (HEA) was used as a coupling agent. They had reported, simple method to evaluate grafting percentage; influence of HEA on various parameters (reaction rate, grafting efficiency, performance properties of hybrid) has also been documented. Morphological study of hybrid shows that, with increasing ratio of AC/PU the particle size of hybrid particles increases. Also with increase in acrylic part, hybrid become more deficient in the carboxylic group which leads to coagulation of particles [303].

Although most of the polyuethane hybrids reported are in field of coatings, recently some paper reports application as pressure sensitive adhesive (PSAs) [304, 305]. PSAs are a distinct type of adhesive, that adheres instantly and firmly to a wide variety of surfaces under the application of only light pressure. This type of adhesive has been traditionally synthesized by solution polymerization, but growing environmental restrictions on volatile organic compound (VOC) emissions have forced the PSA industry to adopt the production of waterborne PSAs.

Lopez, A. [306], synthesized waterborne PU-acrylic hybrid particles, for application as PSAs with a one-step miniemulsion polymerization. Both polyaddition and free radical polymerization
occurred simultaneously in a semicontinuous process. Polyaddition between a reactive urethane prepolymer and a functionalized acrylic monomer allowed compatibilization between both polymers. The shear resistance was substantially raised, when PU was incorporated into the acrylic network, which indicates an increase in film cohesion. However, Further material development is required to achieve a balance between the elastic and viscous properties in order to achieve a higher shear holding power combined with an acceptable level of tack adhesion.

Apart from this major class, the development in organic-organic hybrid approaching towards new ecofrindlly materials for material synthesis. Chitosan is a polysaccharide polymer consisting of 2-amino-2-deoxy-D-glucopyranose as the repeating unit. They offer many advantages over other synthetic polymers because of its biocompatibility, biodegradability, antimicrobial and physiological functions, and non-toxicity. However, Chitosan is a brittle material because of its rigid crystalline structure, which limits its applications. Therefore, modification of Chitosan, by either derivatization, or hybridization with synthetic polymers, is an important field of study. Although Chitosan is not soluble in water, it can easily be dissolved in organic and inorganic acids. Thus, hybrid Chitosan/acrylic resin emulsions using emulsion polymerization with Chitosan dissolved in acrylic acid are reported in the literature [307-312].

Tamaki Wada [313], reported, instead of Chitosan, the quaternary ammonium derivative of Chitosan (q-Chitosan) as a coating binder to the acrylic resin emulsion. Although Chitosan has poor solubility in an acidic solution with a pH higher than 6.5, q-Chitosan is easily soluble in water. With respect to its antimicrobial activity, it is well known that, Chitosan contains many amino groups, which interact with the negatively charged residues of macromolecules at the cell surfaces of bacteria and subsequently inhibit the growth of bacteria. However, Chitosan exhibits its antimicrobial activity only in an acidic medium. In this study, two q-Chitosan composite acrylic resin emulsions were prepared by emulsion polymerization. One is a based on a conventional acrylic resin emulsion as discussed in our previous papers. Another acrylic resin emulsion with a keto group was obtained by copolymerization with diacetone acrylamide (DAAM). The acrylic resin emulsions with a keto group have been used in coatings to modify film properties due to a reaction between the carbonyl group in the resin and dihydrazide. q-Chitosan was fixed in polymer particles by incorporation of the keto group. In addition, the mechanical properties of the hybrid q-Chitosan/acrylic resin film was improved. This result can
be attributed to the fact that, q-Chitosan could Crosslink between acrylic resin particles during film formation.

It seems that, research in organic-organic hybrid field is not pronounced as compared to inorganic-organic hybrid. Reason for this situation is consideration of industrial scientists that, simple polymer blends which are easy to prepare and gives almost the same results as that of hybrids. From an industrial point of view miniemulsion polymerization is not a viable process for hybrid synthesis. There is no doubt that, hybrid system shows significant improvement in properties then physical blend.

Microwave assisted polymer synthesis is growing rapidly, due to their advantages over conventional heating methods. The microwave heating is a promising alternative for conventional heating due to its high heating rates and significant cost and energy savings [314-318]. With microwave assisted reaction immense increase in reaction speed and improved selectivity can be achieved. Microwave reactor has been introduced as a powerful tool for the synthesis of polymers. Consequently, more data will be very likely to be accumulated in the near future, probably focusing on more and more advanced techniques for hybrid synthesis [319]. The field of microwave heating is developing in order to fulfill the industrial applications [320]. This way, reaction times for future polymerizations can be decreased and the way to environmentally benign conditions will be paved.
2.8. Summary and outlook

Emulsion polymerization is a eco-frindly promising and effective strategy for the synthesis of hybrid materials for both classes. The structure, morphology, number and size of hybrids can be more easily controlled compared to other techniques, since, the nucleation and growth are primarily limited into the droplets of monomers. The morphology of hybrid particle can be core-shell, raspberry-like, or multi-core shell structure, thus people can obtain the hybrids as the expected structure and performance.

However, there are some limitations for synthesis of hybrids via miniemulsion polymerization:
(1) the inherent size range of monomer droplets in miniemulsion polymerization confines the encapsulation of large inorganic particles by polymer shell;
(2) The low solid content of hybrid via miniemulsion polymerization also influences its practical applications;
(3) In case of organic-inorganic hybrid the encapsulation efficiency of inorganic material in polymer needs to be enhanced,
(4) Due to difficulty to obtain mini-emulsification of polymer solutions in suitable monomers, mini-emulsion polymerization has been restricted mostly to the laboratory.

It is clear that, the usual method of ultrasonication cannot be applied on an industrial scale. All these deserve to be watched out for in the future research on emulsion polymerization for hybrids, from both scientific and practical viewpoints.