1. Introduction

Ever since their discovery by Otto Bayer and co-workers in 1937, polyurethanes have developed as a unique class of materials and have found use in a wide variety of applications. The name polyurethane was derived from ethyl carbamate, also known as urethane. Besides incorporating the urethane linkage, these materials also sometimes contain several other types of linkages such as amide, urea, ether, and ester. The urethane linkage is formed by the reaction of an isocyanate group of one reactant with the alcohol group of another component. By controlling variables such as the functionality, chemical composition, and the molecular weight of the different reactants, a wide class of materials with significantly varying properties can be obtained. This flexibility has led polyurethanes to find use as synthetic polymers in foams, elastomers, coatings, sealants, and adhesive based products. Some of the applications of polyurethanes lie in the automotive, furniture, construction, thermal insulation, and footwear industries. The 2000 urethanes market was estimated to be of the order of 8.2 million metric tons worldwide (Figure 1.1).

![Figure 1.1 Worldwide Consumption of Polyurethanes](image)

*North American Free Trade Agreement

**Figure 1.1 Worldwide Consumption of Polyurethanes**

In polyurethane synthesis, tuning the ratio and composition of the isocyanate and alcohol components results in a segmented block copolymer consisting of alternating hard and soft blocks. The reaction of an isocyanate group with a chain extender and subsequent phase separation of the hard segments formed from this reaction, results in the formation of hard
blocks; which are referred to as ‘hard’, since they are below their softening temperature at ambient conditions. These hard blocks are covalently bound through urethane linkages to ‘soft’ polyether or polyester segments which are above their softening temperature, $T_g$, at ambient conditions. The phase separation generally leads to good elastomeric properties wherein the hard blocks serve as filler particles and also act as physical cross-linking points.

One of the major sectors of the polyurethane industry are flexible foams, which are manufactured by the controlled expansion of a gas during the polymerization process. Flexible polyurethane foams are designed to be open-celled, i.e., at the completion of foam expansion, the cells open and form a structure composed of interconnected polymer struts, which allow the free movement of a gas within the foam cells. The properties of flexible polyurethane foams depend on both, the elastomeric character of the polymer comprising the foams, as well as the geometry of the cells. Over the years, polyurethane foams have intrigued a broad spectrum of scientists who have tried to provide better solutions to the consumer by investigating the chemistry, physics, engineering, and economic aspects of these materials. As shown in Figure 1.2, flexible polyurethane foams are used in applications such as seating, cushioning, carpet underlayment, fabric backing, insulation, and packaging.

The first commercial production of flexible polyurethane foams, based on the reaction between an aromatic isocyanate and a polyester polyol, was carried out in 1954. However, these
foams were unable to withstand the severe humidity and temperature conditions in which they were used, and thus foams based on polyether polyols were developed. These second generation foams provided better durability as well as comfort. A major advancement in polyurethane technology was the introduction of the ‘one-shot’ system using new catalysts and silicone-based surfactants. In the one-shot process; the isocyanate, polyol, water, and other ingredients are rapidly and intensively mixed and immediately poured to carry out the foaming. Since then, advances in flexible polyurethane foam technology have been numerous, all targeted to provide the customer with enhanced performance properties, while trying to improve processability, increase production rates, and lower costs. The more than five-decade-old technology of polyurethane foams might have been expected to reach a mature growth by now. However, formulations based on newer and more sophisticated applications continue to develop, thus demanding a better understanding of the structure-property correlations. Also, the evaluation of foam morphology using techniques such as atomic force microscopy and x-ray microscopy has opened avenues to improve the understanding of these materials.

Flexible polyurethane foams are produced either by a semi-continuous slabstock process or a batchwise molded process. Currently, both these schemes employ the one-shot method. In the former process, the various foaming ingredients are mixed in a transverse mixing head and sprayed on a conveyor belt. Subsequent foaming reactions lead to the polymerization of the
reacting mixture which gives the foam its integrity; and also release carbon-dioxide, which helps
the entrained air bubbles to develop into foam cells. When the entrapped air bubbles in the
reacting mixture grow large enough to scatter visible light, a visible coloration change, known as
‘creaming’ is observed (Figure 1.3). The point where the majority of the cells open is
accompanied by a ‘sigh back’ of the foam, since at this time, gas can move freely through the
foam cells, and this lets the foam assume its final height. The large buns of foam produced from
this process are then placed in a storage area for a period of at least forty-eight hours to complete
the curing.

Since flexible polyurethane foams expand and flow, at least prior to the onset of gelation,
manufacturers have often found it useful to produce foams using a batchwise molded process.1
This method is especially useful where the final foam product has a complex shape, for example

![Carousel Molding Process](image)

**Figure 1.4 Carousel Molding Process**

in car seats and headrests. The foams produced by this method, therefore, help to save trimming
 costs and minimize wastage. Currently, flexible foams produced by this method account for
 approximately 20% of the total flexible polyurethane foam market. A typical carousel molding
 line is shown in Figure 1.4.

As will be discussed in the following chapter, the formation of flexible polyurethane
foams relies on a complex interaction between physical and chemical phenomena. Perhaps the
most important aspect of flexible foam manufacture is that there are no ‘independent’ chemical
or process variables in producing flexible foams. Therefore, the effect of altering a single variable (such as a foam component or a process condition) cannot be studied, since changing a particular parameter will affect the strong interplay which exists between the different variables.

The next chapter will discuss the contribution of the many workers who have contributed towards the area of flexible polyurethane foams. Wherever necessary, relevant studies that have been carried out in the general area of polyurethane materials will also be discussed.

References

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5. Ade H; Smith AP; Cameron S; Cieslinski R; Mitchell G; Hsiao B; Rightor E; Polymer: 36 (1995) 1843