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Abstract- The manufacture of conventional polyurethanes include the use of isocyanates, which in turn require using toxic and hazardous phosgene. The safety devices are necessary to prepare these monomers. Therefore, the huge investment is inevitable for this process. Also, these monomers cannot be considered as environmentally friendly chemicals. The increasing global awareness for protection of environment from chemical pollutants has created a necessary demand for environmentally benign products. The reaction of cyclic carbonates (polycarbonates) with amines results in formation of hydroxyurethanes that can be taken into account as a unique reaction. This specific reaction has been investigated over last few years. Most chemists have been strongly attracted by this technique that is due to its potential application to prepare the green, non-toxic, non-sensitive towards moisture isocyanate free polyurethanes.

Keywords: *isocyanate free polyurethane, synthesis, mechanism, application.*

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Synthesis and Applications of Isocyanate Free Polyurethane Materials

Mehdi Erfani Jazi [α], Thualfeqar Al-Mohanna [σ] & Fatemeh Aghabozorgi [ρ]

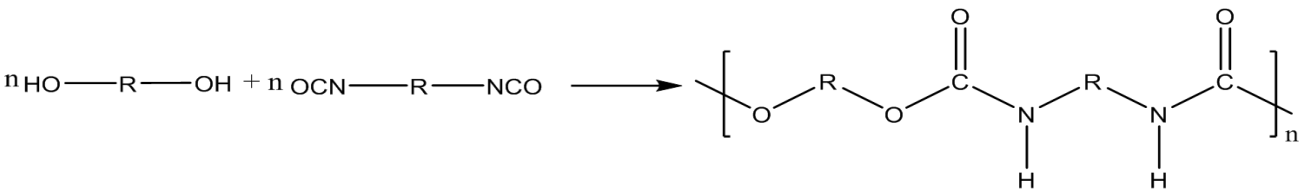
Abstract- The manufacture of conventional polyurethanes include the use of isocyanates, which in turn require using toxic and hazardous phosgene. The safety devices are necessary to prepare these monomers. Therefore, the huge investment is inevitable for this process. Also, these monomers cannot be considered as environmentally friendly chemicals. The increasing global awareness for protection of environment from chemical pollutants has created a necessary demand for environmentally benign products. The reaction of cyclic carbonates (polycarbonates) with amines results in formation of hydroxyurethanes that can be taken into account as a unique reaction. This specific reaction has been investigated over last few years. Most chemists have been strongly attracted by this technique that is due to its potential application to prepare the green, non-toxic, non-sensitive towards moisture isocyanate free polyurethanes. This review is focused on the variety of catalysts used to prepare isocyanate free polyurethanes from five membered cyclic polycarbonates. Also, the reaction mechanism and kinetics for their synthesis have been discussed. In this review, the six-membered cyclic carbonates depicted the higher reactivity rather than five-membered cyclic carbonates for production of non-isocyanate polyurethanes. The various functions of isocyanate free polyurethanes in different fields such as coatings, construction and bio-composites have been summarized.

Keywords: isocyanate free polyurethane, synthesis, mechanism, application.

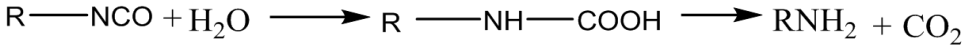
I. Introduction

The polymer materials based on polyurethane segments have attracted a considerable attention in both academic and industrial fields that is due to the versatile features of polyurethane like its high elasticity, thermal and chemical stability, resistant toward abrasion and other excellent properties. These outstanding properties create polyurethane materials asa suitable candidate which can be used in the coating industry[1]. The worldwide utilization of coatings in the various applications in the industry has been successfully attained. There has been a continuous development on synthesis of polyurethane coatings based on bio-materials to remove the health and environmental hazards. These bio-based polymers should have the high performance capabilities in the coatings industry[1].

The utilization of polyurethane compounds which are based on isocyanate chemistry(Scheme 1) has been considerably enhanced in comparison to other polymer materials. The polyurethane materials have distinguished properties but they suffer from some serious issues[2]. The isocyanate based-materials are toxic because they have been synthesized from toxic starting material called phosgene which jeopardizes both environment and human' life[3].Also, polyurethane based-isocyanate materials are sensitive towards moisture and when they are exposed to the environment, an irreversible reaction between isocyanate and water would occur, producing the urea and carbon dioxide which results a useless product (Scheme 2)[2b, 4]. The other negative aspect of conventional polyurethanes is an intrinsic weakness in the hydrolytic bonds of molecules which cause them to be degraded gradually in the environmental conditions. Therefore, the chemical resistance of polyurethane polymers is poor in the environment and it can create a grave challenge for their use in the long period of time[4].



Scheme 1 : Reaction between diols and isocyanates to form linear polyurethanes



Scheme 2 : Hydrolysis of isocyanate in the environment

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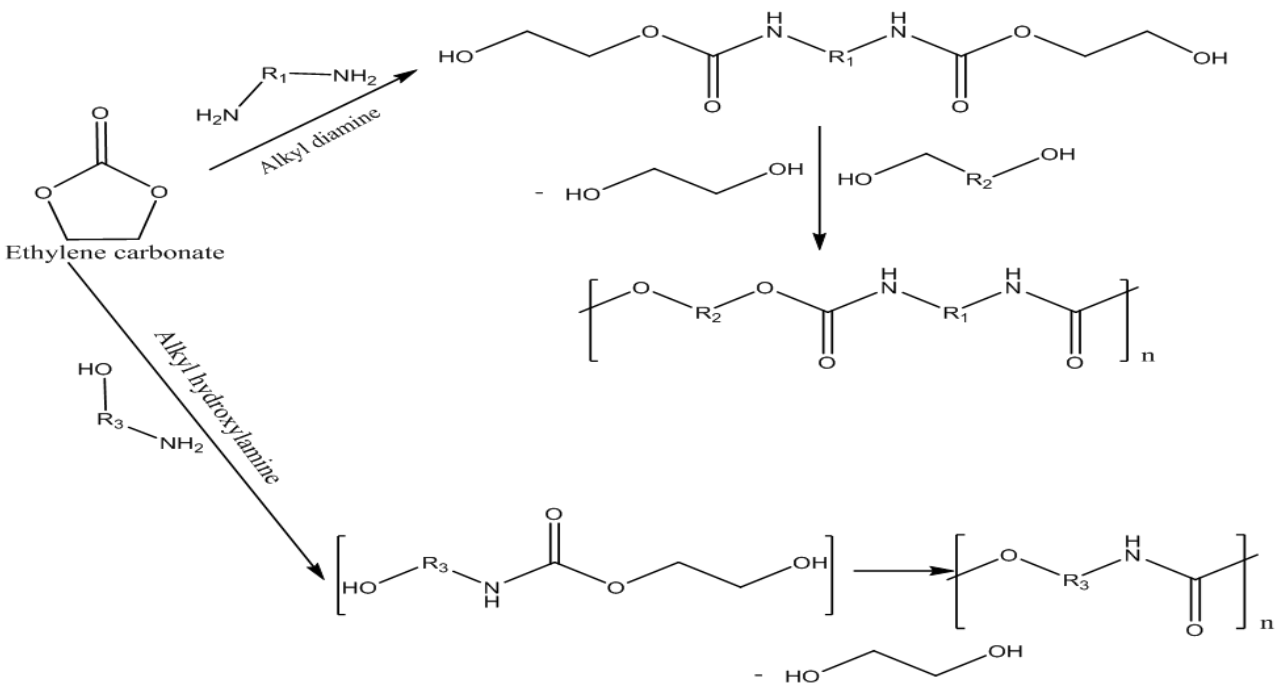
a) Isocyante free polyurethanes

The first use of ethylene carbonate and amines for synthesis and preparation of polymeric polyurethanes has been reported by Dyer and Scott [5]. The ethylene carbonate and primary diamines react with each other to form bis(2-hydroxyethyl carbonate) with release of ethylene glycol as a byproduct under vacuum conditions at 150°C. The catalyst used for this reaction was zinc borate or barium oxide (scheme 3). Also, the preparation of substituted polyurethanes has been achieved by reaction between amino alcohols such as 1,10 aminodecanol or 4-aminomethylbenzyl alcohol and ethylene carbonates through formation of intermediate compounds. In addition, the bis(2-hydroxyethyl carbamate) can be obtained via the transurethanization reaction of ethylene carbonate and 1,4-diaminobutane or 1,6-diaminohexane a long with formation of 1,6-hexanediol or 1,10-decanediol as side products. This reaction is accelerated in presence of tin catalyst [6]. The polyurethane characterization shows both urethanes and urea groups in those products[7].



Scheme 3 : Synthesis of polyhydroxyurethane materials from cyclic carbonates

Another strategy for synthesis of the polyurethanes compounds is reaction between urea and ethyl alcohol. This method is called transesterification reaction because it is similar to the mechanism of transesterification of alcohol with carboxylic acid. The diol organic compounds containing urethane and biureate linkages have been prepared and synthesized based on this strategy[8]. The polyurethane prepolymermaterials contain isocyanate functional groups which are used as the chain extenders that can form urethane bonds in the backbone structure. Basically the diol organic materials obtained from transesterification of urea and ethyl alcohol are employed as the curing agents in the conventional method of polyurethanesynthesis[8a, 9].

Furthermore, several efforts had been performed to synthesize diols organic compounds using urea and monoethanolamine(or urea and ethylene glycol) which can produce the highly viscous diol organic materials. These materials can be used as the cross linking materials which have a capability to react with diisocyantes and melamine formaldehyde in order to produce the rigid and flexible coatings (Scheme 4a)[10]. Consequently, the production of coatings which have similar properties to urethane materials either without any utilization of diisosyanates or a limited use of diisocyanateshas remarkably reduced the consumption of toxic diisocyanates. Nevertheless, these reactions can produce the undesirable byproducts such as ethylene glycol, carbamates and etc (Scheme 4b) [6, 11].

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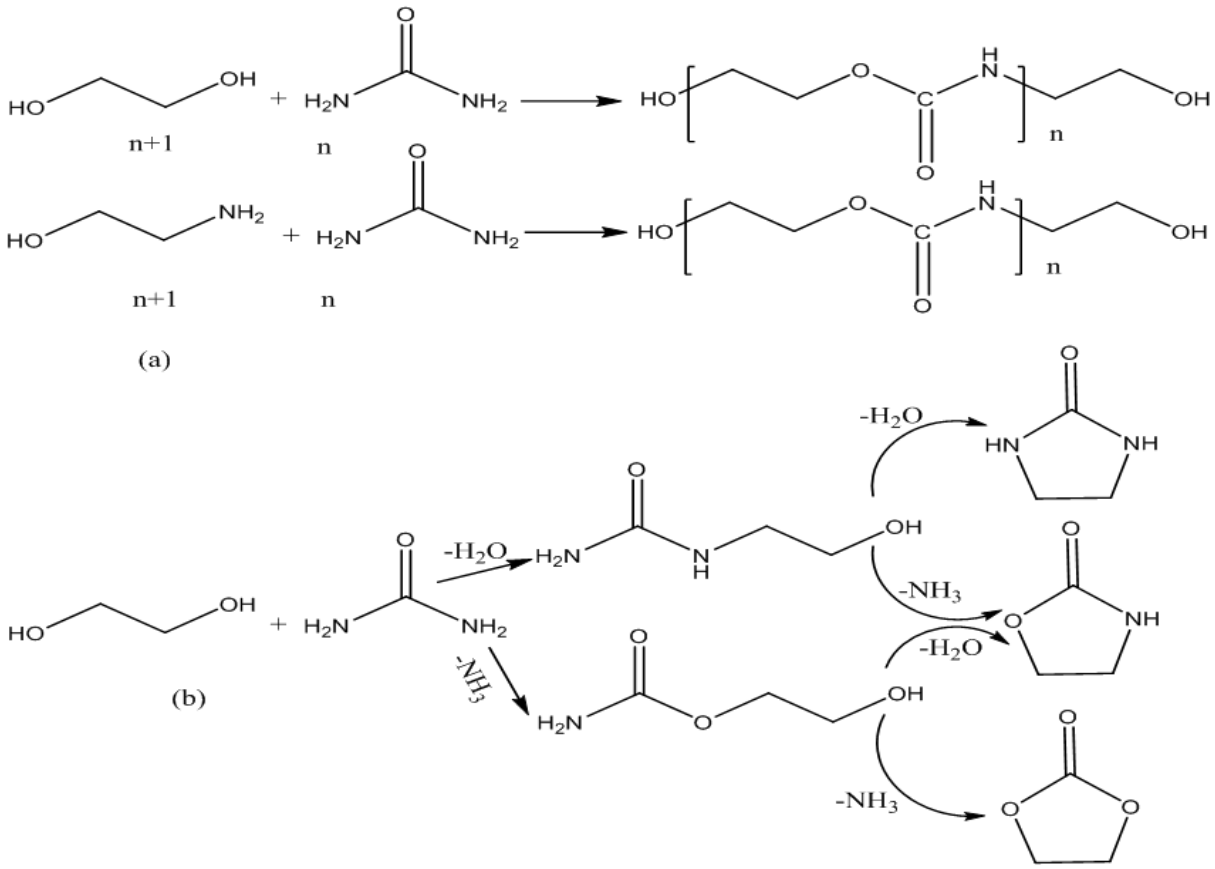
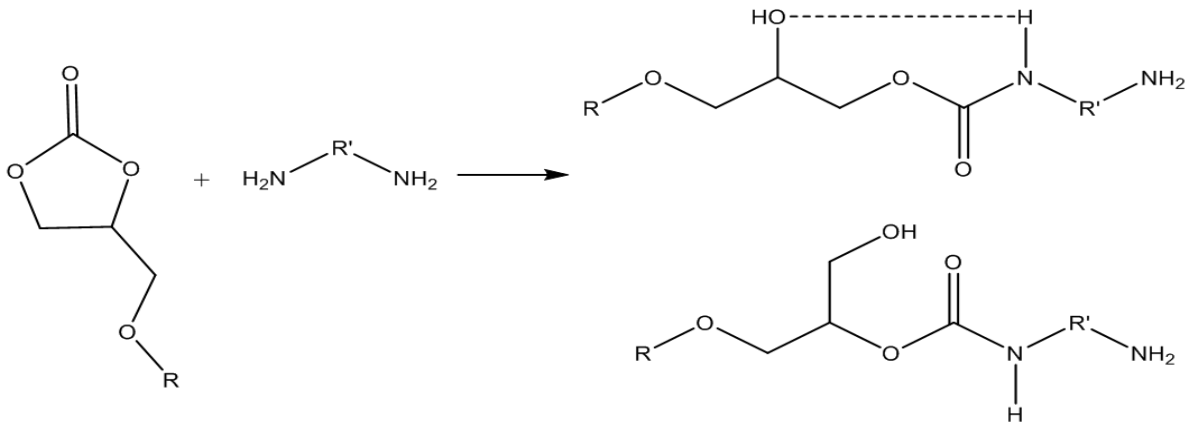


Scheme 4 (a) : Preparation of polyhydroxyurethanes from ethylene glycol or ethanolamine with urea. (b) Formation of side products from reaction of ethylene glycol and urea.

The traditional production of hydroxyurethane is the reaction between cyclic carbonate and amine that can be seen as the best alternative method to produce non-isocyanate polyurethane materials [12]. Particularly, the hydroxyurethane materials are formed through the reaction of five or six membered cyclic carbonates with the materials containing-amine functional groups. The products of this reaction show two isomers which contain both urethane and hydroxyl groups. The main feature of poly(hyroxyurethane) compoundsis presence of hydroxyl groups which have a considerable capability to form intramolecular hydrogen bonds with urethane functions in the backbone structure of polymer (Scheme 5) [2a, 13].

Consequently, the formation of hydrogen bonds between alcohol and urethane functional groups decreases the susceptibility of polyurethanes towards moistureabsorption and deterioration by abrasion that leads to the remarkable enhancement in chemical and thermal stability of polyhydroxyurethanes[13-14].



Scheme 5 : Reaction of diamine with substituted cyclic carbonate and formation intermolecular hydrogen bonds

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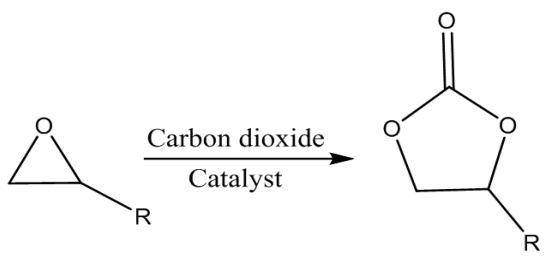
Therefore, the thermal properties of polymers are influenced by hydroxyl functional groups. The compounds with intramolecular hydrogen bonds display the excellent chemical resistance towards the similar compounds without such intramolecular hydrogen bonds [15]. Furthermore, the process of the isocyanate-free polyurethane synthesis is not sensitive to the moisture and thus the coating application of isocyanate-free polyurethane is much better than that of conventional polyurethane compounds [7].

Moreover, there are strict environmental regulations and therefore the application of more environmentally benign procedures to prepare non-hazardous polymer compounds is unavoidable. There has been a limited research for the exploration of new strategies such as utilization of cyclic carbonates materials containing amine functional groups to prepare the high value added polymers. Thus, the utilization of cyclic carbonates, which are produced from the incorporation of carbon dioxide into epoxides, should be considered as an environmental advantage because the carbon dioxide consumption leads to a reduction in the amount of greenhouse gases[16].The basic preparation and synthesis of isocyanate-free polyurethane compounds is based on the reaction of cyclic carbonates with amines or polyamines[17].

II. The Synthesis of Cyclic Carbonates

Basically the cyclic carbonates are starting materials for synthesis of isocyanate-free polyurethanes and there is a variety of methods for preparation of cyclic carbonates. In particular, the main and cost effective method is the incorporation of carbon dioxide into the epoxy rings because the epoxy compounds are easily reacted with carbon dioxide in presence of catalyst at a high temperature to produce cyclic carbonate materials (Scheme 6). Therefore, the cyclic carbonate can be used as a precursor to react with the various amine functional groups to produce different types of linear or crosslinked-isocyanate-free polyurethane networks[18]. For example, the oxirane (ethylene oxide) can react with carbon dioxide which is not a flammable and hazardous reagent in order to form cyclic carbonate [19].



Scheme 6 : Cycloaddition reaction of substituted epoxide with CO_2 in presence of catalyst

III. Reaction of Amines or Polyamines with Cyclic Carbonates

Amines and polyamines display a considerable affinity in presence of catalyst to react with cyclic carbonates thorough the ring opening addition reaction. Particularly the reaction rate of this type of addition reaction is very slow at room temperature in comparison with epoxy-amine reactions. Therefore, the higher temperature can accelerate the reaction rate of amines with cyclic carbonates. Also, in the reaction of amines with cyclic carbonates, the polyaliphatic amines are more reactive than aromatic amines. However, the polyurethane materials containing aliphatic amine functional groups represent the lower tensile strength than ones containing aromatic amine functional groups[20]. The alkyl/aryl amines should possess at least two primary amine functional groups in order to create a cross-linked polymer network with the multifunctional cyclic carbonate materials. However, the secondary and tertiary amine functional groups are not capable to carry out this specific reaction with cyclic carbonate compounds. Polyamines such as polyoxypropylene diamine and polyoxypropylenetriamine and other alkyl amines such as ethylenediamine, tris(2-aminoethyl)amine and heptamethylenediamine have dual amine functional groups in order to react with multifunctional cyclic carbonate compounds [8b, 21].

The backbone structure of polymer and the kind of cross-linking reagents used for polymerization reaction can determine the polyurethane properties. For example, if the structure of cyclocarbonate oligomers only possesses the cyclocarbonate functional groups, this kind of oligomers belong to the non-isocyanate polyurethane compounds while if the backbone structure of cyclocarbonate materials contains other functional groups such as carboxyl, hydroxyl, ether and epoxy groups, this kind of materials can produce hybrid-non-isocyanate polyurethane compounds. Specifically, the backbone structure of these two kinds of polyurethane materials can create the different polymers with various properties[7, 13].

The hydroxyurethane polymer compounds containing the amine functional groups can be synthesized through extra amounts of diamines or amines. These compounds represent different reactivities that can be used as cross-linking reagents or diluents for the adhesives and painting industries[22]. Also, Polyhydroxyurethane materials containing cyclocarbonate functional groups have been synthesized in presence of excess amounts of a bis-glycidyl ether of 1,4-cyclohexanedimethanol with a polyoxypropylenediamine[23].

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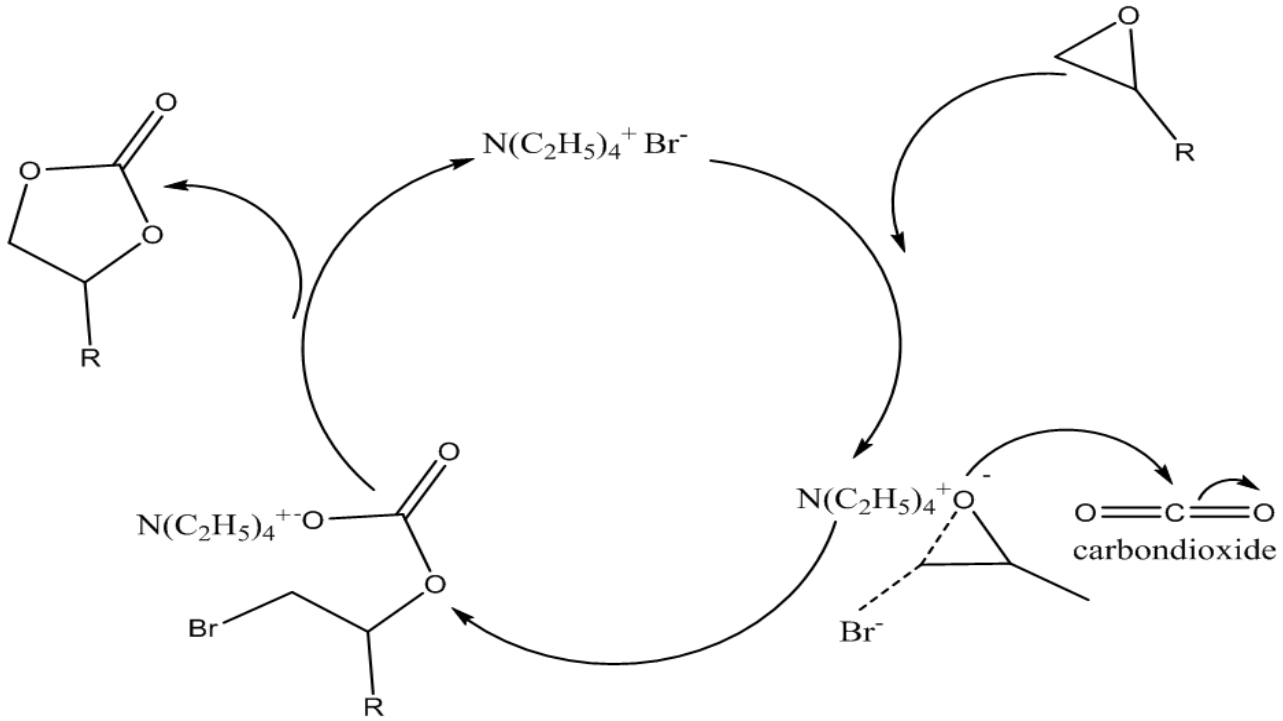
IV. Preparation and Synthesis of Cyclic Carbonate Oligomers and Polymers via Catalysts

The different kinds of catalysts are employedto synthesize the cyclic carbonate materials. The general process of making cyclic carbonate compounds is two step processes including the ring opening of epoxides via a catalyst and a simultaneous incorporation of carbon dioxide into the transition state of catalyst-alkoxides (Scheme 7)[24].



Scheme 7 : The role of quaternary ammonium salt (catalyst) for preparation of cyclic carbonate

The insertion of carbon dioxide into the epoxide groups is an effortless reaction which can produce the considerable yields of favorable compounds (cyclic carbonates) at either atmospheric or high pressure. The catalysts used in this reaction act as a driving force in order to begin (commence) the process by activating either one reactant or both reactants at the same time. For example, the oxygen of ethylene oxide can be activated by Lewic acid. Then, this transition state is attacked by a nuclephilic group leading to the ring opening of etylene oxide[25].

The nickel complexes containing phosphine groups, tribenzene phosphine, quaternary ammonium compounds and ribenzenephosphoniumchloride containing ehter functional groups have been investigated as a ring opener catalyst in the past [26]. Moreover, the homogeneoussalen comlexes including aluminum and chromium salen complexes display the highly active and selective catalysts to activate the reaction of epoxides with carbon dioxide. The zinc complexes containing alkoxide and phenoxide functional groups and also cobalt(III) complexes are shown as the efficient catalysts at low temperatures creating cyclic carbonates from oxiranes and carbon dioxide[27]. The halide salts such as potassium bromide, sodium iodide, lithium bromide and etc, are not relatively soluble in the organic solvents which result the low conversion of oxiranes to the cyclocarbonates[17, 28].However, these halide salts such as potassium iodide are activated as the very effective catalysts in presence of crown ethers [29].

Furthermore, the utilization of tetraalky-ammonium halides such as tetrabutyl- ammonium bromide (TBAB) and tetrabutylammonium iodide (TBAI) is considered as the most commonly used ionic liquids to catalyze the ring opening reaction of epoxies with carbon dioxide [16, 30]. The homogenous ionic liquid catalysts such as TBAB and TBAIcan selectively covert the epoxides to the cyclic carbonates or poly-cyclic carbonates in presence of carbon dioxide. In other words, these homogenous catalysts are strongly contributed in the process of capture of carbon dioxide by epoxides to selectively produce the high yield of desired products (poly-cyclic carbonates)[30b].

Moreover, the heterogeneous catalysts such as quaternary ammonium salts immobilized on the silica supports have been reported to give the remarkable yields of cyclic carbonates materials under supercritical carbon dioxide conditions [18]. The high temperature and pressure are required for this process. Therefore, this

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process is not considered as a cost effective process because it consumes much more energy. Thus, the utilization of silica supported-organic catalysts could be used as an alternative strategy in order to achieve a high yield of poly-carbonate materials which are produced from reaction of epoxides and carbon dioxide under atmospheric pressure[31].

Particularly, the silica surface (Si-OH) possesses the weak acidic reactive sites releasing (which can release) the protonto activate the epoxides and simultaneously the nucleophilic reagent like a halide anion attacks to the epoxy ring to initiate the ring opening reaction[32]. Generally, the organic salts and ionic liquids like phosphonium salts have lower catalytic activities than organic salts/ ionic salts supported onto the silica surface. This phenomenon probably is due to the synergistic effect between hydroxyl groups of silica and acidic sites of organic salts/ionic liquids that can be employed to activate carbon dioxide. Also, the immobilization or functionalization of organic salts/ionic liquids onto the surface of silica materials creates a good opportunity to readily recover the heterogeneous catalysts by a simple filtration and reusing them for several times without loss of their catalytic activity (performance) [32].

In theambient conditions, the catalytic systems including the tetra-nuclear zinc complexes and TBAI have been investigated to synthesize cyclic carbonates via capturing carbon dioxide. These systems represent the highest conversion of epoxides to the cyclic carbonates and the lowest impurities under mild conditions [33].

In the homogenous system, the separation of catalysts from the reaction solution is a main problem. Therefore, the catalytic systems based on the solid-state chemistry have been introduced to overcome with this problem[34]. For example, the different kinds of metal oxide and the ion-exchange resin systems have been investigated to easily recycle the catalysts from the reaction solution [35]. Nevertheless, these catalytic systems based on heterogeneous systems are not recommended because they produce by-products and also they are very expensive.

Recently, the synthesis of the ionic liquids functionalized or grafted onto surface of heterogeneous catalysts has been investigated for production of cyclic carbonates. This catalytic system possesses the properties of both homogenous ionic liquids and heterogeneous solid catalysts to activate both epoxides and carbon dioxide monomer to promote the production of cyclic carbonates. In particular, the ionic liquids such as sodium dodecylsulfate and 1,3-bis-(4-allyl-2,6-diisopropylphenyl) imidazolium chloride are respectively functionalized onto surface of polymer and mesoporous silica materials in order to introduce the ring opening or cycloaddition reaction of epoxides with CO_2[36].

In addition, the carboxylic acid functional groups based on imidazolium ionic liquids have been synthesized and incorporated onto the surface of silica materials for the cycloaddition reaction of carbon dioxide with epoxides[37]. Also, the amino acids have been modified with ionic liquids to investigate the ring opening reaction of epoxides with CO_2[38]. The ionic liquids functionalized onto the chitosan, cellulose and silica supports have been effectively investigated for their catalytic activities in the cycloaddition reaction between CO_2 and epoxides [39].

Moreover, a novel catalytic system based on the polymer supported ionic liquids containing diol functional groups has been developed to promote the cycloaddition reaction rate of CO_2 with epoxide compounds. The remarkable content of adjacent hydroxyl groups on the surface of ionic liquid has been observed to increase the reaction rate through the strong hydrogen bonds between oxygen atom of epoxide and hydrogen atom of hydroxyl groups. In the process of ring opening, this catalytic system has become more effective than Ionic liquids including monohydroxyl functional groups[40].

Basically, the reaction of cycloaddition of carbon dioxide with epoxide is carried out at elevated temperatures in the oil bath. However, the microwave irradiation system under controlled pressure and temperature has provided the more effective heating method than oil bath system. The microwave irradiation system is based on non-thermal effect which uses less thermal energy leading to a remarkable decline in the activation energy of cycloaddition reaction[41].

V. The Addition of Amines or Polyamines to Cyclic Carbonate for Synthesizing Isocyanate Free and Hybrid Polyurethanes

The addition of amines or polyamines to cyclic carbonate is considered as a nucleophilic attack followed by a deprotonation reaction (Scheme 8). Firstly, the nitrogen atom from amine group reacts with carbon atom from carboxyl group of cyclic carbonateto form a tetrahedral transition state. The ring opening reaction of cyclic carbonate using an amine is very slow which is due to the relative chemical stability of cyclic carbonate at a room temperature. In the second stage, another amine functional group is attacked to the tetrahedral transition state to remove the hydrogen atom followed by breaking the carbon-oxygen bond which in turn leads to generation of the alkyl-oxygen anion. Then, this stable compound is rapidly protonated in order to createthe final product[42]. The reaction between the amines and cyclic carbonates mainly produce two different isomers of hydroxyurethane. The major product of this reaction is hydroxyurethane which contain the secondary alcohol. The reaction selectivity towards forming hydroxyure-

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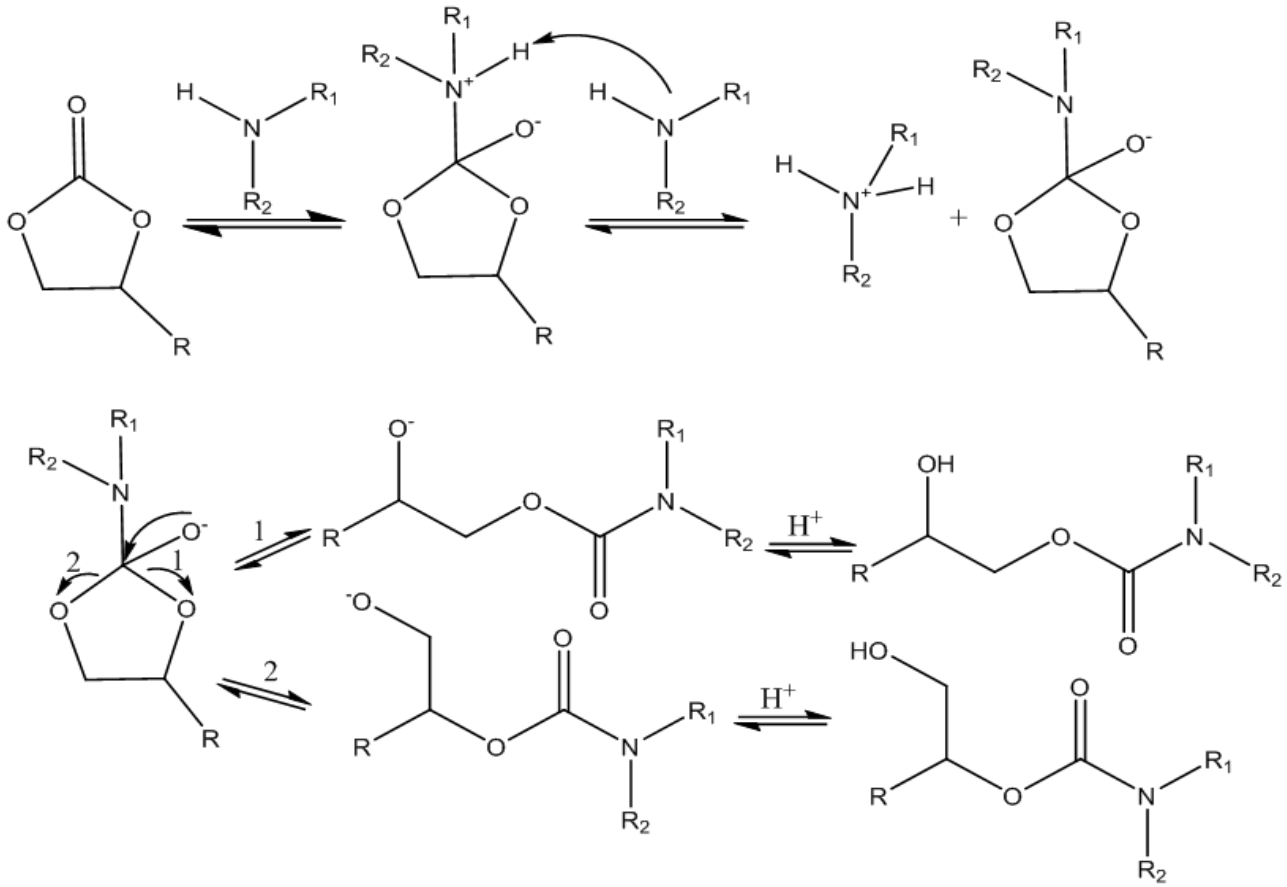
thane containing secondary alcohol is relatively corresponded to types of amines and solvents used for this reaction [43].



Scheme 8 : The mechanism of ring opening reaction of cyclic carbonate with amine

The different resources for synthesis of isocyanatefree polyurethane

a) *Isocyanate free polyurethane from cyclic carbonate polymers*

The utilization of cyclic carbonate for synthesis of polyurethane polymeric compounds is due to elimination of materials containing toxic isocyanate functional groups. Also, the cyclic carbonate materials have a strong capability to react with amine groups in order to produce hydroxyurethanes[17a].

The various types of polyurethane materials, which possess the modest and low molecular weight, are employed to produce different polymeric materials such as synthetic fibers, adhesives, painting and varnishing compounds, thermoplastic and thermosetting polymers. There are several strategies that can be used to synthesize cyclic carbonate compounds which contain five members. Basically, the reaction of oxirane materials with alkali metals containing hydrogen carbonate can produce cyclic carbonates [44]. Moreover, the reaction of ethylene or dimethyl carbonate with 1,2-glycols or glycerol can create cyclic carbonates with different properties. In addition, the reaction of propylene epoxide with butyrolactonecan generate different kinds of cyclic carbonates[45].

Nevertheless, the most facile strategy for synthesis of cyclic carbonates is through the reaction of carbon dioxide with epoxides. There are several examples of cyclic carbonates prepared from carbon dioxide and epoxides (Figure 1).

Vinyl ethylene carbonate is a cyclic carbonate monomer which can be introduced (inserted) to the backbone structure of the vinyl polymer. This monomer is synthesized from reaction of carbon dioxide and 3,4-epoxy-1-butene. Furthermore, this material has a strong capability to carry out the copolymerization reaction with styrene and various types of acrylates such as ethyl or butyl acrylates [46]. Another unsaturated monomer, which is used in the backbone structure of polymer, is vinyl carbonate that can be used in the coating formulation. This compound is synthesized from ethylene carbonate followed by the chlorination and dehyrochlorination reactions [47]. Another type of cyclic carbonate is the glycerol carbonate vinyl ether which is synthesized through the reaction of glycidyl vinyl ether with eitherCO_2 or sodium hydrogen carbonate [47a].

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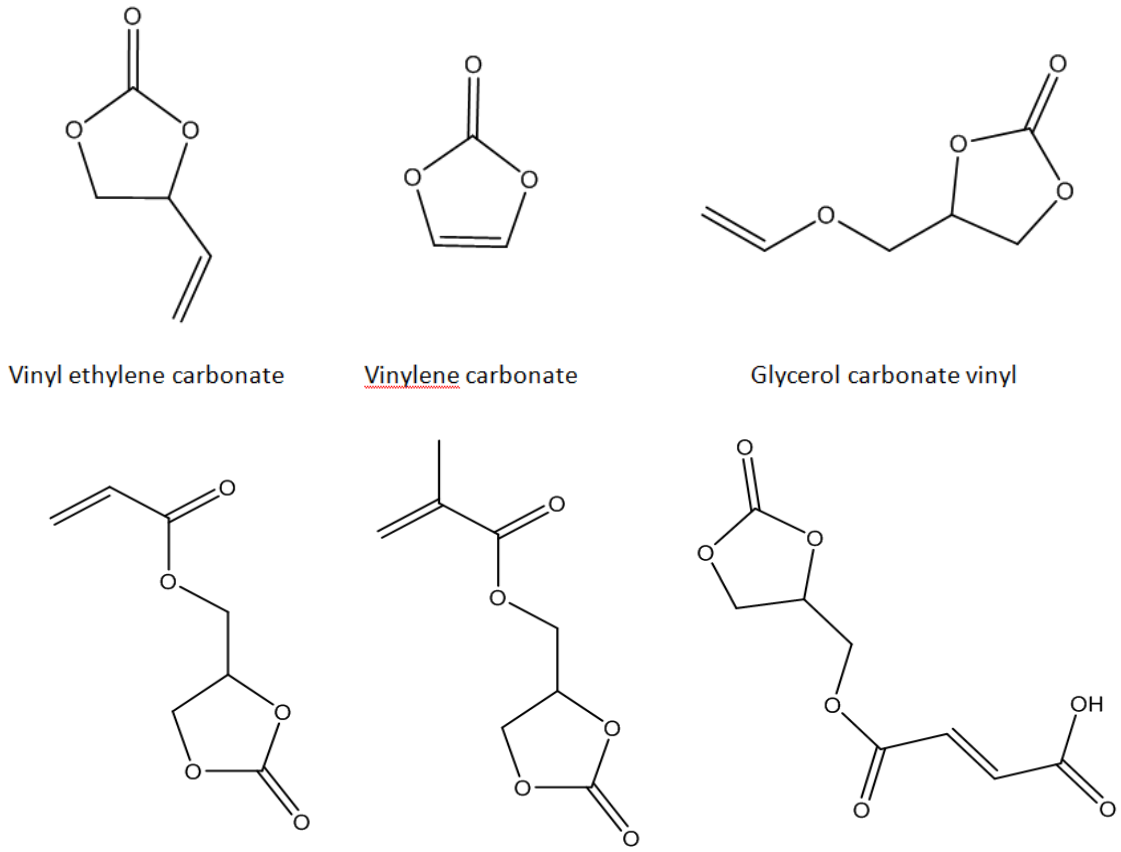
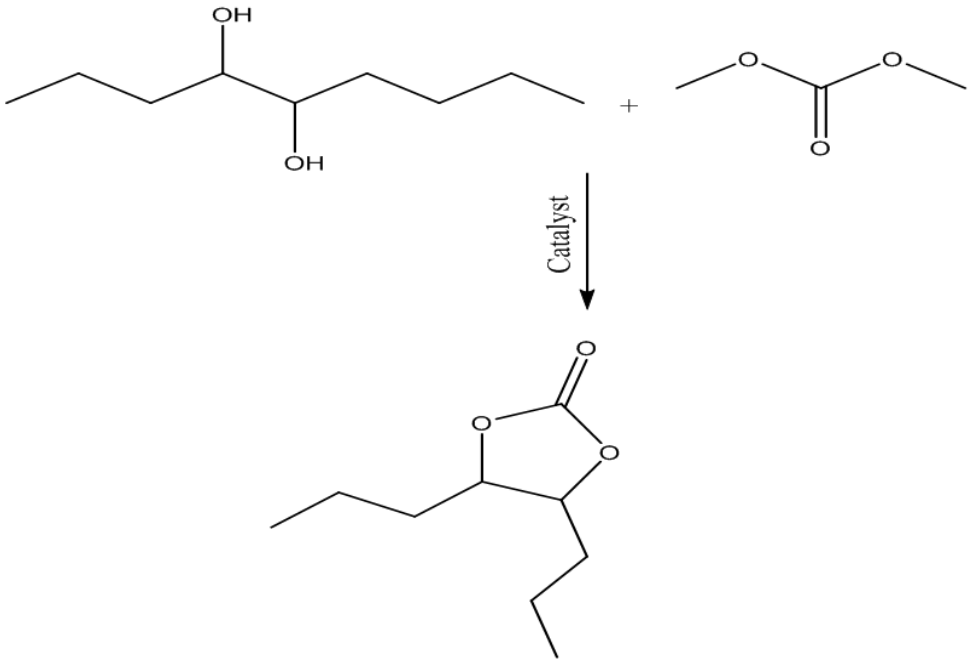


Fig. 1 : General structures of various cyclic carbonate materials

Moreover, the cyclic carbonates can be prepared from the reaction of dimetyl carbonate with the compounds containing vicinal-hydroxyl functional groups such as ethylene glycol and glycerol derivatives. The catalysts such as aluminum and magnesium hydrotalcitesare used to enhance the rate of reaction (Scheme 9)[48]. However, the corrosive and toxic route of cyclic carbonate production is based on phosgenation reaction of compounds containing hydroxyl functional groups in presence of a basic catalyst such as pyridine (Scheme 10) [49].



Scheme 9 : The reaction of dimethyl carbonate with a compound containing adjacent hydroxyl groups

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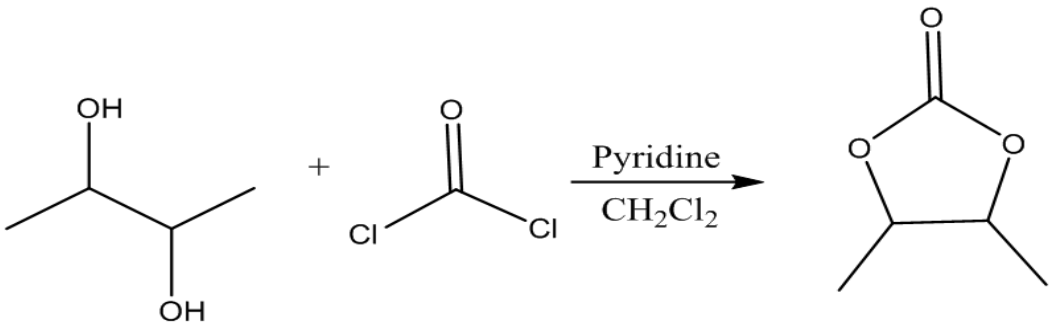

Scheme 10 : The reaction of phosgene with hydroxyl containing material

Furthermore, the glycerol carbonate synthesis displays a green route(which is) based on the transesterification of carbon dioxide with a non toxicdialkyl carbonate such as dimethyl carbonate[41, 50]. The synthesis of glycerol carbonate is a solvent free process (which is) performed in the presence of catalysts such as Magnesium oxide and calcium oxide, zeolites, enzymes, hydrotalcite and alkyl-amine metal oxides [45c, 48b, 51].

The glycerol carbonate can be modified with maleic acid or anhydride through esterification process in order to produce cyclic carbonate materials containing unsaturated acidic moieties which in turn can be used as a monomer in polymer synthesis [45a].

In addition, the halohydrins can react with carbon dioxide in the presence of catalyst in the room temperature to generate cyclic carbonates. Also, the halogenated carbonates in the elevated temperatures can be converted to cyclic carbonate. This reaction is performed in presence of catalyst such as mercuric acetate. The substituted propargyl alcohols undergo the cycloaddition reaction with CO_2. This process leads to synthesis of cyclic carbonates under relatively highertemperature[13, 52].

Moreover, the utilization of bi-functional cyclic carbonate polymers can be taken into account as cross-linking and modifying reagents for adhesive and coating industries. The cyclic carbonates containing reactive functional groups undergo the cycloaddition or condensation reaction with the oligomers containing other functional groups to generate the cyclic carbonate polymers which have outstanding properties. For instance, the esterification reaction of glycerol carbonates and di-functional carboxylic acid materials can produce cyclic carbonate materials containing ester linkages. These materials possess two different functional groups which make (cause) them to be a suitable candidate as cross linking reagents in coatings [53].

Bi-functional cyclic carbonate materials containing thioehthers have been prepared through one step reaction of thiol-ene compounds with glycerol carbonate derivatives. This process is solvent free and can produce the high yield of desirable materials which represent the lower glass transition (T_g) which in turn lead them to be functioned for exterior applications. Also, these materials don't possess the ester linkages and aromatic functional groups. Therefore, they are not hydrolysable and degraded towards the moisture and UV irradiation[54].

VI. Isocyantefree Synthesis of Polyurethanes from Epoxy Resins

The Epoxy resin is considered as a class of polymers which have various applications such as adhesives, coatings and composites. The epoxy resins have remarkable properties which can be used in the various fields. The reaction of the glycidyl ether of bisphenol-A containing terminal epoxy groups and CO_2 is used to generate bis-cyclic carbonate materials (scheme 11)[29a]. These oligomers have been prepared according to the various preparation methods and catalysts. The cyclic carbonate materials based on epoxy resins can be functionalized or cured with amines, diamines and polyamines functional groups to produce polyurethane compounds which can be used in the coating industry [55].

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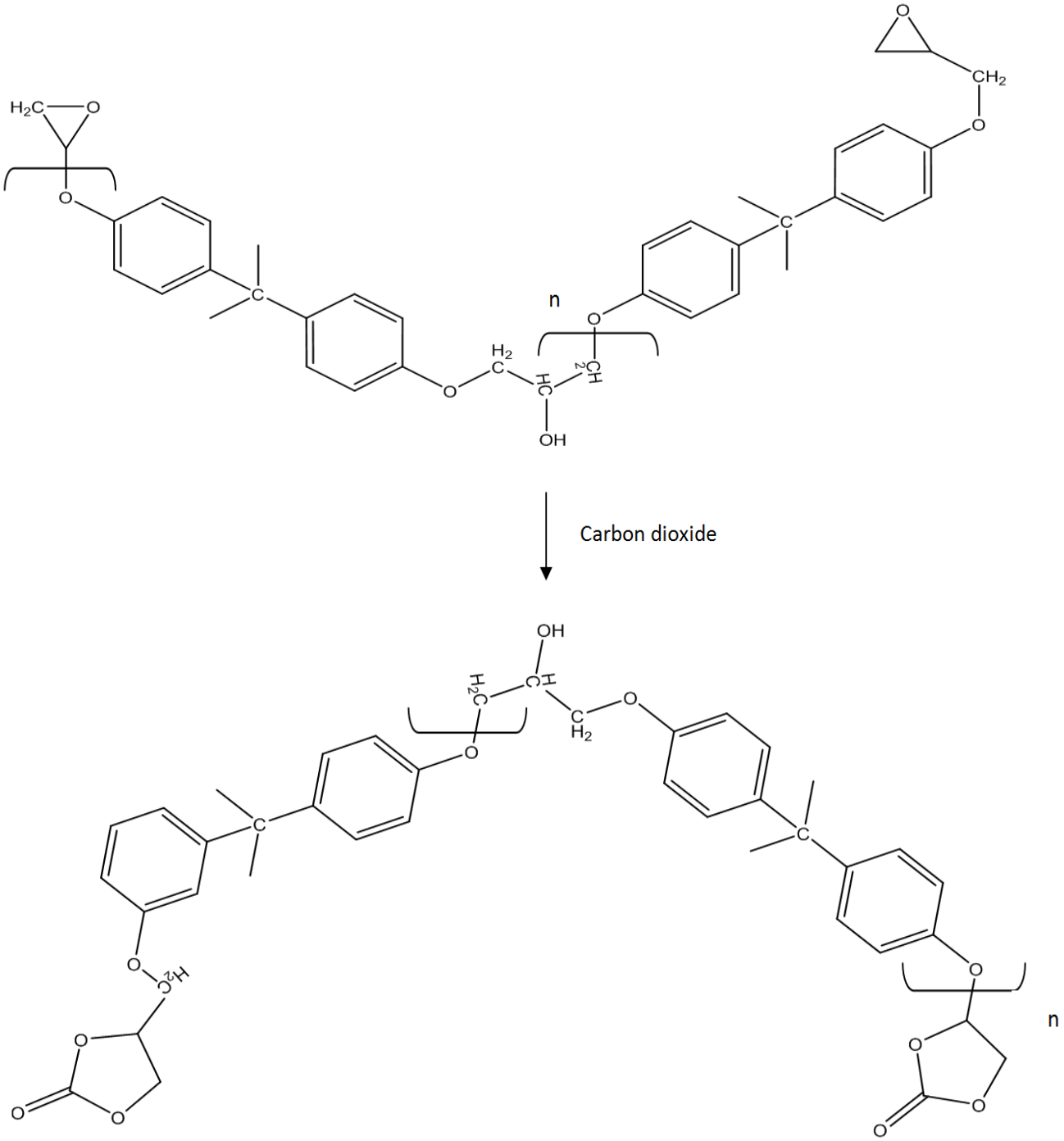

Scheme 11 : Cyclocarbonate synthesis from epoxy resin

The novalac epoxy resin, which is produced from the reaction of phenol with formaldehyde (F/P<1 molar ratio), can be employed in industrial coatings. This type of resin can be used to prepare isocyanate-free polyurethane materials as well (Scheme 12) [56]. These materials should possess outstanding features for both coatings and adhesives industries. Nevertheless, the aromatic ether functional groups which are sensitive to UV irradiation undergo the photo oxidative degradation of this kind of polyurethane compounds. This phenomenon is restricted the use of these materials for only interior applications and therefore they are not used for exterior applications. In addition, the utilization of toxic bisphenol-A (BPA) has been limited. Consequently, there is a serious concern to find alternative bio-resources which are classified asenvironmentally friendly resources to synthesize green polyurethane compounds.

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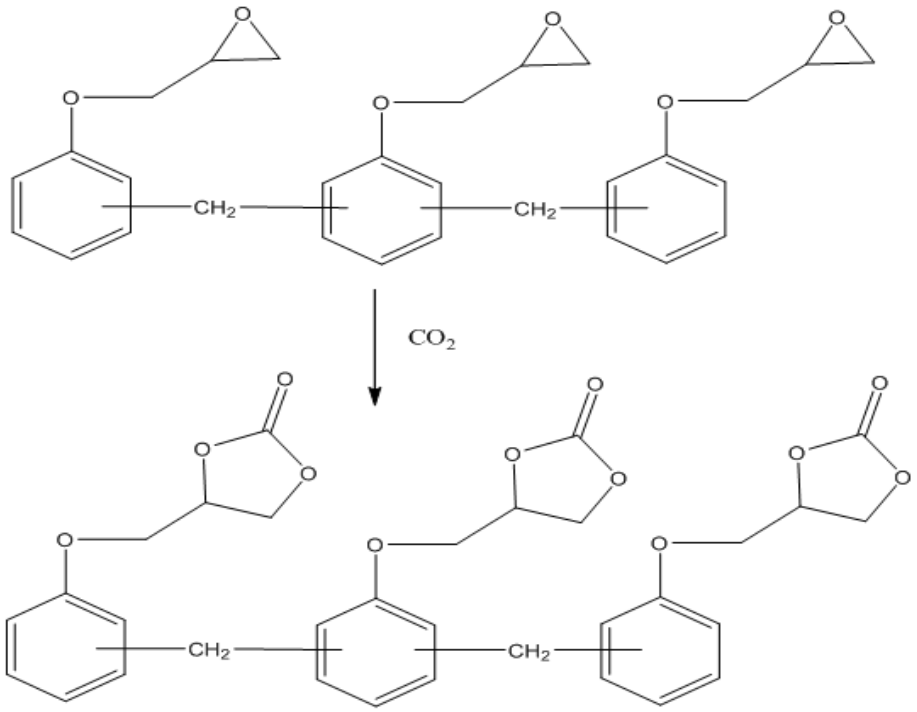

Scheme 12 : Cyclic carbonated materials obtained from epoxy novalac resin

The isocyanate-free polyurethane based polyester resins have been prepared for coating applications. These materials possess high performance. In particular, carboxylic acid compounds such as adipic acid and multifunctional alcohols such as hexanediol and trimethylol propane have been reacted with each other to prepare the acrylated polyester oligomer. Then, this oligomer has been incorporated to the product of the reaction of diamine with cyclic carbonate in order to generate the polyester resins containing flexible urethane segments. The formation of intermolecular hydrogen bonds between amine groups from urethane segments and carbonyl groups from ester groups has enhanced the polymer viscosity and its chemical resistance[57].

The modification of the cyclic carbonate with bis(4-glycidyloxy phenyl)phenyl phosphine oxide (BGPPO), and poly(propyleneglycol)diglycidyl ether (PPG-DGE) has been reported to prepare a novel cyclic carbonate. Then, the hexamethylene diamine was introduced(inserted) to the cyclic carbonate to synthesize a polyurethane material. Subsequently, the sol-gel method is used to incorporate the different concentrations of silica compound into the polyurethane. Therefore, the polyurethane-silica hybrids can be prepared through the isocyanate free strategy. In particular, the modulus and stiffness of polyurethane-silica hybrids were enhanced a long with increasing the concentrations of silica and phosphine oxide. Furthermore, an increase in the char percentage values and degradation temperatures in the thermal gravimetric analysis displays that the thermal stability of nanocomposites was improved[58].

VII. Synthesis of Isocyanate-Free Polyurethane Materials from Bio-Renewable Sources

The most chemicals produced from oil resources are considered as hazardous and toxic materials which can threaten both environment and human' life. Particularly, the rising environmental pollutants caused all people and researchers throughout the world to be concerned toward these serious issues. Consequently, there is a fundamental need to find alternatives to replace the harmful and toxic oil resources. The abundant bio-renewable resources are considered as environmentally friendly assets. Therefore, the use of these resources to produce eco-friendly materials is taken into account as a desirable effort. Also, the utilization of the sustainable bio-resources is being substantially investigated throughout the world[59].

The low price epoxidized soybean oil is considered as an abundant renewable resource which can be used as plasticizer in the production of polyvinyl chloride. The epoxidized soybean oil is efficiently reacted with carbon dioxide to produce the high yield five-membered cyclic carbonate soybean oil (Figure 2). Subsequently, this specific cyclic carbonate material can undergo the amine addition reaction to generate (give) the isocyanate-free polyurethane networks. These

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polyurethane materials based on epoxidized soybean oil possess the high tensile strength and other outstanding properties. The polyurethane characteristics are corresponded to the type of amines and cyclic carbonate oligemers in the polyurethane back bone structure [60].

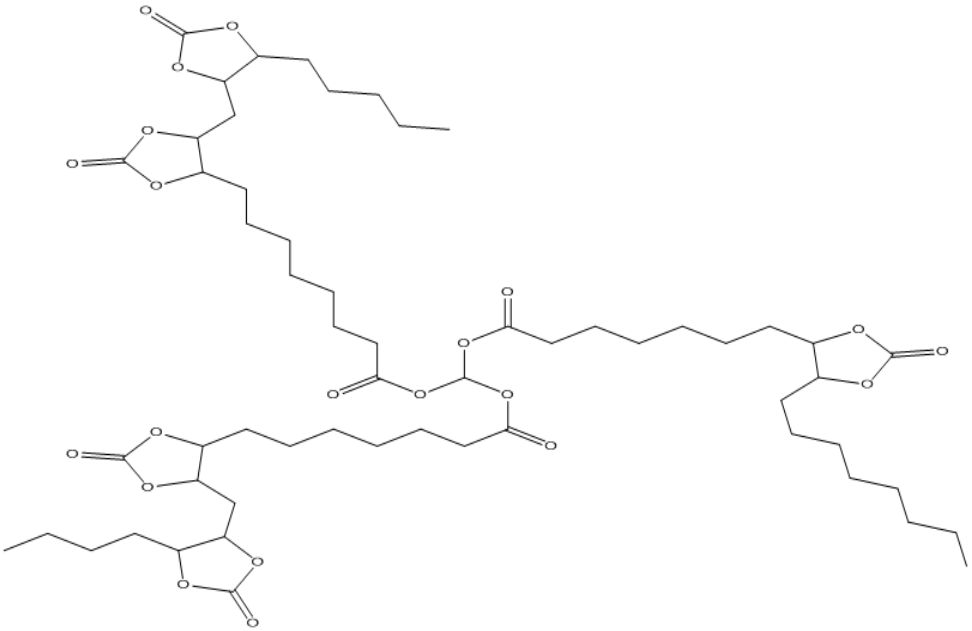

Fig 2 : Molecular structure of carbonated soybean oil

The utilization of different types of amines can affect the polyurethane properties. For instance, meta and para xylyenediamines, aliphatic diamines, cycloaliphatic diamiens can be used as softening reagents in the synthesis of isocyanate-free polyurethane materials. However, the amines or polyamines containing aromatic functional groups can be applied as hardeners in the structure of polyurethane networks because the aromatic functional groups leads to a remarkable increase in the tensile strength and elongation-to-break compared to the aliphatic ones[20].

Furthermore, the preparation of cyclocarbonate linseed oil has been successfully achieved by adding carbon dioxide monomers to epoxide functional groups. In this reaction, the different catalysts such as a homogenous tetra butyl ammonium bromide and the heterogeneous silica materials functionalized with alkyl pyridinium iodide have been employed effectively to accelerate the cycloaddition reaction of $CO_2$with epoxides. Also, in this strategy the catalyst can be readily recovered by simple filtration method which eliminate the solvent extraction process [28].

The number of cyclic carbonate functional groups is considerably high in the carbonated soybean oil, whereas the number of those groups is low in the carbonated linseed oil. A mixture of these two carbonated materials influenced the content of cyclic carbonate groups which in turn altered the concentration of cross-linking agents for curing purposes. Consequently, the variation of cross-linkers concentration has significantly affected the thermal and mechanical features of these novel polyurethane materials. The stiffness and glass transition temperature of polymers are significantly increased with enhancing the curing agent density. In this case, the isophrone diamine enhanced the glass transition temperature for 40°C [61].

Sometimes, the curing reaction of these cyclic carbonate oils can be accompanied with breaking the linkages of ester groups which leads to the remarkable reduction in the network density and tensile strength of polymer structure. Thus, the cyclic carbonate compounds should not have ester linkages for applications which require the high tensile strength[62].

Moreover, the difunctional limonene dioxide is a commercially available compound which originates from limonene. This material can be used as a solvent or diluents in the preparation of epoxy based resins. The limonene belongs to the terpenes family that can be employed as a bio-sustainable resource containing the high number of carbon-carbon double bonds. Also, limonene can be used as a suitable candidate for polyurethane synthesis because it is a free ester material[63]. This highly unsaturated material has a strong capability to react with the large scale of carbon dioxide monomers to generate the cyclic carbonate materials with a high content of cyclic carbonate functional groups.

In particular, the limonene dicarbonate compounds have stiff monomers which can increase the brittleness and the thermal deformation strength of isocyanate-free polyurethane materials[28, 62]. The

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multifunctional amines and diamines can cure the rigid structure of cyclic carbonate polyurethane for generation of stiff and brittle polyurethane networked structure. The high glass transition temperature, high Young's modulus and low elongation at break can reflect the rigid outstanding properties of polyurethane networks[28, 63].

Furthermore, the lignin is takeninto account as the first aromatic sustainable bio-renewable resource and one of the most abundant sustainable bio-polymers composed of different kinds of phenylpropane moieties in the earth[64]. The replacement of petroleum based polyol materials with lignin which is a bio-based polyol compound containing the high content of hydroxyl groupsh as been extensively studied to produce high value added materials[65]. Therefore, lignin can be employed as the bio-polyol resource to produce eco-friendly polyurethane materials.

The synthesis of bio-polyurethane materials obtained from both lignin and cyclic carbonate soybean oil has been successfully achieved. The 3-aminopropyltriethoxysilane has been used as a bridging reagent between lignin and cyclic carbonate soybean oil. This coupling agent can react with cyclic carbonate functional groups to generate the polyurethane segments. Then the lignin can be substituted with hydroxyl groups on the silica surface of coupling agent. This bio-based polyurethane elastomer represents the high tensile strength which is due to incorporation of lignin into the polyurethane network. This material can be used as thermoplastic films, adhesives, coatings and elastomers[66].

In addition, the novel lignin-glycerol based polyurethane materials have been prepared through the addition reaction of amines or diamines to the cyclic carbonate materials. The cyclic carbonate compounds have been extracted from lignin. The lignin-based polyurethane (which is) synthesized from non-isocyanate route has a higher glass transition temperature than traditional polyurethanes synthesized from bisphenol-A based on isocyanate route [67]. This novel isocyanate-free synthesis of polyurethane reveals (opens up) the new horizons in the synthesis of environmentally friendly polyurethanes.

VIII. Application of Isocyanate-Free Polyurethane Materials in Nanotechnology

The excellent performance of non-isocyanate polyurethane systems could be employed in the nanostructured networks. The nanocomposites based silica-polyurethane materials possess the high stiffness, transparency and strength towards break. The silica nanoparticles functionalized with cyclic carbonate compounds, are synthesized from the reaction of tetraethylorthosilicate and cyclic carbonated glycidoxysilanes through the sol-gel strategy. Basically, the silica nanoparticels can act as cross-linking agents in order to strongly increase the properties of nanocomposite coatings and reduce the moisture adsorption on the coating surface[68].

Moreover, the preparation of reactive organic precursors has been successfully archived through isocyanate-free technology. The synthesis of polyurethane materials containing organic silane groups from 1,3 propane diamine and cyclic carbonated glycidoxypropyltrimethoxysilane has been reported. The reactive organic compound possesses six methoxy functional groups, which are susceptible for hydrolysis, can facilitate the sol-gel process. In this process, the coatings containing both organic and inorganic functional groups were applied as a surface protection in the aluminum alloys[69].

IX. Isocyanate Free Polyurethane Materials made of Six-Membered Cyclic Carbonates

The various six-membered cyclic carbonate compounds can be employed effectively in the polyurethane synthesis. The different routes have been used to synthesize these materials. For instance, trimethylene carbonate is produced from reaction of 1,3-propanediol with phosgene derivatives. However, the green route for synthesis of six-membered cyclic carbonate is the carbon dioxide cycloaddition reaction with oxetanes at higher temperature and pressure in presence of a homogenous catalyst[70].

Furthermore, the transesterification of 1,3-diols with dialkyl carbonates that is an environmentally friendly procedure has been offered for synthesis of six-membered cyclic carbonates[70]. In addition, the homogenous metallic catalysts, metal oxides, metal carbonates and phosphazene materials have been employed to synthesize the various types of six-membered cyclic carbonates in the past [71].

Moreover, the green conversion oftrimethyol propane and dialkyl carbonates to six-membered cyclic carbonates through a lipase mediated reaction has been successfully achieved [72]. The six-membered cyclic carbonate materials derived from trimethyol propane could be modified (incorporated) with different functional groups for specific applications.

The six-membered cyclic carbonate materials are susceptible to undergo the ring-opening polymerization in presence of anionic reagents to generate the corresponding linear polycarbonates without the loss of CO_2 and volume degradation. In the presence of anionic reagents, the six-membered cyclic carbonates are less thermodynamically stable than the linear polycarbonates[73]. However, in the presence of cationic reagents the six-membered cyclic carbonates underwent the partial elimination of CO_2 in order to

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produce linear polycarbonates containing the ether moieties [74].

The five-membered cyclic carbonates are not readily polymerized to yield linear polycarbonate materials because they possess the stable five-membered rings but the partial formation of polyethercarbonates could be achieved by loss of carbon dioxide in presence of catalysts such as metal alkoxides, metal acetylacetone and metal alkyls. Nevertheless, the five-membered cyclic carbonates significantly undergo the amine addition reaction to yield the desired polyhyroxyurethanes[75].

The larger ring size of cyclic carbonates leads them to become more susceptible to react with amines or polyamines in order to form hydroxyurethane or polyurethane materials. Therefore, the cyclic carbonates containing six or seven members represent the higher activity for polymerization than five-membered cyclic carbonates [76].

In particular, the reaction of five-membered cyclic carbonates with amines is relatively slow at ambient temperature. Furthermore, the molecular weight of polyhyroxyurethane materials generated from cyclic carbonate is lower than that of conventional polyurethane compounds obtained from diisocyanates and diols. These disadvantages have relatively restricted the widespread utilization and production of isocyanate-free polyhyroxyurethanes[77].

X. Properties of Isocyanate-Free Polyurethane Coatings

The isocyanate-free polyurethane coatings contain very low volatile organic compounds. Also, they can be classified as non-porous materials. They do not react with moisture as well. Therefore, these materials have higher coatings performance compared to conventional polyurethane systems. The chemical and thermal stabilities of these materials are relatively higher than those polyurethanes obtained from conventional method. The basic properties of these specific coatings are strongly dependent to the type of cross-linking agents[78].

Furthermore, the stoichiometric ratios of amine-to-carbonate can generate the regular structured networks in the polymer. These networks have high density, stiffness, T_g and tensile strengths. Nevertheless, the non-stoichiometric ratios of amine-to-carbonate could lead to a significant decrease in coating performance properties. In addition, the samples prepared from the excess amounts of amine or diamine display the higher elongation at break than those obtained from an equal stoichiometric ratio of amine-to-carbonate[79].

Moreover, the various amines or diamines with different molecular weights can considerably affect the properties of polymers. For instance stiffness, hardness and tensile strength of polymers obtained from short chain diamines are much higher than those of polymers obtained from long chain diamines. This phenomenon is related to the different density of cross-linking agents. Also, the different diamines possess the various capabilities to create intermolecular hydrogen bonds in order to increase the chemical resistance of the polymer[78-79].

The isocyanate-free polyurethane materials cannot be employed efficiently in the interior applications such as floor and furniture adhesives because they are not able to perform the fast curing processes in the room temperature. Basically, the cyclic carbonates rapidly react with amines or diamines at elevated temperature. In contrast, diisocyanate materials have a strong capability to react with polyols at any conditions. Also, the mechanical and chemical features of isocyanate-free polyurethanes are comparable to polyurethane materials obtained from traditional conventional system[80].

XI. The Benefits of Isocyanate Free Polyurethanes over Conventional Polyurethanes

The toxic isocyanates are employed in the conventional process of generating the linear and networked polyurethane materials. However, the isocyanate-free polyurethane compounds are produced from diols, polyols, carbon dioxide and diamines which are based on eco-friendly chemical substances. The production process of isocyanate-free polyurethane materials is based on fixation of CO_2 in coatings. These materials don't have any pores and they are not permeable towards chemical solutions and microorganisms. Therefore, they are not easily degraded in the environment. Also once they are exposed to the moisture, they don't react with water on their surfaces. Thus, an essential care, when applying diisocyanates to prevent the carbon dioxide formation resulting inporosity, is not required. Moreover, in the conventional method of polyurethane synthesis the free-solvent curing process should be performed with a great care in presence of diisocyanates to exclude water from atmosphere. This is process is eliminated in the synthesis of isocyanate free polyurethane materials.

XII. Applications of Isocyanate Free Polyurethane Materials

The isocyanate-free polyurethane polymers have some applications in the coatings and polymer industries. In particular, the isocyanate free polyurethane could be functioned for thermo-stable adhesives, UV-resistant coatings and monolithic adhesives or coatings [81]. The main promising way to enhance the chemical and thermal stability of isocyanate-free polyurethane

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materials is utilizing the difunctional hyroxyalkyl urethane glycols as an additive. These glycols containing the urethane bonds can be used as diols for synthesis of polymer materials as well [81-82].

The aminosilanes and cyclic carbonates are specifically used for synthesis of thermosetting polymers. These coatings can be used in the various fields such as non-porous monolithic coatings, the protection against corrosion for coverings and linings, wood and metallic surfaces, retention of color and in the marine environment[81]. The isocyanate-free polyurethane materials can be used as a corrosion protection in a long period of time because they have a non-porous structure which leads them to have an effective performance in the highly basic or acidic conditions. Also, they have much better durability than polyurethanes materials obtained from isocyanate compounds [82a].

The isocyanate-free polyurethane materials are sensitive to light and once they are exposed to light, they may gradually turn to the yellow color. Therefore, they are not suitable for transparent application. Moreover, the UV stable coatings can be synthesized from acrylic materials which contain the cyclic carbonate functional groups. These materials have excellent mechanical properties [83].

The waterborne polyurethane dispersions obtained from non-isocyanate chemistry contain low volatile organic compounds. These specific dispersions have superior mechanical properties. The presence of hydroxyl, carboxyl and urethane functional groups in these materials cause them toact as highly efficient pigment dispersing resins[84].

Moreover, the polyurethane resins are obtained from reaction of multifunctional hydroxyalkylene carbonates with methylene diphenyldiiso cyanates in presence of potassium acetate. These particular polyurethane materials can be reacted again with aliphatic diamines to prepare the highly value-added polyurethane materials with the high content of urethane motifs [24]. The cycloaliphatic diamines are susceptible reagents to react with alkylene carbonates to produce the polyurethane adducts. Then the other terminal amine group is reacted with epoxy-urethane resins to form superior polyurethane coatings without use of diisocyanates[24].

The polyurethane materials obtained from isocyanate-free procedure (process) can be used in the sealants to protect the electronic devices and their components in aircraft and rocket construction towards hydrolysis and gasoline[85]. Furthermore, these materials have the various applications in the civil engineering because they can be employed as glues or adhesives with high performance and longevity to join all kinds of materials such as glass, metal, ceramics. These materials are used as reinforcing and filling polymers in the chemical and civil engineering[86].

Furthermore, the isocyanate free polyurethanes can be functioned in the textile industries for finishing purposes as well. For instance, an isocyanate-free UV-curable polyurethane resin has been recently prepared using polyetheramine and bisphenol based epoxy resin containing cyclic carbonate for treatment of hydrophilic textile[87].

The isocyanate-free polyurethane compounds possess the outstanding adhesive properties and therefore they can be used as adhesives and sealants. The different types of multifunctional acrylate materials containing urethane groups are extensively employed in inks, varnishes and adhesives. These particular compounds can be utilized in the various fields as cross-linking agents. For example, they can be employed for anaerobic adhesives, co-monomers in acrylic materials for laminating coatings and flexibilizers in protective coatings[88].

In addition, the hardeners such as dendro-aminosilanes can be employed in the synthesis of isocyanate-free polyurethane sealants. These hardeners can increase the thermal stabilities of polyurethanes. Also, the organosilaneshave extremely affected the mechanical and viscoelastic properties of isocyanate-free polyurethane coatings which can be employed in the steel and glass industries [89].

The inorganic nanoparticle materials have been functionalized with isocyanate-free polyurethanesto create the hybrid inorganic-organic nanocomposites which can be used in the coating industry. The incorporation of isocyanate-free polyurethane materials onto the surface of zinc oxide nanoparticles has significantly enhanced the mechanical and anticorrosive properties of new materials[90].

XIII. Conclusion

Basically, the chemical industry is increasingly demanding for environmentally benign processes in order to produce the eco-friendly chemicals. The carbon dioxide accumulation can cause global warming. Therefore, there have been several investigations to reduce the carbon dioxide concentration in the atmosphere to reduce the consequences of global warming. Also this useful monomer can be used for synthesis of different polymers. The utilization of isocyanate free strategies for synthesis of polyurethane materials has been attracted the considerable attention because these strategies have not introduced the use of toxic and environmentally dangerous compounds such as phosgene and isocyanates. The isocyanate free processes create a novel route for developing world by incorporation of carbon dioxide into the epoxide rings.

The polyurethane materials, which are generated from isocyanate free procedures, can replace the conventional method of polyurethane synthesis. These materials can be used effectively in a variety of

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applications. In particular, the design of cyclic carbonates backbone structure and their oligomers play an essential role to improve the performance of isocyanate free polyurethane materials. The recent preparations and developments of materials containing cyclic carbonates are providing the new opportunities for synthesis of polyurethane materials. Six-membered cyclic carbonates open a new window for synthesis of isocyanate free polyurethane materials. A variety of cyclic carbonates functionalized with different functional groups have been prepared and polymerized. These novel compounds have high performance properties which can be used for both industrial and household applications. The reaction of peracid or hyrgoen peroxide with unsaturated moieties of polymer compounds leads to the formation of epxides which in turn can undergo the cycloaddition reaction with carbon dioxide to generate cyclic carbonates for synthesis of the green isocyanate free polyurethane materials. This process leads to eco-friendly production of coatings that doesn't apply harmful phosgene and isocyanates. The toxic and hazardous materials have been replaced with safe and nonirritating molecules such as carbon dioxide and hydrogen peroxide.

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