Polymeric Paints and Coatings

Zulfiqar Ahmad Rehan and Ahmad Usman

Abstract Polymeric coatings are applied on surfaces of metal, wood, plastics, and other materials to offer protection, decoration, and specific functionality. Polymeric coating technology is one of the old fields; still, it requires further maturity for perfection. The key trends in polymeric coatings include the production of environment friendly coatings, improving the functionality of existing coatings, and the development of smart coatings with multifunctional properties. Polymeric coatings with such properties are not feasible by conventional formulation and synthesis techniques. Therefore, modern technologies such as controllable graft polymerization, free-radical polymerization, and micro-emulsion polymerization are employed for these coatings. Moreover, the use of novel modified methods, functional pigments and the construction of nano- and micro-surfaces can produce polymeric coatings with multifunctional and enhanced properties. This chapter emphasizes traditional and advanced functional polymer-based coatings.

Keywords Polymeric coating · Latex paint · Elastomer · Water-borne coating · Varnish

1 Introduction

Paints and coatings are polymeric materials applied on numerous substrates through different techniques like dispersion, extrusion, and solution casting methods. The coatings based on polymers offer outstanding physical bonding while shielding from the environment. Polymer coatings are prepared by using components like resin, pigment, solvent, and additives. Each component imparts unique functionality in coatings, e.g., additives improve the functional properties, thinners or diluents lower the viscosity of the solution [1].

There is an ever-increasing demand for polymeric coatings especially in food industry, membranes, aerospace, marine, automobile, storage devices, oil and gas

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industry, etc. Some specific applications include protection against corrosion, breathable coatings in textile industry, encapsulation of electronic circuits, multilayer polymer coatings in infrastructure and transportation applications, and implantable devices [2].

1.1 Features of Polymeric Paint and Coating

In order to achieve gloss, reflectance, colour, flexibility, hardness/strength, and weathering resistance, different surfactants, pigments, fillers, binders and plasticizers are incorporated. The performance of polymer coatings significantly depends upon the interface [3]. When applied to a substrate, three distinct interfaces can be identified, namely interface with substrate at bottom, with air at top and with additives inside the coating. Further interfaces that correspondingly exhibit a role are gas–liquid, solid–liquid, solid–gas and interfaces (e.g., in drying paints) [4].

The chemistry of polymer is different as compared to that of the polymeric coatings. The fascinating characteristics of polymer coatings are that they are certainly spread and controlled. They can be employed as liquids in the case of paints. Certain additional characteristics such as drying, flexibility, and self-healing are the ones where molecular movement performs an essential role [5]. The innovative polymeric coatings are thermosetting in nature, regardless of the fact that majority of polymeric materials are thermoplastics [6].

2 Physically Drying Polymeric Coatings

Latex paint is a broad word for substantially drying paints based on aqueous polymer pigments, dispersions, and fillers. Latex paints are categorized by a Pigment Volume Concentration (PVC) content >40% and latex sheen enamels, through a PVC <40% (Table 1).

Table 1 Classification of latex paints and latex gloss enamels

Paint type	PVC [vol%]	Binder contents [wt%]
1. Latex gloss enamels		
Satin	30–40	38–33
Medium-gloss	15–30	65–38
Glossy	10–15	70–65
2. Latex paints (flat)		
Low-cost interior	80–90	10–5
Interior	60–80	21–10
Exterior (facades)	40–60	33–21

The adhesives are predominantly core dispersions (e.g., styrene-acrylate or pure acrylate). Acrylates of pure origin are ideal for weatherable shine enamels [7].

2.1 Latex Paints

Latex paints for indoor applications of low-cost have a Critical Pigment Volume Concentration (CPVC) $<$ PVC (rarely CPVC $\ll$ PVC) and have an advantage to permeable finishes including a (appropriately) elevated flow of water vapor.

In comparison with other latex paints, superior value latex paints for façade possessed higher value of CPVC than PVC and that leads to high quality non-permeable varnishes with minimal absorption of water. Moreover, latex paints include substantial volumes of (low-cost) additives like titanium dioxide as white pigment, making latex paint more appealing aesthetically. Pigments of inorganic nature having refractive index number of less than 1.7 are mostly known as extenders (fillers), and those including refractive index number more than 1.7 are believed to be pigments of white nature [8]. If the PVC is more than the CPVC, air/filler interfaces are produced in the coating [9]. Therefore, the extenders (fillers) may reduce the strength of hiding over CPVC ("dry-hiding" effect).

2.1.1 Latex Gloss Coating

Latex glossy enamels produce coatings/paints through comparatively superior gloss in comparison to latex paints. Glossy latex enamels produce sheen by three factors:

- The pigment to volume concentration would remain as minimal as possible, and it should be less than 20% for glossy gloss latex enamels.
- The polymer dispersion usually acrylate (pure) must have particle size of 0.1 μm or less.
- Suitable modifier incorporation in latex paints for improved rheological behavior.

Additionally, polymer dispersants are incorporated after grinding the pigment during the production of simple latex and glossy paints in order to avoid agglomeration during pigmentation [10].

2.2 2 K Water-Borne Polyurethanes (PU) Coatings

Poly-isocyanates may possibly react with water in case of water-borne two-components PU paints. Primarily, an unbalanced intermediate mixture, an alternate carbaminic acid, has being produced. Therefore, instantly converted to CO_2 (carbon dioxide) as well as amine (primary). This primary amine develop urea linkages

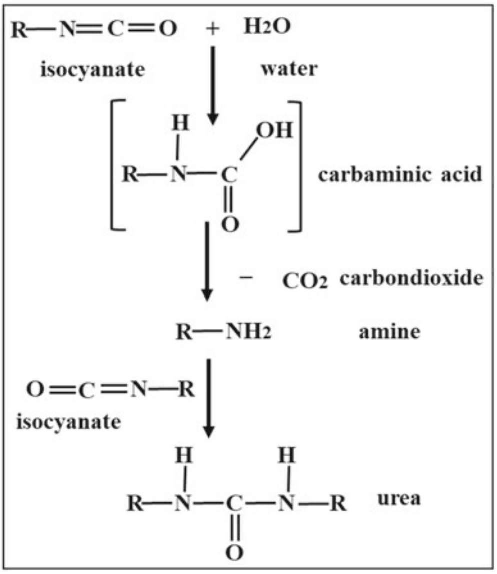


Fig. 1 Reaction of isocyanates with water

through instinctively combination with other isocyanate groups [11]. This reaction kinetics are shown in Fig. 1.

The reaction preferably takes place at the amine groups or hydroxyl groups of resins. The research display that there are likely chances of any reaction happened with the carboxylic groups of water-diluent resins. In order to get the reaction kinetics of these compounds, the two components be dissolved effectively and has significant impact [12]. Usually by the addition of polyisocyanate as hardener to water-borne systems, coarse emulsions are produced. The ingredients are grinded to produce small particles by diffusion methods. That's why, the possibility of an effective crosslinking reaction between the resins and poly-isocyanates exists.

2.2.1 Reaction Kinetics for Poly-isocyanates in Water-Borne Coatings/Paints

The transfer method of hydroxyl-based resins in 2-component PU (polyurethane) processes should never include hydroxyl groups and solvents [13]. Triethyl amines (e.g., Tertiary amine) are ideal that never encompass further active groups, e.g., NH groups or hydroxyl groups, for neutralization. Though the effective homogenization based on the selection of resins and hardeners, its intended use and reactions among isocyanate and water should be taken into account.

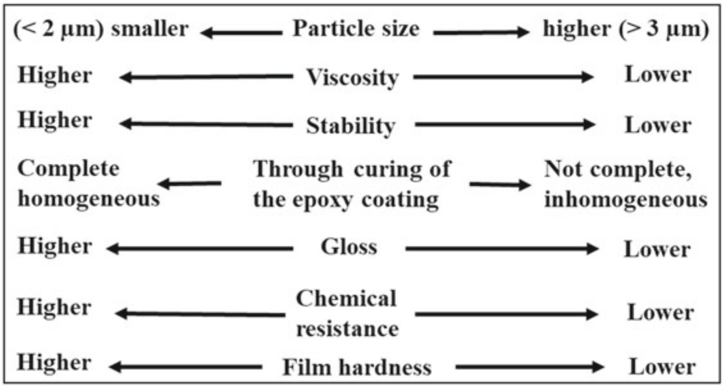
2.2.2 Application Area of 2 K-Component Water-Based Polyurethane Paints

Similar solvent-borne systems, ready to use water-borne polyurethane blended paints have a limited pot-life [14]. They are prominent for tremendous chemical resistance and weather resistance if aliphatic or cycloaliphatic polyisocyanate adducts are selected. Releases of organic compounds (VOC) are substantially lower than in the case of solvent-borne products. Consequently, application fields are those involving high-performance coatings and low emissions [15].

2.3 2 K Water-Borne Epoxy Coatings

In water-borne 2 K-components epoxy paints, hardener (polyamines) as well as the base component (epoxy resin) can be pigmented and diluted with water. The fillers and pigments must have the shortest-potential matter of soluble salts (electrolytes) for all water-borne paint methodologies. The solid-epoxy resins are dispersed in water, termed as emulsifiable epoxy-solid resin are mostly used as liquid coatings. It is already understood that highly viscous resins are difficult to emulsify, so the viscosity must be regulated in order to get better emulsification. Moreover, the performance of epoxy resin emulsion having medium viscosity is much better as compared to high or low viscosity resins. The characteristics of epoxy coatings and epoxy resin emulsions are mostly dependent of particle size of emulsion [16]. The course or rough emulsions have limited performing parameters are compared to fine particle size epoxy emulsions (Fig. 2).

Phase inversion is the best method for the emulsification of epoxy-based resins (Fig. 3). Initially, emulsification of epoxy resin (w/o emulsion) was performed and in



(< 2 µm) smaller ←	Particle size	→ higher (> 3 µm)
Higher ←	Viscosity	→ Lower
Higher ←	Stability	→ Lower
Complete homogeneous ←	Through curing of the epoxy coating	→ Not complete, inhomogeneous
Higher ←	Gloss	→ Lower
Higher ←	Chemical resistance	→ Lower
Higher ←	Film hardness	→ Lower

Fig. 2 Impact of the particle size on the properties of epoxy emulsions and coatings

later stage further addition of water through phase inversion produce the true epoxy resin emulsion in water (o/w emulsion).

It is observed that viscosity goes higher until at maximum value during the phase inversion (Fig. 4). At this moment, the kinetics can be studied in such a way that the particle size of oil/water emulsions can be affected by changing the shearing time and shear force [17].

It is observed that amine hardener doesn't crosslink homogenously with epoxy resin emulsion and coatings. Later on, these two reactants combine or crosslink in such a way that hardeners molecules exist in the epoxy resin emulsion and coatings (Fig. 5). Therefore, the hardeners molecules diffuse into the epoxy resin particles [18]. Hence, simply more than 70% of the reactive groups take part in reaction with each other. So, it can be experimentally stated in case of 2 K-waterborne epoxy coating and paint systems the hardeners are less consumed stoichiometrically.

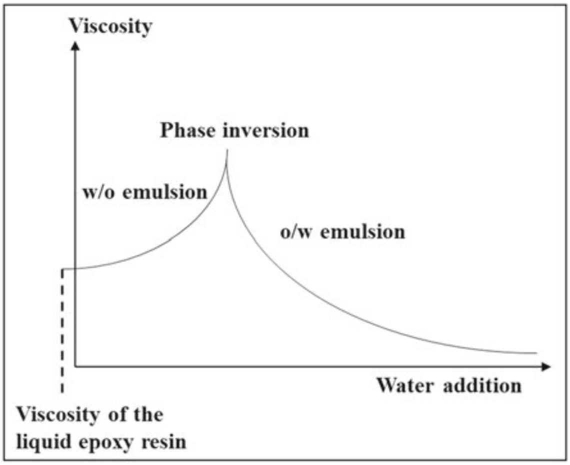


Fig. 3 Basic illustration of the difference in viscosity through emulsification of liquid epoxy resins by phase inversion

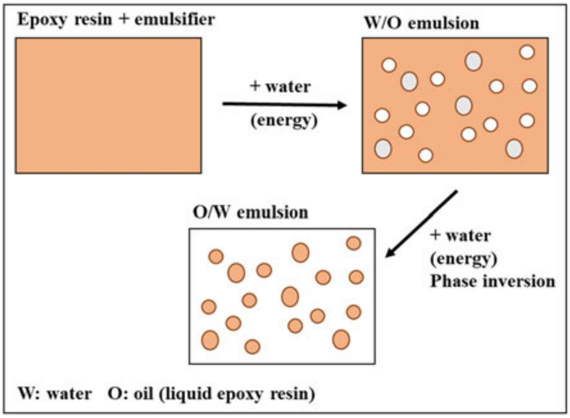


Fig. 4 Emulsification process of liquid epoxy resins by phase inversion

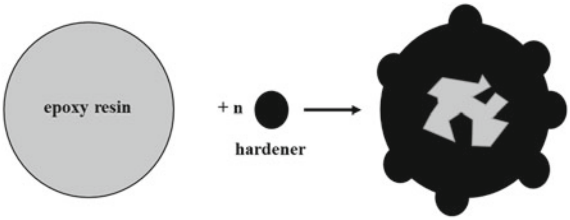


Fig. 5 Basic diagram of the reaction among a single epoxy resin emulsion droplet and amine hardeners

2.4 Water-Borne Stoving Enamels

Stoving enamels are categorized as solvent-borne systems, comprising of two components i.e., cross linkers and hydroxyl resins. Most importantly, these two components should be blended homogenously. All the reaction components should be blended uniformly by diffusion method in water borne techniques due to the colloidal nature as compared to organic coatings/emulsions [19].

2.4.1 Water-Borne Stoving Enamels Based on Amino Resins

Amino resins through non-etherification and etherification with methanol are water soluble in all the case. The studies revealed that resin produced through non-etherification method need special storage facility due to the non-compatibility with other resins. On the other hand, resin produced by methanol etherification are compatible with water-borne paints. The most prominent and well established amino comes under the category of melamine resin. The imino functionalized resin through etherification are relatively more soluble in aqueous media as compared to highly methylolated, fully etherified types (HMMM resins). Though, these methylolated resins are stabilized with anionically stabilized resin or with some general co-solvent [20]. Further the hydrolysis of these imino functionalized resin is resistant to both acidic and basic atmosphere. The mechanism of reaction is shown in Fig. 6 [9].

The alkyd resin are extremely suitable cross-linkers in melamine-based water borne paints. water-borne paints based on alkyd resin consequently give optimal wetting of substrate coats and pigments, the film fabricated through these resins have excellent gloss and durability. The melamine resins are now being used as primer, single coat paint as well water borne upper coat paint [21].

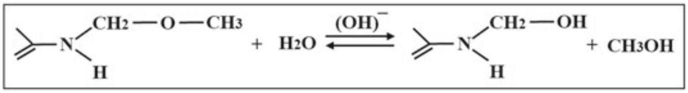


Fig. 6 Hydrolysis of amino resins

3 Solvents-Borne Polymeric Coatings

“Natural drying solvent-borne paint” is a term used to describe paint that is made by dispersing polymeric binder in a solvent-based system and drying naturally over time. The higher molecular mass of the polymer utilized as a binder in paints produces the unique qualities in the paint film. Furthermore, the structural properties of polymers are responsible for maintaining the evaporation rate during paint film formation. One of the drawback of using these polymeric binder is that a huge amount of solvent is use for smooth paint application [22].

Different type of binder is used which includes polystyrene, cellulose nitrate and their co-polymer, some halides and polyester of vinyl-based polymers, derivate of rubber, epoxy and hydrocarbon of higher molecular weight as well as polyamide and polycarbonate-based resin.

3.1 CN (Cellulose Nitrate) Based Polymeric Coating

Naturally occurring cellulose is the main component of all existing plants. It is based on carbohydrate of higher molecular weight comprising of glucose repeating units associated by β-1,4-glycoside linkages. They have higher level of boning as well relatively higher molecular weight molecules (molar mass about 106 g/mol) as shown in above Fig. 7. Cellulose nitrate (CN) was indeed more prominent in polymer class [23]. This polymer is produced through the reaction of naturally produced cellulose with other reactants like water, nitric acid and sometime sulfuric acid as well. The resultant polymer (cellulose nitrate), produced as finished product is similar to wool yarn extensively known as “nitrocotton”. Later on, this product is soaked in different alcohols. Consequently, the chips of cellulose nitrate is produced by reacting plasticizer (phthalate esters) with cellulose nitrate (CN) [24].

The different grades of cellulose nitrate vary with different characteristics like molecular weight and the content of nitrate ester in resultant polymer. One of the impacts of molecular weight is the rise in viscosity of resultant solution. Classification with a high ester content are readily soluble in glycol ether esters, ketones, esters, off course be blended with aromatic hydrocarbons and alcohols [25]. The Chemical structure is demonstrated in Fig. 8.

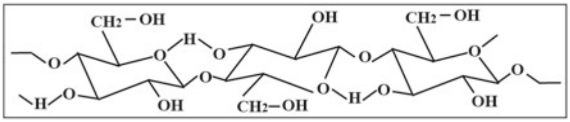


Fig. 7 Molecular formation of cellulose (ß-1,4-glycoside)

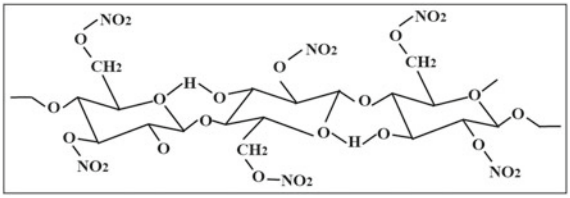


Fig. 8 Molecular formation of an ester-soluble cellulose nitrate

3.1.1 Blend Associates for Cellulose Nitrate

Cellulose nitrate is blended with another particular polyesters established on alkyd resins, and sebacic acid or adipic acid. The mono-carboxylic acids and short oil grades are fatty acids, known as alkyd resin comprise considerable quantities of synthetic acid like oleic, linoleic acid (e.g. based on peanut oil) [26]. Special amino resins (binders) are also appropriate for compatibility with cellulose nitrate. These resins (alkyd) are mostly used to produce pastes of pigment through pigmentation in order to get resultant cellulose nitrate-based paints.

3.1.2 Applications of Cellulose Nitrate Paints

The most well-known, higher molecular weight cellulose nitrate (CN) varnishes are good protectors when applied to metallic surfaces like copper, brass, and silver. These coatings produce clear gloss top layer giving aesthetic feel as well. These cellulose nitrate (CN) paints have also excellent naturally air-drying feature making it more prominent in the field of paints and coatings specially in crackle finishes and hammer finishes. This feature is more visible in printing coatings, topcoats and primers of naturally air-drying wood-varnishes, paper coatings and leather finishes as well [27].

3.2 Elastomeric (Modified Rubbers) Coating

The main component of rubber made from natural sources make up about 35% of its total weight. This type of rubber is produced by unique Euphorbiaceous trees. The chemical name is poly-2-methylbut-2-ene (polyisoprene) and the structure is shown in Fig. 9. The –CH_3 group is coordinated to the hydrogen atom in a cis-position on the isoprene portion. This is of great interest that molecular weight of this polymer could be about 10^6 g/mol. Now, in addition, efforts have been put together by the researchers to provide the appropriate naturally produced for paints and coating applications [28, 29]. There had been great effort in this field and two recently produced naturally rubbers, cyclized rubber (RUI) and chlorinated rubber (RUC) are used as binder in elastomeric paints and coatings applications.

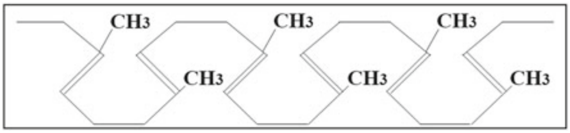


Fig. 9 Structure of rubber (poly-2-methylbut-2-ene) polyisoprene

3.2.1 Cyclized Rubber

This class of rubber is produced through cyclization of rubber at much higher temperature in the presence of catalyst (initiator) usually strong acids. The isoprene units form six-membered ring systems, and the large molecules decay to molar masses of 3,000–10,000 g/mol. Cyclized rubber is a stiff, resin-like material, and melts at temperatures among 120 and 140 °C. It is soluble in aromatic hydrocarbons and aliphatic and in terpenes, thinnable with ketones and esters, but insoluble in glycol ethers and alcohols [30]. For paint formulations, cyclized rubber has to be blended with a plasticizer. The most widely used brand of this class is Syntotex RR 800 (DSM).

3.2.2 Chlorinated Rubber

This class of rubber is prepared by first dissolving natural rubber in solvent carbon tetrachloride (Ccl_4) and then reacting with chlorine (cl_2) to produce chlorinated rubber. The substitution of chlorine occurs while addition and substitution after breaking down the cyclic structure of macromolecule. The chlorine contents are about 67 wt% in the resultant finished product having approximate molar weight from 30 to 180 KD (kilodalton). The composition is mentioned in Fig. 10. Currently chlorinated rubber is now derived from synthetic poly-isoprene and now not produced from natural rubber. This rubber is extremely soluble in ketones, esters and aromatic hydrocarbons and the appearance is usually white powder [31]. Though the product produces films merely by naturally air drying, ultimately excellent resistant to chemical. The film films produced through this class of rubber has excellent adhesion properties with substrate. Some of the types of this rubber having low molecular weight don't need plasticizer for elastic behavior of film. This elastic behavior provides excellent properties in special type of paints. Commercially, this typical rubber is economical product for some of the specialized paints. Few of the commercial products from Bayer (Germany) are Pergut S grades (5, 10, 20, 40, 90).

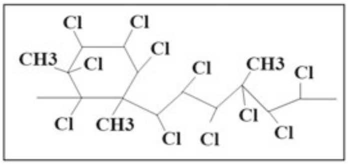


Fig. 10 Molecular formation of a segment of chlorinated rubber

3.2.3 Modified Rubber Applications

In order to produces functional paints against corrosion, rubber is modified with some other active agents. These functional paints based on modified chlorinated rubber are used in marine as well as industrial applications. One of the advantages of these cyclized modified rubber is the uniform permeation inside the concrete and asphalt substrates. Therefore, due to the excellent property of alkali and acid resistance, such functional pains have best application in indoor and outdoor swimming pools and other allied areas. Recently, the different manufactures are utilizing this modified chlorinated rubber into road-marking paint applications.

3.3 Oxidatively Cure Paint

The term air drying, or oxidative drying happens since the previous study reveals about the formation of solid film through transesterification of different vegetable oils and dibasic acids, later on this film is dried in natural air [32]. The chemical kinetic is not simple as the reaction proceeds in two step process and final solid material of characteristics properties are produced through condensation polymerization. The advantage of this functional paint produced through this phenomenon is drying of film formed in natural air/atmosphere.

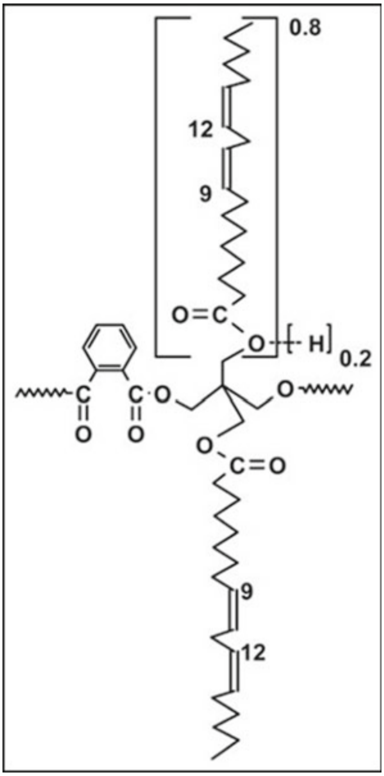
3.3.1 Alkyd Resins

Alkyd or oil based-resins are however the extremely significant category of surface coating adhesive, used in enamel paints. This class of adhesives have commercially available with different grades depending upon their oil length and other components. These resins are produced through transesterification technique. Firstly, intermediate resin is formed through Mono-esterification step by the reaction of polyhydric alcohol (glycerol/glycerin, pentaerythritol and trimethylolpropane) and vegetable/fatty acids. In second step, monoesters are reacted again with dibasic acids like phthalic anhydride, maleic anhydride to produce alkyd resin of specific molecular weight through transesterification step via condensation polymerization [33]. The various classification for naturally drying paints having low –OH contents ($\leq$50 mg KOH/g), and high molecular weight, and low acidic value ($\approx$3–20 mg KOH/g). The classification of alkyd resins is categorized three (03) subclasses depending upon the type and amount of oil/fatty acids.

• Medium oil alkyds	40–60%
• Short oil alkyds	Below 40%
• Long oil alkyds	More than 60% oil or fatty acid

One subclassification is the long oil and is mainly produced by the condensation polymerization of polyhydric alcohol and pentaerythritol. The chemical kinetics

Fig. 11 Fundamental chain of a long oil alkyd resin



depends on the mole ratio of all the reactants. 1.0 (one) mole of polyhydric alcohol i.e., pentaerythritol and 1.8 part of linoleic acid (see Fig. 11), 1 mol phthalic acid, comprises 60.0 wt% fatty acid, 16.8 wt% pentaerythritol and 19.0 wt% phthalic anhydride.

3.4 Alkyd Based Paint

One of the most widely used enamel paints (solvent-borne) is based on alkyd resin.

Alkyd Resin (Long Oil), these kinds of special resin used in decorative enamel paints are manufactured by various kinds of edible oils like sunflower, linseed oil, soyabean oil safflower oil and cotton seed oil as well as the main raw material. These are also termed as fatty acids resins. In addition to decorative domestic paints these resins are utilized for corrosion protection paints. **Medium oil-based resin**, these resins are also prepared from edible oils and fatty acids as well. The amount of oil used in the process of manufacturing resin is less than the contents used in long oil resins. The enamel paint prepared from medium oil resin has the advantage of non-yellowing feature making it best suitable in the area of applications requiring fast-drying of paints, e.g., paints for radiator, agriculture equipment, industrial structures and automotive applications. The third category of resin produced from:

Modified urethane resin, modified urethane is produced for such applications where fast drying is required. They are best applicable for floor varnishes, printing inks and all the wood series coatings and coating including sand sealers [34].

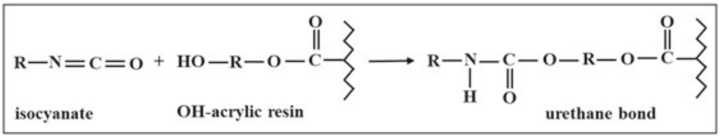
3.5 2 K Polymeric Coatings (PU, Epoxies)

All chemically cured coating techniques have two basic mechanisms. This is possible only in the case where the two polymeric components are blended physically before application comply with the description of a two-component system [35]. The best-known good example is 2 K polyurethane component paints and 2 K epoxy coatings and paints. These coatings are termed as two components-based systems; therefore, it is well understood that one of the components presents in large amount i.e., comprised of pigment is known as base component. Similarly, the other component consists of small amount and known as hardener. The hardener is usually without pigment.

3.6 Two-Components Polyurethane Paints

Reactions of isocyanates: At ambient temperature, coordinated complexes of alcohols, primary and secondary amines with adjacent hydrogen react with isocyanates. Physically blending of isocyanate and hardener with reactive functional groups is taking place here. Commercially, the paint produced by the cross-linking reaction of the urethane group are known as 2 K-polyurethane paints (see Fig. 12). The process can be accelerated towards right side by addition of initiator or catalyst as the reaction kinetics of resin having hydroxyl as functional group with isocyanates proceeds at room temperature.

The film produced through this cross-linking of oligomers of HDI, and hydroxyl functionalized resins are not only had weather resistant properties but also the chemical resistant characteristics. Based on these key characteristics, the generated paints



$$R{-}N{=}C{=}O + HO{-}R{-}O{-}\overset{O}{\overset{\|}{C}}{-} \longrightarrow R{-}\underset{H}{\underset{|}{N}}{-}\underset{O}{\underset{\|}{C}}{-}O{-}R{-}O{-}\overset{O}{\overset{\|}{C}}{-}$$

Fig. 12 Reaction of isocyanates with resins including hydroxyl groups and coatings are best suited for specific applications including automotive painting of vehicles, agriculture equipment, locomotive, repair paints and OEM coatings [36].

3.7 Two-Components Epoxy Paints

All types of paints and coatings produced from epoxy resins must have some excellent chemical resistance. Additionally, they exhibit resistance to abrasion, adhesion, and film hardness of the produced paint on various metallic substrates. One of the excellent features of 2 K paints based on epoxy resin is the protection against metal corrosion and protection in industrial application. The epoxy resin is produced with different ingredients and one of the types of epoxies produced from aromatic bisphenol A resin have comparatively low weatherability. The mechanism of curing of epoxy-based paint is entirely different as the curing mechanism of urethane based occurs by polyaddition of curing agent and hardener at ambient temperature [37].

Base component: Bisphenol A is one of the components used in the production of epoxy resin. This again synthesized by complex reaction of 1.0 mol of acetone and 2.0 mol of phenol. The epoxy, bisphenol A-diglycidyl ether is produced by reaction of 2 mol of ECH (epichlorohydrin) and 1.0 mol of bisphenol A. The epoxy resin can be produced of different molecular weights and such different kind of epoxies can be produced by changing the stoichiometric or mole ratio of these reactants and reaction parameters (Fig. 13).

In normal practices for two-components techniques, the epoxy resins (major ingredient) and hardener (amino functional) are physically blended with each other before applying to some specific area of application. The curing of material takes place after blending the epoxy resin having oxirane group and the later on addition of cross-linker i.e., hardener in 2-K method of paints and coatings. The detail kinetic behavior is shown in Fig. 14. As it is very much clear that the reaction takes place in two steps and in the case of epoxy-based paints and coatings, the first step of the reaction proceeds faster as compared to the second step due to the fact that the primary amines have less steric hinderance as compared to the secondary amine.

The hardeners based on amino functionalization is characterized by the equivalent weight of –NH group. The amino functional molar weight is defined as the molar

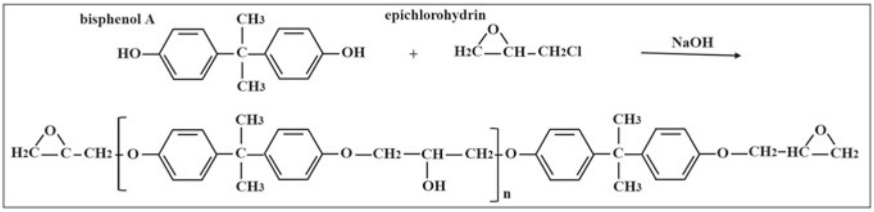


Fig. 13 Synthesis of epoxy resins based on bisphenol A ($n = 0$: bisphenol A—diglycidyl ether)

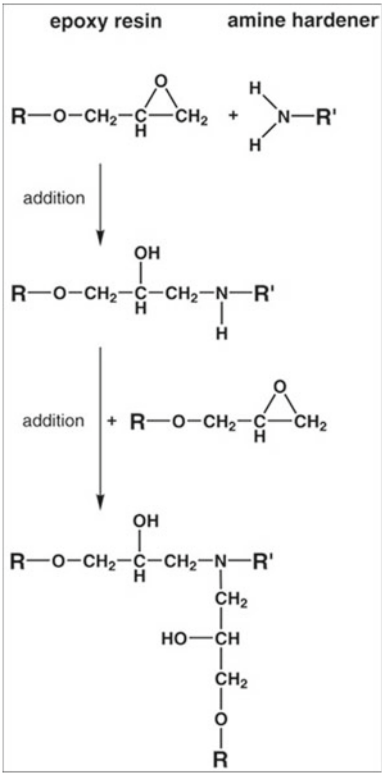


Fig. 14 Curing mechanism of epoxy-based resins

weight of –NH hardener by dividing it with active hydrogen atoms on –NH (amino) group and ultimately termed as 1 mol of active hydrogen [38].

4 Stoving Enamels

The class of paint mostly used in industrial application are termed as stoving paints. They are cured at comparatively high temperature but are best suitable in industrial coatings. For the reason that of the numerous types of techniques in reality, useful baking/stoving parameters. The most important is the temperature and the range of stoving temperature is around 70 and 240 °C. Usually the Stoving/baking cycles is as minimum as one minute and as long as one hour as well. Under these situations—for the duration of film formation—crosslinking takes place.

The mechanism of stoving is very interesting, one or two types of alkyd resins are utilized to react in such a chemical manner that final molecular structure is formed by strong cross-linking with each other. It is also important to mention here that some of the mechanism for stoving paints are through self-crosslinking [39]. The study shows that some of the Stoving enamels are also classified into reactive stoving paints. The stability of paint is one of the saliant feature in stoving paint and hence the components and ingredients of resins are selected in such a way that the final paint remains in useable condition for longer time without any initiation towards gelling at storage temperature [40].

5 Solvent Free Polymeric Varnishes

5.1 *Solvent-Free 2 K Epoxy Varnishes*

Some of the coatings are produced, based on epoxy resin and are cured at room temperature without incorporation any solvent. The cross-linking mechanism is same as found in solvent-based methods. There are two most important variations concerning preparation:

- Low-molecular weight epoxy resins based on liquid epoxy can be produced.
- The different solvents or thinners are added to reduce the viscosity of the final coating solution.

5.1.1 Epoxy Based Liquid Resins

It is already stated above that the epoxy either solid or liquid are based on two major components. One of the components is bis-phenol A and other is epichlorohydrin and the equivalent weight of epoxy for liquid should be greater than 180 as depicted in Fig. 15. The cost and performance depend upon the equivalent weight of epoxy known as di-glycidyl ether epoxy.

The liquid epoxy resin is available commercially in different grades depending upon the molecular weight and the epoxy having low molecular weight have comparatively less shelf life as well as lower drying period. On the other hand, the characteristic features of solid epoxy related to quick drying usually termed as touch to dry phenomenon. This feature is most important due to the use of solid epoxy in certain application like powder coatings.

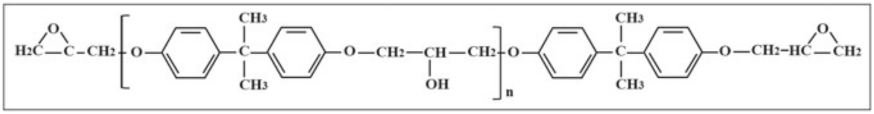


Fig. 15 Bisphenol A-epoxy based resins

5.2 *Radiation Curing Systems*

When certain complexes, primarily those with double conjugated bonds, are exposed to very energetic radiations, applications requiring excellent crosslinking are chosen. For some applications, it is possible to chemically cross link low molecular weight components with higher molecular weight component within the matrix. But the reaction kinetics are highly exothermic and efficient as well. In most cases, low molecular ingredients are low viscous liquid that can be used in solvent-free radiation cure systems recipes as volatile liquids [41]. This system is further subdivided into other two subcategories. One is cured by ultraviolet light (UV) and other through electron beam (EBC).

5.3 *UV Curing*

UV drying appears as paint film comprising unsaturated complexes are cured with UV radiation. There is special UV radiation generator to produce this light of specific wavelength. This specific wavelength radiation react special initiator (UV initiator) also termed as photo initiator to produce free-radicals. These radicals initiate the radical polymerization of conjugated unsaturated complexes. Occasionally, the most important is the blending of photo-initiator with photo-sensitizers. The cross-link or bulk density of coating If the conjugated blend of the coating is dependent on the conjugated crosslinking due to unsaturation of individual component. The cation on later stage could be produced by initially catalyzed reaction through ultra-violet radiation with epoxy resin, facilitating further cross-linking. Now a days this is most favorable reaction process in UV-based coatings and paints. High-voltage electron beams can produce free-radicals in unsaturated complexes immediately. There is another innovation in this field to produces free-radicals by field emission gun or tungsten lamp to produce high energy electron. The advantage of this process is that the photo initiator is not required to build a molecular network through free radical polymerization's cross-linking.

5.3.1 *Mechanism of UV Crosslinking/Curing*

In order to understand the mechanism of UV crosslinking or curing, we must know that the ultra-violet (UV) light is type of electromagnetic radiation that have wavelength in the range of 100–400 nm. The smaller the wavelength, the higher the energy of these radiations. The visible light has little bit higher wavelength. The energy of the whole spectrum of radiation is different as it is related to wavelength. The energy in of UV-radiation is from 300 to 760 kJ/mol. Such energy of UV light can fall on the molecular structure and stimulate the conjugated double bond resulting in initiation of chemical reaction between the chemical components. This is now interesting to

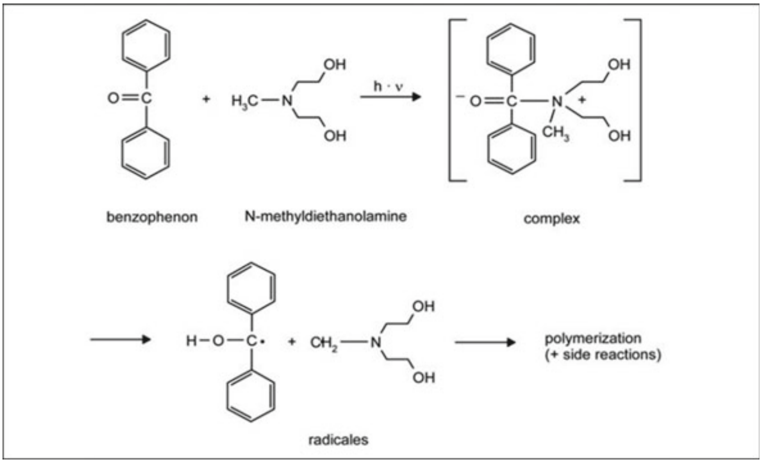


Fig. 16 Formation of free-radical from benzophenone

understand that these high energy in this wavelength region (100–280 nm) cure the paints and coating film initially at the surface via this UV-curing technique. After the partial curing of film at the surface of coating, the complete curing can be performed in visible wavelength region (315–380 nm) [42].

5.3.2 UV Sensitizers and Initiators

The phenomenon of free radical formation is already explained where, UV radiation split the phot-initiator into free-radicals via double bond breaking. One of the interesting features of photo-sensitizer is the absorption of ultra-violet radiation and then fall this absorb energy to other reacting species or molecule to free-radical via intermolecular reaction mechanism [43, 44]. Benzophenone is a well-known ultra-violet initiator. The generation of free-radical through the alky derivative also leads to hydrogen as donor (Fig. 16).

5.3.3 Resins for UV Varnishes

Saturated and unsaturated resins can be used for all kind of coatings but the best ultra-violet curing application, unsaturated resins are the best suitable. These resins can be produced by the polycondensation reaction of maleic and phthalic anhydride with glycols. The unsaturated resin is marketed in diluted form and the best suitable solvent for this resin is styrene. Such class of resins applied in the final application through ultra-violet curing technique need to be modified in order to prevent from oxidation during drying method. (e.g., Isophthalic anhydride, ether modified polyols). Resins with acrylic groups are the following, further significant class of special resins to cure the coating through ultra-violet mechanism. So broadly speaking, unsaturated modified acrylic resins are best applicable actually either polymer or oligomers for this curing methods. Pure acrylic adhesives or resins are produced through the reaction of methacrylic acid or methacrylic esters and the other approach is to produce from acrylic ester or acids. The best suitable for the above-mentioned curing method is through acrylic ester and acids. The unique feature can be incorporated through integrating resin molecular structure with acrylic acid derivatives. The subsequent cross-linked resin occur: polyester acrylates, acrylates based epoxy, acrylates based polyurethane, unsaturated acrylic resins, polyether acrylates, and silicone acrylates [45].

5.3.4 Characteristics and Application of UV Coatings

Coatings based on ultra-violet have astonishing features about the scratch resilience and impact resistance. There is little hard film formed by this technique. In order to develop elasticity or softness in the film, different plasticizers are added in the material that plasticize the structural arrangements of the molecules of resins and also the thinners give addition elastic response to film as well [46]. These additional significant attributes make it best suitable for lamination sheets, wood polish, home and office furniture and sealers as well. The other area of application refers paper coating, foil coating. Similarly, printing inks, laminates, printing sealers can also be prepared by ultra-curing techniques.

5.4 Curing by Electro-Beam

This technique is one of the latest techniques and being used in special applications. The high energy electron is the main source of curing the coating film. These electrons are generated from electron generation source, one of them could be tungsten lamp and other may be field emission gun. The free-radical are created by accelerated voltages from 120 to 500 kV. The active electrons from molecular bonding and the accelerated electron from field emission source react to form cationic configuration though breaking of chemical bond and similarly anionic formation occurs by the addition of electron. So, this phenomenon produces free-radicals from these cation and anions. These accelerated electrons in some condition breakdown the double bond and produce more free radicals. The more the energy of these electron, the more will be free radical formation as well. The energy of these electrons coming from electron source is directly related to the applied voltage to the source. This very well established technique to cure the paints and coating film by electron bombardment [47].

This technique has the benefit of not requiring an initiator for any form of treatment. As we have observed in previous method that there is always a cross-lining phenomenon required for film curing but, in this technique, no need of any cross-linking at the top, or in between two layers of coatings with pigments. As the accelerated voltage of electron beam is higher as compared with ultra-violet radiation, therefore a fast movement of conveyer belt is required for quick action to cure. Unlike the other curing technique, this technique is much better and have excellent surface adhesion properties with plastic substrate. The mechanism behind the adhesion of coating on plastic substrate is the free-radical formation due to the high energy electrons. This reaction is termed as grafting technique [48]. There is only one limitation in this grafting technique i.e., the inert gas is usually required to accelerate the electron. This inert condition reduces the cross-linking efficiency as compared to oxygen or air which facilitate the curing step.

5.5 Powder Coating

In early 1960s, specialized spray gun was employed for powder coatings through the phenomenon of electrostatic deposition. Following this spray gun, the numerous fields were established using powder coating [49]. The markets still emerging in different area of applications. To till date the powder coating is the only solution to get rid of organic solvent spray coatings and as a result green solution for paints application. There are two different approaches for environmentally stable solution. Firstly, coating material from powder are virtually free from any solvent. Secondly, after coating powders can be reprocessed [50].

5.5.1 Manufacture of Powder Coating Materials and Universal Properties

We already studied that powder coating materials are free from any organic solvent; this significance encourages the industries to invest in this technology for bulk production of material. Consequently, the powder is made predominantly in melt methods. First of all, different ingredients are first blended and then pass-through hot melt. The viscosity is the main feature in these hot-melt condition. The more viscous materials were then brought out from these hot chambers or closed reaction towers. Then this highly viscous material is passed through series of dryers to convert this slurry to semisolid form. Later on, this semi dried material is passed though the twin extruders. The extruder converts the material into small portions followed by mixer to produce powder of big particle size. In case, the extruder is operating continuously, it is recommended the mix together all the ingredients prior to extrusion process. One precaution is to avoid using liquid components during the extrusion process [41]. Technically make sure that liquid contents must be incorporated prior to extrusion in hot-melt process. Later on, the master batch is prepared by converting this highly viscous semi solid material into small grains and then this granular mixture is added to another physical mixer to segregate the smaller particle

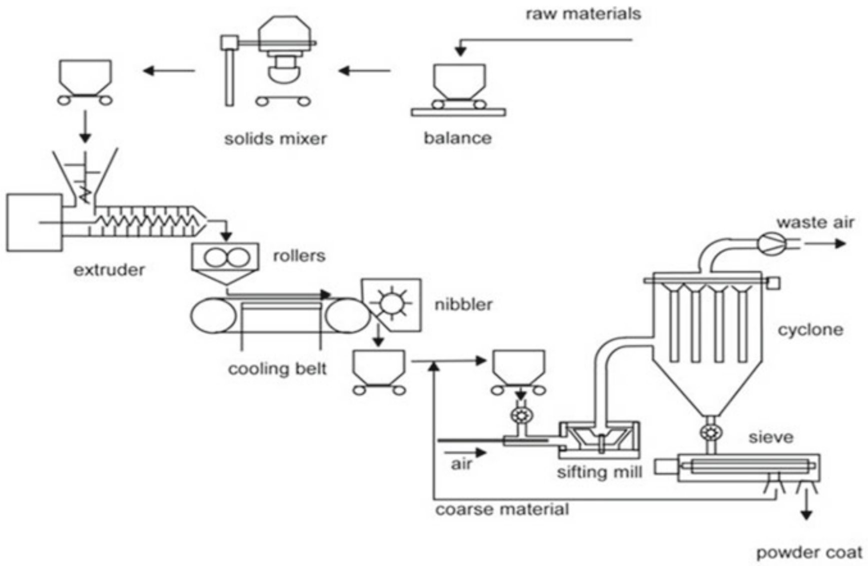


Fig. 17 Procedure for the production of powder coatings

from bigger fractions. In the almost last step, the pigments are also added along with this granular material and consequently, the final shape of the powder coating material is relatively brilliant appearance. The extruded material passes all the way from series of roller forming heavy material block shredded by shredders called nibblers. Special king of pestle and mortar are used to crush the material into fine powder as much possible as can be. The crushed product must be placed in cool place. The fine particle is extracted by special cyclone and the course particles are screened out separately. The objective is to manufacture fine particles with a fine particle size distribution [51]. A graphic illustration of the overall development is described in Fig. 17.

The final particle sizes vary from 15 to 75 μm. While an existing material has a typical size of the particle around 20 μm. The fine particles are then coated through electrostatic spray gun and have thickness of greater than 500 μm. Distinct traditional coatings, usually finds no difficulties with scorching or sagging.

All the manufacturing methods including extrusion, particle size sieve shakers must be such that the softening point which is the most critical parameter should be quite high. Similarly, the other most significant character is the Tg (glass transition) of material and it must fall above 50 °C. The hard resin is then added to the milling stage and thus its significance is limited if meet all above parameters [52].

Film forming of powder coatings brings place by a melt process. The low viscosity after melting is mostly beneficial as the required viscosity for stoving application. This feature of best fit levelling parameters is saliant feature in powder coatings. This is the most excellent condition for optimal levelling [53].

5.6 Composition of Powder Coatings and Superior Characteristics

5.6.1 Thermoplastic Powder Coatings

One of the comparatively cheaper coatings are categorically known as TPC (Thermoplastic powder coatings). These are basically functional coatings and are not too much resistant to chemical and solvent attack as compared to those powder coatings which are chemically crosslinked. Most of the application area of thermoplastic powder coatings are domestic appliances [54].

Polyethylene (P.E) powders are considered most cost-effective finished coatings. P.E powders are primarily utilized by fluid bed sintering. Similar to other application, films are formed at the higher temperature usually around 270–410 °C. If there is special requirement of substrate, specific primer for adhesions is incorporated. There are different primers for different substrate to be applied for coatings, so specific primers for adhesion are applied before final coatings. One of the drawbacks for such coatings that these coatings are not weather resistant. There is another class of polymer-based powder coating originated from polyamide-12 and marketed as Polyamide powders. The method of producing and application is same as the normal powder coating techniques. These powders are also producing films of certain thickness at the temperature ranges from 285 to 415 °C. The resultant film produced from polyamide powder have weather resistant characteristics and also much more chemical resistant as compared to polyethylene powder coatings. Despite of the fact that coating film produced have certain drawback like absorption of moisture and yellowish in appearance, thermoplastic based powder coatings are still the most widely used material. However, they are the utmost frequently used thermoplastic powder coatings. Powder coatings based on PVC are produced from polyvinyl chloride and plasticizer as well. The films are rather elastic, nevertheless are not yellowing resilient. PVC powders are low-cost. They are useful by electrostatic spraying and produce films at 160–200 °C. For various substrates, it is essential to practice an adhesion primer [55].

Powder coatings comprising ethylene–vinyl alcohol copolymers are primarily applied by fluid bed sintering, and their film forming temperatures vary from 200 to 400 °C. The films are recognized by excellent flexibility and adhesion. They are somewhat resistant to corrosion and weathering. Polyester powder coatings comprise of high-molecular, linear, aromatic polyesters. They are generally utilized by electrostatic spraying and form films at 200–240 °C. The films exhibit excellent flexibility, high adhesion, and demonstrate sufficient resistance to water and weathering [56].

6 Functional Polymeric Coatings

In multilayer techniques, functional coatings are typically effective at the several interfaces including, polymer-air, polymer-substrate (wood, metal, glass, or plastic), polymer-liquid (oil or water), and eventually polymer-polymer. Therefore, coatings are made up of fringe structures that are constantly interacting with the environment and users. These structures are aggressively attacked by a variety of factors such as chemicals, bacteria, rain, dust, oils, and wear, which gradually reduces the performance of the ingredients and shortens their shelf life. In this context, efficient coatings have very much in common with the boundary structures of living organisms [57].

6.1 Self-healing Polymeric Coatings

Coatings are frequently employed around a substantial surface area and are hence the extremely possible setting for the initial harms to happen. Numerous self-healing methods have been described for polymers and/or polymeric coatings, which can be categorized in different ways, corresponding to the treatment process: variable versus irrevocable, and intrinsic versus extrinsic healing. The third category seems to be gathering substantial compromise in the coatings field. An extrinsic approach includes the addition of external factors to the technique or preparation, which are not a part of the major polymer group (e.g., microvascular networks or filled capsules). An intrinsic method utilizes curing agent's characteristic to the material which are usually a portion of the system. Mutually methodologies have benefits and drawbacks. The external healing model permits a limited reaction and delivers specific elasticity in opting different external factors, but it is fairly inadequate for numerous healing outcomes. The fundamental attempt may permit several healing and a renovation of the materials to a point which is incredibly near to the unique state [58].

6.2 Antibacterial Polymeric Coatings

Antibacterial and antimicrobial additives are agents efficient enough to eradicate the toxic microorganisms. Antibacterial agents could be classified into further two subcategories on the basis of extent of activity and amount of residue produced: The first category related to killing of bacteria with quick action leaving behind no residue and that's why termed as residue free antibacterial mechanism. The peroxide, aldehyde, alcohols and halogen releasing compounds are excellent example of first class of antibacterial compound. The next class comprises mostly of fresher complexes that leave long-acting residues on the surface to be sanitized and thus have a persistent action and are referred to as residue-producing. Some of the emerging examples are of this group are triclosan, bisphenols, benzalkonium chloride, mercury and silver compounds, tri-chlorocarbon, quaternary ammonium (QA) compounds [59].

6.3 Novel Marine Antifouling Coatings (AF)

The type of coating utilized in special application like marine application are prone to fouling. In order to eradicate the fouling problem, Innovative antifouling coatings are developed and broadly categorized into two sub classes, one is chemically active and termed as biodegradation and other is chemically inert and termed as bio-prevention antifouling techniques. In first class of antifouling coatings, usually special coatings are developed based on enzymes and this is most advance form of the coatings. The later strategy is proposed based on the viewpoint that prevention is preferable to cure. The mechanism of eradication of biofouling from marine is to kill the existing one attached on the surface and also prevent the bacteria to deposit of the surface as well. Chemically inert AF strategies are produced by tuning the surface tensions and/or surface charges, mimicking natural surface topographies, and mixtures of these approaches [60].

6.4 Poly (Zwitterionic) Non-fouling (NF) Coatings

The field of coatings is emerging day by day and in recent innovation, surface coatings based on zwitterionic have taken much attention for the utilization of these coatings as anticoagulant, anti-bacterial purposes. anticoagulant, biomedical diagnostic agent, as well as ultra-filtration membranes. With the recent innovative approaches these coatings are versatile in nature specially, formation of a hydration layer by zwitterionic polymers or mixed charged groups, as depicted in Fig. 18. Generally, there are two types of zwitterionic polymer. One has both positively and negatively charged groups on the same monomer. These include phosphorylcholines and polybetaines. The other has differently charged components on separate monomers, creating a mixed charge complex. These are known as polyampholytes [61]. Polybetaines can be further divided into three major groups based on the negatively charged groups: sulfonate-betaines (SB), carboxylate-betaines (CB), and phosphonate-betaines (PB) (Fig. 19).

These coatings are not only resistant to chemical but also towards cells adsorption, numerous proteins for example, fibrinogen, serum protein, platelet, lysozyme, bacteria (*Staphylococcus epidermidis*, *Pseudomonas aeruginosa*, *Escherichia coli*), and fibroblasts [62].

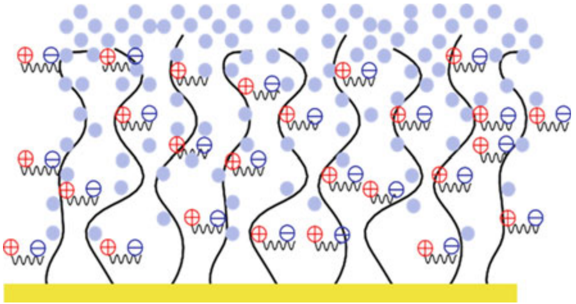


Fig. 18 Illustration of chain hydration and chain flexibility of zwitterionic polymers

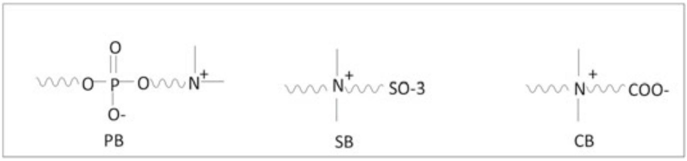


Fig. 19 Chemical structures of phosphonates-betaines (PB), sulfonate-betaines (SB), and carboxylate-betaines (CB)

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