Biobased materials for polyurethane dispersions

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ARTICLE INFO

ABSTRACT

Nowadays, most of the commercially available resins are synthesized from petroleum based stocks. Besides exhibiting excellent properties, synthetic resins are coming under increasing restrictions due to tightening environmental exposure regulations, high depletion rates and exponential rising prices of petrochemical stocks etc. So, considering an increasing ecological and economical issue in the new generation coating industries, the maximum utilization of naturally available resources for polymer/resin synthesis can be an obvious option. These renewable resources can be utilized for number of polymerization reactions due to their reactive functionalities such as hydroxyl groups, carboxyl groups, unsaturation, reactive phenolic structures etc. Therefore, a wide variety of resins can be synthesized from renewable resources, some of them being, alkyd, polyesters, phenolic resins, epoxy resins, polyurethanes, acrylics, vinyl, etc. The present paper discussed the potential of naturally available resources as an environment friendly alternative for petroleum based raw materials as far as coating industries are concerned.

Capsule Summary: Recent trends, developments, and future applications of bio-based materials produced from renewable resources for polyurethane dispersions are discussed. Bio-based polyurethane dispersions are attracting increased attention due to environmental concerns and the realization that global petroleum resources are finite, which not only can replace existing polyurethane dispersions in a number of applications, but also could provide new combinations with improved of properties.

Cite This Article As: V. R. Remya, Deepak Patil, V. K. Abitha, Ajay V. Rane and Raghvendra K. Mishra. 2016. Biobased materials for polyurethane dispersions. Chemistry International 2(3) 158-167

INTRODUCTION

Aqueous polyurethane (PU) dispersion is a binary colloidal system in which PU particles are dispersed in a continuous aqueous media (Mohaghegh et al., 2005). Most conventional PU dispersions are high molecular weight ionic polymers which are commonly prepared by one of two processes: the polyurethane is polymerized in solvent then dispersed in water, or an isocyanate terminated pre-polymer is prepared in the melt or in an aprotic solvent, and is then chain extended with a diamine in the water phase in the presence of a neutralizing tertiary amine. Urethane dispersions are also prepared through the attachment of polyoxyethylene side chains that enable the polymer to be dispersed in water utilizing a non ionic mechanism. We have prepared novel low MW hydroxy/carboxy functional polyurethane dispersions through the use of non-isocyanate chemistry. When crosslinked with a melamine resin these PUR dispersions produce films of more uniform structure and crosslink density (Tramontano et al., 2009). In particular,
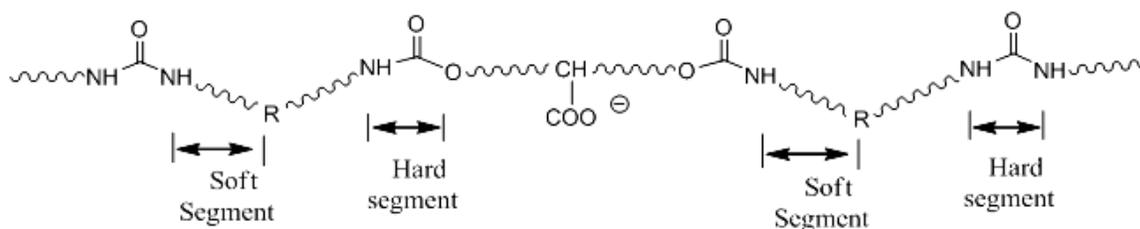
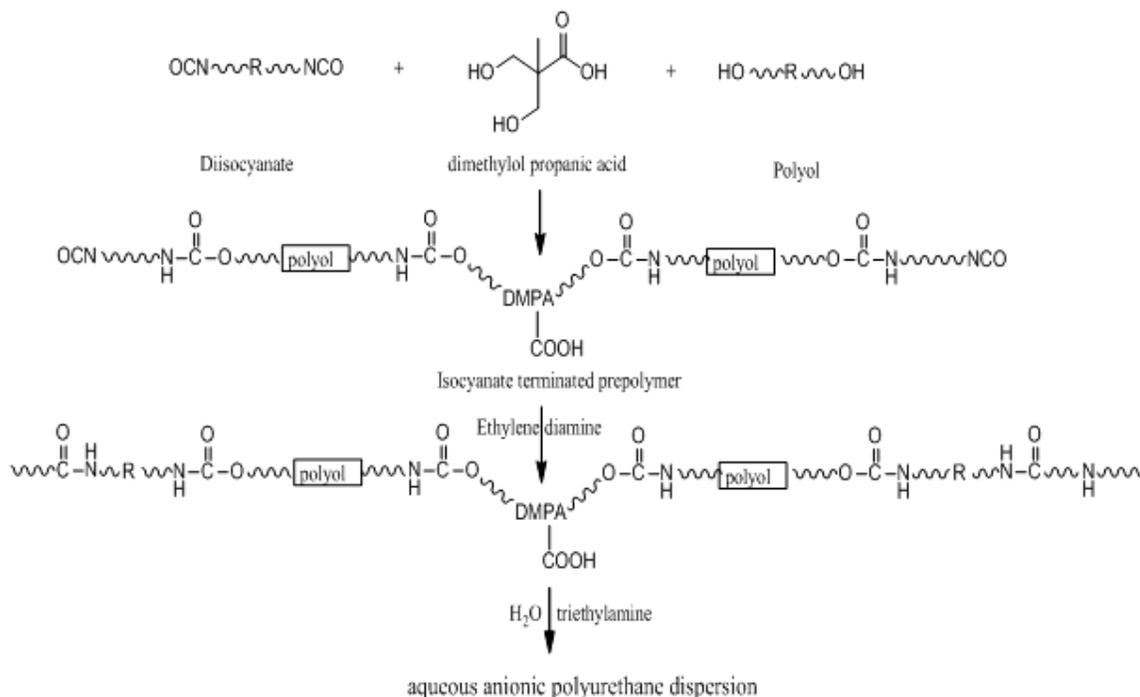**Fig. 1:** Representation of hard and soft segments of PU dispersion

Fig. 2: Representation of Anionic PU dispersion reaction

waterborne polyurethane has emerged as a new chemical technology for ecofriendly adhesive and coatings. PUDs are mainly used as flexible coatings for textiles and hard coatings for wood and metallic surfaces (Choi et al., 2010). Water borne PU dispersion have earned more importance due to their exceptional properties such as glossiness, transparency, quick drying time, flexibility and temperature impact resistance, abrasion resistance, non-flammability, and adhesion with most substrates (Mumtaz et al., 2013). Due to the excellent properties PUDs have established themselves as preferred binder materials for coatings, adhesives, sealants, elastomers, fibers and foams. The preparation of polyurethane aqueous dispersions can be accomplished in several ways. However, it is possible to prepared water borne PUs dispersion with the help of a protective colloid, external emulsifier or by structural modification (Sundar et al., 2004). The first two methods suffer a few disadvantages as they require strong shear force to disperse the polymer, which results in coarse particles and poor dispersion stability. A unique method of dispersing PU in aqueous media is by structural

modification, i.e. incorporating the ionic groups in hydrophobic PU backbone chain (Sundar et al., 2004). The number of advantages of PU dispersion:

- ✓ low solvent content (or in many cases solvent-free)
- ✓ low odor
- ✓ low viscosity at high molecular weight
- ✓ many options for one component applications
- ✓ low temperature drying
- ✓ excellent polyurethane performance

The past few decades have witnessed significant growth in the development of waterborne PU dispersions as environmentally friendly alternatives to solvent-based coatings, but all the PU dispersion are derived from petroleum-based materials and the finite source of petroleum based raw material. One of the possible solutions is the use of bio-based materials for polymer/resin synthesis. The increasing worldwide interest in the use of biomaterials is mainly due to the fact that these materials are derived from natural sources which are abundantly available and their use would also contribute to global sustainability
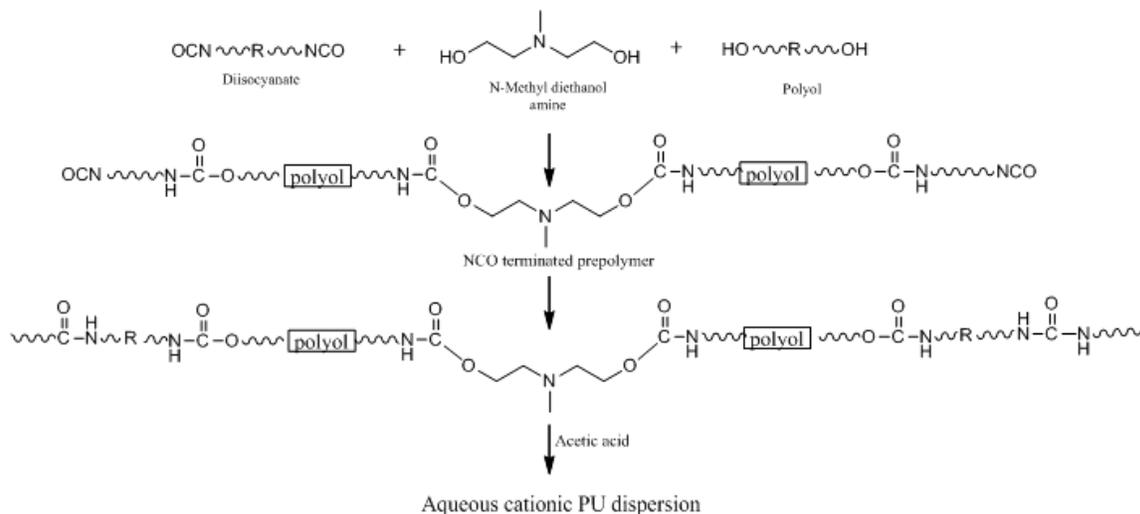
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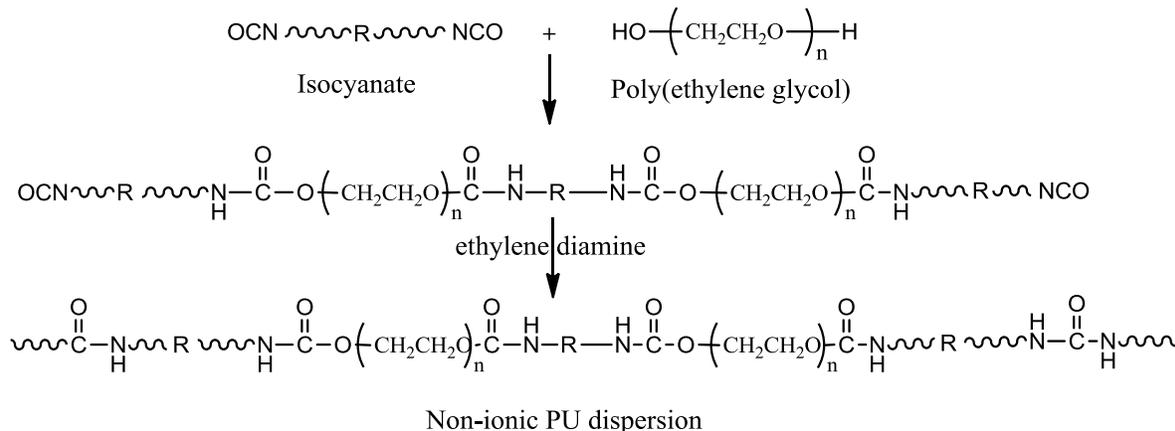**Fig. 3:** Representation of Cationic PU dispersion reaction

Fig. 4: Representation of non ionic PU dispersion reaction

without depletion of scarce resources. Also, biomaterials are comparatively easy to handle with no or less toxicity and health-related issues. PU dispersions from renewable resources have been attracting ever increasing attention over the past two decades, largely because of environmental concerns and finite petroleum resources. The utilization of bio-based materials as such or by chemical modifications for synthesis of PU dispersion has been reported by number of researcher (Suresh et al., 2014). The utilization of bio-based materials as such or by chemical modifications for various applications like resin synthesis, adhesives, paints, coatings, composites, etc., has been well reported. Such materials include cellulose, starch, sucrose, sugar, lignin, plant and animal oils, etc. However, there exists a compound such as Cashew Nut Shell Liquid (CNSL), which can be used as a possible substitute for petroleum-based materials due to its availability, sustainability, cost effectiveness, and reactive functionalities. In this review article we discuss the detail about PU dispersion and preparation method and use of

various renewable raw materials for the synthesis of PU dispersion.

PU Dispersions

PUDs are a binary colloidal system in which the thermoplastic PU chains are dispersed in continuous water phase via incorporating the internal emulsifier in PU backbone. Typically, NCO terminated prepolymer ionomer or non-ionomer is first prepared, which is readily dissolved in acetone. Afterwards, a chain extender is added to react with the terminal NCO groups to increases the molecular weights (figure 1). Chain extension is accomplished by the addition of di or polyamines to the water based prepolymer dispersion and disperse in water under mild conditions. The viscosity of PU dispersion is normally independent of the molecular weight of the polymer. Thus, we can synthesize the high solid content water borne PUDs with a molecular weight high enough to form films with excellent properties. The film formation can occur by simple evaporation
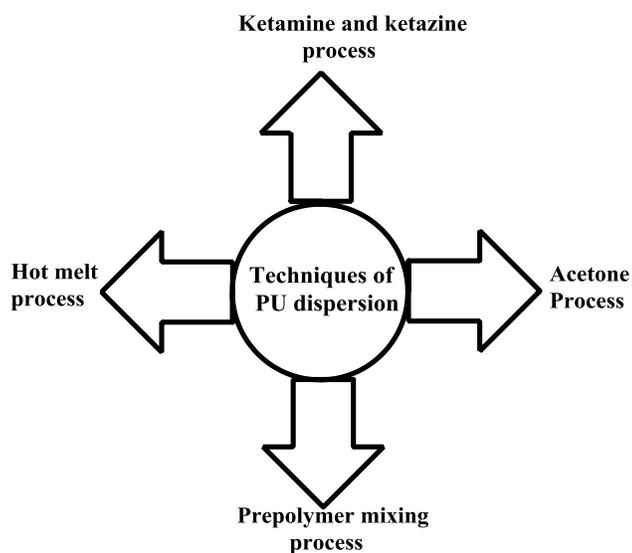
Fig. 5: Techniques for preparation of PU Dispersion

of water even at ambient temperature. In comparison to other waterborne coatings, aqueous polyurethane dispersions have the lowest amounts of organic solvent emissions. The PU dispersions have find the application area include floor coatings, textile coatings, and adhesives.

The PU dispersion chemical composition, chain length, distribution and functionality type plays a vital role in mechanical properties, thermal properties, chemical resistance, water resistance, and also in morphology of dispersions. PU dispersions polymeric backbone chains divided into soft and hard segments. The soft segments cover a large part of PU dispersions chains and it includes mainly polyol chain length and hard segment includes ionic groups, diisocyanates, chain extenders agents (Saalah et al., 2014).

Types and Techniques of PUDs

Depending on the type of ionomers introduced into polymeric chain backbone; PUDs can be classified as anionic, cationic and non-ionic. These ionomers acts as internal emulsifier or self-emulsifiers and makes PU particles to be stable in water media for extended period of time. These anionic and cationic centers could be pendant acid or tertiary nitrogen group respectively, which are neutralized to form salts. Non–ionic dispersions are obtained similar to ionomer dispersions if the ionic centre is replaced by lateral or terminal hydrophilic ether chain. Nonionic type PUDs contains polyethylene oxide as a hydrophilic soft segment pendant group.

Anionic PU dispersions

Among the dispersion, anionic PU dispersions are commercially predominant. In order to obtain anionic PUDs; diols bearing a carboxylic acid or a sulphonate group are usually introduced in hydrophobic PU backbone. These carboxylic functionality bearing PU polymers is subsequently neutralized by tertiary amines, typically triethyl amine (TEA) and self dispersing in

water without the influence of shear force in the absence of dispersants. Generally, anionic PUDs are obtained by using bis(di-hydroxyl-functional) carboxylic acids, monomers having two primary hydroxyl groups that easily react with the isocyanate groups, and a tertiary carboxyl group, with low chemical reactivity due to sterical hindrance as an ionic precursor (figure 2).

The anionic type aqueous PUDs have a fine particle size and hence the stability of the anionic PU dispersion is subsequently higher. The films formed from this dispersion have better mechanical and chemical properties as compared other dispersions (Dieterich et al., 1981).

Cationic PU dispersions

PU cationomers used in aqueous are generally prepared by incorporating tertiary amine functionality into the backbone. The commercially cationic PU dispersions are not used widely at present. There is one additional characteristic feature of cationomers; it is the extensive potential for making structural modifications in their molecules, not only by changing the types of diisocyanate and polyol feeds but also by changing the ionic segments of cationomers which are derived from built-in tertiary amines and counter ions specific for those amines that can produce additional hydrogen bonds and strong ionic effects which influence the interactions within scarcely miscible phases of (urethane and urea) rigid segments and (polyol) soft segments (figure 3). As one of the important consequences of that, changes are observed in the surface free energy (SFE) of the coatings which are obtained from cationomers (Król et al., 2011).

Non–ionic dispersions

Non–ionic dispersions are obtained similar to ionomer dispersions, only the ionic centre is replaced by lateral or terminal hydrophilic polyether chain. In non-ionic dispersion,
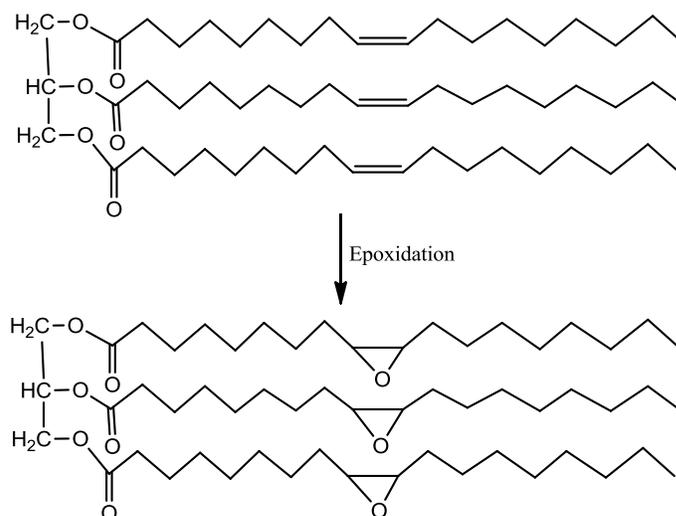

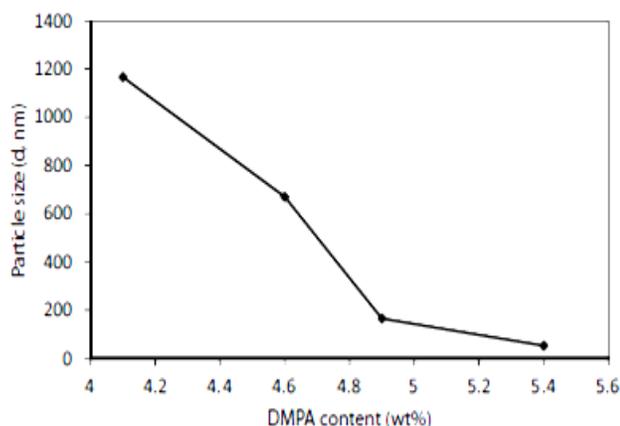**Fig. 6:** Synthesis of Polyol from Oil

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Fig. 7: Effect of DMPA content on particle size of PU dispersion

polyethylene oxide (PEO) polyol are replaced by some part of hydrophobic polyols. In non-ionic dispersion necessary to build a high number of hydrophilic polyether segments into the PU to obtain stable dispersion and hence maximum cured film of non-ionic dispersions are water sensitive. These dispersions have been increasingly used in wood, leather and plastic coating applications. The figure 4 is shown reaction mechanism of non-ionic dispersion. In a straight line, preparation of PU dispersions in water is not possible because of the reactivity of diisocyanates with water (Dieterich et al., 1981). There are numerous techniques have been developed for the preparation of PUDs, some of them gain much attention such as acetone, prepolymer mixing, hot melt dispersion and Ketamine and ketazine process (figure 5). All these have been in common the first step, in which a intermediate molecular weight polymer (the prepolymer) is formed by the reaction of appropriate diols or polyols with a molar excess of diisocyanate.

Prepolymer mixing process

The prepolymer mixing process is most important process in the synthesis of PU dispersions and this process has the advantage of avoiding the use of a large amount of organic solvent. In this process, firstly prepared hydrophilic ally modified prepolymer and it is directly mixed with water. If the mixture viscosity is too high, a small amount of a solvent such as N–methyl pyrrolidone can be added before the dispersion step. Chain extension is accomplished by the addition of di or polyamines to the water based prepolymer dispersion.

Acetone process: In this process; initially the isocyanate-terminated PU prepolymer is prepared in a hydrophilic organic solvent, for example acetone. The chain extended with usually used is sulphonated functional diamine. The solution is subsequently mixed with water and then the organic solvent is removed by distillation. Advantages of this process are the wide varieties of possibilities in the molecular weight build up of the polymer and the control of the average particle size as well as the high quality of the final products. But, in this case the polymer is acetone soluble; the resultant coatings have poor solvent resistance.

Hot melt process: In hot melt process, NCO-terminated ionic modified prepolymer is capped with urea at high temperature (130^0C) to form biuret. This product is then dispersed in water at around 100^0C and chain extension is carried out in the presence of water by reacting it with formaldehyde. These methylol groups can undergo self-condensation producing desired molecular weight.

Ketamine and ketazine process: It is similar to that of prepolymer mixing process. In this process ketamine (ketone blocked diamine) and ketazine (ketone blocked hydrazine) is used for chain extension. Chain extension occurs simultaneously with isocyanate terminated prepolymer during dispersion in water. Ketamine and ketazine hydrolyses and generates free diamines and dihydrazine respectively, which in turn reacts with isocyanate in chain extension. The dispersion prepared by this process yield high performance coatings.

Brief description of development in PU dispersion: Polyurethanes (PUs) are one of the most versatile polymeric materials with variety of applications in both industrial and architectural sector. However, fossil feedstock's based solvents used in PU formulations raised environmental concerns. To reduce volatile organic compound (VOC) emission and to meet Environmental Protection Agency's (EPA) stringent regulations; water borne polyurethane dispersions (PUDs). The PUD based polymeric material offers the freedom to develop unique and broad-ranging portfolio of characteristics including superior hardness, toughness, low temperature flexibility, abrasion resistance and good adhesion.

As discussed, aqueous PUDs present many advantages over conventional solvent based PUDs. Currently, PUDs coatings are derived from petroleum-based materials and the finite source of petroleum based raw material. PU dispersions from renewable resources have been attracting ever increasing attention over the past two decades, largely because of environmental concerns and finite petroleum resources. The utilization of bio-based materials as such or by chemical modifications for synthesis of PU dispersion has been reported by number of researcher (Chintankumar et al., 2014). Various types of renewable resources raw material used in the synthesis of PU dispersion are described in this section.

Vegetable oil
From the early years of coating technology to till date, vegetable oils have been widely explored as sustainable materials in polymers for coatings. Wide variety of vegetable oil based polymers such as epoxy resins, alkyd resins, vinyl polymers, polyanhydrides, acrylic polymers, hybrid latexes and PUs have been developed successfully. Baolian Ni et al initiated to synthesis PU dispersion from oil via incorporating hydroxyl functionality into the backbone chain (Ni et al., 2010). Vegetable oils usually offer two major reactive sites for their incorporate the hydroxyl functionality into chain backbone. These are the double bonds present in the unsaturated fatty acids and the ester
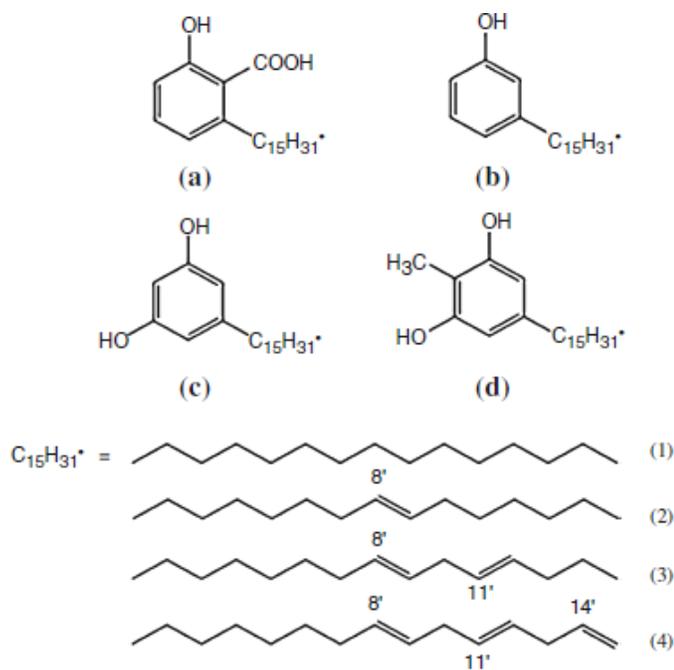
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Fig. 8: Chemical composition of CNSL: (a) anacardic acid (b) Cardanol (c) cardol (d) 2-methyl cardol
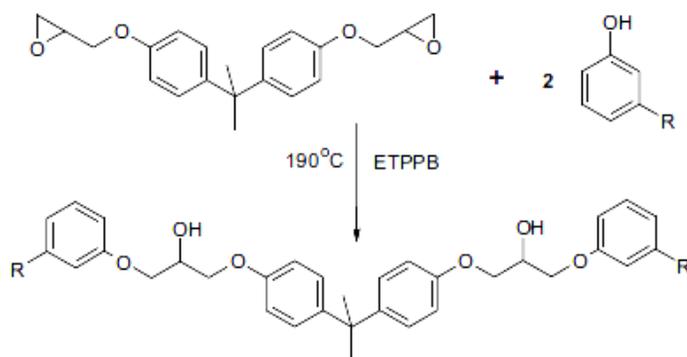

Fig. 9: Synthesis of polyol

groups which link the fatty acid to the glycerol moiety. Generally, the hydroxyl functional oils are obtained either by direct polymerization or by functionalization of the oil through double bond reactions such as epoxidation, hydroformylation and metathesis, or through ester bond breaking reactions. The direct oxidation of the double bonds present in vegetable oils which contain sufficient unsaturation to put the OH functional group in backbone of oil. But, to control the rate of oxidation is difficult and as it produces a number of oxidation by-products such as peroxides, aldehydes, ketone, carboxyl's and other low molecular weight species which are produced by chain scission. The problems of oxidation can be overcome by an epoxidation reaction which introduces epoxy groups exactly at the position of double bonds. Epoxidation of vegetable oils such as soybean,

rapeseed, linseed, safflower, karanja and cotton seed is carried out on an industrial scale to obtain a variety of hydroxyl functional compound (polyols). There are four known technologies to epoxidation the unsaturation of vegetable oils:

[a] epoxidation with percarboxylic acids, the most widely used in industry, can be catalyzed by acids or by enzymes;

[b] Epoxidation with organic and inorganic peroxides which includes alkaline and nitrile hydrogen peroxide epoxidation as well as transition metal catalyzed epoxidation;

[c] Epoxidation with halohydrins, using hypohalous acids and their salts as the reagents for the epoxidation of olefins with electron deficient double bonds; and

[d] Epoxidation with molecular oxygen. The general reaction scheme of epoxidation was given in figure 6.

Hydroformylation is also used to obtain polyols with primary hydroxyl groups. Triglycerides are reacted with carbon monoxide and hydrogen, followed by conversion of the resulting aldehydes groups to hydroxyl groups by hydrogenation. The conversion to polyaldehydes is carried out in the presence of either rhodium or cobalt as the catalyst. Purification of polyols through the removal of byproducts increases the length and cost of the process. In addition, there are risks associated with the handling of reactants such as hydrogen, carbon monoxide, peroxy acids and ozone. Some progress has been made in the development of polyols by the transesterification technique. Transesterification is an important class of organic equilibrium exchange reaction in which one ester is transformed into another by the interchange of the alkoxy moiety. In the transesterification of vegetable oils, the triglyceride is reacted with an alcohol and hence the process is often called alcoholysis. This may be catalysed by acids, bases or enzymes. Glycerol is a trifunctional polyol which is produced by the hydrolysis of vegetable oil and separated by solvent extraction technique. Several aspects, including the type of catalyst, alcohol to vegetable oil mole ratio, temperature and free fatty acid content, have an influence on the progress of the reaction. The transesterification is done with a high excess of a diol in the presence of an organic base (Wang et al., 2013).

In another study, investigation on effect of the various hydroxyl value polyol, ionic content and hard segment content on the PU dispersion properties. As we know, stable dispersion is generally recognized by a smaller particle size and the results obtained in study indicate a significant reduction in particle size as increases the hydroxyl value due to a combination of high hard segment content. As hydroxyl value of the polyol increases, the auther also increases the amount of diisocyanate and DMPA to maintain a constant molar ratio between the NCO and OH groups. However, increasing the amount of IPDI and DMPA in the PU formulation results in a higher hard segment content as well as DMPA content. The results (figure 7) clearly indicate that as the amount of hard segment increases in the PU formulation, the particle size decreases (Sariah et al., 2014).

The preparation of PU coatings from polyols has been the subject of many studies, but limited attention has been paid on the effect of various hydroxyl values on the properties of PU coating. In this regard, author synthesized soybean oil base polyol with various hydroxyl values via the epoxidation method. In this study, the molar ratio of polyol to DMPA was varied from
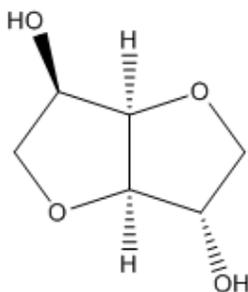
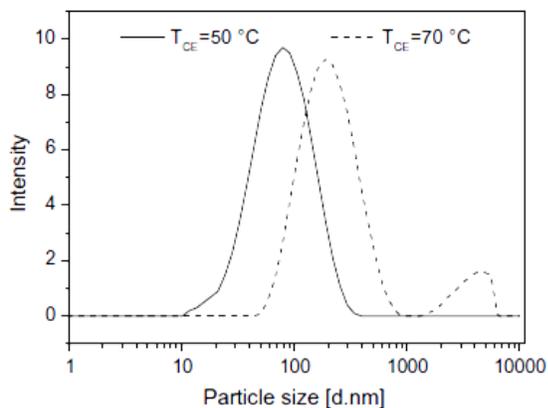**163**

Fig. 10: Isosorbide structure

Fig. 11: Particle size and Particle size distribution of dispersion chain extended with water

1.6 to 2.6 and result revealed that as we increases the mole ratio particle size also increases. At hydroxyl value goes up molecular mass also increases and hence it become more difficult to disperse the particle in water. Thermal properties of the final PU cured samples increased with the hydroxyl value and this is due to the increase the density of crosslinking with hydroxyl value (Sariah et al., 2014).

In another study, Lu et al prepared cationic PU dispersions from soyabean oil based polyol with various hydroxyl functionalities ranging from 2.4 to 4.0. The effects of the hydroxyl functionality of the soyabean oil polyol on the particle size, thermal and mechanical properties of PU dispersion have been studied. The author observed that, the particle size of the PU dispersions containing different OH value might be controlled in two ways. First, the higher OH functionality of polyol can increase the crosslinking of the urethane prepolymer, leading to an increase in the particle size of the dispersion. In PU dispersions preparation, when OH number of the polyol increases, simultaneously the amount of diisocyanate and NMDA also increases to maintain constant molar ratio between the NCO and OH groups. As a result, the content of the NMDA is found to increase, in same manner smaller particle size dispersion was obtained and this may be mainly due to the higher crosslinking (Lu et al., 2008).

The hard segment affected the colloidal characteristics of PUD. The increase in the fraction of hard segment enlarged the particle size of PUD micelles, because the polyurethane chain becomes harder with increasing fraction of hard segment and the formation of polymer micelles in water needs more chains to stabilize the micelle structure. Under a certain fraction of the hard segment, the homogeneous distribution of COOH group in the polyurethane chain results in a small particle size. The amount of COOH groups as hydrophilic unit also influenced the particle size of PUD, indicating that the larger amount of COOH groups led to the smaller particle size of PUD. Moreover, the hydrophilicity and hydration ability of the counter ions affected the particle size of PUD (Ruqi et al., 2014).

Cardanol

Cashew hut Shell liquid (CNSL) occurs as a viscous liquid in the soft Shell of the cashew nut. Cashew nut is the crop of the cashew tree. The seed has two Walls or Shells, the outer one being smooth and somewhat elastic and green in color before maturity. The honeycomb is housed between the inner and outer shell- The kernel is inside the shell and is covered with a brown skin. Industrial grade CNSL is reddish brown in colour. CNSL constitutes about 20 to 25% of the weight of the cashew nut. CNSL is one of the major economic sources of naturally occurring phenols and is regarded as a versatile and valuable raw material for polymer production. CNSL obtained from unroasted shells was first found by Stadeler to consist chiefly of anacardic acid which on heating decarboxylated to cardanol and cardol. Since then, a number of researchers have reported on the chemistry, method of extraction, refining, and compositions of the extracted CNSL. On thermal distillation, CNSL yields a number of phenolic derivatives like anacardic acid (6-pentadecenyl salicylic acid), cardol (5-pentadecenyl resorcinol), and 2-methylcardol (2-methyl 5-pentadecenyl resorcinol) whose main component is cardanol (3-pentadecenyl phenol); a meta-substituted unsaturated hydrocarbon chain having a chain length of C-15, as shown in figure 8 (Balgude et al., 2012).

Besides vegetable oils, cashew nut shell liquid (CNSL), an agricultural by-product of the cashew industry, has also been used in binders for coatings for several years. CNSL is a reddish brown viscous phenolic lipid, which is found in the soft honeycomb structure of the shell of cashew nut. CNSL and their derivatives can undergo number of chemical reactions, some of them being sulfonation, nitration, esterification, halogenation, etherification, epoxidation, etc. (Balgude et al., 2012).

Now days; the chemistry and composition of CNSL have been extensively studied. CNSL and cardanol have been explored in PU for different applications; to the best of our knowledge, cardanol has not been reported for its application in PU dispersions. In these sense; J. Patel et al have been prepared PU dispersion from cardanol base polyol. The synthesis of cardanol polyol via reacting epoxy resin with cardanol (figure 9) at 190° C and reaction was then continued at 190° C until weight percent of oxirane content reduced below 0.3%. The author applied coating on metal substrate from prepared PUDs, with and without drier (catalyst) additive. The cured films have been evaluated for various mechanical and thermal properties, and also studied their corrosion resistance behaviour on steel substrate. The cross-linking in the film showed improvement in the film properties such as hardness, water resistance and solvent

resistance. The corrosion resistance studied by EIS spectroscopy also showed improvement in barrier properties by oxidative cross-linking (Balgude et al., 2012).

In another study, PU dispersion from cardanol diol via acetone method has been synthesized by Suresh et al. The author use cardanol diol as chain extender in various weight percentages and study its effect on particle size, polydispersity and coating properties. As we observed in results; as cardanol weight percentages increases the particle size and polydispersity increases in same manner. The PPU dispersion film obtained with cardanol diol were flexible as compared to the butanediol as chain extender due to the unique molecular structure of cardanol with long alkyl chains and its larger molecular weight compared to butane diol. Author also checked the influence of cardanol diol PPU dispersion surface properties via measuring the water contact angle. The results revealed that cardanol modified or higher cardanol containing PU dispersion given higher contact angle due to the long hydrophobic alkyl chain present in cardanol (Vilas et al., 2010).

Isosorbide

Isosorbide is a diol derived from renewable resources, like cereal-based polysaccharides. With its attractive features, such as rigidity and chirality, and non-toxic nature, Isosorbide has been used to prepare PUs. Due to the damaging effects of VOC emission on environment and hence there is a growing concern about synthesis of water dispersible resin. In that manner; soyabean oil-Isosorbide based PU dispersion has been prepared by varing the weight of diol from 0 to 20 % of total diol content. A typical procedure to prepare PU dispersions includes the NCO-end capped prepolymer synthesis. To synthesis the PU prepolymer diol (Isosorbide and DMPA) reacted with excess mole of HDI and chain extension of isocyanate terminated prepolymer carried out by reacting with Ethylenediamine. The high molecular weight product neutralized with triethylamine to disperse in water and film formation occurs by simple evaporation method. The prepared coating have characterized by dynamic mechanical analysis, differential scanning calorimetry, thermo gravimetric analysis, and mechanical testing. Auther conclude that as we increases the amounts of Isosorbide in coating the glass transition temperature is also increased, and also observed the mechanical properties are improved significantly with the incorporation of Isosorbide. But, the thermal stability decreases slightly with the incorporation of Isosorbide (Ying Xia et al., 2011).

The chain extension of PU dispersions is important step and Li et al studied the effect of chain extension temperature, the sequence of addition of the chain extender with respect to the dispersion step and the utilization of a catalyst on the film properties. In this study; author prepared PU dispersion from diisocyanate, Isosorbide, and DMPA as the internal dispersing agent, and EDA, ADH and/or water as the chain extenders. The free isocyanate groups on particle did not react with the chain extender completely; because the viscosity of dispersions is high at low temperature in the chain extension step and long time require for chain extenders to diffuse into the particle (Li et al., 2014). The temperature at which addition of chain extender

carried out affects the dispersion. Li et al (2014) added chain extender at 50, 60 and 70^{0}C and studied its effect on dispersion particle size. It was observed that at 70^{0}C, the largest average particle size around 195 nm and a bi-modal distribution are observed, while the average particle size of the dispersions obtained at 50^{0}C is approximately 68 nm and the system shows a mono-modal distribution.

The actual maximum chain extension is related to the average particle size of PU dispersion. As a result, the total surface area of particles and the amount of NCO groups on the particles surface increase, and the actual maximum chain extension correspondingly increases. It was found that the average particle size of PU dispersion increases after post chain extension. Therefore the increase in particle sizes reveals that the chain extension mainly takes place on the particle surface. A chain extender molecule has two or multi amino groups and can react with NCO groups located both on the surface of single particle or different particles. So, the single particle size may increase and the particles may also aggregate together because of the bridging effect of the multifunctional chain extenders. In PU dispersion with DETA as chain extender, its particle size distribution is a multiple distribution and some large particles are even detected. It means that trifunctional chain extender DETA promotes the aggregation of particles (Carolina et al., 2008). The TEA influences the dispersion stability; at higher concentration of TEA the electrical bilayer disturb to some extent. As a result of more delocalized positive charges (protonated TEA) below or in the Stern layer, the absolute amount of negatively charged DMPA residues at the particle surface might be reduced (Michael et al., 2013).

Chitosan

Chitosan (CS) is a polysaccharide obtained by deacetylation of chitin, which is the major constituent of the exoskeleton of crustaceous water animals. Chitosan is structurally similar to cellulose and chitin (figure 12). Chitosan is recommended as a functional material, and this natural polymer has excellent properties such as biocompatibility, biodegradability, non-toxicity, and adsorption properties, so it can be used in a wide range of applications, such as membranes, removal of metal ions from wastewater, drug delivery systems, biological applications, tissue engineering, biosensors, scaffolds, and packaging (Mehdi et al., 2010).

Lignin

Lignin is a complex a phenolic polymer derived from wood, and is an integral part of the secondary cell walls of plants. Lignin is possibly third most abundant biopolymer in nature after cellulose and chitin. Lignin is usually considered as a polyphenolic material having an amorphous structure, which arises from an enzyme-initiated dehydrogenative polymerization of p-coumaryl, coniferyl and sinapyl alcohols. Lignin is considered to be the one of the most promising future organic resources because it is renewable and various chemical functional groups present in lignin structure include hydroxyl, methoxyl, carbonyl and
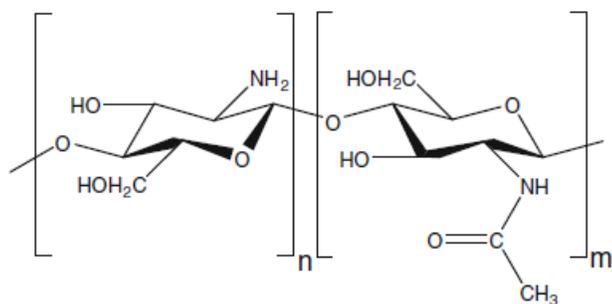
Fig. 12: Structure of chitosan

carboxyl moieties in various amounts depending on its botanic origin (Akriti et al., 2014).

CONCLUSIONS

Considering tremendously increased stringent environmental regulations and dramatic fluctuation in the fossil resources, the exploration of naturally available material can be the obvious option to develop various chemistries for the coating industry. The utilization of such material is only due to the fact that these materials possess reactive functionalities which can be directly utilized to synthesized number of resins such as alkyd, epoxy, polyurethane, polyamide, polyester amide, polyacrylate etc. These chemistries can be further formulated to various types of pigmented coatings for wide variety of applications. Besides huge number of research work, the implementation of bio-materials in coating industry faces some difficulties such as complicated extraction processes, followed by lengthy purifications, higher processing cost of some of the materials and required yield at the end. Although bio-materials possess some limitations, the outlook for replacement of petroleum based raw materials is still promising due to its easy availability, eco-friendliness and easy bio-degradability. Still the commercialization of some of the natural resources will require further research and development for cost effective solutions.

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