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Polyurethanes: Versatile Materials and Sustainable Problem Solvers for Today's Challenges

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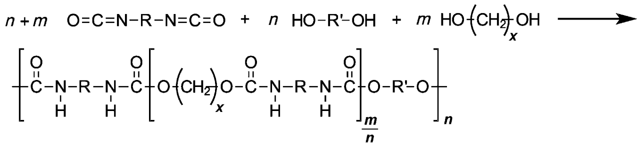
Dedicated to the Bayer company on the occasion of its 150th anniversary

Polyurethanes are the only class of polymers that display thermoplastic, elastomeric, and thermoset behavior depending on their chemical and morphological makeup. In addition to compact polyurethanes, foamed variations in particular are very widespread, and they achieve their targeted properties at very low weights. The simple production of sandwich structures and material composites in a single processing step is a key advantage of polyurethane technology. The requirement of energy and resource efficiency increasingly demands lightweight structures. Polyurethanes can serve this requirement by acting as matrix materials or as flexible adhesives for composites. Polyurethanes are indispensable when it comes to high-quality decorative coatings or maintaining the value of numerous objects. They are extremely adaptable and sustainable problem solvers for today's challenges facing our society, all of which impose special demands on materials.

From the Contents

1. Introduction

Discovered over 75 years ago by Bayer et al.,[1] polyurethanes (PUs) are a class of polymers with very wide-ranging, modular-like polymer structures, and therefore very diverse polymer properties (Figure 1). All industrial polyurethanes are made by the polyaddition of polyisocyanates and macropolyols, whereby polyurethane groups are formed in the polymer backbone. Reactions between polyisocyanates and other polynucleophiles produce related products (e.g. polyamines lead to urea groups), but even these and other products of addition are included in the polymer class of polyurethanes.[2–7] Global polymer consumption in 2011 amounted to 280 million tons, 14 million of which were the polyurethane raw materials, the polyisocyanates and polyols (5%).[8]



$$n+m\ \mathrm{O{=}C{=}N{-}R{-}N{=}C{=}O} + n\ \mathrm{HO{-}R'{-}OH} + m\ \mathrm{HO{\left(CH_2\right)}_x OH} \longrightarrow \left[\overset{O}{\overset{\|}{C}}-\underset{H}{N}-R-\underset{H}{N}-\overset{O}{\overset{\|}{C}} \left[O\left(CH_2\right)_x O-\overset{O}{\overset{\|}{C}}-\underset{H}{N}-R-\underset{H}{N}-\overset{O}{\overset{\|}{C}}\right]_{\frac{m}{n}} O-R'-O \right]_n$$

Figure 1. General structure of linear, single-phase ($m=0$) and phase-separated ($m=1$, 2) polyurethanes on the micrometer scale. Rigid and flexible segments are distributed statistically.

The residues R of the polyisocyanates can be aromatic or aliphatic and usually have a molecular weight less than 200 g mol^{-1}. The most technically important aromatic diisocyanates are toluene diisocyanate (TDI), comprising the isomers 2,4-TDI (**1**) and 2,6-TDI (**2**), and methylene diphenyl diisocyanate (MDI), comprising 4,4′-MDI (**3**) and 2,4′-MDI (**4**; Figure 2). In addition, a few special aromatic polyisocyanates exist, such as 1,5-naphthalene diisocyanate (NDI). The aliphatic representatives are hexamethylene diisocyanate (HDI, **5**), isophorone diisocyanate (IPDI, **6**), and hydrogenated MDI (H_{12}MDI, **7**). The residues R′ from the macropolyols are usually polyether polyols based on propylene oxide (PO), ethylene oxide (EO) with molecular weights of 300–18000 g mol^{-1} and a functionality of 2–6, or polyester polyols with molecular weights of 300–2000 g mol^{-1} and a functionality of 2–3. In addition to the standard grades, there are a number of special grades that contain building blocks such as caprolactone or polycarbonate diols and have a tailored structure. The polyisocyanates as well as the polyether and polyester polyols are adapted specifically to

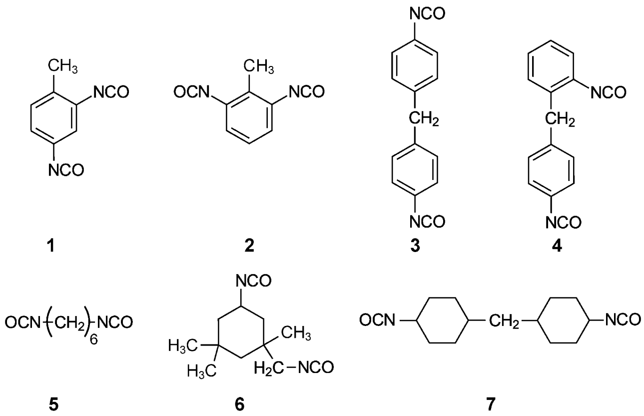


Figure 2. Industrially relevant diisocyanates.

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one another and sometimes designed as so-called prepolymers to achieve optimal product characteristics. In this connection, there are significantly more commercially available polyols (> 500) than polyisocyanates. Apart from the macropolyols mentioned above, many technical applications involve the use of short-chain diol, diamine, and alkanolamine chain extenders to adjust the properties of a polymer precisely. The phase-separated polyurethane copolymers formed in this way, comprising rigid and flexible segments, are typical of thermoplastic polyurethane (TPU) and PU elastomers.

Apart from the linear thermoplastic polyurethanes formed from the difunctional monomers shown in Figure 1, branched and cross-linked polyurethanes (thermosets) are also used in technical applications. Branching can be controlled by the polyol or polyisocyanate component. While the functionality is primarily achieved by the starting material in the case of polyether polyols or higher functional alcohols and/or acids in the case of polyesters, the corresponding, higher functional polyisocyanates are produced by various methods. MDI is obtained from the condensation of aniline and formaldehyde. This reaction also produces polynuclear oligoamines, which are converted into "polymeric" MDI (**8**; Figure 3). The reaction of trimethylolpropane with difunctional TDI under suitable conditions results in an isomeric mixture that contains mostly the trifunctional isocyanate (**9**), as well as higher homologues. Cross-linked polyurethanes can also be generated by a secondary reaction of the isocyanates with the protic urethane groups to form allophanates, with urea groups to form biuret (**10**), or by dimerization into uretdiones or carbodiimides, or trimerization into isocyanurates (**11**) or asymmetrical iminooxadiazindiones. These compounds can be synthesized in situ during the polyaddition reaction by using suitable catalyst systems, or produced specifically and used as building blocks in two-component reactions, as is common with coating isocyanates.

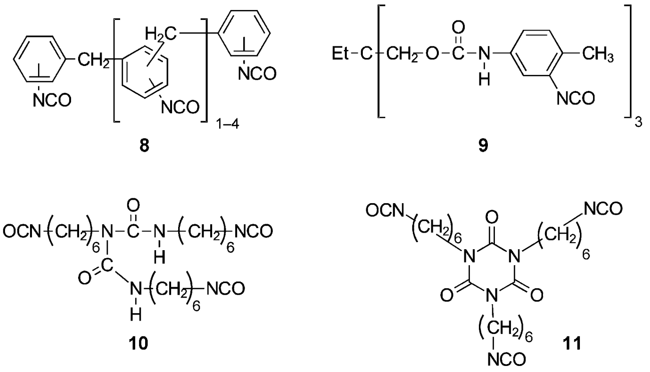

Figure 3. Examples of multifunctional polyisocyanates.

Polyurethane properties are largely determined by the chemical nature of the polymer building blocks, the stoichiometry of the isocyanate/OH components, and the reaction sequence. The choice of catalysts controls the selectivity of the targeted isocyanate reactions. Additives such as foam stabilizers, antioxidants, flame retardants, and the like are critical components in a formulation to achieve the desired properties. In two-component systems there is a need to thoroughly mix the components, and therefore, the mixing equipment plays an important role.

This Review explores the main applications of PUs that are firmly established in the market today and will address the following questions: What is unique about PUs in these applications? How will these PU materials develop? What new material needs in society can be most effectively met by polyurethanes?

Hans-Wilhelm Engels received his PhD in organic chemistry at the University of Cologne with Prof. E. Vogel and started working for Bayer in 1980. He has more than 30 years of experience in various R&D functions in the field of polymer additives, synthetic rubber, polyurethanes, coatings, and adhesives. Currently he is Senior Vice President Strategic Innovation Projects at Bayer MaterialScience. He holds an honorary professorship from the TU Dortmund.

Reinhard Albers studied chemistry at the Technical University in Braunschweig and completed a PhD at the University of Bochum with Prof. W. Sander. After joining Bayer AG in 1997, he started his professional career in the Central Research Department. After several years in Central Research he joined the Bayer MaterialScience's Polyurethane Business Group where he is currently leading the Application Development Group in the EMEA Region for Rigid Foam Applications.

Hans-Georg Pirkl studied chemical engineering and received his PhD in chemical reaction engineering from the University of Erlangen-Nürnberg, Germany, with Prof. H. Hofmann. He joined Bayer in 1993 and moved to the polyurethanes division in 1995, with assignments for polyol and MDI R&D. Since 2001, he has held several positions in MDI production and global technical product management of TDI + MDI. He has headed the application development of flexible foam EMEA since 2011.

Rolf W. Albach studied chemistry in Bonn and Technical University of Munich where he completed his PhD on bioinorganic electrochemistry with Prof. W. A. Herrmann . After postdoctoral studies in Orsay, France, with Prof. J.-J. Gired he joined Bayer in 1994. He has held various positions in research, business development, and sales. Since 2009 he has held an MBA from WHU, Germany, and Kellogg School of Management, USA. He is currently exploring new solutions for lightweight construction in the automotive industry.

2. Polyurethanes in Foam Applications

Over 66 % of polyurethane raw materials (polyisocyanates/polyols) go into foam applications. The reaction between isocyanates and water is the basic step for producing polyurethane foams. The corresponding unstable carbamic acid forms first, which spontaneously decomposes into an amine and carbon dioxide. The amine reacts with additional isocyanate to give a urea; the resulting CO_2 serves as a blowing agent. Additional physical blowing agents can be incorporated as necessary (Figure 4).

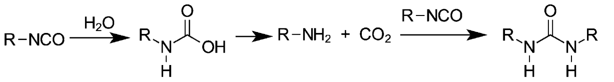

Figure 4. Formation of PU foams from the reaction between isocyanate and water.

2.1. Flexible Polyurethane Foams

Flexible PU foams have become established over the last 60 years as the standard for fabricating furniture cushions, mattresses, and many other technical applications—from molded foam seats in cars to liquid metal filters. The global market for flexible foams grew from 1000 tons in 1952 to 5 million tons in 2011, that is, 36–37 % of the global PU market.[9] The technology for the continuous and batch manufacturing of slab foam, as well as batch manufacturing of molded foam, is used today in virtually all countries around the globe and has been described in monographs.[6] The success of flexible foam was essentially made possible by the following:

a) The variety of foam types.
b) Its long term use characteristics.
c) Its breathability.
d) The efficient manufacturing methods for slab and molded foams.

No competing material today can match the range of properties of open cell flexible PU foams. Market demands are translated by flexible foam developers into technical properties (e.g. density, hardness, elasticity, and haptics) and then into chemical structures and formulations. Flexible PU foams can today be divided into two main foam classes: conventional flexible foams (ca. 55 % of the global market for flexible foams) and highly resilient (HR) flexible foams (ca. 35 % of the global market for flexible foams). There are also ester foams (ca. 4 %) and viscoelastic flexible foams (ca. 6 %).[10]

Conventional flexible foams are mainly characterized chemically by a polyol with a functionality of 3, a molar mass of 3000–4000 $g\,mol^{-1}$, a high propylene oxide content, and a low ethylene oxide content (0–12 %). The polyol typically is structured such that it contains mostly secondary OH end groups, and such systems in the great majority of cases are cross-linked with the help of the diisocyanate TDI. Catalysts (tertiary amines, tin compounds), stabilizers (polyether siloxane copolymers), and water as a chemical blowing agent are also used to control the reaction. The physical properties can be further optimized by adding other polyols. For example, the compressive strength of conventional flexible foam is increased by adding SAN polyols (dispersion of styrene/acrylonitrile copolymers in polyol).

The highly resilient (HR) foams are mainly characterized by a polyol typically with a functionality of 3–6, a molar mass of 4800–12 000 $g\,mol^{-1}$, a lower propylene oxide content, and

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Holger Casselmann studied chemistry at the University of Hannover in Germany and completed his PhD in macromolecular chemistry with Prof. M. L. Hallesleben . He joined Bayer in 1988 and held various positions as a manager for business development and sales within the business unit Coatings, Adhesives, and Specialties. He is currently exploring new sustainable solutions for the application of optical polyurethane systems.

Andreas Hoffmann received his PhD in organic chemistry from the University of Kaiserslautern with Prof. M. Regitz . After three years of postdoctoral studies in the US, Italy, and UK, in the field of supramolecular chemistry he joined Bayer in 1999. In April 2011, he became department head of "Composites" and is now responsible for the development of new polyurethane products and applications.

Jeff Dormish received a BS in chemistry from the University of Dayton and a PhD in chemistry from the Pennsylvania State University with Dr. L. Jackmann. He joined Bayer MaterialScience LLC in 1980, and has held various research and application development positions of increasing responsibility. He is currently responsible for the development of new polyurethane and polychloroprene adhesive applications.

a significant ethylene oxide content (15–20%). The ethylene oxide is incorporated as an end block by polymerization, thus leading to more reactive polyols with mostly primary OH end groups. Added to this are alkanolamines, for example, diethanolamine, as short-chain cross-linkers. In the case of HR flexible foams (Table 1), filler-modified polyols are used, for example, polyurea dispersions and SAN polyols. Both TDI and MDI are used as the isocyanate component. Catalysts (tertiary amines, tin compounds) and polyether siloxane copolymer stabilizers are used to control the reaction, in addition to water as a chemical blowing agent.

Table 1: Characteristics of the flexible foam types (conv. = conventional ether foam, HR = highly resilient ether foam, VE = viscoelastic ether foam, ester = polyester foam).

Flexible foam type	Conv.	HR	VE	Ester
density [kg m^{-3}] (DIN EN ISO 845)	14–100	20–100	40–80	20–60
tensile strength [kPa] (DIN EN ISO 1798)	100–180	60–120	60–100	160–220
elongation at break [%] (DIN EN ISO 1798)	100–400	80–200	80–160	100–500
90% compression set [%] (DIN EN ISO 1856)	2–10	2–10	3–15	5–15

The last two decades have been dominated by customer demands for emission and odor minimization, and by the expansion and refinement of the product range. As in all industrial processes, a focus on costs, foam yield, plant utilization, efficient waste management, and legislative changes has prompted leaps in innovation.

Foam manufacturers have responded to these trends by diversifying their product ranges, and now usually offer over 100 foam grades to optimally serve their local markets. Furthermore, consolidation has led to the formation of large regional corporations, which can exploit the synergies between their local foam production. The pressure to consolidate is expected to continue in established markets. Raw material manufacturers have responded to these market trends and to regulatory changes by improving the PU raw materials and advancing foam technology in partnership with the machine manufacturers.

One example is the abandonment of the CFC blowing agent R11 (trichlorofluoromethane), as prompted by legislators. In the 1990s, machine and raw material manufacturers developed the alternative use of liquid CO_2 by the CarDio or Novaflex methods. The Novaflex technology developed by Hennecke together with Bayer is the most commonly used standard for foams with a low density (Figure 5).[11]

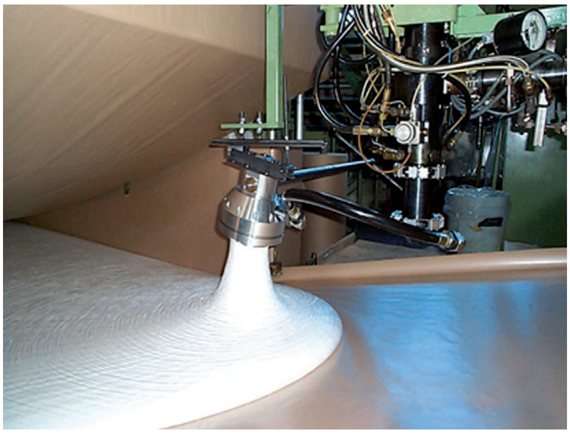
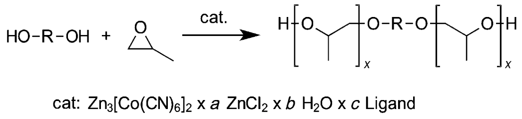


Figure 5. Novaflex technology foams isocyanate and polyol using liquid CO_2 as the blowing agent.

Manufacturers support the trend towards low-emission foams with raw materials (TDI, MDI, polyols) that are subjected to the increasingly complex removal of volatile secondary components. For example, impact technology[12–15] was introduced in 2000 for the industrial-scale manufacture of conventional polyether polyols through double metal cyanide (DMC) instead of KOH catalysis, and with a significantly reduced range of by-products (Figure 6). The polyether polyols produced by this method have become standard in the conventional foam market today. The DMC catalyst must no longer be neutralized and separated in a complex process, which significantly improves the efficiency of the manufacturing process in terms of material.



cat: $Zn_3[Co(CN)_6]_2$ x *a* $ZnCl_2$ x *b* H_2O x *c* Ligand

Figure 6. DMC catalysis for conventional, long-chain flexible foam polyols.[14]

Additive manufacturers make a major contribution by providing products with increasingly reduced emissions. Figure 7 illustrates this trend for flexible molded foams for the automotive industry. The greatest improvements have been made in the field of amine catalysis and silicone stabilizers. Improved polyol production methods have also had an impact. Many countries are experiencing a trend towards more energy efficient and airtight buildings that display lower air exchange rates than conventional buildings. This increases the requirements imposed on low-emission and low-odor flexible foams. At the same time, the chemical analysis of trace concentrations is moving towards ever-lower detection limits. In addition, a network of organizations has been formed which has established quality certificates based

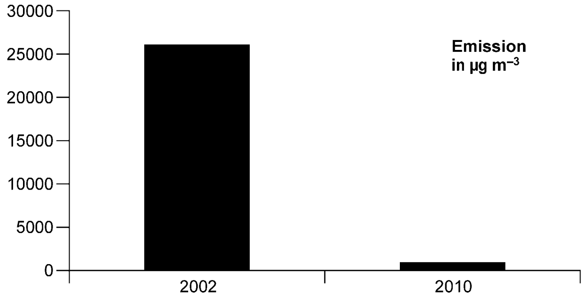


Figure 7. Typical VOC emission values for flexible molded foam according to BMW GS 97014-3 (10/2002).

on high market standards (e.g. Oeko-Tex, LGA, CertiPUR) and which monitors compliance with these standards. This trend will continue over the next few years, thereby providing an incentive for manufacturers to continuously improve their raw materials for flexible foams.

The necessity of improving the resource efficiency and carbon footprint of products has triggered significant efforts over the last 10 years to use naturally occurring vegetable oils as raw materials for polyols.[16] However, these products have only been used to a limited extent up to now. Along these same lines, the processes for manufacturing PU raw materials have been improved continuously at all levels, as demonstrated by products with an improved overall eco-balance industrywide.[17] The entire process chain contributes to this achievement. The TDI process, for example, has benefited from improvements in chlorine electrolysis membranes, optimized catalysis, and efficient energy use in the hydrogenation step to form toluenediamine, as well as innovative phosgenation processes (Figure 8). For example, the commercial use of TDI phosgenated in the gas phase (2011) reduced the solvent cycle by 80% and reduced energy consumption for TDA phosgenation by 40 to 60%.[18] It also enhanced safety on account of the short residence time and the simplicity of process management.

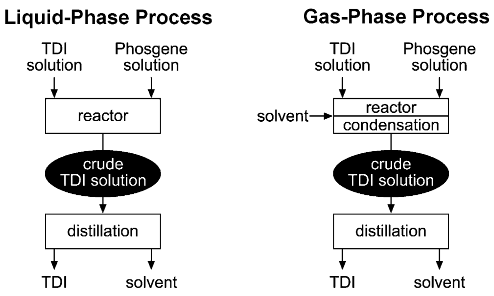


Figure 8. Process comparison of conventional liquid-phase with novel gas-phase technology for TDI.

The next major step in reducing the carbon footprint of flexible foams will be the use of CO_2 as a raw material. This technology originated from Inoue et al. (1969)[19] and was evaluated in the 1980s by Dow[20] and Shell.[21] However, the idea never reached a commercial scale, because it still lacked a suitable catalyst. Bayer later took up this idea to advance its impact technology, which can incorporate CO_2 and PO in the polyol chain statistically and thus generate carbonate functionalities.[22,23] In contrast, Novomer has used a homogeneous cobalt–salen catalyst to develop strictly alternating polyols from PO and CO_2 with up to 43% CO_2 content.[24]

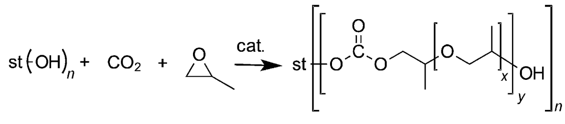


Figure 9. Polycarbonate polyether polyol synthesis by DMC catalysis from starter alcohol (st(OH)$_n$), CO_2, and propylene oxide).

The polycarbonate polyether polyols (Figure 9) display a significant increase in viscosity on account of their higher polarity. As a result, the portion of CO_2 in the polymer is limited with today's processing technology to considerably below 40%. After further basic research, the large-scale functionalization of CO_2 to form flexible PU foam raw materials is expected for the middle of this decade.[25]

In addition to the continued drivers of environmental compatibility and efficiency, tighter demands for flexible PU foams with better recyclability have again emerged after 10 years. The first customers in the EU have responded to the decreasing demand for foam wastes and invested in recycling plants. A chemical recycling facility for flexible foam that uses the glycolysis method to produce rigid foam polyols was installed recently in Germany. The alternative acetolysis method will be commercialized for the first time for 2.5 kt/y of flexible foam polyol from flexible foam waste.[26]

2.2. Rigid Polyurethane Foams

Rigid polyurethane foams have been in use for over 50 years in a variety of applications and in diverse fields of application and industries. The reason behind this is their unique combination of material and processing characteristics. About 30% of global polyisocyanate and polyol demand is for this application.[9]

Rigid polyurethane foams are strongly cross-linked, closed-pore materials produced by treating polyether and/or polyester polyols with polymer MDI grades. The mechanical properties and the processing characteristics can be adjusted over a wide range by using a number of available raw material components and combination options. The density of rigid PU foams can be regulated by adding physical blowing agents or by the formation of carbon dioxide, which is produced by the reaction of water with isocyanates (Figure 4).

Rigid polyurethane foams typically display excellent insulating properties and can be used simultaneously as structural materials. Typical fields of application for rigid PU foams include the construction industry, refrigeration, and the piping/tubing industry.

2.2.1. Rigid PU Foams in Construction Applications

On account of climate change and rising energy costs, many countries are increasing their regulations for saving energy in buildings,[27] a step that is driving up the worldwide demand for better insulating materials. Compared to insulating panels made of polystyrene (extruded: XPS or expanded: EPS), mineral wool, or wood wool, panels made of rigid polyurethane and polyisocyanurate foams (rigid PU/PIR foam) can better serve this trend (Figure 10). Although mineral wool and polystyrene make up the greatest share of insulating materials in the Europe/Middle East/Africa region, the percentage of polyurethane is rising rapidly, from 9.1 to 13.8% between 2000 and 2010 in a growing overall market.[9]

Rigid PU foam displays better insulating properties than any other insulating material that is commercially available today, thus rigid PU foam allows excellent insulating charac-

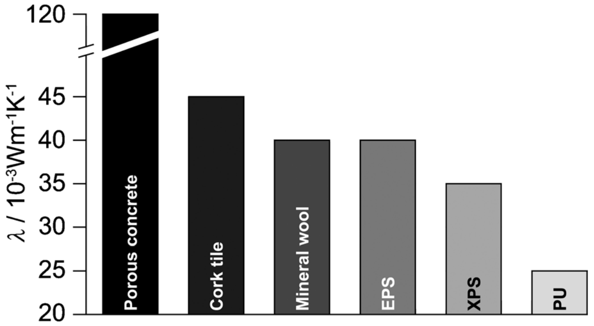


Figure 10. Thermal conductivity values of various insulating materials.

teristics to be achieved with thinner material. This results in lower space requirements, which is an advantage for the construction industry.[28]

The thermal conductivity of rigid PU foam is determined in part by its density, the selected blowing agent, and the pore structure of the foam. Pentane isomers are used most commonly in Europe to manufacture rigid insulating PU foams. With a standard foam density of $30\,\mathrm{kg\,m^{-3}}$ and with pore sizes in the region of 200 μm, over 60 % of the total heat transfer is determined by the thermal conductivity of the pore gas. Since the thermal conductivities of the pentanes (between 0.010 and $0.014\,\mathrm{W m^{-1} K^{-1}}$) fall significantly below that of air,[29] insulating PU panels achieve thermal conductivities as low as $0.024\,\mathrm{W m^{-1} K^{-1}}$ (Figure 10).[30,31]

Apart from excellent insulating properties, the fire performance of the materials is of critical importance in the construction industry. Like all organic materials, including wood and wool, PU is flammable. By adding flame retardants, rigid PU foam can be classified as having low or normal flammability (EU standard) and used as thermal insulation in all kinds of building systems in which materials and systems with low or normal flammability are required. The classifications of fire protection are based on standardized tests, and can vary from country to country. In Europe, for example, the single burning item test (SBI test)[32] has become established in recent years, and is based on the defined flame of a gas burner. The test analyzes ignitability, lateral flame spread, heat release, smoke production, and burning droplets.

Much progress has been made over the last few years in the field of fire protection with PU insulation. If requirements are particularly high, it is primarily insulating panels made from polyisocyanurate (PIR) foams that are used to insulate buildings. PIR structures are formed by the trimerization of isocyanates (see Figure 3). The formation of PIR structures is controlled by the stoichiometry and by the selection of appropriate catalysts. The high thermal stability of isocyanurate structures improves fire protection while reducing the need to use flame retardants. Furthermore, PIR structures contribute to cross-linking and thus to the stability of the foam, whereas in PU foams displaying significantly fewer PIR structures, because of less excess isocyanate, cross-linking is primarily triggered by the polyol components, and the fire protection behavior is more strongly determined by the added flame retardants.

Depending on their structure and the type of facing used, commercial insulating panels achieve classifications of up to C-s2-d0, where s2 is the second-best rating for smoke production and d0 means that the product does not drip when it burns.[32]

Although PU insulating panels are used in conventional installation situations, interest is rising in external thermal insulation composite systems (ETICS), which comprise a single leaf wall with rigid PU panels bonded to it and a suitable plaster system as the outer layer.[33,34] Depending on the thickness of the insulation, diffusion-open ETICS systems with rated values of 0.028 to $0.026\,\mathrm{W m^{-1} K^{-1}}$ ensure constant and high insulating performance over a long period of time. The goal of future developments in this application will be to further increase the insulating performance ratings.

Another major construction application facilitated by the above-mentioned properties of rigid PU foam is PU sandwich–structure composites, also known as sandwich panels. They consist of stiff metal skins made of steel or aluminum, with a core filled with rigid polyurethane foam.[31] The self-adhesive properties of polyurethane result in a strong bond. The panels have very good insulating properties and, thanks to their stability, serve as walling and roofing elements in the construction of industrial, warehouse, and refrigerated buildings. They can be manufactured in a discontinuous or continuous process. Both result in a standardized product with a tongue-and-groove design that enables the rapid assembly of even large buildings.

The mechanical and fire-protection properties of the composite panels are largely determined by the foam core. Typical raw densities are in the region of $38\text{–}42\,\mathrm{kg\,m^{-3}}$. At the same time, flawless optical quality has to be ensured, something that poses a considerable challenge particularly on facings with no texture. In this case, applying an even layer of the reactive foam mixture to the facing is very critical. Tighter fire-protection requirements are the main reason why sandwich panels are increasingly manufactured from polyisocyanurate (PIR) foam.[31] Sandwich panels of this kind can achieve the classification B-s1-d0 in the SBI test (best fire class for organic materials, lowest smoke production, no dripping in the event of fire).[32] Further improvement in the smoke and fire behavior of PU/PIR foams is a key development goal for the future, alongside the ever-present demand for increased efficiency.

2.2.2. *Rigid PU Foams for Technical Insulation*

As a consequence of its very good insulating properties, rigid PU foam is the material of choice for thermally insulating refrigerators with the highest energy efficiency. Over 95 % of all refrigerators manufactured worldwide are today insulated with PU, and the main driver behind innovation is the push to optimize energy consumption even more. Refrigerators are manufactured in a discontinuous process whereby the preformed outer shells are inserted into a support mold. The reactive, liquid PU components are then injected into the cavity, where they foam up and fill the hollow spaces.

The good mechanical properties, good adhesion of the foam to the outer shells used in the refrigeration industry, and the possibility of filling complex cavities inside a housing with foam make rigid PU foam the ideal structural material for affording a refrigerator with sufficient stiffness in conjunction with minimum weight. Optimized PU formulations and manufacturing processes further support the production of refrigerators that achieve maximum cost efficiency and productivity.

The insulating performance of a rigid PU foam depends on its cell size. In general, it can be said that the smaller the diameter of the cells, the lower the thermal conductivity and the better the insulating properties. Conventional rigid PU foams usually have cell diameters of > 180 μm. By continuously optimizing and advancing PU formulations and processing technologies, it recently became possible to obtain rigid PU foams with a very fine cell structure (< 150 μm) and improved insulation performance, without negatively affecting other important material and processing characteristics (Figure 11).[35] Researchers are hoping to make another substantial improvement in the insulating performance by using nanoscale rigid foams with cell diameters of 150 nm, which would be one-thousandth of today's typical size. However, manufacturing foams of this kind requires advanced PU chemistry and adapted processing methods. These developments are currently the subject of research.[36] This type of insulating material has the potential to significantly reduce the energy consumption of refrigerators even further.

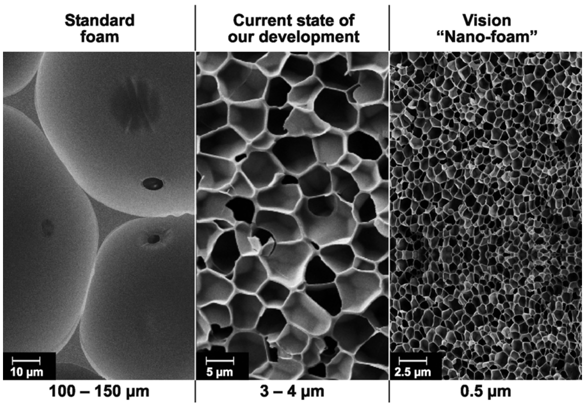


Figure 11. PU foams under a scanning electron microscope.

Finally, rigid polyurethane foams are the standard today for insulating pipes, for example in district heating networks, oil and gas pipelines, and chemical plants, which convey cold or hot media, because they minimize heat exchange between the conveyed medium and the surroundings very efficiently (Figure 12). The high insulating performance and reliability of this insulation method has a direct and positive impact on the cost-efficient operation of pipeline systems. Generally speaking, pipes encased in rigid PU foam can be efficiently insulated over a temperature range from −196 °C to +150 °C. This imposes high demands on the material properties, such as sufficient strength at low temperatures or, in contrast, very high thermal stability for use at high temperatures. With rigid PU foams, the specific properties required for an application can be adapted to an individual need. It should be noted that in Europe, for example, there are laws regulating these material properties. In addition to the very broad temperature range over which rigid PU foam can be used, the foam is further characterized by versatile compatibility with, and good adhesion to, such materials as steel, PE, PP, PVC, and other materials used in this industry.

Figure 12. Pipes insulated with rigid PU foam for the district heating industry.

In addition to the applications mentioned, polyurethane insulating materials play a major role in insulating hot-water tanks, boilers, doors, window sections, and in numerous other applications.

2.3. Noise Control with Polyurethanes

"One day we will combat noise just like the plague and cholera."[37] Polyurethanes are one response to this statement from Robert Koch. Among the variety of dampening materials and absorbers, lightweight polyurethane foams have proven to be indispensable, particularly in motor vehicle acoustics on account of the need to minimize weight. An average of 14 m^2 of a vehicle's interior is insulated with polyurethane foam.

Combination solutions have become established, such as emissions-optimized flexible foams with facings such as a $BaSO_4$-filled elastomer (firewall), an aliphatic PU elastomer or PVC (instrument panel), or textiles (floor covering). The integrated fabrication of such material composites is typical for polyurethane: the flexible PU foam is foamed directly on the second layer, without an adhesive step. A mixture of polyether polyols, water, glycols, ethanolamines, silicone stabilizers, and catalysts able to be incorporated reacts simultaneously with a mixture of various isocyanates in the mold and completely fills even complex cavities. To enable sounds to penetrate them, the cell walls must be opened in an orderly fashion while chemical conversion is still incomplete without the foam collapsing. This is achieved by controlling rigid segment crystallization and stabilizing the rigid segments in the polymer matrix. The kinetics of this self-organization of the various reactants to form an elastomer network is controlled by catalysts, the balance between primary and secondary hydroxy groups, and by the ratio between the 2,4′ and 4,4′ isomers of MDI. In addition, the temperature of the raw materials and the mold play an important role in giving the polymer and pore structure an optimum morphology for noise absorption.

Multilayer absorbers made of several flexible PU foam layers can absorb noise very efficiently. In this case, both the absorption resulting from thermal friction and the phase shift at the boundary layers are critical factors.[38] If at least one of the layers is replaced by an even lighter, open-cell rigid PU foam, a rigid sandwich structure that absorbs noise particularly effectively can be obtained in molding using the one-shot process (Figure 13). These composite materials are self-supporting and, as structural components, can make an important contribution to future lightweight construction.

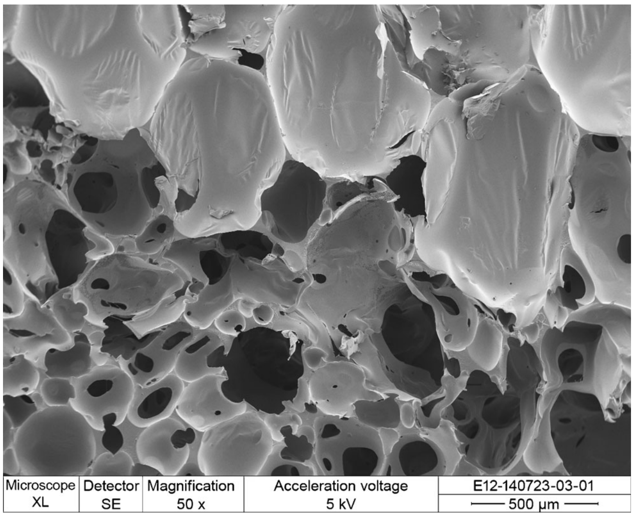


Figure 13. Scanning electron microscope image of the sandwich structure of open-pore flexible foam (bottom left) and rigid foam (top right).

3. Polyurethane Elastomers

When Otto Bayer invented polyurethanes in 1937, the basic idea behind his invention was to produce elastomeric fibers by reacting diols with diisocyanates.[2] Elastomers (about 20% of global PU consumption) have, therefore, accompanied polyurethanes ever since their discovery, as they allow an endless variety of applications. Since that time, cast elastomers have been the basic technology underlying both solid and cellular elastomers.

Cellular elastomers make up about 40% of the elastomers, with footwear elastomers comprising the largest group, followed by integral foam and elastomers for vibration damping. The remaining 60% are divided between solid elastomers, a virtually equal proportion of cast elastomers, thermoplastic PU elastomers (TPU), synthetic leather, and elastomeric fibers, followed by the spray elastomers, RIM elastomers, and millable polyurethanes (Figure 14). Cellular cast elastomers have a raw density ranging between 300 and 700 $kg\,m^{-3}$, which is considerably higher than that of a typical polyurethane foam. In contrast, solid cast elastomers are not foamed and typically have a density of 1200 $kg\,m^{-3}$. Cast elastomers are primarily described below because they best summarize the basic principles of the polyurethane elastomers.

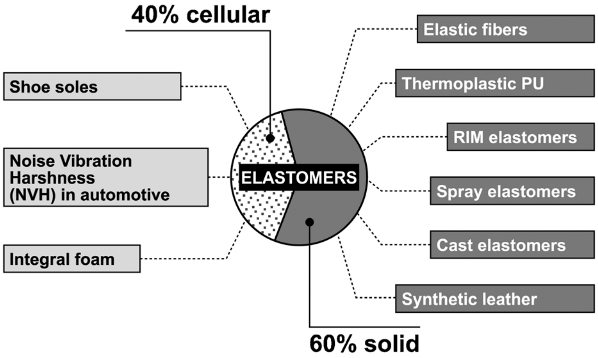


Figure 14. Overview of polyurethane elastomers.

3.1. Cast Elastomers

The first cast elastomers were introduced to the market in 1950 as solid, cast elastomers based on 1,5-naphthalene diisocyanate under the designation “urethane rubber”.[39] A cast elastomer typically comprises the following components: isocyanate, polyol, chain extenders, and additives, which are mixed to create a system with pot lives of 2–10 min and demolding times of 20–60 min. The components are processed in low-pressure mixing machines at temperatures of 40 to 130 °C.

Apart from the NDI mentioned in Section 1, MDI, TDI, PPDI (1,4-*para*-phenylene diisocyanate), TODI (3,3′-dimethyl-4,4′-biphenylene diisocyanate), and aliphatic isocyanates (mostly H_{12} MDI) are used for the isocyanates. The isocyanate components usually have a functionality of 2. The isocyanates are generally manufactured as prepolymers. What is so advantageous about synthesis via prepolymers is that some of the heat of reaction is already generated during the synthesis of the prepolymer, which means that the amount of heat released during formation of the actual polymer is reduced. When it comes to prepolymers, a distinction is made between “full prepolymer systems” with an NCO content of $<12\%$ by weight and “quasi-prepolymer systems” with $>12\%$ NCO by weight.

Polyols in cast elastomers are often based on polytetrahydrofuran diols, polyester polyols, or polyether polyols. The chain extenders can be either short-chain glycols or aromatic diamines. Additives typically include colorants, anti-hydrolysis agents (such as carbodiimides), plasticizers, abrasion-resistance enhancers (such as silicone oils or polyethylene), and flame retardants.

Elastomers are used in applications that depend on good dynamics and low wear. Polyurethane elastomers prove successful because of their good long-term dynamic performance, their high rebound resilience, very low dynamic stiffening, high abrasion and tear propagation resistance, and their excellent resistance to fats and oils. Other positive aspects include their noise- and vibration-damping properties and the numerous processing methods, ranging from casting, spraying, and injecting, to extruding, centrifugal casting, and centrifuging. With these methods, no technical boundaries exist in terms of size and shape. Applications include, for example, micrometer-thick films for electroactive polymers to solid tires weighing several tons for transport vehicles. Unfilled polyurethane elastomers are superior to filled rubber elastomers due to their higher wear resistance, although they do display poorer adhesion to wet surfaces and more unfavorable build-up of heat. Abrasion to DIN 53516 is between 10 and 40 mm^3 for polyurethane elastomers, and between 60 and 150 mm^3 for rubber elastomers. In addition, the processing viscosities of the polyurethanes at <2000 mPa s are much lower than those of the rubber elastomers.

Besides the general properties mentioned above, microcellular elastomers based, in particular, on NDI display a very low compression set, very low temperature increase under dynamic load, and consistent overall properties over a very wide temperature range. The first microcellular elastomer made from 1,5-naphthalene diisocyanate, using water emulsified in fatty acid and a polyester polyol for vibration damping, was introduced in the automotive industry back in 1961 and is used today by 90 % of all automakers.[40] The main reason for its use in the automotive sector is its high compressibility with low transverse expansion in combination with a good noise-vibration-harshness ratio (NVH, vibration damping), which makes this material class unique for installation in very small spaces. The space advantage compared to solid rubber elastomers is in the region of 15–25 %.[41]

In addition to the applications described, polyurethane cast elastomers are found in abrasion-resistant sieve linings, cable sheathing, roller coverings in the steel, printing, and paper industries, rollers for inline skates, pipeline cleaning implements, and in vibration damping for bridges. Solid polyurethane elastomers have high growth potential in offshore applications, which mainly require hydrolytically stable, extensively branched ether systems based on MDI. One illustrative example is the thermal insulation of underwater pipes by using elastomers filled with hollow glass microspheres (syntactic polyurethane) in offshore applications.[42] Other offshore applications for PU include coupling sleeves for underwater pipeline insulation, kink and abrasion protectors for hoses (Figure 15), as well as the use of elastomers to insulate cables and buoys in offshore wind parks.

3.2. Trends in the Development of Cast Elastomers

Although cast elastomers are the oldest class of polyurethanes, there is still a steady stream of product innovations and new applications today. Today's requirements are simple and fast cycle times in production as well as energy-efficient processing at low processing temperatures. The mechanical and dynamic resistance has to be optimized. Systems with optimal environmental compatibility and improved health protection should be available to the market for all applications.

Figure 15. Loading tubes with cable and bend restrictor elements (circled) made of PU elastomers on an offshore loading crane.

TDI prepolymers, which as "full" prepolymers are normally cross-linked using aromatic diamines, have a very wide processing window. However, traditional TDI prepolymers in the past had a free TDI content of approximately 0.2 to 5 %. Adequate two-way ventilation in the workplace is usually required when handling these raw materials to ensure compliance with workplace exposure limits for TDI. So-called "low-free" TDI prepolymers were, therefore, developed in the 1980s. Today, the free TDI content is below 0.1 %.[43] These prepolymers are produced by treating a polyol with excess isocyanate; in a further processing step, any remaining isocyanate is distilled off in a vacuum. Thin-film evaporators are commonly used in this process, which gives rise to the term "thin-film prepolymers." As a consequence of their lower vapor pressure, MDI systems increasingly have been developed in recent years that can be processed, cross-linked, and stored in a similar way as TDI prepolymers. Apart from low-free MDI prepolymers (based on 4,4′-MDI) produced by vacuum distillation,[44] MDI systems based on the 2,4′-MDI isomer were also developed and made available as an alternative.[45] The advantage in both cases is the lower reactivity of the NCO groups; in the case of the low-free MDI prepolymers through the lower percentage of free isocyanate, and in the case of the 2,4′-MDI prepolymers through the lower reactivity of the 2-position compared to the 4-position. This lower reactivity makes it possible to produce stable, one-component systems.[46,47] In this case, a complex of MDA (MDA_3NaCl; MDA = 4,4′-methylenedianiline) serves as a chain extender. The systems are unreactive below 80 °C; the MDA is only gradually released at temperatures above 80 °C, when it then reacts immediately with the isocyanate groups of the prepolymer.

Quasi-prepolymer systems made from MDI prepolymers with a high content of free 4,4′-MDI are used widely in the marketplace. In contrast to the systems just mentioned, these are reacted with one another by using 1,4-butanediol as a chain extender as well as other polyols. As a result of the low activity of the system, latent reactive catalysts are used here. Great efforts have been made in recent years to replace the mercury catalysts used to date with alternatives containing no heavy metals, such as amidine derivatives or metal salt complexes of tin, bismuth, titanium, and zirconium.[48,49]

Another recent innovation is NDI prepolymers with good storage stability.[50] Furthermore, polycarbonate polyol systems are used increasingly in applications requiring high hydrolytic resistance, high mechanical strength and abrasion resistance, and extreme temperature resistance.[51] Polycarbonate polyol systems thus unite the high wear resistance of polyester systems with the high hydrolytic resistance of polyether systems. Low-viscosity polycarbonate polyols[52] with high wear resistance have been gaining increased application in recent years in the offshore and paper industries.

Renewable raw materials are gradually starting to appear in several industries. Initial products are being manufactured from the raw materials succinic acid and 1,3-propanediol, which are obtained by the fermentation of carbohydrates.[53] Up to 80 % by weight of bio-based raw materials can be used in these systems.[54]

New applications have been addressed with aliphatic polyisocyanates in the field of optical lenses, safety glass, and encapsulation of LED light systems. The systems have to be transparent, light stable, and withstand higher temperatures.

4. Lightweight Construction with Fiber Composite Materials Based on Polyurethane

The market for fiber composite materials has grown steadily in recent years. Industry sectors such as aviation, wind, construction, and transportation posted average growth rates of 5 % per year, which means that the overall market has grown to over 8 million tons.[55,56] The development of customized matrix plastics and fiber sizings has made it possible to expand the material properties and increase the efficiency of production processes for fiber composite materials. Polyurethanes thus contribute to the development of new fields of application previously dominated by materials such as metal and wood.

4.1. Polyurethane Matrix for Fiber Composite Materials

The production of fiber composite materials primarily relies on glass fibers (as wovens, nonwovens, bonded fabrics, or chopped fiber strands or rovings) in combination with unsaturated polyester (UPO), vinyl ester (VES), or epoxy (cross-linked with anhydrides or amines) as typical thermoset matrix materials. The matrix determines the functional properties of the fiber composite (e.g. thermal resistance, fatigue behavior) and, as a consequence of rheology (curing kinetics), also the processing conditions and thus the economic efficiency of the entire manufacturing process. Polyurethanes can also serve as matrix alternatives when it is necessary to improve the cost efficiency by progressively automating the production of composite materials (Table 2).

Table 2: Comparison of various matrix materials.[57]

	Glass content [% by wt.]	Module of elasticity [GPa]	ILSS[a] [MPa]	Chemical resistance[b]
polyurethanes	80	49	66	high
polyester, UPO	84	40	30	low
polyester, VES	84	40	48	low
epoxide, anhy.	82	39	49	low
epoxide, amine	81	47	58	low

[a] Interlaminar shear strength. [b] Chemical resistance was tested in about 20 solvents.

Fiber composite materials are manufactured for a wide variety of applications with diverse material requirements and in very different production volumes. An efficiency analysis leads in individual cases to an optimized, component-dependent manufacturing technology. For example, styrene-containing unsaturated polyesters are typically used in combination with chopped glass fibers in a work-intensive spray and lamination process when deep-drawn, thermoplastic films are involved. As a result of the ongoing discussion about the reactive solvent styrene and the associated legal regulations, the use of solvent-free PU spray systems is an increasingly attractive alternative for many manufacturers.

To ensure sufficient rigidity (modulus of elasticity (tension) ca. 3 $\mathrm{kN\,mm^{-2}}$) while using minimum material, the polyurethane can be applied in a sandwich structure, that is, as a combination of solid and foamed layers.[57] Cladding elements for commercial vehicles and sanitary products (Figure 16) are already manufactured by using this method in semi-automated PU spray processes.

Figure 16. Bathtub based on PU spray technology (top) with corresponding sprayhead (bottom).

A combination of spray processes and compression molding is used to manufacture polyurethane sandwich elements. For example, a paper honeycomb is combined on both sides with a random glass fiber mat ($450\,\mathrm{g\,m^{-2}}$) and, following PU spray application, compressed at elevated temperatures (ca. 130 °C), which permanently bonds the different materials together (Figure 17). With this concept, lightweight components can be produced with weights per unit area of $<3\,\mathrm{kg\,m^{-2}}$ at a modulus of elasticity of 2.7 GPa. Today, they already replace wood in applications such as automotive load floors, and currently they are being evaluated for replacing metals in several applications in the transportation sector (automotive roof modules, train cladding components) to help meet weight-reduction targets. Implementing new concepts is contingent upon achieving adequate surface quality and reducing production complexity by integrating functional elements.

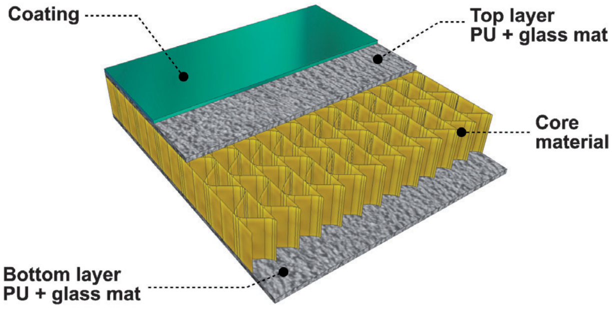


Figure 17. Schematic structure of a sandwich element.

Complex, continuous fiber-reinforced components with a high fiber content by volume (ca. 60 %) can be manufactured by using resin transfer molding (RTM) or infusion techniques. The latter is preferred, for example, for fabricating rotor blades for wind turbines. In fact, as part of an industry project, a rotor blade prototype seven meters long has already been manufactured from a custom PU resin system. Compared with epoxy resins currently in use, significantly faster fiber impregnation was achieved thanks to the extremely low initial viscosity (< 100 mPas). Furthermore, PU composite systems under dynamic/mechanical load display higher damage resistance and better fatigue characteristics (e.g. slower crack propagation).[58]

In contrast to the infusion method, resin transfer molding (RTM) uses closed metal molds. Dry preforms are placed in the cavity, which is then closed, and the resin is injected under pressure (< 80 bar) at temperatures around 80 °C. Since minimum mold cycle times lead to low component costs, new PU systems with so-called "snap cure" catalysts are used. With a low initial viscosity (< 50 mPa s) that does not rise above 200 mPa s during injection, they allow a combination of accelerated curing (ca. 4 min) with a sufficiently long processing time. In this way, faster cycle times can be achieved compared to epoxy resins, especially since thermal post-curing of the component can be eliminated. For use in large-scale, high-volume production (e.g. automotive industry), this method is being developed further with a focus on complex component geometries and the replacement of glass with carbon fibers.[58]

Polyurethane can also be used as a matrix material in continuous production processes. In pultrusion, glass fibers are pulled continuously from rolls through a closed mold (known as an injection box) and impregnated there with the liquid PU matrix. By applying heat (ca. 200 °C), the fiber composite cures completely in the shape determined by the mold and can then be trimmed by a cut-off saw. Pultruded PU sections have been used for window and facade elements for over five years. They not only weigh less than their aluminum counterparts, they also contribute to energy-efficient construction on account of their more favorable insulating values. What is more, entirely new structural ideas can be implemented, thus giving architects greater freedom of design with larger window surfaces and thinner frames (Figure 18). The use of PU sections for floors of shipping containers takes advantage of their good weathering resistance. Their outstanding strength and low brittleness during material processing even makes it possible for them to replace wood in selected fields of application.[57] Pultruded PU sections still offer plenty of potential, and further developments currently aim at replacing metal or wood in applications such as bridges and electrical transmission towers.

Figure 18. Pultruded components with a PU matrix.

4.2. Polyurethane Dispersions for Glass Fiber Sizings

Low-alkali glass with high tensile strength is used most commonly in fiber composite materials. The glass fibers are in the form of fiber strands, known as rovings, and in this state can be incorporated in a plastic matrix as wovens, nonwovens, bonded fabrics, or chopped fiber strands. The rovings are produced with sizings, where various polymers (e.g. polyvinyl acetate, polyester, epoxy- and polyurethane) in solvent-free dispersions are used as the binder component (approx. 0.5 to 1.0 % by weight based on the glass fibers). The purpose of the sizing is to hold the rovings together during fiber production and to ensure optimal function of the fabricated fiber composite. In particular, the adhesion of the matrix to the fibers and the separation of the rovings to allow complete soaking of the individual filaments are decisive factors for break resistance and tensile strength. Some 4 million tons of glass fibers were produced worldwide in 2011, with 28 % going into the reinforcement of extruded thermoplastics.[59,60]

Polyurethane dispersions are preferably used for the binder component in the case of glass fiber sizings combined with the polyamide as the matrix material. The formation of hydrogen bridges between the polyurethane groups and the polyamide is a decisive advantage here, as is the possibility of reacting the blocked polyisocyanates (as the dispersion component) during extrusion by using adhesion promoters. Fiber composite materials produced by these means display optimal hydrolytic resistance and long-term thermal stability, as well as excellent mechanical strength, with the result that the global consumption of PU dispersions for glass fiber sizings has grown to 23000 t (2011).[61]

5. Paints and Coatings

Polyurethane binders, on account of their diverse formulation options and variable properties, are the preferred choice when it comes to formulating high-quality coatings, as illustrated by the following selected examples. The global market share of polyurethane coatings in 2011, excluding architectural paints, can be estimated at nearly 15 %.[62,63]

5.1. Automotive Finishes

Although polyurethanes were quite rare in original equipment manufacturers (OEM) finishes in the 1980s, they are widespread today, with isocyanates and polyurethanes being found in all four layers of a typical coating (Figure 19).

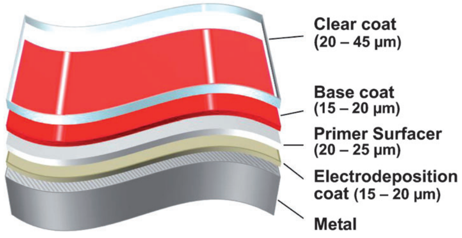


Figure 19. Structure of a typical metallic finish in automotive mass production.

The first layer is deposited electrochemically on the phosphated steel surface in a dip process and serves to protect against corrosion. The water-reducible binder used in this cathodic electrodeposition coating (CED) is made largely of epoxy resin cross-linked with blocked polyisocyanate. The CED emits virtually no volatile organic compounds (VOCs), although it does require baking at high temperatures above 150 °C, normally 180 °C and higher. The subsequent primer surface serves to smooth the surface and protect the underlying CED against stone chipping. Polyurethane binders and blocked polyisocyanates are preferably used in such formulations because of their high impact resistance, particularly at low temperatures. The reactivity of the isocyanate groups is protected in blocked polyisocyanates through reaction with monofunctionalized nucleophiles such as methyl ethyl ketone oxime or 3,5-dimethyl-1,2-pyrazole and react only with the polyol at elevated temperatures. The primer surface is baked at temperatures around 160 °C. Today's modern primer systems are water-borne. The base coat gives a vehicle its color and contains, if desired, pigments for special effects. The base coat can be formulated in solvents or in water; it is usually only semidried before being baked together with the clear coat applied on top (wet-in-wet) at about 140 °C. Modern, high-quality clear coats or top coats are formulated in solvents as two-component polyurethane systems with hydroxyacrylates as the polyols and aliphatic polyisocyanates as cross-linkers. These polyurethane clear coats have proven to be extremely successful because of their high brilliance (wet look) and their high resistance in general. Polyurethane top coats are used today in roughly 30 % of all passenger cars produced worldwide.[64] Various textbooks describe automotive coating technology.[65] Over the years, VOC emissions have been significantly reduced by using water-borne primer surfacers and base coats. However, reducing solvents alone is not sufficient to sustainably optimize OEM finishing, because about 60 % of the primary energy in the entire finishing process is attributable to the spray booths and driers, and only 20 % to the coatings themselves.[66] One important step, therefore, is to eliminate baking ovens or dryers. For example, it has been proven that incorporating the primer function in the base coat saves considerable amounts of energy in the spray booths and drying processes.[67] For the base coat to fulfill the function of the primer surfacer, high-quality polyurethane binders must be used. Another possibility for improving sustainability would possibly be the use of renewable raw materials.[68]

Two-component polyurethane coatings have been a fixture in automotive refinishing for decades. As a consequence of the high productivity resulting from fast drying at 60 °C and the outstanding properties on a par with OEM finishing, there is virtually no alternative to polyurethane technology, particularly for the primer surfacer and clear coat/top coat. For reasons relating to emissions, the colored base coats have almost completely been converted into water-borne systems, and they contain, among other things, high-quality polyurethane dispersions. Converting top coats or clear coats into water-borne two-component polyurethane coatings is technically feasible and basically desirable for reducing VOCs, but there is still a lack of empirical evidence today of practical application.

5.2. Metal Coatings

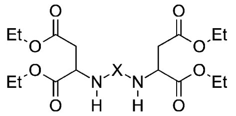
Corrosion protection is one of the most important functions of a coating structure, apart from the color. Numerous coating systems exist for a virtually endless number of applications, so only a few main aspects can be discussed here.

Small and medium-sized parts produced in high volumes and short production cycles are baked to accelerate the curing of the coatings used. Powder coating, frequently used as a one-coat system, has become most widespread, and is an emission-free, low-cost coating system based on polyester or acrylates. Baking temperatures are usually between 150 and 180 °C. Examples include radiators as well as machine and automotive add-on parts. In cases where the size of the parts to be coated no longer permits the efficient use of drying ovens, the coating can only be cured at room temperature or a slightly elevated ambient temperature (forced drying). After further pretreatment of the surface, the typical coating structure for high-quality goods comprises a two-coat system with a two-component epoxy primer for corrosion protection and a two-component polyurethane topcoat for optimal surface quality and weather resistance. Variations on this type of coating structure have become very widespread over the years for large vehicles, railway passenger cars, airplanes, construction machinery, agricultural machinery, and machine components (Figure 20).

Figure 20. High-performance, water-borne two-component polyurethane top coats are state-of-the-art for passenger train coatings.

Although it seemed impossible to incorporate isocyanates into water-borne coatings formulations because of the generation of carbon dioxide, the first patent for two-component water-borne polyurethane coatings was filed 1989. Since then, the systems have been improved continuously,[69–73] and today, water-borne polyurethane topcoats are increasingly being used instead of their solvent-containing counterparts to reduce VOC emissions.

For heavy-duty corrosion protection, thicker layers are required to achieve the desired corrosion protection classes, for example, C3–C5 to DIN EN ISO 12944. In most cases, depending on requirements, finishes on industrial installations, ships, offshore facilities, steel bridges, etc. have a three-layer structure with a two-component epoxy primer as the primary corrosion protection, an intermediate epoxy layer, and an aliphatic two-component polyurethane top coat for weather resistance and a long service life. The polyurethane coatings are often formulated in solvents with high solid contents over 65% to achieve sufficient film thicknesses in a single application. Practical reasons frequently preclude the use of two-component spray systems. In this case, the two-component coating must first be mixed and then applied as a one-pot system. However, because of the reaction between the components, the mixture does not remain stable for long. The desire for faster drying then conflicts with the demand for the longest possible processing window (pot life). It is clear that the drying time of a coating is much longer than the pot life. A more recent development that overcomes this problem involves the polyaspartic acid esters, which are also referred to simply as aspartates. These are sterically hindered amines that are much more reactive with isocyanates than binders containing OH groups (Figure 21).



X = (cyclo)alkylene

Figure 21. Polyaspartic acid esters as reaction components for polyisocyanates in high solids or solvent-free coatings.

In combination with aliphatic polyisocyanates, the aspartates support two-component formulations with a solids content of between 80 and 100 % and thick films in a single application. In some cases, therefore, the subjacent coating layer can be eliminated without compromising corrosion protection. The really unique feature of the two-component polyaspartate coatings, however, is the fact that their pot life is roughly comparable to the drying time of the coating.[74] This apparent contradiction can be explained by the reaction with the polyisocyanate component being catalyzed only after contact with moisture in the air and thus accelerated as soon as the coating is applied over a large surface area. The reduced number of coating layers, the very low emissions, and the faster drying enable high productivity and sustainability along the entire value chain.

5.3. Wood Coatings

Wood is coated primarily to influence its properties for an intended application, to preserve it, and to enhance its appearance. For furniture, parkette flooring, made to measure constructions such as window frames and doors, and other construction elements, the drying time, machinability, as well as abrasion, impact, chemical, and weather resistance are important factors for the performance of the coating. The most frequently used coating resins are nitrocellulose binder combinations, acid-curing systems, polyesters, and polyurethanes. The majority of industrial wood coatings used worldwide are formulated in solvents; the share of water-borne formulations is below 10 %.[63] With a market share exceeding 40 %, polyurethane coatings are the most preferred systems for coating wood on account of their surface quality and not least their great variability.

Among the polyurethane coatings, two-component systems with aromatic polyisocyanates as hardeners, preferably based on TDI, are used most frequently, where the coatings are formulated with a solids content of 25–40 % in solvents such as ketones, esters, and aromatic compounds. These types of coating formulations are very widespread in Southern Europe and Asia. Moisture-curing TDI prepolymers are also used as one-component coatings with outstanding abrasion resistance as an alternative to the two-component formulations. Despite all the positive aspects, the deficits in sustainability arising from the high solvent content in these coatings cannot be overlooked. One of the early developments was unsaturated styrene-based polyesters and later acrylates that permit very fast, radical curing with UV light. Adding flexibility by incorporating urethane groups and using UV-reactive thinners resulted in UV-curing, solvent-free urethane acrylates that display high efficiency and sustainability. Another improvement is the development of low-viscosity urethane acrylates with allophanate structures (Figure 22). These products are solvent-free and can be applied without reactive thinners.[75]

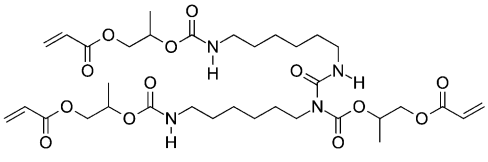


Figure 22. Principle make-up of UV-curing urethane acrylates with an allophanate structure.

A combination of UV-curing and conventional polyurethane addition reactions has been achieved in what are known as dual-cure systems.[76] In contrast, systems that can be pigmented to a variable degree include water-borne one- and two-component polyurethane coatings based essentially on aliphatic isocyanates and acrylate styrene copolymers. They are dried at moderate temperatures between room temperature and 50 °C, contain only very little solvent, and display very high-quality properties.[77,78] More recent developments involve UV-curing polyurethane dispersions that can be dried physically first and then cured with UV light.[79] Coating wood is still associated today with the use of large volumes of solvent. The aforementioned systems offer ecofriendly solutions for high quality and sustainability.

5.4. Coatings for Plastics

Many plastic moldings encountered in everyday life can be colored by incorporating pigments and fillers into the molding compound itself, and the surface morphology determined by the quality of the (injection) mold, such as food processors and other household articles. In these cases, coating is not necessary. However, many plastics are not weather and scratch resistant, and are easily attacked by cleaning agents and solvents. Plastics are coated when they need to have high-quality, durable surfaces. The largest market for plastic coatings is the automotive industry. A coating serves several functions in this context: to match the color of the vehicle, to improve resistance to chemicals, mechanical forces, and weather, possibly to act as a barrier to prevent the migration of plasticizers, and to create visually and haptically attractive surfaces. The demand for coatings for plastics in general is growing at a rate of about 7 % per year. Worldwide, some 60 % of the coatings for plastics are used on motor vehicles and 13 % on consumer electronics.[63]

The coating system must be adapted to the flexibility and surface tension of the plastic substrates, because hard top coats lead to the brittle fracture of otherwise impact-resistant plastics and can be a safety risk under mechanical load. Polyurethane coatings are the ideal solution for top coats and primers on plastics thanks to their properties.[80] In western Europe, some 45 000 t of polyurethane coatings were applied to plastics in 2011.[62] The great majority of polyurethane coatings for plastic are delivered in solvents. The coatings are two-component products based on aliphatic polyisocyanates (preferably HDI-trimerisates) as the hardener component, and combined with acrylate polyols, polyester polyols, or flexibilizing polycarbonate diols, depending on the requirements profile. Examples include automotive bumpers and various body parts, such as mirror housings and roof elements. More recent developments include water-borne two-component polyurethane coatings that are not only equivalent to solvent systems, but also enable formulations for high-quality soft-touch surfaces, for example, for automotive interiors and electronic devices.[81] The environmental compatibility of a plastic coating in a spray application is compromised not only by thermal drying, but also by the high energy consumption for process management and low application efficiency.[82] The latter can be in the region of only 20 % in particularly unfavorable cases.

Although UV-curing systems are known for their fast drying and productivity, most plastics can only be coated with modified UV systems. Incorporating urethane groups into unsaturated acrylates provides for sufficient flexibility. UV-curing polyurethane dispersions are used for highly abrasion-resistant and flexible substrates, such as PVC flooring. As in wood coating, both water-borne and UV-curing polyurethane formulations exist that produce high-quality coating films and allow ecofriendly processing, that is, with only small amounts of solvent, if any at all. It is expected that these systems will replace conventional solvent-borne formulations in the long run.

5.5. Textile Coatings

Textiles are coated to alter their physical and haptic properties. This applies to clothing, as well as to technical textiles and synthetic leather products. Examples include texturizing, embossing, coloring, water/windproofing, abrasion resistance, volume, permeability to water vapor and gases, and chemical resistance. In clothing and synthetic leather, the wearing comfort is the main objective, but in technical textiles it is sometimes the coating itself that generates the targeted function in the first place. This is the case with conveyor belts and sporting goods, for example.

Suitable polymer materials used on a large scale to coat textiles include PVC plastisols, polyacrylates, and polyurethanes. While PVC plastisols by nature contain plasticizers, which can be released into the environment, polyacrylates have a very narrow temperature range in which they are flexible without seeming sticky. If permanent resistance to creasing is required at low temperatures, polyurethane is practically the only material that fulfills this requirement.

The primary methods used in the textile industry require one-component formulations almost exclusively. The binder is typically dried in a temperature range of 150 to 170 °C, or even above 200 °C in the case of PVC plastisols. An overview of the binders used and the application methods can be found in the literature.[83–85]

Among the binders, aromatic polyurethanes in organic solvents are most common for adhesion or intermediate coatings. Aliphatic polyurethanes in organic solvents are used for the top coating or finish to ensure light-fastness. The molar masses of these binders permit only low binder concentrations between 30 and 45 % solids to be used in the targeted viscosity range of the application. The development of water-borne polyurethane dispersions that enable entirely solvent-free application offer an improvement in emissions and include high-performance building blocks as polycarbonate diols and hydrophobic polyethers (PTMGs).[86] The latest developments involve fine-particle polyurethane dispersions (PUDs) with up to 60 % solids, which display very high application efficiency.[87] In the case of the coagulation method for manufacturing synthetic leathers, these PUDs have the potential to replace the polyurethane solutions in dimethyl formamide (DMF) which are used at present.[88] Polyurethane dispersions are likewise used to finish real leather. The global consumption of water-borne polyurethane dispersions for textiles and leather in 2011 was around 75 000 t.[89]

Efficient application processes, the elimination of solvents, and high-grade properties are the requirements for a sustainable coating of textiles that can be fulfilled with modern, water-borne polyurethane systems today.

6. Polyurethane Adhesives

Polyurethane adhesives are known for their high performance and use in a range of demanding applications. These adhesives can be based on essentially the whole range of isocyanates and polyols accessible to the formulating chemist. The optimal raw materials or technologies for a specific end use are driven by the level of performance needed, processing requirements, and cost considerations. Polyurethane adhesives are supplied in solvents, as water-borne dispersions, in 100 % systems, and in high-molecular-weight films. Solvent-based and water-borne adhesive dispersions can be used directly as supplied after drying or can be cross-linked by the addition of an appropriate isocyanate to improve heat stability. 100 % systems are almost always chemically cross-linked. Moisture curing is typical for one-component applications and with two-component systems the isocyanate and polyol components are mixed shortly before the adhesive is applied. The 2009 global market value for polyurethane-based adhesives was estimated at \$2.4 billion (£1.4 billion), and its volume at approximately 640 kt. This accounts for approximately 12 % of the total 2009 adhesive market value and 8 % of its volume.[90]

6.1. Footwear Adhesives

Solvent-borne polyurethane adhesives have been used globally for more than 50 years in footwear applications, particularly for the bonding of soles. These polyurethane adhesives are favored due to their very rapid development of bond strength and ability to bond to a variety of substrates, including those containing a plasticizer and oily leathers.[91] The polymers are based on crystalline polyester polyols (e.g. butanediol adipate) and low-molecular-weight diols (butanediol, hexanediol) reacted with aromatic isocyanates (TDI, MDI). These adhesives are prepared by dissolving the high-molecular-weight polymers in polar solvents (ketones, esters). Specialty solvent-based isocyanate cross-linkers such as triphenyl methane-4,4′,4″-triisocyanate and tris(p-isocyanatophenyl) thiophosphate, can be used with these adhesives to optimize performance.

The heat-activation bonding process can be used for solvent-borne adhesives as well as water-borne adhesives based on a polyurethane dispersion (PUD) with a crystalline backbone.[92] After the adhesive is applied to a substrate and the solvent or water evaporates, an opaque nontacky polymer film is produced. The adhesive layer is ready for bonding after a heat activation process (Figure 23). The adhesive film is heated above the crystalline melting temperature (T_m) and a clear, tacky film results. Activation temperatures range from 45–70 °C depending on the product. At this point, the substrates are mated and the bond line begins to cool. Within seconds there is a development of initial bond strength (I) and within minutes there is another jump in bond strength (II) as the polymer backbone recrystallizes. The cross-linking reaction (III) continues over a period of days and the final properties are obtained. PU film and powder adhesives also utilize the heat-activation bonding process.

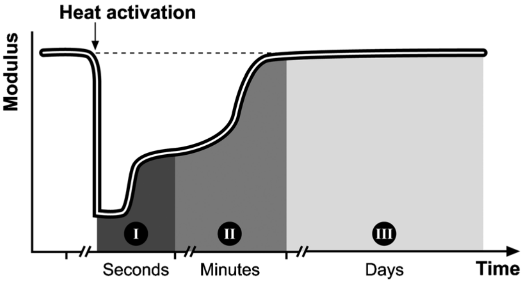


Figure 23. Heat-activation bonding process.

As with many industries, there is a growing interest in moving from solvent-borne to water-borne adhesives and the shoe market is a particular example of this trend. As a result, polyurethane dispersions with 35–50 % solids were developed specifically for footwear applications and are predominantly used in sport shoes. The main component of the polymer is a crystalline polyester polyol which facilitates the fast development of bond strength. Aliphatic polyisocyanates are also used instead of aromatic compounds. This produces a bond line that will not discolor. These dispersions are most often cross-linked with an aliphatic water-dispersible polyisocyanate in a ratio of 20:1 to obtain the required heat and water resistance for the application.[93] These two-part systems will have a typical pot life of 4–8 h.

One-component adhesives based upon a polyurethane dispersion and an encapsulated solid polyisocyanate have been developed.[94] In these adhesives, the cross-linking reaction is initiated at temperatures required for the heat-activation step of the bonding process.

6.2. Flexible Packaging Adhesives

Polyurethane adhesives play a prominent role in flexible packaging applications and are used throughout the world in general- to high-performance applications, particularly for film-to-film and film-to-foil applications. Flexible packaging adhesives must meet country-specific regulations to protect the consumer.[95] Polyurethane adhesives for this market include solvent-borne, 100% solids, and water-borne technologies. Flexible packaging laminates are made from a variety of different films (polyolefins, polyesters, metalized films, and foils). The film type and the number of laminate layers are determined by the requirements of the end-use application. Two-component solvent-borne systems are prepared from polyethers, polyesters, or urethane-modified polyols and cured by isocyanate prepolymers based primarily on aromatic isocyanates. The raw materials are dissolved in solvents to reduce the viscosity and facilitate processing. Since extended shelf-life food pouches are processed at sterilization and retort temperatures ($>121\,°C$), the adhesives used in these applications are required to withstand those temperatures. The adhesives were traditionally two-component solvent-borne systems based on isophorone diisocyanate (IPDI) and polyester polyols. Since aliphatic isocyanates have a slow cure rate, it has been recommended that the laminated films should be stored in a heated environment to reduce the cure time. A faster curing solvent-borne adhesive for retort applications based on an aromatic isocyanate has received regulatory approval.[96]

There has been a transition in the flexible packaging industry to two-component 100% solids adhesives. These systems are very cost-effective; lamination speeds up to $650\,\mathrm{m\,min^{-1}}$ can be achieved. The raw materials are based on low-molecular-weight, low-viscosity components, and require a more extensive curing reaction to take place after the films have been laminated compared to solvent-based adhesives. The raw materials are most often based on diphenylmethane diisocyanate (MDI) prepolymers and polyether polyols. Early versions of these adhesives needed a cure time of 7–10 days or longer before the laminated films could be fully processed (slitting, sealing, filling). The long cure time was needed to insure complete cure and prevent the formation of polyaromatic amines (PAAs) from the reaction of water with uncured monomeric isocyanates. These amines could migrate through the laminated films and into the foodstuff. The most advanced adhesive technology can now reach a PAA level of <2 ppb in 2–3 days. Laminates with a low PAA level are also achieved by treating polyols with advanced prepolymers which have a monomer content of $<0.1\,\%$.[97] These low monomer prepolymers can be prepared by simple distillation or by a synthesis process using asymmetric isocyanates such as 2,4′-MDI.[98] Adhesives based on mixtures of aromatic and aliphatic isocyanates provide a long open time to improve process flexibility while still achieving a quick cure with no PAA generation.

6.3. Construction and Furniture Applications

Moisture-curing 100% polyurethane prepolymer adhesives is a growing technology employed to manufacture load-bearing engineered lumber. These prepolymers are liquid at room temperature and normally based on MDI and polyether polyols. This “glulam” technology involves laminating small pieces of wood to form water-resistant high-strength beams. The beams can be formed into curved shapes and fabricated in lengths up to 30 m. The beams are used in the construction of commercial roof systems, floor beams, and bridges (Figure 24). One-component polyurethane aromatic prepolymers are also used for bonding wood substrates to subflooring (concrete, wood composites) and act as a barrier membrane to prevent moisture transmission from the subfloor. Isocyanate prepolymers are also widely used for the construction of sealants. These sealants adhere to a variety of building materials and are valued for the range of joint movement they can accommodate.

Figure 24. Salt warehouse constructed with engineered lumber (http://www.haring.ch).

Moisture-curing isocyanate prepolymers generate carbon dioxide upon curing. This can lead to foaming in thick films (see Figure 4). In contrast, silane-terminated prepolymers (STP), synthesized from the reaction of PU prepolymers with aminoalkylsilanes or isocyanatosilanes with polyols, release low-molecular-weight alcohols to create a bubble-free adhesive or sealant. The hardness of the adhesive or sealant can be adjusted by varying the molecular weight and functionality of the raw materials used to manufacture the silane-terminated prepolymer.[99]

Water-borne polyurethanes are the primary adhesives used in the three-dimensional lamination of wood composites, such as medium density fiberboard, to polyvinyl chloride (PVC), polypropylene (PP), or acrylonitrile butadiene styrene (ABS) films. A typical application is for kitchen cabinet doors. Fast development of bond strength is required to overcome the stress generated in the deep draw areas of the door. Cross-linking with a water-dispersible isocyanate or an encapsulated isocyanate is typically required to produce an adhesive with the required heat resistance. The adhesive manufacturer formulates a one-component adhesive by blending the encapsulated isocyanate with the polyurethane dispersion. The curing reaction is initiated at the typical temperatures attained during the heat activation process.[100]

6.4. Transportation Adhesives

Polyurethane adhesives are used in the transportation market with applications in the interior trim to structural applications in the automotive, truck, and railway industries. The industry is making use of lightweight metals, plastics, and composites to achieve improved fuel efficiency, and adhesives play a critical role in the success of this approach. One of the largest applications for polyurethane adhesives is the bonding of windshields to the automotive frame. This is accomplished through the use of one-component moisture-curing adhesives. The windshield assembly is designed to act as a structural component of the vehicle's body. Polyurethane adhesives are valued because of their rapid cure rate and their ability to produce strong flexible bonds. Flexibility is of critical importance when adhering substrates with different coefficients of thermal expansion.[101]

A commercial application that makes use of this performance profile involves the bonding of an aluminum roofing assembly to the steel frame. A two-component polyurethane adhesive was chosen for this application over epoxy adhesives because of its flexibility and strength over a wide temperature range. Two-component polyurethane adhesives are used for bonding sheet molding compound (SMC) and resin transfer molding (RTM). A new fast-curing one-component structural adhesive technology is being promoted for automotive applications. It is based on an isocyanate encapsulated in a urea shell. The curing reaction is initiated by heat at temperatures $> 80\,°C$.[102]

Polyurethane reactive hot melts are employed in automotive interior applications. These adhesives are typically based on MDI monomer and crystalline polyester polyols that are reacted to produce prepolymers with low isocyanate content. These products can be processed at temperatures of about 120 °C and moisture cure to a thermoset polymer with high heat resistance. The curing takes place over a few days, but the adhesive develops initial strength in a matter of minutes through recrystallization of the polymer backbone. The rate of recrystallization and open time can be adjusted by blending amorphous and crystalline polyesters.

7. Summary and Outlook

The secret to the success of polyurethane chemistry is the reactivity of the isocyanate groups toward all types of nucleophiles plus the great variability of the polyols and polyisocyanates. The result is a tremendous diversity of possible polymer building blocks, thus enabling an extremely broad range of variations and fine-tuning of material properties and applications.

As one of the major challenges of our time, climate change demands a significant reduction of the greenhouse gases that damage the climate, particularly the CO_2 emissions from the combustion of fossil fuels. Modern polyurethane systems are still made largely with petroleum-based petrochemicals. Substantially improved and, above all, more energy-efficient production processes have steadily reduced the CO_2 footprint of polyurethane raw materials in recent years. The final chapter of this success story has yet to be written. Innovative catalytic and electrochemical processes, adiabatic process management, low-solvent process steps, closed raw material cycles, ever-larger production facilities with improved efficiency are just some examples of why this is true. There are also developments regarding the use of CO_2 as a raw material for polyol synthesis and the use of renewable resources.

It is through their intended use, however, that polyurethanes make their greatest contribution to energy and resource efficiency. Vast amounts of energy are used to heat or cool buildings. Over its service life, PU thermal insulation saves more than 100 times the energy required for the production of the insulating materials.[103] Polyurethane thermal insulation in refrigerators and the logistics chain prevent the rapid spoilage of food. They are an important key to feeding a steadily increasing world population. In mobility, weight savings correspond directly with lower fuel consumption.

Besides contributing to sustainability, PU foams are also indispensable in upholstery/cushioning, for sound absorption, and as a matrix material. The low viscosity of the PU components allows their relatively easy processing into polymer materials, thus making them cost competitive especially in small production runs. The high durability and wear resistance of polyurethanes in coatings extends the service life of the products and enhances their retention of value. PU foams and PU adhesives enable the efficient production of a diverse range of composite materials and are thus a key to modern material concepts, particularly in lightweight structures. More recent examples of attractive applications of polyurethanes include wind turbines, solar thermal energy, and biogas plants.

Polyurethanes have demonstrated their versatility and adaptability to new challenges for over 75 years now, and the potential for future innovations is far from exhausted.

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