Title



© Michael Cohn / stock.adobe.com

When Bonding Becomes Faster Than Welding

Modern production lines require joining processes that reconcile short cycle times in manufacturing with high fatigue strength of components. Fast-curing polyurea adhesives solve the cycle time problem but place high demands on bonding to the substrate. A defined, reproducible adhesion promotion is therefore essential for industrial implementation. Atmospheric plasma polymerization offers a dry, in situ method for this purpose, enabling the direct formation of amine-functionalized intermediate layers on metal surfaces.

Heiko Jung, Thomas D. Michl, Marcel Fischer, Bruno Traber, Sonja Neuhaus, Raphael Schaller

To promote adhesion to aluminum EN AW-6063 (Al-6063), 3-aminopropyltriethoxysilane (APTES) is applied via atmospheric plasma polymerization and subsequently bonded with a fast-curing polyurea adhesive. The adhesive is mixed and dispensed at a temperature of 60 °C, resulting in an open time of 1.5 s. The achieved initial tensile shear strengths of over 17 MPa are on par with resource- and logistics-intensive pretreatments such as coating or cathodic dip coating. This indicates that APTES plasma polymers represent a technically robust, process-integratable bonding agent for rapid aluminum bonding.

Bonding with short cycle times

Bonding and welding have been competing for the same applications for decades, with welding long considered the faster joining technology. Bonding offers several advantages over welding: It is more tolerant of manufacturing tolerances and gap sizes, avoids thermal damage to the component surface, and allows the properties of the overall system to be specifically tailored to the application through the choice of adhesive [1]. In addition, bonding enables the reliable production of hybrid components – such as aluminum-fiber-reinforced plastic composites – which cannot be manufactured by welding and are of central importance for lightweight construction and efficiency in automotive engineering. In high-speed, highly automated processes, however, the process speed of bonding remained the primary limiting factor for a long time. Those who needed to join components at a rate of one per second could not afford traditional adhesive systems for a long time. Fast-curing polyurea adhesives are pushing this limit. The

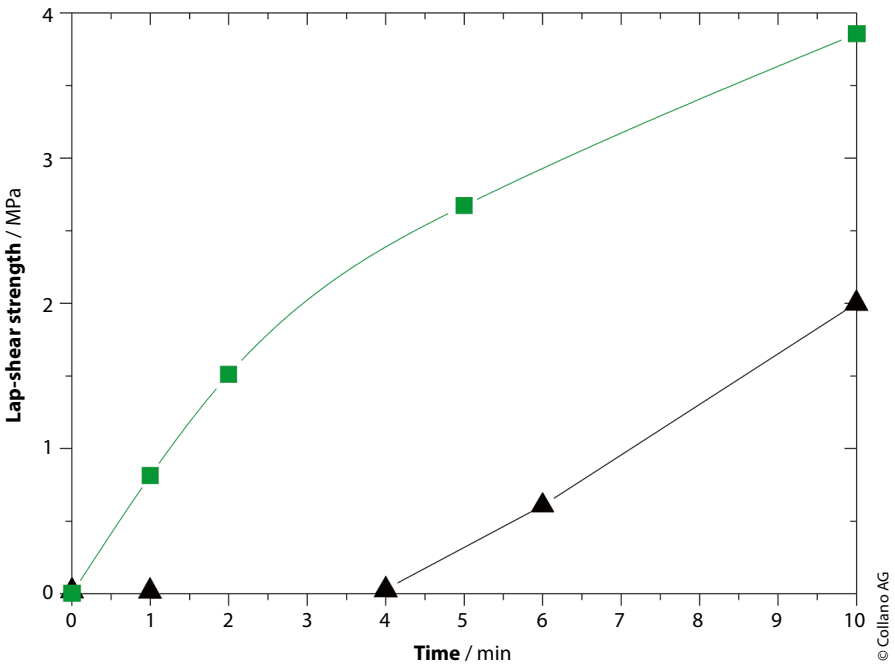
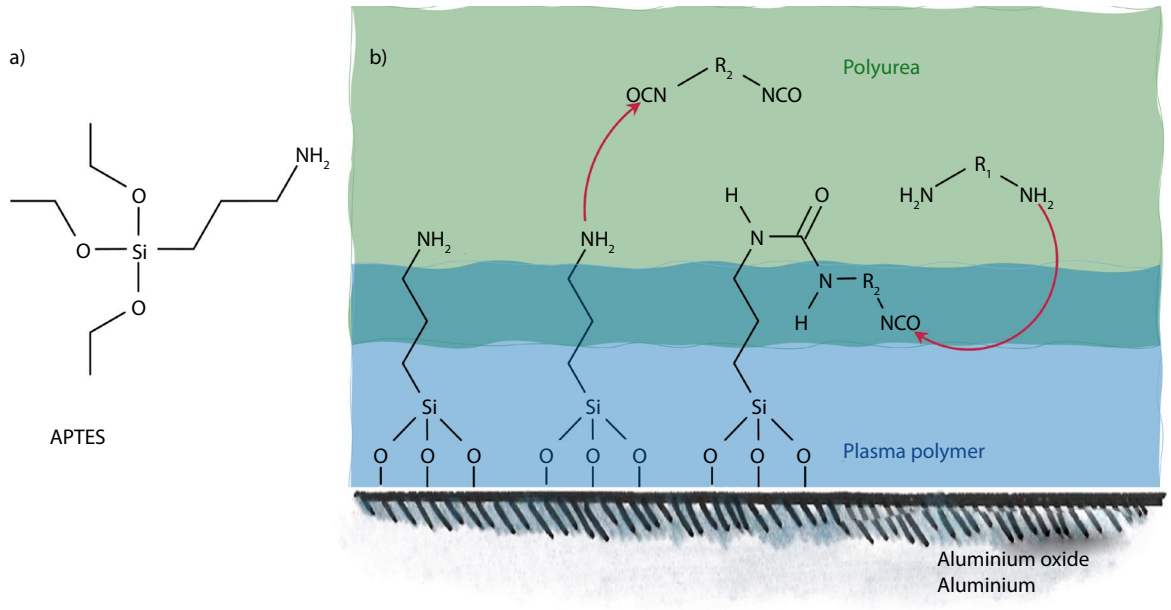


Figure 1 Tensile shear strength as a function of time for two adhesives in a tensile shear test: Strength development of the (■) polyurea compared to a fast-curing (▲) polyurethane.



© Collano AG

Figure 2 Schematic representation of APTES: a) Molecular structure of APTES; b) Plasma-polymerized APTES layer on aluminum oxide with primary amine groups that form covalent bonds with the polyurea isocyanate groups, thereby creating a chemical bridge between the aluminum substrate and the polyurea adhesive. The arrangement shown has been deliberately simplified, as APTES can also form other types of bonds on aluminum and aluminum oxide.

underlying polyaddition reaction between isocyanates and amines proceeds up to about 1,000 times faster than the corresponding isocyanate-polyol reaction in traditional polyurethanes [2], [3]. This acceleration is immediately evident in the rate at which strength develops. The substrate used is EN AW-6063 (Al-6063) aluminum with cathodic dip coating (E-Coat). The polyurea adhesive is mixed at 60 °C and applied at room temperature using a counterflow mixing system. Its open time is 1.5 s.

After just about one minute, the adhesive reaches a tensile shear strength of approximately 1 MPa. In contrast, with a fast-curing standard polyurethane, measurable strength levels are not achieved until four minutes have passed. Even after ten minutes, this adhesive reaches only slightly more than half the strength of the polyurea adhesive (*Figure 1*). From a process engineering perspective, the key factor is that the polyurea bond is strong enough to handle after just about one minute, whereas conventional adhesives such as polyurethane or epoxies require several minutes to reach this stage. Detailed information on polyurea adhesives can be found in the articles by Hug et al. in adhäsion KLEBEN+DICHTEN [4], [5]. With such rapid strength development, cycle times become possible that make bonding fundamentally attractive for highly automated production lines and allow it to penetrate areas that were previously typically reserved for welding. In such applications, the substrates must first be prepositioned so that they can then be bonded together with a material-to-material bond via injection or potting. However, the speed of the adhesive alone does not solve the problem. On the contrary: it shifts the problem to another location, namely the interface between the metal or metal oxide and the adhesive.

Speed alone is not enough

For structural aluminum bonding, cathodic dip coating or industrial coating systems are frequently used today – typically insulating coatings, which also serve as bonding agents [6]. Both processes involve wet chemical pretreatments that require significant energy, time, and material resources and are sometimes carried out outside the production facilities of mass-production manufacturers. This creates additional unknowns and potential quality risks. From the perspective of process integration, the question therefore arises as to whether a dry, process-integratable pretreatment can perform the same interfacial function and thus unlock the potential of fast-curing polyurea bonding directly on metal or metal oxide surfaces for industrial applications. The results presented here are based on an Innosuisse project (102.681 IP-ENG) carried out jointly by the University of Applied Sciences Northwestern Switzerland and Collano. This article also summarizes findings from the work of Michl et al. and contextualizes them within a practical perspective on atmospheric plasma polymerization for the production of bonding agents for fast-curing polyurea adhesives [7].

The fourth state of matter as a tool

Atmospheric plasmas are considered the fourth state of matter, alongside solids, liquids, and gases. They consist of a reactive mixture of ions, free electrons, radicals, and neutral species [8]. This high-energy matter manifests as auroras, flames, or lightning and, when generated in a controlled manner within a plasma jet, can be utilized for surface chemical applications. A fundamental distinction must be made between various applications: plasma activation and plasma polymerization. In plasma activation, the existing substrate surface is merely chemically modified without the formation of a distinct layer. On metals such as aluminum and steel, whose surfaces are covered by a thin oxide layer under ambient conditions, impurities are removed and the oxide layers are chemically activated through the incorporation of additional polar, predominantly

oxygen-containing groups such as hydroxyl, carbonyl, and carboxyl groups [9].

A comparison of plasma activation and plasma polymerization

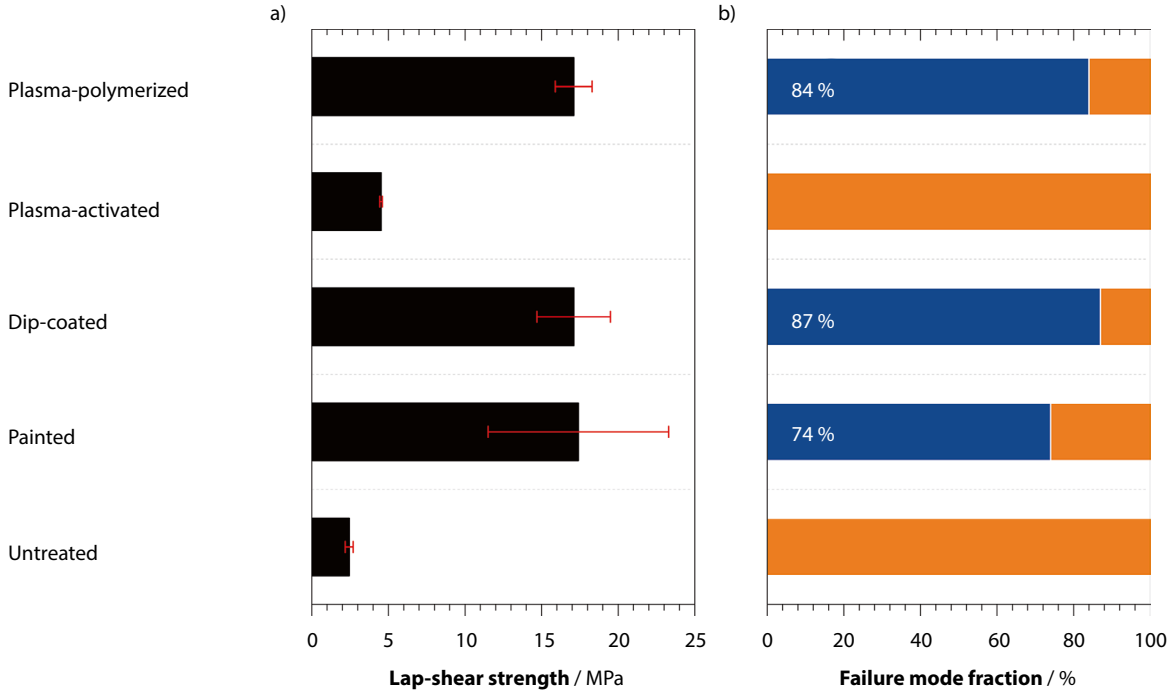
In plasma polymerization, a monomer or monomer mixture is introduced into the plasma nozzle and converted on the substrate into a thin, cross-linked plasma polymer. APTES is of central importance for this application. Its silane structure can bond to oxidic aluminum surfaces, while the terminal amine function reacts rapidly with isocyanates from the polyurea system. This creates a nanometer-thin intermediate layer that is chemically bonded to the metallic surface via silane or siloxane groups on one hand, and coupled to the adhesive via amine-isocyanate reactions on the other. As a result, the polyurea adhesive can be more consistently designed as a load-bearing and energy-absorbing material [10] without having to provide compensation for all irregularities in the metal surface. The result is effectively a three-component adhesive system: the amine and isocyanate components as the main constituents, and the APTES plasma polymer as a nanometer-thin adhesion-promoting layer that covalently bonds to the polyurea (*Figure 2*). It is precisely this difference from mere surface activation that constitutes the core of the approach. The goal is not merely to make a surface more wettable for a short time, but to specifically build a functional, nanoscale interphase with defined chemistry.

The stress test: from 2.5 to 17 MPa

The mechanical performance of the APTES plasma polymer coating was investigated in single-stage tensile shear tests according to DIN EN 1465 on Al-6063 with an overlap of 12.5×25.0 mm. The substrates were first degreased according to standard procedures and then either left untreated, cleaned only with air plasma, or coated with an APTES plasma-polymerized layer, which was deposited in a single pass using an atmospheric plasma jet process (air as the process gas). Al-6063 was used as a reference, as it is typically supplied by system manufacturers in industrial applications – either cathodic dip-coated or painted – and subsequently bonded. A two-component, fast-curing polyurea adhesive with an open time of 1.5 s was used as the adhesive. The adhesive was applied using a high-pressure counterflow mixing system to achieve a defined joint thickness of 5 mm. After 2 h of curing at room temperature, the specimens were post-cured at 80 °C for 4 h. This temperature control served solely to accelerate complete curing and thus shorten the test times; it should not be considered a necessary process step for practical application. The tensile shear strength was determined at room temperature at a feed rate of 20 mm/min; the fracture behavior (adhesive and cohesive) was assessed by visual inspection of the fracture surfaces under UV light. The numbers speak for themselves. Untreated Al-6063 achieves a tensile shear strength of only about 2.5 MPa with polyurea. If pure plasma activation is performed, this value increases to around 4.5 MPa. However, the failure mode remains entirely adhesive, and the bond peels cleanly from the metal substrate without the adhesive itself being subjected to significant stress. With a plasma-polymerized APTES layer on Al-6063, the tensile shear strength increases to about 12 MPa, and the failure mode shifts significantly toward predominantly cohesive failure within the bonded joint. Under optimized conditions, the same combination of APTES plasma polymer and polyurea can even achieve an initial tensile shear strength of around 17 MPa with more than 80 % cohesive fracture. This value approaches the range of conventional pretreatments and comes remarkably close to the level achieved with dip-coated or painted aluminum substrates (*Figure 3*).

A look at the process parameters shows just how precisely this chemistry can be controlled. The film thickness of the APTES plasma polymer decreases exponentially as the nozzle velocity increases, from about 100 nm at very slow travel speeds (about 2 m/min) to about 10 nm at high speeds (about 30 m/min). After solvent washing, 50 to 75 % of the origi-

Advertisement placeholder
Hier steht eine Anzeige.
Hier staat een advertentie.
Advertisement placeholder
Hier steht eine Anzeige.
Hier staat een advertentie.
Advertisement placeholder
Hier steht eine Anzeige.
Hier staat een advertentie.
Advertisement placeholder
Hier steht eine Anzeige.
Hier staat een advertentie.



© Collano AG

Figure 3 Tensile shear strengths and fracture patterns of polyurea bonds on Al-6063 as a function of surface treatment: a) average tensile shear strength with error bars for untreated, painted, dip-coated, plasma-activated, and plasma-polymerized aluminum substrates; b) corresponding proportion of the fracture pattern showing cohesive (blue) versus adhesive (orange) failure modes.

nally deposited film thickness is consistently retained. The remainder consists of loosely bound, uncrosslinked oligomer fragments that serve no mechanical function. For industrial applications, this means that the desired target film thickness can be precisely adjusted both via the travel speed and through multiple coating passes [7].

Less is more

An obvious development approach was to further optimize the APTES-based plasma polymerization layer through the use of comonomers. APTES was combined with hexamethylcyclotrisilazane (HMCTSZ), octamethylcyclotetrasiloxane (OMCTS), trimethylphenylsilane (TMPS), trimethoxyphenylsilane (TMOPS), and 2-aminoethanol (ethanolamine, EA). The selection followed a clear logic. Silazane and siloxane derivatives were intended to increase the degree of crosslinking and the network stiffness of the plasma polymer, aromatic silanes to improve chemical and thermal stability, and ethanolamine to introduce additional amine functionality without completely sacrificing the silane bond to the aluminum. However, the results were unequivocal – and contradicted expectations. Mixtures of APTES with HMCTSZ, OMCTS, TMPS, TMOPS, or ethanolamine consistently resulted in a deterioration of adhesion compared to a pure APTES plasma polymer. In all of the plasma-polymerized monomer mixtures investigated, the tensile shear strengths were clearly below the approximately 12 MPa achieved with the pure APTES plasma polymer on Al-6063 [7]. The key finding is therefore that the simpler approach is superior to the more complex one. Pure APTES plasma polymer apparently provides the optimal balance of accessible amine functions, sufficient crosslinking of the layer, and adequate mechanical integrity of the interphase, thereby forming a robust basis for adhesion between Al-6063 and fast-curing polyurea adhesives.

Surface chemistry is the deciding factor

Why is the simpler system superior to the more complex one? The answer lies deeply hidden in surface chemistry and was only revealed through X-ray photoelectron spectroscopy (XPS) and chemical derivatization XPS (CD-XPS). The composition is given below in atomic percent (at.%). The extent of fragmentation is dramatic. While the APTES monomer itself consists of 64.3 at.% carbon and 7.1 at.% nitrogen, the carbon content in the finished plasma polymer drops to 20 to 35 at.%, depending on the process conditions, while the oxygen content rises to 46 to 65 at.%, leaving only 1 to 4 at.% nitrogen. The plasma effectively breaks the molecule down to its silane-oxygen backbone and reassembles it, resulting in the loss of a large portion of the original amine groups. Nevertheless, sufficient reactive amine groups remain on the surface to mediate adhesion to the adhesive. A threshold behavior is crucial here. Once there are enough accessible amine groups on the substrate surface, adhesion no longer increases proportionally with a higher degree of functionalization. In this range, the cohesion of the plasma polymer and its anchoring to the oxide layer of Al-6063 increasingly determine the resulting strength – not the total nitrogen content alone, which proves to be an unreliable predictor of adhesion.

Several detailed results support this figure. Although switching the process gas from air to nitrogen partially increases the functional nitrogen yield, it does not significantly improve the tensile shear strength. A modified nozzle geometry also does not lead to higher adhesion, despite more favorable chemical signatures.

Surface pretreatment	before PV 1200		after PV 1200	
	Lap shear strength	Cohesive failure	Lap shear strength	Cohesive failure
	MPa	%	MPa	%
Plasma polymerized	17.1 +/- 1.2	84	12.5 +/- 2.5	5
Dip-coated	17.1 +/- 2.4	74	16.3 +/- 2.5	95
Painted	17.4 +/- 5.9	87	17.0 +/- 1.0	99

Table 1 Tensile shear strength and fracture pattern before and after the PV 1200 cyclic environmental test.

© Collano AG

Plasma-polymerized 3-aminopropyldiethoxymethylsilane (APDEMS) was chosen to systematically investigate the influence of a slightly modified terminal group, in which a methyl group replaces an ethoxy group. The effects on fragmentation, network formation, and the stability of the amine-containing functional groups were investigated. Despite lower oxidation, APDEMS performs mechanically worse than the simpler APTES plasma polymer. The overarching conclusion is therefore: It is not the maximum functional density that is decisive, but rather the subtle interplay of chemical composition, degree of crosslinking, and interfacial mechanics.

When Moisture Reaches Its Limit

High initial strength is one side of the coin; durability under real-world climatic conditions is the other. To assess the latter, long-term behavior was examined in a climatic cycling test in accordance with VW PV 1200: The samples underwent several climate cycles (12 h each) involving heating to +80 °C at 80 % relative humidity, followed by cooling to −40 °C (uncontrolled humidity), and a return to room temperature. Atmospheric plasma polymerization with APTES brings the initial strength of polyurea bonds up to the level of established pretreatments; however, it exhibits different aging behavior in the PV 1200 climate cycling test. Prior to the climate cycling test, the tensile shear strengths of the plasma-polymerized, dip-coated, and painted specimens were in a comparable range at approximately 17 MPa, each with high proportions of cohesive failure ranging from 74 to 87 %. After the PV 1200 test, the tensile shear strength of the sample with the APTES plasma-polymerized layer drops to about 12.5 MPa, and the proportion of cohesive fracture decreases to around 5 %, while dip-coated and painted systems maintain both strength and the proportion of cohesive fracture largely stable. Mechanically, this decrease is significant but not catastrophic; more critical is the shift in the failure mode away from cohesive fracture toward increased interfacial failure (*Table 1*).

Supplementary investigations have shown that moisture ingress primarily occurs at the interface between the aluminum substrate and the oxide layer, not at the plasma polymer and polyurea layers [11]. This supports the interpretation that further optimization potential should be sought not so much in the polyurea chemistry or in the APTES plasma polymer itself, but rather at the aluminum-alumina interface and its stability under cyclic humidity conditions. An important limitation here concerns the geometry of the test specimens. Dip-coated and spray-coated tensile shear specimens are completely enveloped by the coating, whereas Al-6063 with APTES plasma polymer exhibits open edges and pores. It therefore remains an open and worthwhile question to what extent the observed under-coating and the loss of cohesive fracture are partly caused by these open edge areas, and whether an adapted edge sealing or geometric design could further improve the long-term behavior of APTES-based plasma polymer coatings.

From the lab to the production line

A technology that shows promise in the laboratory must ultimately prove itself on the production line. Atmospheric plasma polymerization can be directly integrated into the bonding process and is compatible with automated production lines featuring short cycle times (*Figure 4*). An 8-hour endurance test conducted on a laboratory system using APTES in air demonstrated the robustness of this approach. During the test, the system underwent an automated self-cleaning cycle every 30 minutes, in which a fine metal brush kept the nozzle diameter clear, while the internal back pressure at the nozzle was logged hourly to detect gradual clogging at an early stage. Over the entire test period, the coating thickness remained stable within the measurement uncertainty, and no critical problems, such as nozzle clogging, were observed on a small scale [7].

This allows us to specifically describe the benefits compared to conventional pretreatment systems: less wet chemistry, a low monomer volume (approximately 10 g/h), reduced need for drying and oven sections, and better integration with high-speed joining processes. This approach is particularly relevant for applications in the automotive and electric mobility sectors, where cycle time, energy consumption, process robustness, and logistical requirements – such as those for painted or dip-coated components – are evaluated collectively, and entire logistics chains can be eliminated. Initial rough estimates in the context of electric vehicle manufacturing indicate a potential savings of approximately 15 €/module solely through the elimination of time-consuming pretreatment steps, while polyurea adhesives allow components to be manufactured to handling strength within about one minute.

A simple truth and its consequences

The results do not show that all problems with aluminum bonding have been solved. However, they do show that a comparatively simple, APTES-based plasma polymerization represents a robust and industrially viable bonding agent strategy for ultra-fast polyurea adhesives. At the same time, the data provide a clear correction to a widespread development paradigm. More functional groups, more nitrogen, or more complex monomer blends do not automatically lead to better performance and adhesion. Future work should specifically address the effects of salt spray, humidity, and climate, as well as moisture infiltration at the interface between the aluminum substrate and the oxide layer. This study demonstrates the potential of a dry, process-integrated pretreatment for the industrial application of ultra-fast aluminum bonding. //

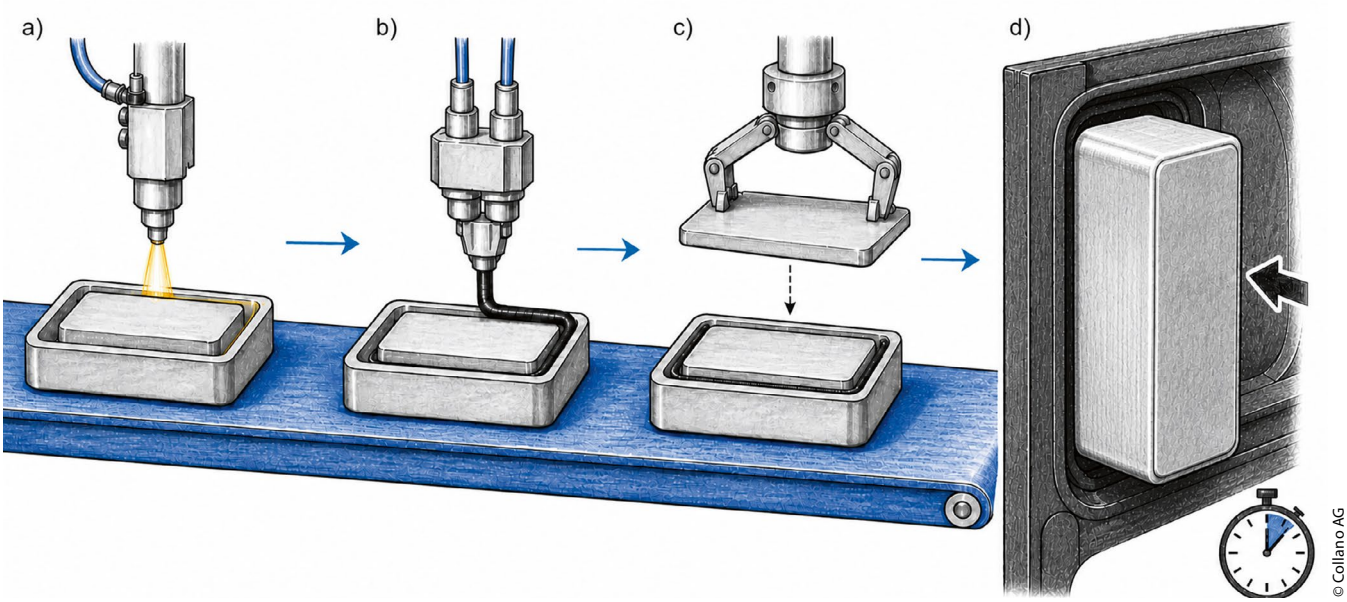


Figure 4 Integration of atmospheric plasma polymerization into an automated bonding process: a) application of a plasma-polymerized bonding agent layer, b) immediate application of the adhesive, for example as a polyurea casting, c) joining and finalization of the component, and d) direct installation shortly after the component reaches handling strength.

References

[1] Habenicht, G.: Kleben – Grundlagen, Technologien, Anwendungen. Berlin/Heidelberg/New York/Tokyo, Springer-Verlag, 1986

[2] Polyurea Elastomer Technology: History, Chemistry & Basic Formulating Techniques. Online: https://thepolyureacompany.com/wp-content/uploads/2022/03/1_WP02.pdf, accessed on 12.08.2026

[3] Oertel, G.: Polyurethane Kunststoff-Handbuch 7. München/Wien, Hanser, 1993

[4] Hug, P.: Schnellhärtende Klebstoffe für die Fahrzeugmontage. In: adhäsion KLEBEN + DICHTEN (2020), Nr. 5-6, S. 14-16

[5] Hug, P.; Jung, H.: Batterien in kurzen Taktzeiten verkleben. In: adhäsion KLEBEN + DICHTEN (2023), Nr. 6, S. 14-19

[6] Peng, H.; Zhou, T.; Fan, Y.; Shangguan, L.; Zhang, N.: Recent advances in aluminum alloy surface treatment technology and bonding properties. In: physica status solidi (a) (2025), Nr. 222

[7] Michl, T. D.; Schwegler, A.; Zvolska, K.; Grob, M.; Keller, P.; Schaller, R.; Jung, H.; Fischer, M.; Frei, P.; Roos, E.; Kresser, K.; Hamedi, Y.; Ben Salem D.; Neuhaus, S.: From plasma chemistry to adhesion strength: Mechanical characterization of pure versus mixed aminosilane films for bonding polyurea to aluminum. In: Plasma Processes and Polymers (2026), Nr. 23

[8] Kroker, T.; Grossmann, M.; Sengstock, K.; Drescher, M.; Wessel-Staarmann, P.; Simonet, J.: Ultrafast electron cooling in an expanding ultracold plasma. In: Nature Communications (2021), Nr. 596, S. 2-8

[9] Yang, R.; Kang, J.; Tian, Z.; Qie, L.; Wang, R.: Plasma cleaning of metal surfaces: From contaminant removal to surface functionalization. In: Surfaces MDPI (2026), Nr. 9, S. 1-26

[10] Ding, L.; Wang, Y.; Lin, J.; Ma, M.; Hu, J.; Qiu, X.; Wu, C.; Feng, C.: Recent advances in polyurea elastomers and their applications in blast protection: A review. In: Journal of Materials Science (2024), Nr. 59, S. 14893-14923

[11] Cavezza, F.; Boehm, M.; Terryn, H.; Hauffman, T.: A review on adhesively bonded aluminum joints in the automotive industry. In: Metals MDPI (2020), Nr. 10, S. 1-32

The Authors | Contact

Heiko Jung, Head of R&D, Collano AG

Marcel Fischer, Head of Applications, Collano AG

Bruno Traber, Know-how Management and R&D, Collano AG

Raphael Schaller, CTO, Collano AG

Thomas D. Michl, Senior Research Fellow, University of Applied Sciences Northwestern Switzerland (FHNW)

Sonja Neuhaus, Professor of Surface Functionalization, University of Applied Sciences Northwestern Switzerland (FHNW)

Collano AG
Neulandstrasse 1
6203 Sempach Station
Switzerland
info@collano.com
www.collano.com

University of Applied Sciences Northwestern Switzerland (FHNW), School of Technology and Environment
Klosterzelgstrasse 2
5210 Windisch
Switzerland
info.technik@fhnw.ch
www.fhnw.ch/de

Advertisement placeholder

Hier steht eine Anzeige.

Hier staat een advertentie.

Advertisement placeholder

Hier steht eine Anzeige.

Hier staat een advertentie.

Advertisement placeholder

Hier steht eine Anzeige.

Hier staat een advertentie.

Advertisement placeholder

Hier steht eine Anzeige.

Hier staat een advertentie.