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SEVENTH EDITION

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Polyurethanes

NORBERT ADAM, Bayer MaterialScience AG, Leverkusen, Federal Republic of Germany (Chap. 7.3)

GEZA AVAR, Bayer MaterialScience AG, Leverkusen, Federal Republic of Germany (Chap. 7.2, 7.4, 8.1 and 15)

HERBERT BLANKENHEIM, Bayer MaterialScience AG, Leverkusen, Federal Republic of Germany (Chap. 10)

WOLFGANG FRIEDERICHS, Bayer MaterialScience AG, Dormagen, Federal Republic of Germany (Chap. 1, 2, 3, 4, 5, 11 and 13)

MANFRED GIERSIG, Bayer MaterialScience AG, Leverkusen, Federal Republic of Germany (Chap. 14.1, 14.2 and 14.3)

ECKEHARD WEIGAND, Bayer MaterialScience AG, Leverkusen, Federal Republic of Germany (Chap. 14.1, 14.2 and 14.3)

MICHAEL HALFMANN, Bergische Universität Wuppertal, Wuppertal, Federal Republic of Germany (Chap. 14.4)

FRIEDRICH-WILHELM WITTBECKER, Bergische Universität Wuppertal, Wuppertal, Federal Republic of Germany (Chap. 14.4)

DONALD-RICHARD LARIMER, Bayer MaterialScience AG, Leverkusen, Federal Republic of Germany (Chap. 12)

UDO MAIER, Bayer MaterialScience AG, Leverkusen, Federal Republic of Germany (Chap. 6)

SVEN MEYER-AHRENS, Bayer MaterialScience AG, Leverkusen, Federal Republic of Germany (Chap. 7.1)

KARL-LUDWIG NOBLE, Bayer MaterialScience AG, Leverkusen, Federal Republic of Germany (Chap. 9)

HANS-GEORG WUSSOW, Bayer MaterialScience AG, Leverkusen, Federal Republic of Germany (Chap. 8.1)

1. Introduction

Polyurethane (PUR) is the collective name for an extensive group of polymers with very different compositions and correspondingly varied property profiles. All PURs are built on a common principle: they are produced by the polyaddition process [1, 2] of (poly)isocyanates typically with (poly)alcohols. The characteristic chain link is the urethane group. In most cases two or more closely positioned urethane groups link poly(alkylene ether) and/or polyester sequences with molecular masses between ca. 200 and 6000 g/mol. Thus, the urethane group usually is only present to a minor extent.

PURs also include polymers produced from polyisocyanates that have urea, isocyanurate, or carbodiimide groups as their characteristic structural unit. As a result of the increasing importance of di- and polyamines and water as reactants, most of the industrially produced PURs contain urea groups (including the isocyanurates as cyclic ureas) as their main property-determining structural units.

A PUR is usually understood to be the fully reacted finished product (e.g., foams and coatings). These products are free from monomeric isocyanates, and unconsumed isocyanate groups, which may be present in small amounts, are bound to the PUR matrix. In adhesives and paints, the isocyanate-containing precursors are often called "PUR adhesive," "PUR hardener," or "PUR paint" to indicate the field of application of the end product produced from them.

The diisocyanate polyaddition process for synthesizing PURs is characterized by the following statements:

1) A large number of different reactants (monomers and oligomers) are available.
2) It is an exothermic reaction that can even take place at room temperature. No byproducts need be separated.
3) The reaction rate can be controlled over a wide range by catalysts, and in some cases a specific reaction can be accelerated by careful choice of the catalyst (e.g., tin compounds catalyze the urethane reaction, tertiary amines catalyze the isocyanate-water reaction; see Section 7.1.1).
4) Intermediates (prepolymers) with reactive end groups can be produced.
5) The stoichiometry influences the molecular mass (see Section 5.2.2).
6) Production and composition can be adapted to various process techniques and extremely diverse product requirements.
7) A large number of end products can be made.

Besides their unique properties, one of the main advantages of PURs is that all types of articles (foams, elastomers, thermosets) can be produced starting from liquid reactive components. This has led to their great industrial importance (see Section 5.2.1 and Chap. 5.2.1 and 15).

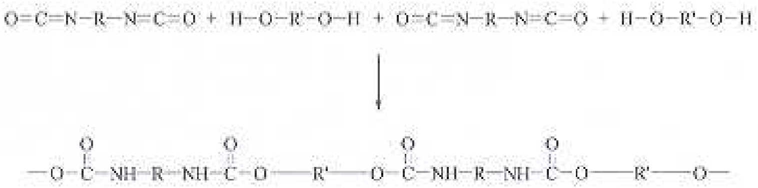
PUR products include highly elastic foams (mattresses, cushions, car seats), rigid foams (insulation materials); rigid and flexible moldings with compact skins (window frames, housings, skis, damping units such as car shock absorbers, front- and rear-end body parts, steering wheels, and shoe soles); engineering moldings with a high hardness and elasticity, ski boots, films, hoses, blow-molded parts, noise shields for trucks, seals for stoneware pipes, roller coatings, sealants, grouting compounds, surfacings for sport and play areas, off-road tires, windsurfing equipment, hydrocyclones, fenders, printing rollers, cable sheathing, catheters, high-quality paints, corrosion protection for steel-reinforced concrete, adhesives, textile coatings, high-gloss paper coatings, leather finishes, poromerics, glass fiber sizes, and wool finishing agents. The number and range of applications are constantly growing. The production, properties, technology, and use of PURs are reviewed in [3–13].

2. Basic Reactions [3, 4, 8]

The addition reaction of an alcohol to an isocyanate to give an urethane (carbamate) has been known since 1849 (Wurtz):

$$R{-}N{=}C{=}O + H{-}O{-}R' \longrightarrow R{-}NH{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}O{-}R'$$

The extension of this reaction to di- and polyfunctional isocyanates and hydroxy compounds by Otto Bayer in 1937 led to the principle of the polyaddition reaction resulting in the formation of linear, branched, or cross-linked polymers:



$$O{=}C{=}N{-}R{-}N{=}C{=}O + H{-}O{-}R'{-}O{-}H + O{=}C{=}N{-}R{-}N{=}C{=}O + H{-}O{-}R'{-}O{-}H$$

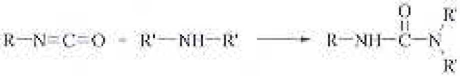
$$\big\downarrow$$

$${-}O{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}NH{-}R{-}NH{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}O{-}R'{-}O{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}NH{-}R{-}NH{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}O{-}R'{-}O{-}$$

In addition to alcohols, the most important group of NCO-reactive compounds are the amines, which lead to the formation of ureas:

$$R{-}N{=}C{=}O + R'{-}NH_2 \longrightarrow R{-}NH{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}NH{-}R'$$

Disubstituted urea



$$R{-}N{=}C{=}O + R'{-}NH{-}R' \longrightarrow R{-}NH{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}N(R')_2$$

Trisubstituted urea

Ureas are also formed by the reaction of water with isocyanates, in which the carbamic acid formed in the first step of the reaction spontaneously decomposes to an amine with elimination of carbon dioxide. This amine then reacts with excess isocyanate to yield symmetrically substituted ureas:

$$R{-}N{=}C{=}O + H_2O \longrightarrow R{-}NH{-}COOH$$

$$\longrightarrow R{-}NH_2 + CO_2$$

$$R{-}N{=}C{=}O + R{-}NH_2 \longrightarrow R{-}NH{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}NH{-}R$$

Disubstituted urea

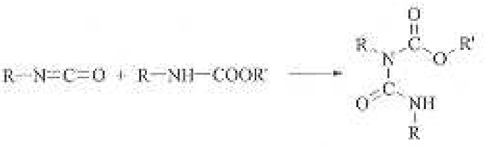
This reaction is the basic reaction leading to PUR foams, especially flexible foams.

Another process which leads to the formation of carbon dioxide is the reaction of isocyanates with organic acids. The reaction product formed in this way is an amide:

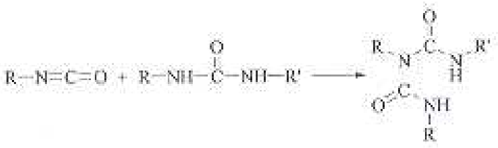
$$R{-}N{=}C{=}O + R'{-}COOH \longrightarrow R{-}NH{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}R' + CO_2$$

Amide

As the urethanes and ureas formed in the reaction mentioned above still contain reactive hydrogen atoms they can react with excess isocyanate to form allophanates and biurets, respectively.



Allophanate



Biuret

These cross-linking reactions are important in the production of PURs and play a key role in the development of polymeric materials with tailor-made properties.

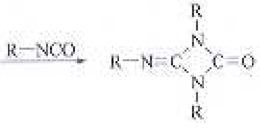
Apart from these polyaddition reactions, the following reactions involving two or more isocyanate groups are also important in PUR chemistry (catalyst in parentheses):

Uretdione

Isocyanurate

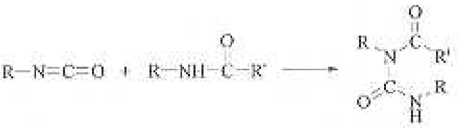
$$2\ \mathrm{R{-}N{=}C{=}O} \xrightarrow[\text{(phospholine oxide)}]{} \mathrm{R{-}N{=}C{=}N{-}R} + \mathrm{CO_2}$$

Carbodiimide

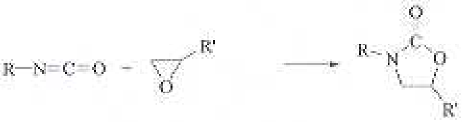


Uretonimine

Due to the high reactivity of the isocyanate group some further reactions are well known but only of minor importance in the production of PURs. Examples are the reactions of amides and epoxides with isocyanates:



Acylurea



Oxazolidone

The tremendous number of different possible reactions not only play a role in the production of the final PUR polymers but also in the production of modified polyisocyanates (see Section 3.1) used as raw materials for PURs.

Usually the reactions described above proceed in parallel. For example, the production of foams is based on the combination of the NCO/ROH reaction leading to urethanes and the NCO/H_2O reaction leading to ureas and causing foaming of the reaction mixture by the evolution of carbon dioxide.

Other methods for preparing PURs which are usually not used in industrial applications are the polycondensation of bis-chloroformate esters and diamines, and the reaction of polyamines with carbonylbiscaprolactam (CBC) or polycyclocarbonates.

Thermally stable *N*-alkyl PURs are formed by the reaction of isocyanates with secondary diamines (e.g., piperazine). Since these products are unable to form hydrogen bonds, their properties are different from those of conventional PURs.

3. Starting Materials [3]

The range of PUR starting materials developed since the early 1950s is based on light petroleum fractions (ethylene, propene, naphtha). To a minor part renewable raw materials (natural products such as sugar, castor oil, etc.) are used [14–16]. The suitability of natural fatty acid esters [17, 18], lignin [19, 20], polysaccharides [19, 21, 22], and chitin as raw materials has been examined for special applications.

3.1. Polyisocyanates

See also → Isocyanates, Organic

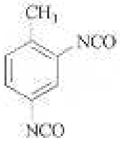
More than 90 % of PURs are produced from aromatic polyisocyanates. Compared to aliphatic and cycloaliphatic polyisocyanates, the aromatic polyisocyanates show higher reactivities towards hydroxyl compounds and give PURs with better mechanical properties.

The aliphatic and cycloaliphatic polyisocyanates are used to obtain PURs that do not become discolored on exposure to light or heat. This is particularly important for coating materials (paints, varnishes, textile coatings, and glass-fiber sizes). The stability of aliphatic or cycloaliphatic polyisocyanates PURs can be improved by incorporating urea, biuret, or hydrazide groups into the polymer [23–25].

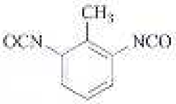
3.1.1. Aromatic Polyisocyanates

Aromatic polyisocyanates are primarily used for a wide variety of PUR foamed plastics, elastomers, thermosets, and adhesives.

2,4-Toluenediisocyanate [*584-84-9*] (TDI), 2,4-diisocyanatotoluene (**1a**), *bp* 121 °C (1.33 kPa), *mp* 21.8 °C.



1a



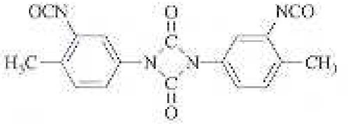
1b

Usually the pure 2,4 isomer or mixtures of 2,4-TDI (**1a**) with 2,6-TDI (**1b**) are used for industrial applications:

TDI 80 (80 % 2,4-TDI, 20 % 2,6-TDI), *bp* 121 °C (1.33 kPa) *mp* 13.5 °C, vapor pressure (25 °C) 3 Pa, equilibrium vapor concentration 30 ppm, MAK value 0.005 ppm (according to TRGS 900).

TDI 65 (65 % 2,4-, 35 % 2,6-), *bp* 121 °C (1.33 kPa), *mp* 5 °C.

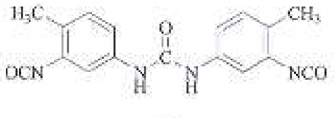
1,3-Bis(3-isocyanato-4-methylphenyl)-2,4-di-oxo-1,3-diazetidine [*26747-90-0*] (**2**) (uretdione of 2,4-TDI, TDI-dimer; Desmodur TT, Bayer MaterialScience), *mp* 153 °C.



2

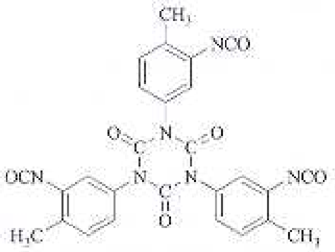
Uretdiones react as blocked isocyanates: the four-membered ring opens at elevated temperature to release the NCO groups.

"TDI-urea" [*5206-52-0*] (**3**) (TDIH, Bayer MaterialScience) *mp* 180–184 °C [26, 27]



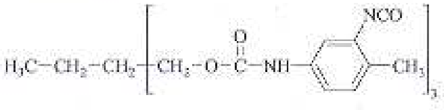
3

1,3,5-Tris(3-isocyanato-4-methylphenyl)-2,4,6-trioxohexahydro-1,3,5-triazine [*20649-21-6*] (**4**) (TDI-trimer), ca. 51 % in butyl acetate (Desmodur IL, Bayer MaterialScience): NCO content ca. 8 %, viscosity (20 °C) 2000 ± 500 mPa · s.



4 (idealized)

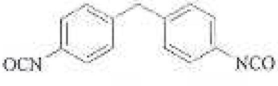
Adduct of TDI and trimethylolpropane [*21092-47-7*] (**5**), 75 % solution in ethyl acetate (Desmodur L, Bayer MaterialScience): NCO content 13 ± 0.5 %, viscosity (20 °C) 2000 ± 500 mPa · s.



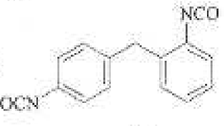
5

Monomeric MDI, 4,4′-Methylene diphenyl diisocyanate [*101-68-8*], 4,4′-methylenebis(phenyl isocyanate), bis(4-isocyanatophenyl)methane, 4,4′-diisocyanatodiphenylmethane (**6a**), Monomer-MDI, *bp* 208 °C (1 kPa), *mp*

39.5 °C, vapor pressure (25 °C) < 1 mPa, equilibrium vapor concentration 0.009 ppm, MAK value 0.005 ppm (according to TRGS 900)



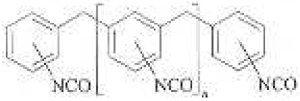
6a



6b

60 % 2,4′-MDI (**6a**), 40 % 4,4′-MDI (**6b**) (Desmodur 1806, Bayer MaterialScience), *mp* 16–17 °C.

Polymeric MDIs (PMDIs) [*9016-87-9*] (**7**) typically contain 30–70 % dinuclear components (n = 0), 14–40 % trinuclear components (n = 1), and 15–30 % higher nuclear components (n > 1), viscosity 50–20000 mPa · s, NCO content 25–33 %.

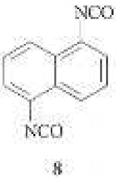


7

Urethanized 4,4′-MDI [*60440-22-4*] (Desmodur PF, Bayer MaterialScience) *mp* 10–15 °C.

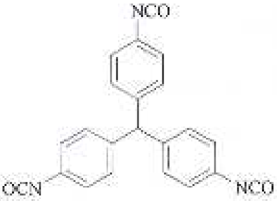
Carbodiimidized 4,4′-MDI [*37353-55-2*], *mp* 10–15 °C (Desmodur CD, Bayer MaterialScience; for carbodiimidization, see Chap. 2).

1,5-Naphthalene diisocyanate (NDI) [*3173-72-6*], 1,5-diisocyanatonaphthalene (**8**), *mp* 127 °C (Desmodur 15, Bayer MaterialScience).



8

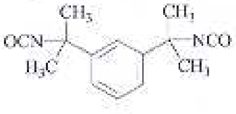
Tris(4-isocyanatophenyl)methane [*2422-91-5*] (**9**), (Desmodur R, Bayer MaterialScience), 20 % solution in ethyl acetate, NCO content 7 ± 0.1 %, viscosity (20 °C) ca. 1 mPa · s.



9

Aromatic isocyanates with the NCO group in the benzylic position behave similarly to the (cyclo-)aliphatic isocyanates with regard to reactivity and light stability:

1,3-Bis(1-isocyanato-1-methylethyl)benzene [*2778-42-9*] (**10**), *m*-tetramethylxylylene diisocyanate (TMXDI, American Cyanamid) [28, 29], *mp* –10 °C, *bp* 150 °C (49.5 kPa).



10

3.1.2. Aliphatic Polyisocyanates

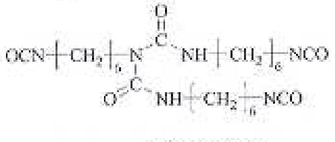
Aliphatic and cycloaliphatic polyisocyanates are used to obtain light-stable PURs. This is particularly important for coating materials (paints, varnishes, textile coatings, and glass-fiber sizes).

Hexamethylene diisocyanate (HDI) [*822-06-0*], 1,6-diisocyanatohexane (**11**) (Desmodur H, Bayer MaterialScience), *bp* 127 °C (1.33 kPa).

$\mathrm{OCN}{-}\!\left[\mathrm{CH_2}\right]_6\!{-}\mathrm{NCO}$

11

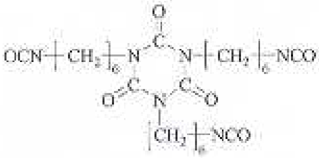
Biuret based on HDI, *N*-isocyanatohexylaminocarbonyl-*N*,*N*′-bis-(isocyanatohexyl) urea [*28182-81-2*] (**12**), biuret triisocyanate (technical mixture), ca. 75 % solution in methoxypropyl acetate/xylene (1/1) (Desmodur N75, Bayer MaterialScience), NCO content 16–17 %, viscosity (20 °C) 250 ± 100 mPa · s.



$\mathrm{OCN}{-}\!\left[\mathrm{CH_2}\right]_6\!{-}\mathrm{N}(\mathrm{C{=}O}{-}\mathrm{NH}{-}\!\left[\mathrm{CH_2}\right]_6\!{-}\mathrm{NCO})\mathrm{-C(=O)-NH}{-}\!\left[\mathrm{CH_2}\right]_6\!{-}\mathrm{NCO}$

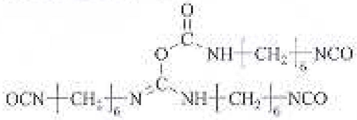
12 (idealized)

Trimer based on HDI, 2,4,6-trioxo-1,3,5-tris(6-isocyanatohexyl)hexahydro-1,3,5-triazine [*28182-81-2*] (**13**), trimeric hexane diisocyanate, ca. 90 % solution in butyl acetate (Desmodur N3390, Bayer MaterialScience), viscosity (25 °C) 2500 ± 500 mPa · s, NCO content 21.5 %, monomer content < 0.5 %.



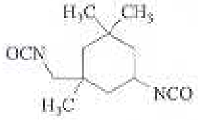
13 (idealized)

Unsymmetrical trimer based on HDI, 2,4-dioxo-3,5-bis(6-isocyanatohexyl)-6-(6-isocyanatohexyl)hexahydro-1-oxa-3,5-diazine [*28182-81-2*] (**14**), unsymmetrical trimeric hexane diisocyanate [30] (Desmodur XP2410, Bayer MaterialScience), viscosity (23 °C) ca. 700 mPa · s, NCO content ca. 24 %, monomer content <0.3 %.



14 (idealized)

Isophorone diisocyanate (IPDI) [*4098-71-9*], 3,5,5,-trimethyl-1-isocyanato-3-isocyanatomethylcyclohexane (**15**) (IPDI, VEBA), *bp* 158 °C (1.33 kPa), 70 % cis, 30 % trans [31, 32]. For reactivity, see [33].

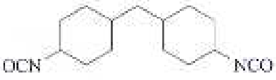


15

Uretdione of IPDI (Crelan TP.LS 2147) [34], *mp* 105–115 °C, ca. 15.4 % NCO.

Trimer based on IPDI, 2,4,6-trioxo-1,3,5-tris(5-isocyanato-1,3,3-trimethylcyclohexylmethyl)hexahydro-1,3,5-triazine [*53880-05-0*], ca. 70 % solution in xylene/methoxypropyl acetate (1/1) (Desmodur Z4470, Bayer MaterialScience), softening range 90–110 °C, NCO content 17 %, monomer content < 0.5 %.

1,1-Methylenebis(4-isocyanatocyclohexane), H12-MDI [*5124-30-1*], 4,4′-diisocyanatodicyclohexylmethane (**16**), trans,trans-4,4′-diisocyanatodicyclohexylmethane, *mp* 83 °C [35]. Technical isomer mixture (24 % *cis,cis*, 43 % *cis,trans*, 20 % *trans,trans*, 13 % 2,4 and 2,2′ isomers): *mp* 15 °C (Desmodur W, Bayer MaterialScience)



16

The short chain polyols usually have OH numbers of 200 mg KOH/g or more, functionalities of up to 6, and molecular weights of 1000 g/mol or less (Table 2).

3.1.3. Blocked Isocyanates [36–39]

Polyisocyanates or prepolymers containing NCO groups are not stable on storage in the presence of atmospheric humidity or compounds that contain reactive hydrogen atoms.

Reaction of the NCO groups with certain organic compounds that have acidic hydrogen atoms such as phenol, cresol, nonylphenol, caprolactam, and methyl ethyl ketoxime leads to "blocked isocyanates," which are stable (storable) at room temperature and labile at elevated temperatures. These adducts are inert to polyols at room temperature and can be mixed with them in one-pack systems. At higher temperatures, usually at 140–180 °C the blocking agent is released, and the free isocyanate reacts as usual with the NCO-reactive components. Due to their thermal lability, uretdiones and uretonimines also behave like blocked isocyanates.

For the physical blocking of solid polyisocyanates by a diffusion barrier layer, see Section 5.4.

3.2. Polyols

Polyols are the largest group of PUR starting materials. The wide range of properties of the resulting PURs is largely determined by the chemical composition and molecular mass of the polyols. The largest group of polyols used for PURs is the group ofpolyethers. The volume of polyesters is much smaller, but they nevertheless have become more important, especially for flame-retarded rigid foams (see Section 7.3.4).

3.2.1. Polyether Polyols

See also → Polyoxyalkylenes

Polyethers (polyether polyols) with terminal hydroxyl groups are produced by addition of cyclic ethers, especially propylene oxide (PO, $R'=CH_3$) and ethylene oxide (EO, $R'=H$), to polyfunctional "starter" molecules.

Usually, the EO and PO units can be structured as homo blocks, produced by batchwise addition of EO and PO to the starter molecule, or as mixed blocks by feeding an EO/PO mixture to the starter. The combination PO block-mixed block-EO block is common.

The structure determines the reactivity, the hydrophobic-hydrophilic properties, the surface activity, and consequently the foaming behavior of the polyethers. Polyols with terminal EO units contain primary hydroxyl groups and consequently have a higher reactivity than polyols with the secondary hydroxyl groups of terminating PO units.

The following starters are typically used industrially: ethylene glycol (EG), 1,2-propanediol (PG), bisphenol A (BPA), Trimethylolpropane (TMP), glycerol (GLY), pentaerythritol, sorbitol, sucrose, water, ethylenediamine (EDA), and diaminotoluene (TDA). Monofunctional polyethers are usually started with 1-butanol.

Depending on their structure, two groups of polyethers can be distinguished: long-chain polyols, mainly used for flexible foams, and short-chain polyols, mainly used for rigid foams.

The long-chain polyols typically have hydroxyl numbers below 100 mg KOH/g and functionalities of 2 to 3, which corresponds to molecular weights of 2000 g/mol or more. The properties of some long-chain polyols are given in Table 1.

Polyethers produced from trifunctional starters and bifunctional cyclic ethers (e.g., epoxy resins) are highly branched and, to some extent, intramolecularly cross-linked [40]. Special polyethers contain, for example, quaternary ammonium or sulfonate groups [41, 42].

An important special polyether is polytetrahydrofuran [43], which is described in detail elsewhere (→ Polyoxyalkylenes). It is used mainly for the production of high-grade elastomers for the engineering field and is liquid above 40 °C [44, 45].

A newer process, known as the IMPACT process, uses double metal cyanides (DMC) as catalysts for the production of especially long chain polyether polyols [46–48] that show improved properties compared to polyols produced by the classical KOH process. During the addition of

Table 1. Properties of long-chain polyether polyols

Starter	Alkylene oxide	Functionality	M_r, g/mol	OH no., mg KOH/g	Viscosity (25 °C), mPa · s
PG	PO/EO	2	4000	28	870
PG	PO	2	2000	56	310
TMP/PG	PO	2.8	3750	42	630
GLY	PO/EO	3	4800	35	860

Table 2. Properties of short-chain polyether polyols

Starter	Alkylene oxide	Functionality	M_r	OH-no., mg KOH/g	Viscosity (25 °C), mPa · s
TMP	PO	3	435	385	600
TMP	PO	3	305	550	1800
EDA	PO	4	350	620	19200
TDA	PO/EO	4	475	470	8000
Sucrose/PG	PO	3.1	385	450	15000

propylene oxide to the starter molecule, base-catalyzed isomerization of propylene oxide to allylic alcohol, which itself can act as starter molecule, leads to a mono-ol containing a double bond. These side products lower the average functionality of the polyols and reduce, for example, their stability against oxidation. The IMPACT process leads to polyols with extremely low mono-ol contents and therefore a low level of unsaturation and results in polyols with functionalities very close to the theoretical number. The IMPACT polyols have become more and more important, especially in the production of flexible foams.

Products based on polyethers have good low-temperature behavior and usually high hydrolytic stability. The viscosity of the liquid polyethers is relatively low (40–15000 mPa · s). A disadvantage of polyether polyols is that they undergo thermooxidative degradation on exposure to heat and atmospheric oxygen; UV radiation is mainly responsible for light-induced degradation changes. Both antioxidants and UV stabilizers counteract this degradation. In some special applications polyether polyols containing hydrazide or urea groups, both of which have a stabilizing effect, are used to avoid thermooxidative degradation.

Polyether dispersions (two-phase systems with a solid polymer as the disperse phase) are a further group of polyethers. Mainly styrene-acrylonitrile polymers (SAN polyols), polyurea, or poly(hydrazodicarbonamide) polymers (PHD polyols) are used as fillers. The dispersions are milky white, of higher viscosity than the corresponding base polyols, and completely stable to sedimentation. The average particle diameter is ca. 1 μm.

3.2.2. Polyester Polyols

Compared with polyethers, polyesters with terminal hydroxyl groups show outstanding resistance to light and thermal aging. PURs produced from them are therefore primarily used for paints, coating materials, and, due to their thermal stability, for flame-retarded rigid foams. Special types are suitable for high-grade PUR elastomers [49, 50].

Polyesters are produced by polycondensation of di- and trifunctional polyols with dicarboxylic acids or their anhydrides. Polyols commonly used are ethylene glycol, 1,2-propanediol, 1,4-butanediol, 1,6-hexanediol, neopentyl glycol, diethylene glycol, glycerol, and trimethylolpropane. Common dicarboxylic acids or anhydrides are succinic acid, glutaric acid, adipic acid, phthalic anhydride, isophthalic acid, and terephthalic acid.

The hydrolytic stability of a polyester urethane is determined by the constitution of the polyester. Polyesters synthesized from glycols and dicarboxylic acids that each contain at least five carbon atoms have good hydrolytic stability. This is because the increase in hydrophobicity of the polyester segments repels moisture [49, 50]. The best results have been obtained with polyesters derived from 1,6-hexanediol and adipic acid.

Common polyesters based on adipic acid and ethylene glycol or ethylene glycol/1,4-butanediol provide inexpensive PUR elastomers of excellent quality. Their hydrolytic stability is lower than that of the polyesters mentioned above and can be considerably improved by appropriate stabilizers (see Section 3.5).

Polyesters have a wide molecular mass distribution and, compared with polyethers, a high viscosity; many are glassy solids (polyphthalates) or crystalline (polyadipates). Polyesters containing diethylene glycol are ether esters; their viscosities are relatively low and their stability to hydrolysis and UV radiation is moderate. The average molecular mass of polyesters is 500–4000 g/mol. For properties, see Table 3.

The polyesters always contain significant proportions of the monomeric glycol used in their synthesis, as well as short-chain oligomers and often nonfunctional cyclic esters. These substances can be removed for a limited time by thin-film distillation, but they are gradually re-formed by transesterification.

3.2.3. Polycarbonate Polyols

Aliphatic carbonate esters (→ Polycarbonates) are produced by transesterification of dimethyl carbonate (DMC) or diphenyl carbonate (DPC) with glycols (e.g., 1,6-hexanediol).

Many investigations have been carried out on the production of polycarbonate by copolymerization of alkylene oxides with carbon dioxide

Table 3. Properties of polyester polyols

Acid	Glycol	Functionality	M_r	OH no., mg KOH/g	Viscosity, mPa · s
Adipic acid	ethylene glycol	2	2000	56	500 – 600 (75 °C)
Adipic acid	diethylene glycol/TMP	2.5	2300	60	900 – 1100 (75 °C)
Phthalic anhydrid/adipic acid	ethylene glycol	2	1750	64	2200 – 3200 (75 °C)
Phthalic anhydrid/adipic acid	diethylene glycol	2	560	200	6300 – 7600 (25 °C)
Terephthalic acid	diethylene glycol	2	450	250	2700 – 7700 (25 °C)

[51–55], but this reaction is not used on an industrial scale as yet.

Polyaddition of caprolactone or pivalolactone to low molecular mass diols yields hydroxy-functional polylactones.

As the susceptibility of polyesters to hydrolysis increases with increasing dissociation constant of the acid on which they are based, the polycarbonates are highly stable against hydrolysis. In particular, polyester urethanes based on 1,6-hexanediol polycarbonate show an unmatched resistance to hydrolysis.

3.2.4. Other Polyols

Other oligomers and polymers with functional groups (OH, SH, COOH, NHR) can also be used for PUR synthesis (e.g., polythioethers, polyacetals, polyester amides, alkyd resins, and polysiloxanes).

Hydroxy-functional poly(1,3-butadienes) contain the hydroxyl function mainly in the terminal position as a result of polymerization with hydrogen peroxide. These compounds yield PURs with moderate mechanical properties but extremely high hydrolytic stability and good low-temperature behavior. Bifunctional poly(1,3-butadienes) can also be obtained by anionic polymerization.

Hydroxyl-bearing polyacrylates based on 2-hydroxyethyl acrylate or methacrylate monomers are used in the production of high-quality, two-component paints [56] (see also → Paints and Coatings, Chap. 2.9).

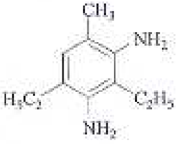
Low molecular mass polyols, in contrast to the higher molecular mass polyols mentioned above (Section 3.2.1), are used as chain extenders. In the production of PUR elastomers they are generally used in the synthesis of the "hard" segment (see Section 3.2.1 and 4.2). Important representatives are ethylene glycol, 1,4-butanediol, 1,6-hexanediol, and 1,4-bis(hydroxyethoxy)benzene.

Trimethylolpropane or glycerol is added to introduce a defined small degree of branching.

3.3. Diamines and Amino-Terminated Polyethers

Diamines are used as building blocks for PURs that contain urea groups. Due to their high reactivity the polyaddition is very fast even without a catalyst, leading to polymers with considerably improved properties compared with "standard" PURs.

For polyaddition in bulk, sterically hindered diamines (e.g., isomeric diaminodiethylmethylbenzenes **17** [57]) or other aromatic diamines with mono- or dialkyl ring substituents [58–61] are preferred.



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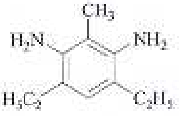

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These amines are liquid at room temperature and therefore suitable for processing in two-component devices (see Section 6.2).

Less reactive diamines with electron-withdrawing substituents are used for producing elastomers by the prepolymer process (see Section 5.2.2); examples include bis(4-amino-3-chlorophenyl)methane [*101-14-4*] (MBOCA) and 2-methylpropyl-4-chloro-3,5-diaminobenzoate [*32961-44-7*] [62–64]. For the toxicological and adverse health effects of MBOCA, see [65].

Amino-terminated polyethers (ATPE) are obtained primarily from the appropriate polyether polyols (see Section 3.2.1) by exchanging the hydroxyl groups with ammonia [66–68] or primary amines [69]. Aminopropoxy end groups are obtained by cyanoethylation of polyols followed by hydrogenation. The high reactivity of the amino groups can be reduced by using their adducts with carbon dioxide (carbonates, carbamates). During the polyaddition reaction the carbon dioxide is released and acts as a blowing agent.

Various processes have been proposed for producing ATPEs with aromatic amine end groups [70]. For example, NCO prepolymers can be hydrolyzed to give the corresponding amino-terminated prepolymers [71]. Other methods include the preparation of N-substituted crotonic acid esters by acetoacetylation of polyols followed by amination [72, 73] and nitrophenylation followed by hydrogenation [74–76].

The adducts of (cyclo-)aliphatic di- and polyamines with ketones are bis- and polyketimines, respectively. They function as capped amines, with which they are in equilibrium in the presence of water (see Section 3.1.3). In the tautomeric enamine form, they also react with NCO groups to form urea and amides. Combinations of ketimines and isocyanates are thus both moisture- and heat-curing [77–79].

Polyether ketimines based on aliphatic polyether amines have a rather low reactivity and therefore a very good processability [80–83].

3.4. Special Building Blocks

Aqueous PUR-ionomer dispersions are synthesized from diols or diamines that contain ionic groups or groups that can be converted to ionic groups by alkylation or neutralization with compounds such as *N*-methyldiethanolamine, 2-(*N*,*N*-diethylaminomethyl)-2-ethyl-1,3-propanediol, and dimethylolpropionic acid, as well as salts of 2-sulfo-1,4-butanediol, *N*-sulfoethylethylenediamine, *N*-carboxyethylethylenediamine, lysine, and glycerol 2-phosphate [84, 85].

Hydroxy-functional polyisobutylene [86, 87], siliconediamines [88–90], and chlorosulfonated polyolefins [91] can be used as oligomer building blocks leading to segmented PUR polymers.

Other special polyols can be obtained by glycolytic degradation of polymer waste [92–94] (see Section 14.3).

3.5. Catalysts and Additives

Catalysts. In order to balance the two main reactions, the isocyanate-water reaction (blowing reaction) and the isocyanate-polyol reaction (gel reaction), various catalysts are used. The reactions of the isocyanate group are extraordinarily sensitive to many different kinds of catalysts:

1) Lewis bases: 1,4-diazabicyclo[2.2.2]octane [*280-57-9*] (DABCO), triethylamine [*121-44-8*], dimethylbenzylamine [*103-83-3*], bis[2-(dimethylamino)ethyl] ether [*3033-62-3*], 1,1,3,3-tetramethylguanidine [*80-70-6*], 1,8-diazabicyclo[5.4.0]undec-7-ene [*6674-22-2*] (DBU), 2,4-bis(dimethylaminomethyl)phenol [*5424-54-4*]
2) Lewis acids: bis(ethylhexanoyloxy)tin [*301-10-0*] (tin dioctanoate), bis(dodecanoyloxy)dibutyltin [*77-58-7*] (dibutyltin dilaurate), dichlorodimethyltin [*753-73-1*]
3) Insertion catalysts: bis(dodecylthio)dibutyltin, organotin alkoxides, organotin oxides, organotin thiolates, organotin sulfides, 1,3-dicarbonyl compounds

Almost every catalyst has a specific "activity profile" [13, 95–99]. The situation is extraordinarily complex, especially since the urethane group itself exerts a catalytic effect. As hydrogen bonds and the nature of solvents used in the reaction influence the reaction rates, most kinetic studies in solvents are not applicable to solvent-free PUR production [100]. Due to the desire to reduce emanations from PUR foams less volatile or reactive catalysts have been developed [101, 102].

Metal catalysts activate the isocyanate groups by making them more electrophilic, while bases make the hydroxyl groups more nucleophilic [103].

Alkali metal salts of organic acids and phenols, as well as phenol Mannich bases catalyze not only the urethane reaction but also the trimerization of the isocyanate group. NCO prepolymers trimerize more rapidly than the corresponding diisocyanates because of the presence of urethane groups which act as cocatalysts (see Section 4.4).

Phosphines are special catalysts which dimerize the NCO group; phospholine oxides cause carbodiimidization.

Additives (see also → Plastics, Additives).

Foam Stabilizers. Besides the chemical structure and molecular weight of the polyols and isocyanates, cell size and fraction of open cells can be controlled to a certain extent by surfactants or foam stabilizers [104]. In some cases, foam formation is virtually impossible without these surface-active compounds. The majority of foam stabilizers are polysiloxane-polyether block copolymers [105–108]. Specific types, e.g., for liquid CO_2 as blowing agent [109], for flame-retarded foams [110], or for other specific foam types are available as well [111, 112].

Hydrolysis Stabilizers [113–116]. Monocarbodiimides, polycarbodiimides, epoxides, cyanates, phenyliminooxazolidines.

Oxidation Stabilizers [113–115], [117–119]. These additives are used in foamed materials, especially in flexible foams, to prevent core scorching. They include sterically hindered phenols, alkylated anilines, phosphites, hydrazides, sulfides, and thioethers.

UV Stabilizers [113–115, 117–119]. Piperidines with bulky substituents in the 2,6-positions, benzophenones, benzotriazoles, cyanoacetate ester derivatives, quenchers, Tinuvins (Ciba-Geigy).

Blowing Agents (see also → Foamed Plastics, Chap. 2.2). According to the implementation of the Montreal Protocol (and the consecutive amendments) blowing agents with an ozone-depleting potential are no longer used as blowing agents for flexible foam by the member states since 1992. Several alternatives have been developed [120–127].

For flexible foams the predominant technology meanwhile is the addition of liquid or supercritical carbon dioxide (e.g., Novaflex by Hennecke, Cardio by Cannon). Another method is the application of varied ambient pressure, e.g., MegaFoam by Hennecke or VPF by Beamech (see Section 7.1.1.2) and depending on regulations of the local authorities, blowing agents like dichloromethane or acetone may be applied as well.

For rigid foams nowadays usually alkanes, namely, n-pentane, isopentane, and cyclopentane are used (see Section 7.3.1).

Flame Retardants (see also → Plastics, Additives, Chap. 6). Various classes of chemicals are used to modify the combustion behavior of PUR flexible foams [128]. The selection of the appropriate flame retardant depends on the test that must be passed, as well as the chemistry of the foam (e.g., polyester vs polyether, HR vs. conventional foam). Most common are phosphorus- and/or nitrogen-containing compounds and halogenated phosphates such as tris(2-chloropropyl) phosphate (TCPP). As in the case of catalysts, less volatile or reactive flame-retardants have been developed in order to reduce the emissions of volatile organic compounds (VOCs) from the finished foam. The liquid flame retardants may be combined with solid ones such as melamine and ammonium polyphosphate. Brominated diphenyl ethers, which have been used for some special foam grades or in some regional markets, will be phased out due to concerns regarding their potential for bioaccumulation.

For rigid foams halogenated compounds such as TCPP, polyesters based on tetrabromophthalic acid, and special bromopolyethers are usually used. The use of polyisocyanurate rigid foams (see Section 7.3.4), which exhibit a superior flame behavior compared to PUR rigid foams, has increased. This has led to a reduction in flame retardant consumption.

Aluminum oxide trihydrate, magnesium hydroxide, and expandable graphite are also used as flame-retardants. The first two act by splitting off water vapor and the latter acts by forming protective layers.

4. Structure and Morphology

Depending on their structure, PURs cover a broad range of properties. Besides the chemical composition, the chain length, and cross-linking, the properties are significantly affected by the interactions between the polymer chains (see Fig. 1), that is to say by the supramolecular structure and morphology.

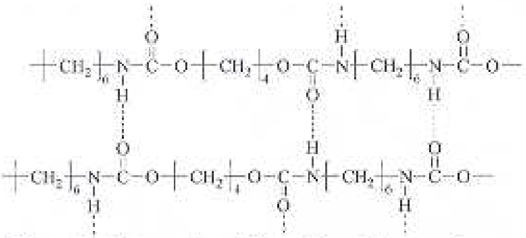


Figure 1. Hydrogen bond interactions between polymer chains of a PUR based on HDI and 1,4-butanediol

4.1. Polyurethanes Without Segmented Structure

The properties of linear PURs, which are produced by polyaddition of monomeric diisocyanates and short- or long-chain diols, are similar to those of polyamides.

Short-Chain Polyols. The polyaddition of hexamethylene diisocyanate (HDI) and 1,4-butanediol leads to a very tough, crystalline material (mp 180–185 °C), which is used for manufacturing of fibers and bristles. The polyaddition of toluene diisocyanate (TDI) and butanediol or diethylene glycol yields very hard, transparent products with low heat resistance.

Long-Chain Polyols. Linear PURs based on diisocyanates (preferably MDI) and long-chain polyester or polyether diols are soft, rubbery, high molecular mass polymers with only a small proportion of urethane groups. Therefore, these materials are homogeneous (single phase), and the intermolecular physical interactions are mainly determined by the polyester and polyether segments (van der Waals forces [129]).

With increasing stiffness of the polyol chain (e.g., highly crystalline polyesters), and decreasing chain length, the resulting PUR becomes harder and less elastic.

4.2. Polyurethanes with Segmented Structure

To obtain PUR elastomers with superior properties, the polyaddition reaction mixture usually contains three components, namely, a diisocyanate, a long-chain polyether or polyester polyol, and a short-chain diol (chain extender). The resulting block copolymer type PURs are characterized by a segmented structure.

The secondary and tertiary structures, and as a consequence, the morphology of these PURs, depend on the chemical structure and the block length of the different segments. Due to the two- or multi-phase morphology, segmented PURs can exhibit extraordinary high-grade properties.

4.2.1. Hard and Soft Segments [12, 130–135]

The reaction of one equivalent of long-chain diol, one equivalent of short-chain diol, and two equivalents of diisocyanate leads to the idealized structure shown in Figure 2.

The long-chain polyols, which are flexible and are usually tangled (soft segments), alternate along the polymer chain with oligomeric rigid urethane units (hard segments).

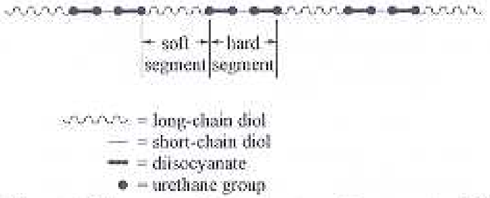


Figure 2. Schematic primary structure of a segmented PUR (idealized)

Usually the structure of the PUR as well as the structure of the soft segment itself is determined by a Flory distribution [136, 137]. This results in a smaller number of larger hard segments than expected in theory. If polyester polyols are used, the low molecular glycols, which are usually present in considerable amounts, even enhance this effect. Further effects leading to deviations from theory include kinetic effects (if end groups with different reactivity are used) and phase transitions due to temperature changes during the polyaddition reaction.

4.2.2. Segregation and Morphology

On cooling, the initially homogeneous PUR melt converts to a two-phase system. This is due to the incompatibility of the polar low-molecular glycols with the low-polarity polyether or

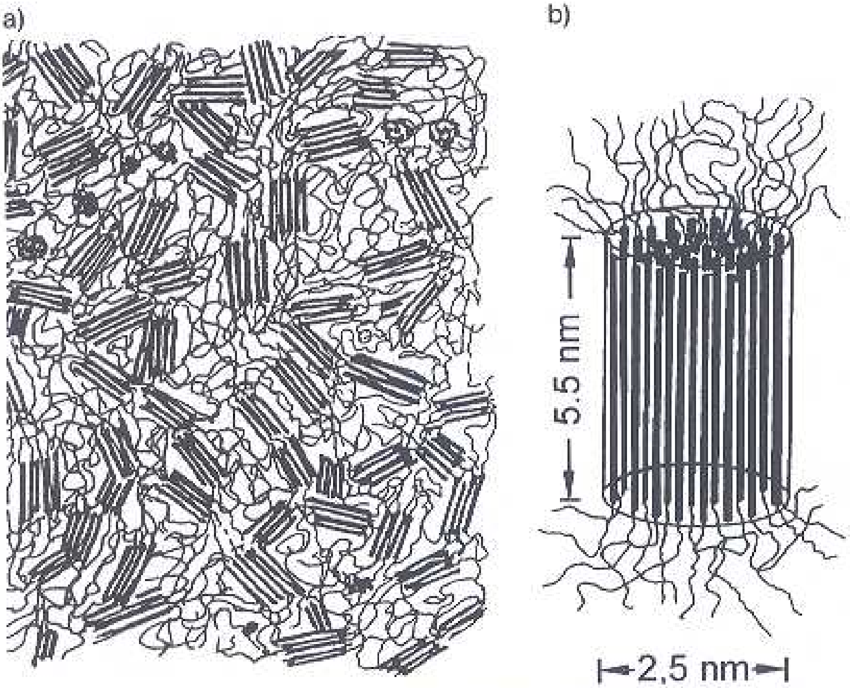


Figure 3. A) Tertiary structure of a linear segmented PUR with polydisperse soft segments and uniform (monodisperse) hard segments; B) Cylindrical model of a hard domain

polyester polyols and polyisocyanates. As the reaction progresses, the formation of polar urethane groups at the ends of the long-chain polyols leads to a certain degree of compatibilization. Nevertheless, the low miscibility of the hard and soft segments leads to segregation, which results in covalently bonded microphases in which paracrystalline oligourethane domains appear (tertiary structure, Fig. 3). On further cooling, these can aggregate and grow to form spherulitic microcrystallites (quaternary structure).

The hard segment domains form three-dimensional cross-linking centers of a noncovalent type (physical cross-linking). The formation of a large number of weak hydrogen bonds results in a high bonding strength, but allows shifts and rearrangements under load, where a covalent bond would rupture. As the hard segments are covalently bonded to the soft segments, flowability of the chains is restricted. This gives the segmented PURs their high elasticity. The hard segments are responsible for tensile strength, tear resistance, hardness, permanent elongation, and compression set, while the soft segments determine the elastic expansion and the glass transition temperature.

The interaction between different hard segment domains is mainly determined by the symmetry of the isocyanates and the nature of the chain extenders, which influence the possibility to form highly organized structures.

Most commercially produced PURs contain urea groups, which often determine the property profile more strongly than the comparatively small content of urethane groups. Since the urea group is more polar than the urethane group, the segregation of hard and soft segments is strengthened, the melting range of the hard-segment domains is higher, and the intermolecular (interchain) interaction stronger [138]. Due to these strong interactions, a single urea group shows hard-segment character. These interactions also explain the superior mechanical properties of polyureas and their low thermoplasticity.

The balance between these hard segment/hard segment interactions and the interactions between hard segments and soft segments determine the degree of segregation. Due

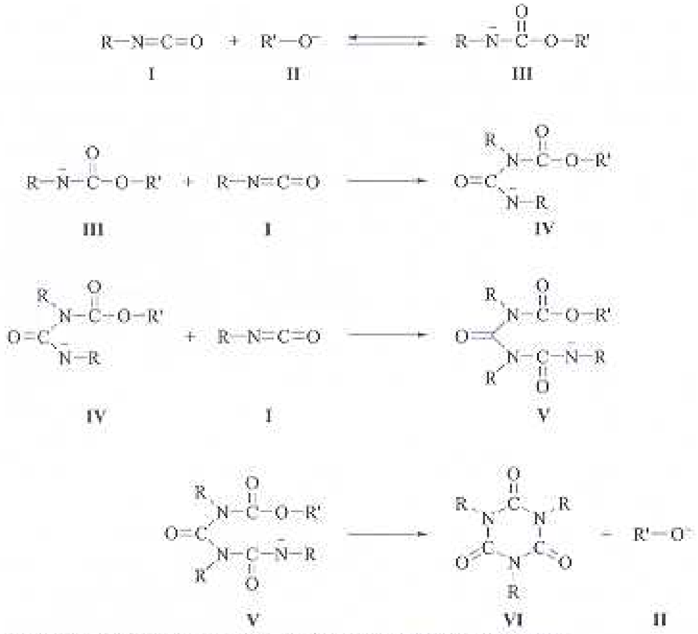


Figure 4. Mechanism of base-catalyzed isocyanate trimerization

to decreasing polarity, segregation increases from polyesters to polyethers to polybutadiene polyethers.

In the soft segments, strain-induced crystallization can be initiated by stretching or disentanglement. This strain-induced crystallization explains the high hysteresis of typical PUR elastomers [139, 140]. The mechanical properties of segmented PUR depend on the melting temperature of the crystalline domains.

Products based on 1,5-naphthalene diisocyanate (NDI) are no longer thermoplastic because the melting temperature of the hard segments is too high. They are usually produced with a small excess of isocyanate as casting elastomers (see Section 8.1). These products have extremely good mechanical properties: high tear strength, high abrasion resistance, high elasticity at high hardness, low damping, high load-bearing capacity, and excellent long-term dynamic endurance (load-bearing property) [135].

High-quality PUR thermoplastic elastomers are produced primarily from MDI. The melting temperature and the solubility of these segmented thermoplastic PURs can be influenced by modifying the chemical composition, especially of the hard segments. Use of a second short-chain diol lowers and widens the melting temperature range, and solubility is also improved.

As the properties of segmented PUR are highly determined by the phase segregation and the crystallinity of the domains, numerous production parameters [130, 131, 141–143] have tremendous influence on the behavior of thermoplastic PUR materials. Even thermoplastic PUR with monodisperse (uniform-length) N-alkylurethane hard segments, which are incapable of hydrogen bond formation show differing morphology and properties depending on their thermal pretreatment [144].

4.3. Cross-linking of Polyurethane

PUR flexible and rigid foams, cast elastomers, and most reactive systems are usually cross-linked. Even if these cross-linked PURs are not thermoplastic, the melting of the hard-segment domains is still observable, e.g., by softening (decrease in shear modulus) at elevated temperatures. With increasing cross-linking, the glass transition temperature increases, whereas the tendency to crystallize decreases.

If the cross-linking is not caused by subsequent reactions (formation of allophanate or biuret), but introduced by the use of highly functional raw materials, then the formation of segregated domains can be disturbed due to the rapid formation of a highly cross-linked PUR network, fixing the polymer chains or at least reducing their flexibility. In this case, even heating to elevated temperatures does not improve the material properties, as domain formation is not possible (e.g., in flexible foams).

4.4. Polyisocyanurates [145]

The general term PURs also covers products that contain cyclic urea structures (isocyanurates), which are formed by cyclotrimerization of isocyanate groups. The mechanism of isocyanurate formation is not completely understood. The most probable mechanism of base catalyzed trimerization [146] is shown in Figure 4.

Addition of the catalyst II to the carbon-nitrogen double bond leads to an urethane anion III, which by subsequent addition of two more isocyanate molecules I is transformed via IV to the adduct V. This adduct collapses into the stable isocyanurate VI and regenerates the catalyst II.

The isocyanurates exhibit improved mechanical properties such as compression strength and dimensional stability and generally show superior fire retardancy [147]. These advantages have led to the increasing importance of isocyanurates, especially since the blowing agent for rigid foams was switched from CFC to pentane (see Section 7.3.4).

5. Production of Polyurethanes

5.1. Stoichiometry

Isocyanates (RNCO) are specified by their percentage NCO content and in some cases also by their equivalent mass (molecular mass of NCO moiety/functionality). Functionality means the number of isocyanate groups per molecule.

$$\text{Equivalent mass} = \frac{\text{molecular mass of RNCO}}{\text{functionality}} = \frac{42}{\%\text{NCO}} \cdot 100 \qquad (1)$$

Polyols are specified by their hydroxyl number (OH no.) and sometimes also by their percentage OH content or their equivalent mass. The OH no. is given in mg KOH/g, owing to the method used for analyzing the OH groups: they are usually treated with acetic anhydride and, after hydrolysis with water, the excess acetic anhydride is titrated with potassium hydroxide. This means that a polyol containing 1 mmol OH groups per gram has an OH no. of 56 mg KOH/g.

$$\text{OH no.} = \%\text{OH} \cdot \frac{56 \cdot 1000}{17 \cdot 100} = \%\text{OH} \cdot 33 \qquad (2)$$

$$\text{Equivalent mass} = \frac{56 \cdot 1000}{\text{OH no.}} \qquad (3)$$

Water, *acids* (acid number AN), and secondary and tertiary amines are also most simply characterized by their equivalent mass. For mixed amines, a mean functionality must be used where necessary. For calculating quantities, 1 gram equivalent isocyanate corresponds to 1 gram equivalent Zerewitinoff-active hydrogen compound (e.g., polyol). In practice, the quantity of isocyanate is calculated almost exclusively for 100 parts by weight of the active-hydrogen compound(s). If the raw materials also contain water, then an additional quantity of isocyanate is required, since the latter reacts with water to form carbon dioxide and substituted urea.

The index (or isocyanate index) is equal to 100 (isocyanate index = 1) if the quantity of isocyanate added equals the amount necessary for reaction with all Zerewitinoff-active hydrogen atoms.

$$\text{Index} = \frac{\text{Used isocyanate quantity}}{\text{Necessary isocyanate quantity}} \cdot 100 \qquad (4)$$

In practice, the index can be used to influence the properties of the PUR decisively, e.g., by "under-" or "over-cross-linking." Under-cross-linking means that free hydroxyl groups remain in the PUR; over-cross-linking means that the urethane moieties undergo consecutive reactions, i.e., the formation of allophanates. High indices of 300 or more are used to produce polyisocyanurates (PIR), in which the isocyanate groups undergo trimerization by reaction with each other (see Section 4.4).

5.2. Reaction without Solvents

The possibility of manufacturing PURs from liquid raw materials without the use of any solvent is one of the biggest advantages of PUR chemistry. As a result, most PURs are manufactured by a mass polyaddition process. This process can be a single-step reaction (one-shot process) or a two- or multiple-step reaction (prepolymer process). The reactivity is controlled by temperature or by the addition of catalysts. Due to the high exothermicity, reaction temperatures of about 100 to 180 °C are not unusual. These high temperatures guarantee good end curing of the molded PUR parts.

5.2.1. One-Shot Process

Bulk reactions without solvents are usually very fast, especially when catalysts are added. Therefore, the production of PUR foams is usually carried out by the one-shot process, in which all components are mixed directly, generally with simultaneous addition of auxiliaries such as catalysts, foam stabilizers, reinforcing agents, fillers, and fire retardants. The reaction is highly exothermic and largely completed in 0.5–30 min, depending upon the catalyst. The final properties, however, are frequently reached only after 24–48 h (post-curing).

The one-shot process requires that the reactivity of all isocyanate species is quite similar. Amines usually lead to excellent PUR properties but react much more rapidly than polyols. If diamines or polyamines are to be used it must be ensured that the urea formed at the beginning of the reaction does not precipitate and is no longer available for incorporation into the hard segments. This means that the use of polyamines is limited to amines which cannot undergo cross-linking (secondary amines), are sterically hindered [57–61, 148], or are deactivated by electron-withdrawing substituents [62–64, 149].

For easy processability all components should be liquid, of low viscosity, and miscible or at least be able to form a homogeneous reaction mixture for the very first moments of the reaction. Usually all the nucleophilic components, that is, polyols and/or polyamines, are premixed and homogenized. If these mixtures are incompatible with the short-chain diols (chain extenders), the miscibility must be enhanced by raising the temperature or adding emulsifiers.

In general, the polyaddition reaction of a multicomponent system by the one-shot process leads to a predominantly statistical structure of the polymer chains.

The term reaction injection molding (RIM) technology usually is used when highly reactive components are mixed and injected into a mold on a very short timescale (see Section 7.4). This technique allows for the handling of reactive systems with pot lives (i.e., the period in which no significant increase in viscosity is observed) of less than 1 s and reaction times of about 10–60 s.

RIM technology has initialized a development, which started with catalyzed highly reactive PUR systems [150], and, by the use of polyurethane-polyurea systems, chain extended by diamines [151–153], led to pure polyurea systems, in which the only isocyanate-reactive components are diamines [154–163].

5.2.2. Prepolymer Processes

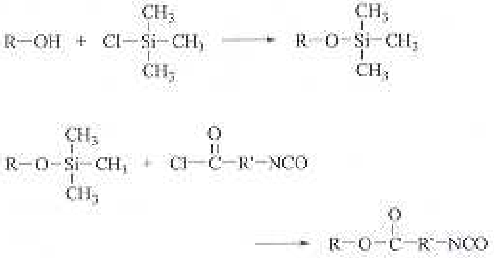
In PUR chemistry, prepolymers are defined as intermediate reaction products of the polyaddition reaction which still contain free isocyanate or isocyanate-reactive groups. In contrast to the one-shot process, the prepolymer process allows for a highly controlled polyaddition reaction, e.g., to construct tailor-made segment structures.

In the first step of the process, polyether or polyester polyols are usually treated with excess diisocyanate to yield homogeneous reaction mixtures, which may contain considerable amounts of unconverted isocyanate groups. If diisocyanates with NCO groups of different reactivity are used (2,4-diisocyanatotoluene, isophorone diisocyanate), the resulting NCO prepolymers exhibit narrow molecular weight distribution with only minor amounts of unconverted monomeric diisocyanate.

If prepolymers free of monomeric diisocyanate are required, the latter must be removed, e.g., by thin-film distillation or extraction with a hydrocarbon solvent which does not dissolve the prepolymer. The monomer content is then lowered to below 0.1 % [164, 165].

The production of storage-stable NCO prepolymers from aromatic diisocyanates is difficult and requires special precautions (e.g., the exclusion of all traces of water and catalysts) to avoid side and consecutive reactions [166].

Low-viscosity, monomer-free NCO prepolymers can be obtained from silylated hydroxy compounds and isocyanates with a carboxylic acid chloride group [167, 168].



$$R{-}OH + Cl{-}\overset{CH_3}{\underset{CH_3}{Si}}{-}CH_3 \longrightarrow R{-}O{-}\overset{CH_3}{\underset{CH_3}{Si}}{-}CH_3$$

$$R{-}O{-}\overset{CH_3}{\underset{CH_3}{Si}}{-}CH_3 + Cl{-}\overset{O}{\overset{\|}{C}}{-}R'{-}NCO \longrightarrow R{-}O{-}\overset{O}{\overset{\|}{C}}{-}R'{-}NCO$$

5.3. Reaction in Solvents

5.3.1. One-Component Systems

Linear or slightly branched PURs or polyurethane polyureas with molecular weights of 50 000 to 150 000 g/mol can be obtained by polyaddition reaction in solution. The PURs are usually isolated by evaporation of the solvents or by precipitation, e.g., by pouring the solution into a nonsolvent liquid.

The choice of solvent for the polyaddition is crucial, as the solvent must be able to dissolve both the soft and hard segments of the segmented PUR structure. Polar organic solvents (dimethylformamide, dimethylacetamide, 1-methyl-2-pyrrolidone, sulfolane, etc.) usually fulfill this requirement. In some cases, ketones like acetone or methyl ethyl ketone are also suitable. The ketones are especially suitable for chain extension of NCO prepolymers with aliphatic diamines as they reduce their activity by reversibly forming an adduct.

In industrial processes, linear PURs containing only urethane groups are usually produced without using solvents, but can be dissolved in a solvent if necessary for the application.

PURs containing urethane and urea groups are mainly produced by a two-step process. In the first step a prepolymer is made without the use of any solvents. In the second step this prepolymer is then treated with chain extenders such as diols or diamines. In the second reaction step, the solvent is usually added stepwise to avoid a too rapid increase in the viscosity of the solution. The obtained PUR solutions have PUR contents of ca. 20 to 30 %.

With increasing viscosity it is very difficult to achieve complete conversion of the functional groups. This problem is overcome by using NCO/OH ratios (indexes) slightly above 100 and running the reaction till the viscosity reaches a specified value, which must be determined empirically for each product. Then the reaction is stopped by adding a monofunctional stopper, e.g., dibutylamine.

If the reaction is carried out in highly polar solvents, especially in mixtures of water and acetone, methyl ethyl ketone, or DMF, even highly reactive aliphatic diamines such as ethylenediamine can be used. With increasing molecular mass the products may tend to gelation or precipitation. The solubility of the PUR can be improved by adding small portions of a second chain extender such as 1,2-diaminopropane, piperazine, or water to disturb the formation of the hard-segment domains.

5.3.2. Two-Component Systems [169]

Two-component systems are of tremendous importance for coatings and for leather and paper finishing. They usually consist of a polyhydroxy compound and an isocyanate cross-linker.

The polyhydroxy compounds are usually obtained by chain extension of common polyether or polyester polyols with diisocyanates; the isocyanate cross-linkers, which for ecological reasons must be free of isocyanate monomers, may be NCO prepolymers made by the reaction of diisocyanates with diols, diamines, or water; or they may be modified isocyanates, e.g., trimerization products of HDI (see Section 3.1.2).

To increase the amount of reactive components in the solvent-containing two-component systems, numerous improvements have been introduced to industrial processes: part of the solvent can be substituted by reactive thinners [170], which are incorporated into the cross-linked PUR. By using new catalysts an unsymmetrical trimerization product of HDI [30], with particularly low viscosity, has been developed, allowing for higher concentrations (high-solids systems) without deterioration in the processability.

5.4. Reactive One-Pack Systems

The term "one-pack system" denotes the storage-stable, ready-to-use formulation of a polymer precursor which cures without addition of further components, e.g., curing agents. Curing generally is caused by humidity, atmospheric oxygen (mainly used in paints), or by the thermal elimination of a blocking agent (see Section 3.1.3), which either vaporizes or remains in the cured polymer.

Other curing systems involve encapsulated materials with a diffusion barrier layer, which is broken, e.g., on heating. They cure without uptake or release of a substance.

Moisture Curing. Relatively low molecular mass NCO prepolymers can be dissolved in small amounts of low-polarity solvents (e.g., 75 % solution in ethyl acetate) and cured by the action of atmospheric moisture. The curing rate depends on the atmospheric humidity and temperature. Usually these solutions are used as paints or coatings, and the carbon dioxide formed as a byproduct escapes from the thin film without bubble formation.

Eliminating Blocking Agents. Mixtures of blocked NCO prepolymers with polyols are stable at storage temperatures (20–50 °C) and are cured by heating (> 120 °C) to eliminate the blocking agent (see Section 3.1.3). The reaction can be conducted in such a way that an isocyanate intermediate does not appear [39]. Appropriate hydrophilic modification can be used to produce such combinations as low-viscosity aqueous emulsions or dispersions, in which one of the components usually has a high molecular mass [38].

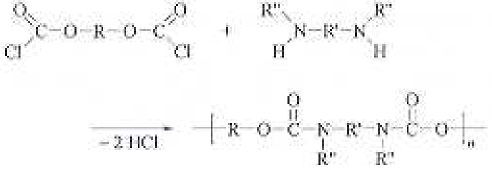
Removal of a Diffusion Barrier Layer. Some solid diisocyanates such as NDI, TDI-urea, and TDI-uretdione (TDI-dimer) can be stabilized by encapsulation with a diffusion barrier layer. The barrier layer is produced by dispersing the solid isocyanate in a solvent and reacting the NCO groups at the particle surface with (cyclo-)aliphatic diamines. After removal of the solvent the encapsulated isocyanates are dispersed in polyols or polyamines.

Liquid, pasty, or granular one-pack systems are produced in this way. They can be stored for several months and are made to react by heat shock, e.g., 1 min at 120 °C. Heat-curable reactive powders can also be produced on this basis [171].

5.5. Other Processes

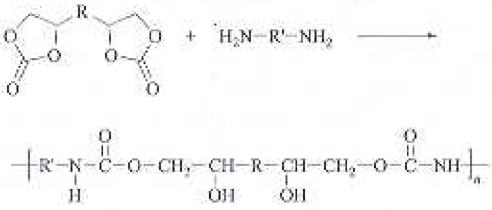
In addition to the industrial isocyanate polyaddition processes described previously and in subsequent sections, several other synthetic methods for PURs or polyureas are of scientific interest [172].

PURs can also be obtained by the polycondensation reaction of bis-chloroformate esters and diamines. This method has the advantage over the polyaddition method that it can be carried out under very mild conditions (at ≤20 °C).



If secondary diamines such as piperazine are used in the polycondensation reaction, thermostable poly(*N*-alkylurethanes) are obtained. This principle has been used to produce, e.g., high-melting PURs [173] for fibers or PURs with liquid-crystalline character [174]. Liquid-crystalline PURs have also been produced from *N*-alkylcarbamic acid chlorides and diols.

Another method for preparing PURs is the ring-opening polyaddition of oligomers with cyclic ethylene carbonate groups and di- or polyamines, which leads to segmented PURs with free hydroxyl groups [175, 176]:



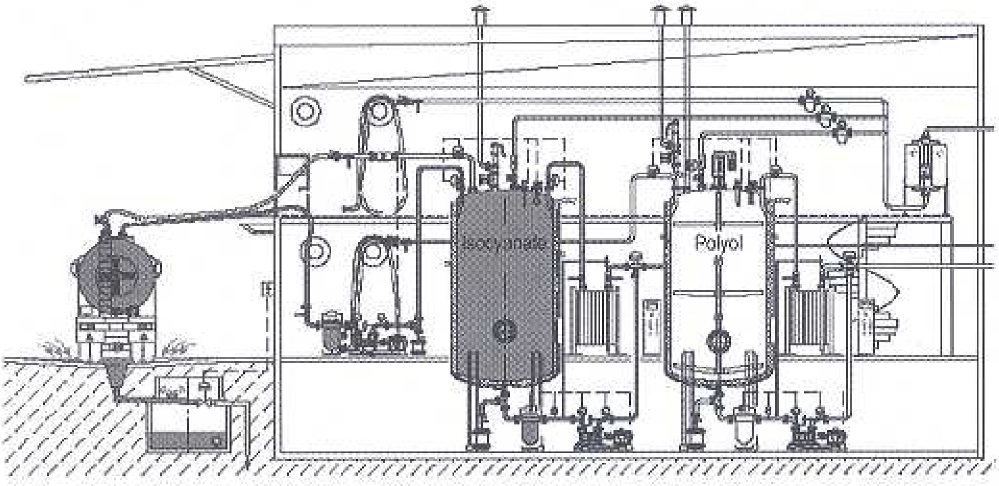


Figure 5. Tank truck unloading and storage tanks

Functionalized PURs can be obtained if carbonylbiscaprolactone (CBC) is used as carbonyl source [177]. Due to its high selectivity, reactions with diamines can be carried out even in the presence of additional hydroxyl groups.

High-molecular mass α,ω-bis(amino) prepolymers for use in RIM technology (see Section 7.4) have been produced by the reaction of α,ω-bis(amino)polyethers with urea [178].

6. Processing of Polyurethanes

6.1. Supply, Storage, and Preparation of Raw Materials

The raw materials are transported in small (< 100 kg) and normal-sized drums (200–250 kg), and (road) tank trucks and trailers (ca. 23 t). The regulations applicable to the transportation of chemicals (including labeling) must be observed, as well as the transportation conditions prescribed by the manufacturer for preserving the quality of the raw materials. If raw materials are delivered by tank truck, storage tanks for polyol and isocyanate should be installed in pairs at the processing site (Fig. 5). The size of the storage tanks should be adapted to the delivery volume (frequently 15 or 30 m^3). Since the raw materials in the tank truck are usually delivered at elevated temperature, they must be cooled to the processing temperature (22–25 °C) in the storage tank. Ordinary thick plate can be used as the tank material.

6.2. Metering and Mixing Technology

In contrast to the machines used for processing thermoplastics, which consist of devices for melting, molding, and solidifying, the machines used for producing PUR moldings or semifinished parts contain all the elements of a chemical reactor.

The raw materials are conveyed from the storage tank, optionally via premixing stations for adding auxiliary materials, to the processing machine. Often the metering and mixing machine is called the wet part of the processing plant. Figure 6 schematically depicts a two-component metering and mixing machine with an impingement mixer as the mixing unit. In practice, machines using the impingement mixing principle are available for mixing up to six components. In the working tanks (a), the raw materials are prepared for processing, i.e., primarily their temperatures are adjusted precisely. Any temperature change, especially of the polyols, results in a viscosity change, which can impair later processing. The working tanks (volume 20–500 L according to the machine size) are therefore usually provided with heating and cooling jackets.

Separate temperature-control circuits via heat exchangers are also common. The working tank is also equipped with an agitator for homogenization as well as an automatic refilling system and indicators for level, pressure and temperature. The conditioned raw materials are conveyed via metering pumps (b) to the most important part of the machine, the mixing head (c), which delivers the liquid reaction mixture.

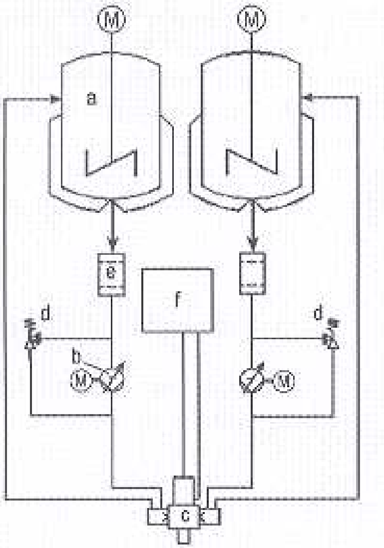


Figure 6. Principle of a high-pressure machine (circulation system)
a) Working tank; b) Metering pump; c) Mixing head; d) Safety valve; e) Filter; f) Hydraulic unit

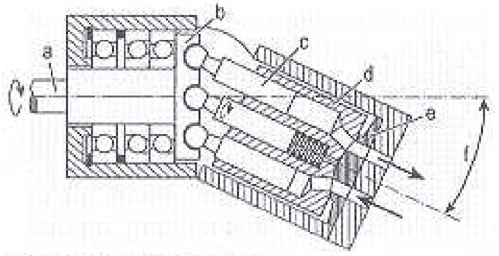


Figure 7. Axial piston pump
a) Shaft; b) Rod plate; c) Piston; d) Cylinder unit; e) Cam plate; f) Angle of inclination to adjust volume flow rate

Depending on the PUR system to be processed, precision metering pumps of various outputs (up to 150 L/min) and pressure ranges (up to 250 bar) are used. The pumps must always satisfy extremely high requirements for metering accuracy in order to maintain a certain reaction mixture. In addition to conventional gear pumps and in-line piston pumps, which have been established in PUR technology for many years, axial piston pumps (Fig. 7) and, for systems containing fillers and reinforcements, slow-running single-cylinder positive-displacement pumps are used (Fig. 8).

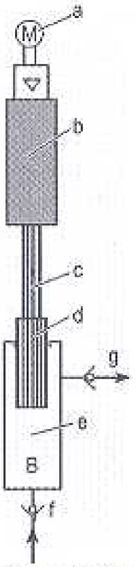


Figure 8. Plunger pump
a) Stepping motor; b) Hydraulic cylinder; c) Hydraulic piston; d) Metering piston; e) Metering cylinder; f) Stop valve: feeding side; g) Stop valve: delivery side

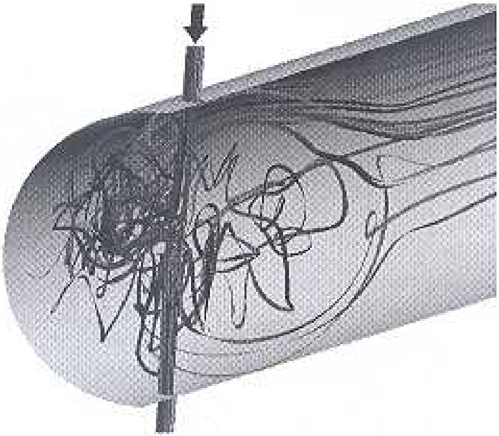


Figure 9. View into an impingement mixer during shot; visualization of streamlines

Two types of mixing principles exist: low-pressure mixing heads with an agitator (3–40 bar) and high-pressure mixing heads (100–250 bar). In mixing heads with an agitator, the raw materials entering the upper part of the mixing chamber are intensively mixed on their way to the outlet by rotating, variable-speed agitators. Agitators include spiked, paddle, or screw agitators, propellers, or turbine impellers. After the end of the shot the agitators are cleaned with a rinsing medium. High-pressure mixing heads operate according to the countercurrent injection principle. The component streams are injected into the mixing chamber via nozzles (Fig. 9) and are mixed by virtue of the kinetic energy used and the chaotic flow behavior created [179].

In controlled-circulation mixing heads, the raw material streams are changed from the "circulation position" (Fig. 10A) (tank → pump → mixing head → tank) to the "injection position" (Fig. 10 B). After injection has occurred, a piston cleans the remaining reaction mixture from the mixing chamber and outlet pipe. These are therefore known as self-cleaning mixing heads.

So-called L-shaped mixing heads are able to improve the homogeneity of the reaction mixture by a perpendicular deflection of the flow direction and simultaneous acceleration of the flow velocity (Fig. 11). Furthermore, the larger

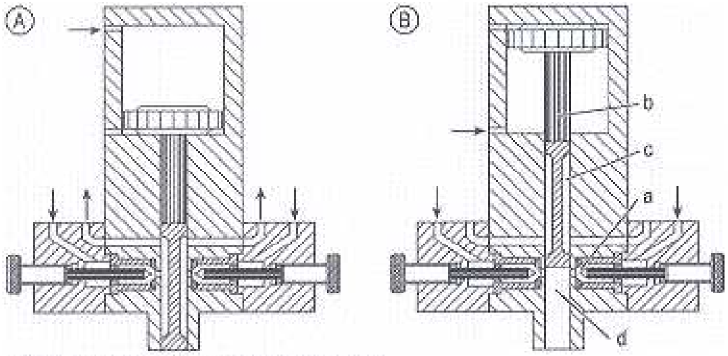


Figure 10. Circulating-groove mixing head
A) Circulation/cleaning; B) Mixing
a) Nozzle; b) Piston; c) Groove; d) Outlet tube

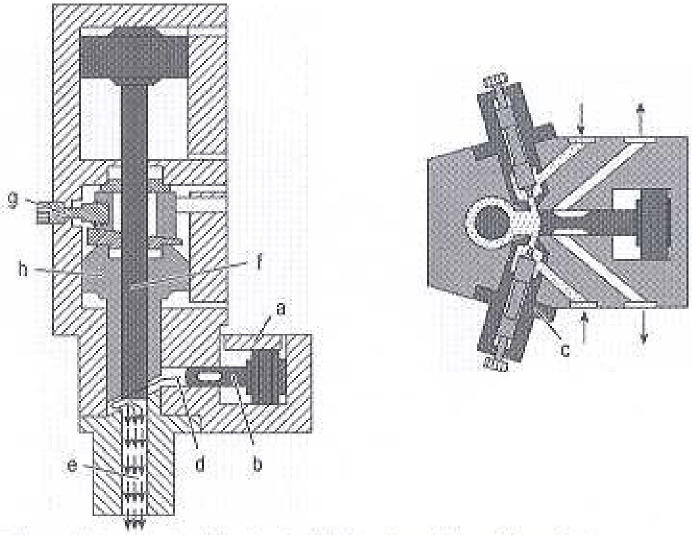


Figure 11. L-shaped mixing head with ring throttle (type Hennecke)
a) Impingement mixer; b) Actuating piston; c) Injection nozzle; d) Mixing chamber; e) Outlet tube; f) Cleaning piston; g) Adjustment of ring throttle; h) Ring throttle

diameter of outlet tube compared with the dimension of the mixing tube allows the required laminar flow out of the mixing head.

6.3. Processing Plants

A two- or multicomponent metering and mixing machine is part of each processing plant. Further equipment and machines define the kind of processing plant.

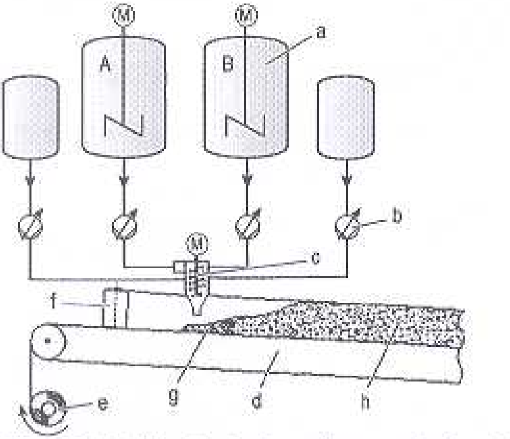


Figure 12. Principle of a plant for continuous production of foam slabs
a) Working tank; b) Metering pump; c) Agitator mixing head; d) Conveyor; e) Bottom paper; f) Side paper; g) Rising foam; h) Cured foam

In continuous plants, semifinished products are produced in the form of blocks, slabs, boards, profiles, etc. The scheme in Figure 12 depicts a plant for the continuous production of foam slabs. Four components are metered, mixed with an agitator mixing head, and poured onto the conveyor belt. The bottom and side paper are used to keep the conveyor belt clean and to avoid sticking of the foam to the conveyor belt during rising and curing. Figure 13 is a three-dimensional view of a plant for the manufacture of rectangular slab stocks.

A three-dimensional drawing of a plant for manufacturing metal sandwich panels (Fig. 14) gives an impression of how large and complex PUR plants can be. The length over all stations of processing steps in this case is ca. 350 m.

Plants for producing moldings operate batchwise. The example in Figure 15 shows a top view of a processing plant: On the left side is the wet part of the plant with a total of six components; a robot handles the high-pressure mixing head, and two clamping units are available for pouring into open moulds.

A distinction can be made between plants with movable (Fig. 16) and those with stationary molds (Fig. 17). Movable molds are supplied by a single mixing head, whereas in RIM plants, several mixing heads are used, each of them being permanently assigned to one (stationary) mold. The plants are preferably automatically controlled with electronic equipment.

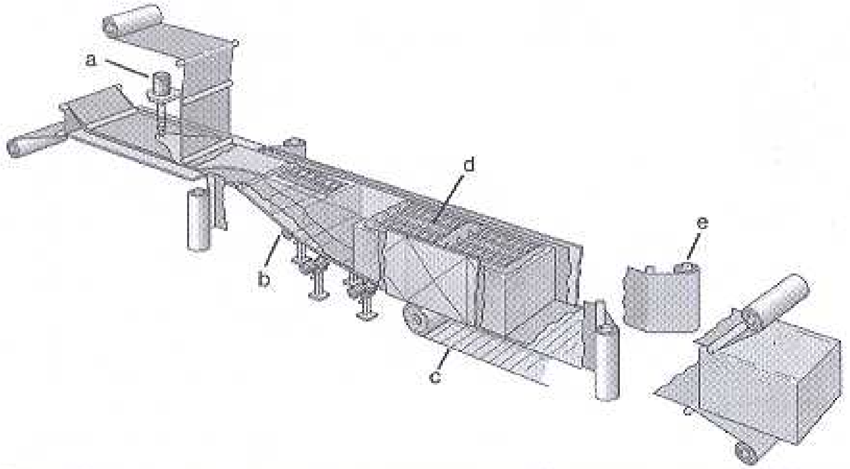


Figure 13. Plant for the manufacture of rectangular slab stocks (Quadro-Foamat-Machine; QFM, source Hennecke) a) Agitator mixing head; b) Fall plate path adapted to foam expansion; c) Conveyor; d) Device to keep block shape rectangular; e) Paper winch

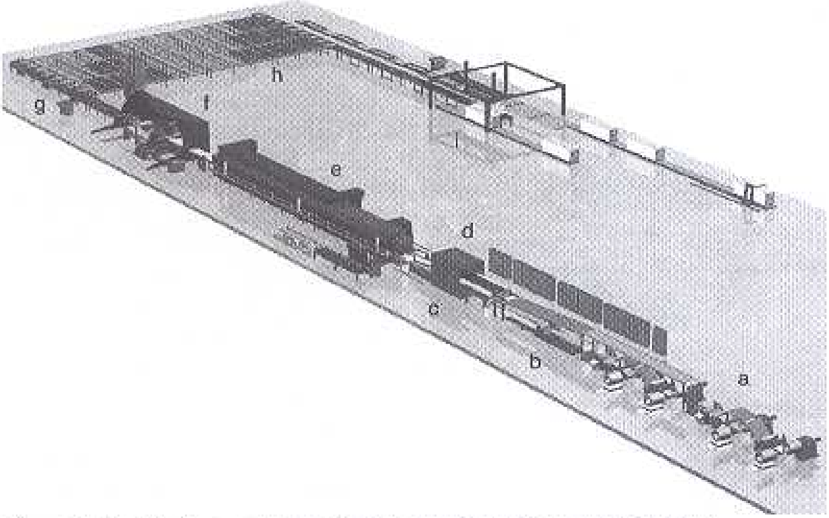


Figure 14. Plant for the manufacture of metal sandwich panels (source Hennecke)
a) Uncoiling station; b) Profiling machine; c) Heater; d) Twin-head foaming portal; e) Laminator; f) Cutting machine/bandsaw; g) Turn over system for roof elements; h) Cooling section; i) Stacker

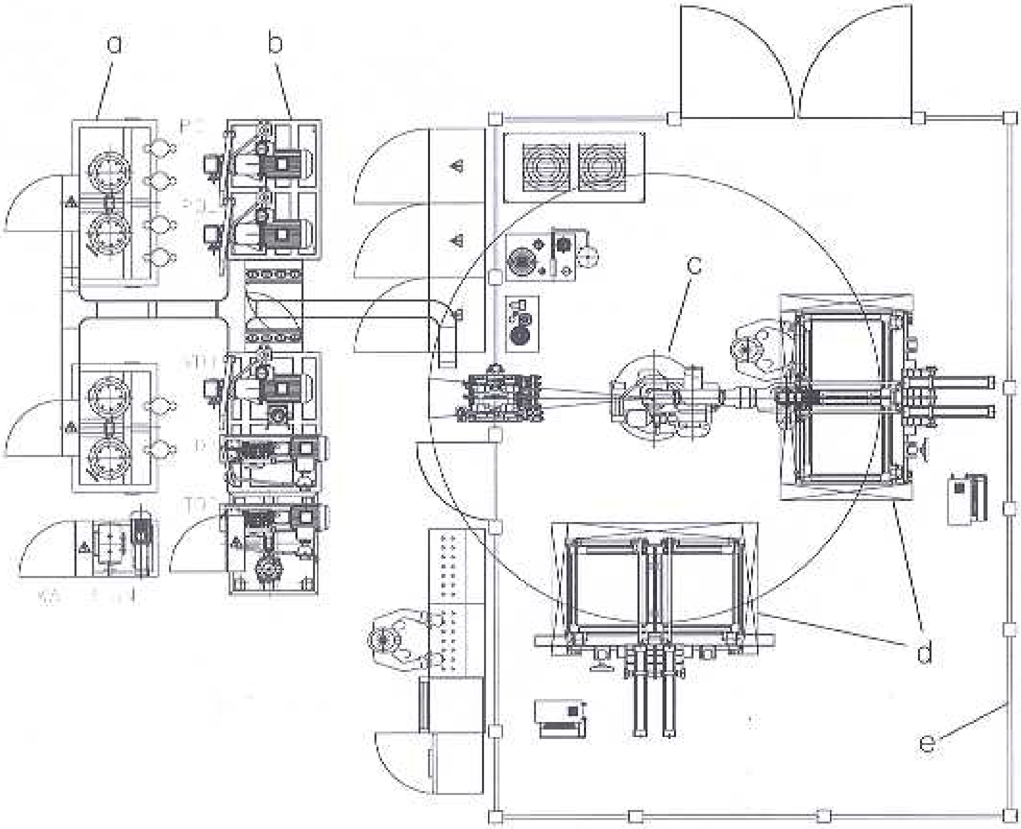


Figure 15. Layout of a plant for producing moldings by open-mold filling technology
a) Tank unit; b) Pump unit; c) Robot with mixing head; d) Clamping units; e) Protective guard

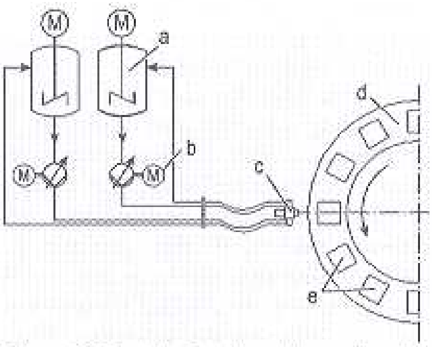


Figure 16. Principle of a plant with movable molds and stationary mixing head
a) Working tank; b) Metering pump; c) Mixing head; d) Turntable; e) Molds

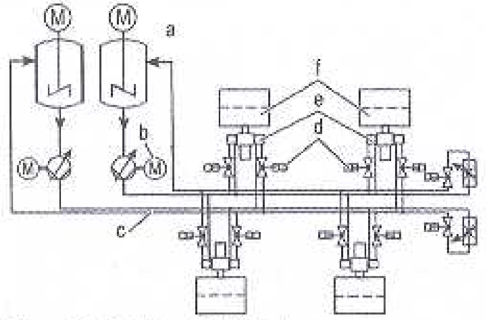


Figure 17. Principle of a RIM plant
a) Working tank; b) Metering pump; c) Circulation system; d) Selection valves; e) Mixing heads; f) Clamping units with tools

7. Foams

Whilst the reaction of isocyanates with water in most PUR applications is an unwanted side reaction, for foams this reaction is of utmost importance, due to the two reaction products formed. These are CO_2, which acts as the blowing agent for foam formation, and the more or less crystalline polyurea domains, which control cell opening and act as reinforcing filler in the PUR backbone. This chemical blowing process was supplemented in the early 1960s by a physical blowing process using low-boiling liquids as blowing agents. These liquids are vaporized by the heat of reaction of the polyaddition reaction between isocyanates and polyols and/or water. The blowing agent vapor is trapped in the viscous reaction mixture and thus leads to the cellular structure of the foam. Since foam formation is a very sensitive and complex process of interdependent chemical, physical, and rheological processes, specific additives and catalysts are required (see Section 3.5).

PUR foams are generally divided into flexible, rigid, and semiflexible products. Integral skin foams, which have a densified surface layer forming an elastomerlike skin and a foamed core, are described in Section 7.4.

Polyols with a relatively high molecular mass (2000–8000 g/mol) and a nominal functionality of 2–6 yield flexible foams. Combinations of these polyols with low molecular mass glycols or amines as chain extenders and preferably polyisocyanates with a functionality of more than two yield semiflexible foams. Highly branched polyols, e.g., polyethers based on sorbitol or sucrose, with a relatively low molecular mass (<1000 g/mol) are the basis of rigid foams.

For all these classes of foams different types of manufacturing processes may be applied. An alternative way of classifying foams is therefore based upon the manufacturing process.

Depending on the processing, a distinction is made between molded foam and slabstock foam. Besides these most prominent groups of flexible foams, other foam types include cavity-filling foam (e.g., filling of cavities in car bodies for acoustical or reinforcing purposes) and spray foam (e.g., for thermal insulation of roofs). The term "filling foam" essentially refers to semiflexible foams behind appropriate overlays, e.g., flexible plastic sheets, films, etc.

7.1. Flexible Foams

Most flexible foams are produced continuously as slabs or batchwise by molding. They are characterized by reversible deformability and an open-cell structure, associated with air permeability.

7.1.1. Flexible Slabstock Foam

7.1.1.1. Raw Materials

Based on different chemistries on the polyol side, three fundamentally different types of slabstock have to be considered: Polyester foams, made from polyester polyols, conventional polyether foam, made from polyether polyols with mainly secondary OH groups and high-resilient (HR) foam, made from polyether foams with mainly primary OH groups.

The isocyanate used for polyester foams is usually TDI 65 (see Section 3.1.1) or blends of TDI 65 and TDI 80; the typical isocyanate for polyether foams is TDI 80. High-resilient slab stock foam is produced from polyethers and TDI 80, both optionally modified.

Main components (parts by weight) of a formulation for flexible polyester foam:

Polyester polyol (OH no. 65), e.g., Desmophen 2200	100
TDI 65 and/or TDI 80, e.g., Desmodur T65, Desmodur T80	variable
Index	95
Water	2.5–4.8
Amine catalyst	0.3–0.6
Foam stabilizer	0.7–1.3

Main components (parts by weight) of a formulation for flexible polyether foam:

Polyether polyol (OH no. 48), e.g., Arcol 1108	100
TDI 80, e.g., Desmodur T80	variable
Index	98–115
Water	2.0–4.5
Amine catalyst	0.15
Tin dioctanoate	0.12–0.28
Foam stabilizer	0.6–1.5

Main components (parts by weight) of a formulation for high-resilient (HR) flexible foam:

Grafted polyol (OH no. 28), e.g., Desmophen 7653	100
TDI 80, e.g., Desmodur T80	variable
Index factor	95–113
Water	1.5–4.0
Amine catalyst	0.10–0.20
Diethanolamine	0.8–1.5
Tin dioctanoate	0.1–0.35
Foam stabilizer	0.3–1.0

The polyesters (M_r 2000–3000 g/mol) are usually based on adipic acid and linear glycols (e.g., diethylene glycol), or triols (glycerol or trimethylolpropane) if slight branching is desired.

The polyethers used (M_r 1000–6000 g/mol) are di- and/or triols with a varying propylene oxide/ethylene oxide ratio, which is tailored to the foam's application. An important factor for polyether foaming is a well-balanced ratio of the metal and amine catalysts, which controls the simultaneous reactions of the NCO group with hydroxyl groups (polyurethane reaction) and with water (blowing reaction). If the polyurethane reaction rate predominates, the foam may shrink due to the formation of a high proportion of closed cells. If the water reaction proceeds too rapidly, the carbon dioxide formed cannot be contained in the cells; splits result and the foam can even collapse.

High-resilient foams are produced from highly reactive grafted polyethers which contain a high proportion of primary OH groups (from ethylene oxide). Grafting is achieved by in situ polymerization of styrene and acrylonitrile to form a stable SAN suspension in the polyol. Another class of grafted polyols is based on the polyaddition of TDI and hydrazine to yield PHD polyols which contain suspended polyhydrazodicarbonamide/polyurea particles. If highly functional (pre-cross-linked) modified TDI types are used, unmodified polyols can be applied, but due to advantages in foam processing, this approach has been generally replaced by grafted-polyol technology.

7.1.1.2. Production

The raw materials are processed in fully continuous plants to give flexible foam slabs up to 220 cm wide, 120 cm high, and of any length. Depending on the slab dimensions, internal temperatures of up to 165 °C are reached as a result of the exothermic reaction. This temperature must not be exceeded, otherwise severe scorching and even self-ignition of open-celled foam may occur. The foaming process is completed after ca. 3 min, and final curing takes from about 10–12 h up to 72 h, depending on the foam type. The slabs are therefore stored in curing storage facilities until they have cooled and attained their final mechanical properties, so that they can be transferred to further processing, fabrication, etc. The length of the slabs varies from 10 m (short slabs) to 120 m (long slabs). To minimize trimming losses of the foam buns, which would

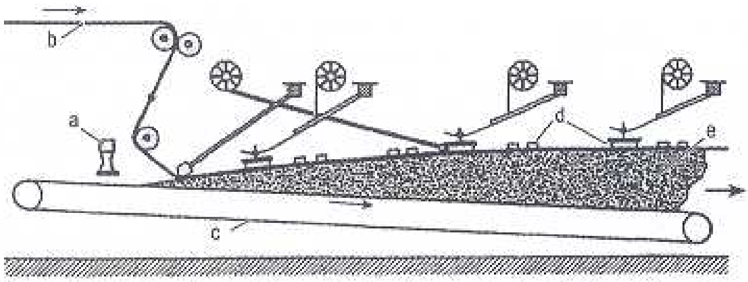


Figure 18. Principle of a plant for production of rectangular flexible foam slab stocks

a) Covering paper; b) Skids; c) Mixing head; d) Conveyor belt; e) Foam

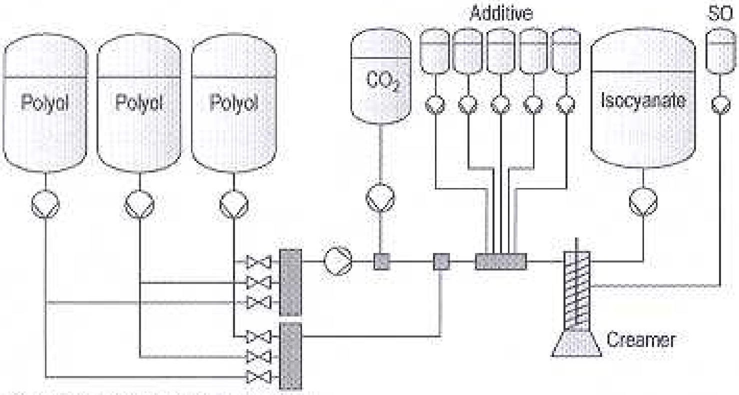


Figure 19. Multistream (Hennecke)

be dome-shaped under free-rise conditions, various technologies are applied to produce rectangular slabs.

Figure 18 shows the principle of a rectangular slabstock plant (Hennecke Planibloc process) [180]. A cover is applied to the rising foam. The pressure of the skids avoids the development of the usual slab dome without the foam becoming compacted. Besides a rectangular slab cross section, this process gives an increased yield of foam due to partial foaming of the mixture at the slab surface, which would otherwise form the surface skin.

In other processes a polyethylene film is drawn up to the slab sides in synchronization with the rising movement of the foam (Draka-Petzetakis) [181, 182]; or the reaction mixture is discharged into a trough with a sloping bottom, in which it rises and then flows off over a downward incline (fall plates) onto the conveyor (Maxfoam) [183]. A more recent development (Multiflex, Quadrofoamat, see Fig. 13) combines the fall plates with liquid laydown principles.

The application of reduced air pressure during the foaming process (variable-pressure foaming, Beamech [184]) or the introduction of carbon dioxide into the mixing chamber (e.g., Multistream (Fig. 19) and Novaflex (Fig. 20), Hennecke [185]) has allowed for the complete elimination of other physical blowing agents such as CFCs.

Rectangular blocks can also simply be produced batchwise by introducing the reaction mixture into metal or wooden boxes and at a given time putting a floating cover on the rising foam. In addition to primitive methods ("box foam"), mechanized box processes are also offered for this purpose with relatively low investment costs and a processing capacity of up to 1000 t/a (e.g., Hennecke Bloc-Foamat BFM 100). Special versions of these batch plants are available so that different ambient pressures can be applied during the foaming stage (e.g., Hennecke Megafoam).

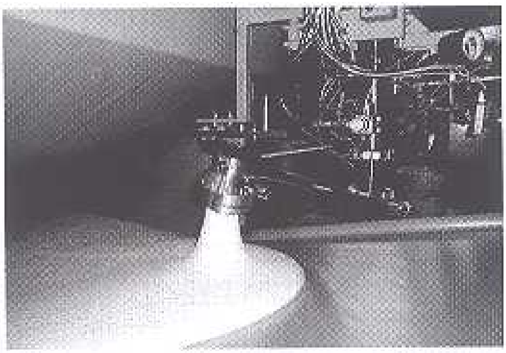


Figure 20. Novaflex creamer (Hennecke)

In addition to the production of blocks with a rectangular cross-section, continuously produced blocks with a round cross section (diameter ca. 120 cm) have become industrially important (Reeves Brothers, General Foam [186, 187]). These buns can be peeled seamlessly.

7.1.1.3. Properties

The mechanical properties of the foam are largely determined by the raw materials and the formulation used and by its apparent density. For flexible foam slabstocks, the usual densities are 20–40 kg/m^3, but extremely light and extremely heavy types of foam (from 16 kg/m^3 and up to 130 kg/m^3) can be produced industrially for special fields. The choice of density is determined by the specific application of the foam: the higher the density, the better the properties or the lower the fatigue of the foam when in continuous use.

The hardness (measured as compressive strength at 40 % compression) is an important characteristic of PUR foams (Table 4). The hardness can be varied within wide limits by altering the formulation. Considerably softer conventional foams are obtained, e.g., by including polyethers of high ethylene oxide content and special additives. Hardness control is also possible through the index or the addition of grafted polyols.

Apart from the hardness, other characteristic values can be derived from the hysteresis loop (Fig. 21). The slope of the loading curve and the area enclosed by the loading and unloading curves (hysteresis) are measures of the elasticity and energy absorption of the foam: the closer the curves are together, the more elastic the foam; and the larger the area, the better the energy absorption or damping properties of the foam. HR slabstock foam has the best elasticity, followed by polyether foam and polyester foam.

Table 4. Relation between apparent density and compressive strength of various grades of flexible foam slab stock

Flexible foam system	Apparent density (ISO 845), kg/m^3	Compressive strength at 40 % compression (ISO 3386), kPa
Polyester foam, based on Desmophen 2200B/Desmodur T65	35	6.5
Polyether foam, based on Polyether 10WF15/Desmodur T80/T65	36	6.0
Polyether foam, based on Arcol 1108/Desmodur T80	36	4.5
HR slab stock foam, based on Desmophen 7619W /Desmodur T80	34	2.7

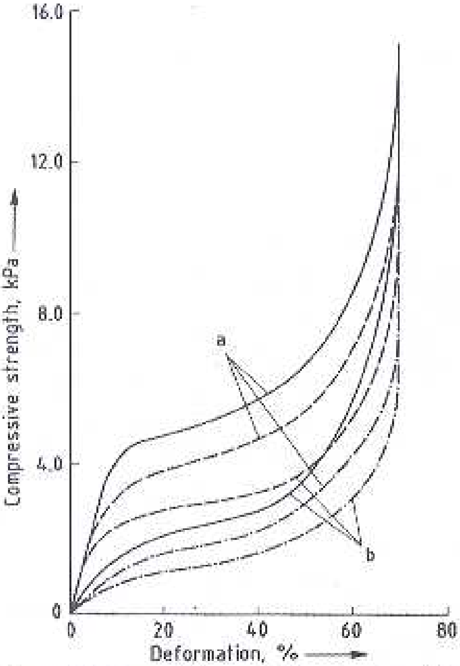


Figure 21. Hysteresis loops of different grades of flexible foam slab stock (apparent density 35 kg/m^3)
a) Loading lines; b) Unloading lines
– Polyester-based foam; – – – Polyether-based foam; – · – · – HR foam

Some important mechanical properties are summarized in Table 5 to demonstrate their range of values. Table 6 shows the values for fatigue in continuous use under the conditions of short-duration tests.

The following list contains some additional properties of flexible PUR slabstock foams:

Thermal conductivity: 0.033–0.040 W m^{-1} K^{-1} (at 0–70 °C and densities of 20–70 kg/m^3)

Temperature stability: from -40 to $+80$ °C without embrittlement.

Open-cell character (see also reticulation capability): 98–100 % with respect to air permeability, not with respect to resistance to air flow.

Chemical resistance to acids and alkalis: polyether foam has a better resistance to acids and alkalis than polyester foam.

Chemical resistance to organic solvents: polyester foam shows a better resistance to organic solvents than polyether foam.

Chemical resistance to atmospheric oxygen: oxygen attacks foam slab stocks only superficially without harming the serviceability. Polyether foam is more easily oxidized than polyester foam. However, if aromatic polyisocyanates and polyether polyols are used for foam production, the foam will decompose over time if exposed to oxygen and light.

Combustibility (see Section 14.4): Flexible slabstock PURs are combustible, like all organic (carbon-containing) materials. By addition of suitable flame retardants the combustion behavior of foams can be adjusted to meet several flammability standards such as MVSS 302, BS 5852 part 2 Crib V, or even Fire Class B1 (DIN 4102). Also a post-treatment with latices containing flame retardants is possible, in particular if demanding tests have to be met. Besides flame retardants, the type of foam (polyester, conventional, or high resilient) is important if certain flammability standards have to be met.

Bactericidal and fungicidal treatment is possible by including appropriate additives in the formulation or by post-treatment.

Reticulation capability (see also open-cell character): the flow resistance can be greatly reduced by using chemical or physical processes (Chemotronics) to remove residual cell membranes (filter foams).

Physiological aspects: According to extensive studies (both dermatological and oral toxicity in animals), flexible PUR foam of defined composition is physiologically harmless.

7.1.1.4. Trimming and Processing

Various possibilities and machines are available for processing the cured slabstock foam to finished articles. The simplest processes for foam blanks are horizontal-cutting (e.g., long-block cutting/peeling), vertical cutting, and angular cutting. These are carried out with continuously rotating knives.

Profile cutting in the form of copy cutting and punching, compression cutting, and milling is used for further forming. With profile cutting tailor-made cuts can be made by following prefabricated templates or drawings (Fig. 22).

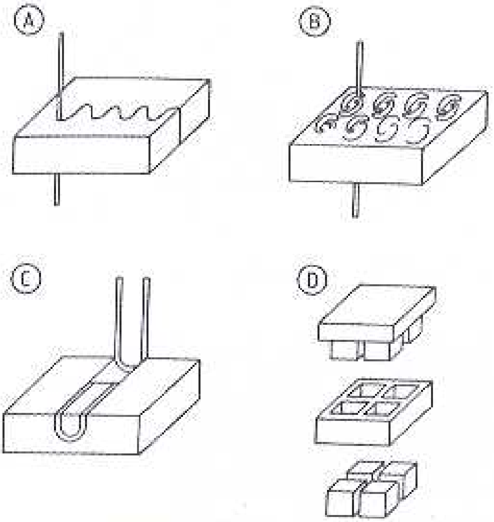


Figure 22. Cutting methods and punching
A) Hot-wire cutting; B) Copy cutting; C) Profile cutting; D) Punching

Compression-cutting is a special variant of profile-cutting. All these processes exploit the easy deformability and excellent recovery of PUR flexible foam (Fig. 23).

Advances in foam trimming equipment such as fully automated CNC processing lines allow for economical conversion of foam buns into very sophisticated contoured parts (Fig. 24). At the same time, trim losses are minimized by specific software [188].

Table 5. Mechanical properties of various grades of flexible foam slabstock

Flexible foam system	Tensile strength (ISO 1798), kPa	Elongation at break (ISO 1798), %	Compressive set (after 90% deformation; ISO 1856), %
Polyester foams	160 – 220	100 – 400	5 – 15
Polyether foams	100 – 180	100 – 400	2 – 10
HR slabstock foams	50 – 120	80 – 200	2 – 10

Table 6. Change of hardness on ageing of various grades of flexible foam slab stock

Flexible foam system	Apparent density (ISO 845), kg/m³	Decrease of indentation load deflection (ISO 3385), %	Decrease of compressive strength (5 d, 90°C, 95% rel. hum.), %
Polyester foams	25	43	35
	35	29	40
	45	26	40
Polyether foams	20	34	10
	25	29	14
	35	19	18
	50	16	16
HR slabstock foams	25	24	8
	35	18	13
	45	16	18

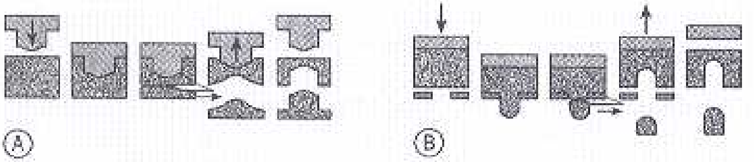


Figure 23. Compression cutting
A) Convoluting process; B) Skiving process

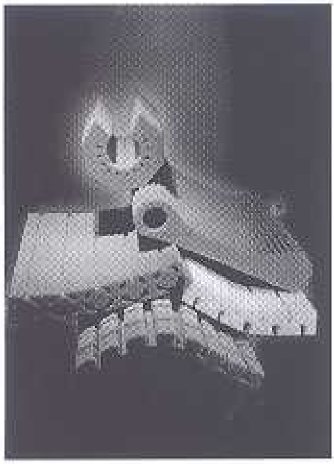


Figure 24. Contoured parts, produced by different trimming technologies

Form milling is used for rounding edges on seat backs and armrests as well as on seat pads. Due to the large variety of milling tools, any shape is possible (Fig. 25).

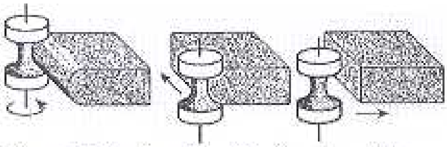


Figure 25. Shaping of flexible foam by milling

Other post-treatment methods include reticulation, impregnation, compression, welding, cementing, laminating with textiles or films by flame lamination or adhesive bonding, quilting, and covering.

The trimmed-off foam is flaked in suitable mills. The flakes can be used as filling material or are bonded to form flake-composite blocks, referred to as rebonded foam. These composite blocks are then fabricated similarly to normal foam slab stocks (see Section 14.3).

7.1.1.5. Applications

The variety of properties and the continuous development of new foam grades and further processing techniques have made slabstock indispensable for many applications.

For furniture, the use of polyether foams extends from complete foam upholstery to the simple seat cushion. Very comfortable cushioning is achieved by combining types with different properties (e.g., density, hardness, or elasticity).

Full PUR foam mattresses at present account for approximately one-third of all mattresses sold in Europe. The relative low weight (e.g., versus latex foam) and the freedom of design by combining various foam types (high resilient, conventional, viscoelastic) and grades (density, hardness) in conjunction with advanced cutting systems have turned these mattresses into high-tech applications. All required grades of hardness are available, from the child's to the intervertebral disk mattress. Even in steel-spring mattresses, a layer of slabstock foam is used as cushioning and lining material.

An important field of application for slabstock foam is the lamination of fabrics. Polyester foams are preferred to polyether foams due to their melting properties and their specific cell structure. The foams can be bonded on one or two sides with textile widths by adhesive or flame lamination and are widely used for automotive interior trim applications such as seat covers or headliners.

Other applications in automotive industry are sun visor fillings, which can be manufactured from semirigid polyester foams, and sound-absorption materials for passenger, engine, and trunk compartments. PUR foams are also used as sealing and filter materials in the ventilation system. All foams for automobiles must satisfy the fire test MVSS 302 (see Section 14.4). Depending on the density and the chemical nature of the PUR foam (HR or conventional foam) flame retardants must be added to the foam formulation to meet this requirement.

In the clothing industry the above-mentioned laminated fabrics are incorporated into jackets and coats. Other applications are paddings in ski and sports boots and underlinings in the purse-making industry.

Flexible PUR foam is particularly suitable as a packaging material for fragile goods. Because of the variety of cutting processes, extremely complicated shapes can be produced for the transportation of goods.

The main application in the household sector is sponges. They are produced from both polyether and polyester foam in very diverse colors and shapes. They can be fine- or coarse-pored and range from extremely flexible to almost rigid. The foam's hydrophilicity can be increased by using special additives. The range of uses in the household includes adhesive, sealing, and jointing tapes as well as undercarpet padding, doormats, and cleaning brushes. Special grades can be obtained by bonding with thermoplastic films by high-frequency welding.

The ability of flexible foams to absorb airborne noise efficiently is exploited for noise abatement. The low thermal conductivity of flexible block foams is used for the thermal insulation of heat accumulators and pipes. For use as filter material, e.g., in ventilation and air-conditioning systems or as dust filter in breathing masks, the flow resistance of the foam must be reduced by post-treatment. Depending on technical requirements, the foam can also be used as a filter for liquids. Since the foams do not absorb X rays, they are an ideal material for the comfortable support of parts of the body during X ray exposure.

7.1.2. Molded Flexible Foam

The foam molding process is used when it is impossible or uneconomic to produce a complex geometry by trimming slabstock foam, or when the incorporation of metal inserts (for fastening cushioning units or coverings) or even steel springs (for furniture applications) is desired. A distinction is made between hot-cure molded foam and cold-cure molded foam.

7.1.2.1. Production

To produce hot-cure foam, trifunctional polyethers with a low content of highly reactive primary OH groups in the molecular mass range of 3000–5000 g/mol are reacted with toluene diisocyanate (TDI) with ca. 80 % of the 2,4′ isomer, e.g., Desmodur T80. The blowing agent is carbon dioxide, which is formed by the water-isocyanate reaction. Polyether polysiloxanes are employed for stabilizing the foam and due to the lower reactivity of the polyols, tin dioctanoate or other tin compounds are used to catalyze the polyurethane reaction, amines are used to catalyze the blowing reaction, and rather high mold temperatures must be applied. The hardness of the foams can be adjusted by adding grafted polyols for increased load-bearing properties or by using special polyols or additives for softer grades. The resulting foam is open-celled and does not require crushing for cell opening.

Cold-cure foams are produced from trifunctional polyethers with enhanced reactivity (high proportion of primary OH groups) in the molecular mass range of 5000–6000 g/mol and grafted polyols. A variety of different isocyanates are used, usually with a functionality exceeding two (modified TDI types, blends of TDI and higher functional MDI; special MDI types). If pure TDI 80 is applied, polyethers with a functionality slightly higher than three are usually used (e.g., Hyperlite). No further blowing agents are used; the carbon dioxide formed from the reaction of water with isocyanate is the sole blowing agent. Due to the higher reactivity of the polyols no metal catalysts are required for curing, and the mold temperatures are relatively low ("cold" cure) compared to hot-cure foam. On demolding the cold-cure foam is closed-celled and must be mechanically crushed to avoid shrinkage and to achieve consistent physical properties.

7.1.2.2. Molding Process

The molding methods for hot- and cold-cure foam systems differ sharply from each other. This is mainly because external heat must be supplied to a hot-cure molded foam to cure the foam's surface fast enough.

Figure 26 shows the individual process steps of the hot-cure foam molding process. This production sequence has a cycle time of ca. 20–25 min, depending on the nature and size of the foam parts.

The molds consist of black iron plate (wall thickness 1.5–2.0 mm), aluminum sheet (wall thickness 4–6 mm), or cast aluminum (wall thickness 6–10 mm). Since the foaming process for this foam type must proceed unpressurized, good mold venting is necessary. The arrangement of the vent holes is determined experimentally. In manufacturing the molds, a volume loss during the curing process of ca. 2 % must be taken into consideration. The precise value is specific for the formulation and must be determined experimentally. Release agents are mainly aqueous wax or soap dispersions. High- or low-pressure machines, operating batchwise, are used for metering the raw materials. The molds are usually heated by hot-air ovens. The heating capacity of the ovens for the full-cure process must be adapted to the mold material and the required cycle time. After removing the molded foam parts, the molds are cooled by water or cold air to the loading temperature.

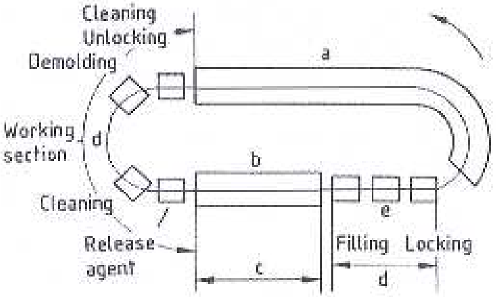


Figure 26. Plant for hot-cure moldings
a) Oven (160–250 °C); b) Recirculating air/water bath; c) Cooling section; d) Working section; e) Inserts

The curing process can be shortened by rapid adjustment of the internal wall temperature of the mold to ca. 120 °C after the end of the rising time. In this case, the molds are heated directly with liquid heating media to conserve energy.

Cold-cure foam systems require much lower mold temperatures. To achieve the optimum quality of the foam skin, the molds are adjusted to the optimum temperature for the mold material and the release agent (between 40 and 65 °C). Cooling equipment is not required (Fig. 27). Depending on the combination of polyols, the isocyanate, the catalyst package, and the shape of the cavity, the foam can be demolded after 2–6 min.

In contrast to open-celled, hot-cure molded foam, the closed cells of cold-cure foam parts must be mechanically opened. This can be achieved by roller crushers with counter-rotating rollers, compressing the parts to a fraction of their original height, or by fast alteration of the ambient pressure in a pressure chamber.

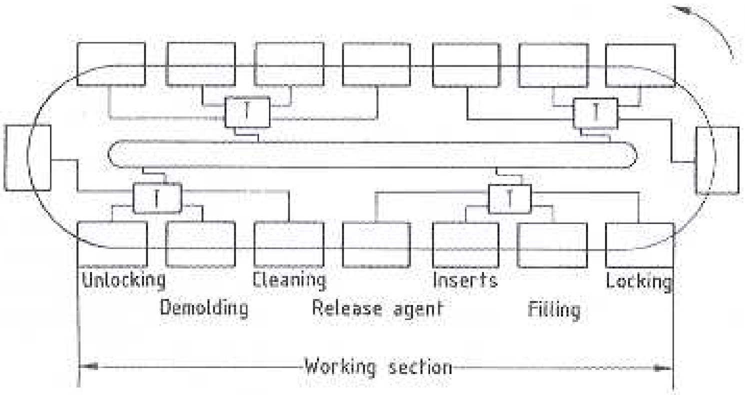


Figure 27. Plant for cold-cure moldings
T = thermostatting units

One hour after demolding, cold-cure molded foams have reached only 50–80 % of their final hardness. Therefore, cold-cure foam parts need to be handled with care in the first few hours after production. Depending on the chemistry and the climatic conditions, final properties are achieved after 5–12 h (for comparison: a hot-cure foam will reach its final hardness within the first 2 h after demolding).

The foam molds must be designed for an internal mold overpressure of 0.3–0.6 bar. When fabricating the master patterns for the mold replica, a loss in volume of the molded part of up to 2 % must be taken into account.

Larger plants (greater space requirement, more molds) are required for the production of hot-cure foam than for cold-cure foam, owing to both the heating/cooling cycle and the longer mold holdup times of ca. 12 min compared to 4–8 min for cold-cure foam. Under ideal conditions, hot-cure molded foam has the advantage of a lower molding mass compared to cold foams at the same compression-load deflection.

7.1.2.3. Properties

Hot-cure and cold-cure foams differ fundamentally in their mechanical properties. The lowest densities can be achieved with hot-cure foam. At the same density, a hot-cure foam will usually provide a higher hardness. However, due to higher venting losses, savings in material for a hot-molded piece of foam are significantly lower than expected based on the simple comparison of apparent densities. The compression load deflection curves of molded foams can be compared with that of free-rise flexible foams (Section 7.1.1.3): the characteristics of hot-cure molded foam are similar to those of conventional slabstock foam; cold-cure molded foam can be compared with HR slabstock. The hysteresis curves show that cold-cure foam has a higher elasticity (narrower hysteresis loop) than molded parts from hot-cure foam. Table 7 gives a general overview of the properties of hot- and cold-cure foams.

With a cold-cure foam cushion, greater comfort is experienced due to its higher elasticity. However, for an automobile seat this higher elasticity means a reduced damping of the vehicle's vibrations. Since the construction of the seat (full foam or combination of foam and springs) and the damping behavior of the vehicle structure must be matched, the question whether to use hot-cure or cold-cure molded foam must be decided for each individual case. A second and more basic difference between hot- and cold-cure foam is their fire behavior. Cold-cure foams down to a density of ca. 35 kg/m^3 usually meet the fire standards of the automobile industry, even without added flame retardants. For hot-molded foam, flame retardants must be used.

7.1.2.4. Applications

Flexible molded foams are principally used in all kinds of seat pads, seat cushions, backrests, bench seats, headrests, etc. in passenger cars (see Fig. 35), motorcycles, and commercial vehicles, aircraft, and railways. Another important area of

Table 7. Average properties for seat grades of flexible molded foams

Property	Hot-cure foam	Cold-cure foam	
		TDI based	MDI based
	HC	HR-T	HR-M
Apparent density (EN-ISO 845), kg/m^3	28 – 40	35 – 50	45 – 65
CLD-Hardness at 40 % (EN-ISO 3386-1), kPa	3 – 7	2 – 8	4 – 12
Compression set 50 %, 70 °C, 22 h (EN-ISO 1856), %	2 – 4	4 – 8	4 – 8
Elongation (EN-ISO 1798), %	120 – 160	100 – 150	90 – 120
Tensile strength (EN-ISO 1798), kPa	80 – 140	130 – 200	100 – 160
Tear strength (ASTM D 3574-F), N/m	200 – 400	200 – 450	160 – 250
Humid ageing (OEM specific)	very good	good	good – very good
Hysteresis (Energy Dissipation)	high	low	medium

application in the automotive industry is sound abatement. Flexible molded foam is used either on its own for absorption of airborne noise or as a composite in conjunction with a heavy layer (EPDM, EVA, or PUR elastomers filled with, e.g., barium sulfate) or as backfilling foam on the vehicle's floor cover. These composites may act either as sound barriers or can be tailored to dampen structureborne noise. In addition, flexible molded foams are used in the furniture industry, e.g., for office chairs, armrests, and in specific combinations with steel springs, which are incorporated into the molded foam. Sealing lips for passenger car tail lamps and for filters can also be produced from molded foams.

7.2. Semirigid Foams

7.2.1. Applications

Semirigid foams are used primarily for improving inner safety and comfort in automobiles. Combined with an external layer of ABS/PVS or PUR skin and a metal or plastic carrier, they are used to produce instrument panels (dash boards), door and pillar covers, armrests, and consoles. The foam has a density range of 80–180 kg/m^3 in the finished part. Key properties are long-term adhesion to skin and carrier, a uniform, fine cell structure, low emission, and high resistance to aging and heat.

Special grades (EA foams) are optimized for energy absorption. On impact, they dissipate the kinetic energy by deformation and thus protect the passengers in a crash (Fig. 28).

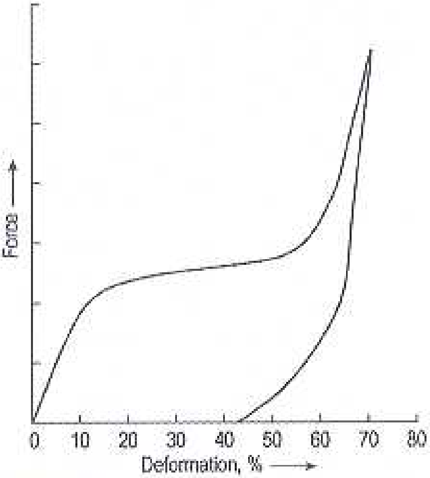


Figure 28. Dynamic force–deformation characteristics of a semi-rigid PUR foam

7.2.2. Production

Parts made of semirigid foam are produced mostly in a two-step process. First, the preformed skin (ABS/PVC by thermoforming or PUR by spraying) is positioned in the cavity of the mold. A plastic or metal carrier is fixed on the lid of the mold. In the second step, the mold is closed and the semirigid foam is injected. Alternately, the semirigid foam is spread in the open mold and the lid is closed before the foam expands.

The two PUR components are mixed by high-pressure machines. The molds are made from aluminum, often coated with epoxy resin. If the foam has contact to the surface of a mold, a wax-based release agent must be used. The demold times are between 1 and 6 min, depending on the size, thickness, and geometry of the parts and on the reactivity of the foam system.

7.2.3. Properties

Semirigid foams are mostly open-celled and have a higher compression load deflection and lower elasticity than flexible foams. Typical properties are:

Apparent density (ISO 845)	80–180 kg/m^3
Tensile strength (ISO 1798)	300–400 kPa
Elongation at break (ISO 1798)	30–60 %
Compression load deflection at 40 % compression (ISO 3386)	80–200 kPa
Compression set at 50 % compression (ISO 1856) 22h at 70 °C	< 10 %

The dynamic impact characteristics (Fig. 28) are important for the dampening and energy absorbing behavior.

7.3. Rigid Foams

Rigid foam is in most cases a closed-cell material that is used for thermal insulation. Besides providing thermal insulation the foam may also have to bear mechanical loads in some applications. Composite structures in which the self-adhesive effect is used to bond the foam to a substrate during the foaming process are often found in the field of rigid foam. This reinforcing sandwich-effect improves the mechanical properties significantly.

Rigid foam is used in many ways. The main applications for rigid foam are appliances (refrigerators, freezers), insulation boards (with and without facings), composite panels (mostly with metal facings), pipe insulation (as insulating shells or as composites), insulated containers, and in situ foam (spray foam).

7.3.1. Raw Materials

Rigid PURs require a highly cross-linked molecular structure. To achieve this, raw materials with high functionalities and low molecular weight are preferred on the polyol and on the isocyanate side. Therefore, short-chain polyether polyols and polymeric MDI are the materials of choice. Low molecular weight polyester polyols are also used.

Typical polyether polyols (see Section 3.2.1) are produced from a highly functional starter molecule (sucrose, sorbitol, glycerol, diethylene glycol, ethylenediamine, and others) or mixtures thereof by adding alkylene oxides, mainly propylene oxide but sometimes ethylene oxide. The resulting products are viscous liquids.

The *polyester polyols* (see Section 3.2.2) are typically based on aromatic acids like phthalic acid. (Di)ethylene glycol is mostly used as alcoholic component. Glycerol or other highly functional alcohol components may be used to increase the functionality. However, the use of starting materials with higher functionalities is limited because of the increasing viscosities of the resulting products.

The *polymeric* MDI types (see Section 3.1.1) that are used have functionalities in the range of roughly 2.5 to 3.5, corresponding to viscosities of about 100 to 1000 mPa · s at 25 °C.

Blowing agents (see Section 3.5) are not only used to create the foam. Since the blowing agent remains inside the closed cells it has a strong influence on the thermal conductivity of the resulting foam. The choice of the blowing agent depends on the most important criteria in the respective application, such as the lowest possible thermal conductivity, processability, or relationship between cost and performance. In most cases, a combination of a physical blowing agent (a low-boiling liquid or a gas) and a chemical blowing agent (mostly carbon dioxide formed by the chemical reaction of water with isocyanate) is used. While, according to the Montreal Protocol, the use of chlorine-containing halogenated hydrocarbons is still allowed in certain areas of the world, the use of these products in Western Europe is banned. Here only fluorinated hydrocarbons such as tetrafluoroethane (R 134a), pentafluoropropane (R 245fa), and pentafluorobutane (R 365mfc) may be used. Hydrocarbons such as n-, iso-, and cyclopentane or mixtures with other hydrocarbons like propane or butane are widely used, despite their flammability. Methods for a safe handling of these products are industrially available and installed. All these blowing agents have very small coefficients of diffusion; they remain within the foam during its lifetime. Where no (metallic) facings are provided, the thermal conductivity increases very slowly because of air diffusing into the foam. Therefore, in some applications, e.g., the construction industry, increments are added to the measured values of the thermal conductivity to take this ageing process into account. In this way it is ensured that a sufficient level of insulation is installed.

Catalysts (see Section 3.5), sometimes called activators, are used to control the foaming process. Products used as catalysts are tertiary amines, organometallic compounds, and alkali metal and quarternary ammonium salts of carboxylic acids. The products may be classified according to their performance-without really being able to draw sharp lines-as blowing, gel, and trimerization catalysts. A few examples taken from a wide range of products are given here: bis[2-(N,N-dimethylamino)ethyl]ether and *N,N*-bis(*N′,N′*-dimethylaminoethyl)methylamine as blowing catalysts; triethylenediamine (dissolved) and dibutyltin dilaurate as gel catalysts and potassium acetate (dissolved) and 1,3,5-tris(3-(dimethylamino)propyl)hexahydrotriazine as trimerization catalysts.

Foam stabilizers (see Section 3.5), also called surfactants, are required to prevent the small bubbles in the liquid reaction mixture from coagulating. Fine-celled foams can be prepared by using these products. To produce foams with a fine cell structure, some air (or other inert gases) may be dispersed into the polyol component or into the reaction mixture for nucleation. A fine cell structure is important for a low thermal conductivity. Chemically, most of the products used in the industry are polyether-modified polysiloxanes. The structural variations possible by using different polyethers and different polysiloxanes lead to the great number of products available on the market, optimized for various purposes. Some of these purposes are: flowability (describes the expansion of the foam into narrow cavities), adhesion to facings (the force required to remove the facing), fine cell structure (small cells of similar size), and flammability (resistivity to flames or high temperatures).

Flame retardants (see Section 3.5) are used to make the foams less flammable. The methods for testing flammability are manifold. However, official requirements regarding flammability are in place for some applications, e.g., in the construction industry. Since PUR foams are based on organic molecules, it is only possible to achieve certain flammability classifications within the group of flammable materials. Flame retardants used in the field are usually substances based on halogens and/or phosphorus. Some products have OH groups, so they can react with isocyanate and are incorporated into the macromolecule; others are nonreactive. Examples of reactive flame retardants are polyethers made from dibromobutenediol and epichlorohydrin or brominated aromatic polyester polyols. Examples of nonreactive flame-retardants are tris(2-chloroisopropyl)phosphate, diphenyl cresyl phosphate, and dimethyl propyl phosphonate. Apart from red phosphorus, which is used in the production of rigid slabstock foam by low-pressure mixing, solid flame retardants have hardly been used in the field of rigid foams. A technique has been developed for processing solid flame retardants continuously on high-pressure machines [189].

7.3.2. Processing

Mixtures of the raw materials mentioned above are processed to produce rigid foams. The foaming process is described and monitored by periods of time taken from the start of mixing:

The *cream time* is the time until the reaction mixture starts to expand. At this point in time, the exothermic reaction has heated the reaction mixture to a temperature at which the blowing agent is starting to evaporate. The gas formed remains in the reaction mixture and forms small bubbles that grow with increasing temperature and further formation of gas.

When the cross-linking of the polymer has progressed to the point where the liquid reaction mixture starts turning into a solid the *gel time* can be observed. This is mostly done by prodding the foam with a small stick. When fibers of polymer are pulled from the rising foam the gel time has been reached.

After that the foam continues to rise to its final height (*rise time*).

The *tack-free time* is the time required for the surface of the foam to lose its tackiness. The tack-free time may occur before or after the rise time.

The time required to cool down the foam depends on its thickness. For slabs 1 m in height it takes more than 24 h until ambient temperature is reached in the core. In all processes the foam applies pressure on the compartment in which it is contained. To keep the parts produced within their specified dimensions, the molds must withstand this pressure until the foam has reached a minimum strength and the part can be demolded (demold time). In continuous processes, the line speed needs to be adjusted to keep the foam in the machine for the time required to cure sufficiently. For thicker parts the demold times are longer than for thinner parts, and therefore the line speeds in a continuous production are slower for thicker parts.

Preblending some of the components-usually into the polyol side-for easier operation can be done at different levels. It can be performed by the raw material supplier or by the processor. This depends mostly on the variability required for the respective process (e.g., adjusting reactivity in continuous processes).

A discontinuous process (sometimes called a one-shot process) is used in cases where particular cavities are to be filled, such as in the production of refrigerators, freezers, insulated containers, and certain sandwich panels. Figure 29 shows the principle of filling refrigerator cabinets.

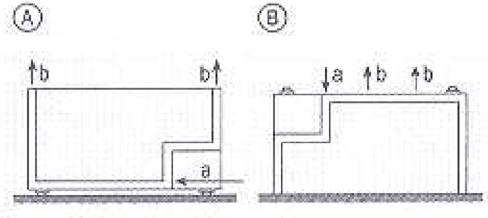


Figure 29. Principle of filling refrigerator cabinets
A) Door opening on top; B) Door opening on bottom
a) Pour-in opening; b) Ventilation openings

Figure 30 shows the discontinuous production of sandwich panels in a multistage press using the mixing head pull technique.

In most of these applications only one type of reaction mixture is used for the whole production range. Here all the necessary components are preblended into the polyol so that only two components, i.e, this polyol formulation and the isocyanate component, must be provided. The components are tempered and metered to the mixing head by high-pressure pumps. The mixing itself is performed by using the high-pressure impingement mixing technique. The amount of reaction mixture necessary to fill the cavity is determined by the volume of the cavity and the density of the foam. The duration of the dosage is then given by the output of the pumps. This shot time must be shorter than the cream time to avoid pumping liquid reaction mixture into an already expanding foam. In so doing, the foam would be partially destroyed with negative effects on all of its properties.

In the continuous production of composite panels and insulation boards on double conveyor belts, the high-pressure impingement mixing technique is also used in most cases. The principle of this process is shown in Figure 31. Here the low weight of the mixing head and the hoses leading to it enable the oscillating of the mixing head across the moving bottom facing for an even distribution of the reaction mixture.

In the special case of the production of insulation boards on high-speed laminators at line speeds of up to 60 m/min, the high-pressure impingement mixing technique is used in most cases, but without oscillating the mixing head. The oscillation frequencies to ensure an even distribution of the reaction mixture on the bottom facing would be too high.

Here even distribution is achieved by passing the reaction mixture through a narrow gap between the top and the bottom facing (calibration technique). By this technique the small voids near the top facing that occur with the oscillating mixing head technique are eliminated. In all these applications it is necessary to adjust the reactivity of the reaction mixture according to the thickness of the board or panel. Also the amount of blowing agent must be adjusted. This means that the degree of preblending is lower than in a discontinuous process. Catalyst, blowing agent, and possibly other additives are metered separately into the polyol stream. Thus, only two components are finally led to the mixing head, keeping the moving weight low for the oscillation.

In the continuous production of rigid slabstock foam low-pressure mixing is used due

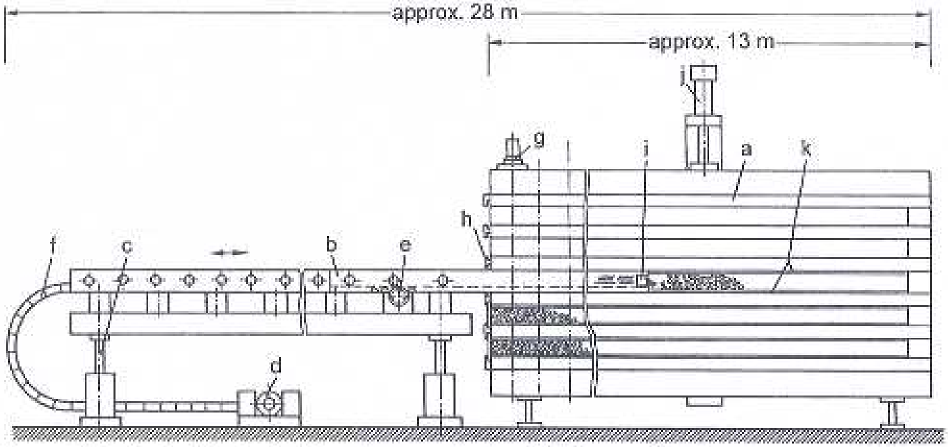


Figure 30. Production line for the discontinuous production of PUR composite elements
a) Plates of the press; b) Carrier on rolls for the hoses leading to the mixing head; c) Lifting device; d) Foam machine; e) Driving elements for horizontal movement; f) Cable holder; g) Device for closing the press; h) Closing cap for each unit; i) Mixing head with hoses; j) Opening device; k) Metal facers

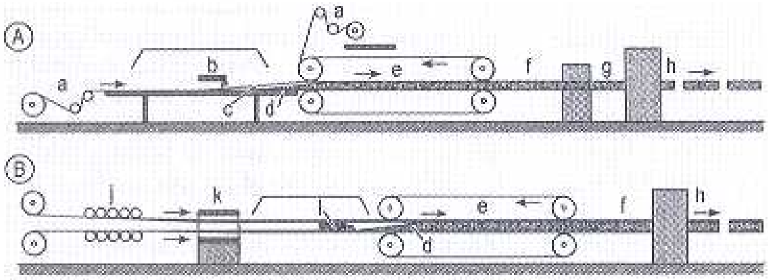


Figure 31. Principle of the continuous production of insulation board
A) With flexible facings; B) With profiled metal facings
a) Unwinding device; b) Lay-down with mixing head; c) Means for folding paper; d) Foaming reaction mixture; e) Compression; f) Cooling area; g) Longitudinal cutting; h) Transverse cutting; i) Coil unwinding; j) Corrugation rolls; k) Heating elements; l) Gate with moving high-pressure impingement mixing head

to the high output. Here the components are metered into a mixing chamber and mixed by a mechanical stirrer. Separate metering of the components into the mixing head can be used. Preparing a polyol component containing all necessary components is also possible and allows for a certain quality control prior to foaming.

7.3.3. Properties

The most important property of rigid PUR foams is its low thermal conductivity, which is the lowest among the different insulation materials available by a significant amount. This allows for a smaller thickness of the insulating layer to achieve the same insulation value. The thermal conductivity of closed-cell PUR foams in the density range 25–60 kg/m^3 depends not so much on the apparent density (usually the thermal conductivity increases slightly with increasing density) but is dominated by the thermal conductivity of the blowing gas. The thermal conductivity can initially be near 0.020 W m^{-1} K^{-1}, and after ageing (cell gas diffusion) typically is in the range of 0.025–0.030 W m^{-1} K^{-1}.

The adhesion to substrates is important for composite constructions. The force needed to remove the foam from the substrate is the criterion used to judge adhesion.

Mechanical properties like compressive strength, tear strength, and shear strength are also important in load-bearing applications. Their values strongly depend on the density and the cell structure (Fig. 32).

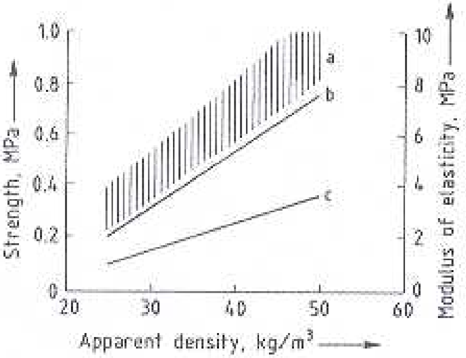


Figure 32. Relationship between typical properties and apparent density of rigid PUR foam (values at room temperature)
a) Modulus of elasticity; b) Tensile strength; c) Compression strength

Dimensional stability must be given under the conditions of use of the respective application. Dimensional stability is tested at low temperatures (e.g., for freezers) and at high temperatures (e.g., for hot water tanks).

Flammability is a very important property of the foam or the composite or both, depending on the test that needs to be passed. Various test methods are in place, most of them in the construction and transportation industries. For example, a harmonized test for the construction industry has been introduced in the EU. The new test procedure comprises a test on the foam (small burner) and the single burning item (SBI) test on the final product under end-use conditions. Other test procedures, e.g., those set up by insurance companies, are also in place.

For the different applications the importance of the various properties is prioritized differently.

For appliances (commercial and domestic refrigerators, freezers, hot water tanks), a low thermal conductivity is of top priority. In these applications a maximum useable space is desired at minimum or given outer dimensions. For this reason, the thickness of the insulation is limited, and only with a foam that offers low thermal conductivity can the energy consumption be minimized. Dimensional stability at low and high temperatures is the other important property here. In the low temperature applications the foam also fulfils a structural task, it forms a type of sandwich structure with the inliner and the outer facing.

Preinsulated pipes are mostly used for district heating. Here the thermal conductivity and the lifetime expectancy are the important properties. Accelerated ageing tests at elevated temperatures are performed to ensure a lifetime of, for example, at least 30 years according to EN 253.

Insulation boards, predominantly those with facings (aluminum foil, mineral fleece, papers) produced on double conveyor belts, also require low thermal conductivity and dimensional stability. On larger insulated areas, e.g., flat roofs, shrinkage would lead to areas without insulation due to gaps between the boards, while swelling might make the boards lift up and break the protective cover. For decorative boards also the appearance is important. Wrinkled facings, mostly aluminum foil, or sink marks due to voids under the facing are unacceptable here. Since most of the products are used in construction, flammability is also an important property.

Composite panels, mostly produced continuously on double conveyor belts with profiled steel sheets as facings, are mainly used in the construction of walls and roofs of large buildings like warehouses or factory buildings. The prefabricated self-supporting panels are attached to a bearing frame construction, so that the complete wall or roof can be put together very fast. The most important properties here are adhesion of the facings, dimensional stability, flammability, and thermal conductivity. The appearance is also important, especially for panels in facades. The thickness of the panels depends on the use of the building. For cold storage houses, where goods are stored at −40 °C, panels up to 24 cm thick are used. The thickness of panels for factories (from about 20 to 100 mm) depends mostly on the local climate. Discontinuously produced panels may have locks for connecting panels with one another that are incorporated into the foam during the foaming process. These panels can be used without bearing constructions, e.g., for walk-in-coolers. Another application is the use of panels in roll-up doors; large ones for truck entrances in industrial buildings, and small ones for private garages.

Slabstock foam is made for applications in very different fields. A few examples are given here: low-temperature insulation (liquid gas tanks, also in ships); refrigerated containments for lorries, where the foam is covered with glass reinforced plastic; insulation for parts that are difficult to mold such as valves and flanges (here the foam is mechanically shaped); wedge-shaped boards to give flat roofs a slope; and others. Different properties are required in these different applications, so rigid slabstock foam is a specialty field. Foams with a range of densities from about 30 to over 200 kg/m^3, different flammability classifications, foams with glass fiber reinforcements, and other variations are found here.

7.3.4. Special Types

Foam from pressurized cans, mainly one-component-foam, is used for mounting and fixing applications such as windows and door-frames. Here all the raw materials, including blowing agent and isocyanate, are blended in the can to form a prepolymer with residual NCO groups. The propellant, that is, liquid under pressure, acts first as thinner for the prepolymer. When expelled the propellant acts as blowing agent to produce the foam. The foam itself is usually an open-cell product.

A few special types of open-cell foam exist, such as thermoformable rigid foam that is used in passenger car headliners, foam for flower-arranging purposes, and packaging foam. Recently some attempts have been taken to evacuate open cell foam to reduce the thermal conductivity even further. One problem here is to find suitable facings that ensure that the vacuum is maintained during the lifetime of the product.

In certain cases the foam must be applied in situ. Two methods are predominant: spraying and layer-by-layer application. Spray foam is mostly used for the industrial insulation of storage tanks or in the insulation of buildings. While spray foam on walls is only for insulation, foam on roofs is also applied for sealing purposes. Two-component systems are used here. The components are fed through heated hoses to the mixing head, which is designed like a spray gun. The reactivity of these systems is so high that the foam cures within a few seconds. In layer-by-layer application the reaction mixture is poured between two substrates, e.g., the outside of a tank and the casing. This method is used where the application of the foam in a factory is not possible, e.g., because of the size of the tank. Here also two-component systems are used. In both cases special attention must be paid to temperature and humidity conditions. Foams should not be applied on cold or moist surfaces. Otherwise, problems with bonding the foam to the substrate may result.

Polyisocyanurate (PIR) foams [190–195], more precisely to be understood as polyisocyanurate-modified PUR foams, are products in which isocyanurate structures are incorporated into the macromolecule. These structures are formed due to the reaction of excess isocyanate with itself. Special (trimerization) catalysts are required. Three NCO groups form the cyclic isocyanurate structure, which shows a higher decomposition temperature than PUR groups. Therefore, these foams are used where flammability or heat resistance is an issue. However, this highly cross-linked structure increases the brittleness of the foams. The overall cross-linking density is controlled by the use of low-functionality polyols. In the continuous production of insulation boards on double conveyor belts, which is the major application for this type of foam, the PIR structure is usually combined with (aromatic) polyester polyols. The higher decomposition temperatures of esters compared to ethers also leads to an additional positive effect on the flammability of the foam. In the manufacturing of these foams, special attention must be paid to the temperature of the laminator because the trimerization only takes place at temperatures above 60 °C. Apart from the reduction of brittleness the polyols have the task of heating the reaction mixture by their exothermic reaction with isocyanate. When the required temperature is reached, the trimerization starts, which can often be observed as a second phase in the expansion of the foam.

7.4. Integral Skin Foams and RIM Materials [196–198]

Integral skin or self-skinning foams are products with a cellular core and a cell-free surface that are formed in a mold in a single operation (Fig. 33). Parts made by the reaction injection molding (RIM) process are microcellular materials with a high surface quality that are mostly painted.

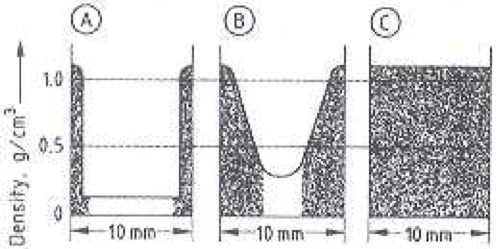


Figure 33. Principle of density distribution for integral foam boards of 10 mm thickness and various apparent densities: A) 0.2 g/cm^3; B) 0.6 g/cm^3; C) 1.1 g/cm^3

7.4.1. Applications

Flexible self-skinning foams are used mainly in the automotive, furniture, and footwear industries. Typical automotive applications are steering wheels and gearshift knobs, but also armrests and headrests (Fig. 34). In the footwear industry, integral skin foams are used for soles of sport, leisure, and safety shoes.

RIM materials are used for exterior auto parts like fenders (Fig. 35A), panels, side protection and window encapsulation, but also for other exterior parts in agricultural machines or recreational vehicles like snowmobiles (Fig. 35B).

Rigid integral skin foams or RIM materials can be used in many different applications, mainly for structural parts. They can favorably compete with wood, thermoplastics, thermosets, and metals. They are used for furniture, skis, pump housings, window frames, decorative applications, and housings, just to name a few characteristic applications.

7.4.2. Production

Integral skin foams are mostly manufactured in metallic (aluminum) or epoxy molds. Skin formation is controlled by addition of a low-boiling solvent in amounts of about 2–10 wt %, relative to the polyol mixture. After the banning of CFCs and HCFCs, currently HFCs (hydrofluorocarbons) or alkanes are used. When using alkanes, special precautions must be taken because of their flammability.

Thermodynamic equilibrium between the liquid and gaseous phases of the blowing agent in the reaction mixture is crucial for the formation of the closed surface. The mold temperature is kept between 40 and 60 °C, and the reaction mixture in the vicinity of the mold surface has a lower temperature than the core (up to 140 °C). In the core the blowing agent vaporizes, while near the edge it condenses, with formation of the solid surface.

The quality of the surface depends very much on the quality of the mold, but precise control of the processing pressures and temperatures is also required.

In special cases formation of an integral skin is possible without the addition of physical blowing agents. For this, temperature-controlled carbon dioxide formation from the NCO/H_2O reaction must be achieved.

High-pressure metering and mixing units are necessary for manufacturing of RIM parts. The processing of these materials, which are mostly of high reactivity, also requires closed, metallic molds and a clamping unit. To obtain void-free parts without porosity the reaction mixture must enter the mold cavity through a gate designed to ensure laminar flow. Also, correct venting of the mold at the highest points and nucleation of the reaction mixture by air or nitrogen are important for good quality.

After demolding, the parts must be trimmed, and gate and flash must be removed. The surface is prepared for painting by removal of the release agent by washing or sanding.

7.4.3. Properties

Depending on the field of use, soft-elastic moldings have densities of 100–300 kg/m^3, flexible molded articles 400–600 kg/m^3, and the relatively hard, microcellular elastomers 900–1100 kg/m^3.

Technical data for a typical soft integral skin foam of low density:

Density (ISO 845)	400 kg/m^3
Shore A hardness (DIN 53505)	35
Tensile strength (DIN 53504)	0.8 MPa
Elongation at break (DIN 53504)	85 %
Tear resistance (ISO 34)	1.4 kN/m
Compression set (25 %/70 h, RT; ISO 1856)	2.5 %

Mechanical properties of a flexible molding of medium density used in the footwear industry (e.g., polyester system):

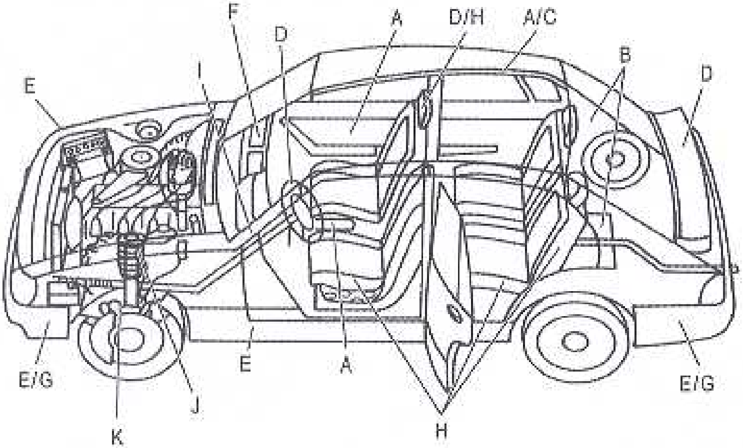


Figure 34. Use of PURs in the passenger car
A) Rigid integral foam; B) Rigid integral foam, glass-mat reinforced; C) Hot-moldable rigid foam; D) Semi-flexible integral foam; E) Semi-flexible integral foam, glass-fiber reinforced; F) Semi-flexible filling foam; G) Semi-flexible filling foam, impact-energy-absorbing ; H) Flexible molded foam; I) rigid foam; J) Hot-curing PUR elastomer; K) PUR rubber

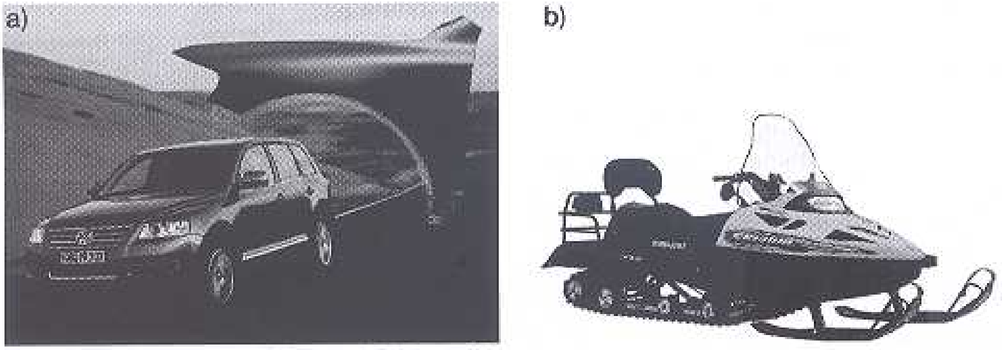


Figure 35. Use of integral skin foams and RIM materials
A) Fender of the VW Touareg; B) Snowmobile

Density (ISO 845)	500–600 kg/m^3
Shore A hardness (DIN 53505)	ca. 50
Tensile strength (ISO 1798)	6–8 MPa
Elongation at break (ISO 1798)	450–550 %
Tear propagation strength (ISO 34)	10–15 kN/m
Abrasion loss (DIN 53516)	50–100 mg

Mechanical properties of a microcellular elastomer molding of high density (e.g., automotive body parts):

Density (ISO 845)	1100 ± 50 kg/m^3
Shore D hardness (DIN 53505)	64 ± 3
Tensile strength (DIN 53504)	35 ± 3 MPa
Elongation at break (DIN 53504)	300 ± 30 %
Tear propagation strength with cut (ISO 34)	80 ± 10 kN/m
Modulus of elasticity according to Roelig	
at −30 °C	1400 ± 100 MPa
at + 20 °C	600 ± 50 MPa
at + 65 °C	360 ± 30 MPa

The technical data of rigid integral skin foams depend very much on the density, which can be anywhere between 150 and 1100 kg/m^3. Typical properties of a low-density rigid integral skin foam, as used for imitation wood follow:

Density (ISO 845)	400 kg/m^3
Shore D hardness (DIN 53505)	58
Flexural strength (ISO 178)	20 MPa
Flexural modulus of elasticity (ISO 178)	520 MPa
Impact strength (ISO 6603)	10 KJ/m^2
Heat deflection temperature (ISO 75)	90 °C

High-density rigid RIM materials, which are typically used at wall thickness between 3 and 5 mm, have the following characteristics:

Density (ISO 1183)	1100 kg/m^3
Shore D hardness (DIN 53505)	76
Flexural strength (ISO 178)	25–45 MPa
Flexural modulus of elasticity (ISO 178)	2000 MPa
Tensile strength (ISO 527)	53 MPa
Elongation at break (ISO 527)	14 %
Impact strength (ISO 179)	45 KJ/m^2
Heat deflection temperature (ISO 75)	115 °C

When flame retardancy tests are also considered, RIM materials are capable of passing burning tests such as UL 94 V-0 (Underwriters' Laboratories) or B2 (DIN 4102) by the addition of flame retardants.

Both flexible and rigid RIM materials can be reinforced with short or long glass or mineral fibers and also glass mats or mats made of natural fibers. These composite materials show considerably higher stiffness and especially impact strength.

8. Noncellular Polyurethanes

Although the term "noncellular" is unambiguous, the terminology of the products treated in this chapter requires explanation. "Cellular Vulkollan," well known from the early days of PURs, already breached the borderline of precise definition. In practice, this material was not considered a "foam," although it can be undoubtedly classified as a foam from a strictly physical viewpoint because of its cellular structure, however small the few cells may be. The RIM technology has made the definitions even less distinct due to the terminology of "microcellular elastomers" on the one hand and "solid integral parts" on the other. In this chapter the problem of definition is solved as follows: All products which are based on a formulation that usually leads to a foam are classified as "foams," even if cell-free solid materials can be obtained by raising the apparent density (less blowing agent). Similarly, products which are based on formulations that usually result in noncellular materials are classified as noncellular PUR, even though they may be cellular, and these materials are treated in this chapter.

There are two different processing technologies for manufacturing these noncellular PURs. Liquid, low molecular mass raw material systems are converted to high molecular mass products by the reaction of the polyol and polyisocyanate components by cold or hot curing. Linear, high-molecular-mass raw material systems are either thermoplastically processable pellets or urethane rubber are processed by vulcanization technology.

8.1. Cast Elastomers

Cast elastomers are mostly solid, noncellular materials, produced in a low-pressure casting process from ester or ether prepolymers of MDI, TDI, and NDI (see Section 3.1.1) and a cross-linker such as butanediol. If water-containing cross-linkers are used, cellular elastomers can also be obtained.

8.1.1. Applications

The highest quality elastomers are those derived from NDI [Tradenames: Vulkollan (Bayer MaterialScience), Cellasto (Elastogran)]. They are used where materials must meet extremely high requirements regarding durability and mechanical properties. Examples are high-load rolls and wheels for forklift trucks and machines, hydraulic seals, membranes, valve seats and balls, scrapers, and sieves. Cellular NDI-based elastomers are widely used in the automotive industry for bouncers and spring supports (Figs. 34 and 36).

Hot-curing elastomers based on MDI or TDI are used, e.g., for bottle stars in automatic filling machines, cutting wheels for fiber production, roll covers for the paper and printing industry, and wheels for in-line skates and skateboards.

Cold-curing PUR elastomers are used as binders for the surface of playgrounds and sport tracks. These surfaces are very durable, require little maintenance, can be used under all weather conditions, and reduce the risk of injuries. Other applications are seals for stoneware pipes, polishing disks, protective edges, and permanent fenders for boats. Cold-cure elastomers can also be sprayed on concrete or metal for corrosion protection and are used for the surfacing of bridges, parking decks, and terraces and for lining of wagons and trucks.

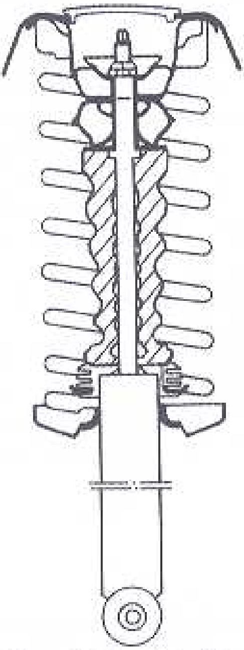


Figure 36. Use of cellular Vulkollan as supplementary spring in the passenger car

8.1.2. Production

The raw materials used are low molecular mass glycols or amines, polyester or polyether polyols, and (modified) MDI-, TDI-, or NDI-type isocyanates.

The elastomers can be manufactured in a two-step or a one-step procedure. Figure 37 shows a typical line for the production of high-quality elastomers, as is used for NDI-based high-performance materials. The system passes through several stages: dehydration of the polyester (a), production of prepolymer from polyester and diisocyanate (b), degassing of the feed component (c), admixing of cross-linking agent (d), atmospheric-pressure casting in open molds (e, f), and fully curing the molding at 100–300 °C for several hours (g). This processing technique even allows the production of voluminous and thick-walled parts in relatively simple, inexpensive molds with low energy consumption. Depending on the system to be cast, steel, aluminum, and in special cases plastics or wood can be used as the mold material.

For MDI and TDI stable prepolymers are commercially available, so that a one-step process can be used. The reactivity of the raw materials varies widely. Casting times between 2 and 60 min can be realized.

Cold-casting systems are usually processed with a casting machine. For some formulations that have a sufficiently long pot life, the starting components can also be hand mixed and cast. In this case the charge volumes are limited to a few liters. The reaction mixtures cure, without an external heat supply, within widely differing cure times, from less than 10 min to a maximum of 24 h. The castings reach their final strength after ca. 7 d storage at room temperature.

8.1.3. Properties

NDI-based elastomers have a temperature range for continuous use between −30 and +80 °C. At temperatures below 0 °C the material becomes increasingly hard and inelastic, though there is no danger of fracture. Embrittlement occurs only at very low temperatures (below −30 °C).

NDI elastomer (Vulkollan) is resistant to mineral oils, grease, gasoline, and most organic solvents. Gasoline and some solvents cause some swelling, but this does not impair its mechanical properties if the solvents are able to re-evaporate. Concentrated acids, alkalis, and other hydrolyzing media attack NDI elastomers. By incorporating additives or using special polyesters the hydrolytic stability can be increased so that the service life of the elastomers becomes adequate for a variety of uses even under extreme conditions. Mechanical properties of NDI elastomers are listed in Table 8.

Cellular NDI elastomers can be produced with densities of 300–700 kg/m^3 and are characterized by their high capability of absorbing energy on impact. The material can be compressed by up to 80 % of the original volume without damage. Damping units with various compression deformation characteristics can be manufactured from cellular Vulkollan by varying its apparent density, preferably in the range 300–600 kg/m^3.

Hot-casting systems with a base other than NDI are produced with Shore hardness grades from ca. 55A to 65D. The other mechanical properties and the chemical stability are basically comparable with those of NDI elastomers without reaching the same levels, especially in

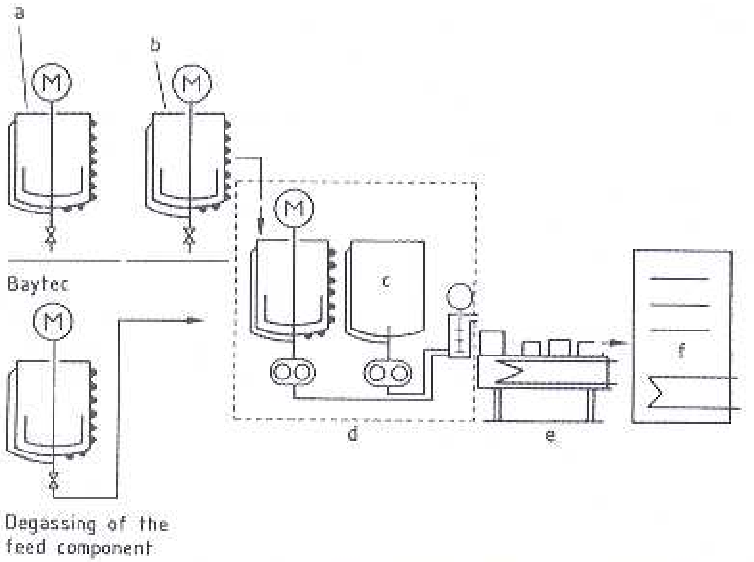


Figure 37. Flow chart for production of high-quality elastomer (e.g., Vulkollan/Baytec)
a) Dehydrogenation of the polyester; b) Prepolymer production; c) Cross-linker; d) Casting machine; e) Mold frame; f) Heating oven (thermal posttreatment)

Table 8. Mechanical properties of a hot-casting system (e.g., Vulkollan)*

Property	Vulkollan type			
	18/40	18	30	50
Shore hardness A/D (DIN 53505)	68/20	83/31	92/36	96/58
Density (ISO 1183), kg/m^3	1.25	1.25	1.26	1.26
Abrasion loss** (DIN 53516), mm^3	45 – 50	45 – 50	40 – 50	43 – 48
Tear propagation strength according to Graves (ISO 34), kN/m	20 – 30	40 – 55	67 – 85	85 – 96
Impact resilience (DIN 53512), %	48 – 55	45 – 50	45 – 50	45 – 50
Tensile strength (DIN 53504), MPa	42 – 49	50 – 60	37 – 45	40 – 43
Elongation at break (DIN 53504), %	600 – 700	630 – 750	550 – 650	330 – 370

*The properties listed here can only be regarded as approximate. For Vulkollan articles on the market, the quality characteristics specified by the manufacturer are applicable.
**Relative to abrasion-resistant grade of natural rubber (= 100).

dynamic stability. They do not, however, reach the high values of Vulkollan in all points, as is also clear from the lower dynamic stability under load. MDI and TDI elastomers cannot replace Vulkollan but are used as supplementary products, primarily in fields where the high quality of Vulkollan is not absolutely necessary, where a system with long casting time is advantageous for producing large-volume and thick-walled moldings, and where short demolding times are desirable for producing large series.

Cold-curing products have a good elasticity, high flexibility, and a variable Shore hardness in the range of ca. 20A to 65D. They are highly resistant to aging and microorganisms and are not attacked by dilute acids and alkalis, mineral oils, soaps, or detergents. Organic solvents cause various degrees of swelling.

8.2. Thermoplastic Polyurethane Elastomers (TPU)

See also → Rubber, 3. Synthetic, Chap. 7.3, → Thermoplastic Elastomers, Chap. 2

Production. Diisocyanate (usually MDI), polyols (polyester and polyether polyols), chain extenders (butanediol), and the necessary auxiliaries are reacted in continuous plants via mixing heads or in reaction extruders. After solidifying, the product is processed further to pellets. The TPU can be processed further by, e.g., injection molding, extrusion, calendering, or blow molding to give finished or semi-finished products.

Properties. The principle of "tailor-made plastics" applies to the properties of thermoplastic PURs, as to all PURs. A very wide range of properties is available by careful choice of the starting materials. This is shown in Figures 38 and 39 as well as Table 9 for three selected examples.

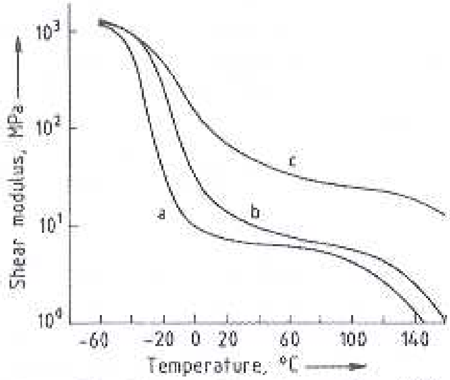


Figure 38. Shear modulus for various TPUs (e.g., Desmopan)
a) Type 385; b) Type 790; c) Type 460

Uses. The TPUs are valued as high-grade polymeric materials in many industrial branches for a great variety of constructional parts. Table 10 shows examples of their use in relation to their Shore hardness. Glass-fiber reinforced types are used for bodywork units.

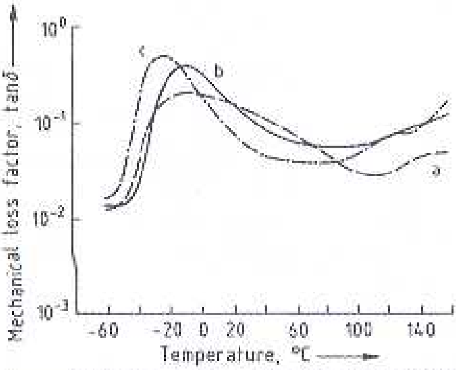


Figure 39. Mechanical loss factor for various TPUs (e.g., Desmopan)
a) Type 385; b) Type 790; c) Type 460

Table 10. Typical applications for different grades of TPU

Hardness range		Uses
Shore A	Shore D	
75 – 90	< 35	membranes, seals, damping units, sieve units, hoses, cable sheatings
90 – 95	35 – 45	animal identification markings, roll coverings, toothed belts, sport shoe soles
> 95	45 – 55	seals, flanges, rolls, pneumatic hoses
	55 – 70	bearings, bushes, connectors, ball sockets, seals, coupling units, ski bootlegs, heel pieces

Table 9. Mechanical properties of different types of TPU (e.g., Desmopan)

Property	Desmopan system		
	385	460	790
Shore hardness A/D (ISO 868)	86/33	97/59	92/42
Density (ISO 1183), kg/m^3	1200	1210	1210
Tensile strength (ISO 527-1/-3), MPa	40	35	55
Elongation at break (ISO 527-1/-3), %	450	350	450
Tear propagation resistance (ISO 34-1), kN/m	80	120	85
Impact resilience (ISO 4662), %	42	35	32
Abrasion loss (ISO 4669), mm^3	30	40	30

9. Polyurethane Coatings [199–201]

See also → Paints and Coatings, Chap. 2.9

PUR coatings offer a large variety of outstanding properties, which make them suitable for many high-performance applications. PUR coatings have polymeric structures with urethane, urea, biuret, or allophanate coupling groups. They are generated either from reactive systems by polyaddition of oligomeric polyisocyanates with polyol components, or from high molecular mass adducts which are further cross-linked by physical drying or other mechanisms. The nature of the isocyanate building blocks (aliphatic or aromatic) and the structure of the backbone are important. Film mechanical properties are dependent on the structure of the polymer (segmented, interpenetrated networks) and cross-link density. PUR coatings are available solvent-borne and, as a result of the trend to reduced emission systems (low VOC), as high-solids, waterborne, solvent-free, and powder systems. Important PUR systems are summarized below.

Two-component coatings are the most important (solvent-borne) PUR paint systems. The primary component is always polyisocyanate (mainly HDI, IPDI, or TDI derivatives). The other component consists of polyols (polyester, polyacrylic) or amines or a mixture thereof and any additional ingredients such as pigments or solvents. The reactive components must be kept separate. Mixing, preferably of an equimolar equivalent, is done immediately before application. The coatings system can be applied by all conventional coating methods, but preferably by spraying or, industrially, with automatic two-component equipment. The solids contents of the coatings are usually higher than with standard coatings and can reach 80 % (pigmented high-solids), depending on the formulation. Curing takes place at ambient temperature, but can be accelerated by heat. Outstanding film properties such as high mechanical resistance, high chemical resistance, and, with aliphatic polyisocyanates, excellent lightfastness and weather resistance, open up a broad range of uses. Major areas of application are transportation (large motor and rail vehicles, aircraft, automobile finishes and refinishes), the building sector (wood and mineral substrates), industrial paints, and steel construction.

One-component coatings include air-drying and stoving systems. The most important are solvent-borne, isocyanate-terminated prepolymers of higher molecular weight made from aromatic or aliphatic isocyanates (MDI, TDI, HDI, IPDI) with polyols. They react with atmospheric moisture to form urea linking groups. Although the final properties are comparable to those of two-component PURs, curing of these systems is slower, which limits their use mainly to wood-flooring coatings, corrosion protection, and applications on mineral surfaces.

The reaction of TDI or IPDI with polyol-modified drying or semi-drying oils generates urethane alkyds, which can be cured oxidatively (by air drying) like alkyds.

The isocyanate groups of prepolymers can be reacted with agents containing, e.g., acidic CH or NH groups to form blocked isocyanates (see Section 3.1.3). Their mixtures with polyols are stable at room temperature, but react at elevated temperatures (120–220 °C, depending on the nature of the blocking agent). The resulting films have a very high mechanical resistance. They are particularly important for automotive finishes, industrial goods and coil coating.

Powder coatings consist of a combination of solid polyols (mostly polyester or polyacrylate polyols) and solid blocked polyisocyanates as the cross-linker. ε-Caprolactam was the most commonly used blocking agent but is being replaced by other blocking agents. An alternative method, avoiding the use of an added blocking agent is the dimerization of the isocyanate groups to uretdiones. During stoving (10–25 min at 150–210 °C) isocyanate groups are liberated and undergo cross-linking. PUR powder systems are used in many industrial applications.

Waterborne coatings are growing continuously in importance, due to the requirement that emissions should be reduced. A variety of systems are available, comparable to solvent-borne coatings. One-component systems are based on self-emulsifying polyurethane or polyurethane-polyurea dispersions. They are manufactured by processes which allow the production, in contrast to solvent-borne PURs, of any molecular weight without having a significant impact on viscosity, and with only small contents of solvents or no solvent at all. These products are used in physically dried films for more flexible substrates like textile, paper, and plastics. One-component polyurethane/polyacrylate dispersions based on aliphatic or aromatic isocyanates are used for coating parquet flooring. In addition, UV-curing PUR acrylate dispersions are used in industrial wood and furniture finishes.

One-component stoving systems contain blocked polyisocyanates emulsified in OH- or NH-containing dispersions (epoxy polyester, acrylic). Important applications are automotive coatings (electrodeposition coating, primer surfacer) and other industrial coatings.

Reactive waterborne two-component systems are based on polyisocyanates (HDI, IPDI) and aqueous OH-functional dispersions (polyacrylate, polyester, polyester polyurethane). Self-emulsifying polyisocyanates reduce interfacial tension between the components and ease homogenization. The film properties are influenced by the extent of side reactions, which can occur in the presence of water. The main applications of these reactive systems are in all types of industrial, wood, and plastic coatings.

10. Polyurethane Adhesives [202–204]

See also → Adhesives

PUR adhesives exhibit unique properties due to their wide variety of compositions, their excellent adhesion to most polar substrates (ability to form hydrogen bonds), and the possibility of chemical cross-linking.

To achieve good cohesive strength of the adhesive bond, high molecular weight polymers are necessary. On the other hand, for good adhesion to the substrate, efficient wetting of the surface is essential. This can be done either by "liquefying" the polymer by the use of solvents, aqueous dispersions, or heat or by in situ polyaddition of low-viscosity polyols and polyisocyanates to give high molecular weight products. Depending on the application, the adhesives can be differentiated as follows:

Solvent-borne adhesives are made by dissolving granules of a linear high molecular weight OH-terminated PUR in a solvent like methyl ethyl ketone, acetone, ethyl acetate, or mixtures thereof to a solids content of up to 15–20 %. The PUR building blocks are crystalline polyester diols or polycaprolactones, aromatic diisocyanates (mainly MDI or TDI), and possibly a low molecular weight chain extender like butanediol or hexanediol. After evaporation of the solvent a nonblocking adhesive film results on the substrate. Due to the crystalline nature of the polyester soft segment, this adhesive film can be thermally reactivated at temperatures between 50 and 80 °C, and in this tacky state bond formation to a second coated and activated substrate can be achieved. On cooling down again, recrystallization leads to high initial and final bond strength ("physical setting"). To improve properties such as heat resistance, resistance to solvents, water, oils, or plastisizers, two-component processing is possible. This is achieved by adding a solvent-based triisocyanate (e.g., Desmodur R-Series, Bayer MaterialScience, cf. Section 3.1.1) to the adhesive solution shortly before application, which results in chemical cross-linking by reaction with the OH groups of the base polymer and other isocyanate-reactive groups on the substrate (including water). The main application for this kind of adhesive is in the footwear industry (bonding shoe soles to uppers).

Waterborne adhesives usually consist of a 40–50 wt. % aqueous dispersion of a high molecular weight PUR made by the acetone or the prepolymer mixing process. Besides crystalline polyester diols, aliphatic isocyanates such as HDI or IPDI and ionic or hydrophilic groups containing chain extenders are used as starting materials. Properties and processing are comparable to those of solvent-borne adhesives. Crosslinking can be achieved by using solvent-free emulsifiable polyisocyanates (e.g.- Desmodur D series, Bayer MaterialScience). The main applications are in sport shoe fabrication, the furniture industry (MDF kitchen cabinet door lamination with PVC films), and the automotive industry (lamination of interior trim parts with films).

Hot-melt adhesives are available in nonreactive and reactive form. The starting materials for nonreactive systems are similar to those used for solvent-borne adhesives, but instead of dissolving the granules, these are either directly extruded onto the substrate or (co)extruded to form hot-melt films or fleeces. Another possibility for bringing the adhesive polymer into intimate contact with the substrate (without using solvents or water as a carrier) is cold grinding of the granules. The resulting powders (particle size < 600 µm) can be easily brought onto the surface by scatter coating. Common to all these nonreactive hot melt application forms is the (in this case only one-component) processing by the thermoactivation procedure described above. Application fields are textile and film lamination.

Reactive hot melts are prepolymers of a crystalline or high-T_g polyester with an excess of a diisocyanate (mostly MDI-based). They are applied at temperatures of 60–80 °C higher than the melting point of the soft segment and combine the aforementioned advantages of physical setting and chemical cross-linking (NCO/water reaction). Typical application areas are bookbinding, woodworking, packaging, and the automotive and construction industries.

Reactive adhesives can be divided into one- and two-component systems. One-component reactive adhesives liquid at room temperature are NCO-terminated prepolymers of (usually) polyether polyols and an excess of an aromatic polyisocyanate (mainly MDI derivatives). Setting occurs by reaction with humidity and therefore requires at least one porous substrate. Applications are foam rebonding, rubber crumb bonding, and in the construction and transportation fields.

Two-component reactive adhesives consist of a liquid polyether polyol (or a low-viscosity polyester polyol) and a polyisocyanate (mainly polymeric MDI). The two components are either mixed and applied immediately before use by an automatic machine or by using a hand-held double cartridge/static mixer combination. A broad spectrum of polyisocyanates and polyols is available, and the mixing ratio of the two components can be varied over a wide range. Thus, it is possible to design the adhesive for the individual substrate/bond requirements, e.g., from flexible to rigid. Application fields are again transport and construction, and flexible packaging/film lamination (no porous substrate necessary).

11. Polyurethane Fibers [205]

See also → Fibers, 4. Synthetic Organic, Chap. 3

Synthetic fibers containing at least 85 wt % of high molecular weight segmented PUR [206] are known as Elastane or in the USA as Spandex. The segmented structure (see Section 4.2) gives these fibers high elasticity and makes them easy to stretch. The properties are determined not only by the raw materials used, but also by the synthesis conditions, the spinning process, and the post-treatment.

Compared to rubber fibers, the PUR fibers exhibit superior properties such as the ability to form fine filaments, good colorability and chemical resistance, and high resistance to physical impact.

They are produced by a two step process. In the first step, long-chain diols are reacted with aromatic diisocyanates; in the second step, the high-melting urethane and/or urea groups which are necessary for the high-level properties are introduced by chain extension with short-chain diols or diamines (see Section 4.2) [207–211].

In industrial production, usually poly(tetraethylene glycol) [212, 213], manufactured by ring-opening polymerization of tetrahydrofuran, is used as the long-chain polyol. In some cases, copolyethers of tetrahydrofuran and 3-methyltetrahydrofuran are used [214]. If polyesters are used as diols, they are usually based on adipic acid and mixtures of ethylene glycol, propylene gylcol, butylene glycol, and/or 1,6-hexandiol.

Aromatic diisocyanates, mainly 4,4′-MDI and in some cases 2,4-TDI, are used exclusively. Due to its unsymmetrical structure, 2,4-TDI leads to a weaker segmented structure and therefore to lower thermostability. Aliphatic diisocyanates, e.g., HDI, are only used in small amounts as modifiers.

Chain extension with diamines usually gives high-performance Elastane [215–218]. Mostly primary cycloaliphatic or aliphatic diamines such as ethylenediamine and 1,2-propylenediamine are used. Modification of the hard segments is achieved by adding small amounts of, e.g., 1,3-diaminocyclohexane.

12. Polyurethanes and Isocyanates as Binders [219]

Panels and molded parts made of wood chips, fibers, and veneers are used extensively in the furniture, building, packaging, and automotive industries. These products are produced under heat and pressure by using a variety of organic binders. PURs are excellent starting materials for composite binders and are used extensively in their production. They are classified according to binder type as polyurethane and polyurea bonding agents.

Polyurethane bonding can be accomplished with one-component moisture-curing systems or two-component ambient-cure systems. The latter can be adjusted in reactivity to meet processing conditions.

PUR dispersions are also utilized in special cases. In addition to adhesion, PUR dispersions exhibit excellent film-forming properties. This is an especially important characteristic for the sizing of glass fibers. PUR dispersions meet very specific requirements regarding film formation and glass adhesion, critical for "matrix" bonding. The properties of glass-reinforced plastic depend to a high degree on the adhesion of the polymer to the surface of the glass fibers.

In polyurea bonding, polyisocyanates are transformed into polyureas at high temperatures in the presence of moisture and, if necessary, catalysts. In addition to the physical adhesion properties of polyureas, there is also the possibility of adhesion by way of chemical reactions between polyisocyanate and reactive groups of the substrate material. Compared to the PUR binders, polyureas are more rigid and hydrophobic.

Binders based on polymeric diphenylmethane diisocyanate (PMDI) have been industrially used in the wood composite industry since 1973. PMDI binders are used worldwide in the manufacture of particleboard, oriented strand board (OSB), laminated strand lumber (LSL), medium-density fiberboard (MDF), and other specially engineered wood composites, as well as panel products based on annual plants, e.g., straw and sugar cane bagasse. The manufacture of straw-based panels was indeed first made possible with PMDI binders.

The success of PMDI binders in the wood and straw composites industry has its origin in the unique properties of the polyurea bond.

Moisture resistance: polyurea is highly cross-linked, chemically stable, and hydrolytically resistant. PMDI binders are one of two binders listed in the European standard for particleboard EN 312-3/5, option 2 that require no special testing to prove hydrolytic resistance.

Dimensional stability: polyurea is also hydrophobic and lends wooden panels improved dimensional stability. This was demonstrated on particleboard during three years of outdoor exposure, where they showed the lowest moisture absorbance and weight changes. This favorable behavior was also confirmed by long-term stress bending (creep testing) under severe conditions of 40 °C and 95 % R.H.

Emission-free: PMDI wood binders contain no formaldehyde. The resultant polyurea bond in the finished panel is free from emissions.

High-strength properties: The excellent adhesion properties of polyurea and the deep anchoring of the bond in the wood structure leads to the high strengths of the different wood composite panels.

During the manufacture and processing of rigid PUR foams, cutting and milling about 5–25 % of scrap is generated. Utilization of this scrap is possible by bonding it into panels or molded parts with varying properties. This can technically be realized with the aid of the hot-press technique employing PMDI binders, analogous to the manufacture of wood composites. The physical and mechanical properties of articles made from rigid PUR foam scrap can be varied over a wide range. The properties depend upon the type and pretreatment of the raw material, the amount of bonding agent, and the density.

Cork granulates and remilled rubber waste, especially peeled tire tread from the recapping process, as well as recovered scrap from milling of frozen old tires, can be converted with PUR bonding agents to composite materials. The bonding agents are isocyanate-terminated, one-component, moisture-curing prepolymers or reactive two-component systems. They form elastic films during curing. The prepolymers are synthesized from long-chain linear or slightly branched polyethers and MDI types or toluene diisocyanate and/or from mixtures of both. The one-component prepolymers generally have an NCO content of ca. 10 % and a viscosity of 1500 to 3000 mPa · s at 23 °C.

The most important properties are elasticity, flexibility, damping capacity and void content. They can be varied over a broad range through the shape and size of the rubber particles, type and amount of binder, and degree of compaction.

13. Special Products

PURs are particularly suitable as wall materials for microcapsules (see also → Microencapsulation). Capsules can be impermeable or permeable to the core material. The capsule wall is usually produced by interfacial reaction of multifunctional isocyanates or NCO prepolymers and multifunctional amines at an oil/water interface. The microcapsules have a diameter of 1 to 5000 μm, depending on the droplet size of the emulsion used for polymer formation. The capsules are used for a wide variety of purposes, e.g., for the production of carbonless copying paper or for the delayed release of plant-protection products.

Polyoxazolidinone polyisocyanurates are produced from polyisocyanates and epoxy resins in the presence of special catalysts (see Chap. 2). They have high fire resistance, high long-term heat resistance, and excellent electrical insulation properties [220, 221].

Water-soluble PURs are of interest as retaining agents and dyeing auxiliaries, thickeners, paper-sizing agents, and other sizers.

Oligourethanes with unsaturated (e.g., acrylate) groups can be cured by UV radiation in the presence of photoinitiators [222]. Systems based on acrylate groups containing blocked NCO prepolymers have been developed. They can be cured either by heat or by radiation (dual curing [223–227]) and are used especially for automotive refinishing paint.

14. Safety and Ecology

PUR-containing products have become an essential part of modern living. For production and processing of all of these varieties of PUR, it is estimated that worldwide well over 500 000 people are handling PUR raw materials every day. For the toxicology of the raw materials, see also → Isocyanates, Organic, Chap. 10 and → Polyoxyalkylenes, Chap. 4.

Health, safety, and environmental aspects, especially for MDI and TDI (see Section 3.1.2), are described in [228].

14.1. Safety Precautions when Handling the Raw Materials

When building and operating plants for producing PUR, all laws, decrees, and regulations in force for chemical plants must be observed. Many years' experience in handling the raw and auxiliary materials for PUR has shown that these products can be handled safely. It is a prerequisite for this, however, that the persons working with them are supplied with all the necessary information and above all, that the required technical and personal protective equipment is available and used.

All isocyanates, activators, and most alkanes and haloalkanes are regarded as products having acute or chronic harmful properties.

Di- and polyisocyanates have only a moderately acute oral and cutaneous toxicity. Di- and polyisocyanates are known to have allergenic potential, and the human health risk due to the acute or chronic effect of isocyanate vapors and aerosols (of liquid and dust forms) is considerably higher. Therefore, it is of extreme importance that appropriate safety measures, e.g., protective clothing and ventilation, are provided.

Occupational exposure limits have been set in many countries. As examples, the currently (2003) MAK values for Germany are listed in Table 11.

Table 11. German air concentration limits (according to TRGS 900) for typical polyisocyanates (see Section 3.1)

Isocyanate	Air concentration limit	
	ppm	mg/m^3
TDI (2,4-/2,6-)	0.005	0.035
MDI	0.005	0.050
NDI	0.010	0.087
HDI	0.005	0.035
IPDI	0.010	0.092
H12-MDI	0.005	0.054

The vapor pressures of the industrially most important isocyanates at their usual processing temperatures are listed in Table 12.

Many years' experience in handling the various isocyanates has shown that very effective air-extraction systems must be present at all workplaces where TDI is processed at room temperature or MDI and NDI at temperatures above 40 °C. If, for any reason, the aforementioned maximum value at the workplace is exceeded

Table 12. Vapor pressures of the industrially most important isocyanates at processing temperature

Isocyanate	Processing temp., °C	Vapor pressure, Pa	Conc. of saturated vapor, mg/m^3
TDI (2,4-/2,6-)	25	3	255.5
PMDI	25	$< 10^{-2}$	< 0.1
MDI	42	6×10^{-2}	0.65
NDI	130	ca. 120	7850

(e.g., on construction sites), the persons present in the working area must be protected against inhaling isocyanates, wherever possible by wearing suitable masks. TRGS 430 is a special German guideline on how to analyze and monitor isocyanates at workplaces where PURs are produced or processed.

More information can be obtained from literature available from the isocyanate producers, or their associations e.g.,

ISOPA: http://www.isopa.org
API: http://www.polyurethane.org/

Polyols have been well studied with respect to their toxicity and, if used according to relevant regulations, do not present an industrial hygiene problem. Aminopolyethers are moderately irritating to the eyes and skin, and thus contact with them should be avoided.

Auxiliary Materials. The ready-to-use polyol preparations, which are used to a large extent nowadays, contain the auxiliary materials necessary for PUR production (especially activators, emulsifiers, and stabilizers) in quantities of up to ca. 1.5 wt %. Toxicological studies have shown that these small quantities of the auxiliary materials scarcely affect the biological behavior of the polyols.

Polyols and polyol preparations have an exceptionally low vapor pressure; a health hazard via inhalation is therefore not to be expected. If, however, they contain readily volatile aliphatic amines as activators, an unpleasant odor can be expected.

For the *tertiary amines* used as catalysts, occupational threshold values in air (MAK) defined by the German TRGS 900 (2003) are available only in some cases, e.g., triethylamine: 1 mL/m^3 (ppm) corresponding to an eight-hour average value of 4 mg/m^3. However, the intense odor of most tertiary amines gives a clear warning of excessive concentrations.

Low-boiling chlorofluoroalkanes were used as blowing agents for producing rigid and flexible foams in the past. Since these substances are suspected of damaging the ozone layer, their use was phased out in the late 1980s. These substances have therefore been replaced by alkanes and to some extent by partly halogenated alkanes, because the blowing process cannot be carried out with carbon dioxide (from the NCO/H_2O reaction) in all cases. Since direct contact of partly halogenated alkanes and alkanes with the skin leads to intense defatting and roughness, it is important to wear impermeable gloves and to take good care of the skin. The inhalation of vapors from these blowing agents in high concentrations can lead to intoxication.

14.2. Emissions, Accidental Release, and Waste Disposal [229]

The emission of PUR raw materials into the atmosphere during production and processing is usually small. In special cases (e.g., filling of storage tanks, flexible foam slabstock production), measures to reduce emissions are advisable or required. Since a certain concentration limit of a harmful substance must not be exceeded in the air at the workplace, the air is extracted at the processing plant, and this is one source of emissions. The volatility of the raw materials determines the extent of emission. Hence blowing agents (e.g., carbon dioxide, halogenated hydrocarbons, hydrocarbons) and tertiary amines are the main constituents, whereas isocyanates normally do not play a significant role. Since the carbon dioxide formed from the reaction of water with isocyanate is a natural constituent of air, it presents no problem. The other blowing agents are discharged into the atmosphere in varying quantities depending on the foam type. The emissions of volatile organic chemicals are being increasingly regulated in industrialized countries. National regulations must be observed.

During storage, tank-filling, and transportation of PUR raw materials, discharge due to accidents or leaks cannot be entirely ruled out. Should this happen, as a standard precaution, the accidentally released raw material should be prevented from entering soil or water by suitable measures (e.g., covering sewers). Spilled product should be covered with a liquid-binding material such as a chemical binder based on hydrated calcium silicate (e.g., Hybilat), sand, or sawdust. This can then be transferred to a waste container. In the case of spilled isocyanates, the liquid-binding material should be moist and the material in the waste container stored under moist conditions in a secure place in the open air. The lid of the container must not be tightly sealed because of danger of bursting (CO_2 evolution). The polluted areas must then be decontaminated (see below). In all cases, the waste collected in the containers is best disposed of by incineration in a suitable facility (see below). In the unlikely event that a large pool of escaped isocyanate has formed, all unauthorized persons should be kept away from the scene of the accident. Persons downwind should be evacuated. Further evaporation of isocyanate can be prevented very effectively by covering the pool with protein foam. Large quantities of liquids can be pumped into waste containers, before the procedure given above is applied to the remaining residues. Nevertheless, in the case that isocyanate raw materials have leaked into the soil or water, inert polyurea is the major end product of their reaction with water. According to a three-month soil study with ^{14}C-labeled TDI and MDI, degradation products (e.g., amines) were at no time detected in the aqueous extract.

An experimental pond study indicated low environmental risk arising from spillage of polymeric MDI into a natural aquatic ecosystem. No direct ecotoxic effects and no bioaccumulation of MDI or MDA were observed. Furthermore no MDI or MDA could be detected in water.

Waste Disposal. Liquid or solid PUR production wastes which are not completely reacted are categorized as hazardous waste and should not be dumped but burned in industrial waste incineration facilities, equipped with state-of-the-art flue-gas scrubbing.

Drum decontamination. Any isocyanates residue in "empty" containers that are to be sent for reconditioning or disposal can be rendered harmless with a special neutralizing solution (for formulations, see the specialist literature). The same solution can also be used to decontaminate clothing, equipment and floors. Fully cured PUR end-product wastes, such as trimming waste from flexible foam slabs, can be recycled or recovered (see below). Wastes for which no utilization is yet possible can have their energy content recovered in appropriate incineration plants or can be disposed of in landfill sites, as a last resort (and as long as local regulations do not exclude organic materials from landfilling).

14.3. Recycling/Recovery of Polyurethanes

Because of their excellent durability, PURs in general contribute significantly to a long service life of the products containing them. This is an important contribution to waste minimization. To handle PUR wastes that cannot be prevented, technologies for recycling or recovery have been developed by many industrial associations, joint ventures, and cooperations between producers and users of raw materials throughout the world, e.g., the Polyurethane Recycle and Recovery Council (PURRC, USA), European Isocyanate and Polyol Producers Association (ISOPA, Europe), Tecpol (Germany), and the Japan Urethane Industrial Institute (JUII, Japan). The most appropriate method may vary from case to case, and depends on the properties of the PUR, the intended application, and the related capacity of the market for the recycled material, and very much on logistical, economic, and ecological factors. After all, recycling should not only serve to minimize waste; it ought to contribute also to the saving of resources and to the reduction of environmental burdens. Only then can recycling be counted as a contribution to sustainable development. Currently, the following possibilities for recycling/recovery of PUR exist.

Mechanical Recycling. Mechanical (or physical) recycling of PURs means one of the many forms of "particle recycling." The rebonding of flexible foam or adhesive pressing of rigid foam, for example, involves binding roughly 90 wt % of particles with about 10 wt % PUR binders under heat and pressure. Particle bonding uses up to 70 wt % PUR as the matrix for any kind of particles (e.g., rubber chips for sports ground surfaces). PUR powder can be incorporated into new PUR articles at a loading of round about 20 wt %. PUR powders/particles are also being reused as oil binders.

Feedstock Recycling/Chemical Recycling. Large-scale feedstock recycling processes recover oil and gas products from mixed plastic waste streams of a hundred thousand tons per year or more, of which PUR materials can be one constituent. These processes include pyrolysis, hydrogenation, synthesis gas generation, and reduction of iron ore in blast furnaces. When smaller, but pure streams of particular polymers are available, "chemical recycling" processes can be applied. It is thus possible to obtain liquid degradation products from PURs that are suitable, together with new material, for the manufacture of new PURs. For example glycolysis has been applied more often in favorable case where a suitable application for the glycolysate has been identified. Much research has resulted in several process variations [230]. Some of them include purification and chemical processing of the regenerate before use in PUR applications. Observation of appropriate industrial hygiene and safety is essential, because hazardous substances could be formed.

Energy Recovery. Combustion, or incineration with the recovery of energy, is currently the most effective way to reduce the volume of organic material which otherwise would have to be sent to landfill. Combustion is suitable for all materials for which material recycling is ruled out on ecological or economic grounds or simply because of logistical difficulties. Rotary kilns, fluidized beds, and mass burning equipment, for example, have been shown to be suitable for combustion of plastic scrap. These processes are applied, e.g., in cement production, in industrial power stations, and in municipal solid waste combustors. The heat content of PURs (lower heating value 24–30 MJ/kg) is comparable to that of coal. Numerous test runs have shown that this energy content is recovered in an environmentally sound manner in modern plants equipped with state-of-the-art flue-gas treatment facilities.

14.4. Fire Performance of Polyurethanes [128], [231]

The fire performance of a product is characterized at the various stages of a fire by the parameters ignitability, flame spread, and heat release, and by phenomena such as smoke density and the toxic potency of the combustion products. The dripping behavior, the amount of debris in general, and the corrosive effect of effluents are also determined. Fire test methods differ greatly from country to country, and also depend on the field of application. Different requirements exist, e.g., for the electrical, transportation, furniture, and building sectors. Fire testing, classification and regulatory requirements are very complex and reference must be made to summarizing literature.

In general, the fire hazards posed by a PUR foam and its fire effluents are comparable to those of natural materials like wool and wood. The chemical composition of the material is not the main determining factor. The behavior of the material in fires depends on, e.g., the relative surface of the material (e.g., massive wood compared to sawdust), the combination of materials, thermal conductivity, nature, duration, and intensity of ignition sources, and ventilation.

The qualitative and quantitative composition of fire effluents depends on the decomposition conditions (temperature and ventilation) as well as the amount of material involved. Comparative tests taking into account different stages of a fire have confirmed that the toxicity of fire effluents from PUR products is similar to that of other natural products like wood, cork, and wool. Fire effluents of natural and artificial organic products always pose a toxic hazard irrespective of the type of burning material.

As effluents from PUR do not differ greatly from natural materials, a similar effect on the environment is assumed. Due to their reactivity, isocyanates are rapidly decomposed photochemically or converted chemically.

A special fire risk from PUR is not evident: risk of ignition and flame spread as well as emissions mainly depend on the scenario and the amount of burning material, and are not determined by the specific material involved.

15. Economic Aspects

Even though PUR makes up only for ca. 6 % of the total consumption of plastics, the annual production reached the 10×10^6 t level in 2004. The growth rate since 1970 (Fig. 40) on average exceeded 5 % and thus grew faster than GDP. The fastest growing market over the last few years was Asia, in particular China with growth rates exceeding 10 %.

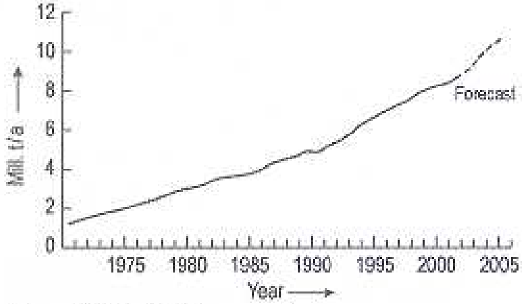


Figure 40. World PUR consumption

Figures from 2001 show that there is still a big difference in per capita consumption between the regions (Fig. 41), which allows an optimistic outlook for further development.

Figure 42 gives an overview of the main application areas of PURs and Figure 43 the split for the basic raw materials MDI, TDI, and polyethers.

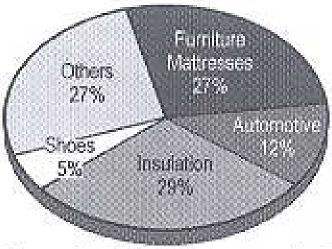


Figure 42. World PUR consumption 2004 by applications (total: 10×10^6 t/a)

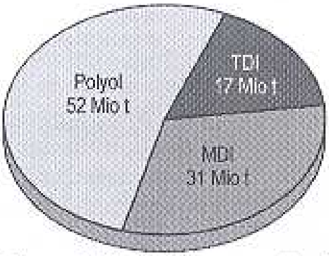


Figure 43. World PUR consumption 2004 by raw materials (total: 10×10^6 Mio t/a)

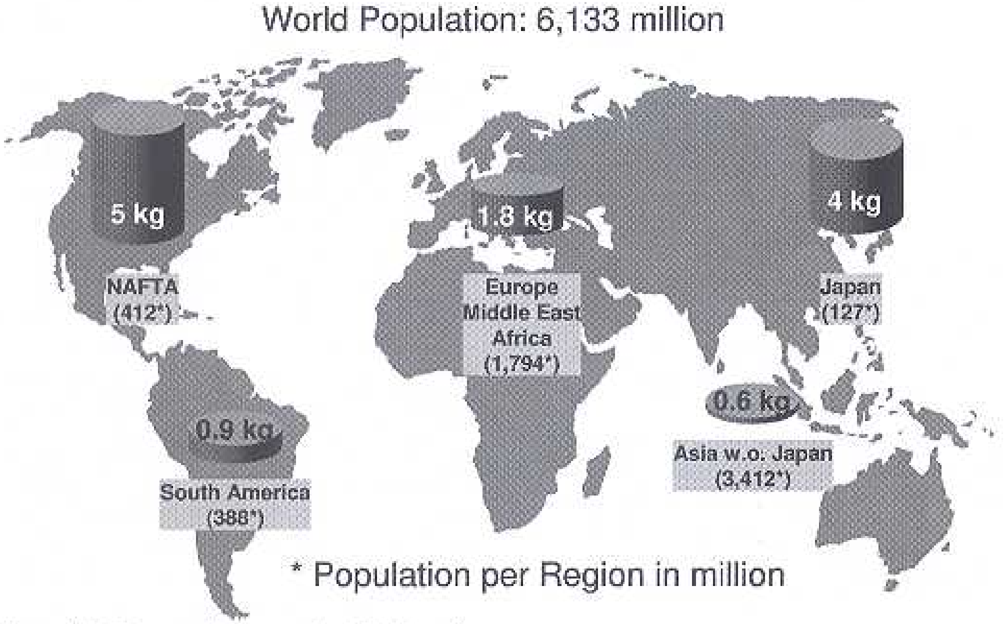


Figure 41. PUR per capita consumption 2001 by regions

Table 13 lists trade names of raw materials.

Table 13. Trade names of raw materials (exemplary)

Type	Tradename	Company
Isocyanates	Caradate	Shell
	Cosmonate	Mitsui Takeda
	Desmodur	Bayer MaterialScience
	Isonate	DOW
	Lupranate	BASF
	Mondur	Bayer MaterialScience
	Rubinate	Huntsman
	Suprasec	Huntsman
	Takenate	Mitsui Takeda
	Tedimon	DOW
	Voranate	DOW
Polyols	Acclaim	Bayer MaterialScience
	Actcol	Mitsui Takeda
	Arcol	Bayer MaterialScience
	Caradol	Shell
	Daltolac	Huntsman
	Desmophen	Bayer MaterialScience
	Isonol	DOW
	Jeffol	Huntsman
	Lupranol	BASF
	Lupraphen	BASF
	Multranol	Bayer MaterialScience
	Pluracol	BASF
	Rubinol	Huntsman
	Tercarol	DOW
	Voranol	DOW
Catalysts	DABCO	Air Products
	Desmorapid	Bayer MaterialScience
	Jeffcat	Huntsman
	Niax	Witco
	Polycat	Air Products
	Toyocat	Tosoh

16. References

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