2. Literature Review

2.1 Flexible Polyurethane Foam Chemistry

This section focuses on the basic chemical reactions involved in the formation of flexible polyurethane foams. Since flexible polyurethane foam production requires a variety of chemicals and additives, this section will review specific chemicals and their importance in the foaming process.

2.1.1 General Chemical Reactions

Flexible polyurethane foam chemistry particularly features two reactions – the ‘blow’ reaction and the ‘gelation’ reaction. A delicate balance between the two reactions is required in order to achieve a foam with a stable open-celled structure and good physical properties. The commercial success of polyurethane foams can be partially attributed to catalysts which help to precisely control these two reaction schemes. An imbalance between the two reactions can lead to foam collapse, serious imperfections, and cells that open prematurely or not at all.

2.1.1.1 Blow Reaction

The first step of the model blow reaction (Figure 2.1) involves the reaction of an isocyanate group with water to yield a thermally unstable carbamic acid which decomposes to give an amine functionality, carbon dioxide, and heat. In the second step (Figure 2.2), the newly formed amine group reacts with another isocyanate group to give a disubstituted urea and additional heat is generated. The total heat generated from the blow reaction is approximately 47 kcal per mole of water reacted, along with the carbon dioxide released in the first step and
serves as the principal source for ‘blowing’ the foam mixture, though some auxiliary blowing agents are also usually utilized. Also, since the typical isocyanates utilized in foam production are difunctional, the second part of the blow reaction serves as a means to chain extend the

\[
R\equiv N\equiv C\equiv O + R'-NH_2 \xrightarrow{-\Delta} R-N\equiv C\equiv N\equiv R'
\]

Isocyanate Amine Disubstituted Urea

**Figure 2.2 Second Step of the Blow Reaction**

aromatic groups of the typically used isocyanate molecules to form linear hard segments. However, it should be noted that this reaction scheme can also produce covalent cross-linking points when molecules with functionality greater than two, such as diethanol amine, are added to the formulation.

There are other secondary reactions, involving the formation of biuret and allophanate linkages which could lead to the formation of covalent cross-linking points. In the formation of

\[
R\equiv N\equiv C\equiv O + R-N\equiv C\equiv N\equiv R' \xrightarrow{\Delta} R-N\equiv C\equiv N\equiv R'
\]

Isocyanate Disubstituted Urea Biuret

**Figure 2.3 Formation of a Biuret Linkage**

biuret, a hydrogen atom from the disubstituted urea reacts with an isocyanate group to form a biuret linkage, as shown in Figure 2.3. The allophanate forming reaction is discussed in the next section.

**2.1.1.2 Gelation Reaction**

The gelation reaction, also sometimes called the polymerization reaction, involves the reaction of an isocyanate group with an alcohol group to give a urethane linkage as shown in Figure 2.4. The heat of this reaction is reported to be approximately 24 kcal per mole of urethane
formed. Since polyurethane foams usually utilize polyfunctional reactants (typically difunctional isocyanates and trifunctional polyols), this reaction leads to the formation of a cross-linked polymer.

\[
R\overset{\equiv}N=C=O + R'CH_2OH \xrightarrow{\triangle} R\overset{\equiv}N-C-O-CH_2R'
\]

Isocyanate                   Alcohol                  Urethane

**Figure 2.4 The Gelation or Cross-Linking Reaction**

The reaction of a urethane group with an isocyanate group to form an allophanate group is another possible way to further cross-link the polymer as shown in Figure 2.5. In uncatalyzed systems this reaction is known to be insignificant. Also, this reaction is generally not favorable under the catalytic conditions used for flexible foam production.

It is important to note that both reaction schemes described above occur simultaneously, and therefore it is critical to control the relative rates of these reactions in order to obtain a foam with a stable cellular structure and good physical properties. If the blow reaction takes place too fast in comparison to the gelation reaction, it would result in the cells opening before there is sufficient viscosity build-up to provide the foam struts with enough strength to uphold the foam, leading to the collapse of the foam. On the other hand, if the gelation reaction is faster than the blow reaction, it may result in a foam with closed cells, which is not desirable. The relative rates of reaction of the isocyanate component with other foam reactants at 25 °C under uncatalyzed conditions are provided in Table 2.1. These can serve as a guideline to make appropriate catalyst adjustments to achieve a suitable balance of the two reaction schemes.
Familiarity with the above two reaction schemes is adequate to develop a fundamental understanding of the solid-state morphology which develops in flexible polyurethane foams. As discussed in Section 2.1.1.1, the blow reaction not only helps in foam expansion, but also leads to the generation of urea hard segments. The gelation reaction covalently bonds these urea hard segments to soft polyol segments. When the concentration of the hard segments exceeds a system dependent solubility limit, the hard segments phase separate out and form what are commonly referred to as ‘urea microdomains’. Due to the asymmetric nature of the isocyanates

<table>
<thead>
<tr>
<th>Active Hydrogen Compound</th>
<th>Typical Structure</th>
<th>Relative Reaction Rate (Uncatalyzed at 25 °C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Primary Aliphatic Amine</td>
<td>RNH₂</td>
<td>100,000</td>
</tr>
<tr>
<td>Secondary Aliphatic Amine</td>
<td>R₂NH</td>
<td>20,000-50,000</td>
</tr>
<tr>
<td>Primary Aromatic Amine</td>
<td>ArNH₂</td>
<td>200-300</td>
</tr>
<tr>
<td>Primary Hydroxyl</td>
<td>RCH₂OH</td>
<td>100</td>
</tr>
<tr>
<td>Water</td>
<td>H₂O</td>
<td>100</td>
</tr>
<tr>
<td>Carboxylic Acid</td>
<td>RCOOH</td>
<td>40</td>
</tr>
<tr>
<td>Secondary Hydroxyl</td>
<td>R₂CHOH</td>
<td>30</td>
</tr>
<tr>
<td>Urea</td>
<td>RNHCONHR</td>
<td>15</td>
</tr>
<tr>
<td>Tertiary Hydroxyl</td>
<td>R₃COH</td>
<td>0.5</td>
</tr>
<tr>
<td>Urethane</td>
<td>RNHCOOR</td>
<td>0.3</td>
</tr>
<tr>
<td>Amide</td>
<td>RCONH₂</td>
<td>0.1</td>
</tr>
</tbody>
</table>

Table 2.1 Reactivity of Isocyanates with Active Hydrogen Compounds

Figure 2.6 Schematic Representation of the Phase Separation Behavior in Polyurethane Foams
utilized in foam manufacture (discussed in detail in Section 2.1.2.1), these microdomains are not crystalline but have been suggested to possess ordering of a paracrystalline nature. In addition, at higher water contents (and thus at higher hard segment contents), the urea microdomains are known to aggregate and form larger urea rich structures commonly termed ‘urea balls’ or ‘urea aggregates’. These urea balls are regions which are richer in urea as compared to the general surrounding polyol matrix which also contains dispersed urea microdomains. A schematic representation of this phase-separated morphology is provided in Figure 2.6, and should be kept in mind while further reading this review. Further aspects of this phase-separation behavior and its influence on physical properties of foams will be discussed in section 2.3.

2.1.2 Basic Foam Components

There are many different components needed to synthesize a flexible foam. The seven major ones are isocyanate, polyol, water, physical blowing agents, catalyst, surfactants, and cross-linking agents. The desired end properties of the foam dictate the choice of specific components along with their required quantities. For example, one way to adjust foam modulus would be by controlling the percentage of hard segments formed from the water-isocyanate reaction. In other cases, it might be required to have a foam with more cell openness – this would be possible by controlling the type and quantity of surfactant used. Table 2.2 lists the

<table>
<thead>
<tr>
<th>Component</th>
<th>Parts by Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyol</td>
<td>100</td>
</tr>
<tr>
<td>Inorganic Fillers</td>
<td>0-150</td>
</tr>
<tr>
<td>Water</td>
<td>1.5-7.5</td>
</tr>
<tr>
<td>Silicone Copolymer Surfactant</td>
<td>0.5-2.5</td>
</tr>
<tr>
<td>Amine Catalyst</td>
<td>0.1-1.0</td>
</tr>
<tr>
<td>Tin Catalyst</td>
<td>0.0-0.5</td>
</tr>
<tr>
<td>Chain-Extender</td>
<td>0-10</td>
</tr>
<tr>
<td>Cross-Linker</td>
<td>0-5</td>
</tr>
<tr>
<td>Additive</td>
<td>Variable</td>
</tr>
<tr>
<td>Auxiliary Blowing Agent</td>
<td>0-35</td>
</tr>
<tr>
<td>Isocyanate</td>
<td>25-85</td>
</tr>
</tbody>
</table>

Table 2.2 Formulation Basics for Flexible Polyurethane Foams
components which are commonly involved in a formulation and gives a typical range of quantities for each component utilized. As can be seen from the table, the quantities of all components listed are based on the amount of polyol utilized in the formulation. For example, water is typically used in the range of 1.5-7.5 parts per hundred polyol (pphp). However, the isocyanate added to the formulation is usually reported by an index number. An isocyanate index of 100 indicates that there is a stoichiometric amount of isocyanate added to react with functional groups from the polyol, water, and cross-linkers added in the formulation. In the following subsections, each type of component will be discussed in detail.

2.1.2.1 Isocyanates

The two most common sources of isocyanate functionalities in foam production come from toluene diisocyanate (TDI) and diphenylmethane diisocyanate (MDI), of which the former is more commonly used in North America, whereas the latter one has a greater market demand in European countries. TDI exists in two isomeric forms, as shown in Figure 2.7, both of which are used in foam production. The two isomers differ mainly in two ways. Firstly, as indicated in Figure 2.7, the relative reaction rates of the different isocyanate groups on each molecule differ considerably. The reactivity of the ortho position in the 2,4 isomer is approximately 12% of the reactivity of the para position due to the steric hindrance caused by the methyl group. However, when the reaction temperature approaches 100 °C, steric hindrance effects are overcome and both the positions react at nearly the same rate. In comparison, the NCO groups on 2,6 TDI have equal reactivities though the reactivity of the second isocyanate group drops by a factor of around 3 after the first group reacts. The second way in which the two isomers differ is that the 2,6 isomer is symmetric as compared to the 2,4 isomer and therefore is expected to form
hard segments with better packing characteristics. Chapter 7 in this dissertation addresses the structure-property relationships of slabstock foams with varied TDI isomer ratios.

The production of TDI, as shown in Figure 2.8, involves the nitration of toluene followed by reduction and phosgenation steps. Routes not utilizing phosgene are commercially unattractive. Depending on the pathway chosen between these two steps, three industrially common mixtures of the two isomers of TDI can be generated – 65:35 2,4/2,6 TDI (TDI-65), 80:20 2,4/2,6 TDI (TDI-80), and 100% 2,4 TDI (TDI-100). Of these mixtures, the 80:20 blend is, by volume, the most important. Foam properties can be modified to a certain extent by modifying the isocyanate used. For example, after suitable catalyst adjustments are made to enhance the relatively low reactivity, the 65:35 isomer blend has been noted to form foams with higher load-bearing properties.

Several issues with regard to the isocyanate have been addressed and are available in the literature. Knaub et. al. have presented the challenges which MDI based foams face over conventional TDI foams. Dounis et. al. have discussed the effect of TDI index on the morphology and physical properties of flexible slabstock polyurethane foams. Determination of residual isocyanate in flexible foams via FTIR has also been described.

2.1.2.2 Polyols

The soft phase of polyurethane foams is usually a polyfunctional alcohol or polyol phase which on reacting with isocyanate groups covalently bonds with urea hard segments through

Figure 2.8 Routes for the Production of Commercial TDI Blends

![Diagram of TDI production process]
urethane linkages. Glycols such as ethylene glycol, 1,4-butanediol, and 1,6-hexanediol are relatively much lower in molecular weight as compared to the polyols used in flexible foam production. These are more commonly used for chain extension to form hard segments (in polyurethane elastomers) and therefore will be referred to as ‘chain extenders’. Polyols used for flexible foam formulations are higher molecular weight (ca. 3000 to 6000 g/mol) and have average functionalities in the range of 2.5 – 3. Polymerization processes allow production of a wide range of polyols, differing in molecular weight, functionality, reactivity, and chain structure. Selecting the right polyol is an important issue, and the choice is governed by the desired foam properties and economics.

The first polyether polyol which was sold for the production of flexible polyurethane foams was polyoxytetramethylene glycol. Although the use of this polyether polyol resulted in good overall foam properties, extensive use of the same was restricted due to the high costs involved. At present, there are two kinds of polyols commercially available for flexible foam production, hydroxyl terminated polyethers and hydroxyl terminated polyesters. The polyether polyols are produced by ring opening propoxylation or ethoxylation onto a variety of starting materials called initiators. Around ninety percent of the flexible polyurethane foam market utilizes polyether polyols based on propylene oxide in comparison to polyester polyols, because of their lower cost, better hydrolysis resistance, and greater ease in handling. Also, polyurethane foams, due to their low density cellular structure, expose a large surface area to the atmosphere. This further makes polyether polyols advantageous over polyester polyols due to the known greater hydrolytic stability of the polyether backbone. Finally, polyether based flexible foams contribute lower T_g values, are softer and more resilient, making them suitable candidates for bedding and seating applications.

![Figure 2.9 Repeat Units of the Common Polyether Polyols Used in Flexible Foam Production](image)

The common polyether polyols used in flexible foam production utilize ethylene oxide (EO) and propylene oxide (PO) as the repeat units (Figure 2.9). The polyols produced are typically random heterofed copolymers of EO and PO, though in some cases where high
reactivity of the polyol is required, the polyol is EO end-capped. This is because primary hydroxyl groups are approximately three times more reactive towards isocyanates as compared to secondary hydroxyl groups. The reason behind producing polyols utilizing both EO and PO monomers is argued as follows. Though polyols based solely on PO have relatively low reactivities, they are superior as compared to all-EO based polyols in terms of possessing lower water absorption. On the other hand, EO based polyols become important where water solubility is required. Thus by making polyols incorporating both repeat units, the resultant polyol gives a balance of required properties, i.e., lower water swelling is obtained due to the PO repeat units in the backbone, where as the EO repeat units provide good mixing of the water, isocyanate, and the polyol. In addition, if end-capped with the primary EO groups, the polyol has a high reactivity which is of importance for production of high resiliency (HR) foams.

The anionic polymerization of PO and EO for the production of a polyether polyol involves the successive reaction of an organic oxide with an initiator compound containing active hydrogen atoms (Figure 2.10). This requires the addition of the alkylene oxide through anionic (basic) catalysis or cationic (acidic) to the initiator molecule. Commercial production is usually carried using a base such as KOH which catalyses the ring opening and oxide addition.

![Figure 2.10 Base Catalyzed Production of Poly(propylene oxide)](image)

![Figure 2.11 Mechanism of Base Catalyzed Ring-Opening Polymerization](image)
which is continued until a required molecular weight is achieved. The number of active hydrogen atoms on the initiator plays an important role in determining the functionality of the polyol, as can be seen in Figure 2.10. A wide variety of initiators are utilized commercially, such as ethylene glycol and 1,2-propylene glycol in the production of diols, and glycerine and trimethylolpropane for the production of triols. It is also common to blend the above mentioned initiators to achieve desired control over average functionality. Some other initiators which contain a larger number of active hydrogen atoms such as sucrose and sorbitol are also utilized, generally to increase the average functionality. The mechanism for the polymerization process is shown in Figure 2.11. The reaction is carried out at ca. 100 °C. Water removal is an important step. Since the epoxide monomers and polyether polyols are easily oxidized, air is excluded from the manufacturing process. When the polymerization is complete, antioxidants are added to prevent the oxidation of the polyether. The probability of nucleophilic attack taking place at the first carbon atom of propylene oxide is ten times greater as compared to the attack taking place at the second carbon atom. This leads to the polyether backbone containing predominantly head to tail units, though some head to head and tail to tail defects are present.

When the polyol production is carried out by feeding a mixture of ethylene oxide and propylene oxide, a polyol results with random EO and PO units along its backbone, and is commonly referred to as a ‘heterofed polyol’. In another production scheme, the EO and PO are fed in a batch wise manner, and this results in a ‘block polyol’.

The production of a pure polyol from a selected initiator is hindered due to the occurrence of two side reactions. One side reaction involves the formation of a diol on addition of an oxide to water, which is sometimes present as an impurity in the catalyst, initiator, or oxide feeds. Thus, a good control over moisture content in the incoming feeds is required to achieve polyols with desired functionalities and molecular weights. The other side reaction (Figure 2.12) occurs due to the isomerization of propylene oxide to form an allyl alcohol, which leads to the formation of monohydroxy molecules with unsaturated end groups, also called as ‘monols’.

Thus, it can be visualized, that the presence of monols and diols from the two side reactions mentioned above would play an important role in determining the average functionality of the polyol, which for flexible foam production is generally desired to be in the range of 2.5 to 3. Various workers have employed different schemes to calculate the average functionality based on monol and diol content and these can be found in references. Also, routes to synthesize
polyols with lower monol contents and thus better functionality control have been reported in the literature.\textsuperscript{14,15}

![Side Reaction Resulting in a Monofunctional Chain (Monol)](image)

**Figure 2.12 Side Reaction Resulting in a Monofunctional Chain (Monol)**\textsuperscript{2}

**Modified Polyether Polyols**

There are three main types of modified polyether polyols each of which is used to make foams of higher hardness as compared to foams based on unmodified polyols. These are the polyvinyl-modified polyethers or ‘chain-growth copolymer polyols’, polyols containing polyurea dispersions or Poly Harnstoff Dispersion (PHD) polyols, and polyols containing polyurethane dispersions or Poly Isocyanate Poly Addition (PIPA) polyols. Filled polyols are also known to aid foam processing by improving the cell-opening.

Chain-growth copolymer polyols (CPPs) contain stabilized dispersions of ‘polyvinyl’ fillers which are in-situ “graft” polymerized by a chain-growth mechanism. The preparation of these involves the break down of an initiator molecule, typically an azobis aliphatic nitrile compound, to form free-radicals. The radicals then react with the monomer molecules to rapidly form a high molecular weight polymer. CPPs contain three types of polymer: the vinyl polymer, unmodified polyether polyol, and some vinyl polymer grafted onto the polyether macromolecules. Chain transfer agents are often added to prevent the formation of ultra high molecular weight vinyl polymers. The first commercial CPPs utilized acrylonitrile as the sole
monomer. A significant deficiency of using 100% acrylonitrile as the filler was the discoloration (yellowing) of the foams. This led to the development of styrene-acrylonitrile (SAN) azeotropic copolymer as the favored systems for making the CPPs.

Polyurea modified polyols, or PHD polyols, are composed of the conventional polyether polyols and dispersed polyurea particles. The polyurea is formed from the reaction of a diamine (hydrazine) and TDI in a step growth mechanism. Therefore, unlike the chain-growth CPPs, the molecular weight build up does not occur in a rapid manner in PHD polyols. The polyols produced in this manner typically contain 20% dispersed polyureas. The dispersed polyureas also may react with the TDI during foam manufacture, thereby increasing the cross-linking of the final polyurethane.

PIPA polyols are conceptually similar to PHD polyols except for they contain dispersed particles of polyurethanes formed by the in-situ reaction of an isocyanate with an alkanolamine, for example triethanol amine. In addition to the three main copolymer polyols discussed above, there are also available the epoxy dispersion polyols, polyisocyanurate dispersion polyols, and melamine dispersion polyols.

2.1.2.3 Water

Water acts as a chemical blowing agent and reacts with an isocyanate group resulting in a primary amine and carbon dioxide as discussed previously in section 2.1.1.1. Increasing the water content influences both the cell structure and the solid-state morphology of the foam. Higher water contents typically result in foams with lower density due to the increased blow reaction, as seen in Figure 2.13 (presented in the next sub-section). Also, since the hard segment content is also increased on reacting more water with the isocyanate, this increases the stiffness of the polymer composing the foam struts. This effect will be discussed in greater detail in section 2.3. However, in general, it is observed that increasing the water content while maintaining other variables constant does not drastically affect the load bearing properties of the foam. For example, the hardness of the foams corresponding to curve A in Figure 2.13 have been reported to be in the range of 250-350 N as the water content is varied from 2.0 to 5.0 pphp. This is due to the fact that the two opposing factors discussed above compensate each other, and by and large, the load bearing properties remain unchanged.
2.1.2.4 Physical Blowing Agents

Although the carbon dioxide produced from the water-isocyanate reaction acts as the principal source to blow the foam, some formulations also employ physical or auxiliary blowing agents. These are low boiling solvents, inert towards chemical reactions, and they are generally used to produce softer foams by reducing the foam density. As the foaming reactions proceed, the temperature reaches ca. 130 °C, and this is high enough to vaporize the low boiling solvents and provide supplementary gas to expand the foam. Addition of a physical blowing agent while maintaining the water/isocyanate content constant typically results in larger cells and a greater degree of cell openness, which results in a decreased foam density generally leading to an increase in foam softness. This observation has been reported in the literature and is reproduced in this report in Figure 2.13. However, foams can be produced with similar cellular structures and varying foam softness. This can be done by partially substituting the CO₂ produced from the water-isocyanate reaction with a physical blowing agent – the foam incorporating the physical blowing agent would be softer due to a comparatively lower hard segment content.

Until the early 1990’s the auxiliary blowing agent primarily used to produce soft low-density foams was chlorofluorocarbon CFC-11 (CFCl₃). This blowing agent was, however, phased out in 1995 due to the environmental concern it caused regarding the depletion of the ozone layer, especially over Antarctica. Nevertheless, at that time, there existed a replacement, hydrochlorofluorocarbon HCFC-141b (CH₃CFCI₂), which had performance and

![Figure 2.13 Slabstock Polyether Foams water/CFC-11/density/hardness relationship.](image)

handling characteristics similar to that of CFC-11, and was reported to have a depletion effect which was only 1 to 2% of that of CFC-11. Although HCFC-141b had a much lower ozone depleting potential as compared to CFC-11, it was seen as a temporary solution until suitable nondepleters such as hydrofluorocarbons (HFCs) could be developed for flexible polyurethane foam production. Also, amongst the currently used HCFCs, 141b has the highest ozone depleting potential, and is currently targeted to be phased out by Dec. 2002, while other HCFCs have until 2010.

The above chain of events, along with other concerns projected by the EPA, has led companies which produce or utilize blowing agents to find suitable alternative measures. Technology for using methylene chloride as a blowing agent exists; however, appropriate adjustments in the catalyst package are required to overcome processing problems. Other alternatives involving the use of acetone and liquid carbon dioxide have been suggested in the literature. Blowing agents such as pentane have been tried to replace CFCs although they are less satisfactory and also raise flammability concerns. Workers have also proposed the use of certain additives to achieve softer foams by partially disturbing the formation of the precipitating polyurea.

2.1.2.5 Catalysts

Since polyurethane foam production relies on two competing reactions, a balance between them is required to make foams with good open-celled structures and desired physical properties. While it is true that these reactions may proceed in the absence of catalysts, they generally proceed at rates too slow to be practical. Suitable catalysts are thus used to carry out these reactions in a faster, controlled, and balanced manner. This correct balance is required due to the possibility of foam collapse if the blow reaction proceeds relatively fast. On the other hand, if the gelation reaction overtakes the blow reaction, foams with closed cells might result and this might lead to foam shrinkage or ‘pruning’. Catalyzing a polyurethane foam, therefore, involves choosing a catalyst package in such a way that the gas produced becomes sufficiently entrapped in the polymer. The reacting polymer, in turn, must have sufficient strength throughout the foaming process to maintain its structural integrity without collapse, shrinkage, or splitting.

The role of a catalyst in controlling the balance between the two reactions, as discussed above, is more conveniently represented by workers in terms of its selectivity. Since the
number of equivalents of water and alcohol present in the reacting mixture is different, yields of urea and urethane, which are representative of the blow and gelation reaction respectively, cannot be compared directly, but require to be normalized with respect to their limiting yields. Therefore, the selectivity of a catalyst is defined in terms of ‘normalized’ blowing and gelation rates.

Normalized Blowing Rate = (% urea yield at time t)/(limiting urea yield) \hspace{1cm} (2.1)

Normalized Gelling Rate = (% urethane yield at time t)/(limiting urethane yield) \hspace{1cm} (2.2)

Then the blow to gel selectivity can be defined as:

Blow to Gel Selectivity = (Normalized Blowing Rate)/(Normalized Gelling Rate) \hspace{1cm} (2.3)

Selectivity values greater than 1 are indicative of a strong preference towards blowing, while selectivities less than 0.4 are suggestive of a strong gelling catalyst. Intermediate selectivity values indicate more balanced catalysts.

Polyurethane foam formulators generally choose catalysts from two major classes of compounds – tertiary amines and metal salts, primarily of tin. Since catalysts differ both in activity and selectivity towards the polyurethane foaming reactions, the two kinds are combined not only to provide the desired balance of ‘blowing’ vs. ‘gelation’, but also to tune these reactions according to the needs of the production equipment.

In any chemical reaction, there are certain positions on reacting molecules which are more susceptible to attack by other added co-reactants. These positions are, therefore, more likely to undergo a given reaction. Catalysts characteristically function at these positions. In the formation of polyurethane foams, the catalyst forms an activated complex with the reactants thus making it easier for the isocyanate moieties to chemically react with the active hydrogen containing compounds.

**Tertiary Amine Catalysts**

Tertiary amines, by definition, are compounds which contain a nitrogen atom having three substituent groups and a free pair of electrons. Though these catalysts are generally thought of as blowing catalysts, they are known to catalyze the gelation reaction as well. The catalytic activity of the amine is determined by the availability of a free electron pair for complexation. The catalysis mechanism involves the donation of these electrons by the tertiary nitrogen of the catalyst to the isocyanate group leading to the formation of an intermediate complex. The
availability of the electrons is a function of both, the steric hindrance caused by the substituent groups, as well as the electron withdrawing or electron releasing nature of the substituent groups. Groups which tend to withdraw electrons reduce the accessibility of the electrons and thus reduce the catalytic activity. N,N-Dimethylcyclohexylamine (Figure 2.14) is an example where the methyl groups have an electron releasing effect resulting in good catalytic activity.\textsuperscript{[3]} The requirements for good catalytic activity are a) nucleophilic enough to attack the carbon of the isocyanate group, b) ability to form an active hydrogen amine complex, and c) solubility in water with the ability to form hydrogen bonds with water.

Since electron accessibility is also usually measured by the basicity, the catalytic activity is found to generally increase as the basicity increases.\textsuperscript{[23]} Thus, a plot of pH vs. catalytic activity usually yields linear behavior. However, exceptions exist, such as triethylenediamine (Figure 2.15) in which the substituent groups on the nitrogen are pulled back, thereby reducing steric strain, and thus making the electron pair on the nitrogen atom easily accessible.\textsuperscript{[23]} Thus, the catalytic activity exhibited by this compound is greater than expected from its basicity. A substantial amount of work has been done to study the functioning of catalysts and their complexation with the different foaming components. However, much of this work has investigated the reaction mechanism of model compounds in dilute solutions at fixed temperatures.\textsuperscript{[11]} Also, polar solvents are thought to increase the reactivity of the isocyanates by stabilizing the polarization of the isocyanate group.\textsuperscript{[11]}

Besides the electronic effects discussed above, the role of a catalyst is also determined by other physical and chemical properties. For instance, catalysts which have low boiling points, such as triethylamine, are readily volatized in the exothermic reactions taking place and are thus
lost from the reacting mixture.23 Once they volatilize, it leads to a decrease in the catalytic effect. Other catalysts, which contain hydroxyl groups, such as dimethylaminoethanol, chemically react with the growing polymer chain, and thus are no longer able to find their way to a reaction site.23 This again leads to a loss in the catalytic activity. Therefore, it is often helpful to use a mixture of catalysts, such that the reactions proceed at a reasonable rate at all times during the foaming as well as curing stages.

Organometallic Catalysts

While the amine catalysts discussed above exert some influence on the isocyanate-hydroxyl reaction, organometallic salts favor this reaction almost exclusively and are thus called gelation catalysts. The catalytic activity is explained by three complimentary mechanisms.1 The first mechanism describes the activation of the polyol into a tin alkoxide which then reacts with the isocyanate to yield a urethane linkage. The urethane linkage further reacts with a polyol – thereby propagating the polyol and regenerating the catalyst. In the second mechanism, the isocyanate molecules get activated and are in turn attacked by the polyol to again propagate the polymer and regenerate the catalyst. The third mechanism involves the formation of a tin-amine complex which accepts a polyol molecule and further activates the complex. This complex then reacts with an isocyanate group to yield a carbamate linkage. Detailed discussions on these mechanisms can be found in references 1, 2.

Unlike the tertiary amine catalysts, which usually volatilize during the foaming reactions, tin catalysts can remain in the foam permanently. However, they are also known to undergo certain chemical changes. Stannous salts are known to oxidize into their stannic form, which promotes the oxidative degradation of flexible foams.23

Flexible foams which employ auxiliary blowing agents also require appropriate adjustments in their catalyst package. The blowing agent sometimes hinders the formation of the activated complex discussed previously, and is also known to act as a heat sink, since it absorbs some of the heat generated by the foaming reactions. Thus foams utilizing auxiliary blowing agents, in general, require higher amounts of catalysts.23 Also, some blowing agents in the presence of flame retardants are known to have an acidity effect which reduces the basic nature of the amine and hinders its catalytic activity.23
Molded foam applications often employ delayed-action catalysts which allow complete filling of intricate parts of the mold by delaying the gelation reaction and thus maintaining a low viscosity of the foaming mixture. These catalysts show low activity at room temperature, but become more activated once the reaction exotherm builds. Examples of these catalysts are tertiary amine salts in solvents such as water or low molecular weight glycol.

2.1.2.6 Surfactants

Flexible polyurethane foam production relies greatly on the performance of non-ionic, silicone based surfactants which are added to realize a variety of functions. In fact, the largest commercial application of silicone surfactants is in the area of polyurethane foams with worldwide production quantities of 30,000 metric tons/year for the polyurethane foam industry. Some of the main functions performed are reducing surface tension, emulsifying incompatible ingredients, promoting bubble nucleation during mixing, stabilization of the cell walls during foam expansion, and reducing the defoaming effect of any solids added. Of these functions, perhaps the most important is the stabilization of the cell walls, without which the foam would behave like a viscous boiling liquid. The processing window for surfactants is generally in the range of 0.5-2.5 parts per hundred polyol (pphp), and the actual quantity of surfactant added is

![Figure 2.16 Effect of Surfactant Concentration on Foam Stability](image)
dependent on the type of surfactant used as well as on the other constituents of the foam formulation. Below a certain minimum concentration of surfactant, the foam can result in serious imperfections such as splitting, densification, or collapse. Addition of more than required quantities of surfactant has its own drawbacks. This usually results in an over-stabilization of the foam, resulting in closed cells, which result in a decreased airflow through the foam (Figure 2.16). Also, a high number of closed cells in the foam leads to foam shrinkage on cooling, which is undesirable.

Although the first “defoamers” used in flexible foams were low viscosity siloxane oils based on poly(dimethylsiloxane), current surfactants employ graft copolymers of polysiloxane-polyoxyalkylene. The siloxane block is known to lower the bulk surface tension where as the polyoxyalkylene promotes the solubilization of the surfactant into the polyol and aids in emulsification of the foaming components. Also, the polyoxyalkylene part is adjusted according to the type of foam application. This is done by varying the percentage and arrangement of ethylene oxide units and propylene oxide units which make up the polyoxyalkylene. By doing so, desired levels of affinity of surfactant for water, and solubility of surfactant in the foam polyol, can be achieved. In addition, surfactants can be tailored to meet required needs of foam systems by altering their chain architecture (topology). AB, ABA, comb-like, or branched structures are produced and utilized to meet desired requirements. The flexibility of siloxane chemistry facilitates the production of the broad range of surfactant structures mentioned above.

There are four main types of silicone surfactants, the structures of which are shown in Figure 2.17. These include silicone oil, ABA block copolymers, graft copolymers, and surfactants possessing a highly branched structure. Table 2.3 lists the structural features of the surfactant for slabstock as well as molded foams. As noted from this table, the molecular weight of the surfactants used in slabstock foam production is much higher as compared to those used for molded foams. This is because stability of the liquid foam as it rises is of primary importance in slabstock systems. Also, in molded foams, the liquid foam is stabilized mainly by the higher bulk viscosity of the system which results from the use of higher molecular weight polyether polyols and the addition of cross-linking agents. The polyethers used in slabstock foam surfactants are fairly high in molecular weight, ca. 1000-4000 g/mol, as compared to molded foam surfactants which have polyether molecular weights less than 800 g/mol. The polyethers of slabstock foam surfactants also possess almost an equimolar ratio of EO and PO contents. This is
because surfactants which are based on all EO polyethers do not lower the surface tension of the polyether polyols and are therefore not practical. Surfactants based on all PO polyethers are less hydrophilic and have shown to be inefficient in slabstock foams.

\[
\text{Me}_3\text{SiO-}(\text{SiMe}_2\text{O})_x-\text{SiMe}_3 \quad (a)
\]

\[
\text{Me}_2\text{SiO-}(\text{SiMe}_2\text{O})_x-\text{SiMe}_2-(\text{CH}_2)_3(\text{EO})_a(\text{PO})_b\text{OR} \quad (b)
\]

\[
\text{(CH}_2)_3(\text{EO})_a(\text{PO})_b\text{OR}
\]

\[
\text{Me}_3\text{SiO-}(\text{SiMeO})_y-\text{SiMe}_3 \quad (c)
\]

\[
\text{(CH}_2)_3(\text{EO})_a(\text{PO})_b\text{OR}
\]

\[
\text{SiMe}_2\text{-O-}(\text{SiMe}_2\text{O})_x-\text{R} \quad (d)
\]

\[
\text{O}
\]

\[
\text{Me-Si-O-}(\text{SiMe}_2\text{O})_y-\text{R}
\]

\[
\text{O}
\]

\[
\text{SiMe}_2\text{-O-}(\text{SiMe}_2\text{O})_z-\text{R}
\]

**Figure 2.17 Structural Types of Silicone Surfactants**

a) Silicone Oil or Polydimethylsiloxane  
b) ABA Block Copolymer Structure  
c) Graft Copolymer Structure  
d) Branched Structure

The preparation of a flexible polyurethane foam involves ongoing processes at the interfacial level as well as within the bulk. Surfactants play a crucial role in influencing both these processes. The interfacial processes come into play as early as when the initial bubbles are formed in the liquid. These bubbles are not spontaneously nucleated, but rather require agitation. As the CO\(_2\) is evolved due to the reaction of the isocyanate with the water, these bubbles, which were initially on the scale of a few \(\mu\)m, expand to few hundred \(\mu\)m in size. This expansion leads to an increase in the net surface area and therefore the surface energy of the
foam. To maintain a low overall surface energy, the addition of silicone surfactants reduces the surface energy per unit area, i.e., the surface tension.

<table>
<thead>
<tr>
<th>Application</th>
<th>Surfactant molecular weight</th>
<th>Weight percent silicone</th>
<th>Polyether molecular weight</th>
<th>Weight percent EO in polyether</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molded</td>
<td>300-1500</td>
<td>30-100</td>
<td>0-800</td>
<td>0-100</td>
</tr>
<tr>
<td>Slabstock</td>
<td>20,000-80,000</td>
<td>15-30</td>
<td>1000-4000</td>
<td>35-65</td>
</tr>
</tbody>
</table>

**Table 2.3 Molecular Weights and Copolymer Compositions of Silicone Surfactants Used for Flexible Polyurethane Foams**

Surfactants are thought to stabilize the air-liquid interface as well as the liquid-liquid interface. Their addition retards processes such as bubble coalescence, liquid drainage, and diffusion of gas from smaller to larger bubbles (Ostwald ripening). Bubble coalescence is slowed down by retarding the excessive thinning of films between adjacent bubbles to an extent which leads to film rupture. Thinning of films can be offset by transport of surfactant and/or bulk material to the thinned regions, an adequately viscoelastic surface layer, or by a high bulk viscosity of the system.

At the air-liquid interface, the adsorption of the surfactant changes the mechanical behavior of the interface, in particular, its surface tension and viscoelasticity. At a molecular level, the surfactant conformationally orients at the interface, through bond rotation and bending, thereby reducing the surface energy. This is due to the very low Si-O bond rotation energy of the siloxane backbone. The surface tension of the polyols, which form the bulk of the foaming liquid, is typically in the range of 33-40 mN/m, and cannot be considerably lowered by adding hydrocarbon based surfactants. Silicone based surfactants, however, can reduce the surface energy to much lower values of 21-25 mN/m.

During the initial stages of foam formation, at the liquid-liquid interface, surfactants have been shown to promote the interfacial mixing of the water and the polyol. At the latter stages, when urea hard segments are generated, the surfactant has been shown to stabilize the precipitating urea phase. This has been shown in studies by Rossmy and coworkers who demonstrated that when a silicone surfactant was present, the urea phase separation does not lead to foam collapse, as it does when a surfactant is not present.

In the bulk, surfactants are speculated to micellize in the water-polyol-isocyanate mixtures. This hypothesis stems from the observation that a plot of surface tension versus...
surfactant concentration often display break points similar to those noted at the critical micelle concentration (CMC) for surfactants in aqueous solutions.\(^{25}\) However, to the authors best knowledge, there is no experimental evidence in the literature – such as any light scattering/SAXS/SANS studies, which support the formation of micelles in polyurethane foams.

### 2.1.2.7 Cross-Linking Agents

Cross-linking agents in flexible polyurethane foams are usually low molecular weight species with hydroxyl and/or amine groups and have functionalities greater than or equal to 3. An example shown in Figure 2.18 is diethanol amine (abbreviated as DEOA), a commercially utilized cross-linker, which is commonly used in molded foam applications as it helps in a faster viscosity build-up and thus in achieving shorter demold times. Also, since molded foam applications utilize high molecular weight polyols and slightly higher catalyst doses (as compared to slabstock formulations), using typical foam surfactants leads to an over-stabilization of the cell walls. Thus, lower potency surfactants are utilized in molded-foams, to counteract this over-stabilization effect. Since these surfactants are not potent enough to give dimensional stability to the foam, the addition of cross-linking agents helps achieve foam stability.

Addition of a cross-linking agent generally leads to a reduction in the stiffness of the foam. This is because the additional covalent linkage resulting from the cross-linking agent interferes with the phase separation behavior of the foam. A systematic study initiated by Dounis and Wilkes\(^{29}\) and continued by Kaushiva and Wilkes\(^{30}\) using DEOA as a cross-linking agent revealed that the hard segment ordering was lost on addition of DEOA, thus leading to the observed softening of the foam. Thus it needs to be realized, that even though some components might be added in small concentrations, the role they play in influencing foam properties can be very significant and needs to be well understood.

### 2.1.2.8 Other Additives

Various additives are added to flexible polyurethane foam formulations depending on the required properties and the end use of the foam. Some additives are added for aesthetic reasons
(for example colorants) where as others are added to improve product performance. Since polyurethane foams have a significant amount of aromatic content, UV stabilizers are added to retard the yellowing of foams on exposure to light. Bacteriostats and flame retardants are also added in some formulations. Some other additives include the use of non-reactive plasticizers to reduce viscosity, cell-openers to prevent shrinkage of the foam on cooling, and compatibilizers to enhance the emulsification of the reactants. The use of antistatic agents to minimize the build up of static electrical charges is important for foams used to package electronic devices. A detailed discussion of these additives can be found in references [1] and [2].

2.2 The Foaming Process

FTIR has been extensively used to study the sequence of the foaming reactions. In general, there is agreement amongst different workers that the water-isocyanate reaction takes place sooner and faster as compared to the polyol-isocyanate reaction. This is supported by a growing urea carbonyl absorption at ca. 1715 cm⁻¹ early in the reaction which is observed to shift to ca. 1640 cm⁻¹ once half the foam rise height is reached. Model studies carried out on diphenyl urea have indicated that the urea carbonyl absorption in a good solvent (DMF) and a poor solvent (THF) appears at 1715 and 1640 cm⁻¹ respectively. This suggests that a stage is reached when the polyurea being formed is no longer soluble in the foaming mixture and phase separation takes place. Bailey and Critchfield observed that the urea formation takes place quickly with most of it taking place within the first 5 min of the foaming process. The urethane formation, however was not significant in the first 5-10 min, but was found to increase at a steady rate for the next 30 min. These results were also confirmed by Rossmy and co-workers who observed that the ratio of isocyanate to water consumption was 2:1 in the early part of the foam reaction, indirectly indicating that urethane formation was not significant in earlier stages. The same workers also confirmed, using reactive and non-reactive polyols, that the heat generated by the urethane reaction in the earlier stage was negligible.

McClusky and coworkers used a vibrating rod viscometer as a probe to examine the rheology of the reacting foam mixture. Based on their investigation, the reaction scheme was divided into three regimes. During the first regime, which began from mixing of the reagents and continued up to the point of cell opening, it was observed that there was a continuous reduction in the system viscosity due to the increase in temperature resulting from the exothermic nature of
the reactions. In the second regime, a rapid increase in the viscosity was observed, due to the precipitation of the urea which led to the formation of a hydrogen bonded physically cross-linked network. The third regime displayed a gradual increase in the system viscosity, due to the formation of the covalent network in the polymer.

The rigidity of rising foams was measured by Bailey and Critchfield based on the BB-drop test developed by Rowton. This test consists of dropping BB’s from a constant height on the foam sample at different times during the foaming process. The distance traveled by the BB after hitting the foam can be related to the integrity of the foam. It was observed that the BB’s sank through the foam until the precipitation of the urea occurred. The phase separation of the urea, therefore, was responsible to give the foam its structural integrity. It has also been observed by Rossmy and coworkers that cell rupture took place just after the urea precipitation. In light of this observation, it has been suggested that the precipitation of the urea destabilizes the foam mix and aids in cell opening.

Workers have also used different techniques to try and identify the event of cell-opening. The simplest method to do so is by visual observation of ‘blow-off’ which is marked by a sudden cessation of the foam expansion and a release of the gas under pressure. Bailey and Critchfield identified cell opening by measuring the escaped blowing agent concentration above the foam by using IR spectroscopy. Miller and Schmidt used a porosimeter to measure bulk permeability of the foam, and identified cell-opening with a sudden increase in foam permeability. In a more recent work, Macosko and Neff used a parallel plate rheometer to study cell opening. They observed that the normal force exerted by the expanding foam mixture on the rheometer plates was a function of both, the rate of foam expansion, as well as the foam modulus. Their work suggested that the visually observed blow-off of the foam coincided with a sudden drop in the normal force which marked the cell opening event.

2.3 Morphology

The physical properties of flexible polyurethane foams are a function of both, the cellular structure, and the phase separated morphology of the polymer comprising the struts of the foam. These two factors are intimately related because both are influenced by the forces exerted during the expansion and stabilization of the foam. There has been considerable effort to try and understand how these two factors influence the physical properties of the foam such as load
bearing, compressive stress-relaxation, creep, and also how these properties are a function of varied temperature and humidity conditions. While testing polyurethane foams, workers have often found it difficult to separate the effects of cellular structure and the solid state polymer morphology on the foam properties. For this reason, some investigators have worked on plaques based on flexible polyurethane foam formulations with an attempt to deconvolute the effect of polymer morphology on foam properties.

2.3.1 Cellular Structure

As stated earlier, the properties of flexible polyurethane foams are a strong function of its cellular structure. A complete knowledge of the cellular structure of a foam would require the exact size, shape, and location of each cell. Since obtaining this information is difficult, and impractical, certain approximations are employed. Mean cell diameters and average cell volumes are often used to characterize cell size, since a distribution in cell size is always noted. Earlier researchers described the shape of the foam cells similar to that of a pentagonal dodecahedron, which has twelve five-sided faces. However some four- and six-sided faces are also observed in real polyurethane foams, and thus the cell geometry might be better approximated using the fourteen-faced tetrakaidecahedron space filling model. Another variable of importance for flexible foams is the degree of cell openness. This is usually characterized using air-flow measurements.

Optical microscopy as well as SEM has been used to study the detailed features of cellular structure. The SEM images for a typical slabstock foam are reproduced in Figure 2.19. It is observed that the foam has an open-celled structure and very few closed cells. Also, a geometrical anisotropy in the cell structure, parallel and perpendicular to the blow direction can be observed. The cells parallel to the rise direction appear circular, where as those perpendicular appear elliptical with their major axis aligned along the foam rise direction. This structural anisotropy is known to effect bulk foam properties, such as load bearing. A comparison with the micrographs of a typical molded foam (Figure 2.20), suggests that molded foams have a significantly greater number of closed cells. This observation has been confirmed by Dounis et. al., using air flow measurements, which were observed to be 5 ft³/min and 1 ft³/min for slabstock and molded foams of comparable composition. It was also observed in the same study that the cell struts in the molded foam were thicker, thus resulting in a somewhat higher density foam.
Finally, there was no geometric anisotropy in cell structure noted in the molded foam, probably because the molded foam operation involves pressurization of the reactants from all directions into the mold.

Figure 2.19 Typical SEM micrographs of a conventional slabstock polyurethane foam. a) parallel to the rise direction b) perpendicular to the rise direction

Confocal microscopy has been used by workers to collect two-dimensional images of the cellular structure at different ‘depths’ of the foam, with an objective to provide a realistic three-
2.3.2 Polymer Morphology

As discussed above, the cellular structure observed in flexible polyurethane foams plays an important role in determining its physical properties. If not greater, of equal importance is the dimensional reconstruction of the foam network. The use of NMR microscopy for cellular structure evaluation has also been reported in the literature.

Figure 2.20 Typical SEM micrographs of a conventional molded polyurethane foam. a) parallel to the rise direction b) perpendicular to the rise direction

2.3.2 Polymer Morphology

As discussed above, the cellular structure observed in flexible polyurethane foams plays an important role in determining its physical properties. If not greater, of equal importance is the
morphology of the polymer which comprises the solid portion of the foam. Over the years, workers have utilized several techniques to investigate this solid state morphology. Until the early 1980’s IR spectroscopy was the primary characterization technique. The last 20 years, however, have seen the application of SAXS, WAXS, TEM, and more recently AFM and XRM to gain further insight into the unique morphology of these materials at the molecular, domain, and in most cases at a superstructure level. In conjunction, thermal characterization using DSC and DMA has often been found helpful.

2.3.2.1 Urea Microdomain Considerations

As discussed earlier in section 2.2, the isocyanate-water reaction proceeds faster as compared to the reaction between the isocyanate and the polyl. This leads to the formation of oligomeric polyurea species which are termed as urea hard segments. When the molecular weight of these urea hard segments exceeds a system dependent solubility limit, thermodynamic boundaries are surpassed, resulting in a transition from an initial inhomogeneous disordered state to an ordered microphase-separated state. Workers have suggested using in-situ SAXS measurements that the microphase separation transition follows the kinetics associated with spinodal decomposition. The characteristic properties of flexible polyurethane foams depend much less on the covalent cross-linking points present in the polyl phase and more on the cohesive strength of the microphase separated urea hard domains, which provide physical cross-linking points. Hydrogen bonds occur readily between the proton donor NH- groups of the urethane and urea linkages and their electron donor carbonyl groups. These hydrogen bonds strongly influence the cohesive strength of the urea hard domains. Other factors; such as the symmetry, molecular weight, and molecular weight distribution of the aromatic polyurea segments also strongly influence the nature of packing of the urea hard segments.

Small angle x-ray scattering (SAXS) has been successfully utilized to prove the existence of the microphase separation discussed above. An observed shoulder in the SAXS profiles of flexible polyurethane foams corresponds to an interdomain spacing (average center-to-center distance between urea hard domains) of ca. 80-120 Å. Workers have also demonstrated using MALDI mass spectroscopy that the urea hard segments consist of ca. 4-6 repeat units thus suggesting that the hard domains are ca. 30-60 Å long. The ordering or the packing of the urea hard segments, has been attributed to the presence of bidentate hydrogen bonding. This was
confirmed in a recent study by Kaushiva et. al. on analyzing the FTIR spectra and WAXS patterns of a polyurea powder and a polyurea powder prepared in the presence of a surfactant. In that study it was observed that the polyurea powder without surfactant exhibited many peaks in the WAXS pattern, as would be expected from a crystalline material, and also showed the presence of an absorbance at 1640 cm\(^{-1}\), indicating the presence of bidentate hydrogen bonding. However, on preparing a powder with surfactant in it, workers observed via WAXS that the only periodicity which remained corresponded to a spacing of ca. 4.7 Å, while the 1640 cm\(^{-1}\) absorbance remained unaffected. This study therefore strongly suggested that the local ordering of the hard segments within the urea microdomains can be examined via the 1640 cm\(^{-1}\) IR absorbance and the 4.7 Å WAXS reflection.

Moreland et. al. investigated the viscoelastic properties of flexible polyurethane foams under varied temperature and humidity conditions. Their work suggested that the observed increase in creep on increasing the relative humidity was a result of water acting as a hard domain plasticizer. They also observed that an increase in relative humidity had a greater effect on the rate of creep at higher temperatures. Interestingly, they also reported that the creep rate was higher for the higher hard segment containing foams, while maintaining the same initial deformation level and testing conditions. This difference in creep rates was attributed to the greater amount of hydrogen bonds available for disruption in the higher hard segment containing foams. In short, their work elucidated the importance of the presence and stability of urea hard domains in controlling the properties of flexible foams.

Dounis et. al. investigated the mechano-sorptive behavior of flexible polyurethane foams undergoing a creep experiment. On subjecting the foams to cyclic humidity conditions between 10 and 98 %, the workers showed that the compressive strain increased in subsequent steps, with larger deformations observed during the desorption portion of the humidity cycling. They suggested that during the dehumidification process, regions of free volume were introduced in the urea hard domains, promoting chain slippage and increases in strain. Once more, weakening of hydrogen bonding was shown to have a marked effect on the viscoelastic properties of flexible foams.

Not only temperature and humidity, but also the addition of certain cross-linking agents and additives tends to disrupt the physical associations of the urea hard segments. This was demonstrated by Kaushiva et. al. on observing that addition of diethanol amine (a commercial
cross-linking agent utilized in molded foams, commonly abbreviated as DEOA) had a disrupting effect on the hydrogen bonding within the urea microdomains.\textsuperscript{30} Their work suggested that DEOA primarily resides in the urea microdomains and thus reduces the extent of segmental packing of the urea hard segments. These changes in structure at the microdomain level thus provided an explanation for the lower rubbery moduli and lower load-bearing properties exhibited by the foams containing DEOA.

In another study, Moreland et. al. studied the effect of LiCl as an additive in slabstock foam formulations.\textsuperscript{53} The presence of LiCl was shown via WAXS to disrupt the packing of the urea microdomains. It was also shown using SAXS that the LiCl containing foams were microphase separated and possessed an interdomain spacing similar to the foam without LiCl. This study therefore suggested that LiCl acted as a localized ‘hard segment plasticizer’ thus explaining why the foams which incorporated LiCl exhibited faster rates of compressive load decay and lower moduli. NMR relaxation times, which can map the motion of an entire polymer molecule, suggested that in the LiCl containing foams, the hard segments restricted the motion of the soft segments, as compared to the foams not incorporating LiCl.\textsuperscript{54}

\subsection*{2.3.2.2 Urea Aggregate Considerations}

The previous section discussed the importance of urea microdomains in determining foam properties. There is another structure which is known to exist in flexible polyurethane foams which needs to be addressed. Urea rich regions, sometimes called ‘urea aggregates’ or ‘urea balls’, which are ca. 2000-5000 Å in diameter, have been observed by workers via TEM\textsuperscript{1,3} and XRM.\textsuperscript{45,46} The exact composition and size of these urea aggregates would be expected to vary from one foam formulation to another. A study carried out by Armistead et. al. on slabstock foams revealed that as the hard segment content was increased, the urea aggregates increased in both size and number.\textsuperscript{3} The micrographs from that study are reproduced in Figure 2.21. It has also been commonly observed that this urea aggregation behavior is not so pronounced in molded foam formulations,\textsuperscript{1,44} a point which will be discussed later.

Not only the composition, but also the mechanism of formation of urea aggregates is not clear. Currently, there are two mechanisms proposed.\textsuperscript{1} One mechanism suggests that the formation of the urea aggregates takes place in two steps. According to this two-step mechanism,
phase separation takes place in the first step whereby the urea microdomains are formed. The second step then involves the diffusion of the microdomains to form larger urea rich aggregates.

The second, and more widely accepted mechanism, suggests that the formation of urea

![Figure 2. 21 TEM micrographs of slabstock foams varying in water content^3](image)

Figure 2. 21 TEM micrographs of slabstock foams varying in water content^3
aggregates takes place in regions with higher water-isocyanate concentrations. Since the solubility of the water in the polyol phase is limited, there may form regions with locally higher water concentrations. Reaction of the water with the isocyanate in these regions would then lead to the formation of aggregates which are high in urea content.

Rossmy et. al. have suggested that the presence of these large urea macrophases aids in the cell-opening of flexible foams. They observed that a visible macrophase separation, marked by a loss in optical clarity, occurred in the bulk liquid just before cell-opening. However, it is not clear how these urea macrophases (aggregates) induce cell opening. One hypothesis suggests that some of the urea aggregates may reach a size where they themselves rupture cell windows or destabilize their surfaces.

The above discussion therefore partially explains why molded foams have more closed cell windows as compared to comparable slabstock formulations. The high reactivity ingredients used in molded foams; along with the high molecular weight polyols, which also have higher EO contents as compared to slabstock polyols; inhibit the formation of large urea aggregates. This results in the removal of one of the mechanisms which helps in cell opening and thus results in foams with numerous closed windows. For this reason, it has often been found useful to add particulate fillers such as copolymer polyols (CPP) to restore this cell opening mechanism. In other cases where these filler particles are not added, it is common industrial practice to mechanically crush the foam pads between rollers to open the cell windows.

In another study, Moreland et. al. studied the effect of LiCl as an additive on the morphology and properties of flexible slabstock foams. They observed via TEM that addition of LiCl, even in amounts as low as 0.1 pphp, prevented the formation of urea rich aggregates. In agreement with the current discussion, it was observed that foams which contained LiCl (i.e. the foams in which urea aggregation did not take place) had more closed windows as compared to the foams without LiCl. This observation further emphasizes the destabilizing effect which urea aggregates might have on cell windows which could lead to their rupture.

2.4 Summary

The reactive processing of water-blown flexible polyurethane foams involves a complex combination of both physical and chemical events. Attempts to understand the development of a supramolecular architecture of a solid foam from a liquid mixture of low molecular weight
compounds has perplexed researchers working in this area. Based on the findings of workers over the last five decades or so, the current understanding of the morphological features present in flexible polyurethane foams is depicted in Figure 2.22. As will become apparent from reading subsequent chapters, this schematic representation is just a guideline, and might not be truly representative of the actual morphology of flexible polyurethane foams.

Figure 2.22 Simplified Model for the Morphological Features Found in Flexible Polyurethane Foams

- $d_2 \sim 4,000,000 \text{ Å (0.015 INCH)}$
- $d_1 \sim 6,000,000 \text{ Å (0.024 INCH)}$
- $d_3 \sim 500,000 \text{ Å (0.001 INCH)}$
- $d_4 \sim 5000-30,000 \text{ Å}$
- $d_5 \sim 2000-5000 \text{ Å}$
- $d_6 \sim 3000 \text{ Å (Absent in HR foams)}$
- $d_7 \sim 20-50 \text{ Å}$
- $d_8 \sim 65-125 \text{ Å}$
- $d_9 \sim 30-50 \text{ Å}$
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