3

Structure–Property Relations in Polyurethanes

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The most specific definition of a polyurethane is any polymer with a plurality of carbamate (urethane) linkages. The terms polyurethane and polyisocyanates are general names for the segment of the plastics industry that manufactures use. The name polyurethane is almost universally applied to the final (polymeric) products of that segment of the industry.\textsuperscript{1}

Polyurethanes, also called urethanes, are used to form a broad range of products, including flexible and rigid foams, elastomers, coatings, and adhesives. For our purposes, we will define a polyurethane as a large family of polymers, based on the reaction products of an organic isocyanate with compounds containing a hydroxyl group.

Polyurethane characteristics are controlled by the molecular structure and include degrees of flexibility/rigidity, density (foamed or solid), cellular structure, hydrophilicity or hydrophobicity, processing characteristics, and end-use properties. The processing characteristic is controlled by their basic plastic nature, that is, whether the material is thermoplastic (linear molecular structure) or thermostet (cross-linked molecular structure). Figure 3.1 presents the universe of structure–property relationships in polyurethane polymers.

The general principles of the structure–property relationship can be summarized as follows:

1. \textit{Molecular weight}. As the molecular weight increases, some properties such as tensile strength, melting point, elongation, elasticity, glass transition temperature, and so on increase up to a limiting value and then remain constant.

2. \textit{Intermolecular forces}. The weaker bonds such as hydrogen bonding, polarizability, dipole moments, and van der Waals forces may form, in addition to the primary chemical bonds, and these weaker bonds are affected by temperature and stress. If there is repulsion between like charges or bulky chains, or if there is high cross-link density, the effect of intermolecular forces will be reduced. Figure 3.2 shows the effect of hydrogen bonding in the hard segments of polyurethanes. Figure 3.1 is an idealized three-dimensional representation of hydrogen bonds in an aromatic polyurethane.

3. \textit{Stiffness of chain}. Presence of aromatic rings stiffens the polymer chains and causes a high melting point, hardness, and a decrease in elasticity. On the other
FIGURE 3.1
hand, the presence of flexible bonds (such as ether bonds) favors softness, low melting point, low glass transition temperature, and elasticity.

4. **Crystallization.** Linearity and close fit of polymer chains favor crystallinity, which leads to reductions in solubility, elasticity, elongation, and flexibility, and increases in tensile strength, melting point, and hardness. Figure 3.3 presents an idealized view of crystallization in polymers, including polyurethanes (bundle crystallization). Crystallization depends on the level of stretch induced in the polymers. Figure 3.2 shows the transient morphologies of segmented polyurethanes on stretching.

**FIGURE 3.2**
Polyurethane elastomer structure, crystallization, and hydrogen bonding.

**FIGURE 3.3**
Mechanisms of crystallization in polymers.
5. **Cross-linking.** Increases in the degree of cross-linking cause an increase in rigidity, softening point, and modulus of elasticity for amorphous polymers, and reduces elongation and swelling by solvents.

Table 3.1 summarizes key structure–property interactions in polyurethane polymers, and the key effects related to polymer structure.

### 3.1 Monomers, Reactions, and Structures

Commercially, the most attractive feature of polyurethanes is the unparalleled versatility offered by isocyanate chemistry for tailoring properties to specific end-use requirements. At room temperature (and up to 50°C), isocyanates react with hydroxyl groups to produce polyurethanes, while with amines and/or water they will produce urea linkages. At higher
temperatures (up to 150°C), further reactions produce allophanate, biuret, and isocyanate linkages. Polyurethanes can be considered as mixed amide esters of carbamic acid, and thus their properties are between polyesters and polyamides. This versatility has allowed polyurethanes to be utilized in a broad range of applications, including automotive, architectural, aerospace, office machinery, agriculture, mining, marine, electrical, communication, footwear, and medical.

The primary reactions of isocyanates with active hydrogen compounds occur with remarkable ease at ordinary temperatures with the evolution of heat. If a linear polyurethane is desired, the application of the lowest temperature is required. If high cross-linking and branching through secondary reactions is desired, higher temperatures (100–150°C) are needed. At about 180°C, aromatic polyurethanes start to revert. For aliphatic polyurethanes, this reversion takes place at around 160°C. At temperatures above 250°C, all polyurethanes start to decompose. Decomposition yields free isocyanates, alcohols, free amines, olefins, and carbon dioxide.

Polyisocyanates are very reactive substances, even reacting with water. As a result, the reaction between polyisocyanates and polyhydroxy compounds is complicated by the presence of moisture. The presence of water first causes the formation of unstable carbamic acid, which then disintegrates into amine and carbon dioxide. The formation of gas gives rise to foam production. Further reaction between amine and isocyanate leads to the formation of urea groups.

Polyurethane elastomers can be prepared by two basic processes. The simplest and most obvious method is to mix a liquid diol, a polyol, and diisocyanate, and to cast the mixture in a mold while still liquid. Curing of the cast mixture yields an elastomeric product. To obtain a thermoplastic elastomer, the reactants should be chosen such that they produce a linear structure. This is called the one-shot process. Figure 3.4 presents a schematic representation of the differences between the prepolymer method and the one-shot method of polyurethane preparation. Figure 3.5 compares thermal proprieties of polyurethanes prepared by the one-shot versus prepolymer methods.

The second method involves the reaction of a linear hydroxy-terminated polymer with an excess of diisocyanate to form an isocyanate-terminated polymer called a prepolymer, as shown in Figure 3.6. A prepolymer is either a viscous liquid or a low-melting solid.

![FIGURE 3.4 Prepolymer and one-shot methods of polymerization.](image-url)
Figure 3.7 is a schematic representation of the equipment used for the full-scale preparation of prepolymers.

The next step is chain extension and network formation with a small-molecular-weight polyol or amine called a chain extender. If the NCO/OH ratio is greater than 1, then this step is usually accompanied by some allophanate and/or biuret branch point formation. Figure 3.8 shows the theoretical relationship between molecular weight and NCO/OH ratio.

The development of cross-linking in elastomers also depends on the reaction of some isocyanate groups with atmospheric moisture to form urea groups, which then react with other isocyanate groups to form biuret cross-links. To obtain the required amount of cross-linking, a more useful procedure is to use formulations with at least one component having more than two reactive end groups.

FIGURE 3.5
DSC comparing one-shot to prepolymer-based elastomers using PTMEG 1000 and 2000 MW.

FIGURE 3.6
Preparation of polyurethane elastomers.
Relatively simple linear polymers may be obtained by using compounds with two active groups such as diisocyanate and diols. In each polymerization reaction, however, secondary reactions take place to a certain extent. Polyurethanes contain urea, allophanate, biuret groups, and aromatic rings in addition to urethane groups. These groups affect the properties of the resultant polymer.

The reactions between a diisocyanate, a linear long-chain dial, and a low-molecular-weight chain extender lead to the production of elastomers. The properties of the elastomers are determined mainly by the chain structure, the degree of branching of the polymeric
intermediate, and the stoichiometric balance of the components. The ratio of NCO to OH for optimum mechanical strength is usually 1.0–1.1. As the ratio falls below 1.0 the mechanical strength, hardness, and resilience decrease and elongation and compression increase very sharply. Resultant linear polyurethanes behave as cross-linked polymers, and are termed virtually cross-linked, as shown in Figure 3.9.

Useful polyurethanes are produced over a durometer range of 55A to 75D. They can be solubilized in a variety of solvents or made resistant to solvents and other fluids. Polyurethanes can be environmentally stable or biodegradable, hydrophobic, or hydrophilic. Useful service temperature ranges from below −100 to over +125°C.

Polymer chemists can synthesize polyurethanes in many interesting ways. However, commercial manufacture is based primarily on the addition reactions of polyols with polyisocyanates. Diols and diisocyanates produce linear polymers. Triols, triisocyanates, and/or monomers of still higher functionality produce branched and cross-linked polymers. These reactions generally proceed readily at room temperature, particularly with the help of amine catalysts and/or organotin catalysts. This is the most general reaction for the production of polyurethanes, as shown in the following reaction:

\[
\text{Isocyanate} + \text{Alcohol} \rightarrow \text{Urethane}
\]

The properties associated with the polyurethanes are due to the presence of urethane linkages in the molecular backbone. The urethane linkage is shown in Figure 3.10. The type of diisocyanate, glycol, and solvent used may affect the rate and the type of the reaction as well as the properties of the product. Polyols give high flexibility to the backbone of the network chains. Therefore, they are called soft domains or soft segments. Conversely,
isocyanate and chain-extender components give rigidity to the chains and are called **hard domains or rigid segments**. Physical and mechanical properties of polyurethane that contain these types of segments can be explained in terms of morphological structure, that is, rigid domains dispersed in a flexible segment matrix. The two isocyanates most frequently used in the synthesis of polyurethanes are MDI and TDI. The isomeric structures of TDI are shown in Figure 3.11. These diisocyanates are exhaustively covered in Chapter 4.

Because the hard and soft blocks are partly incompatible with each other, the elastomer shows a two-phase morphology, although there is a significant level of mixing of the hard and soft blocks. At low temperatures, the soft matrix having a low $T_g$ influences the properties.

**FIGURE 3.9**
Virtually cross-linked network.

**FIGURE 3.10**
Urethane linkage.
Hard segments in the domains act as cross-link points as well as reinforcing filler entities, and these govern the mechanical performance of the material at elevated temperatures.

### 3.1.1 Polyols

Polyol compounds used in polyurethane production are generally compounds with molecular weights in the range of 400–5000 Da. Depending on the chain length of these diols or glycol, the properties of the polyurethane change. If the polyol has a low molecular weight, it creates hard plastics, and if it has a high molecular weight, it creates flexible elastomers. The reactivities are not the same for all hydroxyl groups. Primary alcohols react readily at 25–50°C, while the secondary and tertiary alcohols are about 0.3 and 0.005 times less reactive than the primary ones, respectively. Figure 3.12 presents some commercially important polyols.

![Diagram of difunctional aromatic isocyanates](image)

**FIGURE 3.11**
Difunctional aromatic isocyanates.

![Diagram of polyols](image)

**FIGURE 3.12**
Some important polyols.
The reaction between a hydroxyl group and an isocyanate is catalyzed by mild and strong bases, by many metals, and by acids. Bases such as sodium hydroxide, sodium acetate, tertiary amine, and certain metal compounds (especially tin compounds such as dibutyltin dilaurate and stannous octoate) are the most commonly used catalysts.

Polyfunctional alcohols (those containing more than one hydroxyl group) are known as polyols. Polyols are involved in the synthesis of polyurethanes. The following three families of structures are commonly used to provide the polyols for the manufacture of polyurethane: polyethers, polyesters, and hydrocarbon backbones.

### 3.1.1 Polyethers

The most common polyether polyol is poly(oxypropylene) glycol made by alkaline polymerization of propylene oxide; this provides good flexibility and low cost, the molecular architecture of poly(oxypropylene glycol) is shown in Figure 3.13.

For higher strength, poly(oxytetramethylene) glycol, better known as polytetra methylene ether glycol (PTMEG) is frequently used, as shown in Figure 3.14. PTMEG is made by acid polymerization of tetrahydrofuran. Polyurethane products made from PTMEG can be characterized as high-performance polymers exhibiting high engineering toughness, resiliency, high abrasion resistance, inherent hydrolysis resistance, and superior low-temperature properties, when compared to other polyether-based polyols.

### 3.1.1.2 Polyesters

Linear aliphatic polyesters are common structures such as poly(ethylene adipate) shown in Figure 3.15. These polyols are used to provide high strength to polyurethane elastomers. Polyester-based urethanes’ thermal behavior is dependent upon the concentration of ester groups on the polyester. An increase in ester group concentration leads to reduced flexibility at low temperatures, higher hardness, higher modulus, and a marked increase in permanent elongation. Conversely, reducing the ester group concentration improves the low-temperature flexibility and reduces the tear strength. Glass transition temperatures of polymers prepared with poly(1,4-butylene adipate) and poly(1,5-pentylene adipate) are significantly lower than that of the poly(ethylene adipate) elastomer.

![Figure 3.13](image1)

**FIGURE 3.13**
Poly(oxypropylene glycol).

![Figure 3.14](image2)

**FIGURE 3.14**
Poly(oxytetramethylene glycol).

![Figure 3.15](image3)

**FIGURE 3.15**
Poly(ethylene adipate).
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Table 3.2 shows the effect of isocyanate structure on the properties of polyester urethanes that are prepared by using 0.1 equivalents polyethylene adipate molecular weight 2000, 0.32 equivalents diisocyanate, and 0.2 equivalents 1,4-butanediol chain extender.5

Polyester structure also affects the properties of the product. For a special polyurethane series prepared from diphenylmethane diisocyanate, 1,4-butanediol (as chain extender), and different polyesters, the properties can be summarized as shown in Table 3.3.

For improved resistance to hydrolysis, polyester polyols such as polycaprolactone or polycarbonate are used; the structures of these polyol is shown in Figure 3.16.

### Table 3.2

<table>
<thead>
<tr>
<th>Diisocyanate</th>
<th>Tensile Strength (psi)</th>
<th>Elongation (%)</th>
<th>Modulus at 300% (psi)</th>
<th>Tear Strength (lb/in)</th>
<th>Hardness (Shore B)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NDI</td>
<td>4300</td>
<td>500</td>
<td>3000</td>
<td>200</td>
<td>80</td>
</tr>
<tr>
<td>p-PDI</td>
<td>6400</td>
<td>600</td>
<td>2300</td>
<td>300</td>
<td>72</td>
</tr>
<tr>
<td>TDI</td>
<td>4600</td>
<td>600</td>
<td>350</td>
<td>150</td>
<td>40</td>
</tr>
<tr>
<td>MDI</td>
<td>7900</td>
<td>600</td>
<td>1600</td>
<td>270</td>
<td>61</td>
</tr>
<tr>
<td>TODI</td>
<td>4000</td>
<td>400</td>
<td>2300</td>
<td>180</td>
<td>70</td>
</tr>
<tr>
<td>DMDI</td>
<td>5300</td>
<td>500</td>
<td>600</td>
<td>40</td>
<td>47</td>
</tr>
<tr>
<td>DPDI</td>
<td>3500</td>
<td>700</td>
<td>300</td>
<td>90</td>
<td>56</td>
</tr>
</tbody>
</table>

Table 3.3

<table>
<thead>
<tr>
<th>Polyester</th>
<th>Tensile Strength (psi)</th>
<th>Elongation (%)</th>
<th>Tear Strength (lb/in)</th>
<th>Hardness (Shore B)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly(ethylene adipate)</td>
<td>6900</td>
<td>590</td>
<td>240</td>
<td>60</td>
</tr>
<tr>
<td>Poly(1,4-butylene adipate)</td>
<td>6000</td>
<td>510</td>
<td>280</td>
<td>70</td>
</tr>
<tr>
<td>Poly(1,3-butylene adipate)</td>
<td>3200</td>
<td>520</td>
<td>100</td>
<td>58</td>
</tr>
<tr>
<td>Poly(1,5-pentylene adipate)</td>
<td>6300</td>
<td>450</td>
<td>60</td>
<td>60</td>
</tr>
<tr>
<td>Poly(ethylene succinate)</td>
<td>6800</td>
<td>420</td>
<td>200</td>
<td>75</td>
</tr>
<tr>
<td>Poly(2,3-butylene succinate)</td>
<td>3500</td>
<td>380</td>
<td>ND</td>
<td>85</td>
</tr>
</tbody>
</table>

(a) OH(CH₂)nCOO(CH₂)nOH
(b) OH(CH₂)nOCO(CH₂)nOH

**FIGURE 3.16**

Polycaprolactone (a) and polycarbonate (b).
A naturally occurring polyester polyol often used in polyurethane is castor oil, shown in Figure 3.17.

### 3.1.1.3 Hydrocarbons

For lower polarity, better electrical insulation, and higher resistance to hydrolysis, aliphatic hydrocarbon polyols are sometimes synthesized in structures such as hydroxy-terminated polybutadiene glycols,

\[
\text{HO(CH}_2\text{CH=CHCH}_2\text{CH}_2\text{CH})_n\text{OH}
\]

and their hydrogenated derivatives,

\[
\text{HO(CH}_2\text{CH}_2\text{CH}_2\text{CH})_n
\]

### 3.1.1.4 Triols and Higher-Functionality Polyols

Polyols with three hydroxyl groups, such as glycerine, are known as trihydroxyl polyols or triols. When triols are reacted with an isocyanate, the resulting polyurethane is cross-linked. The amount of cross-linking affects the stiffness of the polymer. If a rigid foam is required, the polymer structure must be highly cross-linked; for flexible foams, less cross-linking is needed, as shown in Figure 3.18a. Branching and cross-linking are most commonly accomplished by the use of higher-functionality polyols. These are most conveniently based upon a triol or hexol backbone as shown in Figure 3.18b.

### 3.1.2 Isocyanates

The most common diisocyanates are toluene diisocyanate (TDI) and methylene bis diphenylisocyanate (MDI), plus higher oligomers for increased functionality and cross-linking. For resistance to ultraviolet light and outdoor weathering resistance, aliphatic polyisocyanates such as hexamethylene diisocyanate (HDI) and hydrogenated MDI (HMDI) are useful, even though these aliphatic diisocyanates involve lower polymerization reactivity and much higher cost.

The reactions between a diisocyanate, a linear long-chain polyol, and a low-molecular-weight chain extender lead to the production of elastomers. The properties of the elastomers are determined mainly by the chain structure, the degree of branching of the polymeric intermediate, and the stoichiometric balance of the components. The ratio of NCO to OH for optimum mechanical strength is usually 1.0–1.1. As the ratio falls below 1.0, the mechanical strength, hardness, and resilience decrease, and elongation and compression set increase very sharply.
The reactivity of isocyanates depends on their chemical structures. Aromatic isocyanates are generally more reactive than aliphatic ones. The presence of electron-withdrawing substituents on the isocyanate molecule increases the partial positive charge on the isocyanate carbon and moves the negative charge farther away from the site of reaction. This makes the transfer of the electron from the donor substance to the carbon easier, thus causing a faster reaction. On the other hand, the presence of electron-donating substituents on isocyanate compounds can cause slower reactions. Bulky groups in the ortho positions of aromatic isocyanates, and bulky and branched groups in aliphatic isocyanates, retard the reaction because of strike hindrance. In the reactions of disiocyanate, the reactivity of the second isocyanate decreases significantly after the first has been reacted. The difference in the reactivities is less if the two isocyanates belong to different aromatic rings or are separated with an aliphatic chain.

### 3.1.2.1 Prepolymers

Mixing all the reactants at once—a one-shot process—provides the fastest, simplest, and most economical manufacturing technique, and is most often favored in highly competitive commodity fields such as flexible foam. Conversely, two-step or three-step processes give the manufacturer much greater control over toxicity, reactivity, structure, properties, processibility, and finished product quality. In a typical two-step process, the first step is the production of a prepolymer, as shown in Figure 3.19.

Prepolymers (isocyanate intermediates between monomers and the final polymer) are the reaction product of a polyol or blend of polyols with excess isocyanate. A prepolymer describes a polyol–isocyanate adduct with a free isocyanate content of 1–15% by weight. Prepolymers are made by the slow addition of the polyol or blends of polyols to the isocyanate at a controlled temperature, usually 60–70°F, followed by reaction to a constant free isocyanate content. Catalysts may be used to accelerate the reaction.
Prepolymers are useful in the production of urethane elastomers, coatings, adhesives, sealants, reaction injection molding, binders, and so on, where the lower reaction exotherm produced when using a prepolymer is a crucial advantage. Since the reaction between a hydroxyl group (–OH) and an isocyanate (–NCO) to form a urethane linkage develops approximately 25 kcal/mol. The use of a prepolymer is distinctly advantageous to lower the overall reaction exotherm.

The last step is a reaction of the prepolymer with a chain extender such as a diol or a diamine to produce high-molecular-weight polymers. In many cases, controlled cross-linking is introduced as the second or third step.

### 3.1.2.2 Quasiprepolymers

A quasiprepolymer is the reaction product of a polyol or blend of polyols with a large excess of isocyanate. The term quasiprepolymer is used to describe a polyol–isocyanate adduct with free isocyanate contents between 16% and 32% by weight. Quasiprepolymers are extensively utilized in the production of foams. It is important to distinguish a prepolymer from a quasiprepolymer; this is done primarily by observing the nomenclature regarding free isocyanate contents as follows:

<table>
<thead>
<tr>
<th>Percent free isocyanate</th>
<th>Prepolymer</th>
<th>Quasiprepolymer</th>
</tr>
</thead>
<tbody>
<tr>
<td>1–14</td>
<td>Elastomers, coatings, sealants, adhesives</td>
<td>16–32</td>
</tr>
</tbody>
</table>

### 3.1.3 Chain Extenders and Cross-Linking Agents

For stepwise extension (cure) reactions, the three most common additives are 1,4-butane-diol, diamines, and water. Thus, these additives function as chain-extender and/or cross-linking agents, depending on the functionality of the prepolymer and the overall stoichiometry of the reaction.

In vulcanizing polyurethane elastomers, rubber compounders also use conventional sulfur cure, producing sulfide and polysulfide links between polyurethane chains, and sometimes peroxide cure, producing direct C–C links between the polyurethane chains.

### 3.1.3.1 Indigenous Cross-Linking Reactions

Aside from higher-functionality polyols, polyisocyanates, and/or polyamines, there are several reactions that can contribute significant cross-linking during polymerization and
cure of polyurethane. There are three indigenous cross-linking reactions: allophanate, biuret, and isocyanurates.

3.1.3.1.1 Allophanate
When a polyurethane is formed in the presence of excess polyisocyanate, the urethane group itself can supply an active hydrogen to react with the isocyanate, thus forming a branch point. Obviously, a diisocyanate could similarly form a cross-link between two vicinal polyurethane chains. These cross-links are not as stable as the conventional cross-links formed from polyfunctional polyols and polyisocyanates; allophanate cross-links are thermally labile and open quite easily at higher temperature.

3.1.3.1.2 Biuret
When polyurea is formed in the presence of excess polyisocyanate, the urea group can supply active hydrogens to react with the isocyanate, thus forming a branch point. Obviously, a diisocyanate could similarly form a cross-link between two polymer chains. These cross-links form more readily than allophanates and are somewhat stabler than allophanates, but they are still thermally labile and open fairly easily at higher temperatures.

3.1.3.1.3 Isocyanurate
Under proper conditions, excess isocyanate forms cyclic trimers that are called isocyanurates. When the isocyanate is a diisocyanate or higher polyisocyanate, these isocyanurate rings act as extremely stable cross-links in the polyurethane network. Isocyanurates are frequently used to produce polyurethane of high heat stability and flame retardance.

3.1.3.1.4 Block Copolymers
When small comonomer units are assembled randomly into a polyurethane molecule:

```
~~~~~ABAABABBAAAABBAB~~~~~
```

the resulting random copolymer has an overall average structure that is fairly uniform and forms a single homogeneous phase containing this average composition and structure. When the growth of a copolymer molecule produces fairly large areas (blocks) of one monomer structure alternating with fairly large areas (blocks) or another monomer structure:

```
~AAAABBBB~
```

these blocks will tend to separate into microphases or domains, and each type of domain will contribute independently to the properties of the block copolymer. In polyurethane, the polyl generally forms fairly large blocks even before they are reacted with the polyisocyanate. Furthermore, in step synthesis of polyurethane, the first-stage prepolymer forms one type of block (often called the soft block), while the reaction of short-chain extender with isocyanate forms another type of block (often called the hard block). Thus, polyurethanes are block copolymers. In many cases, the separation of these blocks into domains has a major synergistic effect on the properties of the resultant polymer.

3.1.4 Heteroblock Copolymers
The stepwise synthesis of polyurethane, with active hydroxyl, amine, and/or isocyanate end groups remaining after each intermediate step, provides the polyurethane chemist with the additional possibility of combining these polyurethane blocks with blocks of
other polymer structures, to unite the best properties of polyurethane with the best properties of the other polymers as well. Some of the most common may be described briefly as follows:

- **Acrylic esters.** Acrylic esters that contain hydroxyl groups are readily combined with polyurethane that contains isocyanate groups to produce acrylic–urethane block copolymers.

- **Epoxy resins.** Some epoxy resins contain hydroxyl groups, and most of them form hydroxyl groups during cure. These react readily with excess isocyanate groups of polyurethane to form block copolymers. Conversely, polyurethane containing terminal hydroxyl or amine groups can act as curing agents for epoxy resins, again forming block copolymers.

- **Drying oils.** Drying oils are often transesterified with glycerol to form mono- and diglycerides, containing both drying oil groups and hydroxyl groups. These copolymerize readily in the presence of catalysts with excess isocyanate groups in polyurethane to form drying oil urethanes, the most common form of polyurethane coatings.

- **Silicones.** Cure of silicone elastomers and resins proceeds through a transient intermediate silanol stage. At this point, the silanol can react with the hydroxyl and isocyanate end groups of polyurethane to form silicone-urethane heteroblock copolymers, which combine some of the best properties of each polymer.

Thermal analysis comprises a group of techniques in which a physical property of a substance is measured as a function of temperature while the substance is subjected to a controlled-temperature program. A complete modern thermal analysis instrument measures temperature and energy of transitions, weight loss, dimensional changes, and viscoelastic properties.

In differential thermal analysis (DTA), the temperatures of the sample and a thermally inert reference material are measured as a function of temperature. Any transition that the sample undergoes will result in the liberation or the absorption of energy by the sample, with a corresponding deviation of its temperature from that of the reference. This tells us whether the transition is endothermic or exothermic.

In differential scanning calorimetry (DSC), the sample and a reference material are subjected to a closely controlled, programmed temperature variation. In case of a transition in the sample, thermal energy is added or subtracted from the sample or reference container to keep both at the same temperature. Recording of this balancing energy yields a direct calorimetric measurement of the transition energy.

Thermogravimetric analysis (TGA) provides a quantitative measurement of any weight change associated with a transition.

Thermomechanical analysis (TMA) provides measurements of penetration, expansion, contraction, and extension of materials as a function of temperature.

Dynamic mechanical analysis (DMA) detects transitions associated with movement of polymer chains. The technique involves measuring the resonant frequency and mechanical damping of a material forced to flex at a selected amplitude. Mechanical damping is the amount of energy dissipated by the sample as it oscillates, while the resonant frequency defines the Young’s modulus of stiffness. Loss modulus and the ratio of loss modulus to elastic modulus can be calculated from the raw frequency and damping data. In general, modulus and frequency, as well as damping, change more dramatically than heat capacity.
of thermal expansion during secondary transitions. For example, dynamic mechanical analysis is helpful in determining the effectiveness of reinforcing agents and fillers used in thermoset resins.

Since polyurethanes are made up of three types of ingredients (isocyanates, polyhydroxy compounds, and chain extenders) that can be selected from a wide variety of chemicals, generalization of their thermal properties is not a simple task. Still, three endothermic peaks, one for the glass transition temperature of the soft segments and two for the dissociation of the short- and long-range order of the hard segments, can be observed in most polyurethane. For a two-phase block copolymer, the width of the soft-phase glass transition zone provides a qualitative measure of soft-phase homogeneity. At higher temperatures, melting of the hard-segment microcrystallites may also be observed. In the DSC of an MDI, 1,4-butanediol, and polytetramethyleneoxide (molecular weight 1000) polyurethane, these four peaks were observed at 35°C, 71°C, 176°C, and 193°C, respectively. However, the lack of high-temperature endotherms related to hard-segment ordering is commonly reported for MDI-based polyurethane block copolymers, especially when asymmetric chain-extender diols are used.

The chemical structure and the linkages present in polyurethane have a significant effect on thermal behavior. If diamines are used as chain extender, urea linkages will form rather than urethane linkages, which leads to an increase in hydrogen bonding and results in stronger resistance to thermal disruption. The hydrogen bonding promotes greater cohesiveness of the hard-segment domains. In DMA analysis of polyurethaneimides, an increase in the storage modulus $E$ was observed with an increase in the fraction of the hard phase.

All this polyurethane chemistry produces a broad spectrum of polymer structures that contribute many interesting and useful properties for many fields of technology. On the one hand, the study of polyurethane structure and properties has contributed greatly to our understanding of polymer structure–property relationships in general. On the other hand, systematic organization of our understanding of polymer structure–property relationships in general contributes to a sounder understanding of the specific practical relationships in polyurethane polymers and end products. These are best reviewed from smallest to largest structural feature, starting with submolecular structure and continuing on to larger and larger structural features such as molecular weight, molecular flexibility, intermolecular order, intermolecular bonding, and finally supermolecular structures.

### 3.1.5 Submolecular Structure: Atoms and Functional Groups

Polyurethane may contain aliphatic, aromatic, ether, ester, carbonate, urethane, hydroxyl, amine, urea, biuret, isocyanate, and isocyanurate groups during processing and/or use of the finished product. They may also contain plasticizers and other additives along with variable amounts of water. All of these contribute individually to many properties. A brief review of some of the more important effects is instructive.

### 3.1.5.1 Processibility

Polyurethanes are the leading prototype of reactive processing, including all their foams and reaction injection molding (RIM), along with most of their elastomer, castings, coatings, and adhesives. These are high-speed processes based on the high reactivity of aromatic isocyanates. Reactions are fastest with aliphatic amine, and slower with aromatic amine. Reactions with polyols and water are fairly competitive, depending on the choice of the
catalyst (amines favor water, organotins favor hydroxyl groups). Primary hydroxyl groups are more reactive than secondary, whereas aromatic hydroxyls (phenols) are slower and more likely to revert on heating. Reactions with urea and urethane groups are more difficult, but they can form biuret and allophanate cross-links at higher temperature. Use of aliphatic isocyanates in place of aromatic isocyanates, for UV and weather resistance, generally requires considerably more time, temperature, and a higher concentration of catalysts to obtain full polymerization.

Moisture is a ubiquitous impurity that causes hydrolytic waste of isocyanates, unbalanced stoichiometry, and poor properties in end products. Thus, all ingredients and process conditions must be scrupulously dry, and most processors routinely add several percent excess isocyanate to account for all wasteful side reactions.

Thermal reversion is most noticeable when urethane groups are formed from phenols, somewhat less with allophanate, and still less with biuret, but significant in all these structures. Even normal urethane groups can open at higher process temperature. Such reversion can actually be useful when the rubber processor wants to recycle light thermoset scrap.

The N–H groups in urethane and urea structures are still reactive enough for derivatization, grafting, and cross-linking reactions. These are used in isocyanate and biuret cross-linking, epoxy copolymerization, heparinization for antithrombotic in vivo plastics, and controlled release of drugs.

### 3.1.5.2 Mechanical Properties

Mechanical properties are most openly controlled by molecular flexibility, crystallinity, and cross-linking. It is possible to soften polyurethane elastomers by addition of compatible plasticizers such as isodecyl pelargonate (Table 3.4), similar to conventional PVC technology, but such techniques have not been of commercial importance. Water absorption provides plasticization here as it does in nylon but, since most polyurethanes are already flexible, the added plasticization is not usually significant, except in medical applications, where the softening effect of water can provide advantageous properties.

1. Static tests. Loads are applied slowly enough so that quasistatic equilibrium of forces is maintained.

\[
\begin{array}{|c|c|}
\hline
\text{IDP Content (%)} & \text{Glass Transition Temperature (°C)} \\
\hline
0 & -52.5 \\
5 & -57.5 \\
10 & -61.5 \\
15 & -63.5 \\
20 & -66.5 \\
\hline
\end{array}
\]

2. Cyclic tests. Loads are applied and then (a) partly or wholly removed or (b) reversed a sufficient number of times to cause the material to behave differently than under static loading.

3. Impact tests. Loading is applied so rapidly that the material must absorb energy rather than resist a force.

The simplest mechanical test is the tensile test, generally carried out with an Instron tensile tester, in which the specimen is gradually elongated under an applied stress, and the resulting changes in length are recorded. The stress is the force applied per unit cross-sectional area of the specimen. The strain is the fractional change in the length of the specimen. It can be measured as linear strain, $\varepsilon$, which is the change of length per unit length, or as shearing strain, $\lambda$, which measures the change in angle from the original right angle. In a tensile test, a specimen is subjected to a progressively increasing tensile force until it fractures. At the beginning, the test material extends elastically. The strain is directly proportional to the stress, and the specimen returns to its original length immediately on the removal of the stress. In this region, loads are not great enough to cause permanent shifting between the atoms. Beyond the elastic limit, the applied stress produces plastic deformation, so a permanent extension remains after the removal of the applied load. The material either fractures or undergoes some change in shape due to flow of the material. In the elastic region, the stress and strain are linearly proportional to each other. Stress is called normal stress, when it acts perpendicular to a given area and the slope, $E$, of the line defined as $E = \delta/\varepsilon$, where $E$ represents the Young’s modulus. When a shear stress that acts in a plane other than normal to the plane is applied, the relation between the shear stress, $\tau$, and shear strain, $\gamma$, is given as $G = \tau/\gamma$, where $G$ is the shear modulus.

The amount of deformation in any direction depends on the magnitude and direction of the loading, and on the condition of the material. When the stress reaches a critical value, the atomic bonds fail across an atomic plane. The relationship between stress and strain departs from linearity, and plastic deformation begins accompanied by a reduction in the cross section known as necking. As deformation continues, the applied load increases until the tensile strength or ultimate strength is reached. This strength is the maximum point shown on the stress–strain curve. Polymers have a wide spectrum of mechanical properties ranging from hard brittle materials to gel-like structures, from flexible elastomers to tough materials, and from porous foam structures to nonporous rigid materials. The applied force may cause fractures on the material. The fractures form under either constant-stress (creep) or fluctuating-stress (fatigue) conditions.

Creep tests are carried out under certain combinations of stress and temperature. All materials, when subjected to a constant stress, will exhibit an increase of strain with time. This phenomenon is called creep. Most materials creep to a certain extent at all temperatures. High temperatures lead to a rapid creep, which is often accompanied by microstructural changes.

Fatigue test is the measurement of the failure of a structure under the repeated application of a constant stress smaller than that required to cause failure in one application. The material initially suffers some microstructural damage. Eventually, the cyclic application of load leads to the formation of cracks, which grow larger with every application of load. A series of specimens of the material are tested to failure by the application of different values of stress. Properties such as fatigue lifetime, number of cycles to failure after crack initiation, permanent set, and total elongation are also measured. Generally, logarithms of the stress are plotted versus the logarithms of the number of cycles to failure.
Impact test measures the brittleness of the material. In this test, a standard notch is cut in a standard test specimen, which is then struck under impact conditions by a heavy weight forming the end of a pendulum. The notch serves to introduce triaxial tensile stresses into the specimen, encouraging brittle failure to occur. The weight is released from a known height so as to strike the specimen on the side opposite the notch and to induce tensile stresses in it. After breaking the specimen, the pendulum swings on, and the height to which it rises on the other side is measured. Thus, the energy absorbed in breaking the material under high-speed loading can be determined and, if it is low, the specimen is called brittle.

The techniques of continuous and intermittent stress relaxation measurement have been used successfully for studying the thermal behavior of elastomers. In these tests, with continuous stress relaxation, a strip specimen of an elastomer is held at a fixed extension while it is being exposed to a constant elevated temperature. The tensile force or stress at constant extension and temperature is monitored continuously. If the temperature is high enough to induce random thermal session of the elastomers’ network chains, the measured force of stress will decrease with time at a rate that is proportional to the rate of chain session. Such a stress decay process is often referred to as a chemorheological or simply a chemical stress relaxation.14

Continuous stress relaxation data are often fitted to a simple exponential Maxwell model, expressed as

\[ f_t = f_0 e^{(9-t/\tau)} , \quad E_t = E_0 e^{(-t/\tau)} \]

where \( f_0 \) is the initial tensile force measured at constant extension and constant temperature, and \( \tau \) is the tensile force measured after some relaxation time \( t \). In the second expression, \( E_0 \) and \( E_t \) are relaxation modulus values initially and at time \( t \). \( \tau \) is a characteristic relaxation time constant. Stress relaxation technique measures the rate of network chain session but does not give information about the rate of reversible reactions. Recombination of thermally cleaved chains might occur in a relaxed condition. Therefore, continuous relaxation measurements are often supplemented by intermittent relaxation measurements. The specimen is maintained in a stretched position at widely spaced intervals of time, and the resulting stress is rapidly measured, after which the strip is immediately returned to its unstretched state.

The mechanical properties of polyurethanes can be controlled by using components of different chemical structure at appropriate molar ratios. The final reformational properties of segmented polyurethane rubber result from the combination of segment flexibility, cross-linking, chain entanglement, orientation of segments, rigidity of aromatic units, hydrogen bonding, and other van der Waals forces. These parameters affect the applied force and lead to different types of deformations. There is a correlation between morphological structure and stress–strain behavior. The modulus decreases with decreasing hard-segment content in poly(ethylene oxide)-based elastomers extended with either ethylenediamine or phenylenediamine. Such trends are explained in terms of greater degree of domain formation with increasing hard-segment content. Decrease in hard-segment content causes a decrease in modulus but, in some cases where the hard content value is less than 10%, crystallization of soft segments may occur and create an unexpectedly high modulus.

Temperature affects the tensile properties and demonstrates a decrease of stress at a given strain with increasing temperature. This negative temperature coefficient of stress...
can be explained in terms of the viscoelastic softening of hard-segment domains, resulting in a decrease in effective physical cross-links.

Due to dissimilarity in the chemical structure of the hard and soft segments, there is a thermodynamic incompatibility between these segments. There is a driving force that causes them to form separate phases. This effect is, however, limited due to the presence of covalent links. It forms domains or leads to microphase separation.

Experiments carried out with small-angle x-ray scattering showed that microphase separation for segmented poly(urethane urea) is improved with an increase of average molecular weight of poly(tetramethylene glycol). Some processing parameters of the casting method also affect the morphology. The temperature of the prepolymer synthesis as well as the temperature of the mold, strongly influence the phase segregation. Generally, the spherulites are bigger if the temperature of the mold is higher.8

Polyurethane, especially the linear segmented polyurethanes, show significant time-dependent changes in their physical properties. Time dependency is observed in stress–strain behavior. For the samples annealed at certain temperature and then rapidly cooled, it was observed that the Young’s modulus value was much lower than before annealing. With increase in time after annealing, the Young’s modulus increases, but complete recovery is not observed.9

Stress relaxation measurement is a practical method for the examination of viscoelasticity of the polymer. Processes of breaking and rebuilding polymer network as well as changes occurring in molecular structures can be examined by this method. In stress relaxation processes, many reactions may happen. Some of these reactions are

1. Breaking of urethane or allophanate-type linkages
2. Disruption of hydrogen bonds or other secondary bonds
3. A decrease in the number of free entanglements

During stress relaxation, it has been observed that cleavage of polymer chain occurs most readily in groups having nitrogen atoms. When the length of the diols increase, it is observed that relaxation speed increases. When cross-linking density and hard-segment content increase, relative relaxation speed decreases with a parallel influence on the disappearance of viscoelastic properties.10

The molecular weight of the macroglycol is another parameter that affects the properties of the polyurethane. For example, for a sample prepared with polyoxyethyleneglycol, MDI and 1,5-pentanediol, the molecular weight of polyether was changed between 600 and 2000. With longer polyether chains, the system was more flexible and more hydrophilic, and had lower elastic modulus. Water absorption percent was increased from 9.9 to 62.4, with an increase in the molecular weight of polyether from 600 to 2000. For the same polyurethane, experiments to measure shear modulus were carried out in saline solution at 37°C, where relaxed and unrelaxed modulus showed an increase from 0.33 to 0.92 GPa and 0.57 to 2.58 GPa, respectively. An increase in shear modulus values with a decrease in the molecular weight of the polymers was observed.11

Like the isocyanates, polyols have an important effect on the properties of the polyurethane. The mechanical properties of polyurethane prepared from different polyols as the backbone for polyurethane are given below. The preparation mixture consisted of 2 mol of DMI, 1 mol of backbone diol, and 1.02 mol of either 1,3-propanediol or 1,4-butanediol as chain extender12 as shown in Table 3.5.
Changing the backbone from polyester to polyether glycol leads to different properties. Such differences are shown in Table 3.6 for polyethylene adipate and polypropylene glycol urethane. For the given set, it is observed that polyester urethane is far superior to its polyether counterpart of the same molecular weight. However, reducing the molecular weight of the polypropylene glycol improved the properties, although the tensile strength was still greatly inferior to the polyester compound.

A more detailed study on the effect of the polyether polyurethane molecular weight on the mechanical properties involved polyurethane prepared from a range of polypropylene glycol of different molecular weights, 2,4-toluene diisocyanate and 4,4′-methylene bis(o-chloroaniline) (MOCA). As observed in the previous example, a decrease in the molecular weight leads to increases in the tensile and tear strengths, and in the modulus. The results are tabulated in Table 3.7.

In polyurethanes, cross-linking can occur by the use of trifunctional chain extenders, by alphanate formation, or by biuret formation. It is assumed that cross-linking by isocyanurate formation is of little importance. Increasing the amount of cross-linking by decreasing the molar ratio of chain extender results in hysteresis loss, lower heat buildup, and lower flex–fatigue resistance. The molecular weights between branch points (molecular weight between crosslinks (Mc)) and modulus has been found to vary in opposite directions for some polyurethanes as shown in Table 3.8.

### Table 3.5
Effect of Molecular Weight and Diol Structure on MDI–MOCA Polymers

<table>
<thead>
<tr>
<th>Polyl</th>
<th>Polyethylene Adipate (MW 1040)</th>
<th>Polycaprolactone (MW 1050)</th>
<th>Poly(Tetramethylene Etherglycol) (MW 808)</th>
<th>Poly(Trimethylene Glycol) (MW 658)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile strength (psi)</td>
<td>5650</td>
<td>6410</td>
<td>5840</td>
<td>3875</td>
</tr>
<tr>
<td>100% Modulus (psi)</td>
<td>705</td>
<td>656</td>
<td>765</td>
<td>780</td>
</tr>
<tr>
<td>Ultimate elongation (%)</td>
<td>1035</td>
<td>1000</td>
<td>930</td>
<td>830</td>
</tr>
<tr>
<td>Hardness (Shore A)</td>
<td>81</td>
<td>81</td>
<td>82</td>
<td>83</td>
</tr>
<tr>
<td>Melt temperature (°C)</td>
<td>200</td>
<td>197</td>
<td>172</td>
<td>140</td>
</tr>
</tbody>
</table>

### Table 3.6
Effect of Molecular Weight and Diol Structure on MDI–MOC Polymers

<table>
<thead>
<tr>
<th>Diol</th>
<th>Tensile Strength (psi)</th>
<th>100% Modulus (psi)</th>
<th>Elongation (%)</th>
<th>Hardness (Shore A)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polypropylene glycol</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MW 2000</td>
<td>148</td>
<td>650</td>
<td>560</td>
<td>83</td>
</tr>
<tr>
<td>MW 1500</td>
<td>2400</td>
<td>1060</td>
<td>690</td>
<td>88</td>
</tr>
<tr>
<td>Polyethylene adipate</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MW 2000</td>
<td>5050</td>
<td>880</td>
<td>930</td>
<td>88</td>
</tr>
</tbody>
</table>
Chemical cross-linking can be controlled by varying the proportion of diol to triol. The data in Table 3.9 was obtained by substituting trimethylol propane for butanediol, and it shows the effect of increasing average molecular weight per cross-link unit.

The number of repetitions and the length of the chains of the hydrocarbon, ether, and ester groups appear to control the properties. Table 3.10 summarizes some known effects of the various groups. To control properties, the technologist must not only have the means to correctly and accurately identify qualitatively and quantitatively these groups in the end polymer, but must also be able to evaluate them as they form in the polymerizing mass.

### 3.1.5.3 Thermal Properties

Thermal stability of polyurethane depends primarily on the polymerization ↔ depolymerization equilibria of the functional groups in the polymer molecule. Urethane groups made from phenols revert quite readily at higher temperatures. Allophanate and biuret cross-links also reopen quite readily on heating. Conventional urethane and urea links decompose at considerably higher temperatures, and isocyanurate rings are the most stable.

Flammability of polyurethane is a frequent concern, particularly in flexible foam bedding and upholstery and in rigid foam insulation. Burning is effectively retarded either by reactive flame retardants (such as polyols containing phosphorus, chlorine, or bromine) that are built right into the polyurethane molecule during polymerization, or by additive flame retardants such as phosphate esters, halogenated phosphate, and halogenated hydrocarbons, either liquid (plasticizers) or solid (fillers). When a halogen is used, either as a reactive or additive flame retardant, addition of antimony oxide produces excellent synergism.\(^{16}\)
3.1.5.4 Electrical Properties

Polyurethanes contain many polar groups that tend to orient in an electrical field, and most polyurethane molecules have enough flexibility to permit their polar groups to orient in this way, producing high dielectric constants. On the other hand, molecular flexibility and the resulting polar group mobility are very sensitive to frequency and temperature, so dielectric constants are far from constant, and electrical–mechanical hysteresis produces considerable and variable dielectric loss. Thus, polyurethanes are not generally used as

### TABLE 3.9

Effect of Mc on the Properties of Polyurethane Elastomers

<table>
<thead>
<tr>
<th>Mc</th>
<th>Tensile Strength (psi)</th>
<th>Elongation (%)</th>
<th>100% Modulus (psi)</th>
<th>Tear Strength, Graves (lb/in)</th>
<th>Hardness (Shore B)</th>
<th>Compression Set (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2100</td>
<td>1800</td>
<td>170</td>
<td>540</td>
<td>30</td>
<td>57</td>
<td>1.5</td>
</tr>
<tr>
<td>3100</td>
<td>1750</td>
<td>200</td>
<td>420</td>
<td>25</td>
<td>53</td>
<td>16</td>
</tr>
<tr>
<td>4300</td>
<td>1450</td>
<td>280</td>
<td>300</td>
<td>30</td>
<td>49</td>
<td>10</td>
</tr>
<tr>
<td>5300</td>
<td>2800</td>
<td>350</td>
<td>270</td>
<td>30</td>
<td>46</td>
<td>5</td>
</tr>
<tr>
<td>7100</td>
<td>4500</td>
<td>410</td>
<td>330</td>
<td>40</td>
<td>51</td>
<td>25</td>
</tr>
<tr>
<td>10,900</td>
<td>5600</td>
<td>490</td>
<td>460</td>
<td>60</td>
<td>55</td>
<td>40</td>
</tr>
<tr>
<td>21,000</td>
<td>5500</td>
<td>510</td>
<td>500</td>
<td>140</td>
<td>56</td>
<td>45</td>
</tr>
<tr>
<td>∞</td>
<td>6750</td>
<td>640</td>
<td>630</td>
<td>300</td>
<td>61</td>
<td>55</td>
</tr>
</tbody>
</table>

### TABLE 3.10

Effects of Different Groups on Properties

<table>
<thead>
<tr>
<th>Hardness</th>
<th>Elongation</th>
<th>Tensile Strength</th>
<th>Tear Strength</th>
<th>Abrasion Resistance</th>
<th>Chemical Resistance</th>
<th>Heat Resistance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrocarbon</td>
<td>G</td>
<td>NK</td>
<td>NK</td>
<td>NK</td>
<td>G</td>
<td>G</td>
</tr>
<tr>
<td>CH₂</td>
<td>E</td>
<td>F</td>
<td>E</td>
<td>G</td>
<td>E</td>
<td>G</td>
</tr>
<tr>
<td>Aromatic</td>
<td>E</td>
<td>P</td>
<td>G</td>
<td>G</td>
<td>F</td>
<td>G</td>
</tr>
<tr>
<td>C₆H₄</td>
<td>E</td>
<td>P</td>
<td>G</td>
<td>G</td>
<td>F</td>
<td>G</td>
</tr>
<tr>
<td>Urea</td>
<td>E</td>
<td>P</td>
<td>G</td>
<td>G</td>
<td>F</td>
<td>G</td>
</tr>
<tr>
<td>Disubstituted</td>
<td>G</td>
<td>P</td>
<td>G</td>
<td>G</td>
<td>F</td>
<td>G</td>
</tr>
<tr>
<td>Alphanate</td>
<td>F</td>
<td>G</td>
<td>P</td>
<td>P</td>
<td>G</td>
<td>F</td>
</tr>
<tr>
<td>Biuret</td>
<td>F</td>
<td>G</td>
<td>G</td>
<td>G</td>
<td>F</td>
<td>P</td>
</tr>
<tr>
<td>Substituted</td>
<td>F</td>
<td>P</td>
<td>G</td>
<td>G</td>
<td>F</td>
<td>G</td>
</tr>
<tr>
<td>Substituted</td>
<td>E</td>
<td>G</td>
<td>G</td>
<td>G</td>
<td>F</td>
<td>G</td>
</tr>
<tr>
<td>Acyl urea</td>
<td>G</td>
<td>P</td>
<td>G</td>
<td>G</td>
<td>G</td>
<td>G</td>
</tr>
<tr>
<td>Ester</td>
<td>G</td>
<td>G</td>
<td>G</td>
<td>G</td>
<td>G</td>
<td>G</td>
</tr>
<tr>
<td>Ether</td>
<td>G</td>
<td>G</td>
<td>G</td>
<td>G</td>
<td>G</td>
<td>G</td>
</tr>
<tr>
<td>Amide</td>
<td>G</td>
<td>G</td>
<td>G</td>
<td>G</td>
<td>G</td>
<td>G</td>
</tr>
</tbody>
</table>

Note: NE = no effect, G = good, NK = no known effect, F = fair, E = excellent, P = poor.
high-performance electrical insulation. However, they are often used as outer sheathing to protect electrical insulation from abrasion and attack by fuel and oil.

### 3.1.5.5 Optical Stability

Aromatic polyurethanes absorb ultraviolet light from the sun but are unable to cope with the excess energy, and they degrade to quinoid structures that discolor and often suffer loss of mechanical properties. Where weather resistance is important, particularly in coatings, most manufacturers replace aromatic isocyanates by aliphatic isocyanates to solve this problem.

### 3.1.5.6 Chemical Properties

Strong polarity and hydrogen bonding make polyurethanes highly resistant to hydrocarbon fuel and oil, a major advantage for polyurethane elastomer over conventional hydrocarbon rubbers. They also enjoy another major advantage because their saturated structure is resistant to ozone and exudative aging, whereas most diene-based rubbers have serious problems in this respect.

Linear polyurethanes dissolve, making these elastomers useful in solution processing of fibers, coatings, and adhesives. Cross-linked polyurethane only swell, in polar organic solvents. But in general, polyurethanes are not widely used in the production of chemically resistant products.

Water absorption and hydrolysis, especially at higher temperature, cause aging problems in polyurethane, particularly polyester urethane. In polyester-based PUs, hydrolytic resistance can be improved by the use of polycaprolactone, polyethers, or hexamethylene polycarbonate-based polyols (see Table 3.11). More often, this problem is minimized by changing from polyester to polyether polyols, and occasionally even to hydrocarbon-based polyols.

Biodegradation can attack the aliphatic polyester segments of polyurethane, degrading them to much smaller molecular units via hydrolytic attack. This is a problem in long-term implantable products, but it is useful in controlled release of drugs and a possible solution to solid waste disposal problems. Biostability is greatly increased by changing to polyether

<table>
<thead>
<tr>
<th>TABLE 3.11</th>
<th>Hydrolytic Stability of PU Elastomers</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Polyol</strong></td>
<td><strong>Hydrolytic Stability</strong></td>
</tr>
<tr>
<td>Esters</td>
<td></td>
</tr>
<tr>
<td>Poly(diethylene glycol adipate)</td>
<td>Poor</td>
</tr>
<tr>
<td>Poly(ethylene adipate)</td>
<td>Fair</td>
</tr>
<tr>
<td>Poly(1,4-butylene adipate)</td>
<td>Good</td>
</tr>
<tr>
<td>Polycaprolactone</td>
<td>Good</td>
</tr>
<tr>
<td>Ether</td>
<td></td>
</tr>
<tr>
<td>PTMEG</td>
<td>Excellent</td>
</tr>
<tr>
<td>Polycarbonate</td>
<td></td>
</tr>
<tr>
<td>Poly(hexanediol-1,6-carbonate)</td>
<td>Excellent</td>
</tr>
</tbody>
</table>

polyols and by the addition of biocides and biostats. Biodegradation can be promoted by the use of short straight-chain aliphatic polyester units, and by inoculation, humidity, and temperature control in solid waste disposal units.

### 3.1.6 Molecular Weight

As the molecular weight increases, some properties (e.g., tensile strength, melting point, elongation, elasticity, and glass transition temperature) increase up to a limiting value and then remain constant.

A high molecular weight is the most distinctive structural feature that differentiates between polymer molecules and all other types of materials. The effects of molecular weight on polymer properties are commonly generalized by the rule that lower molecular weight is easier to process, but higher molecular weight gives better end-use properties. Many properties change from low to medium molecular weight but then approach an asymptote and become fairly constant from high to very high molecular weight. In the polyurethane field, it is generally assumed that final molecular weights are in the high to very high range, and therefore molecular weight is not a significant variable affecting polyurethane properties.

While this may be true in respect to many properties, there are some properties that depend significantly on molecular weight. These deserve careful consideration and are discussed in the sections below.

#### 3.1.6.1 Processibility

Most polyurethane processing is based on the use of low-molecular-weight liquid monomers or prepolymers, which are easily handled at atmospheric or low pressure in lightweight equipment, before rapid reactions convert them into solid end products. Liquid viscosities are a direct function of prepolymer molecular weight, so specific process techniques dictate the optimum molecular weight that can be used.

Solution processing of fibers, coatings, and adhesives depends on optimum solution viscosity, which is controlled by polyurethane molecular weight and solution concentration. Generally, it is desirable to work at maximum concentration to minimize solvent problems such as flammability, toxicity, recovery, and cost. Thus, lower molecular weights are generally desirable. Often, these are achieved by the use of reactive monomers.

Melt processing viscosities depend on polymer molecular weight. This is important in the extrusion of fibers and in extrusion and injection molding of thermoplastic elastomers. Often, the lower molecular weight required for easy melt processing conflicts with the higher molecular weight required for end-use properties. Some thermoplastic elastomers are designed with some residual reactivity, which permits them to be melt processed at lower molecular weight and then polymerized or cross-linked up to higher molecular weight to improve end-use properties. Reaction injection molding takes the extreme position, mixing and injecting low-molecular-weight prepolymers and then polymerizing and cross-linking them rapidly in the mold to produce the best end-use properties.

The largest usage of polyurethane is in the production of flexible and rigid foams by reactive processing. Here, low-molecular-weight reactive prepolymers are mixed and poured, with polymerization, foaming, and curing happening in rapid overlapping succession. The dynamic balance between increasing viscosity and gas bubble formation is very critical for optimum foam formation. If gas bubbles form at too low a viscosity, they grow irregularly, burst, and collapse. If they form at too high a viscosity, the gas pressure is insufficient to
produce full expansion, and the foam is too dense. The optimum dynamic balance is achieved in flexible foam by balancing catalysis of the isocyanate–polyol action versus the isocyanate–water reaction. In rigid foams, this delicate equilibrium is achieved by balancing polymerization rate and exotherm against volatility of the physical blowing agent.

### 3.1.6.2 Mechanical Properties

Modulus, strength, extensibility, creep resistance, lubricity, and abrasion resistance generally increase with increasing molecular weight. This is particularly true in thermoplastic polymers, and these effects are particularly applicable to thermoplastic polyurethane elastomers. In thermoset polymers of infinite molecular weight, they would tend to approach high-level value, which would then become a function of cross-linking rather than of molecular weight itself.

### 3.1.6.3 Thermal Stability

Thermal stability is generally greater at higher molecular weight, because higher molecular weights have less mobility and reach asymptotic properties that are less sensitive to scission. Such effects might be observed in thermoplastic polyurethane, but in cross-linked polymers, stability depends primarily on cross-link concentration rather than on the molecular weight itself.

### 3.1.6.4 Solubility

In many linear polymers, low-molecular-weight products are soluble in a fairly broad range of solvents; as the molecular weight increases, the choice of solvents becomes more restricted (as predicted from thermodynamic theory), and solution viscosity rises rapidly. This is undoubtedly true in solution processing of thermoplastic polyurethane. For cross-linked polyurethanes, solubility becomes irrelevant; if they are exposed to solvents of similar polarity and hydrogen bonding, the degree of swelling is proportional to the degree of cross-linking. Nevertheless, as a rule, the greater the cross-link density, the lower the degree of swelling.

### 3.1.7 Molecular Flexibility

- **Intermolecular forces.** The weaker bonds, such as hydrogen bonding, polarizability, dipole moments, and van der Waals forces may form, in addition to the primary chemical bonds. These weaker bonds are affected by temperature and stress. If there is repulsion between like charges or bulky chains, or if there is high cross-link density, the effect of intermolecular forces will be reduced.

- **Stiffness of chain.** The presence of aromatic rings stiffens the polymer chains and causes a high melting point, hardness, and a decrease in elasticity. On the other hand, the presence of flexible bonds (such as ether bonds) favors softness, low melting point, low glass transition temperature, and elasticity.

The inherent flexibility of the individual polymer molecule is an important theoretical concept, and it has many consequences in practical properties. The subject is best divided into these two separate aspects.
3.1.7.1 Effect of Structure on Molecular Flexibility

The structure of the individual polymer molecule determines its inherent flexibility (Table 3.12). In the absence of crystallinity, intermolecular attractions, or cross-linking, the polymer molecule is free to exhibit all its inherent flexibility, and this unrestricted freedom has major effects on polymer properties. Even in the presence of such conflicting factors, the inherent flexibility of the polymer molecule is still very important, but the evidence for it is more obscure, and the practical effects are more complex. To better understand this phenomenon, let us consider the simple concept of the inherent flexibility of the individual polymer molecule.

Molecular flexibility depends on the freedom of rotation about the single bonds in the main chain of the polymer molecule; restriction of rotation reduces molecular flexibility. A linear aliphatic chain, as shown in Figure 3.20, is fairly free to rotate about its C–C bonds but is restricted by (a) the 109° angle between C–C–C bonds and (b) the electropositive repulsion between adjacent H atoms requiring some energy to rotate them past each other. When a –CH₂– is replaced by an oxygen (–CH₂–O–CH₂–), rotation around the C–O bond does not bring H atoms into conflict with each other, so rotation is easier, and the molecule is more flexible; this occurs in polyethers, polyesters, and even polyurethane linkages.

Sulfide links (–CH₂–S–CH₂–), although less common, have a similar effect. When methyl side groups are attached to the aliphatic main chain in an amorphous polymer, as shown in Figure 3.21, steric hindrance restricts rotation around the main chain, and the molecule stiffens. It should be noted that, in crystalline polymer, random methyl side groups reduce regularity and crystallinity and thus make the solid mass of polymer molecules more flexible. When aromatic groups are present, particularly in the main chain, they introduce large flat rigid units that greatly reduce molecular flexibility (see Table 3.13).

When the aromatic rings are conjugated with adjacent unsaturated groups in the main chain, the entire conjugated resonating unit becomes much larger, and the stiffening effect is much greater, as shown in Figure 3.22.

### Table 3.12

Molecular Flexibility of Ether Groups

<table>
<thead>
<tr>
<th>Glycol Reacted with Hexamethylene Disocyanate</th>
<th>Polyurethane Melting Point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HO(CH₂)₅(OH)</td>
<td>151</td>
</tr>
<tr>
<td>HO(CH₂)₁₀(CH₂)₂OH</td>
<td>120</td>
</tr>
<tr>
<td>HO(CH₂)₁₅(CH₂)₂OH</td>
<td>132</td>
</tr>
</tbody>
</table>

![Figure 3.20](linear-aliphatic-chain.png)

Linear aliphatic chain.

![Figure 3.21](amorphous-polymer.png)

Amorphous polymer.
Likewise, in polyaromatic systems such as naphthalene units, the stiffening effect extends further and becomes much greater (Table 3.14). These effects are most clearly seen in amorphous polymer of low intermolecular attraction and no cross-linking; when these complications occur, they interact with molecular flexibility and often overpower it so that its effects are no longer clearly seen.

### 3.1.7.3 Mechanical Properties

Without the complications of crystallinity, intermolecular attraction, and cross-linking, molecular flexibility generally permits the polymer molecules to disentangle and flow
more easily when mechanical stress is applied. This generally produces lower hardness, modulus, strength, creep resistance, and lubricity, along with higher extensibility and friction (see Tables 3.15 through 3.17).

### 3.1.7.4 Thermal Properties

For any given molecular structure, increasing temperature means increasing atomic and molecular motion, greater free volume, higher energy to overcome electronic repulsion and steric hindrance, and thus greater molecular flexibility. Thus, practical molecular flexibility is the summation of (a) inherent molecular flexibility plus (b) thermal mobility. Conversely, polymers with inherent molecular flexibility retain this flexibility down to lower temperatures, giving lower glass transition temperature, retaining flexibility or toughness down to lower temperature, but suffering lower heat deflection temperature, and greater loss of strength and creep deformation at high temperatures.

Thermal stability tends to correlate with molecular rigidity because chemical reaction and degradation depend on molecules moving and meeting each other, and this becomes more difficult when the molecules have less flexibility.

### 3.1.7.5 Electrical Properties

As noted earlier, molecular flexibility permits polar groups to orient in an electrical field, producing high dielectric constant; molecular rigidity prevents orientation, producing low dielectric constant. Since practical molecular flexibility and rigidity depend not only on molecular structure but also on temperature and frequency, polyurethane do not have constant dielectric constant. In the transition region, they have considerable dielectric loss, so they are not generally used in highly demanding electrical insulation applications.
3.1.6 Infrared Spectroscopy

Bending, stretching, and rotation about bonds in the polymer molecule occur at frequencies and energies primarily found in the infrared region of the electromagnetic spectrum. Since each bond absorbs energy at very specific frequencies, this provides sensitive analytical techniques to characterize the structure of polyurethanes. Conversely, for rapid preheating during processing, infrared radiation with these specific frequencies provides a very convenient technique for bringing polyurethane up to processing temperatures.

Some of these properties depend only on the inherent flexibility of the individual polymer molecule. Other structural features, however (particularly crystallinity, intermolecular attraction, and cross-linking) can immobilize polymer molecules and thus exert controlling effects on many practical properties. These will now be considered in detail.
3.1.8 Intermolecular Order: Crystallinity

The linearity and close fit of polymer chains favor crystallinity, which leads to reductions in solubility, elasticity, elongation, and flexibility, and to increases in tensile strength, melting point, and hardness.

3.1.8.1 Factors Affecting Crystallinity of Polyurethanes

In the melt and in solution, polymer molecules tend to form random coils more or less entangled with each other but relatively free to disentangle, uncoil, recoil, and exhibit more or less liquid flow. On cooling from the melt, evaporation, or coagulation of the solution, irregular molecular structures [such as poly(oxypropylene) as shown in Figure 3.23 and urethanes from 2,4-toluene diisocyanate] remain in the form of random entangled amorphous coils and come closer together, with less free volume and less mobility, gradually becoming rubbery and then glassy in properties.

In contrast, regular molecular structures of reasonable flexibility, such as poly(oxytetramethylene), polyesters, and urethanes from diphenyl methane 4′-diisocyanate (MDI), on cooling from the melt or coming out of solution, tend to organize and pack into regular dense crystalline lattice structures, which immobilize the polymer molecules and greatly restrict their inherent flexibility, producing much harder, stronger, chemically resistant products. Even in elastomeric polyurethane, such crystallization may become very apparent in low-temperature stiffening and embrittlement. Thus, crystallinity plays a major role in practical properties, often overpowering the significance of inherent molecular flexibility.

Several types of structural features affect the ability of regular polymer structures to fit and pack into the tight regular lattice required for crystallization. On the positive side,

1. A reasonable degree of molecular flexibility makes it possible for polymer molecules to disentangle from random coils and conform and fit into the precise positions required for lattice formation.
2. Intermolecular attractions help to bind the polymer molecules into the crystal lattice, making it stronger and more resistant to mechanical, thermal, and chemical stresses.
3. Monomer units with an even number of atoms in the main chain tend to pack and fit more neatly and densely than those with an odd number, giving stronger crystalline structures.

Several other types of structural features have negative effects on the ability of polyurethane to fit and pack into the crystal lattice:

1. Short side groups such as CH₂ make it more difficult for polymer backbones to fit neatly and tightly into the crystal lattice, and thus reduce or prevent crystallinity.

![FIGURE 3.23 Polyoxypropylene.](image-url)
2. When side groups become much longer, they may tend to form little crystallites among themselves, generally referred to as side-chain crystallization, which restrict molecular mobility and usually give stiffer, more waxy type of properties.

3. Introduction of cross-linking into a regular linear polymer produces branch points that reduce its regularity, decreasing and even preventing crystallinity. The result is a softening of mechanical, thermal, and chemical properties at first; however, as the degree of cross-linking is increased further and further, it eventually immobilizes the polymer molecules so effectively that properties revert and become harder again.

3.1.8.2 Effects of Crystallinity on Properties

3.1.8.2.1 Processibility

Crystalline polymers are held together by a high accumulation of intermolecular attractions, which requires more energy to separate the polymer molecules and permit them to flow during processing. In melt processing, this means higher temperatures. In solution processing, it means much more difficulty in dissolving the polymer molecules into the solvent and keeping them there. In highly crystalline polyurethane, this can make processing difficult to impossible, thus placing limits on the enthusiasm of the synthetic organic polymer chemist. On the other hand, fast crystallization from the melt can solidify molded and extruded products much faster than the gradual stiffening of amorphous polymers and thus helps to shorten processing cycles handsomely.

3.1.8.2.2 Mechanical Properties

Crystallization packs and immobilizes even highly flexible polymer molecules, making them much more resistant to mechanical stress. This produces higher hardness, modulus, strength, lubricity, and resistance to creep. All these are desirable in rigid products, but loss of softness and flexibility can be a major concern in flexible foams and elastomers.

3.1.8.2.3 Thermal Properties

The attractive forces between polymer molecules tend to hold them into the crystal lattice. Temperature represents the vibrations of atoms and molecules that tend to free them from the crystal lattice and into the mobility of the random coil. Thus, the balance of these factors determines the melting point of the crystal structure, \( T = \Delta H/\Delta S \), and the contrast between properties above and below this point.

Molecules with high inherent flexibility tend to remain amorphous, soft, and flexible at ambient temperatures. If they are regular in structure, cooling reduces vibrations and encourages crystallization, producing serious stiffening and embrittlement of flexible elastomeric products. In fact, random uncrystallizable structures can retain their soft, rubbery properties down to much lower temperature.

Molecules with high intermolecular attractions tend to form more stable crystals and resist thermal vibrations up to higher temperatures, retaining higher hardness, modulus, strength, and creep resistance, before they eventually melt. However, melting point is often accepted as a direct evidence of intermolecular attraction.

3.1.8.2.4 Chemical Resistance

Polar solvents are attracted to polar polyurethane molecules. In random amorphous coils, these solvents can easily penetrate the free volume in the random coils, separate them from each other, and dissolve them. In a tightly packed crystalline lattice, on the other
hand, there is no room for solvent molecules to penetrate, and the accumulation of attractive forces between polymer chains in the crystal lattice is too great for solvent molecules to compete with it. Thus, crystalline polymers have much greater solvent resistance.

3.1.9 Intermolecular Attraction

In a solid product made of linear polymer molecules, the ability to resist mechanical, thermal, electrical, and chemical stress depends on the attractive forces between the polymer molecules, which transfer these stresses from one molecule to another throughout the solid mass. These secondary attractive forces cover a spectrum from weak long-distance attractions up to fairly strong close-range forces (see Table 3.18).

The order of intermolecular attractions may be arranged as follows:

1. *London dispersion forces*. London dispersion forces are due to the interaction between nonpolar electron cloud bonds, typically the C–C and C–H bonds in the hydrocarbon portions of polymer molecules. They are generally 1–2 kcal/mol in strength and 3–5 Å in length.

2. *Permanent dipoles*. Permanent dipoles exist in polyurethane bonds such as C–O, C=O, C–N, O–H, and N–H. Attractions between such dipoles are typically about 3 kcal/mol in strength and 3 Å in length.

3. *Hydrogen bonds and ionic bonds*. Hydrogen bonds form when an electronegative atom in one molecule pulls electrons away from a hydrogen, leaving the hydrogen relatively electropositive and electron deficient, and an electronegative atom in another molecule shares its extra electrons with the electropositive hydrogen atom. Such hydrogen bonds are very important in polyurethane, and are typically 1.5–6 kcal/mol in strength and about 3 Å in length (see Figure 3.24).

Ionic bonds may occur occasionally in polyurethanes and are typically 10–20 kcal/mol in strength and 2–3 Å in length.

3.1.9.1 Total Intermolecular Attraction

Total intermolecular attraction is a critical concept and may be expressed in the form

\[ I = S \times C \times M \times F \]

where \( I \) is the total intermolecular attraction per unit volume, \( S \) is the strength of a single intermolecular attraction as given above, \( C \) is the concentration of such groups in the polymer

<table>
<thead>
<tr>
<th>Group</th>
<th>Cohesive Energy (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>–CH₂— (Hydrocarbon)</td>
<td>0.68</td>
</tr>
<tr>
<td>–O— (Ether)</td>
<td>1.00</td>
</tr>
<tr>
<td>–COO— (Ester)</td>
<td>2.90</td>
</tr>
<tr>
<td>–C₆H₄— (Aromatic)</td>
<td>3.80</td>
</tr>
<tr>
<td>–CONH— (Amide)</td>
<td>8.50</td>
</tr>
<tr>
<td>–OCONH— (Urethane)</td>
<td>8.74</td>
</tr>
</tbody>
</table>
molecule (the size of the repeat unit), $M$ is the molecular weight of the polymer (which determines the number of such groups in the molecule), and $F$ is the frequency with which such potential intermolecular attractions come close enough to each other to actually form. Thus, for example, London dispersion forces individually have low-strength $S$, but their concentration $C$ is so ubiquitous that they add up to a major portion of the total intermolecular attraction in all polymer molecules; in fact, in hydrocarbon polymers, they alone account for the useful properties of such widely used polymers as polyethylene, polypropylene, and polystyrene.

For another example, in polyurethane, the strength $S$ of polar and hydrogen bonding attractions is great enough to accumulate and give useful properties even at rather modest molecular weight $M$, whereas in polyolefins, the lower strength $S$ of London dispersion forces requires much higher molecular weights $M$ before they can accumulate to produce useful properties. Additionally, in the random coils of amorphous polyurethane, the polar and hydrogen-bonding groups ($S$) of adjacent polymer molecules only rarely come close enough to function (low $F$), leaving such polymers soft and flexible, whereas, in the neatly packed area of crystalline polyurethane, the same groups ($S$) occur close to each other with high frequency ($F$), producing much greater total attraction and much greater strength and heat resistance. In general, it is the total intermolecular attraction that best explains effects on practical properties.

3.1.9.1.1 General Effects on Properties

In general, increasing intermolecular attraction makes procession more difficult, requiring higher melt temperatures and more polar, higher-boiling solvents to overcome these attractions and produce good flow. As intermolecular attractions increase, they bring increasing hardness, modulus, strength, and creep resistance. They decrease low-temperature flexibility but increase hot strength and melting point. They also increase resistance to non-polar fuels and oils, a major advantage over conventional hydrocarbon elastomer and foams (see Tables 3.19 and 3.20).

### TABLE 3.19

<table>
<thead>
<tr>
<th>Urethane weight (%)</th>
<th>8.4</th>
<th>9.3</th>
<th>10.9</th>
<th>13.6</th>
<th>17.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile strength (psi)</td>
<td>110</td>
<td>110</td>
<td>140</td>
<td>250</td>
<td>2000</td>
</tr>
<tr>
<td>Ultimate elongation (%)</td>
<td>190</td>
<td>180</td>
<td>220</td>
<td>340</td>
<td>720</td>
</tr>
<tr>
<td>Glass transition (°C)</td>
<td>-51</td>
<td>-48</td>
<td>-43</td>
<td>-34</td>
<td>-24</td>
</tr>
<tr>
<td>Swelling in benzene (%)</td>
<td>524</td>
<td>492</td>
<td>450</td>
<td>368</td>
<td>300</td>
</tr>
</tbody>
</table>
A few examples from polyurethane structure–property relations can serve to illustrate some of these principles.

- Polymers alone have oxygen to serve as electron donors, but only meager amounts of electropositive hydrogen to serve as electron acceptors; for this reason, aliphatic polymers tend to be weak and low-melting. When aliphatic polymers are used in polyols to make polyurethane, however, the N–H groups provide electropositive hydrogen to act as electron acceptors; the resulting hydrogen bonding in polyester urethanes makes them the optimum choice for high-strength elastomers.

- Hydrogen bonding in polyurethane is sufficient to provide good properties, but hydrogen bonding in polyureas is much stronger and gives much higher strength and melting points. Thus, in making high-performance polyurethane elastomers, the use of diamines to create urea group contributes even more to performance than the urethane groups, which take total credit in conventional nomenclature. Even in flexible polyurethane foams, the use of water plus diisocyanate to produce CO₂ for foaming also incidentally introduces diamine, which then reacts to introduce polyurea units into the foam and contributes greatly to its strength.

- Introducing ionic bonding between polyurethane chains has been observed to increase hardness, modulus, strength, and glass transition temperature, along with decrease in elongation (see Table 3.21). All of these effects are evidence that ionic bonding serves to immobilize the polymer molecules and make them more resistant to mechanical and thermal stress.

### Table 3.20

<table>
<thead>
<tr>
<th>Urethane weight (%)</th>
<th>10.5</th>
<th>8.3</th>
<th>5.3</th>
<th>3.1</th>
<th>2.7</th>
</tr>
</thead>
<tbody>
<tr>
<td>100% Secant modulus (psi)</td>
<td>30</td>
<td>16</td>
<td>12</td>
<td>7</td>
<td>6</td>
</tr>
<tr>
<td>Tensile strength (psi)</td>
<td>30</td>
<td>21</td>
<td>18</td>
<td>22</td>
<td>15</td>
</tr>
<tr>
<td>Ultimate elongation (%)</td>
<td>100</td>
<td>130</td>
<td>155</td>
<td>295</td>
<td>340</td>
</tr>
<tr>
<td>Compression load at 75% psi</td>
<td>8.3</td>
<td>4.3</td>
<td>2.1</td>
<td>1.6</td>
<td>0.9</td>
</tr>
<tr>
<td>Rebound (%)</td>
<td>16</td>
<td>15</td>
<td>44</td>
<td>42</td>
<td>—</td>
</tr>
<tr>
<td>% Swelling in dimethylacetamide (DMAC)</td>
<td>145</td>
<td>170</td>
<td>237</td>
<td>350</td>
<td>—</td>
</tr>
</tbody>
</table>

### Table 3.21

<table>
<thead>
<tr>
<th>Degree of quaternization (%)</th>
<th>10</th>
<th>30</th>
<th>60</th>
<th>100</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shore A hardness</td>
<td>48</td>
<td>65</td>
<td>73</td>
<td>82</td>
</tr>
<tr>
<td>100% Secant modulus</td>
<td>110</td>
<td>320</td>
<td>730</td>
<td>940</td>
</tr>
<tr>
<td>Tensile strength (psi)</td>
<td>670</td>
<td>2800</td>
<td>3170</td>
<td>4250</td>
</tr>
<tr>
<td>Ultimate elongation (%)</td>
<td>1280</td>
<td>1000</td>
<td>790</td>
<td>710</td>
</tr>
</tbody>
</table>
3.1.10 Cross-Linking

The ultimate intermolecular force is a primary covalent cross-link, and these are generally used in the vast majority of polyurethane products.

3.1.10.1 Cross-Linking Reactions

Cross-linking increases the degree of cross-linking and leads to an increase in rigidity, softening point, and modulus of elasticity for amorphous polymers, thus reducing elongation and swelling by solvents.

It is possible to use more than one polycomponent to vary the formulation, and hence the processing characteristics and the properties, of the product. This affects the degree of branching and also the order of interaction of the polyols with the diisocyanate. It is also possible to vary processing factors such as temperature, viscosity, rate of setup, curing of the casting mix, or incorporation of fillers. Addition of low-molecular-weight polyols such as glycerol or trimethylol propane may introduce branching.

Generally, in the preparation of polyurethane, the excess diisocyanate may first react with polyol to form isocyanate-terminated prepolymer, which is stable in the absence of moisture and catalyst. This prepolymer reacts with more polyol at the casting stage. Therefore, by varying the polyol component added in this stage, it is possible to change the properties of the resulting elastomer. Depending on the chemical composition and the amount of cross-linking and branching, it is possible to obtain products ranging from soft elastomers to hard resinous materials.

The chain structure of the polymerized intermediate determines the level of mechanical properties. Fillers, if used, may increase hardness and modulus of elasticity and reduce elongation, but they do not have a very substantial effect on strength.

For a given set of diols and triols and a given NCO/OH ratio, the molecular weight per branch point may be altered by varying the proportions of diols and triols. The molecular weight per branch point may be varied while retaining the same proportion of polyisocyanate, either by using polyols that are the same equivalent weight or by simultaneously varying the equivalent weights of the polyols to give a combination of the same average equivalent weight. An increase in the proportion of polyisocyanates results in a decrease in the molecular weight per branch point and an increase in tensile strength, modulus of elasticity, and hardness, while decreasing elongation.

Besides the triols, cross-linkage and branching will also take place at the urethane and the urea groups. When the NCO/OH ratio is low, the branching will occur at the urethane linkage. At higher NCO/OH ratios, the probability for the formation of urea linkages will be high and, thus, branching will occur at the urea linkages. The presence of higher atmospheric pressure and relative humidity assures the presence of ETO linkage and branching at the urea groups, and the percentage of urea to urethane will be higher than at lower NCO/OH ratios.

Most often, cross-links are introduced by the use of trifunctional or higher-functional polyols as shown in Figure 3.25.

In flexible urethane foams and cast elastomers, the polyol is a long, linear Y-shaped triol. In rigid urethane foams, it may be a short-chain polysaccharide hexol. Here, the cross-links have the same chemical composition and stability as the main chains.

Second in importance is the use of low-molecular-weight polyisocyanates made from aniline–formaldehyde oligomers. These are used primarily in the production of rigid foams. Here again, the cross-links have the same chemical composition and stability as the main chains.
Often, the cross-links are produced by using excess allophanate in the formulation and allowing it to react with urethane groups already formed to produce allophanate cross-links, or with urea groups already formed to produce biuret cross-links. In this case, the cross-links form somewhat reluctantly and are less heat stable than the main chains, tending to open and revert upon heating.

The stablest cross-links are formed by using excess isocyanate in the formulation and causing it to form cyclic trimers called isocyanurates. These are by far the stablest types of cross-links, and they are used to produce products with maximum heat and flame resistance.

Cross-linking may be induced by peroxides, either by abstraction of hydrogen (which is quite difficult) or by introduction of vinyl groups into the polyurethane (which requires extra synthetic effort). Either way, the cross-links formed are C–C bonds, which are as stable as the main chain itself.

Rubber processors sometimes buy thermoplastic polyurethane elastomer gums and cross-link them as they would conventional rubber, using sulfur and accelerators. Such sulfur cross-linking is difficult using saturated elastomers; it can be improved by synthesizing the polyurethane with some vinyl groups to permit conventional sulfur vulcanization reactions. However, such sulfur cross-links appear to be less heat stable than the more common conventional polyurethane cross-linking systems.

### 3.1.10.2 Mechanical Properties

The introduction of cross-links between polyurethane molecules produces a definite quantitative restriction of molecular mobility. At low degrees of cross-linking, where long
segments of the backbone molecule are still free to move, there is little loss of soft flexible
rubbery behavior, and there are distinct improvements in strength and creep resistance
(see Tables 3.22 and 3.23). In crystalline polymers, low cross-linking destroys regularity
and reduces crystallinity, and thus actually produces softer properties. With increasing
degree of cross-linking, modulus increases and extensibility decreases, giving tough,
flexible products. At still higher degrees of cross-linking, the polymer molecules are thor-
oughly immobilized and become rigid thermoses plastic (see Table 3.24). Thus, cross-
linking alone can develop a broad spectrum of polyurethane properties and products.
Figure 3.26 presents the mechanism of cross-linking via dicumyl peroxide.

### 3.1.10.3 Thermal Properties

Increasing cross-linking draws polymer backbones closer together, reduces molecular
mobility, and raises glass transition temperature. Thus, flexible elastomers begin to stiffen
at low temperatures. However, where secondary attractions permit weakening and creep at
high temperatures, these are both controlled by the introduction of permanent cross-links.

**TABLE 3.22**

Low Cross-Linking of Polyether Urethane Elastomers

<table>
<thead>
<tr>
<th>MW between cross-links</th>
<th>2500</th>
<th>4500</th>
<th>8500</th>
<th>12,500</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile strength (psi)</td>
<td>200</td>
<td>220</td>
<td>130</td>
<td>160</td>
</tr>
<tr>
<td>Ultimate elongation (%)</td>
<td>110</td>
<td>190</td>
<td>260</td>
<td>310</td>
</tr>
<tr>
<td>Glass transition (°C)</td>
<td>−59</td>
<td>−59</td>
<td>−59</td>
<td>−59</td>
</tr>
<tr>
<td>Swelling in benzene (%)</td>
<td>294</td>
<td>342</td>
<td>384</td>
<td>467</td>
</tr>
</tbody>
</table>

**TABLE 3.23**

Low Cross-Linking of Polyester Urethane Elastomers

<table>
<thead>
<tr>
<th>MW between cross-links</th>
<th>2100</th>
<th>4300</th>
<th>7100</th>
<th>21,000</th>
<th>∞</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shore A hardness</td>
<td>57</td>
<td>49</td>
<td>51</td>
<td>56</td>
<td>61</td>
</tr>
<tr>
<td>Tensile strength (psi)</td>
<td>1800</td>
<td>1450</td>
<td>4500</td>
<td>5500</td>
<td>6750</td>
</tr>
<tr>
<td>Ultimate elongation (%)</td>
<td>170</td>
<td>280</td>
<td>410</td>
<td>490</td>
<td>640</td>
</tr>
<tr>
<td>100% Secant modulus</td>
<td>570</td>
<td>300</td>
<td>330</td>
<td>500</td>
<td>630</td>
</tr>
<tr>
<td>Tear strength (pli)</td>
<td>30</td>
<td>30</td>
<td>40</td>
<td>140</td>
<td>300</td>
</tr>
<tr>
<td>Compression set (%)</td>
<td>2</td>
<td>10</td>
<td>25</td>
<td>45</td>
<td>55</td>
</tr>
</tbody>
</table>

**TABLE 3.24**

High Cross-Linking Produces Rigid Thermoset Polyurethane Plastics

<table>
<thead>
<tr>
<th>Hexol/diol ratio</th>
<th>80/20</th>
<th>90/10</th>
<th>100/0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shore D hardness</td>
<td>77</td>
<td>85</td>
<td>91</td>
</tr>
<tr>
<td>Tensile strength (psi)</td>
<td>4300</td>
<td>8800</td>
<td>13,250</td>
</tr>
<tr>
<td>Ultimate elongation (%)</td>
<td>4</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Tensile modulus (psi)</td>
<td>170,000</td>
<td>410,000</td>
<td>600,000</td>
</tr>
<tr>
<td>Flexural strength (psi)</td>
<td>7000</td>
<td>16,700</td>
<td>18,000</td>
</tr>
<tr>
<td>Heat deflection temperature (°C)</td>
<td>52</td>
<td>78</td>
<td>87</td>
</tr>
<tr>
<td>Swelling in acetone (%)</td>
<td>27.4</td>
<td>17.9</td>
<td>0.3</td>
</tr>
</tbody>
</table>
At higher temperatures, the weaker, less stable types of cross-links tend to reopen and revert to linear structures. This is noticed first in allophanates, then in biurettes. Sulfur vulcanization cross-links are less stable than conventional polymer cross-links. When direct C–C cross-links can be formed, these have very good stability. Generally, the stabllest are those formed by isocyanate cyclic trimerization into isocyanurate rings. Isocyanurates are most commonly used for heat- and flame-resistant products.

### 3.1.10.4 Chemical Resistance

Even the lightest degree of cross-linking will prevent individual polymer molecules from dissolving in a solvent. Since there is still strong attraction between polyurethane and polar solvents, lightly cross-linked polymers will absorb large amounts of solvent and swell to soft gels. Increasing degree of cross-linking produces less free lump for absorption of solvent molecules, and less freedom for polymer chains to move apart to accept them. Thus, there is a precise quantitative relationship between swelling and cross-linking (Table 3.25), which can actually be used to calculate the concentration of cross-links in the polymer. A high degree of cross-linking can even produce considerable improvement in resistance to polar solvents.

Water absorption should similarly be reduced by cross-linking. Furthermore, the degrading effects of hydrolysis on molecular weight and properties should be retarded by the presence of cross-links to maintain the molecular weight above the critical level needed for

#### Table 3.25

<table>
<thead>
<tr>
<th>MW between cross-links</th>
<th>1650</th>
<th>1070</th>
<th>690</th>
</tr>
</thead>
<tbody>
<tr>
<td>Swelling in acetone (%)</td>
<td>116</td>
<td>90</td>
<td>83</td>
</tr>
</tbody>
</table>
useful properties. The extent of such improvement in individual products must be determined experimentally.

3.1.11 Supermolecular Structure

A number of larger structural features are of major practical importance in the properties and use of polyurethane, and some of them are also fairly well understood at the theoretical level as well.

3.1.11.1 Latex

Polyurethane coatings, adhesives, and fibers are frequently processed by conventional organic solution techniques. Such use of solvents introduces growing problems of cost, toxicity, flammability, disposal, and recycling, problems that create growing pressure to reduce or eliminate the use of organic solvents. One attractive alternative is to disperse the polyurethane in aqueous medium, apply in place, and remove the water to deposit the solid polyurethane product. A variety of techniques have been studied to accomplish this.

Finished thermoplastic polyurethane can be emulsified and used in latex form. Fatty isocyanates of low polarity can be emulsified in water without suffering hydrolysis and then formulated into reactive systems. Isocyanates can be temporarily blocked to make them stable in water; then, the blocking reaction is reversed to liberate the isocyanate for the curing reaction.

3.1.11.2 Copolymers

The versatile reactivity of polyols and polyisocyanates invite the preparation of copolymers with various other polymer systems to combine the best properties of each. Thus, there are occasional reports of polyurethane copolymers with other common polymer systems. Most important are probably the polyurethane drying oils, which combine conventional drying oil processibility with the high performance of polyurethane. Also popular are acrylic polyurethanes, which combine the easy radiation cure of the acrylics with the end-use performance of the polyurethane. More specialized are copolymers with epoxy resins (Table 3.26), polyester (Table 3.27), and silicones. Most of these systems are fairly homogeneous one-phase copolymers and thus not truly supermolecular structures.

3.1.11.3 Block Copolymers

Polyurethanes are generally made up of polyol segments of lower polarity, plus polyurethane and/or polyurea segments of higher polarity. When the segments are fairly short, the polymer may have a fairly random homogeneous structure. When the segments are

<table>
<thead>
<tr>
<th>TABLE 3.26</th>
<th>Copolymers of Urethane Elastomer with an Epoxy Resin</th>
</tr>
</thead>
<tbody>
<tr>
<td>Urethane/epoxy ratio</td>
<td>'100/0</td>
</tr>
<tr>
<td>Shore D hardness</td>
<td>39</td>
</tr>
<tr>
<td>Flexural modulus (psi)</td>
<td>4230</td>
</tr>
<tr>
<td>Flexural strength (psi)</td>
<td>393</td>
</tr>
<tr>
<td>Volume resistivity</td>
<td>4 x 10^11</td>
</tr>
<tr>
<td>Dielectric constant</td>
<td>7.2</td>
</tr>
<tr>
<td>Dissipation factor</td>
<td>0.048</td>
</tr>
</tbody>
</table>
longer, the resulting block copolymer will tend to separate into microphases. The phase present in larger amount will tend to form the continuous matrix and control most of the properties, while the phase present in smaller amount will tend to segregate as discrete domains and contribute specific properties to the composite structure.

Generally, the polymer blocks are of lower polarity, long and flexible, and frequently referred to as soft segments; they form the continuous matrix and make the majority of polyurethane soft, flexible, and rubbery. In some cases, very regular polyols such as poly(oxytetramethylene) and poly(ethylene adipate) will tend to crystallize, giving higher-strength elastomers, but stiffen when cooled to lower temperatures.

The polyurethane and polyurea blocks are generally higher in polarity and hydrogen-bonding, short and bulky, and are frequently referred to as hard segments. They form the dispersed domains, contribute strength and creep resistance, and retain these to higher temperatures. Irregular structures such as 2,4-toluene diisocyanate and polymethylene polyphenyl isocyanates generally give glassy hard segments, held together by steric hindrance, polar attraction, and hydrogen bonding. Regular structures such as diphenylmethane-4,4′-diisocyanate tend to give crystalline hard segments, also held together by steric hindrance, polar attraction, and hydrogen bonding.

Thus, block copolymer structure and microphase separation permit polyurethane to combine the best properties of both the soft polyol continuous matrix and the hard urethane and/or urea dispersed domains. This supermolecular structure is a major reason for their high performance and versatility.

### 3.1.11.4 Polyblends and Interpenetrating Polymer Networks

When two polymers are mixed, the requirement for thermodynamic miscibility at equilibrium is a decrease in free energy ΔG:

\[
\Delta G = \Delta H - T \Delta S
\]

where ΔH is the enthalpy of mixing (attraction between the two polymers) and ΔS is the entropy of mixing (gain in statistical randomness). Two unlike polymers will generally repel
each other, making $\Delta H$ unfavorable, unless there is some specific group attraction between them such as hydrogen bonding. Mixing of large polymer molecules does not produce much gain in randomness $\Delta S$, because all the atoms in a polymer molecule remain attached to each other during the process. Thus, most polymer blends are not miscible at the molecular level and tend to separate into microphases. If the interface between these microphases is strongly bonded, each phase may be free to contribute some of its best properties to the blend, and such two-phase blends can benefit from synergistic balance of properties. This has turned polyblending into one of the fastest-growing segments of the polyurethane industry.

Polyurethanes contain aliphatic, aromatic, ether, ester, urethane, and urea groups, offering a wide range of polarities and hydrogen-bonding possibilities, which should promote miscibility, or at least strong interfacial bonding, with a wide variety of other polymers. Blends with acrylonitrile styrene-butadiene (ABS) combine the melt processibility/rigidity and heat deflection temperature of the ABS with the classic recovery and abrasion resistance of the polyurethane. Blends with polyvinyl chloride (PVC) combine the rigidity and flame retardance of the PVC with the impact resistance of the polyurethane (Table 3.28); in more miscible blends, the polyurethane acts as a permanent polymeric plasticizer. Blends with epoxy resins combine the rigidity and heat and chemical resistance of the epoxy with the ductility and impact resistance of the polyurethane (Table 3.29).

When a polymer is lightly cross-linked and swollen with a second monomer, and the second monomer is then polymerized in the swollen network, the resulting interpenetrating polymer network (IPN) contains the two polymer phases in a controlled degree of dispersion. IPN synthesis benefits from the use of two distinctly different polymerization mechanisms. Since polyurethanes are formed by a unique chemical reaction, they can conveniently form one of the two polymer phases in IPNs and have proved to be one of the

### TABLE 3.28

<table>
<thead>
<tr>
<th>PU</th>
<th>PVC</th>
<th>Sb$_2$O$_3$</th>
<th>Oxygen Index (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>0</td>
<td>0</td>
<td>22.0</td>
</tr>
<tr>
<td>100</td>
<td>10</td>
<td>0</td>
<td>22.0</td>
</tr>
<tr>
<td>100</td>
<td>5</td>
<td>5</td>
<td>29.1</td>
</tr>
<tr>
<td>100</td>
<td>0</td>
<td>10</td>
<td>23.5</td>
</tr>
<tr>
<td>100</td>
<td>20</td>
<td>0</td>
<td>21.4</td>
</tr>
<tr>
<td>100</td>
<td>15</td>
<td>5</td>
<td>31.0</td>
</tr>
<tr>
<td>100</td>
<td>10</td>
<td>10</td>
<td>31.3</td>
</tr>
<tr>
<td>100</td>
<td>5</td>
<td>15</td>
<td>29.4</td>
</tr>
<tr>
<td>100</td>
<td>0</td>
<td>20</td>
<td>23.5</td>
</tr>
<tr>
<td>100</td>
<td>40</td>
<td>0</td>
<td>22.1</td>
</tr>
<tr>
<td>100</td>
<td>35</td>
<td>5</td>
<td>27.9</td>
</tr>
<tr>
<td>100</td>
<td>30</td>
<td>10</td>
<td>32.6</td>
</tr>
<tr>
<td>100</td>
<td>25</td>
<td>15</td>
<td>32.2</td>
</tr>
<tr>
<td>100</td>
<td>20</td>
<td>20</td>
<td>29.8</td>
</tr>
<tr>
<td>100</td>
<td>15</td>
<td>25</td>
<td>31.5</td>
</tr>
<tr>
<td>100</td>
<td>10</td>
<td>30</td>
<td>27.5</td>
</tr>
<tr>
<td>100</td>
<td>5</td>
<td>35</td>
<td>26.8</td>
</tr>
<tr>
<td>100</td>
<td>0</td>
<td>40</td>
<td>22.3</td>
</tr>
</tbody>
</table>
most popular polymer systems in IPN research. Surprisingly, many polyurethane IPNs, particularly with acrylics and polyesters, have shown remarkable synergistic improvement of tensile strength, as compared with the individual polymers involved. Much IPN research has been directed toward broad-spectrum damping of noise and mechanical vibration.

3.1.11.5 Reinforcing Fillers

The use of fibers to produce high-performance reinforced composites has been developed primarily in epoxy resins and thermoset polyesters. In reaction injection molding (RIM), addition of short glass fibers produces reinforced RIM (RRIM), with much improved rigidity and strength (Table 3.30). Similarly, addition of short glass fibers to rigid urethane foam produces major improvements in modulus and strength (Table 3.31). The most extreme reinforcement is, of course, observed when flexible polyurethane foam is coated onto cloth, for upholstery and clothing, combining the high planar modulus, strength, and dimensional stability of the cloth with the high transverse flexibility, softness, and thermal insulation of the foam.

3.1.11.6 Foams

When gas bubbles are dispersed in a solid polymer to form a foam, it is possible to combine some of the best properties of each phase and to produce some synergistic benefits as well. In polyurethane, the gas contributes light weight, thermal, and electrical insulation. The thermal insulation is used in rigid foams for refrigeration and freezer applications in flexible forms for winter outerwear clothing. In closed-cell foams, the gas contributes flotation,
rigidity and strength, and impact absorption, while in open-cell foam, the fluidity of the gas contributes softness, elastic recovery, impact absorption, noise damping, filtration, and sponge performance. Thus, the gas phase, negligible in weight but most prominent in volume, contributes many useful properties and uses that the polyurethane alone did not have.

3.1.11.7 Coatings

Thin polyurethane surface films contribute useful properties far beyond their thin dimensions. They are easy to apply by a variety of techniques and can have a wide range of modulus as desired. They have strong adhesion to many substrates. They are strong, impact resistant, extremely abrasion resistant, and resistant to hot aging, aqueous solutions, fuels, oils, and many other chemicals. When aliphatic isocyanates are used, they are also very resistant to weathering. Aliphatic-based polyurethane coatings find increasing use in corrosion-preventive maintenance coatings.

3.1.11.8 Adhesives

Polyurethanes combine the fluidity needed to wet irregular substrates, the cure reactions needed to convert them into high-molecular-weight materials of strong cohesion, and the range of polarities and hydrogen bonding needed to form strong adhesive bonds with many types of surfaces. For these reasons, they have proved useful in a wide range of specialty adhesives.

3.2 Surface Analysis

Theoretically, a surface is an infinitely thin layer separating two phases. Surfaces are generally examined with spectroscopy, which involves probing a sample target with a flux of energetic particles and detecting characteristic particles emitted from the surface after interaction.

Activation may be achieved by electromagnetic radiation, as in electron spectroscopy for chemical analysis (ESCA); by a beam of incident ions, as in secondary ion mass
spectrometer (SIMS) and ion scattering spectroscopy (IS); or by an incident electron beam, as in Auger electron spectroscopy (AES) or by electron microprobe (x-ray fluorescence) analysis.

Infrared spectrophotometry (IR) measures the energies involved in the twisting, bending, rotating, and vibrating motions of asymmetrical chemical bonds in a molecule. Upon interaction with infrared radiation, portions of the incident radiation are absorbed at particular wavelengths. These wavelengths correspond to particular vibrations of the bonds and thus yield information about the chemical structure of the absorbing species. A Fourier transform infrared spectrophotometer (FT-IR) makes use of computer technology and yields much higher resolution through processing of very large amounts of data obtained through numerous runs. IR and FT-IR give information about the chemical bonds present in the bulk structure. On the other hand, an attenuated total reflectance infrared spectrophotometer (AT-IR or ATR-IR) gives information about the chemical bonds present on the surface.

Adsorption and segregation depend on surface chemistry as well as on surface free energy. Determination of contact angles (advancing, receding, or critical) by the use of a goniometer is a convenient and simple method of measuring the surface free energies of the polymeric samples.

Polyurethanes have very widely varying structures, depending on the components used in the formulation. The aromatic isocyanates will give more urea groups in the finished structure than will the aliphatic diisocyanate. Excess NCO in the formulation will react with atmospheric moisture to form urea and barrette groups in the structure. Aromatic diamines will produce a great amount of urea groups in the structure of the polymer, with some amide groups and aromatic rings. Polyester components will give far more urethane groups, along with a few ester groups in some cases, and the urethane linkages will be predominant. Polyether components give a very large number of elephant groups in the polymer, with a few ether groups, and, in some cases, a few ester groups. The amount of these groups in comparison with the urethane linkages can be varied easily by choice of the individual polyether. Other groups such as urea and barrette can be decreased by reacting these hydroxyl components with an aliphatic diisocyanate at very near to the stoichiometric 1:1 ratio by avoiding any further reaction with atmospheric moisture and by using completely anhydrous components.

The structure of the diisocyanate and the structure of the hydrogen donors have a great influence on the final properties. NCO/OH ratios, the manner in which they are reacted, the presence of catalyst, and the cure conditions all have large degree of influence on the end product.

Although the types of ingredients are much more varied in polyurethane than other polymers, some analytical techniques, such as IR, are quite useful in the chemical characterization of polyurethanes. In IR analysis (or AT-IR or FT-IR), the wavelengths of the absorption bands for some groups can be summarized as in Table 3.32.

However, interferences and shifts caused by the neighboring groups may be encountered. In large polymers such as polyurethane, the characteristic spectra become diffuse, and identification of small amounts of any given functionality becomes increasingly difficult.

The effect of secondary valence internal bonding through polar internees and hydrogen bonding is also manifested in the modulus of elasticity and hardness of the cured product, which increase markedly with increases in the proportion of diisocyanate to glycol. Although this increase is accompanied by some loss in resilience, it is possible to obtain very hard products that still retain elastomeric character. In the production of high-grade, high-modulus elastomers, symmetrical diisocyanate such as naphthalene-1,5-diisocyanate,
phenylene-1,4-diisocyanate, and diphenylmethane-4,4’-diisocyanate, and symmetrical glycol such as 1,4-butanediol, 1,6-hexanediol, p-bis(β-hydroxy ethoxy)benzene, 1,5-bis(β-hydroxy ethoxy)napthalene are useful.

Unsymmetrical diisocyanate and glycol result in very different processing characteristics and physical properties. Low proportions of the diisocyanate–glycol urethane segment yield elastomers that are substantially softer and of lower modulus than analogous compositions based on symmetrical diisocyanate. Interruption attractive forces between rigid segments are very high because the urethane group is highly polar and exhibits a strong tendency to hydrogen bonding between the –NH– and the –COO– parts of the group. Consequently, it has a strong tendency toward association and a high energy of cohesion. Regular polyurethanes are generally similar in character to other polymers containing regularly occurring groups with high energy of cohesion.

References