Studying on the mechanism and raw materials used to manufacturing polyurethane

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ABSTRACT

Polyurethanes (PU) are present in various aspects of advanced life. They represent is a class of polymers that have found a propagate use in the medical, automotive and industrial fields. Polyurethanes are produced by the polyaddition reaction of a polyisocyanate with a polyalcohol (polyol) in the presence of a catalyst and other additives. In this case, a polyisocyanate is a molecule with two or more isocyanate functional groups, $R-(N=C=O)n\geq2$ and a polyol is a molecule with two or more hydroxyl functional groups, $R'-(OH)n\geq2$. The reaction product is a polymer containing the urethane linkage, -RNHCOOR'. Though the properties of the polyurethane are determined mainly by the choice of polyol, the diisocyanate exerts some influence, and must be suited to the application. The cure rate is influenced by the functional group reactivity and the number of functional isocyanate groups. The mechanical properties are influenced by the functionality and the molecular shape. Diazobicyclo [2.2.2]octane (DABCO) was used to comprehension of PU preparation mechanism when two monomers are stiring the together.
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INTRODUCTION

Polyurethanes (PU) are present in various aspects of advanced life. They represent is a class of polymers that have found a propagate use in the medical, automotive and industrial fields. Polyurethanes can be found in products such as furniture, coatings, adhesives, constructional materials, fibers, paddings, paints, elastomers and synthetic skins. TABLE1 shows how polyurethanes are used (according to US data from 2004)[70].

Polyurethanes are replacing older polymers for various reasons. The United States government is phasing out chlorinated rubber in marine and aircraft and coat-

TABLE 1 : Used polyurethanes (US data from 2004):[71]

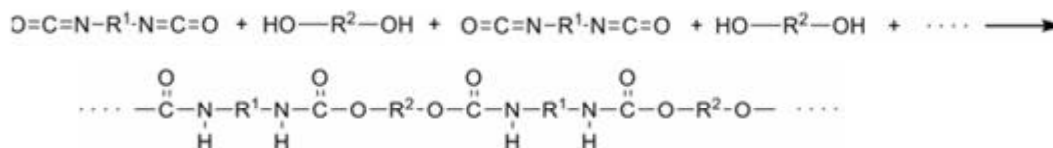| Application	Amount of polyurethane used (millions of pounds)	Percentage of total
Building and construction	1,298	23.8%
Transportation	1,298	23.8%
Furniture and bedding	1,127	20.7%
Appliances	278	5.1%
Packaging	251	4.6%
Textiles, fibers and apparel	181	3.3%
Machinery and foundry	178	3.3%
Electronics	75	1.4%
Footwear	39	0.7%
Other uses	558	10.2%
Total	5,444	100.0%

Figure 1: PU polymer formed by reacting a diisocyanate with a polyol

ings because they contain environmentallyhazardous volatile organic compounds[1,6,67]. Auto manufacturers are replacing latex rubber in car seats and interior padding with PU foam because of lower densityand greater flexibility[2,44-48]. Other advantages of PUs are that theyhave increased tensile strength and melting points making them more durable[3,49]. Their resistance to degradation by water, oils, and solvents make them excellent for the replacement of plastics[4]. As coatings, they exhibit excellent adhesion to many substances, abrasion resistance, electrical properties and weather resistance for industrial purposes[44,50-52].

Polyurethane foam (including foam rubber) is often made by adding small amounts of volatile materials, so-called blowing agents, to the reaction mixture. These simple volatile chemicals yield important performance characteristics, primarily thermal insulation. In the early 1990s, because of their impact on ozone depletion, the montreal protocol led to the greatly reduced use of many chlorine-containing blowing agents, such as trichloro fluoromethane (CFC-11). Other haloalkanes, such as the hydrochlorofluorocarbon 1,1-dichloro-1-fluoroethane (HCFC-141b), were used as interim replacements until their phase out under the IPPC directive on greenhouse gases in 1994 and by the volatile organic compounds (VOC) directive of the EU in 1997. By the late 1990s, the use of blowing agents such as carbon dioxide, pentane, 1,1,1,2-tetrafluoro ethane (HFC-134a) and 1,1,1,3,3-pentafluoropropane (HFC-245fa) became more widespread in North America and the EU, although chlorinated blowing agents remained in use in many developing countries[7,53-59].

Polyurethanes are in the class of compounds called reaction polymers, which include epoxies, unsaturated polyesters, and phenolics[8,9,10,11,12,41,42,59]. A urethane linkage is produced by reacting an isocyanate group, -N=C=O with a hydroxyl (alcohol) group, -OH. Polyurethanes are produced by the polyaddition reaction of a polyisocyanate with a polyalcohol (polyol) in the pres-

ence of a catalyst and other additives. In this case, a polyisocyanate is a molecule with two or more isocyanate functional groups, $R-(N=C=O)_n \geq_2$ and a polyol is a molecule with two or more hydroxyl functional groups, $R'-(OH)_n \geq_2$. The reaction product is a polymer containing the urethane linkage, -RNHCOOR'-as shown in figure 1.

Isocyanates will react with any molecule that contains an active hydrogen. Importantly, isocyanates react with water to form a urea linkage and carbon dioxide gas; they also react with polyetheramines to form polyureas. Commercially, polyurethanes are produced by reacting a liquid isocyanate with a liquid blend of polyols, catalyst, and other additives. These two components are referred to as a polyurethane system, or simply a system.

Property of raw matterials

1. Isocyanates

Isocyanates are highly reactive chemicals and create several chemically different products when combined with -OH and -NH functional substances. Desired products and side products are formed in different amounts. The basic reactions of isocyanate with different reagents are shown in figure 2. The high reactivity of isocyanate groups toward nucleophilic reagents is mainly due to the pronounced positive character of the C atom in the cumulative double bond sequence consisting of nitrogen, carbon and oxygen, especially in aromatic systems. The electronegativity of the oxygen and nitrogen imparts a large electrophilic character to the carbon in the isocyanate group. The common reactions of isocyanates can be divided into two main classes:

(1) The reaction of isocyanates with compounds containing reactive hydrogen to give addition products, and

(2) the polymerization of isocyanates, i.e., self-addition reaction.

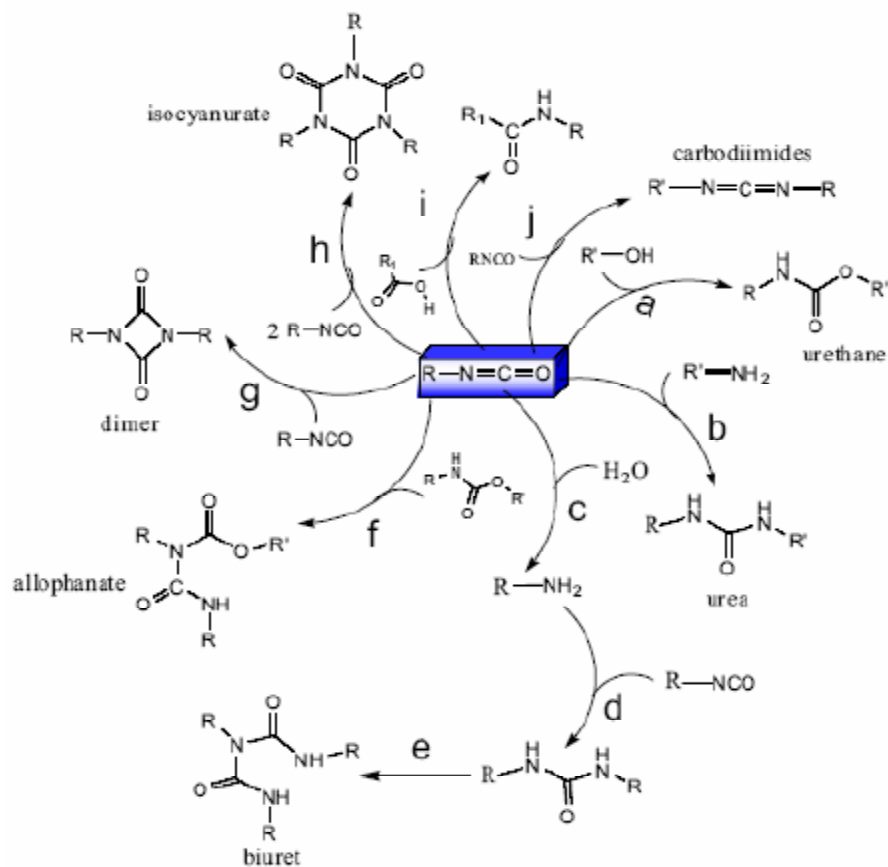Isocyanates react with hydroxyl compounds to give

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Figure 2: Basic reactions of isocyanate with different reactants[24]

urethanes (a) and with amines to give ureas (b). For primary and secondary alcohols, the uncatalysed reaction proceeds readily at 50-100ºC, tertiary alcohols and phenols react more slowly. Typical primary and secondary aliphatic amines and primary aromatic amines react rapidly with isocyanate at 0-25 ºC to form urea functional substances. Similarly, water reacts with a diisocyanate and initially forms of an unstable carbamic acid, which decomposes and produces an amine (c). Amine is a nucleophilic reagent and further reacts with an isocyanate function to produces urea linkage (d). The availability of a lone pair of electrons on the nitrogen atom of urea group makes them nucleophilic centers, which upon reaction and fruitful collision with one molecule of isocyanate produces biuret (e). Similarly, isocyanates react with urethanes and produce allophanates (f). Different secondary reactions shown in figure 2, occur to a lesser extent than the primary reactions. Reactions leading to the formation of allophanates and biurets are influenced by the reaction

condition such as temperature, humidity level and the type of isocyanate used. The self-condensation of isocyanate results in uretidione rings (dimer-, g), isocyanurate (trimer-, h) or carbodiimide (j).

The formation of carbodiimides is not usually considered a polymerization reaction, but it could be classified as a condensation polymerization between isocyanate molecules with elimination of CO_2. This is due to degradation of isocyanates taking place at high temperatures[13,60-63]. When isocyanate reacts with carboxylic acids, the mixed anhydrides break down and form amide groups (i). The trimer isocyanurate rings, unlike uretidione rings, are exceptionally stable. The high reactivity of isocyanates may cause detrimental secondary reactions and uncontrolled condensations leading to the formation of unworkable crosslinked materials that are difficult to process. Therefore, blocking of isocyanate capped material or monomer may sometimes helps for improving the stability[14,64]. The blocked isocyanate can be converted to the active isocyanate form
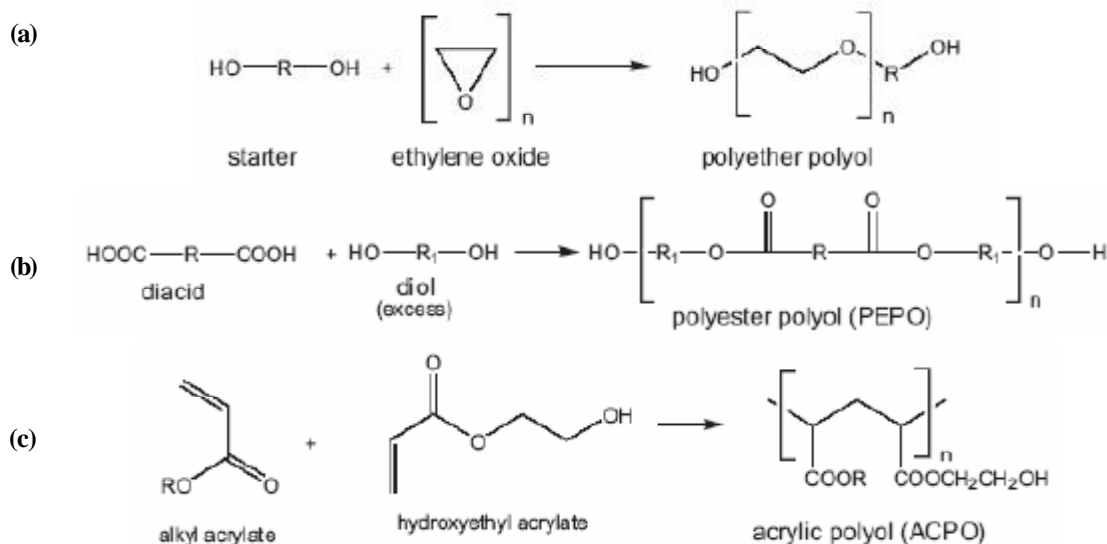
Figure 3: Synthetic methods for the preparation of polyether polyol, PEPO and ACPO

when required. More recently, commercial availability of blocked isocyanates has increased greatly. In particular, these reagents are suitable for light-stable two-component and single package blocked adduct urethane coatings in which high temperatures (>100ºC) are used to regenerate the isocyanate and the blocking agent. The regenerated isocyanates react with hydroxyl or amine functionalized co-reactants to form thermally stable urethane or urea bonds, respectively[15-17]. Blocked isocyanates used in the literature were phenol, oxime[15], caprolactam[18,65], imidazoline[19,66], tetrahydropyrimidine, imidazole[20,67], pyrazole[21,68], etc. In order to avoid the release of volatile isocyanate blocking agents, a self-blocked concept has also applied[22,69].

The polyfunctional isocyanate used to prepare PU coatings can be aromatic, aliphatic, cycloaliphatic or polycyclic in structure. The commonly used isocyanates in the manufacture of PUs are TDI, MDI, 4,40-dicyclohexylmethane diisocyanate (H12MDI), xylene diisocyanate (XDI), tetramethylxylylene diisocyanate (TMXDI), hydrogenated xylene diisocyanate (HXDI), naphthalene 1,5-diisocyanate (NDI), p-phenylene diisocyanate (PPDI), 3,3′-dimethyldiphenyl-4,4′-diisocyanate (DDDI), hexamethylene diisocyanate (HDI), 2,2,4-trimethylhexamethylene diisocyanate (TMDI), isophorone diisocyanate (IPDI), norbornane diisocyanate (NDI), 4,4′-dibenzyl diisocyanate (DBDI), etc. Aromatic isocyanates have high reactivity than ali-

phatic or cycloaliphatic diisocyanates. Different diisocyanates contribute to the PU properties in different ways. For example, aromatic diisocyanates give more rigid PUs than do aliphatic ones, but their oxidative and ultraviolet stabilities are lower[23].

2. Diols/polyols

The polyol component of the PUs can be a polyfunctional polyether (e.g., polyethylene glycol, polypropylene glycol, PTMG or polycaprolactone diol), polyester polyol (PEPO), acrylic polyol (ACPO), polycarbonate polyol, castor oil or a mixture of these. A wide variety of branched or crosslinked polymers can be formed since the functionality of the hydroxyl-containing reactant or isocyanate can be adjusted. The simplest polyols are glycols, such as ethylene glycol,1,4-butane diol (BDO) and 1,6-hexane diol. The low molecular weight reactants result in hard and stiff polymers because of a high concentration of urethane groups. On the other hand, the use of high molecular weight polyols as the main reactants produces polymer chains with fewer urethane groups and more flexible alkyl chains. Long-chain polyols with low functionality (1.8-3.0) give soft, elastomeric PU while short chain polyols of high functionality (greater than 3) give more rigid, crosslinked product. Polyether polyols are produced by the addition of either ethylene oxide or propylene oxide to a polyhydroxy 'starter' molecule in the presence of a catalyst (figure 3a). Typical starter molecules

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include glycerol, ethylene glycol, propylene glycol and trimethylolpropane. PEPOs are produced by the condensation reaction of polyfunctional carboxylic acids or anhydrides with polyfunctional alcohols (figure 3b).

ACPOs are produced by free radical polymerization of hydroxyethyl acrylate (HEA)/methacrylate with other acrylic precursors[25,44,68] (figure 3c). Depending on the field of application, PEPO, ACPO or polyether polyols have generally been chosen. In commercial applications, it is common to find polyesters prepared from a mixture of two or more diacids reacted with two or more glycols, which gives ample scope for a range of very complex products[26,27,45]. Though PEPO and ACPO-based PUs are vulnerable to the gradual hydrolysis of the ester group but they are sufficiently stable against natural weathering. The hydrolysis takes place at the ester groups, which reverts to the carboxylic acid and alcohol. Additionally, the in situ formation of carboxylic acid catalyzes further ester hydrolysis, thus accounting for an autocatalytic effect[28] and therefore a significant reduction of average molar mass and, consequently, deterioration of mechanical properties occur on prolong exposure to humid atmosphere. To slow down the hydrolysis of polyester groups, polycarboimides can be added to poly (ester urethanes) that act as acid scavengers and suppress the autocatalytic effect[29,30]. PU coatings derived from PEPO have excellent heat stability, adhesive properties and oil resistance. Additionally, the lower manufacturing cost has made widespread application of polyester type PU coatings.

3. Chain extenders and cross linkers

Chain extenders (f=2) and cross linkers (f=3 or greater) are low molecular weight hydroxyl and amine terminated compounds that play an important role in the polymer morphology of polyurethane fibers, elastomers, adhesives, and certain integral skin and microcellular foams. The elastomeric properties of these materials are derived from the phase separation of the hard and soft copolymer segments of the polymer, such that the urethane hard segment domains serve as crosslinks between the amorphous polyether (or polyester) soft segment domains. This phase separation occurs because the mainly non-polar, low melting soft segments are incompatible with the polar, high melting hard seg-

ments. The soft segments, which are formed from high molecular weight polyols, are mobile and are normally present in coiled formation, while the hard segments, which are formed from the isocyanate and chain extenders, are stiff and immobile. Because the hard segments are covalently coupled to the soft segments, they inhibit plastic flow of the polymer chains, thus creating elastomeric resiliency. Upon mechanical deformation, a portion of the soft segments are stressed by uncoiling, and the hard segments become aligned in the stress direction. This reorientation of the hard segments and consequent powerful hydrogen bonding contributes to high tensile strength, elongation, and tear resistance values[32,33,34,35,36]. The choice of chain extender also determines flexural, heat, and chemical resistance properties. The most important chain extenders are ethylene glycol, 1,4-butanediol (1,4-BDO or BDO), 1,6-hexa nediol, cyclohexane dimethanol and hydroquinone bis (2-hydroxyethyl) ether (HQEE). All of these glycols form polyurethanes that phase separate well and form well defined hard segment domains, and are melt process able. They are all suitable for thermoplastic polyurethanes with the exception of ethylene glycol, since the its derived bis-phenyl urethane undergoes unfavorable degradation at high hard segment levels[37,40]. Diethanolamine and triethanolamine are used in flex molded foams to build firmness and add catalytic activity.

4. Catalysts

Polyurethane catalysts can be classified into two broad categories, amine compounds and organometallic complexes. They can be further classified as to their specificity, balance, and relative power or efficiency. Traditional amine catalysts have been tertiary amines such as triethylenediamine (TEDA, also known as 1,4-diazabicyclo[2.2.2]octane or DABCO), dimethylcyclo hexylamine (DMCHA), and dimethylethanolamine (DMEA). Tertiary amine catalysts are selected based on whether they drive the urethane (polyol+isocyanate, or gel) reaction, the urea (water+isocyanate, or blow) reaction, or the isocyanate trimerization reaction. Since most tertiary amine catalysts will drive all three reactions to some extent, they are also selected based on how much they favor one reaction over another. For example, tetramethylbutanediamine (TMBDA) prefer-
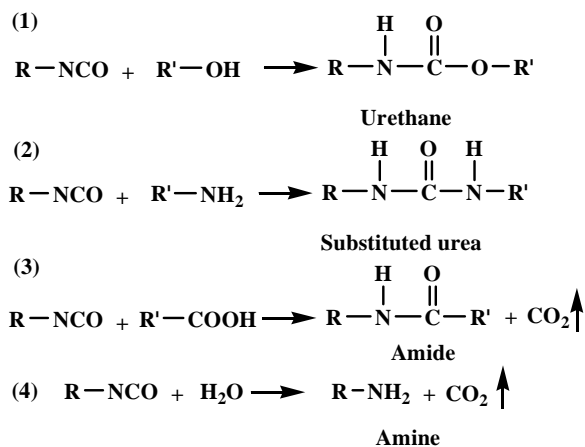
(1)

$$R-NCO + R'-OH \longrightarrow R-\underset{\underset{H}{|}}{N}-\underset{\overset{O}{||}}{C}-O-R'$$

Urethane

(2)

$$R-NCO + R'-NH_2 \longrightarrow R-\underset{\underset{H}{|}}{N}-\underset{\overset{O}{||}}{C}-\underset{\underset{H}{|}}{N}-R'$$

Substituted urea

(3)

$$R-NCO + R'-COOH \longrightarrow R-\underset{\underset{H}{|}}{N}-\underset{\overset{O}{||}}{C}-R' + CO_2\uparrow$$

Amide

(4) $R-NCO + H_2O \longrightarrow R-NH_2 + CO_2\uparrow$

Amine

Figure 4: Primary reactions

entially drives the gel reaction over the blow reaction. On the other hand, both pentamethyldipropylenetriamine and N-(3-dimethylaminopropyl)-N,N-diisopropanol amine balance the blow and gel reactions, although the former is more potent than the later on a weight basis. 1,3,5-(tris(3-dimethylamino)propyl)-hexahydro-s-triazine is a trimerization catalyst that also strongly drives the blow reaction. Molecular structure gives some clue to the strength and selectivity of the catalyst. Blow catalysts generally have an ether linkage two carbons away from a tertiary nitrogen. Examples include bis-(2-dimethylaminoethyl)ether and N-ethylmorpholine. Strong gel catalysts contain alkyl-substituted nitrogens, such as triethylamine (TEA), 1,8-diazabicyclo[5.4.0]undecene-7 (DBU), and pentamethyldiethylenetriamine (PMDETA). Weaker gel catalysts contain ring-substituted nitrogens, such as benzyldimethylamine (BDMA). Trimerization catalysts contain the triazine structure, or are quaternary ammonium salts. Two trends have emerged since the late 1980s. The requirement to fill large, complex tooling with increasing production rates has led to the use of blocked catalysts to delay front end reactivity while maintaining back end cure. In the United States, acid- and quaternary ammonium salt-blocked TEDA and bis-(2-dimethylaminoethyl)ether are common blocked catalysts used in molded flexible foam and microcellular integral skin foam applications. Increasing aesthetic and environmental awareness has led to the use of non-fugitive catalysts for vehicle interior and furnishing applications in order to reduce odor, fogging, and the staining of vinyl coverings. Catalysts that contain a hydroxyl group or an active amino hydrogen,

such as N,N,N′-trimethyl-N′-hydroxyethyl-bis (aminoethyl)ether and N′-(3-dimethylamino)propyl)-N,N-dimethyl-1,3-propanediamine that react into the polymer matrix can replace traditional catalysts in these applications[38,39].

Organometallic compounds based on mercury, lead, tin (dibutyltin dilaurate), bismuth (bismuth octanoate), and zinc are used as polyurethane catalysts. Mercury carboxylates, such as phenylmercuric neodeconate, are particularly effective catalysts for polyurethane elastomer, coating and sealant applications, since they are very highly selective towards the polyol+isocyanate reaction. Mercury catalysts can be used at low levels to give systems a long pot life while still giving excellent back-end cure. Lead catalysts are used in highly reactive rigid spray foam insulation applications, since they maintain their potency in low-temperature and high-humidity conditions. Due to their toxicity and the necessity to dispose of mercury and lead catalysts and catalyzed material as hazardous waste in the United States, formulators have been searching for suitable replacements. Since the 1990s, bismuth and zinc carboxylates have been used as alternatives but have short comings of their own. In elastomer applications, long pot life systems do not build green strength as fast as mercury catalyzed systems. In spray foam applications, bismuth and zinc do not drive the front end fast enough in cold weather conditions and must be otherwise augmented to replace lead. Alkyl tin carboxylates, oxides and mercaptides oxides are used in all types of polyurethane applications. For example, dibutyltin dilaurate is a standard catalyst for polyurethane adhesives and sealants, dioctyltin mercaptide is used in microcellular elastomer applications, and dibutyltin oxide is used in polyurethane paint and coating applications. Tin mercaptides are used in formulations that contain water, as tin carboxylates are susceptible to degradation from hydrolysis[40].

Structural property of PU

The structure of polyurethane can be complex and diverse containing "hard" and "soft" segments, which contribute to the balance between rigid and elastomeric properties. Polyurethanes are synthesized by two methods namely, prepolymer method and one- shot method. In prepolymer method, the polyisocyanate and polyol
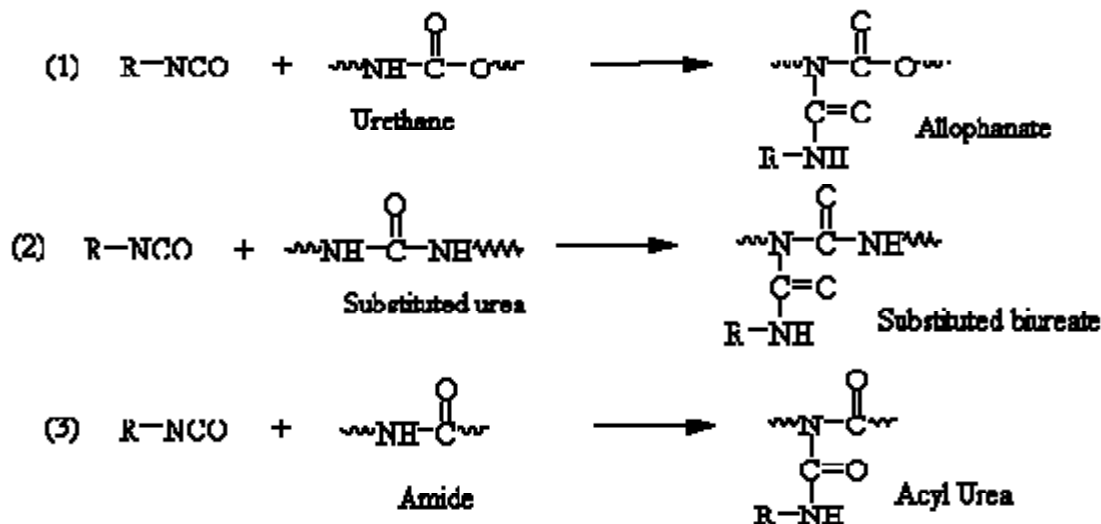
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Figure 5: Secondary reactions

are reacted to form an intermediate polymer called "prepolymer". It is then converted into final high molecular weight polymer by further reaction with diol or diamine chain extender. In the 'one-shot' method, the polymer formation is carried out by simultaneous reaction of polyol, polyisocyanate and chain extender.

1. Primary reactions

Primary reactions are relatively faster and occur at relatively lower temperatures compared to the secondary reactions. The various primary reactions of isocyanates shown in figure 4 are described as follow.

Isocyanate reacts with hydroxyl group as shown in figure 4(1) to produce urethane linkage. This reaction is exothermic. Isocyanates reacts readily with primary hydroxyl groups than secondary ones. Isocyanates reacts with amino groups at 0-25°C to form substituted urea as shown in figure 4(2). Primary amino groups have higher reactivity with isocyanate than secondary ones. Reaction of isocyanate with carboxylic acid shown in figure 4(3) leads to the formation of amide linkage, which is similar to urethane linkage. This reaction produces carbon dioxide gas.

Isocyanates readily reacts with water to produce amines and carbon dioxide gas as shown in figure 4(4). The evolved carbon dioxide gas causes foaming and is undesirable in synthesis of polyurethane elastomers. Therefore all the reactants and apparatus used in polyurethane synthesis needs to be dried thoroughly.
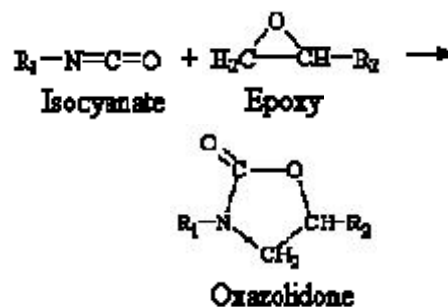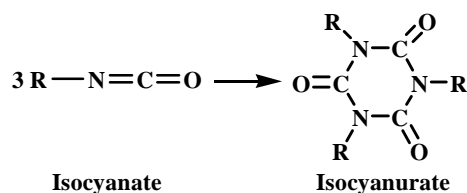

Figure 6: isocyanate reaction with epoxide group

2. Secondary reactions

Isocyanates react with the secondary amino group of urethanes, ureas, and amide forming allophanates, substituted biurets, and acyl ureas respectively as shown in figure 5. The secondary reactions of isocyanate leads to cross-linking, and the resulting polyurethane becomes insoluble and infusible. Thus the temperature control during polyurethane synthesis is critical to avoid secondary reactions and thereby cross-linking.

The isocyanurate, which is a six-member ring is thermally most stable and enhances fire resistance of the polymer. However, it increases the functionality of the

system, which forms a crosslinked network, which is undesirable in the present study.

The isocyanate also reacts with epoxide group to form oxazolidone linkage as shown in figure 6. Oxazolidone is a saturated, five-member heterocyclic group. This cyclic structure is very stiff which imparts rigidity and excellent thermal properties to the polymer. Isocyanurate and oxazolidone formation have been studied extensively.

4. The PU preparation mechanism

As mentioned before, polyurethanes achieved from two monomers, a polyol/diol and a polyiisocyanate/diisocyanate. With the help of a little molecule called diazobicyclo[2.2.2]octane, or DABCO for short, we
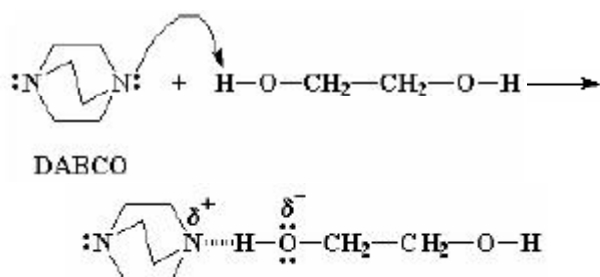

Figure 7: Emerged partial positive and negative charge When DABCO H-bonds with the alcohol

can make these two polymerize. When we stir the two monomers together with DABCO, something nifty happens. DABCO is a very good nucleophile, it has a pair of unshared electrons that would just love to attach themselves to a vulnerable nucleus. electrons have negative charges, and the nuclei of atoms have positive charges. It is well known negative charges and positive charges attract, So DABCO's electron look around, and they find a nucleus on the alcohol hydrogens of the diol. These hydrogens are vulnerable, because they are bonded to oxygen atoms. Oxygen is electronegative. This is to say it pulls electrons away from other atoms. So it pulls electrons away from its neighbor the hydrogen atom. This leaves the positive charge of its nucleus unbalanced. The electrons would have balanced the positive charge with their own negative charges, they've been sucked away by the oxygen. This leaves a slight positive charge on the hydrogen as shown in figure 7.

So DABCO's electrons see this and they just can't help themselves. They rush over and form a hydrogen bond between the hydrogen and DABCO's nitrogen. This H-bonding leaves a partial positive charge on the nitrogen, but more importantly, a partial negative charge on the oxygen[41]. This partial negative charge makes the oxygen really hot to reaction. The oxygen has an
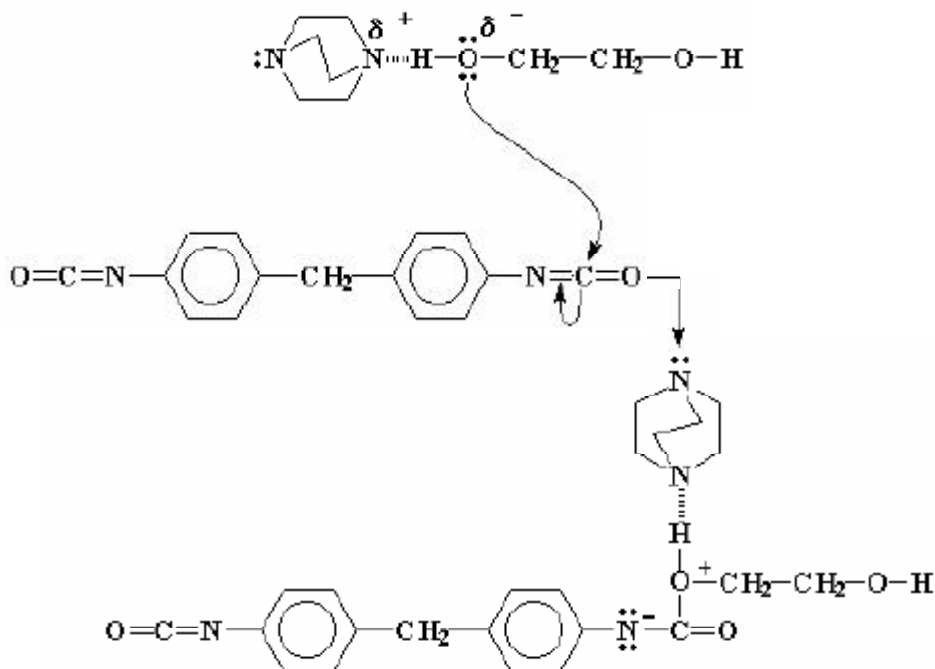

Figure 8: The oxygen with a partial negative charge donates a pair of electrons to the electron-poor isocyanate carbon, setting off a flow of electron which leaves with a positive charge on oxygen, and a negative charge on the nitrogen
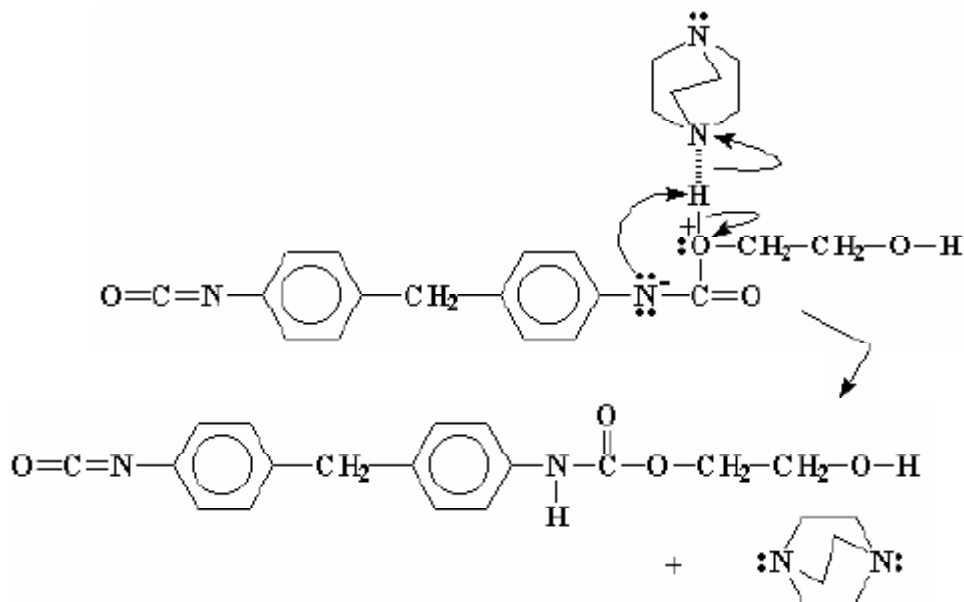
Figure 9: The negative charged nitrogen swipes the hydrogen away from the alcohol

urethane dimer

The urethane dimer can react with either a diol or a diisocyanate to form a trimer. It can even react with other dimers, trimers and higher oligomers.
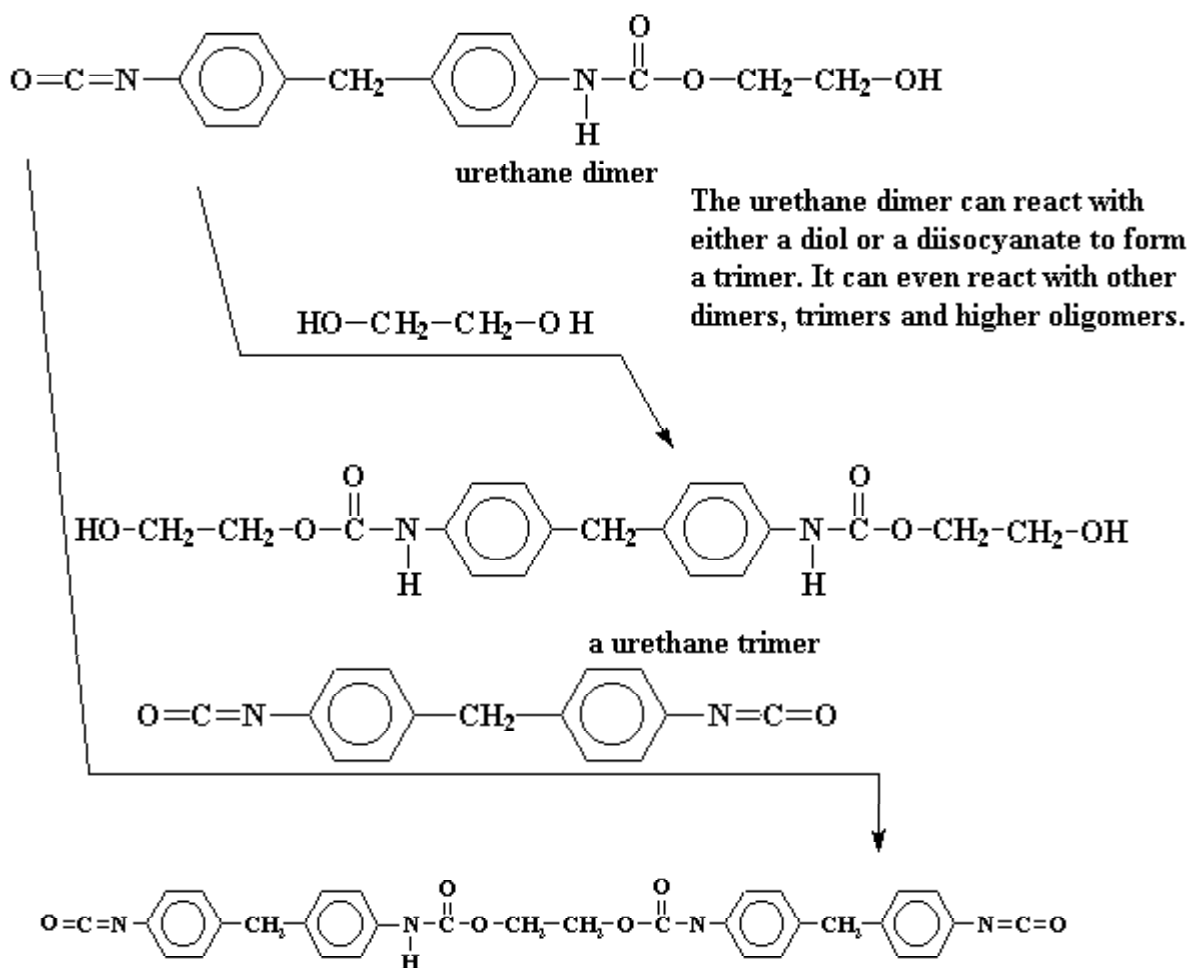
HO−CH₂−CH₂−O H

a urethane trimer

Figure 10: monomers and oligomers combination to get high molecular weight polyurethane
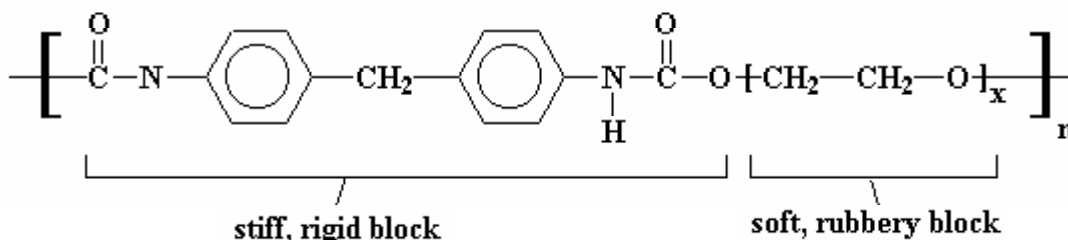
Figure 11: A polyurethane made from a polyglycol

excess of electrons, so it will react with something that is poor in electrons. it can be seen that the carbon in the isocyanate group is sandwiched between two electrone-gative elements, oxygen and nitrogen. This means that this carbon is going to be very poor in electrons indeed. So oxygen wastes no time in reacting with it. It throws a pair of electrons to that carbon, and a bond forms as shown in figure 8.

Of course this pushes a pair of electrons out of the carbon-nitrogen double bond. This pair situates itself on the nitrogen, giving it a negative charge. Our oxygen meanwhile, having donated an electron pair, is left with a positive charge.

Now there isn't much that a nitrogen atom likes less than to have a negative charge. So it's going to try to get rid of it as soon as it can. This forms a bond between that hydrogen and the nitrogen.

The electrons that the hydrogen had shared with the oxygen now belong to the oxygen alone. This elimi-nates that old positive charge that the oxygen was car-rying. When it's all over we're left with a brand new urethane dimer.

This urethane dimer has an alcohol group on one end, and an isocyanate group on the other, so it can react with either a diol or a diisocyanate to form a tri-mer. Or it can react with another dimer, or a trimer, or even higher oligomers. In this way, monomers and oli-gomers combine and combine until we get high mo-lecular weight polyurethane as shown in figure 10.

This makes it a step growth polymerization. Also, because no small molecule by-products are produced, it is an addition polymerization

Polymers within polymers

Sometimes, instead of using a small diol like ethyl-ene glycol, it used a polyglycol, one with a molecular weight of about 2000[42,43].
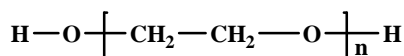
Poly(etylene glynol)

This gives us a polymer within a polymer so to speak, and we have a polyurethane that looks something like in figure 11.

CONCLUSION

For the manufacture of polyurethane polymers, two groups of at least bifunctional substances are needed as reactants; compounds with isocyanate groups, and compounds with active hydrogen atoms. Polyurethane can be made in a variety of densities and hardnesses by varying the type of monomer(s) used and adding other substances to modify their characteristics, notably den-sity, or enhance their performance. The physical and chemical character, structure, and molecular size of these compounds influence the polymerization reaction, as well as ease of processing and final physical properties of the finished polyurethane. In addition, additive such as catalysts, surfactants are used to control and modify the reaction process and performance characteristics of the polymer. Polyurethanes are synthesized by two methods namely, prepolymer method and one- shot method. In prepolymer method, the polyisocyanate and polyol are reacted to form an intermediate polymer called "prepolymer". It is then converted into final high molecular weight polymer by further reaction with diol or diamine chain extender. In the 'one-shot' method, the polymer formation is carried out by simultaneous reaction of polyol, polyisocyanate and chain extender. With the help of a little molecule called diazobicyclo [2.2.2] octane, or DABCO for short, the mechanism of polymerization can be achieved.

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