POLYURETHANE FOAMS

B. VENKATARAMANI Defence Science Laboratory, Delhi

INTRODUCTION

"The history of mankind has been a fascinating story, beginning with the simplest materials and unfolding with the passage of centuries into a variety of complex materials deliberately made by man to suit his particular needs". Few branches of science have made such a stupendous progress as that of High Polymers. In fact the technology and commercialisation of polymers have advanced with such a remarkable speed in the past three or four decades that the acceptance of polymers has been closely linked with the civilization and social communities that man has fashioned. Polyurethanes, sometimes called Isocyanate resins or urethane plastics, are widely used in diverse fields such as elastomers, adhesives, surface coatings, rigid and flexible foams etc. An elaborate account of all the uses of urethane materials and their respective technologies will definitely cover a voluminous number of pages. Popular and detailed reviews on different characteristics of urethane foams are available in literature. However, the purpose of this article is to bring to light the various aspects of polyurethane foams, their properties and their potential defence applications.

BASIC REACTIONS IN POLYURETHANE FOAM FORMATION

The term urethane^{16,17} was originally coined to denote the ethyl ester of carbamic acid NH₂·COOC₂H₅ and now gradually it has become customary to refer to all the esters of carbamic acid as urethanes. These esters are easily formed by the reaction of isocyanates with compounds containing reactive hydroxyl groups. Though the basic chemistry of urethane formation was described over a hundred years ago, yet its technological application is of comparatively recent origin and is mainly due to the availability of polyisocyanates. The major advantage, of these isocyanates as a group is their ability to enter into reaction with a wide variety of compounds containing active hydrogen atoms. ^{18,19} In essense the reaction involves the migration of an active hydrogen atom to the nitrogen of the isocyanate and the basic reaction with a hydroxyl group can be represented by the equation (1).

The most important reactions of the isocyanates which ensure their entry into the commercial fields are those with hydroxyl group and with water. With water, isocyanate reacts through an intermediate stage of substituted carbamic acid and its subsequent break down into an amine and carbon dioxide (equation 4). The reactivity of isocynates is such that the reactions are highly exothermic and require little heat to initiate them, but on the contrary they have to be controlled by judicious use of catalyst. However, at temperatures of 100°C and above, isocyanates react²⁰ not only with the relatively reactive amines, alcohols, carboxylic acids and water (equation 2 to 4) but also with less reactive compounds such as ureas, urethanes and amides (equation 5 to 7).

$$R-NCO+HO-R'---\rightarrow R-NH-COOR'$$
(1)

$$R-NCO+R'NH_2 \longrightarrow R-NH-CO-NHR'$$

$$R-NCO+R'COOH\longrightarrow R-NH-COR'+CO_{2} \tag{3}$$

$$R-NCO+H_{2}O\longrightarrow (R-NH-COOH) \tag{4}$$

$$R-NH-COOH\longrightarrow R-NH_{2}+CO_{2}$$

$$R-NCO+R-NH-CO-NHR'\longrightarrow R-NH-CO-N-CO-NHR' \tag{5}$$

$$R$$

$$(a Biuret)$$

$$R-NCO+R-NH-COOR'\longrightarrow R-NH-CO-N-COOR' \tag{6}$$

$$R$$

$$(an Allophonate)$$

$$R-NCO+R-NH-CO-R'\longrightarrow R-NH-CO-N-CO-R' \tag{7}$$

It is readily noted from the above equations that these reactions are actually the combination of isocyanates with initial reaction products from isocyanates with amines, carboxylic acid and alcohols respectively. Furthermore, the active hydrogen has not still disappeared and it is probable that such a sequence of reactions may take place in an uncontrolled reaction. However, the rates of reactions of isocyanates with active hydrogen compounds are sufficiently different to permit the commercial exploitation of any of these reactions individually. Another possibility, ²⁰ is the occurrence of self condensation leading to the formation of a dimer (I), a trimer (II) and carbodiimide (III).

Though the insight into the fundamental reactions of polyurethane foam formation was gained much earlier, the possibility of polymer formation was not realised until 1938. O. Bæyer and Colleagues,²¹ then studied the reactions of dihydroxylic compounds and diisocyanates and judiciously combined this reaction with the water reaction to result in the formation of a back bone polymer which trapped the carbon dioxide evolved. A combination of a simple dihydroxylic compound with diisocyanate will result in a material having

some isocyanate end groups. However, if the choice is so made that the hydroxylic groups are by themselves a part of the polymer, the physical and chemical properties of the resulting foam make them useful commercially. The nature of the foams produced in these reactions are mainly governed by the location of hydroxyl groups in the initial polymer. By a suitable choice of isocyanate-polymer reaction, the resulting product can be made to take different forms like flexible or rigid foams, fibres, adhesives, coatings...etc. The chemical reactions involved in the foam manufacture are very complex^{22, 23} and they can be roughly represented as in Chart I.

It is evident from the above considerations that the foam formation is subjected to the interplay of so many undesired side reactions and these have to be minimised by careful control. Therefore two fundamental reactions namely the polymer formation and $\rm CO_2$ liberation must be so balanced that the back bone polymer structure is just formed in time to trap the carbon dioxide that is evolved.

RAW MATERIALS

Resins6, 24-26

Polyurethane foams can be broadly divided into two categories, namely rigid and flexible. Resins suitable for foaming are normally made by condensing a diabasic acid with polyhydric alcohol. The use of polyesters with increasing branching leads to rigid foams while flexible foams are made from essentially linear polyesters. Changes in the ultimate quality of the foams are brought about by changes in the back bone structure of the polyhydroxylic part of the polymer. For example, the number of cross linking points in a structure is mainly dependent on the use of an alcohol having a functionality greater than two, in the polyester manufacture and the greater the cross links greater is the rigidity of the foams.

Diisocyanate modified polyester foams were not entirely satisfactory in some of their performance tests. Hence, a detailed investigation of the other hydroxyl ended polymer was pursued with tremendous pace, until the use of polyether or polyols in the foam production had gained commercial acceptance. Tetrahydrofuran polymerisation⁶ (equation 8) to polytetra ethylene glycol and its use as the back bone structure in the foam manufacture is the earliest example of deviation from the polyester structure. The commercial exploitation of this process was handicapped by the high cost involved in this manufacture. Later, more easily obtainable ethers such as polyethylene and polypropylene glycols (equation 10 and 11) were investigated^{25, 27}. Foams from the for ner did not possess much hydrolytic stability while the one derived from the latter was much more hydrophobic in nature and its economics was also favourable. As polypropylene glycol is a linear polymer, its reaction with isocyanate should normally give rise to only a linear polymer without much technical value. However, it has been shown that the isocyanate reaction with urethane or urea to form allophonate and biuret (equations 6 and 5) lends opportunities for cross linking and thereby imparting technical value to the products.

. การ (ก. 1831) เลยที่ เดืองที่สารที่สารคามที่ทำวันเรียกให้เกี่ยวการสารที่เป็นเปรียกให้ และ เวลา (การที่สารที่สุดสมาชาวันสาราว (การที่สารที่สารที่สารที่สารที่สารที่สารที่สารที่สารที่สารที่สารที่สารที่สา

agamarak Mag

Still a distinct advance²⁸ in polyurethane foam technology is the utilization of a triol (equation 11) as a resin part. It is to be noted here, that the hydroxyl groups in polyester are mainly primary and as such possess the same reactivity towards isocyanate and water. But in the case of polypropylene glycols the hydroxyl groups are now mainly secondary and their reactivity towards isocyanate is comparatively less than in the earlier case. In consequence, the urethane and gas formation could not be so easily balanced as in the case of polyester. However, this difficulty was overcome by the introduction of certain specific catalysts to increase the rate of the reaction between isocyanate and the secondary hydroxyls.

$Isocyanates^{29-34}$

One of the necessary conditions for the proper choice of raw materials for foam production, is that they should all be liquid at ambient temperature. Tolylene diisocyanate (TDI) is one of the easily available isocyanate and its low volatility and low molecular weight make it ideally suited for use in the urethane foam manufacture. Among the other isocyanates used, diphenyl diisocyanate methane (VI), is worth mentioning here. Of the six possible

isomers of TDI, the 2:4 (IV) and 2:6 (V) isomers are of technical importance. Commercially, TDI is available in three categories, the proportions of each one being controlled by initial nitration stages. (100 per cent, 2:4, isomer, 80:20, 2:4 and 2:6 isomer mixture and 65:35, 2:4 and 2:6 isomer mixture)

Detailed investigations³² have been carried out on the effect of different isomer mixture on the quality of the foam and it has been shown that though these particular ratios may differ from an entirely different formulation, but there is an optimum isomer blend (which is very nearly 80: 20) to yield a quality foam. It is interesting to refer, at this stage to recent work^{33, 34} on the effect of diisocyanate structure on the physical properties of urethane foam. The introduction of polymethylene polyphenyl isocyanate (PAPI) is a marked advance in recent times.³⁵ Because of its high functionality and its inherent thermal stability, PAPI has found large scale application in the production of heat resistant urethane foams.

Other Ingredients

In addition to water and the above two raw materials, other ingredients that are used are (a) a catalyst or combination of two catalysts to balance the isocyanate and foaming reaction (b) emulsifiers and surface active agents. These are used to hasten the mixing and to control the cell size and consequently the structure of the foam.

Catalyst³⁷—³⁹

The use of basic catalysts to accelerate the formation of polyurethane foam is well established. 18,19 The role of the catalyst and its influence on the course of urethane reaction have been studied in considerable detail and the essential steps are depicted b8,36

The base-isocyanate complex possibly reacts⁸ with alcohol followed by release of the catalyst. Interestingly, alcohol here plays the part of an acid by the addition of the proton to the negatively charged nitrogen and addition of the OR to the carbon of the NC bond. It is evident from the above mechanism that the stronger the base, the more powerful it would be, as a catalyst in this reaction. As already mentioned, with the introduction of polyethers as back bone structure for foam production the necessity of balancing the two fundamental reactions was great. With polyester, the function of the catalyst is merely to speed up the reaction. However, with polyethers and the common tertiary amines as catalyst, the viscosity is not readily built up to trap the gas that is liberated from the reaction between isocyanate and water. However, the use⁴⁰ of triethylene diamine (VII) is a singular example of a tertiary amine catalyst in polyether foam manufacture though it is reported⁴¹ to present considerable difficulty in satisfactory commercial production.

The advent⁴² of organo tin compounds as catalysts for the isocyanate hydroxyl reaction, has revolutionised the very technology of polyurethane foam production. The main advantage of these catalysts is that they do not strongly catalyse the isocyanate-water reaction and thereby they provide an opportunity for the liberated carbon dioxide to be trapped in the resin, which by itself is formed by the interaction of polyether hydroxyls and isocyanate under the influence of the catalyst. However, the use of dibutyl tin laurate or stannous octoate singly as catalyst was found to produce marked degradation of the urethane polymer. Fortunately, the action range of organo tin catalysts can be extended by the synergistic effect of a tertiary amine (e.g., dimethyl amino pyridine) and thereby the concentration of tin compound can be regulated to a desirable minimum without affecting the life of the foams.

Surface Active Agents

Sulphated fatty acids are the commonly used surface active agents in the case of polyester based urethane foams. Recently, with the introduction of polydimethyl siloxanes, as a separate class of surface active agents, it has been possible to produce foams with marked improvement in their physical properties. However, substantial contribution has been made by the water soluble silicones⁴³ in the manufacture of polyether flexible foams by the one shot method. These are polyalkylene-poly-dimethyl siloxane block to copolymer such as—

$$C_2H_5-Si-\left(egin{array}{c} CH_3 \ -(O_-Si)_x\cdot\ (OC_3H_6)_y\cdot\ (OC_2H_4)_z\cdot\ (OC_4H_9) \ CH_3 \end{array}
ight)_3$$

The exact mode of action of silicone is not clear but data have been recorded 44 about the marked reduction in surface tension of the resin (polyether) with various polydimethyl siloxanes. The effect of different type of silicones on both the prepolymer and one shot method have been studied in detail. It has been observed that the use of silicone is very often desirable in the manufacture or rigid foam with a maximum number of closed cells.

The main reaction that takes place during foaming is the reaction between isocyanate and water which results in the liberation of carbon dioxide. The density of the foam is determined by how much carbon dioxide is evolved and consequently how many urea linkages are formed. However, it is known that the latter controls main physical properties like feel, compression load etc. and thus by a choice of a particular density foam necessarily restricts the physical properties obtainable from the resin. Blending of a volatisable liquid in a foam mixture would then assist in reducing the overall density of the foam.

Foam Blowing Compounds

Fluorochlorohydrocarbons have several advantages over the other volatisable solvents that they are non-inflam nable, non-toxic and do not react with the foam physically or chemically except acting as a blowing agent.⁴⁵ In addition to causing density reduction, the use of freons leads to many important technical effects especially in a rigid foam. For example, with Cl₃FC/CO₂ blown foams pressures built up during the foaming process is much lower than that of fully carbon dioxide blown foams. In the preparation of these foams, the fluorotrichloromethane is usually dissolved in either the resin or the isocyanate.

Thermal conductivity^{46, 47} of a foam is generally governed by the gas content of the cells and is a function of molecular weight and cross section.

 T	ABLE I
Air	0·168 B. Th. U/hr/ft²/°F/in.
And the second of the second o	0·102 Do. 0·058 Do.

It is evident from the above Table I that by this process improved thermal insulation properties are imparted to the foam. However, with carbon dioxide blown foams the

thermal conductivities are found to increase (from 0·15 to 0·22 B. Th. U.) on ageing the foam and this is mainly due to the diffusion of carbon dioxide from the cell walls. In this connection it is interesting to refer to the studies^{48, 49} that have been made on the transmission of carbon dioxide through plastic films and also the low permeability of fluorochlorohydrocarbons.

METHODS OF MANUFACTURE

Basically, two different methods are used in the manufacture of urethane foams. Prepolymer process.⁵⁰ The main object of this process is to control the reaction in two steps. In the first, the resin, either polyether or polyester, is reacted with isocyanate to give a known amount of isocyanate terminated polymer. This prepolymer and the activator (water, surface active agents etc.) are sold separately and can be mixed as and when the foam is required. The main disadvantage of this process is that with a given resin, the prepolymer preparation step must be made so adjustable that it is capable of giving a variety of foams with wide range of properties. On the other hand, in the one shot method, ^{51,52} the components namely resin, activator and diisocyanate are mixed simultaneously and foamed. Though the process was earlier applicable to only polyester foams, the advent of organo tin catalyst has made possible the manufacture of polyether foams also by this method.

The commercial production ^{53, 59} of polyurethane foam is a highly specialised field and warrants engineering and technical skill of a high order. Essentially, the system must be capable of metering out accurately different foam producing components to the mixing head and the mixture should not be allowed to fall on a material which has already started foaming. Many methods of mixing have been investigated, but rotating stirrer of different types are the common ones which are used technically. The problems of mixing and metering require careful adjustment owing to the differing viscosities and quantities of the different materials. Details of different machinery and other advantages are available with the various suppliers and in some non-technical reviews. Perfect care and thorough checks up of all the components and machinery are absolutely essential. Even slight changes in the foam formulation or in the speed of the stirrer are likely to affect the physical properties of the foam to a considerable extent.

Testing of the foams is of significant importance in assessing its quality and suitability for different uses. The methods of testing of the rigid and flexible foams, have been dealt with elaborately in various publications. $^{60-63}$

CHEMICAL & PHYSICAL PROPERTIES 7,62

Before discussing the applications of urethane foams, it is necessary to review their properties. Naturally, the properties of these foams vary depending upon the raw materials used for fabrication. A characteristic advantage of polyure thane foam is the ease with which the density can be varied within a wide range by the suitable choice of the resin, blowing agents etc.

Durability

These foams are unaffected by minor changes in temperature and have a tear resistance which is twice greater than that of foam rubber of equivalent weight. In general, they possess good resistance to a wide range of organic solvents such as glycol, glycerol, linseed oil etc. Particularly, urethane foams are resistant to oxygenand ozone and this is a decided advantage over foamed rubber latex. Their degradation under the influence of ultraviolet and sunlight is also negligible though they undergo discolouration but without any change in physical properties.

It is interesting to note⁶⁸ that rigid foams have good resistance against microbiological deterioration. A test sample of urethane foam was sandwiched between the layers of cork and subjected to the action of microorganism under standard conditions. The fact that the foam itself under these conditions remained free from mould growth clearly proves that rigid foam is highly resistant to microbiological attack even when it is in close contact with the materials that are themselves susceptible to attack.

Moisture effects

In general, urethane foams are hydrophobic in nature, but continued exposure to water results in moisture absorption. It has been observed that a newly made rigid foam absorbs more water than the aged foam. It is considered to be due to the presence of carbon dioxide in the open cells of newly made foam. The carbon dioxide being water soluble causes a pressure gradient which forces water into the foam. Though five fold reduction in the water vapour transmission coefficient has been recorded using the effect of 'skins', it is necessary that complete protection against ingress of water vapour must be ascertained.

Sound Absorption

Frequency range between 125 C/S to 4,000 C/S is normally encountered in domestic and industrial noise. One of the characteristic property of these cellular structures is the capacity to absorb sound. ⁶⁵ Table II shows the fraction of incident sound energy absorbed by the foam and it is evident that the reduction of sound level intensity is more easily achieved at higher frequencies. Sound absorption appears to be mainly a function of the ratio of open and closed cell structure. Fully open system (e.g., flexible foam) have better sound absorption properties since the rigidity is low enough to prevent the setting up of the transmisson of vibrations.

 ${\bf TABLe~II}$ Reverberation Absorption coefficient for frequency bands 125 to 4,000 C/S.

				125	250	500	1,000	2,000	4,000
301.14.4 3.4 4. 4. 4.									P
Rigid foam 2 lb/eu. ft	. • •	• •	••	••	0.79	0.99	0.97	••	••
2.6-2.8 lb/cu ft	• •	• •		0 · 20	0.40	0.65	0.55	0.70	0.70
6 lb/cu ft	•	••			0.20	$0\cdot 22$	0.22	••	
10 lb/cu ft Flexible	••	• •	•	0.25	0.20	0.22	0.31	••	••
Polyester type 2 · 2 lb/cu f	`t	••		0.25	$0 \cdot 50$	0.85	0.95	0.90	0.90
Polyether type 2·2 lb/cu	ft			0.25	0.45	0 · 75	0.90	0.75	0.85

Thermal properties

The inherent thermal conductivity of rigid foam is very low and is almost similar to that of glass wool or granulated cork.^{8, 47, 66} Further, by the use of flurochlorohydrocarbon, foams are manufactured which have still lower thermal conductivity of the order to 0.01 to 0.03 B. Th. U.

The changes in thermal conductivity of foams with temperature have also been studied in detail. One of the main advantage with urethane foams is their superior heat ageing properties ⁶⁷ compared to those of either natural rubber latex or P.V.C. Polyester foams are quite serviceable even after having been kept at 150°C for 21 days, while both latex and P.V.C. collapsed within the first day itself. Besides, the coefficient of expansion⁶³

of polyurethane rigid foam is 6×10 cm/°c only and correctly, formulated foams withstand a considerable amount of thermal shock produced by the rapid fluctuations in temperature.

Adhesion 68

The liquid mixture just before the foaming starts in the manufacture is known to be an excellent adhesive. In this case, a decided advantage is that the surface need not be prepared for adhesion. Table III depicts bond strength of rigid feams of varying densities. This particular property of the rigid feam has been exploited in the commercial fabrication of sandwiched structures.

m.		TTT
I A	BLE	111

 Foam density lb/ou	ft					2	5	10	 20
Bond strength, PSI				••		••		• •	••
To Aluminium	••	••	•	•••	in ee in territoria. Orași tă n in de t	10	27	56	158
To glass	••					9	25	50	142
To steel	••	••	••.,		• ••	12 .	. 29	62	146
To wood	••	••	••	••	••	17	29	. 62	170

APPLICATIONS

Polyurethane foams constitute a major discovery in the realm of high polymers and their unique and versatile properties make it easy to adapt it for a variety of applications and even in areas hereto dominated entirely by non-synthetic materials.^{69—72}

Rigid Foams

The low thermal conductivity and water uptake of closed cell rigid foams have ensured their entry into the thermal insulation field both in industrial and domestic appliances^{73—80} such as refrigerators, land cold stores, insulated vans for roads and rail transport, hatch covers, storage tanks, insulation for liquid gas pipelines chemical plants etc. The value of an insulant in practical insulation to prevent the transmission of heat depends not only on the magnitude of thermal conductivity and but also on the ease of application to the installation in situ. Urethane foams serve exceptionally well as they possess the advantage of being foamed in situ. When foamed like this, a continuous skin is formed on the outside surface of the foam and these help to reduce the water intake. Resistance to burning is an important property of an insulant and the initial experiments conducted by ICI show that there will be negligible rise in temperature on the inner surface of the insulation even during welding through the foam. A marked advance in this direction has been the use of tri-β-chloroethyl phosphate in the foam manufacture which confers self extinguishing properties to finished foam.

An attractive defence application⁸¹⁻⁸³ of rigid foam is in the construction of troop shelters, which can be built in a convenient place and can be transported to remote areas by helicopter and this is made all the more easy by the good binding strength of polyurethane foam to light weight structural materials. The U. S. Army Engineers of Research and Development laboratories have produced an experimental building and it is reported that these foam buildings have low thermal conductivity and negligible water absorption. From the Army's point of view, the outstanding contribution of this concept is the logistical problem it may solve. A change in the formulation provides material for producing structure suitable for tropic and moderate climates. In addition to its use in this particular fashion it can also be used to make beams, roofing and foundation materials.

The commercial applications of rigid foams in radomes in high speed aircraft and radar scanner have been developed mainly because of the ability of the foam to allow magnetic and electrical beams, to pass through it efficiently. The high dielectric constant and low weight of rigid foams make them ideally suited for applications in the electronic industry such as potting and encapsulating electrical components, microwave absorbers, etc. Apart from void filling and structural reinforcements a practical industrial use is for the embedment of electronic component and circuits⁸⁴. Either precut foam shapes or prepolymer for inplace spray foaming can be used for these operations.

Fabrication of sandwiched panels 85-87 using polyure than e foams are finding increasingly wide application in many diverse fields, where a combination of a high strength to weight ratio and excellent thermal insulation are required. This has been completely exploited in the manufacture of light weight roofs, doors, and floors in road, rail and air transport.

Open cell rigid foams have become widely accepted 88 as filter mediums particularly in room air conditioners. These are produced by a special process. These filters are oil resistant and can be conveniently cleaned without matting or separation. Heat resistant urethane rigid foams have already found a large scale application in U. S. A. missiles and aircraft where high temperatures are encountered. Because of the low density of urethane rigid foams, they have been used in many buoyant structure. The U. S. Army has recently reported the use of urethane rigid foams in "flying boots" which enable the troops to cross water without any difficulty. This obviously depends both on the percentage of closed cells and on the inherent strength of the foam as such.

Semi-rigid and flexible urethane foams have found commercial acceptance in industrial packagings such as for protection for precision optical and electronic instruments, missile components, missile containers for transporting missiles and cushions for recoverable targets drone during parachute landing.....etc.

Flexible Foam^{89.93}

The principal application of flexible foams is in upholstery of various types and this uses the capacity of foam to cushion the effect of variable loads. In general, open and inter connecting cellular structures are the necessary characteristics of cushioning materials. Though springs by themselves supply cushion, obviously they do not give comfort. When a load is applied to a flexible foam the cell walls in the indented area are either compressed or stretched resulting in the air displacement from one section to another and thus the innu merable tiny springs spread the load in such a way that additional padding is not recessary.

Adherence to stress-strain relationship is one of the basic properties that is measured to give an indication about the suitability of the material for cushions. Detailed study of this has shown that urethane foams have stress-strain curve which differ from that of foamed latex. However, with latex foam, performance is usually related to the density of the foam, the lower the density the lower is the weight it supports at the same compression. But urethane foams can be manufactured with the same density and wide range of compression characteristics. In general, polyester foam is stiffer than latex and hence it is not much useful in parts where applied forces are small. However, by a special treatment called 'profiling' it has been possible to improve the shape of the curve. Polyether foam curve very closely approaches that of latex and thereby presents a keen competition to the latter. It is significant to note here that urethane flexible foams have comparatively low permanent set and are quite resistant to repeated flexing.

Hysteresis curves for flexible foams based on polyether have been compared with that of latex foam. Polyether and latex foam have almost similar pattern of hysteresis curve while polyester presents a marked deviation. The initial stress required to deflect a polyester foam is greater than that of latex and polyether foams and the unloading curve has a low energy return. Since the area between the loading and unloading curves is the effective energy absorbed by the foam, flexible polyester foams can take a greater shock without transmitting it. Flexible foam show a 370 % higher RMA compression resistance than foam latex of equal density though its elongation value is much poor compared to natural rubber.

The above two characteristic properties of flexible foams coupled with the general properties of urethane foam (such as thermal, acoustic insulation) ensure their commercial application in diverse fields. To name a few are, seat cushion, seat toppers, upholstery paddings, crash pads for tanks interiors and military vehicles of all types, life jackets, mattresses, non-skid table covers, protection coating for glassware, radio valve and other delicate instruments, thermal and acoustic insulations, sleeping bags, packaging materials over head safety padding in automobiles, radiation absorbers ⁹² etc.

A recent development in textile industry is the introduction of fabric/foam laminates. In this field, polyester flexible foam provide an apparel trade with a light weight insulating material having a softness and drape qualities unmatched by many conventional textiles. Using foam between 1/16 and 3/32 in. in thickness it has been found that cotton fabrics are given the warmth and recovery of wool and light weight wools are given the characteristics of heavier weights wool fabrics. On the basis of comparative experiments on several representative textile insulating fabrics, it has been possible to establish that for comparable thickness urethane foams can be as warm as most textile substitutes at only half the weight.

Apart from the latex foam, cellular cellulose acetate, Vinyl, phenolic, polystyrene and epoxy foams are direct competitors of urethane flexbile and rigid foams in the market. Table IV depicts the comparative properties of three competitive foams and it is clearly seen therein that polyurethane foams with their characteristic advantage of the situ foaming has a wider scope for applications in diverse fields compared to the other two.

CONCLUSION

It is clear from the above account that the amazing versatility of urethane foams foresees a bright and brilliant future. The upward trend in world usage of natural latex was reversed since 1959, largely as a result of the fall in consumption in U. K. and U. S. A. This coincides with the appearance of synthetic foams as competitors in these countries. The consumption of rubber latex by the end of the third five year plan is expected to reach the figure of 54,000 tons and yet a sizable portion of it has to be imported. In this connection, any effort to substitute the foam latex with newer indigenous synthetic materials will be of relief on our foreign exchange. Hence it will be greatly advantageous if investigations are undertaken to develop and produce urethane foams from indigenous raw materials and translate their notable properties into commercial use at least to meet the Defence needs.

TABLE IV

Serial	Properties	Urethane foam	Latex foam	Vinyl foam
No.				
1	Foaming action	Due to chemical reac-	Mechanical or chemical	Blowing agents.
2	Foaming in place	tion. Ideal	(in mould). Impossible	Limitations due to cur-
3	Heat curing	Not necessary	Necessary	Necessary
4	Formulation range	Very wide	Very limited	Wide
5	Moulds	Difficult	easy	eary
6	Ageing (high tem- perature)	very good	poor	very good
7	Solvent resistance	very good	poor	good
8	Density	2-3.0	6-7	7.0
9	Compression set at 70°C	17	4.6	**
	at 25°C	3	4.1	
10	Hysteresis loss o/°	57.8	23.2	44.8
11	Resilance	good 30—60	very good 64	34
12	Tear strength lbs/in.	very good 2·0	Fair 1.2	good 1.9
13	Tensile strength PSI	very good 20—27	Fair 10—20	good 20
14	Elongation% _	250	380	190
15	Low temperature properties.	good	very good	good
16	Thermo plasticity in welding.	very good	poor	good
17	Maximum service tem- perature °F (dry)	260	160	160
	PAPI Urethane foams st	and much higher tempera	tures.	
18	Microbiological attack	Resistant	Easily attacked	Resistant
19	Ozone	not attacked	attacked	not very stable

CHART I

(a) Chain extension

$$\begin{array}{c|c} \text{OCN-R-NH-C-O-(Polyester)}_{n} - \text{O-C-NH-R-NCO} \\ \text{Polyester-Urethane} \end{array}$$

(b) Reaction of -NCO with water

 ${\rm (Polyester-urethane)}_m{\rm -NCO} + {\rm H}_2{\rm 0}$

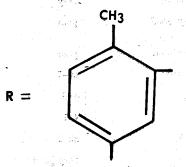
 ${\rm (Polyester_urethane)}_{m} - {\rm NH_CO-NH_(Polyester_urethane)} + {\rm CO}_{p}$

Control (1911) and state of the lead of

(c) Cross linking

$$\label{eq:polyester} \begin{split} \text{(Polyester-urethane)}_m - & \text{NH-CO-NH-(Polyester-urethane)}_m \\ + & \text{OCN-R-NH-CO-O-(Polyester)}_n \end{split}$$

and similarly further cross linkings.



Acknow'edgement—The author is greatly indebted to Dr. V. Ranganathan, Deputy Chief Scientist, Ministry of Defence and Dr. K. Subba Rao, Asstt. Director, Defence Science Laboratory, for their valuable suggestions, keen interest and kind encouragement.

REFERENCES

- 1. BAYER, O., Modern Plastics, 24 (10), 149, 250 (1947).
- 2. BAYER, O., Angew. Chem., 59, 257 (1947).
- 3. BJORKSTEN, J.A., TOVEY, H. and HOLLARD, M. L., Modern Plastics, 31 (8), 143, 228, 223 (1954).
- Katz. I., Technical Papers, 11th Annual National Technical Conference, Society of Plastic Engineers, 1, 149 (1955).
- 5. FAICHNEY, L. M., Modern Plastics Encyclopedia, 119 (1960).
- 6. Dombrow, B., Polyurethanes, Reinhold Publications (1958).
- BEUTEL, A. C., BRINKMAN, R. J., DUFF, R. O., DUMON, J. G., ELIEZER, J. S., GORHAM, R. O., HEXTER, R. M., JOHNSON, V. J. and MILLER, W. S., Polyurethanes (Polyurethanes Association).
- 8. BUIST, J. M., HURD, R. and LOWE, A., Chem. and Ind., 1544 (1960).
- 9. Buist, J. M., Plastic Inst. Trans., 30 (86), 100 (1962).
- 10. Buist, J. M., Rubber J. and Inst. Plast., 135, 792 (1958).

- 11. GHATGE, N. D., Plastic Progress in India (Annual) 42 (1961).
- 12. Hurd, R. and Hampton, H. A., Plastic Inst. Trans., 29 (84), 204 (1961).
- 13. Duno, G. and Shelton, G. G., Chem. & Ind., 1158 (1962).
- 14. Cooper, A., Plastic Inst. Trans., 29 (80), 39 (1961).
- 15. Anon., British Plastics, 35, 58 (1962).
- 16. GATTERMANN, L., Ann., 244, 30 (1888).
- 17. Basterfield, S., Woods, E.L. and Wright, J., Am. Chem. Soc., 48, 2371 (1926).
- 18. SAUNDERS, J. H. AND SLOCOMBE, H. N., R. J., Chem. Revs., 43, 203 (1948).
- 19. Arnold, R. G., Nelson, J.A. and Verbane, J. S., Chem. Revs., 57, 47 (1957).
- 20. SAUNDERS, J. H., J. RUBB. Chem and Tech., 32, 337 (1959).
- 21. BAYER, O., Ann., 549, 286 (1941).
- 22. WHITE, G. S., J. Soc. Dyers and Colourists, 70, 481 (1954).
- 23. Hopkins, R. P., Rubber Age, 78, 239 (1955).
- 24. BJORKSTEN, J. A., TOVEY, H., HARKAR, B. AND HENINNG, J., Polyesters and their applications, Reinhold Publications, 225 (1956).
- SAUNDERS, J. H., STEINGISER, P. G. GEMEINHARDT, A. S., MORECFROFT, S. AND HADY, E. D., Ind. Eng. Chem., 3, 153 DS (1958).
- 26. Saunders, J. H. et. al., Chemical Abstracts, 57, 6121.
- 27. PACKER, E. A. AND WOOD, J. F., Rubber and Plast. Age, 41 (10), 1174 (1960).
- 28. SEIZINGER, R. K., DAVISS, MCCLELLAN, J. M. AND FRISCH, K. C., Rubber Age, 85, 997 (1959).
- 29. Stevenson, A. C., Rubber Age, 77, 63 (1955).
- 30. Swensson, S., Brit. J. Med., 12, 50 (1955).
- 31. Fromandi, K., Rubber Age, 73, 527 (1953).
- 32. GMITTER, G. T. AND GRUBBER, Rubber Age, 83, 83 (1959).
- 33. COOPER, W., PEARSON, R. W. AND PARKER, S., Industrial Chemist, 36, 121 (1960).
- 34. SMITH, C. H. AND PETERSON, C. A., Society of Plastic Engineers Journal, 18, 455 (1962).
- 35. Sunto, G., Rubb. and Plast. Age, 43, 458 (1962).
- 36. BAKER, J. W. AND HOLDSWORTH, J. B., J. Chem. Soc., 713 (1947).
- Heiss, H. L., Saunders, J. H., Morris, M. R., Davis, B. R. and Hardy, E. E., Ind. Eng. Chem., 46, 1498 (1958).
- 38. ALZNER, B. G. AND FRISCH, K. C., Ind. Eng. Chem., 51, 715 (1959).
- 39. GMITTER, G. T. AND GRUBBER, E. E., Society of Plastic Engineers Journal, 15, 957 (1959).
- 40. FARKAS, A., MILLS, G. A., ERNER, W. E. AND MAERKAR, J. B., Ind. Eng. Chem. 51, 1299 (1959).
- 41. SAUNDERS, J. H., J. Rubber Chem. and Tech., Rubber Reviews, 33 (5), 1259 (1960).
- 42. HOSTETTLER, F. AND COX, C. E., Rubber World, 140, 87 (1959).
- 43. SAUNDERS, J. H., J. Rubb. Chem. and Tech., Rubber Reviews, 33 (5), 1293 (1960).
- 44. Frensdorff, H. K., Rubber Age, 83, 813 (1958).
- 45. Klesper, E., Rubber Age, 84, 84 (1958).
- 46. Buist, J. M., Proc. Inst. of Refrigeration (1959-60.)
- 47. DOHERTY, D. J., HURD, R. AND LESTER, G. R., Chem. & Ind. 1340 (1962).
- 48. Brown, W. E., AND SAUBE, W. J., Modern Plastics, 36 (12), 107 (1959).
- 49. PARMALEE, H. M., XLIVth Semi Annual meeting of ASRE, Chicago (1957).
- FERBARI, R. J., SINNER, J. W., BULL, J. C. AND BRUCOKSCH, W. R., Ind. Eng. Chem., 50, 1041 (1958).
- 51. ERNER, W. E., FARBAS, A. AND HELL, P. W., Modern Plastics, 37 (6), 107 (1960).
- 52. Duno, G. K. And Shelton, C. G., Chem. and Ind., 1158 (1962).

- 53. Anon., Modern Plastics, Encyclopedia, 1107 (1961),
- 54. Buist, J. M., Rubber and Plast. Age, 41, 38 (1960).
- 55. Anon., Rubb. and Plast. Age, 42, 1460 (1961).
- 56. Anon., Rubb. and Plast. Age, 42, 520 (1961).
- 57. WATTS, J. T., Plastic Inst. Trans., 26, 289 (1958).
- 58. EISENNMANN, K. H., Rubber and Plastic Age, 43, 459 (1962).
- 59. Anon, Rubber and Plastic Weekly, 143 (13), 465 (1962).
- 60. A. S. T. M., D 1564-59 T.
- 61. B. S. 3379 (1961).
- 62. Buist, J. M. and Lown, A., Plastics Inst. Trans., 27 (67), 13 (1959).
- 63. Hurd, R., Bulletin of International Institute of Refrigeration, 195 (1957-1).
- 64. I. C. I. Technical Literature, Pe/U 5.
- 65. I.C.I. Technical Literature, Pc/U 21.
- 66. HARDING, H, AND JAMES, B. F., Modern Plastics, 39 (7), 133 (1962).
- 67. Buist, J. M., Trans. I.R.I., 33, 102 (1957).
- HARRINGTON, C. J., Technical Papers, 12th National Technical Conference, Society of Plastic Engineers, 2, 1380 (1956).
- 69. Anon., Modern Plastics, 36 (7), 91, 36 (8), 109 (1959).
- 70. VOORHEES, H., Modern Plastics Encyclopedia, 734 (1960).
- 71. Dombrow, B., Modern Plastics Encyclopedia, 286 (1960).
- 72. SIMONS, L. F., Modern Encyclopedia, 216 (1960).
- 73. BROCHAGEN, F. K., British Plastics, 35 (3), 131 (1962).
- 74. HALLIMAN, M. R., HIMMLER, W. A. AND KAPALAN, M., Paint India, 15 (June 1962).
- 75. Buist, J. M., Modern Refrigeration, 62, 735 (1959).
- 76. Anon., Society of Plastic Industry Cellular Plastics Div. Ra (N.Y.), 79, 803 (1956).
- 77. Anon., Materials in Design Engineering, 54 (1), 10 (1961).
- 78. ABBOTSON, W., BUIST, J. M. AND LOWE, A., World Refrigeration and Air Conditioning, 12, (8), 38 (1961).
- 79. Anon., Modern Plastics, 38 (8), 96 (1961).
- 80. Anon., Chemical Processing, 8, 26 (1962).
- 81. SWENSON, S. B. AND MACCLARANCE, J., Modern Plastics, 38, (12), 78 (1961).
- 82. Anon., Plastic World, 68 (Feb 1962).
- 83. Anon., Plastic World, 135 (Oct. 1961).
- 84. JENNINGS, R., Society of Plastics Engineers, 319 (1960).
- 85. Anon., British Plastics, 35 (5), 234 (1962).
- 86. Anon., Rubber and Plastic Age, 343 (10), 1140 (1962).
- 87. Anon., Chemical Age, 88, 230 (1962).
- 88. RILEY, M. W., Materials in Design Engineering, 53 (3), 119 (1961).
- 89. CARR, J. A. AND WILLIAMS, B., Modern Plastics, 33 (1), 114 (1955).
- 90. Anon., Modern Plastics, 32 (12), 102 (1955).
- 91. Anon., Bedding Upholstery and Furniture, 27, 264, 323 (1962).
- 92. Anon., Modern Plastics, 35 (4) 200 (1958).
- 93. WHINSTOCK, L., Man-made Textiles, 38 (444), 46 (1961), 38 (446), 50 (1961).
- 94. Rulber Trends, 14th (June 1962).