doi:10.2533/chimia.2008.826

Chimia 62 (2008) 826–831
© Schweizerische Chemische Gesellschaft
ISSN 0009–4293

Adhesives: Polymer Chemistry at Work

Christof Arz, Andreas Dobmann, Olaf Meincke, Adrian Schulthess*, and Willi Schwotzer

Abstract: Successful adhesive technology relies on the diligent engineering of adhesive and cohesive forces. Polymers thereby play the dominant role as they largely determine the chemical and physical properties of the adhesive joint. A wide range of polymer systems is available, each having special properties in its own right. The art of adhesive formulation lies in the right choice of the appropriate polymer and its modification to suit the purpose. This article provides several examples of adhesive applications in demanding industry segments.

Keywords: Adhesives

1. Introduction

Collano AG, a privately owned company specialized in adhesive bonding technologies, is based in Sempach Station, Switzerland, and employs 330 persons. The enterprise was founded in 1947 by Dr. Marcel Ebnöther and originally incorporated as Ebnöther AG. In 1978, the company changed ownership in a management buyout, a transaction not widely reported at that time. The former head of marketing and sales, Gerry Leumann, and the technical director, Walter Heublein, transformed the former local player into an internationally active company. After Walter Heublein retired in 1994, Gerry Leumann became the sole owner. In 2007, he entrusted the function of CEO to his son Stefan. Apart from Sempach Station, the company operates four more production and development sites in Switzerland, Germany, and France. In 2008, Collano AG was restructured into three companies: two sales companies in different markets, each with a research & development (R&D) department, and a service and production company. With this reorganization, Collano assumed a holding structure. The three companies, nolax AG, Collano Adhesives AG and Collano Services AG were incorporated under its umbrella.

The three companies focus their development on different objectives, each of them aiming to be the leaders in their industry: nolax on system innovations, Collano Adhesives on speciality products, and Collano Services on services. Table 1 shows key figures for the years 2005, 2006, and 2007.[1]

The Collano group maintains four technology platforms: water-based dispersions and adhesives, hot melt adhesives, reactive systems, and adhesive films.

The examples presented below illustrate the scope and innovation potential of modern adhesives.

2. UV-Curable Hot Melt Pressure Sensitive Adhesives (HMPSAs) for Direct Skin Contact

2.1. *History*

The first adhesive products with pressure sensitive properties were introduced to the market by Oscar Troplowitz in the early 20th century. He developed a solvent-based adhesive based on natural rubber with colophony resins. He also recognized that the addition of zinc oxide helped neutralize the free acid groups of the abietic acid in the colophony, which was a big improvement in terms of long-term stability and skin compatibility. After World War II, solvent-based acrylics were developed. The big advantage of this class of pressure sensitive adhesive (PSA) was their excellent long-term stability and also the high water vapor transmission rate, which allowed plasters to stay on skin over a long period of time.

2.2. *Hot Melt Pressure Sensitive Adhesives*

With the development of solvent-free hot melt pressure sensitive adhesives (HMPSA) and with growing environmental awareness, thermoplastic rubber-based adhesives (base polymer: styrene block copolymers) reached the breakthrough in the field of direct skin contact applications in the late 1990s.

HMPSAs based on thermoplastic rubber were able to replace most of the solvent-based natural rubber adhesives as well as many solvent-based acrylics.

The main drawback of thermoplastic rubbers is their hydrophobic nature since high water vapor transmission is generally requested. Human skin evaporates between 500–2000 g water per square meter and day. Thermoplastic rubber-based HMPSAs

Table 1. Key indicator figures of the Collano Group

		2005	2006	2007
Sales worldwide	in CHF million	115	125	137
Operating profit (EBIT)	in CHF million	0.7	2.2	7.2
Employees		328	332	340
Full-time jobs		299	311	315
Employee satisfaction		82%	82%	80%
Sales share generated in Switzerland		30%	29%	28%

**Correspondence:* Dr. A. Schulthess
Collano AG
Eichenstrasse 12
CH-6203 Sempach Station
Tel.: +41 26 497 81 11
Fax: +41 26 497 81 01
E-mail: adrian.schulthess@collano.com

are only able to transport up to about 100 g/m^2/d of water through a 60-micron thick layer. Open coating patterns or needling of the adhesive layer is a possible solution for achieving higher values. However, this technique is not always favored as it interrupts the bacterial barrier of the adhesive layer. Other adhesives are therefore sought.

An eligible solution is provided by thermoplastic hot melt acrylic adhesives. These raw materials have been available since 1980 but they exhibit quite a high level of cold flow at room temperature which entails the deposition of adhesive residues on human skin from bandage or tape applications. This disadvantage was overcome in the early nineties when BASF introduced UV-curable, thermoplastic acrylic polymers. This new class of compounds combines the benefits of hot melt adhesives with those of cross-linked systems. For medical applications in particular, they offer the following benefits: i) excellent cohesion and high temperature resistance, ii) excellent long-term stability, iii) very good skin compatibility due to the absence of free photo initiators.

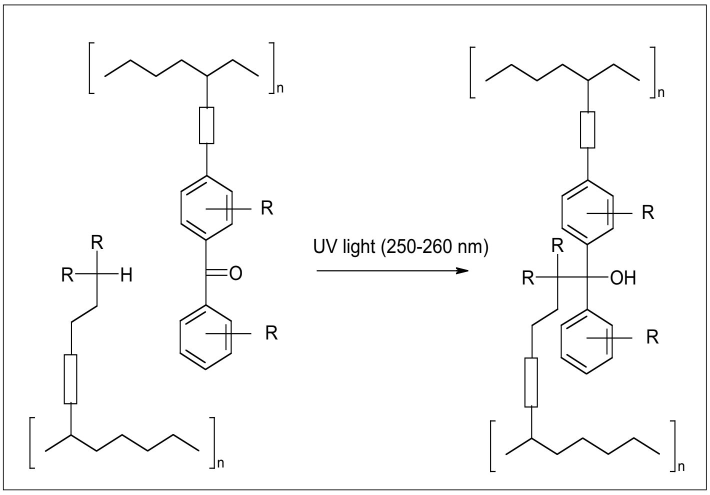
However, adhesion to certain substrates, especially human skin, needed to be improved in order to be commercially successful in this field. By using the right additives and formulation technique, it was possible to tailor adhesion characteristics to meet the high demands of this industry.

2.3. *UV-Curable Hot Melt Pressure Sensitive Adhesive*

2.3.1. *Chemistry and Formulation Techniques*

The UV-cross-linkable polymer backbone is based on butyl-acrylate, ethyl-hexyl-acrylate and other acrylic monomers. The photo-reactive group is bound directly onto the backbone polymer with a defined spacer group. By irradiation with UV light (UV-C with 250–260 nm wavelength) the polymer chains cross-link according to Scheme 1.

Typically, a dose of 5–50 mJ/cm^2 of UV-C radiation is applied. A curing thickness up to 100 microns is achievable. The melt viscosity of such a polymer before cross-linking is in the range between 10 and 50 Pa·s at 130 °C. Standard tackifiers (hydrogenated resin esters, low molecular styrene resins or hydrocarbon resins based on C_5/C_9 fractions) for acrylic polymers can be used to increase the specific adhesion to skin. The additives must have a high UV transparency at 250–260 nm in order not to interfere with the cross-linking reaction. Additionally, for medical applications, these tackifiers must comply with regulations on biocompatibility. Additional additives like polyvinyl ethers, polyvinyl-pyrrolidone *etc.* may help increase the adhesion and other desired properties of the adhesive.[2]



Scheme 1. Cross-linking reaction

2.3.2. *Application and Cross-linking of UV-curable HMPSAs*

The thermoplastic, non-cross-linked HMPSA precursors can be coated onto the substrate at 100–140 °C. Typically, a slot die nozzle is used to achieve a uniform coating pattern. Coating weights between 20 and 60 g/m^2 are mostly used in medical applications. The adhesive is applied to a release liner (siliconized paper or film), followed by exposure to UV light for a dwell time <1 s and lamination to the desired carrier (non-wovens, textile, polyurethane films, *etc.*) Coating and cross-linking speeds of 100 to 200 m/min can be reached, depending on thickness and available UV dose (5–50 mJ/cm^2 is recommended).

2.3.3. *End Product Performance*

The cross-linked adhesives are successfully tested for biocompatibility pursuant to ISO 10993 (cytotoxicity, skin irritation and sensitization). Collano is able to formulate adhesives based on this technology with peel strengths from low (<2 N/25 mm, 180° peel against steel) up to very high strengths of >20 N/25 mm. Typical application weights for these tests are 25 g/m^2. The required peel strength depends on the intended application. For children's or elderly people's skin a lower peel level is requested, because their skins are more fragile. Depending on the formulation, a moisture vapor transmission rate (MVTR, open cup test method) of 1200 g/m^2/d can be attained with a coating weight of 50 g/m^2. The UV-cured adhesives are no longer thermoplastic. They can withstand steam sterilization at 121 °C for 25 minutes without changing their properties. Gamma sterilization (tested up to 60 kGy) and ethylene-oxide gas sterilization can also be used.

2.4. *Application Examples for UV-curable HMPSAs*

2.4.1. *Incision Films with Breathable Adhesives*

In order to prevent microorganisms from migrating from the surroundings into the wound, a surgical technique has been developed in which, prior to surgery, a flexible film is bonded to the skin. This film is referred to as an incision film and is composed primarily of polyurethanes with high breathability. The transection is then conducted through the film and the skin with the film still adhering to the edges of the transection zone. After surgery, a new film is applied to protect the fresh wound which gives the patient the benefit of being able to shower very soon after surgery. These films remain on the human skin for 4–5 days and therefore must exhibit a high MVTR value as well as excellent skin compatibility. If MVTR is too low, maceration of the skin could occur which could inhibit the self-healing process of the skin. In this application, UV-curable HMPSAs based on acrylics were able to replace solvent-based adhesives due to their superior properties.

2.4.2. *Adhesives with Moisture-absorbing Properties*

Incorporation of water-absorbing polymers like carboxylated cellulose (CMC) or polyacrylic acid/sodium polyacrylate into a UV-curable HMPSA leads to a new class of hydrocolloid adhesives.[3] These adhesives are capable of absorbing body fluids in amounts up to 200–300% of their own weight. The hydrocolloid adhesives are used in the treatment of chronic wounds. Due to the cross-linking process which leads to high cohesion in the adhesive matrix, the integrity of the adhesive patch is outstanding. No particles of CMC or other water-absorbing polymers contaminate the wound.

2.4.3. *UV-Curable HMPSAs with Antimicrobial Properties*

Due to the polar nature of the UV-curable HMPSA based on acrylic polymers, silver-containing substances can be included in the adhesive layer. Elution tests with isotonic sodium chloride solution show a controlled release of Ag^+ ions over time. Ag^+ ions are well known for their antimicrobial function against gram-positive as well as gram-negative bacteria. In a contact test (test method JIS Z 2801:2000, *Staphylococcus aureus* ATCC 6538P) a bioburden reduction of >99.99% was achieved. The introduction of an antimicrobial function into an adhesive illustrates the current trend in the industry: the demand for multifunctional adhesives.

3. Adhesives off the Roll: Thermoactivable Adhesive Films

In addition to the hot melt technology described above, Collano has developed the technology of thermoactivable adhesive films. These films consist of thermoplastic polymeric materials which are produced on either cast or blown-film extrusion lines. This product line was introduced in the market in 1968 by the former Xiro AG in Schmitten which in 2002 became a member of the Collano group. The range of polymers used in the formulation of adhesive films extends from polyolefins to copolyamides and thermoplastic polyurethanes, thereby covering a broad range of physical and chemical properties. Generally, these products are non-tacky at room temperature. At elevated temperatures from 60 °C up to 180 °C, they can be brought to adhere to a variety of surfaces. The concomitant bonds exhibit a temperature resistance up to 160–180 °C with an exceptional adhesive and cohesive performance. Peel forces up to 10 N/mm are no exception.[4] The application range of thermoactivable adhesive films is very broad, covering liners for the garment industry and textile laminates to chip embedding for the smart card industry as well as safety components for the automotive industry.

3.1. *Multilayer Films*

Collano's recent efforts in this technology are focused on the development of multilayer adhesive films. This concept permits the incorporation of features to the adhesive in addition to adhesive properties. An anisotropic glue line with a left and a right side is obtained when two adhesive layers of different chemical nature are combined. This allows the bonding of substrates with substantially different surface properties. For example, the difficult bonding of polyethylene to aluminum is achieved with a multilayer film in a satisfactory manner. More recently, concepts have been developed to incorporate further functionalities such as selective barriers for gas or water vapor. Among others, these concepts are applied to airbags in the automotive industry. In modern cars, airbags are an integral part of passenger safety systems. Initially, these passenger restraint devices were installed as front collision airbags on the driver side only, followed by the installation also on the passenger side. The most recent technology involves side curtain airbags. They are engineered to prevent injuries resulting from direct impact on the heads of the passengers or from objects penetrating through the side windows. Unlike front airbags, these safety devices have to stay inflated for several seconds in order to protect the passengers even in case of several roll-overs of the vehicle. Therefore, air tightness of the textile laminate is a critical feature of these devices. Fig. 1 shows a side curtain airbag with several cushion zones for head protection.

Fig. 1. Side curtain airbag module with Collano® adhesive film

Airbags are composed of highly oriented technical fibers, *i.e.* nylon 6.6, which are hard to bond to. In addition, these airbags have to stay operational for more than 10 years at conditions ranging from –40 °C up to 90 °C, resulting in high requirements concerning heat stability and toughness. First attempts to solve the problem of air tightness for this application using a thermoplastic film are described in the patent literature in 1999.[5] In cooperation with a major supplier of airbag systems, Collano developed a multi-layer film that fulfills all requirements. In this film a polyether-block-copolyamide is used as the sealant layer in a multilayer structure that guarantees the air tightness, however this layer needs to be bonded to the technical textile. For this task, a polyolefinic adhesive layer was developed that shows superior adhesive performance over the entire relevant temperature range. The performance of these layers is outstanding especially at temperatures below –30 °C due to the high flexibility of the material and its low glass transition temperature. Fig. 2 shows a DMA measurement of this polyolefin adhesive layer. A maximum in the loss factor and loss modulus shows a broad glass transition region between –60 °C and –40 °C. Furthermore, this product shows a low storage modulus within the application range of the film (–40 °C to 90 °C). The use of such a designed adhesive film was patented by Collano in 2005, and in the meantime this product has been successfully commercialized.[6]

4. Structural Adhesives: Polyurethanes, Polyureas, and Silane/Urethane Hybrids

If an adhesive is submitted to substantial mechanical stress over a prolonged period of time, the cohesive forces within the bond line must be strong. Consequently, the polymer chains must be either cross-linked or sufficiently long in order to prevent creep fatigue. Yet the liquid state during application is a precondition for an adhesive in order to wet the surfaces and develop adhesion forces. As shown above, the answer to this seeming dilemma is to either apply the adhesive in solution or as a melt. Alternatively, liquid prepolymers can be applied which then cross-link during a curing process. A broad choice of precursors for such *in situ* polymerization reactions is available. They react by radical, condensation, or addition mechanisms depending on their chemical nature. Among them, isocyanates are especially attractive as they provide many possibilities to literally engineer the adhesive to its purpose.

The chemistry of isocyanates, which was brought to commercial significance through the work of Otto Bayer in the late 1930s, opens a plethora of opportunities to the adhesive chemist.

Isocyanates react with a wide range of functional groups which contain an active hydrogen atom. Of practical importance in the adhesives world are the addition reactions which yield polyurethanes and polyureas. The most simple reaction principles are outlined in Table 2.

4.1. *Polyurethane Adhesives*

In order to form cross-linked networks upon curing, the isocyanate component contains two or more isocyanate groups which are separated by an organic moiety. The fragment to which the isocyanate group is linked determines its reactivity. During the polyurethane forming reaction, aromatic isocyanates are up to ten times more reactive than aliphatic ones. For this reason, several million tonnes of the aromatic di-isocyanates TDI (toluene-di-isocyanate) and MDI (diphenyl-methane-di-isocyanate) are produced globally and are used in many polyurethane products including adhesives. Aliphatic isocyanates are also readily available. In the field of polyurethane adhesives, they are used for specialties such as medical adhesives or applications where discoloration of the adhesive joint upon aging plays an important role. Apart from the substituent effects, the reaction mechanisms of isocyanates are significantly influenced by catalysts. They not only affect the reaction rates but also, through their selectivity, the final properties of the polymer. Two di-isocyanates units can be combined with a diol moiety

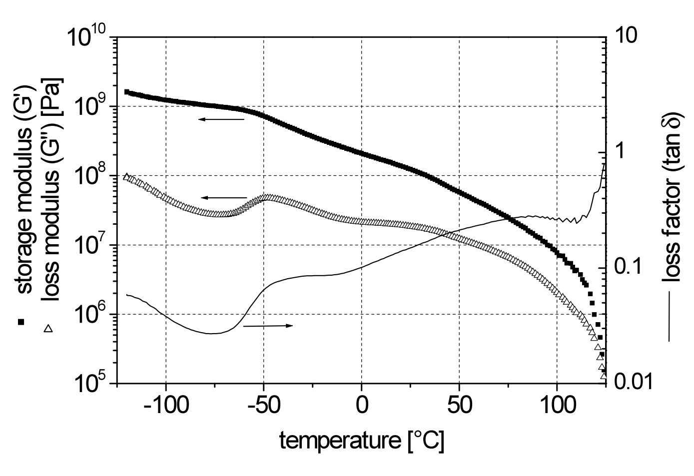
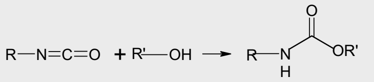
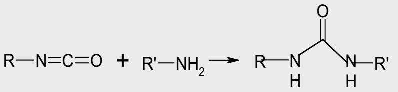
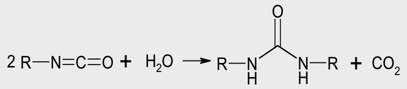
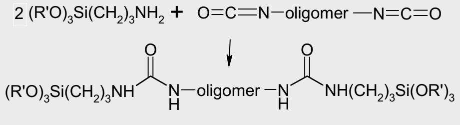
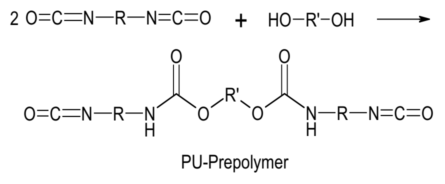


Fig. 2. DMA measurement of adhesive layer of Collano® multilayer film

Table 2. Reactions of isocyanates

Reaction with	Reaction scheme	Product
Alcohol		Urethane
Amine		Urea
Water		Urea
Amino-silane		Silane-terminated polyurea/ urethane hybrid (SPUR)

to form a prepolymer which still contains two reactive sites for further polycondensation, as shown in Scheme 2.



Scheme 2. Formation of a PU prepolymer

The nature of the diol component will strongly influence the properties of the adhesive formulation, and the choice is almost unlimited. Typically, polyester- or polyether-polyols are employed, but natural diols such as castor oil also find their specific niches.

Polyurethanes (PU) are available as moisture-curing one-component and two-component systems or as thermoplastic, non-reactive systems.[7]

Traditional one-component systems are formulated with pre-polymers and suitable additives to fit the required adhesive profile. Such systems are stable for months in the absence of humidity but are rapidly hydrolysed, forming CO_2 and a primary amine. Since the reaction rate of the resulting amine with an isocyanate is up to 100 times higher than that of water, the amine will immediately combine with the isocyanate groups present. The prepolymers used in reactive 1C systems can be both in liquid or solid form. The latter are moisture-curing hot melts. The pertinent prepolymers are formulated in such a way that the molecular weight is high and/ or the employed polyester-ols are crystalline (*e.g.* poly-caproclactones (CAPA®)). Due to the crystallization of the matrix such compounds behave like traditional hot melts. They exhibit a reasonable initial strength which increases over several days through the slow cross-linking of the isocyanate groups.

For obvious reasons, one-component polyurethanes must be stored in the complete absence of moisture which requires special containers and procedures. Moreover, a certain degree of foaming in the glue line and concomitant reduction of cohesive strength always occurs due to CO_2 formation during the hydrolysis step. Additionally, at least one moisture-providing surface must be present, which excludes the use of such systems for the bonding of air-tight surfaces such as metals, glass, or plastics. In order to circumvent these obstacles, so-called two-component systems are often used in which the PU prepolymer and the polyol are stored in separate containers and are mixed immediately prior to application. Often a catalyst is added to the isocyanate component as described above to adjust the setting time of the mixed system. In addition to the described aromatic isocyanates (TDI and MDI), aliphatic isocyanates can also be formulated into adhesives, *e.g.* hexamethylene-di-isocyanate (HDI), isophorone-di-isocyanate (IPDI), and 2,2,6-trimethyl-hexamethylene-di-isocyanate.

Thermoplastic polyurethanes (TPU) are mostly applied as solutions in solvents or increasingly as water-based dispersions. Another application form of thermoplastic polyurethanes are adhesive films as described in Section 3. Recently, Bayer Material Science have introduced a TPU dispersion containing a solid iscocyanate. A dried film of the above-mentioned dispersions is also commercially available.[8]

4.2. *Pre-applicable (Latent) Reactive PU Systems*

Pre-applied adhesive systems are widespread in most areas of activity because of their convenience. They are encountered in the form of adhesive tapes, pressure-sensitive labels, self-sealing envelopes, *etc*. Another well known form of pre-application are heat sealing adhesives which are widely used in the packaging and textile industry. All these systems have the advantage of the ease of application. The end user is not encumbered with the task of bringing the liquid adhesive onto the surfaces which are to be joined. However, all the above-mentioned systems are thermoplastic and therefore subject to cold flow (creep) behavior. There are not suitable for bonds which are exposed to permanent load, *i.e.* structural bonds. In order to avoid creep in adhesive bonds, their matrix has to be cross-linked as realized in many structural adhesives such as epoxies, polyurethanes, and others. For obvious reasons, this cross-linking must occur in the bond line which means that in reactive systems for pre-application the conditions of storage and reaction, respectively, must be distinctively different. The sites of cross-linking must be latently reactive in order to be deliberately triggered by conditions different from those during storage, *e.g.* light irradiation or temperature.

The first thermally latent reactive polyurethane system was introduced to the market 10 years ago under the trade name Collano HCM®. It consists of a dispersion of a solid isocyanate in a mixture of different poly-caprolactones. EP 0 598 873 contains the details of the formulation.[9] In principle, crystals of a solid isocyanate are deactivated on the surface by a thin layer of urea. This coating prevents the reaction with the polyester–polyol matrix even in the melt, up to temperatures of approximately 100 °C. Only above this threshold temperature the solid isocyanate begins to dissolve and reacts with the matrix polyol.

This sequence of events can be conveniently monitored by differential scanning calorimetry (DSC). At 65 °C the melting

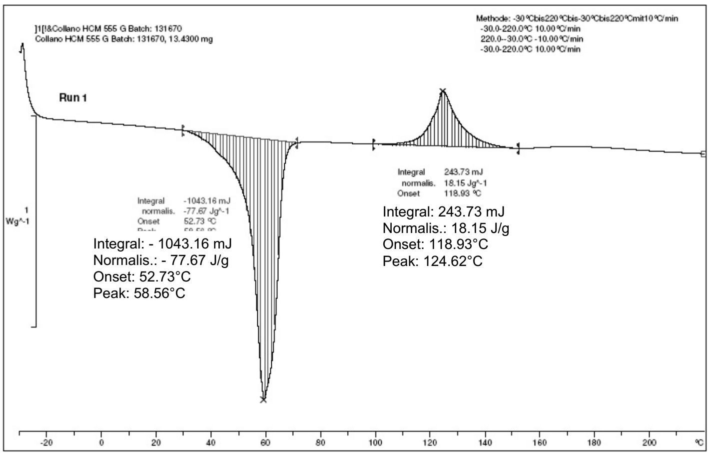


Fig. 3. DSC spectra of HCM 555 from –30 to 220 °C

of the crystalline polyol matrix (an endothermic peak) and at 125 °C the reaction of the liberated di-isocyanate (an exothermic peak)[10] are observed (Fig. 3). The surface-deactivated solid isocyanate can be heated to about 70 °C without loss of reactivity. At that temperature, the crystalline polyol matrix is melted and can be applied through a slot die or by roller coating. The coated adhesive is non-tacky and can be stored without special protection.

In order to activate the reaction of the isocyanate, a heat pulse at temperatures above 120 °C is required. The system was extensively studied by thermoanalytical methods and the data analyzed by advanced thermal analysis methods.[11,12] On the basis of these data, the reaction can be modelled under any given system conditions.

Collano HCM® is available as granules for extrusion coating or as a powder for scattering applications. Most of the applications are in the automotive industry. Examples are pillar linings, door panels, dashboards, seats, or headliners. Such applications require a heat resistance of 90–120 °C while the heat sensitivity of the substrates excludes the use of classical hot melt adhesives.

4.3. *Polyurea Adhesives*

While polyurethane adhesives are commercially available in large abundance, information on polyurea adhesives is still scarce, which prompted us to apply for a European patent (application date 6.02.07). To our knowledge it is the first one on record describing the preparation and application of two-component polyureas for adhesive purposes. The reason for the virtual absence of the polyurea technology is in all likelihood the high reaction rate at which curing occurs. Table 3 summarizes the relative reaction rates of a given isocyanate with respect to molecules with an active hydrogen group.

The high reaction rate observed for polyureas requires totally new concepts of adhesive application technology.[13] The components have to be mixed with high-speed equipment, applied within seconds thereafter, and joined in-line in a continuous press. At present, there is no commercial equipment available which would permit continuous high-speed line production involving polyurea technology. However, the concept was proven on a prototype production line used in a joint project between Collano and the University of Applied Science at Biel. In an experimental set-up, solid wooden boards are assembled at a speed of 60 meters per minute.

4.4. *Silane Terminated Polyurethanes (SPURs)*

The versatility of the polyurethane chemistry for adhesive purposes is further demonstrated by a fairly novel class of commercially available products commonly referred to as ‘silane terminated polyurethanes’, SPURs. The compounds are obtained by reaction of an isocyanate containing prepolymer with a suitable silane, see Table 2 (reaction of an isocyanate with aminosilane).

Applied to a surface, the silicon alkoxides will hydrolyze to form unstable silanol groups. These will consequently either react with hydroxy functions on the surface or cross-link among themselves.

The resulting products combine to a certain degree the properties of polyurethanes and those of silicones. They are highly elastic and robust. These properties are exploited in commercially available parquet adhesives where the sound-deadening property of the glue line is a supplementary benefit. Since silanes are adhesion promoters in their own right, SPURs show excellent adhesion properties to many substrates such as glass, ceramics, metals, *etc.* Other properties of SPUR adhesives are improved UV-stability and weatherability, immediate paintability, and improved resistance to automotive fluids.

5. Emulsion Polymerization

Polymers from aqueous emulsion polymerizations are used in water-based adhesives as well as binders in paints and coatings. A common denominator of all these applications is a high affinity of the polymer film to the target surfaces and a high degree of cohesive strength. For the latter purpose, polymer emulsions have a distinct advantage over polymer solutions. Emulsion polymerization allows the preparation of high molecular weight polymers at high concentrations and still workable viscosity ranges. Additionally, emulsion-based systems are environmentally friendly due to the absence of organic solvents.

5.1. *Technology*

Emulsion polymerization is a type of radical polymerization that usually starts with an emulsion phase consisting of water, monomers, and surfactants. The most common type of emulsion polymerization is an oil-in-water emulsion in which droplets of monomer (the oil) are emulsified (with surfactant) in a continuous phase of water. In the nucleation step, an initiator triggers the formation of radicals which start the polymerization. These radicals react in a chain reaction with additional monomers to create the polymer (Fig. 4). The first successful theory to explain the distinct features of emulsion polymerization was largely developed by Smith and Ewart[14] in the 1940s, based on their studies on polystyrene. Fig. 4 shows the three intervals according to the theory of Smith and Ewart. The diagram

Table 3. Relative reaction rates of isocyanate with nucleophiles

Nucleophile	Formula	Relative reaction rate uncatalyzed at 25 °C
Primary aliphatic amine	$R\text{-}NH_2$	1000
Secondary aliphatic amine	$R_1R_2\text{-}NH$	200–500
Primary aromatic amine	$Ar\text{-}NH_2$	2–3
Primary hydroxyl	$R\text{-}CH_2\text{-}OH$	1
Water	H_2O	1
Secondary aromatic amine	$R_1Ar\text{-}NH$	1
Secondary hydroxyl	$R_1R_2\text{-}CH\text{-}OH$	0.3

was taken from a brochure published by Dechema.[15]

The choice of monomers depends on the intended application of the polymer and on the available production technology. For example, wood adhesives are traditionally based on vinyl acetate and stabilized with polyvinyl alcohols. Other protective colloid systems involve cellulose derivatives. Alternatively, emulsions can be stabilized with anionic, cationic and/or non-ionic surfactants. The stabilizers are not only responsible for good stabilization, they also determine the particle size of the polymer particles, the pigment bonding properties, the water resistance of the polymer film, and the storage stability of the emulsion. The composition of the monomers, on the other hand, determines hardness, flexibility, chemical resistance, weatherability, *etc.*

5.2. *Self-cleaning Surfaces*

Self-cleaning surfaces have recently attracted broad attention after products with the so-called lotus effect became commercially available. The term 'lotus effect' stems from the properties of the leaves of the lotus flower which are washed clean by rain. The surface structure of the lotus leaves is quite intriguing in that it contains waxy humps on a nano scale which prevent dirt particles from firmly adhering to the surface. To a certain extent, the commercially available products mimic this effect.

A potential alternative to this strategy consists in creating a highly hydrophobic surface in order to minimize all interactions with polar dirt particles and to repel water droplets which then will wash off the particles. Polymer films composed of the monomers VeoVa and acrylates can be designed in a way that fulfills this condition. The structure of VeoVa (versatic acid vinyl ester, a branched monomer produced by Hexion, the former chemical subsidiary of Shell) is shown in Fig. 5. The bulky hydrocarbon groups entail a high degree of water and alkali resistance. The down side of the steric loading is a lower reactivity during the polymerization process. Poly-VeoVa 10 exhibits a fairly low T_g value of –3 °C, but when combined with so-called hard acrylic monomers (*i.e.* with high T_g value), a broad range of polymer properties can be covered.

These unique properties of the VeoVa-type monomers in combination with suitable acrylates were used to achieve the goal of making self-cleaning and water-repellent surfaces. The traditional silicone-based additives are no longer needed as hydrophobicity now is an intrinsic property of the VeoVa/Acrylate polymer film. Fig. 6 demonstrates the effect of a high VeoVa content for self-cleaning applications when compared to a 'normal' indoor paint on a terpolymer of vinyl acetate, VeoVa, and acrylates.

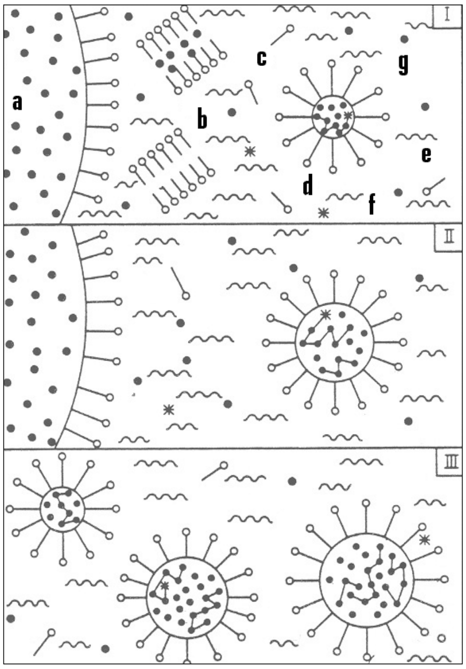


Fig. 4. Steps in emulsion polymerization. I) Nucleation with a) monomer droplets, b) micelles, c) surfactant, d) polymer particles, e) water, f) radicals, g) monomer, II) growth, and III) termination.

6. Conclusion

For many years, the market for adhesives has expanded at a rate that clearly exceeds average economic growth. The reason for this proliferation is the availability of customized adhesive solutions which replace traditional bonding technologies such as welding, riveting, or screwing. The key to success in the development of speciality adhesives is a profound understanding of the chemical and physical properties of polymers. In the adhesives world, we can see how the results of basic research are translated into practice in a straightforward way.

Received: May 8, 2008

---

[1] Collano AG, Annual Report **2007** at *www.collano.com.*

[2] A. Dobmann, *Adhesives Age* **2002**, *45*, 26.

[3] P. Frei, J. Nyffeler, A. Dobmann, EP 1616583 (A1), **2006**.

[4] O. Meincke, K. Jud, *Adhäsion* **2007**, *7–8*, 20.

[5] Gebrauchsmusterschrift DE 29906538, **1999**.

[6] A. Schulthess, EP 1518761(A1), **2005**.

[7] U. Meyer-Westhues, 'Polyurethane, Lacke, Kleb- und Dichtstoffe', Vincentz Network, Hannover, **2007**.

[8] G. Büchner, W. Henning, *Adhäsion* **2007**, *6*, 16.

[9] T. Abend, EP0598873, **2002**.

[10] D. Fuhrer, W. Probst, W. Schwotzer, *Adhäsion, Kleben und Dichten* **1999**, *10*, 22.

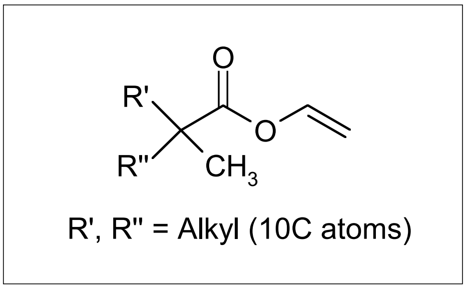


Fig. 5. Structure of VeoVa

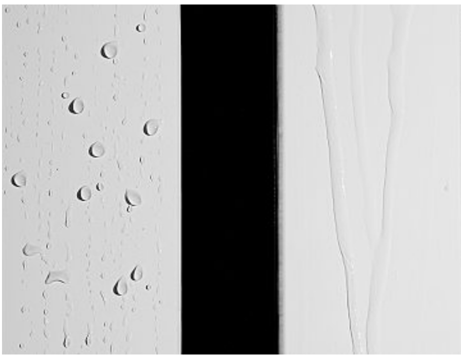


Fig. 6. Different hydrophobicity of indoor paints

[11] AKTS AG, at *www.akts.ch.*

[12] D. Ferrand, Presentation at the Symposium 'Swissbonding', Rapperswil, **2006**.

[13] W. Schwotzer, Proceedings of the World Adhesive Conference, Miami, **2008**.

[14] W.V. Smith, R. H. Ewart, *J. Chem. Phys.* **1948**, *16,* 592.

[15] Dechema, 'Polymerisationstechnik', **1989**.