

Polyurethanes (PUs)

7.1 INTRODUCTION

PUs, as commercial polymers, constitute one of the most complete and versatile class of polymeric materials known today. The term polyurethane is extended to all complex reaction products of isocyanates and polyhydroxy compounds. From the chemical point of view they contain a diversity of functional groups along with the urethane group ($-\text{NH}-\text{CO}-\text{O}-$), which sometimes is not even the principal group present. Many other groups such as ether, ester, amide, urea, biuret, allophanate, uretidione, carbodiimide and isocyanurate enter the chemical composition.

PUs are synthesized by a step growth polymerization process in which the chain length of the polymer increases steadily as the reaction progresses.

The polymer chains may be linear or slightly branched as in thermoplastic PUs or they may have a crosslinked network leading to thermosetting products.

A large diversity of raw materials has been employed to produce PUs. They may be classified in three principal groups: isocyanates, polyols and chain extenders. The synthesis of the polymer is always based on the utilization of at least one component of each principal group. Complementary materials, such as water, blowing agents, catalysts, structure regulators and solvents, have been used to manufacture specific products (elastomers, foams, coatings). Commercial formulations may also include other additives such as anti-aging compounds, fillers, colorants, flame retardants and others.

A large spectrum of properties that can be tailored by the selection of raw materials, formulations and manufacturing processes, has led to a broad variety of end products that are in continuous diversification. The following major types of commercial PU are produced: flexible foams, rigid foams, integral (or self-skinning) foams, elastomers, fibers, surface coatings, adhesives and sealants.

PUs date from 1937 when fiber forming polymers were produced by the German chemist, O. Bayer (I.G. Farbenindustries), by reacting diisocyanates

with aliphatic diols. No extensive commercial importance was reached until after the Second World War when elastomers (1950) and foams (1952) were developed at Bayer. But the expansion of the market started after 1957 when American companies introduced polyether–polyol based foams at a lower price and with a wider range of properties. The production volume of PUs has been growing continuously since then as new and valuable applications have been found [1].

PUs are among the top ten global polymers with a volume of 5.1 million tons per year in 1990 and an estimated demand of 8.5 million tons in 2000 [2]. The principal consumers of PUs are Western Europe with 2 million tons, the USA with 1.5 million tons and the Far Eastern countries with 1.2 million tons [2]. Flexible foams accounted for about 50% of the market, rigid foams for 30% and the remainder is covered by elastomers, adhesives, coatings and sealants.

7.2 RAW MATERIALS

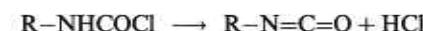
7.2.1 Isocyanates and their chemistry

The specific raw material for polyurethane production are isocyanates, more precisely di- and polyisocyanates. Many preparative reactions are known to synthesize isocyanates [3,4] but they are used exclusively on a laboratory scale. The only methods that have acquired commercial importance consist of the phosgenation of the appropriate amines or amine hydrochlorides.

The phosgenation is usually carried out in a solvent inert to isocyanate, i.e. does not contain active hydrogen atoms (usually *o*-dichlorobenzene). The process is run continuously or in batch in two stages known as the cold and the hot stages. In the cold stage (25–100°C) a 20% solution of the appropriate amine is reacted with a solution containing a 20–50% excess of phosgene. Intermediate carbamoyl chloride is formed:



Then the carbamoyl chloride is thermally decomposed to isocyanate in the hot stage (150–160°C) and the hydrogen chloride and excess phosgene are removed with nitrogen:



At the end, pure isocyanate is separated from the solvent by fractional distillation, by crystallization or by sublimation.

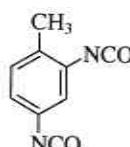
As isocyanates are very reactive compounds, side reactions may occur, especially if unreacted amine is present, leading to the formation of a urea:



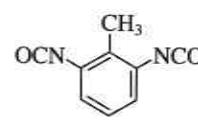
To minimize this reaction, amine hydrochloride can be used instead of amine and excess phosgene is maintained during the process.

The most important commercial isocyanates are given below.
(a) The group of toluene diisocyanate (TDI) which comprises

- 80:20 TDI, a mixture of two isomers, 80% 2,4-toluene- and 20% 2,6-toluene diisocyanates;
- 65:35 TDI, a mixture of 65% 2,4- and 35% 2,6- isomers;
- 2,4-TDI which is pure 2,4- isomer.



2,4-Toluene diisocyanate
(2,4-TDI)



2,6-Toluene diisocyanate
(2,6-TDI)

These different mixtures of isomers are obtained by various ways of conducting the dinitration of toluene. The mixtures of 2,4- and 2,6-dinitrotoluenes are subsequently reduced to diaminotoluenes without any fractionation and then phosgenated to diisocyanates.

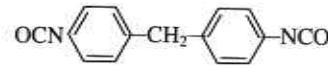
TDI mixtures are liquids at ambient temperatures that have the melting range at 5–15°C; while pure 2,4-TDI melts at 22°C. The 4-isocyanato group is more reactive than either 2- or 6- position groups at ambient temperature and in the absence of catalysts.

TDIs are respiratory toxic materials and the toxicity is closely related to their vapor pressure. Safety measures should be taken in handling these materials.

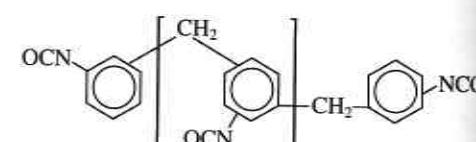
TDI mixtures are extensively used for the production of polyurethane flexible foams, elastomers and adhesives.

(b) The diphenylmethane diisocyanate group is composed of

- pure 4,4'-diphenylmethane diisocyanate (MDI);
- 'polymeric' diphenylmethane diisocyanate (PMDI);
- modified diphenylmethane isocyanates.



4,4'-Diphenylmethane diisocyanate
(MDI)



Polymeric diphenylmethane diisocyanate
(PMDI)

As the melting point of pure 4,4'-MDI is 37–38°C, some liquid derivatives have been prepared. The so called 'polymeric' diphenylmethane diisocyanate

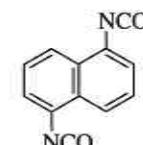
(PMDI) is a crude liquid mixture with the functionality 2.3–3.1, composed of around 55% MDI (4,4'- and 2,4'- isomers), 25% triisocyanates and 20% higher polyisocyanates. The mixture results at the step of amine preparation which is realized by the acid catalyzed condensation of aniline with formaldehyde and its composition depends on the aniline to formaldehyde ratio. By the phosgenation of the whole mixture, polymeric PMDI is obtained in quantitative yield. Pure 4,4'-MDI is separated from PMDI by continuous thin film distillation.

Using various chemical modifications of pure MDI, stable liquid derivatives with free isocyanate groups have been prepared. They are prepolymers with polyesters or polyethers, carbodiimide modified or isocyanurate modified MDI derivatives [5].

All these products are less toxic than TDI isocyanates as their vapor pressures are lower.

Crude PMDI oligomers are mainly used in the production of rigid insulation foams. Pure MDI is used in the manufacture of elastomers.

(c) Naphthalene, 1,5-diisocyanate (NDI) is a solid compound melting at 128°C. It was first prepared in Germany and is used almost exclusively in Europe for the production of Vulkollan type elastomers:

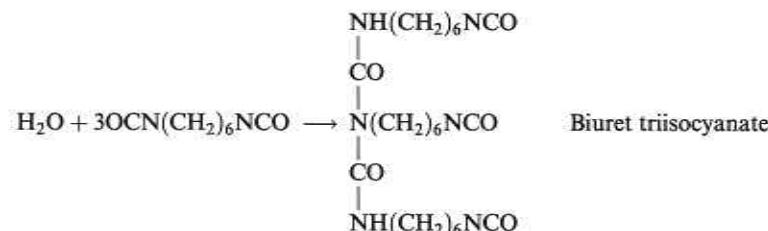


1,5-Naphthalene diisocyanate (NDI)

(d) Hexamethylene diisocyanate (HDI) is a volatile and high vapor pressure liquid; consequently, it is a toxic product:

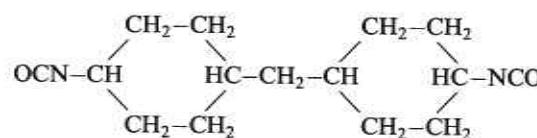


In order to reduce its volatility, hexamethylene diisocyanate is reacted with a controlled amount of water resulting in a triisocyanate with biuret structure:



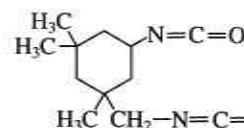
Light stable non-yellowing PU are obtained from HDI and its derivatives due to the absence of aromatic structures and therefore aliphatic isocyanates are used for coatings.

(e) Another diisocyanate for the production of polyurethanes with improved resistance to discoloration and to thermal and hydrolytic attack is 4,4'-dicyclohexylmethane diisocyanate ($H_{12}\text{MDI}$), a mixture of stereoisomers obtained on the hydrogenation of 4,4'-diaminodiphenylmethane:



4,4'-Dicyclohexylmethane diisocyanate ($H_{12}\text{MDI}$)

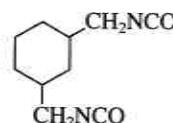
(f) Isophorone diisocyanate (IPDI), 3-isocyanatomethyl-3,5,5-trimethylcyclohexyl isocyanate, has both isocyanate groups attached to saturated organic groups:



3-Isocyanatomethyl-3,5,5-trimethylcyclohexyl isocyanate (IPDI)

It is a liquid less volatile than TDI and is used for light stable flexible coatings.

(g) 1,3-bis(isocyanatomethyl) cyclohexane ($H_6\text{XDI}$) is another commercial isocyanate suitable for non-yellowing PU applications:



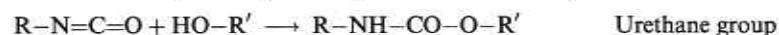
1,3-Bis(isocyanatomethyl) cyclohexane ($H_6\text{XDI}$)

(h) A more recent technological development is the preparation of polymeric aliphatic isocyanates obtained by the copolymerization of styrene with 2-isocyanatoethyl methacrylate and other suitable acrylic acid esters [6].

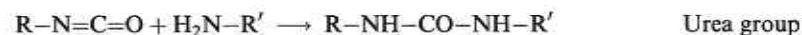
The isocyanate group is very reactive and gives rise to a large number of reactions. Only those reactions employed in different polyurethane technologies are presented below. They may be classified as follows:

- addition reactions involving active hydrogen compounds (1–7);
- self-cycloaddition reactions (8 and 9);
- self-condensation reactions (10).

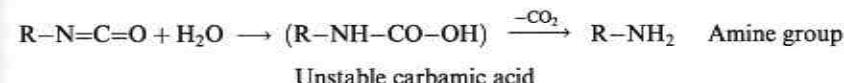
1. With alcohols and phenols (R' is aliphatic or aromatic):



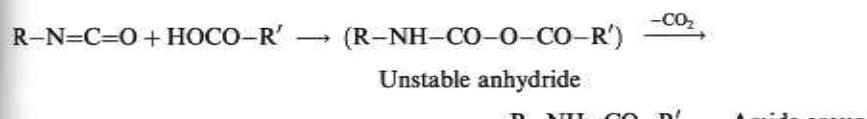
2. With amines:



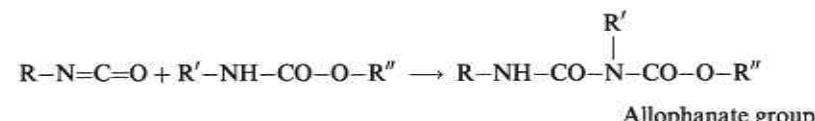
3. With water:



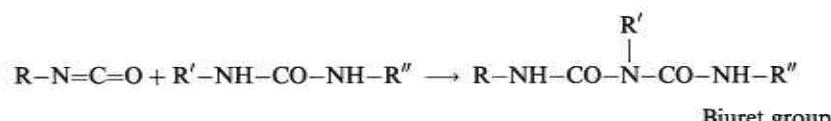
4. With carboxylic acids:



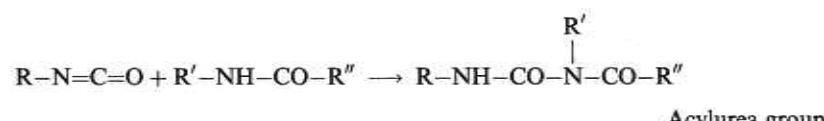
5. With urethanes:



6. With ureas:

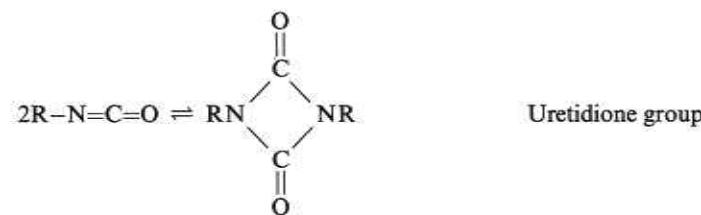


7. With amides:

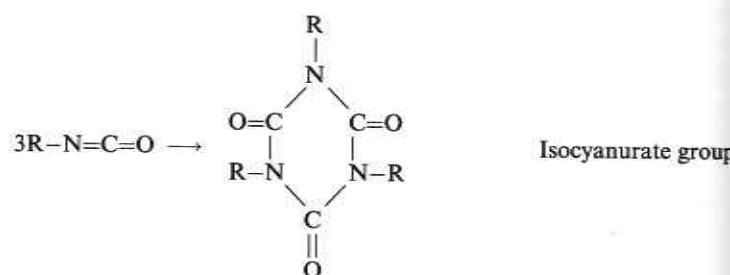


As can be seen, reactions (1–4) lead to linear chains whereas reactions (5–7) result in branched chains.

8. Dimerization:



9. Trimerization:

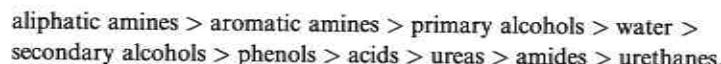


10. Self-condensation:



These reactions may also be used to modify the isocyanates in order to make them more versatile for various technologies or to introduce certain groups such as carbodiimide or isocyanurate into the end products.

It should be noted that the reaction rates depend on the structures of the involved compounds. The reactivity of the isocyanate group is enhanced by the presence of electron withdrawing groups on the isocyanate molecule whereas the electron donating substituents reduce the reactivity [7]. Aromatic isocyanates are much more reactive than aliphatic ones. Steric hindrance also influences the rate of isocyanate reactions. Contrary to isocyanates, the active hydrogen compounds are activated by the presence of electron donating groups on their molecules. The active hydrogen compounds can be arranged in decreasing order of their nucleophilicities which are proportional to their reactivities toward isocyanates:



The above considerations are true only in the absence of catalysts; their presence can substantially modify the rate of each individual reaction as well as their relative rates.

7.2.2 Polyols

Besides isocyanates, the other major components of all types of PU products are hydroxyl-containing compounds known as 'polyols'. Polyols can also be used as intermediates or modifiers for other polymers such as epoxy resins or unsaturated polyesters, as well as for non-polymer domains as surfactants and functional fluids.

Polyols are oligomeric products with MW in the range 250–8000 and a hydroxyl functionality from 1–8. The composition and the structure of the polyol polymeric backbone, the hydroxyl functionality and its distribution,

and the hydroxyl equivalent weight are all essential characteristics of polyols that are reflected in the properties of the resulting PU polymers.

A large variety of polyols is used in PU manufacture. They are homo- or copolyethers, homo- or copolymers, polyester-polyethers or polyisobutylene polyols. Another category of polyols are the so called 'polymer polyols' that are polyether polyols containing dispersions of organic fillers as an integral part of the polyol. Polyether amines have been introduced more recently for RIM technologies. The choice of polyol is imposed by the end application of the product. For example, PU that require hydrolytic stability and thermal resistance are based on polyether polyols, whereas a better resistance to solvents is imparted by the use of polyester polyols.

As a general guideline, linear or slightly branched polyols are used for the manufacture of elastomers and flexible foams, whereas moderately and highly branched polyols are used for coatings and rigid foams.

The technology of polyols for PU applications described particularly in patents has been reviewed extensively [8–12].

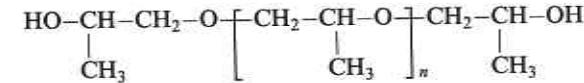
(a) Polyether polyols (PEPs)

PEP represent around 90% of the total polyols used for PU. They consist in a variety of linear or branched compounds with polyether backbone and hydroxyl functional groups. PU based on PEP have better hydrolytic resistance than those prepared from polyester polyols [13].

(a) The bulk of PEPs most widely used for PU are poly(propylene oxide) polyols (PPOs) and propylene oxide/ethylene oxide random or block copolymers. Two main categories of these polyols are prepared. For low modulus PU such as flexible slabs, elastomers (including RIM) and coatings, linear or slightly branched PEPs are prepared, with a 2–3 hydroxyl functionality and MW in the range of 1000–8000. High modulus highly crosslinked PU such as rigid foams, hard coatings, microcellular or solid plastics require highly branched, low MW polyols (250–1000), with an average hydroxyl functionality of 3–7.

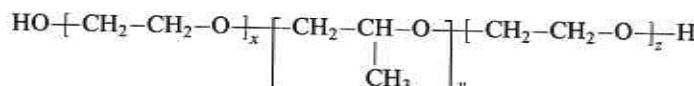
PEP can be synthesized by anionic, cationic or coordinate catalytic mechanisms [14]. Commercially PPOs are produced by anionic polymerization of propylene oxide initiated by different glycols (starters). The functionality of the initiator determines the hydroxyl functionality of the polyol.

With propylene glycol as initiator linear PPOs are obtained:



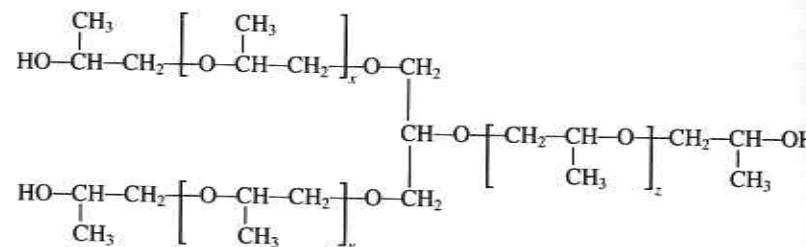
Secondary hydroxyls which are less reactive toward the isocyanates can be replaced by more reactive primary hydroxyls by copolymerizing propylene oxide with ethylene oxide so that the chains are tipped with ethylene oxide

units:

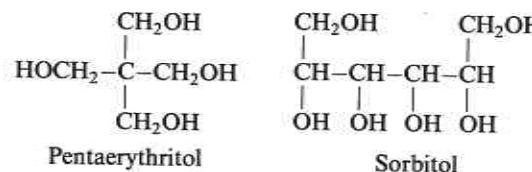


PEPs based exclusively on ethylene oxide are too hydrophilic to be satisfactory for PU.

To prepare branched PPO, it is common practice to initiate the polymerization of propylene oxide by triols such as glycerol, 1,1,1-trimethylolpropane or 1,2,6-hexane triol. When glycerol is used as the initiator, the resulted PPO are triols such as:



For even more branched structures, polymerization is initiated by polyfunctional initiators such as pentaerythritol or sorbitol with four and six hydroxyl groups, respectively:

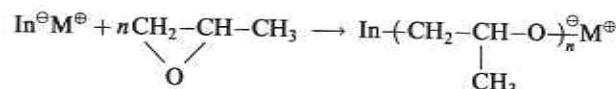


Amines and other active hydrogen compounds can act as initiators.

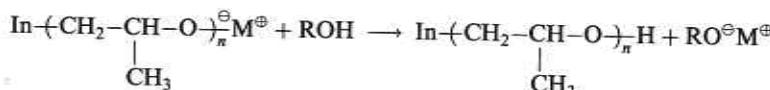
The initiation step of the anionic polymerization is the formation of the alkoxide ion (alcoholate) of the initiator in the presence of a basic catalyst, most frequently potassium hydroxide:



Propagation takes place by the addition of alkylene oxide units to the desired MW:

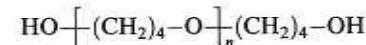


Chain growing is concluded by chain transfer and termination:



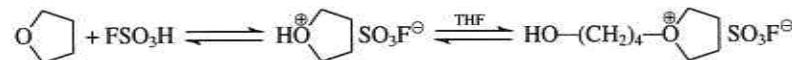
The manufacturing process can be run continuously or in semibatch operations and it is controlled extensively by instrumentation in order to obtain consistent products. Reaction temperatures are in the range 80–150°C. Polyols for PU must have a very high level of purity in order to ensure the control of subsequent reactions with isocyanates. The removal of catalyst traces has to go as far as 5 ppm for the majority of PPO applications, and abundant patent literature describes a variety of purification processes [12]. PPOs are stabilized with proprietary inhibitor antioxidants (hindered phenols, aromatic amines, phenothiazene and other compounds), saturated with nitrogen and stored hot. A flow chart of the preparation of PEP is presented in Figure 7.1.

(b) Another PEP is poly(oxytetramethylene) glycol (PTMG) or poly(tetrahydrofuran) (PTHF) introduced on the market in 1955:

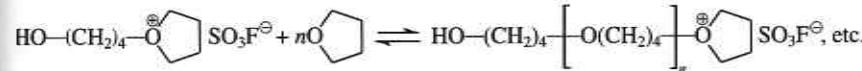


It is prepared by acid catalyzed, cationic, ring opening polymerization of tetrahydrofuran (oxacyclopentane) [15,16]. The most commonly used catalyst for the commercial polymerization is fluorosulfuric acid [17]. The initiating species is the oxonium ion and the propagation involves nucleophilic attack of monomer with simultaneous ring opening.

Initiation:



Propagation:



Commercial PTMGs have MW in the range 600–3000, a functionality of two and only primary hydroxyls. It is the most frequently used polyol for the preparation of PU thermoplastic elastomers and fibers due to its low T_g (-84°C), the regularity of its chain structure and its ability to crystallize upon extension.

(c) Filled PEPs have become major polyol raw materials for PU foams. This group of products consists of dispersions of different reinforcing polymers which are not additives but integral parts of the polyol [18]. They are made *in situ* in the liquid polyol through either free radical polymerization or step polyaddition reactions. Many commercial compositions of these particulate PEPs are prepared. Styrene-acrylonitrile or other copolymers grafted on PEP are known as ‘polymer polyols’. Other filled PEPs contain particulate dispersed phases based on polyureas, polyurethanes or epoxy resins.

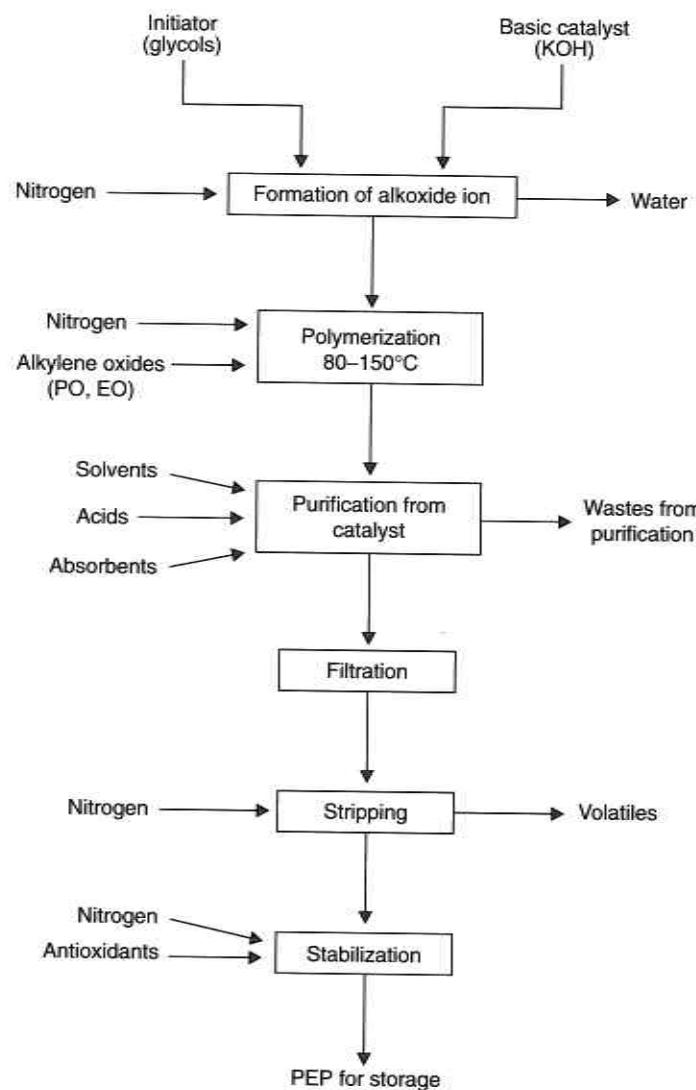


Figure 7.1 Preparation of polyether polyols.

Similar to the filler effects in composite materials, filled polyols enhance the load bearing characteristics of high resilience flexible PU foams and the strength properties of PU elastomers.

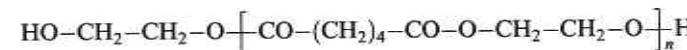
(d) Amine terminated PEPs have been prepared more recently and used in different polyurethane/polyurea technologies such as RIM applications, foam and cast elastomers, in epoxy resins as well as in many other non-polymeric fields [19]. Primary and secondary hydroxyl groups can both be

minated with ammonia in the presence of catalysts. These polyetheramines have increased reactivities toward isocyanates allowing shorter manufacturing cycles and, in many applications, the use of catalysts can be avoided [20,21]. The resulting polyurethane/polyurea products exhibit better mechanical properties.

(b) Polyester polyols (PESPs)

Chronologically PESPs are the first polyols used for the preparation of PUs [11]. Besides this main application, they are also used as components of epoxy, alkyd or unsaturated polyester resins.

Two different categories of PESPs are manufactured and intended for specific applications [22]. High purity PESPs with MWs in the range 2000–4000 are prepared by the condensation of dibasic acids such as adipic, sebacic, phthalic and aliphatic diols: ethylene glycol, diethylene glycol, propylene glycol, 1,4-butanediol, 1,5-pentanediol and 1,6-hexanediol. Slightly to highly branched PESPs are prepared from the same acids with polyhydric alcohols such as glycerol, trimethylolpropane or pentaerythritol. A typical polyester is poly(ethyleneadipate) diol:



Polycaprolactone diol is another PESP prepared by the ring opening polymerization of ϵ -caprolactone and diol or triol initiators:



Castor oil, a natural compound of ester type largely composed of glyceroltriricinoleate, is a triol specifically used in the manufacture of PU adhesives and coatings.

The composition and MW of PESP determine their physical properties, such as the ability for hydrogen bonding, the presence of crystalline regions, the melting temperatures and the viscosity of the melt. The hydrolytic stability of PESP depends on the concentration of the ester groups. The PESPs are used for PU elastomers, coatings and fibers with high tensile properties, excellent abrasion resistance and flex fatigue.

The manufacture of PESP is operated in batch or continuous reactors. The polyesterification of acids and glycols is conducted in two stages. In the first stage, the temperature is raised from 135°C to above 200°C in order to remove 90% of water from the condensation reaction. The second stage is conducted at a reduced pressure of 0.4–2 kPa which removes water and drives the polyesterification to the desired degree of conversion [11]. The preparation of PESP is presented in Figure 7.2.

The second category of PESPs consists of low MW aromatic PESP prepared by the transesterification of wastes of poly(ethylene terephthalate) or

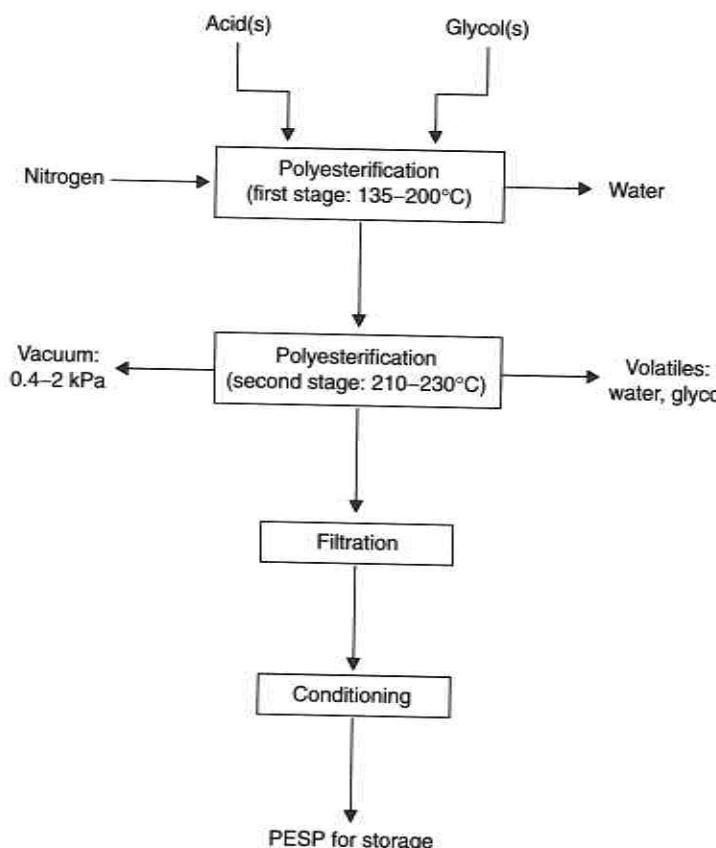
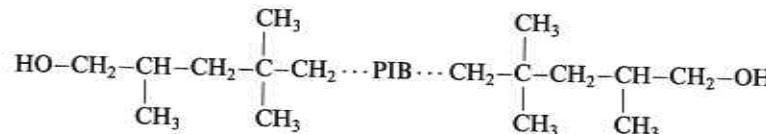


Figure 7.2 Preparation of polyester polyols.

dimethylterephthalate distillation bottoms [22]. Poly(ethylene terephthalate) (from recycled film or bottles) or dimethylterephthalate are transesterified with a glycol in a ratio determined by the desired MW. In addition to the low cost, the flammability of these PESPs is reduced due to their aromatic content. They are successfully used for rigid PU foams with improved burn characteristics.

(c) Polyisobutylene glycols

Polyisobutylene glycols are linear or branched hydroxyl terminated hydrocarbon chains:



They are prepared by the polymerization of isobutylene in the presence of bi- or trifunctional initiating transfer agents (called inifers) in conjunction with Friedel–Crafts acids [23]. They have recently become commercially available and are intended for polyurethanes for medical and engineering applications [24]. Polyisobutylene based polyurethanes exhibit improved hydrolytic and oxidative stabilities and excellent gas barrier properties due to low water absorption and low moisture permeability of hydrophobic hydrocarbon domains [25].

7.2.3 Chain extenders

Chain extenders play a major role in determining the final properties of PU even though they are relatively minor components in the formulations. They contribute to the nature and the density of chemical crosslinks as well as to the nature and size of the so called ‘hard segments’ that are responsible for physical crosslinks in linear thermoplastic polyurethanes.

Aromatic diamines and aliphatic or aromatic hydroxy compounds are used as chain extenders.

The selection of the chain extender depends on the formulation (diisocyanate and polyol), the ultimate properties and cost intended for the PU, as well as the processing characteristics. Aromatic diamines are very reactive toward the isocyanate groups and, as a general rule, they are used with prepolymers or systems that are less reactive, such as TDI–polyol prepolymers or for those technologies where very short gel times are required. Less reactive hydroxy extenders are used with more reactive MDI–polyol prepolymers [26]. Aliphatic diamines are too reactive to be used in practice.

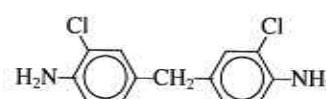
In diamine extended PU, the rigid aromatic rings and the highly polar urea groups formed in the reaction with the isocyanates, impart high mechanical strength to the material. Similar properties are obtained when aromatic hydroxy extenders are used. On the other hand, aliphatic short chain glycols are used as extenders when softer and medium strength products are desired [27]. Table 7.1 illustrates the general characteristics of urethanes cured by the two principal types of curatives.

Table 7.1 Influence of glycol and amine chain extenders on PU properties

Glycols	Property	Amines
	Reactivity of the system	→*
	Tensile strength	→
	Modulus	→
	Hardness	→
	Abrasion resistance	→
	Compression set	→
←	Resilience	→

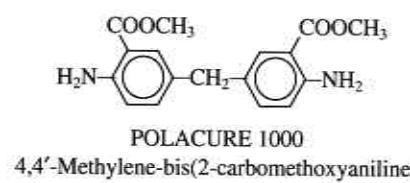
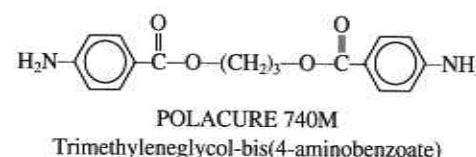
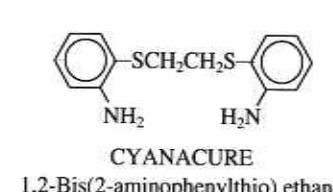
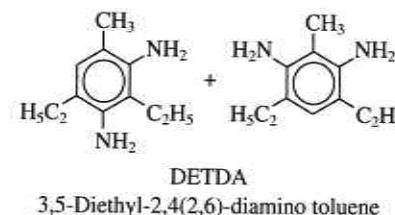
*low → high

The most extensively used diamine is 4,4'-methylene bis(2-chloroaniline) known under the trade name MOCA:



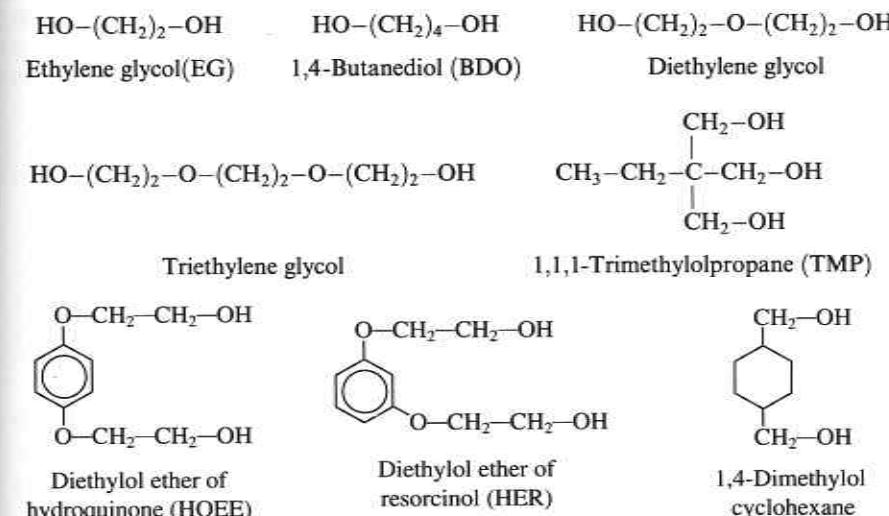
Because of concerns over the potential health hazards to humans, MOCA has to be handled with special care and its use is avoided whenever possible. In 1985 MOCA was labeled a 'probable human carcinogen' by the US Environmental Agency [28].

During the past few years, several new aromatic substituted diamine extenders became available commercially as a result of the intensive research work done to replace MOCA [27,28]. Electron withdrawing substituents on the aromatic ring in addition to their steric hindrance further reduce the reactivity of the amino groups and also lower the toxicity of the amines. Chemical formulas and trade names of the most common amine extenders are presented below:



Even if they have been found to be safer than MOCA, they are more expensive, require narrower processing parameters and are designed to more specific applications. In RIM formulations amines and particularly DETDA are the chain extenders of choice because they provide not only processing advantages over the glycol extenders, but also yield products with superior physical properties [29]. Gel times as short as 0.8–1.4 s have been practiced in PU/polyurea RIM technologies. For more processing latitude, mixtures of amines or of amines/glycols can be used.

Some of the more common hydroxy chain extenders are presented below:



When water is used as in flexible PU foams, in addition to the extension of the chains through urea linkages, the evolution of CO_2 from the reaction of water and isocyanate provides the gas that raises the foam.

1,4-Butanediol is by far the most used aliphatic diol for the preparation of thermoplastic PU elastomers [27,28]. Low hardness elastomers are obtained with TDI based prepolymers whereas high hardness products result with MDI prepolymers.

The two aromatic diols, HQEE and HER, yield products with increased thermal resistance and better retention of properties at elevated temperatures, and exceptionally good compression set.

Trimethylolpropane and glycerol used either alone or mixed with diols introduce additional chemical crosslinking in polyurethanes.

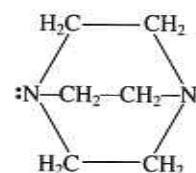
7.2.4 Catalysts

The utilization of catalysts is essential in many commercial procedures in order to achieve the desired processing parameters and physical properties.

During the preparation of PU, more than one of the previously mentioned isocyanate reactions take place simultaneously; therefore, the relative rates of all reactions should be controlled very carefully as they have an important bearing in determining the final structure and the properties of the resulting PU. It is thus evident the importance of the utilization of the appropriate catalyst or mixture of catalysts.

Many classes of compounds have been investigated as catalysts but only tertiary amines and some tin, mercury and bismuth compounds have acquired practical importance [11].

The catalytic activity of amines depends not only on their base strength but even more on steric hindrance at the nitrogen atom [30]. Amines with a less hindered lone pair of electrons on the nitrogen (with smaller or no substituents) are stronger catalysts. Thus, triethylenediamine (1,4-diazabicyclo-2,2,2-octane or DABCO) is a weak base but a powerful catalyst:



More specific tertiary amine catalysts with delayed initiation or heat activation have been developed recently [31].

The rates of various isocyanate reactions are influenced to a different extent by various catalysts, as can be seen from Table 7.2. The reaction (a) corresponds to OH/NCO reaction (growing of the polymer chains); (b) is a HOH/NCO reaction and results in the formation of amine groups with simultaneous evolution of CO₂ and the blowing of the foam, and (c) leads to crosslinking and to the formation of the final polymer network. A comparison between the relative rates of the three reactions for each individual catalyst is given in the fourth column. It is

Table 7.2 Effect of various catalysts on isocyanate reactions [32]

	<i>Relative rates of isocyanate reaction with</i>			
	<i>n-Butanol (a)</i>	<i>Water (b)</i>	<i>Diphenylurea (c)</i>	<i>a:b:c</i>
None	1.0	1.1	2.2	0.45: 0.5: 1
Triethylamine	86	47	4	21.5: 11.7: 1
Tetramethyl-1,3-butanediamine	260	100	12	21.6: 8.3: 1
Triethylenediamine	1200	380	90	13.3: 4.2: 1
Tributyltin acetate	80 000	14 000	8000	10.0: 1.7: 1
Dibutyltin diacetate	600 000	100 000	12 000	50.0: 8.3: 1

evident that metallic compounds, and particularly dibutyltin diacetate, are the most powerful catalysts and they selectively speed up the formation of polymer chains while the amines promote more strongly the gelling reaction, the reaction with water and the subsequent blowing of the foam. When used in mixture, tertiary amines and tin compounds are synergistic, i.e. their catalytic activity is more than twice the sum of their separate activities.

Furthermore, various classes of isocyanates respond in a different way to the action of catalysts. The relative rates of reaction of aromatic and aliphatic isocyanates are not strongly modified by tertiary amines. Tin and lead compounds provide a more pronounced catalytic activity on aliphatic isocyanates making them as reactive as the aromatic ones whereas iron, cobalt and titanium compounds make aliphatic isocyanates even more reactive than the aromatic ones [33].

As for the polyols, certain catalysts manifest a selective promoting effect on the reactivity of either primary or of secondary hydroxyl groups.

Hexahydrotriazines, potassium carboxylates and quaternary ammonium hydroxides are the catalysts of choice to introduce isocyanurate structures in PU-isocyanurate foams, whereas phospholene oxides catalyze the formation of carbodiimide structures in low density poly(carbodiimide) and PU-carbodiimide-isocyanurate foams [34].

7.3 POLYURETHANE ELASTOMERS

On the market there is a large spectrum of PU elastomers from highly flexible and resilient to hard, plastic-like materials [26]. The application of analytical techniques during the last years has led to a comprehensive understanding of structure–property relationships in PU and of the kinetics of formation processes. These two types of information have resulted in a high level of control of formulations and manufacturing.

The variation in properties is based on the balance of two kinds of structures in the PU macromolecule: a ‘soft segment’ block and a ‘hard segment’ block. The soft segments are formed from the isocyanate and the high MW polyol; the hard segments are formed from the isocyanate and the chain extender. In linear or slightly crosslinked polymers these two blocks are phase separated, giving rise to the outstanding properties of PU elastomers. On the other hand, crosslinked PUs are single phase, amorphous and non-elastomeric materials.

Different types of PU elastomers include cast elastomers both non-cellular and microcellular, thermoplastic elastomers, RIM elastomers and millable gums. PU elastomers can also be formulated into coatings, sealants and adhesives [2]. The main categories of PU elastomers are presented below.

7.3.1 Cast urethane elastomers

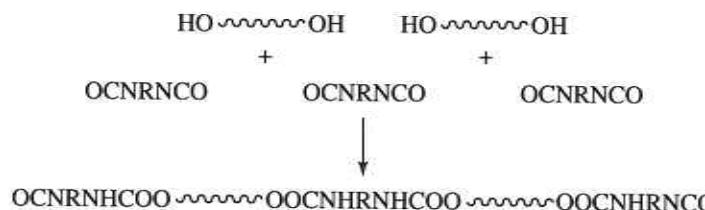
Casting as a manufacturing technique represents one of the major methods of preparing PU elastomers and foams. Casting involves a precise metering of chosen components, their thorough mixing and then pouring the reaction mixture into a heated mold wherein the crosslinked tridimensional polymer structure is simultaneously formed and molded in the desired size and shape. The final requirements of the product properties as well as the economical aspects dictate the selection of basic raw materials (isocyanate, polyol and extender), other ingredients as well as the manufacturing technology.

Linear or branched polyether and polyester polyols are used in thermoset PU elastomers with MWs in the range 2000–6000 [26]. Pure, crude or polymeric MDI as well as TDI mixtures are the isocyanates used according to the application. As for the chain extenders, they consist of both amine and glycol types (ethylene glycol, diethylene glycol, 1,4-butanediol).

The casting procedure generally follows two basic techniques known as the prepolymer route and the one-shot technique [26]. The reaction injection molding (RIM) procedure has evolved from the one-shot casting technique and will be discussed separately.

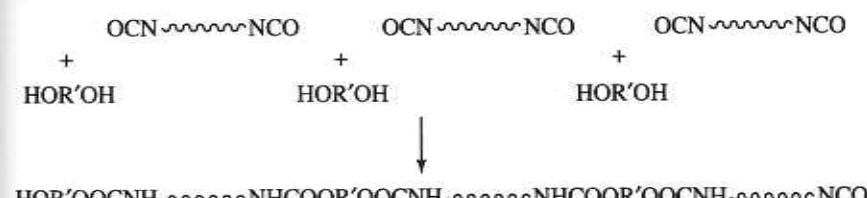
The prepolymer technique is by far the most commonly used for elastomers. The predried polyol is reacted with a molar excess of isocyanate (20–40%) resulting in a prepolymer that consists of two to three polyol molecules joined together by diisocyanate molecules and urethane linkages and terminated with isocyanate end groups. This is termed ‘full’ prepolymer and it results in extremely high viscosities. A variation of this method consists of the preparation of a ‘quasi’ prepolymer using only a part of the polyol so that higher ratio isocyanate/polyol is obtained. After the reaction, the mixture is composed of isocyanate capped polyol plus free, unattached isocyanate and the viscosity is much lower. The remaining polyol is mixed up with the chain extender and the other ingredients so that the overall stoichiometry is not changed. Metering and mixing operations are easier in the quasi prepolymer technique due to better balanced volumes to be mixed and to lower viscosities of the quasi prepolymer compared to the full prepolymer [26].

Chemical reactions in the preparation of a full prepolymer are presented below:

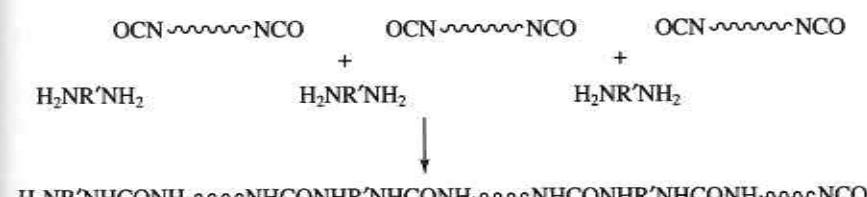


Storage stable prepolymers with isocyanate end groups are now available commercially [27].

In the second step of the process the liquid or molten prepolymer, which is in fact a ‘macrodiisocyanate’, is mixed and reacted with the previously heated and degassed chain extender. The time of mixing, known as ‘pot life’, depends on both the extender and the temperature and it generally takes some minutes. A very efficient mechanical mixing head in a mixing chamber is used to thoroughly mix the components. After each shot, the mixing chamber is cleaned with a solvent or an air blast. The mixture is poured into a heated open mold before the viscosity of the melt starts to grow significantly (gel time). During this stage the macrodiisocyanate reacts with the chain extender with the formation of new urethane or urea linkages that extend the polymer chains. The amount of chain extender is smaller than the equivalent of free isocyanate groups on the prepolymer so that free isocyanate groups still remain on the extended polymer chains. A schematic representation of glycol chain extension is illustrated below:



Diamine chain extension is represented schematically below.



In the curing stage that takes place in the mold, these free isocyanate groups react with the urethane or urea groups present on the polymer chains resulting in a crosslinked tridimensional structure. After demolding, additional postcuring at elevated temperatures is necessary in order for the products to acquire their final physical properties.

The flow charts of the preparation of casting polyurethane elastomers by the full prepolymer and quasi prepolymer methods are presented in Figures 7.3 and 7.4, respectively.

In the one-shot system all the ingredients are mixed together simultaneously and the rate of different reactions is carefully controlled by the use of catalysts. A flow chart of the preparation of cast elastomers by the one-shot method is illustrated in Figure 7.5.

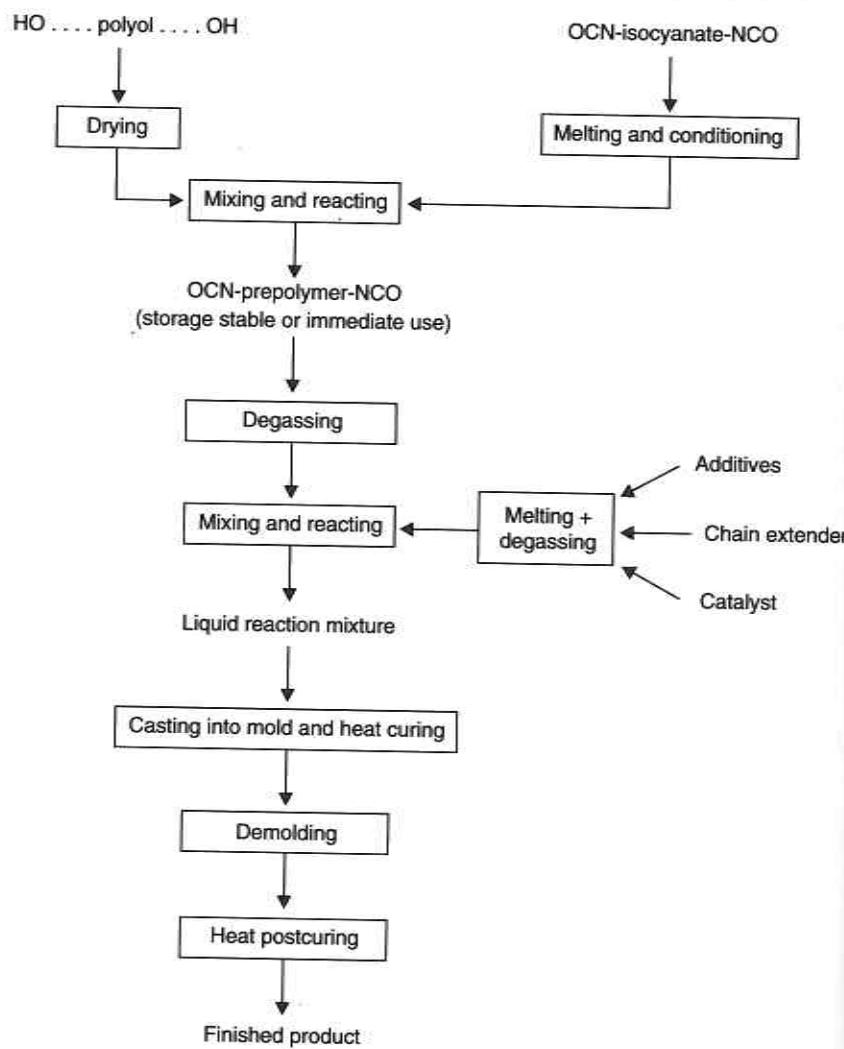


Figure 7.3 Preparation of PU cast elastomers by the full prepolymer method.

The overall stoichiometry of reactants in any PU system is expressed by the isocyanate index which is the molar ratio (NCO/all OH) × 100 and must be controlled accurately. When all the components are bifunctional and the index is 100, the resulted polymer is linear and thermoplastic. If the index is less than 100, the end groups are –OH. An index higher than 100 means that after the reaction with the chain extender, the polymer chains are –NCO terminated and crosslinking occurs on curing by allophanate or

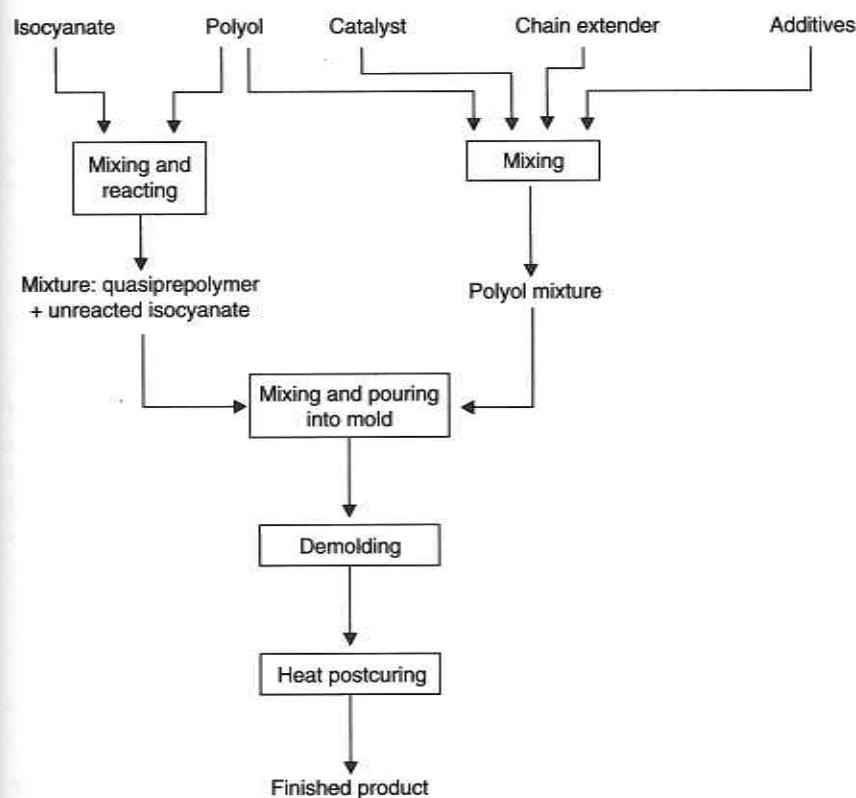


Figure 7.4 Preparation of PU cast elastomers by the quasi prepolymer method.

biuret structures. The degree of crosslinking is controlled by the isocyanate index [26].

Another way to introduce crosslinking is the utilization of polyols, isocyanates or extenders with functionalities higher than two (branched polyester or polyether polyols, polymeric or modified MDI compounds or trihydroxy extenders).

An example of typical formulations and of reaction conditions for casting polyurethane elastomers is given in Table 7.3.

A broad range of properties can be obtained by selecting appropriate formulations and reaction conditions. Among the most outstanding properties of polyurethane elastomers are high abrasion resistance, tear strength and tensile strength as well as excellent resistance to aliphatic hydrocarbon fuels, oils, oxygen and ozone. They are also good electrical and thermal insulators. They may be formulated from hard materials (50 Shore D) to very soft elastomers (10 Shore A). Hardness is controlled by the amount of hard segment that results from the reaction of the isocyanate and chain extender (Table 7.4) [35].

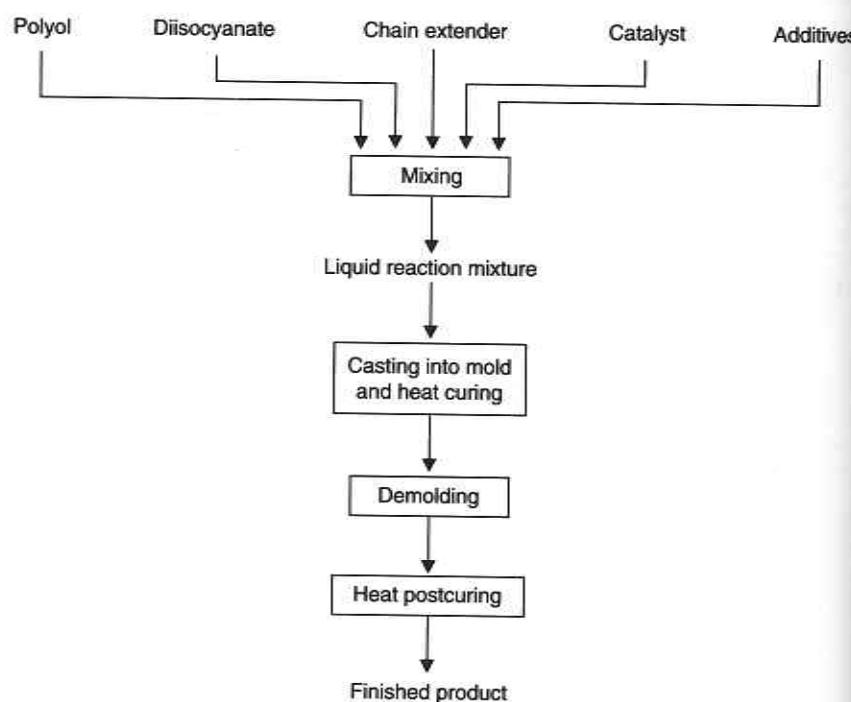


Figure 7.5 Preparation of PU cast elastomers by the one-shot method.

Some properties of a PU cast elastomer based on a 6000 MW polyether triol chain extended with 1,4-butanediol are given in Table 7.5.

Major shortcomings of PUs are their low resistance to steam, aromatic and chlorinated solvents and strong acids and bases. The maximum service temperature is 120°C.

Table 7.3 A typical formulation and reaction conditions for casting polyurethane elastomers

	<i>Parts by weight</i>	
Prepolymer (PTMG/TDI), 4.2% NCO	100	100
MOCA	12.5	—
1,4-Butanediol	—	4.0
Trimethylolpropane	—	0.3
	<i>Conditions</i>	
Prepolymer temperature (°C)	100	100
Extender temperature (°C)	115	100
Pot life (min)	12	45
Demolding time at 100°C (min)	30–45	90
Postcuring at 100°C (h)	16	20

Table 7.4 Effect of the amount of chain extender on some PU properties [35]

Hard segment (%)	Hardness (Shore A/D)	Flexural modulus (MPa)
25	82 A	4.3
50	60 D	484
75	78 D	1382

Common applications for cast PU elastomers are printing and industrial rollers, pipes and impellers for mining and quarrying industries, flexible tooling molds, recreational surfaces (in multisports halls, tennis courts and children's playgrounds), solid industrial tires for fork and lift trucks, skateboard and roller skate wheels, soft cast elastomer (tire filling material for heavy vehicles), sealing gaskets and oil field equipment, diaphragms and a variety of other mechanical applications [36].

Microcellular elastomers obtained by the incorporation of a blowing additive are prepared by different technologies and will be discussed with the RIM elastomers.

7.3.2 Thermoplastic polyurethane elastomers (TPUs)

TPUs represent about 9.8% of the total of thermoplastic elastomers [37]. TPUs have become the second most important class of urethane elastomers. They are linear block copolymers that can be processed on conventional plastic processing equipment by any standard method used for thermoplastics such as injection and compression molding, extrusion, calendering and film blow molding. They are supplied as dry granules [38].

TPUs are synthesized from the general types of PU components, namely a diisocyanate, a polyol and a chain extender. The preferred isocyanates

Table 7.5 Some properties of PU cast elastomer based on a 6000 MW polyether triol chain

Property	Value
Density	1.10 g/cm ³
Tensile strength	24 MPa
Elongation	275%
Modulus 100%	13.7 MPa
Hardness (Shore A)	95

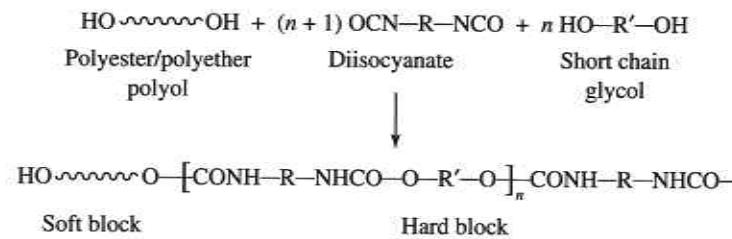
are MDI for general applications and H₁₂MDI for color-stable coatings. The most used polyols are poly(tetrabutylene adipate) glycols, poly(caprolactone) glycols and poly(oxytetramethylene) glycols. 1,4-Butanediol is the choice chain extender. Reaction stoichiometry is calculated based on the complete reaction of isocyanate groups with all hydroxyl groups, from the polyol and the chain extender (isocyanate index 100), so that linear chains are formed.

Full prepolymer, quasi prepolymer or one-shot techniques are all applied in the manufacture of TPUs. A typical formulation (by weight) based on 1/3/2 equivalent ratio of polyol/diisocyanate/extender are given below:

- Polycaprolactone (MW 2000), 1000;
- MDI, 375;
- 1,4-Butanediol, 90.

Using the two-step full prepolymer or quasi prepolymer routes, all or some of the predried polyol is reacted with the isocyanate at 110–130°C for about two hours and the resultant prepolymer is then mixed with the predried diol (chain extender or chain extender plus the remaining polyol) at 100°C. The mixture is poured continuously onto a heated endless belt and is removed after 20 minutes. After cooling, the product can be chopped or granulated and stored in air-tight containers. In the one-shot method, all the components are mixed together simultaneously and polymerization is allowed to proceed. The polymerization may alternatively be conducted in an extruder with intensive mixing.

The polyaddition reactions in the preparation of TPUs are illustrated schematically below:



TPUs are (AB)_n block copolymers. They are composed of 'soft segment' blocks and 'hard segment' blocks. The soft blocks are formed from the high MW polyols (polyester or polyether diols) and isocyanate and they are connected through urethane linkages to the hard blocks that are formed from the chain extender and isocyanate. TPUs have the properties of a vulcanized elastomer although they are thermoplastic. Many studies have been done to elucidate the morphology of thermoplastic elastomers and to explain their properties. During the polymerization, phase separation

occurs due to the basic thermodynamic incompatibility of the soft and hard segments [39]. Recent studies on the morphology of various TPUs show that the hard segments tend to cluster or aggregate with each other into crystalline, hard and rigid domains through hydrogen bonding which is due to the polar nature of urethane or urea linkages [40,41]. These hard domains are dispersed within the soft rubbery matrix composed of soft segments and act as filler particles reinforcing the matrix. They function as 'virtual crosslinkers' of TPU preventing permanent deformations of the elastomeric soft segments.

DSC measurements also evidenced the two-phase structure of TPUs by the presence of two separate T_g values corresponding to the soft and hard domains and a melting endotherm for the crystalline hard segment [42].

As in thermoset PUs, the hard segments control the hardness, modulus and tear strength while the soft segments provide flexibility, low temperature properties and solvent, oil and hydrolysis resistances [43–45].

Chain extenders play a major role in the final elastomer properties as they determine the nature of the hard segments. The content of the hard blocks is determined by the free unattached isocyanate content in the prepolymer.

Some properties of TPUs based on polycaprolactone polyester with different hardnesses (hard block content) are given in Table 7.6 [41].

TPUs have quite similar properties to those of cast PU rubbers but the absence of true covalent crosslinks results in higher values of compression set and in a more pronounced loss of strength with increasing temperature.

TPUs are used for the preparation of polyurethane engineering thermoplastics that are polyblends of TPUs and a variety of other polymers such as nylon, PVC, ABS, SAN, PC, PET, PBT, acetals and those reinforced with glass or mineral fillers [46–48]. For medical purposes, siloxane modified TPUs are being investigated [5].

The variety of applications is extensive. Among the most important are wire and cable jacketing, sheet and film, household gadgets, gears, various backing pads in abrasive applications, components for mining and drilling machinery and for agricultural equipment, medical devices, rolls and diaphragms [27,38,48]. TPUs are used not only as elastomers, but also for the preparation of adhesives, coatings and films.

Table 7.6 Some properties of TPUs based on polycaprolactone polyester

Hardness	80 Shore A	55 Shore D
Tensile strength (MPa)	52	43
Elongation (%)	490	350
Modulus 100% (MPa)	6	20

7.3.3 Polyurethane fibers

PU fibers are known under the generic name of Spandex fibers, which are composed of at least 85% segmented block TPU [38]. Long chain polyols are polyethers such as PTMG or linear polyesters that are reacted with TDI and/or MDI to form the prepolymer. For chain extension aliphatic amines (ethylene diamine), aromatic amines (*m*-phenylenediamine) or hydrazine are usually used. Spandex fibers are prepared by either solution or reaction spinning [38].

In solution spinning, the NCO terminated prepolymer is dissolved in a highly polar solvent such as *N,N*-dimethylformamide or *N,N*-dimethylacetamide, and the chain is subsequently extended by the addition of aliphatic diamines or hydrazine. Additives and stabilizers are also added to the solution, which is then pumped through a spinnerette plate into a hot atmosphere where the solvent diffuses out to form the filaments.

In reaction spinning, the additives and stabilizers are added to liquid prepolymer, which is then extruded into a coagulating bath that contains the amine chain extender which extends the polymeric chains and forms the fiber.

Crosslinks are produced through biuret and allophanate structures at elevated temperatures during the curing of fibers.

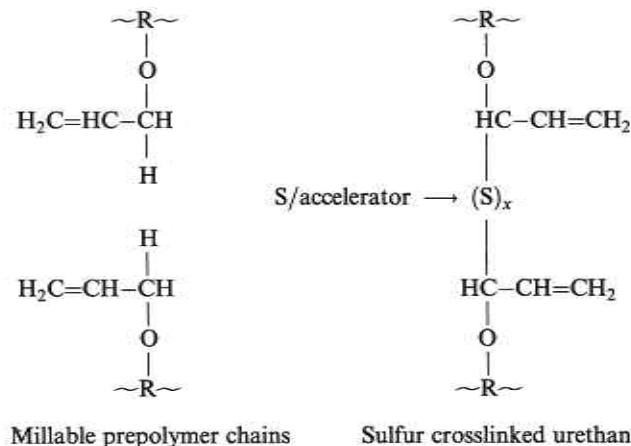
The basic characteristics of Spandex fibers are softness, high modulus, elongation and instant recovery when the stress is released, excellent resistance to oxidation, body oils and dry cleaning solvents and good dyeability. Spandex fibers have surpassed the properties of any elastomeric fiber known and they have replaced natural rubber fibers in many applications.

7.3.4 Millable polyurethane elastomers

Vulcanizable PU gums are used in small volume. They are processed on conventional rubber machinery. Before vulcanization they are essentially linear rubber-like compounds. They are prepared as storage-stable prepolymers with hydroxyl terminal groups (isocyanate index lower than 100) from linear polyols such as poly(ethyleneglycol adipate) or PTMG and MDI or TDI. In the next step these prepolymers are compounded on two roll mills with the other ingredients. Crosslinking is achieved by one of the three ways of curing used with PU millable elastomers, namely by sulfur, peroxides or blocked isocyanates [26].

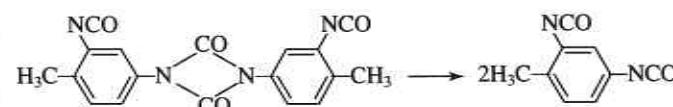
Better properties are obtained by conventional sulfur vulcanization in the presence of accelerators and activators. Special prepolymers with pendant carbon–carbon double bonds are prepared using unsaturated chain extenders such as the monoallyl ether of glycerol, $\text{H}_2\text{C}=\text{CH}-\text{CH}_2-\text{O}-\text{R}(\text{OH})_2$. A schematic representation of sulfur vulcanization is

presented below:



Curing with peroxides (e.g. dicumyl peroxide) by a free radical mechanism is used with prepolymers based on MDI. Free radicals which are produced on the polymer chains at the site of the active methylene group in MDI, join together in a crosslinked network.

The third way of curing is done by incorporation on the rolls of a blocked or 'latent diisocyanate' which is a dimer of toluene-2,4-diisocyanate. During the molding at about 150°C the dimer dissociates into free isocyanate:



which reacts with the urethane or urea groups on the prepolymer backbone and crosslinking occurs via allophanate or biuret linkages.

Millable PUs are compounded with reinforcing fillers such as carbon blacks, silicas and clays, as well as with other additives, just as other rubber materials are. Their properties are not generally as good as those of cast elastomers and they are of limited importance [2].

7.4 POLYURETHANE FOAMS

Polyurethane foams are by far the most versatile of all the polymeric foams. They may be manufactured in forms from the very soft to the very rigid. Properties can be tailored by the selection of suitable raw materials and formulations. The requirements for particular applications dictate the density of the foams [49].

Flexible and rigid foams are manufactured with different equipment, using different techniques and entirely different raw materials and formulations. In flexible foams, the chains are long and the crosslinks are farther apart, permitting more movement. In rigid foams, the crosslinks are close together creating a tight network and restricting movement. As a result, flexible and rigid polyurethane foams are very different in properties and uses and they will be discussed separately.

7.4.1 Flexible foams

These foams can be made with a large range of densities, flexibilities, elongations and compressive strengths. They are slightly crosslinked or even thermoplastic materials. The flexible foams are open celled [49,50].

Two categories of flexible foams are manufactured, hot molded and cold molded, high resilience (HR) foams. Hot molded foams are based on TDI and less reactive polyether polyols containing secondary hydroxyls. Their molding temperatures are from 80–120°C and cycle times from 20–30 minutes. Cold molded, high resilience (HR) foams are based on more reactive MDI or PMDI and primary hydroxyl-containing polyethers. Enhanced reactivity of HR foam components leads to molding temperatures of only 30–50°C and 4–20 minutes cycle times. HR foams have a higher resiliency and comfort for cushioning applications. Special polyethers, which contain grafted organic polymers such as acrylonitrile/styrene copolymers or polyurea dispersions, are used in HR foams in order to enhance the load bearing capacity.

Saturated polyesters such as poly(ethylene adipate) glycols or poly(propylene succinate) glycols are used in the higher grade foams especially for cloth lining where higher temperature resistance and dry cleaning solvents resistance are needed.

Water is by far the most successful blowing agent for flexible foams as it plays a double role. It reacts with isocyanate groups with the evolution of CO₂ gas that blows the foam and introduces urea groups on the polymer chains. The latter act as chain extenders and subsequently lead to biuret crosslinking and to tridimensional elastomeric foams. In some formulations additional physical blowing agents such as fluorocarbons and methylene dichloride can be introduced for lower density foams. The heat of the water–isocyanate and polyol–isocyanate reactions help to expand the CO₂ and to evaporate the added blowing agent. The density of the foam can be evaluated by the blowing index, I_B , calculated with an empirical relationship based on the overall amount of blowing agent per 100 parts of polyol [49]:

$$I_B = [\text{water}] + [\text{CCl}_3\text{F}] / 10 + [\text{CH}_2\text{Cl}_2] / 9$$

Foam formulations include at least one catalyst; however, with polyether polyols, which contain in the majority less reactive secondary hydroxyl

groups, a dual catalyst system is required. This is composed of a tertiary amine such as triethylene diamine, bis-(dimethylaminoethyl) ether or other similar amines and a metallic salt, usually dibutyltin dilaurate or stannous octoate [51]. The two catalysts are synergistic. Their ratio is very critical as each one preferentially promotes a different type of reaction. Tin compounds are particularly effective on the formation of urethane links, i.e. on polymer chain growth and gelation. Tertiary amines favor isocyanate–water reaction and CO₂ evolution and blowing. If the tin concentration is too high, gelation is too fast and the foam results tight, with closed cells and low air flow. At higher amine concentrations, the foam blows too fast and may collapse from lack of gel strength. Delayed action or heat activated catalysts, introduced more recently, are used for the manufacturing of large objects where mold filling is essential [31]. Latent catalyst systems have been created by the adsorption of conventional amines on molecular sieves (zeolite) [5].

Other important components in foam formulation are surface active agents, used at 1% level, which decrease the surface tension, facilitate the dispersion of water, and stabilize and control the structure of cells. The most used agents are water soluble polyether siloxane block or graft copolymers.

An example of formulation of a flexible polyurethane foam is given in Table 7.7.

Flexible polyurethane foams are manufactured almost exclusively by the one-shot process in which the ingredients are all mixed simultaneously or are previously preblended. The mixing head is the heart of the equipment. They are of two types: the recirculating type used in high pressure impingement RIM mixing machines and the non-recirculating, low pressure mechanical mixing machines. Both types are provided with sophisticated control system to monitor pressures, temperatures and flow rates and automatic flow control. Most slabstock foams are produced with non-recirculating heads with mixer speeds in the range 2000–6000 rpm. Their disadvantage is the need to flush the head with solvents after each shot. The reactive liquid mixture is poured continuously onto a conveyer system yielding foam slabstocks up to 2.2 m wide and 1.25 m high. The conveyer

Table 7.7 A formulation of a flexible polyurethane foam

	Parts by weight
Polyether triol (PPO MW 3000)	100
80/20 TDI, 110 index	41
Water	3
Triethylenediamine	0.3
Stannous octoate	0.15
Silicone block copolymer	1.0

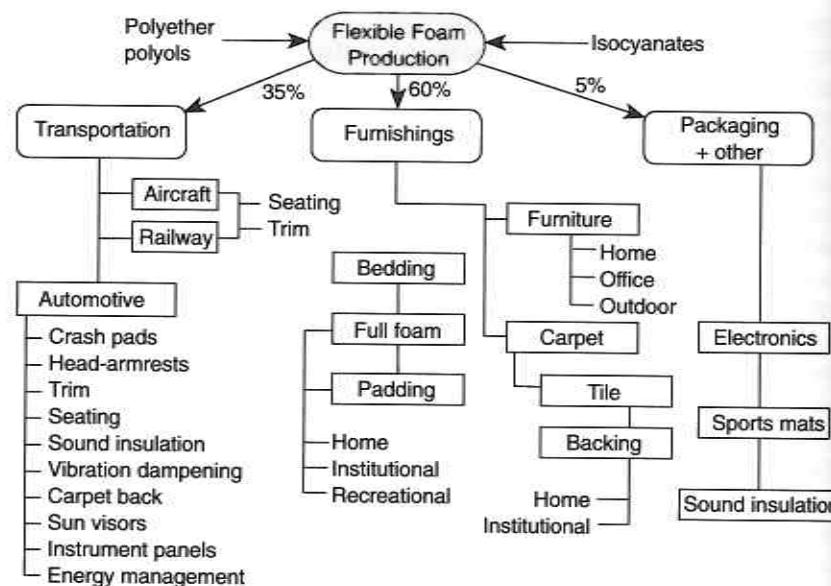


Figure 7.6 Application areas for PU flexible slabstock foam [52]. (Reprinted by permission of Carl Hanser Verlag from *Reaction Polymers* by W.F. Gum, W. Riese and H. Ulrich (eds), 1992, Carl Hanser Verlag Munich-Cincinnati.)

and the mixing head are located in a ventilated tunnel. After 5–10 minutes, the foam can be cut and handled. The slabstocks are then heat cured for 24 hours and then cut into different sized products and shapes.

When the product shape is more complex or contains inserts, the polymerizing liquid is poured into molds; the mixture foams and fills the mold. Another application is in foam carpet cushioning and is realized by pouring the mixture directly onto the carpet that has been previously coated with an intermediate layer.

A recent review of foam morphology studies has shown that the polymer that composes the foam is phase separated PU/urea that contains a soft segment phase, a hard segment or microdomain and a precipitated, aromatic polyurea discontinuous phase [52]. The polymer is a lightly crosslinked (AB)_n block copolymer with excellent elastomeric properties similar to that of elastomers. Dynamic mechanical spectroscopy (DMS) and differential scanning calorimetry (DSC) clearly demonstrated the presence of a transition T_g at -60 to -40°C from the soft polyether block and a high T_g at about 250°C attributed to the polyurea hard phase. In addition to this physical crosslinking due to phase separation, some chemical crosslinking is present from branched polyols and from biuret and allophanate links.

The geometry of the cells is a very important factor in the foam's ultimate properties. The first step in cell formation is the nucleation, i.e. the initiation

of the bubbles, which is done by the gases already present in reactants. The next step is the growth of the bubbles by thermal expansion and by evolution of CO₂ from the water-isocyanate reaction. Spherical bubbles grow and are transformed into pentagonal dodecahedral cells [49]. The process ends by the rupture of cell walls and the opening of the cells. In a good foam, a majority of cells have open pentagonal windows with tridimensional triangular cross-section struts in between.

The final mechanical properties of a flexible foam depend both on the macroscopic cell geometry and on the morphology of the polymer contained within the structural elements of the foam. In cushioning applications, a low hysteresis and a high resiliency are of major importance in compressive loading. Proper formulation will achieve low hysteresis values based on the advanced phase separation. Increasing the density of the foam increases the durability of the foam measured by tensile, tear, elongation and fatigue tests.

Flexible urethane foams are manufactured with densities in the range 0.016–0.048 g/cm³; semiflexible foams range from 0.096–0.192 g/cm³ and high resilience foams (HR) are in the range 0.028–0.048 g/cm³.

Based on the broad range of load bearing capacities and resiliencies, the largest volume of foam is used for cushioning applications for furniture, automobiles, aircraft, bedding and carpet underlay. Polyether based foams are preferred as they have a higher resilience than polyester based foams. The applications of flexible PU foams are summarized in Figure 7.6. On the other hand, flexible foams based on polyesters perform better for textile applications as laminates for cold weather clothing; they are particularly resistant to dry cleaning solvents.

Other major uses include packaging of military hardware, electronic parts and delicate products, acoustic and thermal insulations and safety equipment. An important use for these open cell foams is as filters for oils, chemicals and various air pollution control devices.

7.4.2 Rigid polyurethane and polyisocyanurate foams

Rigid PU and polyisocyanurate foams are highly crosslinked materials in contrast with flexible foams, which are only lightly crosslinked. They are mainly used for insulation purposes on account of their high insulating efficiency and their high strength to weight ratio that provides significant structural integrity. The raw materials used in flexible and rigid foams are quite different.

The rigidity is provided by the high functionality of both the isocyanate and the polyol components. The majority of isocyanates used are crude and undistilled, such as PMDI or its mixtures with modified TDI, and mixtures of MDI with its oligomers [53,54]. The functionality of the isocyanate component is between 2.6 and 3.2. The isocyanate index in different

formulations is of the order of 250 or even as high as 450–500 in PU/isocyanurate compositions.

Three basic types of polyols are generally used: polyester, polyether and halogen- or phosphorus-containing polyols. Polyester polyols have a better flammability performance due to an increased formation of char that serves as a heat barrier for inner foam. They are derived from aliphatic or aromatic dicarboxylic acids and their derivatives such as phthalic anhydride, dimethyl terephthalate residues and poly(ethylene terephthalate) scrap by transesterification with short chain diols [55]. For some applications polyethers are preferred to polyesters; they are branched and polyfunctional compounds with MW as low as 500. The short distance between the hydroxyl groups of the polyol accounts for an increased density of crosslinks in the final polyurethane foam. The functionality of polyols may be even as high as eight when they are synthesized in the presence of polyfunctional initiators such as pentaerythritol or sorbitol. Polyethers have better compatibility with chlorofluorocarbon blowing agents than polyesters.

Polysiloxane-polyether block copolymers are used as surfactants providing nucleating sites for bubble formation and regulating the size, shape and distribution of cells. Common catalysts for PU rigid foams are tertiary amines and only infrequently metallic salts. When PU/isocyanurate are prepared, specific isocyanate trimerization catalysts are used such as carboxylic metal salts (e.g. potassium acetate or octoate) [56].

The choice of the blowing agent for PU rigid foams is of major importance for the insulating efficiency. Rigid foams are closed cell and, at a density of 0.032 g/cm³, 97% of their volume is occupied by gas. The overall thermal conductivity of a foam or the *K*-factor, expressed in watts per meter and Kelvin (W/m · K), depends on three contributions:

$$K = K_g + K_s + K_r$$

where K_g = the gas contribution, 45–50%; K_s = the solid polymer contribution, 25%; K_r = the radiative heat transfer contribution, 30–35%.

Solid polymer has relatively high thermal conductivities of 0.180–0.250 W/m · K but it contributes only a small fraction (about 25%) due to its small volume fraction in the foam matrix. K_s is only slightly affected by changes in polymer composition [57]. Radiative heat transfer K_r increases strongly with decreasing foam density owing to thinner cell walls. The contribution from gas thermal conductivity is by far the largest.

Thermal conductivities in W/m · K of some gases are

- air, 0.024;
- carbon dioxide, 0.014;
- fluorocarbons, 0.008–0.010.

For thermal insulating properties, trichlorofluoromethane (CFC-11 b.p. = 23.8°C) is the best blowing agent due to its low thermal conductivity.

It remains incorporated in the closed cells of the insulating foam. Concern for depletion of stratospheric ozone layer by CFC-11 imposed its partial to total replacement during the present decade [58]. To date, only two halocarbons, partly hydrogenated, have been found to be satisfactory blowing agents, namely 1,1-dichloro-2,2,2-trifluoroethane (HCFC-123) and 1,1-dichloro-1-fluoroethane (HCFC-141b) [59]. They are environmentally safer as they can be destroyed in the troposphere. More recently a technique has been developed for the cleavage of partly hydrogenated halocarbons at 2000°C in an oxyhydrogen flame to afford HF, HCl and CO₂ without formation of polychlorinated dioxins and furans [5].

Water is used in addition to halocarbons, and CO₂ gas produced in the water-isocyanate reaction acts as a blowing agent. The resulting polyurea structures contribute to increased mechanical strength of the foam.

The initial values of thermal conductivities of PU/isocyanurate rigid foams are ranging from $K = 0.015\text{--}0.020\text{W/m}\cdot\text{K}$, but these values deteriorate over time [53,59]. The cell gas consists mainly of CFC-11 and CO₂. The cell membranes are permeable to each of the gases present, although to a different degree. CO₂ diffuses completely out of the cells in a few days. The larger and heavier CFC-11 molecules diffuse much more slowly and remain in the foam for years. As time progresses, the concentration of CFC-11 in the cell diminishes as air permeates into the foam and its concentration increases until an equilibrium is reached at a 1/1 ratio of CFC-11/air in the cell. The net effect of the dilution of CFC-11 with air is a gradual increase in the thermal conductivity of the foam. Halocarbon blown foams have ultimate thermal conductivities significantly lower than those of CO₂ blown foams, as can be seen from the values in W/m · K below:

- CFC-11 blown foam (final), 0.024;
- CO₂ blown foam (final), 0.035.

Strength characteristics of a foam depend mainly on the polymeric phase whereas its thermal conductivity depends on the gas phase [60]. When structural strength is required, the foam is blown by CO₂ from the isocyanate-water reaction that introduces PU/urea units and biuret additional crosslinks. In thermal insulation foams, where thermal conductivity is the most important characteristic, halocarbon blowing agents are additionally used.

A common formulation for thermal insulation PU rigid foam is shown in Table 7.8.

Another important characteristic required for thermal insulation foams is combustibility. The behavior of polyurethane foams in fire is not good. Improved flame resistance is achieved by the incorporation of either reactive or additive-type fire retardants. Chlorinated or phosphorus-containing polyols may be used as reactive hydroxy compounds. Phosphorus promotes

Table 7.8 A common formulation for thermal insulation PU rigid foam

<i>Parts by weight</i>	
Polyether polyol	100
Glycerol	10
PMDI	stoichiometric + 5%
CFC-11	50
Triethylenediamine	0.5
Silicone block copolymer	1.0

char formation which serves as a protective barrier. On the other hand, halogens are free radical scavengers that suppress flame propagation.

An even more significant improvement was introduced by the isocyanurate rigid foams which are based on isocyanate cyclotrimerization presented in Section 7.2.1 [61]. Cyclotrimerization results in highly crosslinked foams that are too brittle. Trimerization was coupled with urethane formation resulting in polyurethane-isocyanurate rigid foams and composite materials. Isocyanate trimerization was found to be a slower process than either urethane or urea formation and thus it takes place at the end of the polyaddition process with the remaining isocyanate groups in the presence of specific catalysts.

Some properties of polyurethane-polyisocyanurate foams are given in Table 7.9.

Polyurethane-polyisocyanurate foams have good resistance to burning and flame spread and very good hydrolytic stability [61,62].

Besides trimerization, isocyanates can react with each other in the presence of suitable catalysts to form carbodiimide structures (Section 7.2.1). The simultaneous evolution of carbon dioxide gives rise to foamed products. As carbodiimide groups further react with free isocyanate groups, the resulting foams are crosslinked rigid materials with densities of 0.016–0.020 g/cm³ and high flame resistance, and good thermal and acoustical insulation characteristics. Among their applications are underfloor sound insulation, pipe insulation and thermal insulation between cavity walls [62].

Table 7.9 Some properties of polyurethane-polyisocyanurate foams

<i>Property</i>	<i>Value</i>
Density	0.024–0.096 g/cm ³
Initial <i>K</i> -factor	0.019 W/m·K
Equilibrium <i>K</i> -factor	0.024 W/m·K
Service temperature	–185 to 150°C (compared to –40 to 95°C for rigid PU foam)
Compression strength	0.14–0.28 MPa
Shear strength	0.10–0.24 MPa

Rigid polyurethane foams can be produced by a large number of methods either in plant or by portable equipment and pour-in-place methods. One-shot, prepolymer and quasi prepolymer techniques can all be used. Besides continuous slabbing (pouring into large blocks onto a moving conveyor system), other processing alternatives include pouring in place, spraying, frothing and laminating. Foam density is largely a function of the concentration of the blowing agents.

The rigid urethane foams have proved to be far superior to any other polymeric foam in thermal insulation properties over a wide range of temperatures. They are extensively used in home and building insulation for walls, roofs and structural components [60], for refrigerated trucks, trailers and railway cars, for refrigerators and freezers (household, commercial and industrial), for insulation of storage tanks and pipes, and for insulation in automobiles, aircraft and ships. Another application is for flotation in barge compartments, small boats and in the oil industry.

Less expanded, high density structural and decorative foams, the so called 'simulated wood' (different wood grains may be captured perfectly on the foam surface) are used for doors, windows and other accessories, and in furniture manufacture [60,63].

The recent abundant patent literature demonstrates the effort to find various ways for the reutilization of PU waste materials [5]. Glycolysis is the general chemical method for the processing of large amounts of waste. On the other hand, the physical method consists of the production of reutilizable PU powder. For example, the foam originating from disused refrigerators is already recuperated as powders.

7.4.3 Polyurethanes by the reaction injection molding process

A development of one-shot injection molding gave rise to the independent process known as 'reaction injection molding' (RIM) which has become a high productivity manufacturing process. The RIM technique is applied to produce parts made from PU that range from high density, high modulus elastomers to lower density structural foam parts [64–67].

The RIM process consists of a precise and individual metering of all the components, which must be liquid, and their thorough and extremely rapid mixing; the highly reactive liquid mixture is poured into molds where the reactions take place, and the polymeric material is formed and shaped into the final products.

The considerations made before on raw materials and additives, as well as on isocyanate reactions, all apply to RIM components. RIM polyols are di- and trifunctional polypropylene oxide capped with ethylene oxide, MW = 4000–6000, as well as amine terminated polyethers, MW = 2000–5000. The resulted soft segments of urethane or urea-type respectively, impart good low temperature impact, elongation, tear strength and abrasion resistance.

Glycol and amine chain extenders are both used. The most widely used chain extender is 2,4/2,6-diethyltoluene diamine, 80/20 isomer mixture (DETDA) that forms urea hard segments contributing characteristics of stiffness and thermal stability [68]. Full polyurea RIM formulations are so reactive that the reactions occur almost instantaneously (0.8–1.2 s) in the RIM mix head and the use of any catalyst can be avoided. For a better control, the reaction can be slowed down by blending low levels of amine terminated polyethers with polyether polyols. When the use of catalysts is necessary, their selection is even more critical in order to balance the speed of each individual reaction in the highly reactive system. Typical catalysts are organometallics such as dibutyltin dilaurate and tertiary amines, especially DABCO.

A comparison of the relative reactivities of amine and hydroxyl end groups toward the isocyanate group is presented in Table 7.10. The isocyanate component is a liquid carbodiimide modified MDI or other liquid glycol modified MDI derivative.

Individual components are continuously recirculated from their storage tanks through the delivery lines, mix head and return lines to ensure their temperature consistency within a $\pm 1^\circ\text{C}$ limit.

The mixing head is the critical point of the system. It is a $0.3\text{--}4\text{ cm}^3$ chamber where the components are continuously introduced and mixed. Mixing is realized by high pressure ‘impingement’, i.e. a counter-current introduction of component streams at 10–20 MPa and their highly efficient turbulent mixing. The simple configuration of the impingement mixing head avoids the need of cleaning the head and delivery lines between shots (self-cleaning system). The resultant polymerizing liquid mixture, which is highly reactive, is then injected into molds that are part of the RIM processing system. Reaction rates and injection times are adjusted to achieve a gelation time at the point of complete fill of the mold, which is in the range of 1–2 s.

The reaction between $-\text{OH}$ and $-\text{NCO}$ groups to form urethane linkages is highly exothermic (approximately 104 kJ/mol) and it takes place in the molds. The molds are provided with good thermal conductivity

Table 7.10 Relative reactivities of hydroxyl and amine groups toward isocyanates [2]

Reactive group	Relative reactivity
Secondary hydroxyl	1.0
Primary hydroxyl	5–10
Primary aromatic amine	10–100
Secondary aliphatic amine	2000–3000
Primary aliphatic amine	10 000

Table 7.11 Typical conditions for reaction injection molding [69]. (Reproduced by permission of Taylor & Francis, Inc. from *Principles of Polymer Systems* by F. Rodriguez, 2nd edn, 1982, pp. 354. All rights reserved)

Formulation	Parts by weight
Resin stream:	
Polyols	150
Dibutyltin dilaurate (catalyst)	0.045
Amine (cocatalyst)	0.6
Isocyanate stream:	
Polyfunctional isocyanate	96
Blowing agent (Freon type)	3
Methylene chloride	1
Processing parameter	Condition
Resin temperature	54°C
Isocyanate temperature	21°C
Mold temperature	57 ± 3°C
Resin pressure	120 atm
Isocyanate pressure	100 atm
Throughput	1.1 kg/s
Demolding time	1–2 min
Postcure	1 hour at 120°C

(metallic molds) and are designed with temperature control. Table 7.11 illustrates a typical formulation and the operation conditions for a RIM process [69].

Further productivity improvements have resulted in the introduction of internal mold release (IMR) based on zinc stearate solubilized in the polymerizing mixture by the presence of the amine-type compounds (amine polyether and amine chain extender) [68]. When the amine compatibilizers are rapidly consumed on contact with the isocyanate, zinc stearate precipitates as a uniform dispersion in the reaction mass. The IMR minimizes the time spent for mold preparation.

Milled glass up to 40–50%, treated with aminosilane adhesion promoter, fibrous calcium silicate mineral or treated mica are used as fillers in reinforced RIM (RRIM) to provide a high flexural modulus and low thermal expansion coefficient, especially in thin parts. Some properties of unfilled and glass filled PU/urea RIM polymer are presented in Table 7.12.

When RIM is used to produce microcellular or foamed parts, the reaction mixture is injected into the mold without filling it completely. Filling the mold is completed by the expansion of the material, which can vary from 5–10% expansion for microcellular elastomers to 60–75% expansion for structural foam systems. Surfactants such as

Table 7.12 Some properties of PU/urea RIM for automotive applications [68]

<i>Property</i>	<i>Unfilled</i>	<i>15.8% Glass filled</i>
Density (g/cm ³)	1.02	1.07
Hard segment content (%)	41.1	30.9
Flexural modulus (MPa)		
-29°C	849	618/392*
22°C	405	360/194*
70°C	304	260/137*
Tensile strength (MPa)	26.7	15.2
Elongation (%)	195	125/180*
Coefficient of thermal expansion ×10 ⁻⁶ /°C (from 66°C to 121°C)	170	51/145*

* parallel/perpendicular

polyoxyalkylene polysiloxane copolymers are used to facilitate the formation of a fine cell structure.

Low boiling halogenated alkanes such as CFC-11 or the environmentally safer CFC-123 are used as blowing agents. They are vaporized by the reaction heat in the interior of the mold but are condensed in the surface layer by contact with the cooled mold. An expanded foam core is formed in the interior of the part that compresses the exterior layer of material to the mold walls, resulting in a continuous skin-like surface. These self-skinning foams produced by RIM technology are also called integral skin or structural foams. The densities of RIM foamed products may range from 0.2 g/cm³ to 1.2 g/cm³ for microcellular elastomers.

The same variations as practiced in the manufacture of cast elastomers and foams are encountered in RIM processes, namely:

- true one-shot system: all components are individually and simultaneously introduced into the mixer;
- two-component system: isocyanate constitutes component A, and all other ingredients are premixed and constitute component B;
- quasi prepolymer system: the isocyanate is reacted with a part of polyol to give the quasi prepolymer (component A); the remaining polyol is premixed with all other ingredients and constitutes component B.

PU, polyurea, PU/urea and PU/isocyanurate elastomers and foams produced by RIM and RRIM processes have found numerous applications in the automotive industry for the production of exterior large size components such as front and rear bumpers, instrument housings, head rests, steering wheels, pneumatic tires for tractors and other parts. The shoe industry utilizes RIM microcellular elastomers or flexible and semiflexible foams with or without an integral skin to produce shoe soles. Rigid foams are used in the furniture and building industries.

7.5 POLYURETHANE COATINGS, ADHESIVES AND SEALANTS

Polyurethanes are largely used for coatings, adhesives and sealants owing to their outstanding properties such as abrasion resistance, toughness, flexibility, tear strength, adhesive properties and solvent resistance.

The chemistry of PU coatings, adhesives and sealants is similar to that encountered with other urethane materials. TDI, MDI or PMDI are the isocyanates used for non-light exposed applications. Aliphatic and cycloaliphatic isocyanates such as isophorone, hydrogenated MDI, biuret or isocyanurate derivatives of HDI and a number of newer isocyanates are chosen in those applications where weatherability and appearance are important. Polyethers, polyesters, acrylic polyols, glycols and amines are used in prepolymers and for chain extension. For some applications, the formulation is based on thermoplastic PU. Besides the PU resin, catalysts, fillers, pigments, plasticizers and other additives and sometimes solvents compose the formulation.

To meet pollution and safety regulations, an increasing importance is given to PU water dispersions for coatings and adhesives, thus avoiding the utilization of organic solvents [26].

Available systems are classified as one-component and two-component [70,71]. The one-component system actually consists of several components mixed and stored together and can be cured by oxygen (air), moisture or heat. They are based on PU with high MW but which are still soluble. The two-component systems are stored as two separate components that contain ingredients terminated in active groups and they are mixed just before the application (short pot life) and then cured. Two-component systems are used in more demanding applications for physical characteristics.

7.5.1 Coatings

The US consumption of PU coatings in 1990 was 111 000 tons [2]. They can be formulated into a large number of types of coatings; the early attempts to classify them have been outgrown [70].

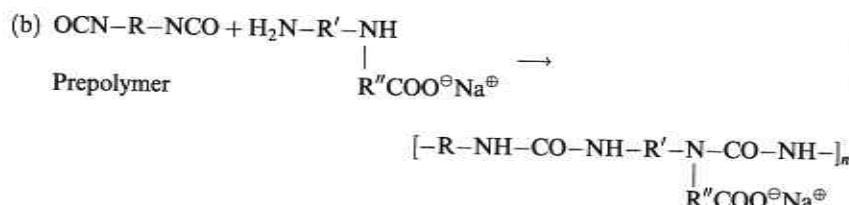
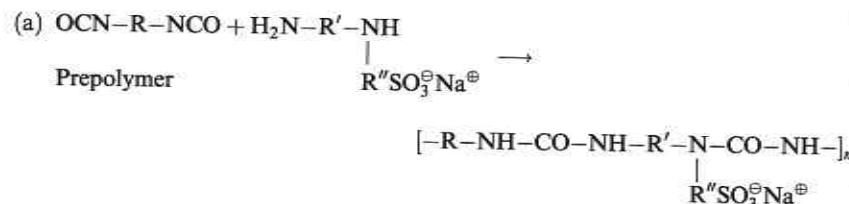
Several one-component systems are available on the market. Uralkyds are urethane modified alkyd resins cured by atmospheric oxygen and used as wood finishes and enamels. Moisture cured coatings based on NCO terminated prepolymers are limited to thin films and in places with relative humidities of 40–75%. Major markets are for concrete and wood seamless floors [60]. Coatings based on blocked isocyanates can be cured at room temperature (phenol blocked and amine coreactants) or at 190°C (alcohol blocked and hydroxylic coreactants). These coatings are also available as water dispersions.

The most important types of PU coatings are based on two-component systems: an isocyanate prepolymer and a polyol. They need meter-mix equipment. Clear topcoats have recently entered the automotive market. PU coatings are largely used for aircraft, heavy machinery, buses, trucks and maintenance coatings.

Coatings based on high MW thermoplastic PU dissolved in a solvent are used on textiles and leather (equally as water dispersions) and for magnetic media coatings used for audio, video and computer tapes and computer floppy disks [2]. They are cured by the evaporation of the solvent. Other PU coatings are formulated for radiation cure (flooring), vapor cure (foundry molds) or as urethane powder coats (appliances and metal furniture).

The water dispersions of PU elastomers are of growing importance. They are non-toxic, non-flammable and do not pollute air or waste water [26]. They are based on PU ionomers which have hydrophilic ionic groups incorporated into the polymer. These ionic groups function as an ionic emulsifier making unnecessary the use of external emulsifiers. Due to the absence of low MW emulsifiers, these systems show extremely good film forming properties even in the case of especially hard PUs such as air drying lacquers.

PU ionomers are prepared to form anionic or cationic dispersions. Anionic ionomers have sodium sulfonate (a) or sodium carboxylate (b) ionic groups attached to side branches. They are prepared by the chain extension of NCO terminated prepolymers with special diamines that contain the respective ionic groups:



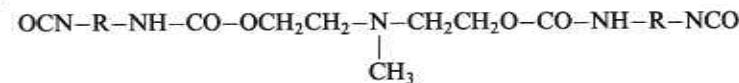
These ionomers can be readily melt dispersed into water (without the use of any solvent) and subsequently crosslinked by the polycondensation of the urea groups from the polymer chain with formaldehyde.

Cationic PU ionomers are prepared from NCO terminated prepolymers chain extended with alkyl substituted ethanolamines such as

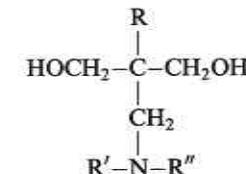
N-methyldiethanolamine, $\text{CH}_3-\text{N}(\text{CH}_2\text{CH}_2\text{OH})_2$:



Prepolymer



Significantly more light stable PUs are obtained from aminodiol which contain the tertiary nitrogen atom in a side branch such as 2-alkyl-2-dialkylaminomethyl-1,3-propanediol:



Emulsification occurs when these extended prepolymers are added to 3% aqueous acetic acid under high speed mixing. The subsequent curing of the latex takes place by the reaction of terminal free isocyanate groups either with water or with water soluble diamines [11].

Another way to prepare cationic dispersions from the above mentioned extended prepolymers is by quaternization of tertiary nitrogen atoms. They can react readily with formaldehyde in the presence of water to form crosslinked products.

Ionomers with a high percentage of ionic groups are excellent dispersants, superior to the usual surface active agents for the emulsification of non-ionic PU. The hydrophilic ionomer component forms the surface layer of the dispersed particles.

7.5.2 Adhesives

PU adhesives are complex mixtures containing PU resin, fillers, pigments and plasticizers. The USA's consumption of PU adhesives in 1990 was 88 000 tons [2]. PUs manifest very good adhesion to materials as varied as rubber, other plastics, synthetic fibers, wood, glass, cements and metals. Adhesive properties may be attributed to the polar nature of the compounds used in their formulation. Furthermore, the isocyanates present in PU compositions may react with any active hydrogen present in the adherent or with the thin films of water often present on the surfaces of materials such as ceramics, glass and metals. These reactions permit the attainment of high bond strength [71]. PU adhesives are very useful when elastomeric bonds are required on flexible substrates such as rubber or plastic.

The best of PU adhesives are superior in performance to virtually any other adhesive type at cryogenic temperatures. They maintain their shear

strength and toughness at temperatures far below those that cause serious embrittlement of adhesives designed for use at ambient temperatures and above [60]. Polyurethanes have the drawback of poor chemical and thermal stability and loss of bond strength at temperatures above 80–100°C.

The oldest types were based on triphenylmethane-4,4',4''-triisocyanate or NCO terminated prepolymers as solvent-borne or 100% solids, cured by air moisture. They are used today in rebonded foam, tire cords and furniture. Conventional hot melt adhesives are based on high MW TPU in solution and are used in the shoe industry. After the evaporation of the solvent, heat and pressure are applied to melt the polymer and press the parts for adhesion. Reactive hot melt adhesives also contain some free isocyanate groups that will moisture-cure and contribute to some crosslinking [72].

Two-component adhesives result in more flexible and softer elastomers. One of the components is an NCO terminated prepolymer and the other is a polyol or polyamine. They are extensively used in the automotive industry, to laminate panels for construction, foam to textiles, or plastic films together for food packaging. Hybrid adhesives have been prepared from PU-polyepoxy or PU-acrylics.

Aqueous PU latex adhesives are growing in importance in order to avoid the use of large amounts of volatile organic solvents in open systems. PU latices can be prepared in several ways. In one instance, a thermoplastic PU made in solution is emulsified in water, then the solvent is removed. Or an isocyanate terminated prepolymer is blocked with an appropriate isocyanate blocking agent and subsequently emulsified in water. Chain extension and crosslinking are accomplished by water or diamines present in water, and they take place within each particle of the dispersion. Eventually particles are considered to form a macromolecule. Adhesive latices can also be prepared from PU ionomers in a similar way to that presented in Section 7.5.1.

7.5.3 Sealants

Sealants are materials introduced into joints in order to prevent the transmission of water vapor and air, and to absorb the expansion and contraction of the joint. They contain 30–50% PU resins, the remainder being fillers, pigments, plasticizers and other additives. They can be formulated as one-component moisture cured systems or as two-component fast curing systems. PU sealants exhibit low modulus, low hardness (10–50 Shore A), excellent adhesion, 100% elasticity (high joint movement capability), high abrasion resistance, low temperature flexibility and low moisture transmission.

The USA's consumption of PU sealants was 30 000 tons in 1990 with a growing demand in modern high rise construction for insulated glass windows, for sealing windshields and clay sewer pipes, for highway and airport sealants and different marine applications [71].

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