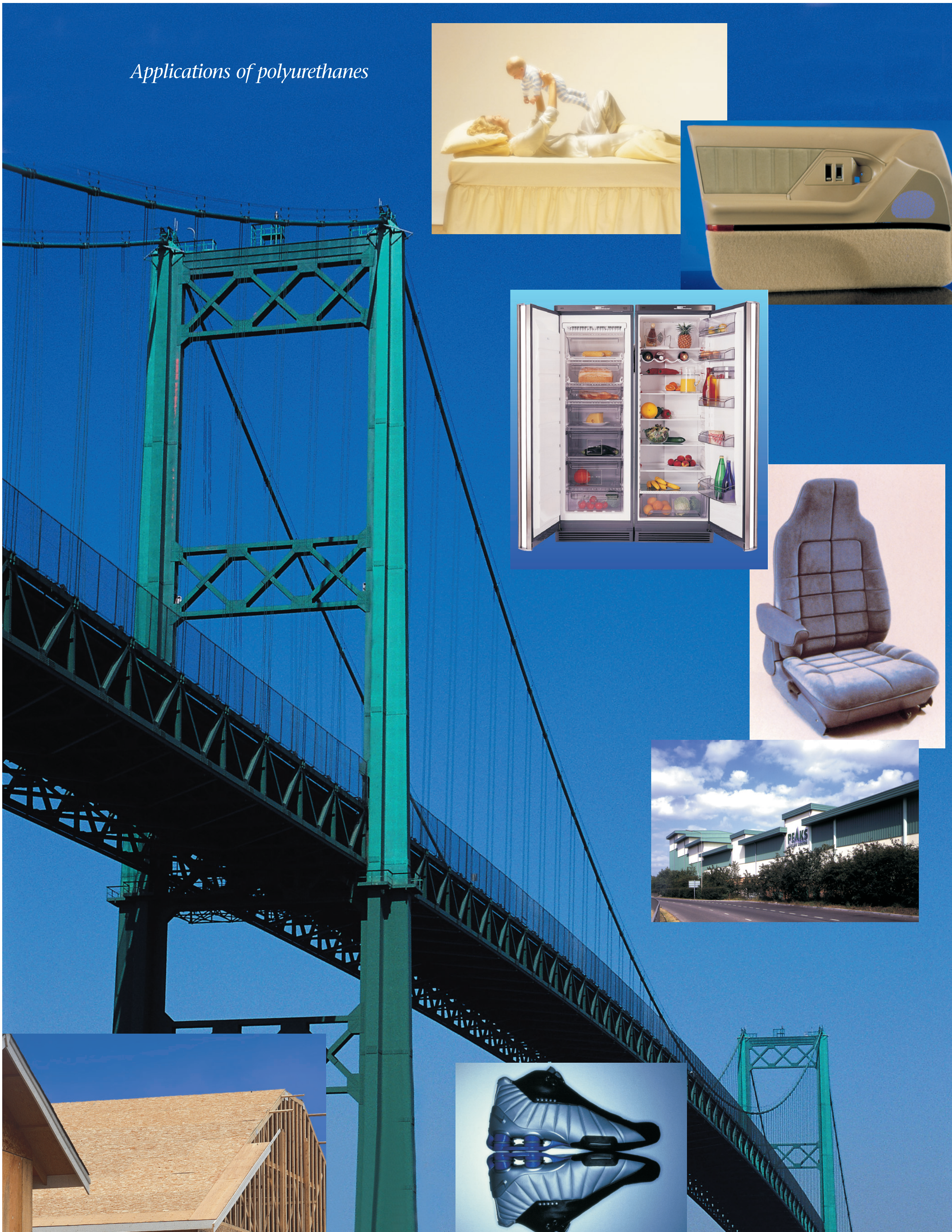
1. Introduction to polyurethanes

Although the reaction between isocyanate and hydroxyl compounds was originally identified in the 19th Century, the foundations of the polyurethanes industry were laid in the late 1930s with the discovery, by Otto Bayer, of the chemistry of the polyaddition reaction between diisocyanate and diols to form polyurethane. The first commercial applications of polyurethane polymers, for millable elastomers, coatings and adhesives, were developed between 1945 and 1947, followed by flexible foams in 1953 and rigid foams in 1957. Since that time they have been finding use in an ever-increasing number of applications and polyurethanes are now all around us, playing a vital role in many industries – from furniture to footwear, construction to cars. Polyurethanes appear in an astonishing variety of forms, making them the most versatile of any family of plastic materials.

Comfortable, durable mattresses and automotive and domestic seating are manufactured from flexible foam. Rigid polyurethane foam is one of the most effective practical thermal insulation materials, used in applications ranging from domestic refrigerators to large industrial buildings. Polyurethane adhesives are used to make a wide variety of composite wood products from load-bearing roof beams to decorative cladding panels. Items such as shoe soles, sports equipment, car bumpers and 'soft front ends' are produced from different forms of polyurethane elastomers.

Many of us are clothed in fabrics containing polyurethane fibres or high-performance breathable polyurethane membranes. Highly demanding medical applications use biocompatible polyurethanes for artificial joints and implant coatings. Polyurethane coatings protect floors and bridges from damage/corrosion and adhesives are used in the construction of items as small as an electronic circuit board and as large as an aircraft. Advanced glass and carbon fibre reinforced composites are being evaluated in the automotive and aerospace industries. Examples of typical applications are shown on page 2.

Commercially, polyurethanes are produced by the exothermic reaction of molecules containing two or more isocyanate groups with polyol molecules containing two or more hydroxyl groups. Relatively few basic isocyanates and a far broader range of polyols of different molecular weights and functionalities are used to produce the whole spectrum of polyurethane materials. Additionally, several other chemical reactions of isocyanates are used to modify or extend the range of isocyanate-based polymeric materials. The chemically efficient polymer reaction may be catalysed, allowing extremely fast cycle times and making high volume production viable.



Applications of polyurethanes

Cost and processing advantages

Although a unique advantage of polyurethanes lies in the very wide variety of high-performance materials that can be produced, they also differ from most other plastic materials because the processor is able to change and control the nature and the properties of the final product, even during the production process. This is possible because most polyurethanes are made using reactive processing machines, which mix together the polyurethane chemicals that then react to make the polymer required. Changes in the detailed chemical nature of the polyols, isocyanates or additives allow the user to produce different end polymers. Minor changes in the mixing conditions and ratios allow for a fine-tuning of the polymers produced. The polymer is usually formed into the final article during this polymerisation reaction and this accounts for much of the versatility of polyurethanes. They can be tailored with remarkable accuracy to meet the precise needs of a particular application.

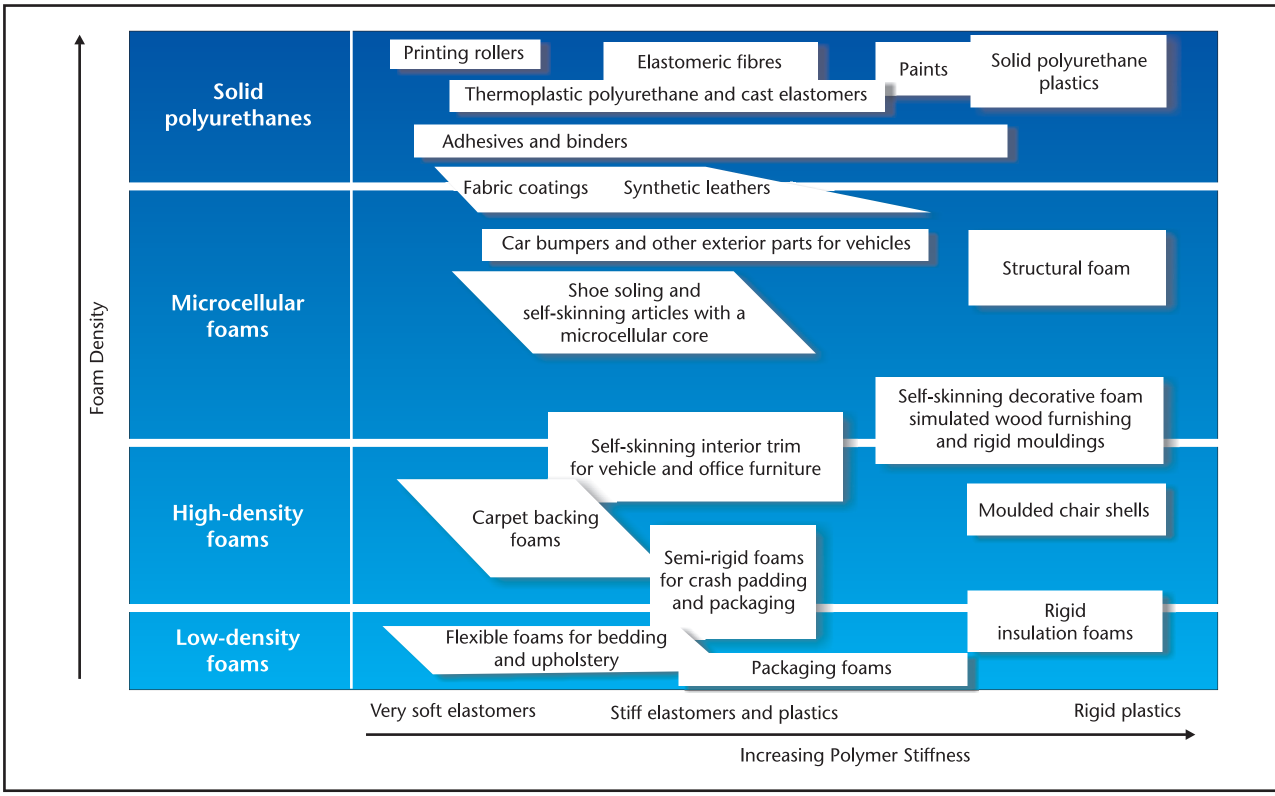
Another important property of polyurethane reaction mixtures is that they are powerful adhesives. This enables the simple manufacture of strong composites such as building panels and laminates, complete housings for refrigerators and freezers, fully integrated instrument panels for vehicles and reinforced structures in boats and aircraft. It is, in part, this dual functionality that makes the material so valuable for manufacturing industries since it is possible to eliminate a number of complex and expensive assembly steps when using polyurethanes rather than alternative polymers.

It is this combination of high material performance coupled with processing versatility that has resulted in the spectacular growth and wide applicability of the polyurethane family of materials. The processing benefits enable polyurethanes to compete with lower cost polymers since raw material costs are not the only consideration in the total cost involved in producing an article. Factors of at least equal importance are cycle time, the cost of tooling and finishing as well as reject rates and opportunities for recycling. As polyurethane reaction moulding requires only comparatively low pressures, moulds can be made of less expensive materials such as aluminium or glass reinforced polyester rather than steel. This is of particular importance for low volume production, but also allows the simple and rapid production of inexpensive prototypes for the development of new products and processes or the refinement of established ones.

Properties of polyurethanes

Polyurethanes can be manufactured in an extremely wide range of grades, in densities from 6 to 1,220 kg/m^3 and polymer stiffness from flexible elastomers to rigid, hard plastics. Although an over simplification, the following chart, Figure 1-1, illustrates the broad range of polyurethanes, with reference to density and stiffness.

Figure 1-1 *Property matrix of polyurethanes*



Types of polyurethanes

A consideration of particular properties of certain grades of polyurethanes and the way these are used serves to demonstrate their versatility.

Foamed

By itself the polymerisation reaction produces solid polyurethane and it is by forming gas bubbles in the polymerising mixture, often referred to as 'blowing', that a foam is made. Foam manufacture can be carried out continuously, to produce continuous laminates or slabstock, or discontinuously, to produce moulded items or free-rise blocks.

Flexible foams can be produced easily in a variety of shapes by cutting or moulding. They are used in most upholstered furniture and mattresses. Flexible foam moulding processes are used to make comfortable, durable seating cushions for many types of seats and chairs. The economy and cleanliness of flexible polyurethane foams are important in all upholstery and bedding applications. Strong, low-density rigid foams can be made that, when blown using the appropriate environmentally acceptable blowing agents, produce closed cell structures with low thermal conductivities. Their superb thermal insulation properties have led to their widespread use in buildings, refrigerated transport, refrigerators and freezers.

A fast, simple moulding process can be used to produce rigid and flexible foam articles, having an integral skin, that are both decorative and wear resistant. Fine surface detail can be reproduced in the integral skin of the foam allowing for the simple manufacture of simulated wood articles, 'leather-grain' padded steering wheels and textured surface coatings.

Three foam types are, in quantity terms, particularly significant: low-density flexible foams, low-density rigid foams and high-density flexible foams, commonly referred to as microcellular elastomers and integral skin foams.

Figure 1-2
Scanning electron micrograph showing the open cells of flexible foam

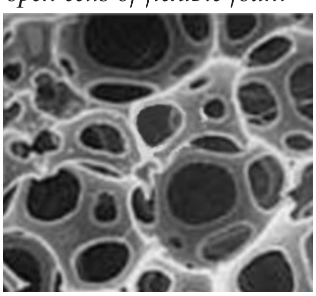
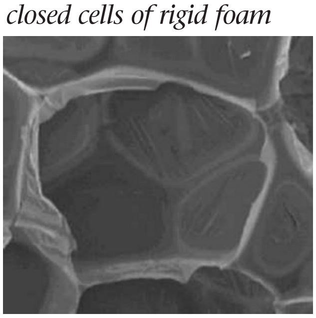


Figure 1-3
Scanning electron micrograph showing the closed cells of rigid foam



Low-density flexible foams have densities in the range 10 to 80 kg/m^3, made from a lightly cross-linked polymer with an open cell macro structure. There are no barriers between adjacent cells, which results in a continuous path in the foam, allowing air to flow through it. These materials are used primarily as flexible and resilient padding material to provide a high level of comfort for the user. They are produced as slabstock, which is then cut to size, or as individually moulded cushions or pads. There are semi-rigid variants of this material, where the chemistry of the building blocks has been changed, and these are mainly used in energy management systems such as protective pads in cars. An example of the cellular structure is shown in Figure 1-2.

Low-density rigid foams are highly cross-linked polymers with an essentially closed cell structure and a density range of 28 to 50 kg/m^3. The individual cells in the foam are isolated from each other by thin polymer walls, which effectively stop the flow of gas through the foam. These materials offer good structural strength in relation to their weight, combined with excellent thermal insulation properties. The cells usually contain a mixture of gases and depending on their nature and relative proportions the foams will have different thermal conductivities. In order to maintain long-term performance it is necessary for the low thermal conductivity gases to remain in the cells, consequently more than 90 per cent of the cells need to be closed. An example of the cellular structure is shown in Figure 1-3. Recently, fully open celled rigid foams specifically developed for vacuum panel applications have been developed.

High-density flexible foams are defined as those having densities above 100 kg/m^3. This range includes moulded self-skinning foams and microcellular elastomers. Self-skinning or integral skin foam systems are used to make moulded parts having a cellular core and a relatively dense, decorative skin. There are two types: those with an open cell core and an overall density in the range up to about 450 kg/m^3 and those with a largely closed cell or microcellular core and an overall density above 500 kg/m^3. The microcellular elastomers have a much more uniform density in the range of 400 to 800 kg/m^3 and mostly closed cells, which are much smaller than those in the low-density applications. The biggest applications for integral skin and microcellular elastomers are in moulded parts for upholstery, vehicle trim and shoe soling. Another similar material is the microporous elastomer in which the porous structure is often created in ways other than by the expansion of gases. Often produced in thin films these materials have an open cell like structure, which allows movement of gases, but have the appearance and physical integrity of a solid film.

Solid
Although foamed materials account for a substantial proportion of the global polyurethanes market there is a wide range of solid polyurethanes used in many, diverse applications.

Cast polyurethane elastomers are simply made by mixing and pouring a degassed reactive liquid mixture into a mould. These materials have good resistance to attack by oil, petrol and many common non-polar solvents combined with excellent abrasion resistance. They are used amongst other things in the production of printing rollers and tyres, both low speed solid relatively small units and to fill very large, pneumatic off-road tyres.

Polyurethane elastomeric fibres are produced by spinning from a solvent, usually dimethylformamide (DMF), or by extrusion from an elastomer melt. The solvent process is the dominant one and has two forms, one in which the completed elastomer is dissolved and then a fibre spun as the solvent is removed and the other in which the isocyanate and polyol are mixed into a DMF solution and the fibre spun as the reaction occurs. The major applications are in clothing where these fibres have effectively replaced natural rubber.

Thermoplastic polyurethanes are supplied as granules or pellets for processing by well-established thermoplastic processing techniques such as injection moulding and extrusion. By these means elastomeric mouldings having an excellent combination of high strength with high abrasion and environmental resistance, can be mass-produced to precise dimensions. Applications include hose and cable sheathing, footwear components and high-wear engineering applications. Recent advances have shown the possibility to foam the polymer during injection moulding, extending even further the range of applications.

Polyurethanes are also used in flexible coatings for textiles and adhesives for film and fabric laminates. Paints and coatings give the highest wear resistance to surfaces such as floors and the outer skins of aircraft and for the automotive industry. Binders are used increasingly in the composite wood products market for oriented strand board and laminated beams for high performance applications.

Applications of polyurethanes

A detailed breakdown of the markets for polyurethanes is given in Chapter 2, but the versatility of this material can be demonstrated by looking at the applications in five major areas.

Automotive
The use of polyurethanes in this area is now well established to the benefit of both the manufacturer and the end consumer. Applications include seating, interior padding, such as steering wheels and dashboards, complete soft front-ends, components for instrument assemblies and accessories such as mirror

surrounds and spoilers. Door panels, parcel shelves, sun roofs, truck beds, headliners, components mounted in the engine space and even structural chassis components are now made from polyurethanes.

Furniture

The market for cushioning materials is mainly supplied by polyurethane flexible foam, which competes with rubber latex foam, cotton, horse hair, polyester fibre, metal springs, wood, expanded polystyrene, propylene and PVC. Polyurethanes are also ideal where strong, tough, but decorative integral-skinned flexible or rigid foam structures are needed.

Construction

When sandwiched between metal, paper, plastics or wood, polyurethane rigid foam plays an important role in the construction industry. Such composites can replace conventional structures of brick, concrete, wood or metal, particularly when these later materials are used in combination with other insulating materials such as polystyrene foam, glass fibre or mineral wool. Technically advanced wood composites can be produced for use in load-bearing applications and wood construction boards for flooring and roofing.

Thermal insulation

Rigid polyurethane foam offers unrivalled technical advantages in the thermal insulation of buildings, refrigerators and other domestic appliances and refrigerated transport. Competitive materials include cork, glass fibre, mineral wool, foamed expanded and extruded polystyrene and phenol formaldehyde.

Footwear

Soles, some synthetic uppers and high performance components for many types of footwear are produced from polyurethanes. These compete with traditional leather and rubber, PVC, thermoplastic rubber and EVA. Polyurethane adhesives are widely used in shoe manufacture and coatings are used to improve the appearance and wear resistance of shoe uppers made from both real and synthetic leather.

Industry structure

The industrial base for polyurethanes that has evolved over the last half century is driven by two key factors. The first is the economies of scale associated with the raw material manufacture. The process to make isocyanates, starting from chemicals such as benzene or toluene, is complex and expensive. As with all chemical processes there are many safety and environmental issues to be considered and it is essential to have the lowest possible cost base for production of these large volume chemicals. Consequently, the manufacture resides in the hands of a few major global chemical companies. The situation for the polyol side is more complex since the production of propylene oxide (PO), ethylene oxide (EO) and polyesters is more wide spread, in part due to the wider variety of processes available and the suitability to run economically, at a relatively smaller scale. In addition, both PO and EO can be purchased on the open market and then used to manufacture polyols whereas the isocyanates are produced and sold by the major companies. It is, of course, still beneficial to have world-scale production economics for the polyol components.

The second factor is the diversity of the market and the routes to serve that market. Although all the major isocyanate manufacturers are also basic in PO and EO and make and sell polyols, there are strategic choices made about the way that the chemical 'package' is delivered to the customer. This choice is governed principally by economics and supply chain logistics. In addition, the customer is not always the end producer. An illustrative example of this is the automotive industry where there are a number of 'tiers' of manufacturers all creating more complex product offers as they move towards the final specifiers/ designers: the car companies, often referred to as OEMs (original equipment manufacturers) who assemble and sell cars under their own name and brands. Thus, a chemical manufacturer could be providing a fully-formulated system, isocyanate and polyol with a full additive package to a flexible foam seat moulder, who will then provide the cushions to another company to finish the seat assembly. This, in turn, goes to the car company, which will fit the seat into the car.

To some customers the chemical manufacturer will provide only the basic isocyanate and polyol and the customer, using its own, in-house expertise, will formulate a system and then manufacture the end article itself. An alternative approach is the use of a 'system house', either independent or aligned, which buys in the base chemicals from a number of sources, designs and manufactures a formulated system and then sells it on to the end polyurethane producer.

Future trends

The future of the polyurethanes industry will be driven by the continued innovation in both the chemistry and the polymer physics of this highly versatile material and research and development will continue to provide new capabilities. The integration of raw material supplies, such as propylene to propylene oxide to polyols, will have an effect on the cost base of the major chemical manufacturers. At the same time, as the economics of production improve and market development into previously unexplored end uses identifies new targets, so the growth of the industry will be fuelled not only by economic growth, but also by the replacement of other materials in existing markets.

An example of this is the progress being made in the area of composite materials, where metals and other engineering plastics are being displaced by polyurethane composites offering superior properties and processing advantages.