POLYURETHANE FLEXIBLE FOAMS

Polyurethane foam is the most widely used flexible foam plastic. It is used to produce a wide variety of items including thermal insulation and packaging materials, comfort cushions, bed mattresses, carpet backings and resilient floor coverings.

Tolylene diisocyanate (TDI) and polyalcohols are the basic ingredients for the production of polyurethane foam. The basic reaction is as shown below:

\[
\text{OCN} - \text{NCO} + \text{HO-R-OH} \rightarrow \text{HO-R-OH} + \text{H-O-C-N-C-O-R-O}
\]

Blowing agent, such as methylene chloride and water, and various additives are also required.

**Step 1 - Mixing of the raw materials**
During production, the raw materials (TDI, polyalcohol, blowing agents and additives) are pumped from their own storage tank to a common mixing chamber. Adequate dispersion can be achieved by the stirring of high speed impeller installed in the mixer.

**Step 2 - Foam forming and settling**
The foam gradually solidifies when travelling up the settling chamber by the action of paper conveyor. It is then cut into 2.2 m long blocks by an electric cutter after the foam is hardened.

**Step 3 - Curing**
The newly formed foam blocks are still very hot when transported to the storage area. They must be cured at room temperature for at least 18 hours before further processing.

INTRODUCTION

Solid foam is formed when gas is blown through solidifying plastic. Depending on its ability to retain original shape after compression, solid foam can be classified as either flexible or rigid. Polyurethane foam is the most widely used flexible foamed plastic, being used for thermal insulation and packaging materials, cushions, bed mattresses, carpet backings and resilient floor coverings.

There are four major polyurethane foam manufacturers in New Zealand. This article is based on the process used by Dunlop Flexible Foam in Auckland, although all manufacturers use a similar process. Dunlop has been using a continuous process since 1985, and has a daily capacity of more than 15 tonnes of polyurethane foam.

The chemistry of polyurethane foam formation
Flexible polyurethane foams are open cell materials that allow free movement of air between the foam cavities. They are commonly available in density of 13 - 80 kg m\(^{-3}\).

TDI and polyalcohol are the basic ingredients for polyurethane foam production. A range of additives, blowing agents and water are also added.
TDI is the abbreviation for toluene di-isocyanate, a mixture of toluene-2,4-diisocyanate and toluene-2,6-diisocyanate with the 2,4- isomer being the major component. Polyalcohol (HO—R—OH) is the other important ingredient in foam production, and the structure of the R group in the alcohol is largely responsible for the final properties of the final product. Generally speaking, using a longer R group will improve the flexibility of the resulting foam. The relative molecular mass of polyalcohol for flexible foam production is as large as 20000.

When TDI reacts with polyalcohol, polyurethane forms in a highly exothermic reaction:

$$\text{OCN} - \text{NCO} + \text{HO} - \text{R} - \text{OH} \rightarrow \left[ \text{O} - \text{H} - \text{N} - \text{C} - \text{O} - \text{R} - \text{O} \right]$$

This is a nucleophilic addition of RO-H across C=N.

The polymeric chain crosslinks with others via the following reactions:

$$\text{R} - \text{N} - \text{C} - \text{R} + \text{O} - \text{C} = \text{N} - \text{R}$$

TDI

$$\text{R} = \text{other parts of the polymeric chain}$$

This is a nucleophilic addition of >N-H across C≡N.

Hard polyurethane plastic (such as that which many electric switches are made of) would be formed in the above condensation reaction if the reaction is carried out without blowing agent.

Two different types of blowing agents are added to the polymer - carbon dioxide and methylene chloride. Carbon dioxide (the primary blowing agent) is produced in the reaction mixture as water reacts with the isocyanate group:
Due to its low reactivity and low boiling point (b.p. 40.7 °C), methylene chloride (CH₂Cl₂) is selected as a supplementary blowing agent. It vapourises and leaves cavities in the plastic framework after the exothermic reaction begins.

In practice, a range of additives are blended with the raw materials. A tin based additive is used to stabilise the foam while a few amine based additives are added to control the extent of cross linkage and the rate of reaction. Dyes are also added to distinguish different grades and batches of foams.

**THE MANUFACTURING PROCESS**

Dunlop Flexible Foam produces polyurethane from a continuous production line. Unlike conventional machines that extend horizontally for tens of metres, the polyurethane forming machine in Dunlop adopts a vertical profile to save space.

A schematic diagram of the machine is shown in Figure 1 below.

![Figure 1 - Schematic diagram of the Dunlop polyurethane process](image)

**Step 1 - Mixing of the raw materials**

TDI and polyalcohol are transported to the plant by road tankers. They are stored in cylindrical tanks before use.
Since the melting point of TDI is about 17 °C, it would solidify in uninsulated tank during winter. Therefore the contents in the tank are kept at 25 °C to solve the material handling problem.

During production, the raw materials (TDI, polyalcohol, blowing agents and additives) are pumped from their own storage tank to a common mixing chamber. An impeller driven by a fast rotating motor is installed in the mixer to aid dispersion. Despite its small size (less than 1 L in volume) the mixer can process more than 50 kg of raw materials each minute.

Step 2 - Foam forming and settling
Due to the foaming effect of the blowing agents, the reacting mixture expands rapidly on ejection from the mixer. Since the mixture is still in liquid form when pumped to the bottom of the settling chamber, it picks up the shape of the chamber readily.

The foam gradually solidifies when travelling up the settling chamber by the action of a paper conveyor. It takes approximately nine minutes for the foam to travel from the bottom to the top of the machine. By this time, the foam is fully hardened. It is cut into 2.2 m long blocks by an electric cutter mounted on top of the settling machine.

Step 3 - Curing
The newly formed foam blocks are still very hot when transported to the storage area. Although the peripheral of the foam is cooled to room temperature, the centre of the block can still be hotter than 100 °C. It must be cured at room temperature for at least 18 hours before further processing.

Fully cured foam blocks are either directly delivered to the customers or cut into smaller sizes according to orders. Due to its low density, foam products are bulky and expensive to transport. To save space, vacuum packing is prevalent during transportation. Being flexible the foams reduce in size and revert to their full size when returned to atmospheric pressure.

THE ROLE OF LABORATORY
To assure the product quality, the laboratory performs routine tests on selected batches. Most of the tests, such as density measurement, tensile and compression strength tests are mechanical in nature.

Since expansion of polymer into a cellular state greatly increase the surface area, reaction of the foam with environmental agents, e.g. moisture and air, are correspondingly faster than that in solid polymer. Ageing problem is thus serious for polyurethane foam. The life time of foam can be estimated from accelerated tests by keeping foam samples in an oven.

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1 Since TDI is a mixture of the two isomeric forms of toluene diisocyanate, it does not have a sharp melting point.
ENVIRONMENTAL IMPLICATIONS

TDI is a confirmed carcinogen. Its emission is closely monitored by the local council. TDI tape detectors are installed around the factory. To minimise the emission of TDI, most of the process equipment is shielded.

Traditionally CFC (chlorinated fluorocarbons) based solvents were used as blowing agents. In the late 80's, the ozone layer depletion effect of CFC based chemical was established. The use of CFC was gradually banned. Methylene chloride, which is inert to ozone, is used as a substitute for CFC.

Lots of "offcuts" are generated in the foam cutting process. They are collected and sent to the associated recycle plant to produce a lower grade flexible foam. This type of foam is widely used in the production of carpet backings and packing materials. By this way the net amount of waste produced in the process can be minimised.

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