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Injection bonding of structural components with fast-curing two-component PUR-systems

Gerrit Conermann[1*] and Klaus Dilger[2]

*Correspondence: gerrit.conermann@daimler.com
[1] Daimler AG, HPC F150, 71059 Sindelfingen, Germany
Full list of author information is available at the end of the article

Abstract

When someone joins large structural components, the importance of the joining technology increases. Well-known joining processes such as welding and classic adhesive bonding reach their limits with respect to cycle times and tolerances. A new two-component polyurethane injection process based on the reaction in mold technology, offers an alternative and has the potential to reduce costs and compensate tolerances. The objective of this paper is to characterize and evaluate this process for potential applications so that it is possible to set the parameters as necessary. The example that was chosen for this research is the battery housing for electric vehicles. The advantage that this process does not only join the parts within seconds, but also will seal or fill long gaps if necessary, makes it particularly interesting for the industry. Classic adhesive technology applies the adhesive on one part, then takes the second part for the joining process, grouts the adhesive to a defined gap and afterwards, it still has to cure in a geometrically-defined tool. The PUR injection process fixes the two components in a tool with a defined gap and afterwards, injects the PUR that then reacts in the gap and joins the two parts within seconds. The adhesion and as well the rheology decreases with an increase in crosslinkings. These two parameters are therefore described relative to time and temperature. A steep increase in viscosity is detected after just a few seconds. With higher adherend temperatures the increase in viscosity appears earlier and steeper. The property for adhesion to the surface is decreasing the longer the PUR takes to hit the surface. These dependencies are described in this paper to develop a reproducible application process with a battery housing for electric vehicles as a case study.

Keywords: Injection bonding, Battery housing, Two-component PUR-systems, Rheology of adhesives

Introduction

With regard to the joining of large structural components in particular, joining technology is becoming increasingly important. The weighting of the cycle time, the associated costs and the influence of component tolerances pose special challenges for classic joining technologies. Although classic adhesive bonding processes can join different materials while also compensating for tolerances and different coefficients of thermal expansion, they always involve design limitations for the joining process and long curing times. For classic 2C PUR adhesives the curing times reach from 10 min up to several hours. The aim of this research is to obviate these disadvantages by using PUR systems that cure within seconds. In order still to obtain a robust joining process, the adhesive is injected. A low viscosity in the initial seconds allows the PUR material to flow into bonding gaps and it does not need pressing of the two adherends. Figure 1 shows how the low-viscosity material flows into a gap and cures there within a few seconds. Picture (a) shows how the nozzle is positioned right above the gap and in picture (b) you can see how the nozzle actually moves along the gap and applies the liquid adhesive. After just a few seconds you get to picture (c). In picture (c) the low-viscosity adhesive is already cured, the two parts are joined with an adhesive bond and the gap is sealed. The parts can now be further manufactured.

The aim of this work is to develop an injection bonding process for large structural components that guarantees, among other things, leak tightness and handling strength between the adherends after just a few seconds. Further requirements are media resistance, crash resistance and also a certain elongation at fracture, which allows different coefficients of thermal expansion to be compensated. To this end, the most advanced applications from many different areas of the PUR-processing industries are brought together, intelligently combined and further developed.

The injection bonding process is developed on the basis of Window Spray Technology® [2, 3] for the forming of sealing lips on solar panels or glass panels for the automotive industry. This open process allows defined geometries to be produced with the aid of the low-viscosity PUR material without the need for sealing under pressure. The sealing under pressure is necessary for the Reaction in Mold (RIM) process [4]. This calls for an intelligent tool concept for forming the mold and the associated play with the force of gravity and the flow paths of the PUR material [5]. Two other injection bonding processes in the automotive industry use adhesives with a higher viscosity and fill the gap with pressure [6, 7]. Due to the higher viscosity the adhesive doesn't flow away by the force of gravity, but it also needs at least 10 min of curing to reach handling strength. The material system chosen is a further developed 2C PUR system based on the PUR system used for the Window Spray Technology with the properties shown in Fig. 2. The chemistry of the components were adapted to comply the requirements of the mixing technology described in the second building block.

The second building block is high-pressure countercurrent mixing [8]. This technology mixes polyol and isocyanate in a turbulent flow and allows the components to cross-link within seconds. The mixing head allows stable, low-maintenance operation without the need for flushing between application cycles. This technique is used for injection bonding in the furniture industry, where a fast 2C polyurea adhesive is injected into a cavity and cures within seconds [9].

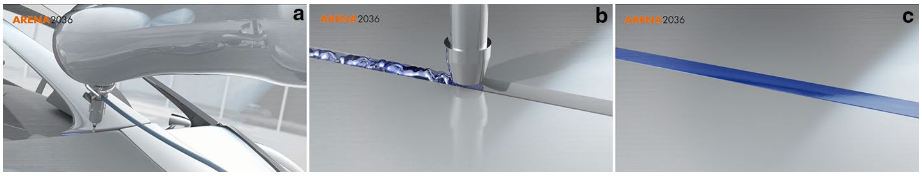

Fig. 1 Vision injection bonding [1]

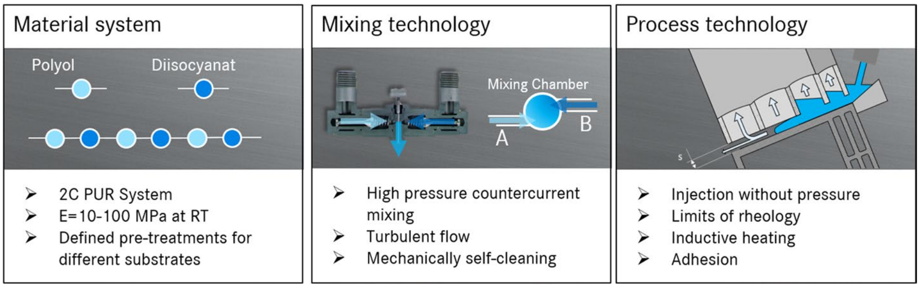

Fig. 2 The 3 building blocks of injection bonding

Table 1 Properties of the two different polyurethane materials

Properties at 25 °C	2C PUR 1	2C PUR 2
Density (g/cm^3)	1.08	1.07
Mixing ratio A (Poly):B (Iso)	100:78	100:58
Viscosity of the components (mPas)	A: 900 B: 150	A: 1080 B:125
Tensile strength (N/mm^2)	33.5	12
Elongation to fracture (%)	280	185
E-modulus (N/mm^2)	40	25

The third building block shall visualize properties that need to be regarded for a successful implementation as an injection bonding process. A relatively fast bonding process with 2C PUR can be found in the automotive industry, such as in the CFRP hybrid trunk lid of the Mercedes SL AMG, where cross-linking is accelerated and controlled by means of inductive heating immediately after application, with handling strength being obtained after 180 s [10]. The induction technology in general was proved to be the most adequate heating technique for fast curing adhesives in metal bonds and is therefore a relevant part of the third building block, the process technology. It achieves high heating rates and enables a drastic reduction of the curing times [11]. Due to the low viscosity PUR material it is also important to know flow paths and therefore understand the limits of rheology. And of course a good adhesion is always a necessary requirement for every adhesive joint. The picture shown in this building block will be explained in "Case study" section in detail.

Using the three building blocks presented in Fig. 2, the aim is to develop a process that makes it possible to join complex structural components within seconds. With this injection bonding process, the first step is to describe the flow behavior of the highly reactive 2C PUR material, especially in the seconds after impact on the surface of the adherend.

Experimental details

The adhesives used in this work are two non-commercial two-component polyurethane materials. The properties are listed in Table 1. Both materials were specially designed by the suppliers for the use with the high-pressure countercurrent mixing in combination with the planned injection bonding process. The polyurethane dosing system is a PSM3000 with a GP600 mixing head [8].

The test setup for the rheology experiment uses a plate/plate measuring system according to DIN 53019 [12], which specifies a constant shear rate. The rheometer used is a MCR300 by Anton-Paar. Due to the difficulty of pouring the PUR material in a defined manner into the measuring gap of the rheometer, Fig. 3 shows how the adhesive can be injected, with the result that the injection process itself has only a minimal influence on the measured viscosity. Starting from the centered hole, the material floods the entire gap within 0.1 s.

A second experiment in this work is used to describe the adhesion in dependence on the time t before the PUR comes into contact with the surface. For this reason a test setup was developed, that lets the material travel for a certain time from the outlet of the application nozzle to the surface of the specimen. Tubes with defined length and cross-section for the respective open times bridge the path between application nozzle and adherend. This test setup can only display open times up to 4 s. The effort to change the material on the used processing equipment is comparably high, therefore the test is carried out only for the faster 2C PUR 1 material. If an influence on the adhesion property is detected it will be clearer with the more reactive 2C PUR 1. The dimensions of the specimen are shown in Fig. 4 and the parameters for the test are listed in Table 2. The specimen were heated to a temperature of 60 °C. Thick adherend lap shear specimen were chosen to eliminate the bending at the end of the lap [13].

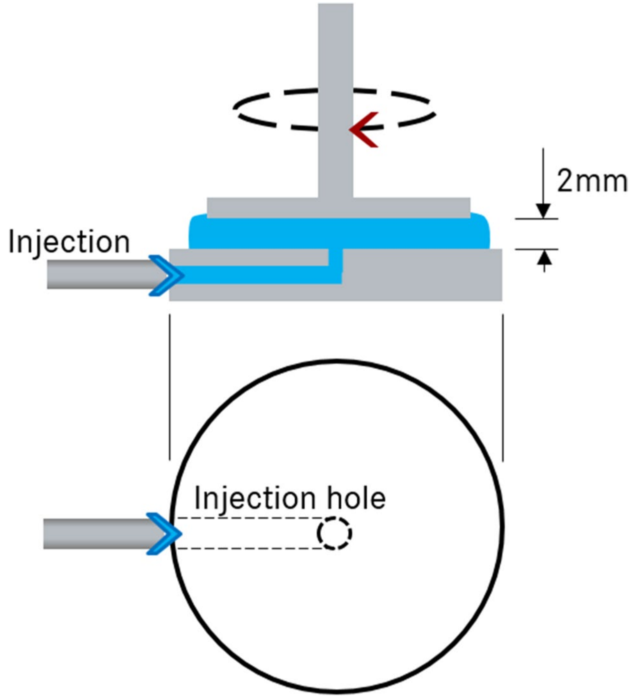

Fig. 3 Test setup for plate/plate

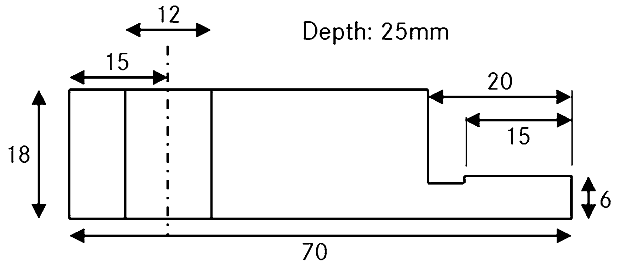

Fig. 4 Dimensions of thick lap shear specimen

Table 2 Tensile testing parameters with thick lap shear specimen

Adhesive	2C PUR 2
Adherend material	St-37
Surface	Cathodic dip-paint coating
Bonding	25 × 15 × 6 mm
Testing	Tensile test
Testing rate	20 mm/min
System	Zwick 1464
Aging	> 10 days RT
Surface temp.	60 °C

Results and discussion

Rheology

Only a robust bonding concept, with an adhesive that can be easily processed and which cures reliably, enters into consideration for use in series production. Other injection bonding processes with classic 2C adhesive systems have already been tested on several occasions [6]. With open times of over 10 min and an almost constant in-process viscosity, rheology plays a minor role and these processes are a lot easier to handle [14]. With open times of 5 s, the viscosity increases steeply from the moment the components come into contact. This viscosity increase is highly temperature-dependent and the rheological behavior must therefore be determined for a reproducible injection or application process.

Rheology describes the deformation and flow behavior of materials. When flowing, molecules and particles are forced to slide along each other. They exhibit a flow resistance force caused by internal friction. Larger components of a liquid cause correspondingly higher viscosity values. The same applies to cross-linking plastics, which also exhibit higher viscosity values in the course of the reaction with an increasing degree of cross-linking [15].

With regard to the injection bonding process, it is necessary to find out how the viscosity value behaves over time for different adherend temperatures. With the aid of these curves, it is possible to design bonding gaps with better geometries and thus prevent errors in the early phases of product development.

Normally a constant shear stress is specified. The disadvantage is that the resulting rotational speed decreases continuously as the viscosity increases. The rate of deformation would therefore no longer be constant. This, however, is decisive for the comparability of the effect of shear on the test specimen [15]. Therefore the shear rate is kept constant. The measuring temperature is kept constant and, with the aid of a disposable measuring system, consisting of a disposable plate and a disposable dish, it is possible to measure several specimens without having to go to the effort of removing the hardened adhesive. The time-dependent viscosity function is evaluated as the result. Here, the time t_s (start time) when the curve begins to rise is of special interest. Likewise, the slope of this curve can be compared for the respective substrate temperatures.

Figure 5 presents for two 2C PUR materials the exothermic polyaddition reaction. It starts with the point where the PUR is injected in the measuring gap at 4 s. Afterwards it is additionally accelerated at higher substrate temperatures. This behavior can be explained with the aid of Brown's molecular movement [16]. It can also be clearly seen that, at a substrate temperature of 80 °C, although the viscosity of 2C PUR 1 is lower in the first 6 s, it is subsequently higher due to the further-advanced cross-linking and it also rises faster. This value of 6 s before the viscosity increase, compared to the around 10 s at a substrate temperature of 60 °C, is excellently suitable for the design of the process for the respective components and flow paths. A substrate temperature of 40 °C is

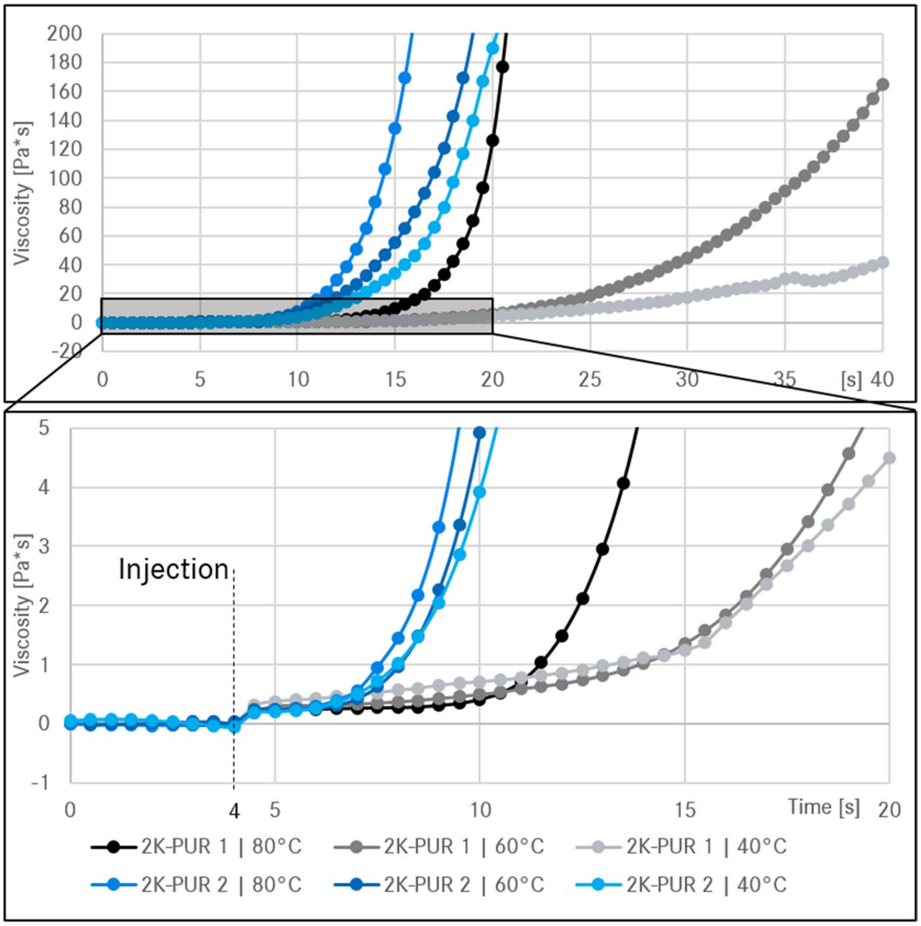

Fig. 5 Viscosity/time for different adherend temperatures

not advisable for the 2C PUR 1 material due to the slow curing. The 2C PUR 2 material is significantly more reactive due to a higher proportion of catalysts and exhibits a correspondingly lower temperature dependency. However, the faster cross-linking also means that there are soon fewer reactants for an adhesive bond with the active centers of the substrate surface [17]. As the goal of the injection bonding process is still fast demolding and further processing, it is necessary to find the break-even point between sufficient adhesion and short curing time.

Also to be considered is the influence of the heat resulting from the exothermic reaction. The more PUR is injected in relation to the adherends surface through which heat can be dissipated, the lower the influence of the adherends temperature. The influence of the adherends temperature also decreases in the case of faster-curing PUR systems, such as the 2C PUR 2 material, where the difference is very small at the various adherends temperatures. The material can also react faster on adherends with lower thermal conductivity. An example would be fiber-reinforced plastics in comparison to aluminum.

The rheological behavior of a 2C PUR material for the injection bonding process can be very well described, especially in the first seconds, with the test setup developed in this work. With the aid of the viscosity curves, the adhesive system, adherend geometry and tool temperature can be better matched to each other. This can save time and money, especially in the early phases of product development.

Adhesion

The adhesion between adhesive and adherend is dependent on many parameters. These parameters are sufficiently described in the literature [17] for classic bonding processes with longer curing times. However, the flow paths with injection bonding, along with the extremely fast curing, present the bonding process with new challenges. Due to the very fast cross-linking of the PUR system used here, the functional molecule groups responsible for the formation of the bonding forces rapidly decrease. In those cases where the degree of cross-linking is already too far advanced prior to contact with the surface of the adherend, the number of possible intermolecular bonds is reduced and therefore also adhesion forces are reduced [17].

In the described injection bonding process, flow paths of up to 120 mm are to be covered. In this case, the material flows for several seconds until the surface at the end of the gap is also wetted. To know what time t can be allowed to elapse before the PUR comes into contact with the surface, the test setup described in “Experimental details” section was created.

The result of the lap shear tests with thick lap shear specimens is presented in Fig. 6. The open time denotes, in theory, the time after application during which a serviceable bond can be made at room temperature. This definition gives no indication of how the term “serviceable bond” is to be interpreted. The limit of usability of a reaction adhesive mixture is determined by two factors: viscosity increase and formation of adhesive forces [17]. For the 2C PUR 2 material under investigation here, this means that the open time is just under 3 s. As can be seen in Fig. 5, the viscosity of this material increases after just 3 s. As shown in Fig. 6, the thick lap shear specimens, too, exhibit an increasingly adhesive fracture behavior in the case of open times of 3 s or over or sometimes of even 2 s or over. For all three open times were at least three thick lap shear specimen tested.

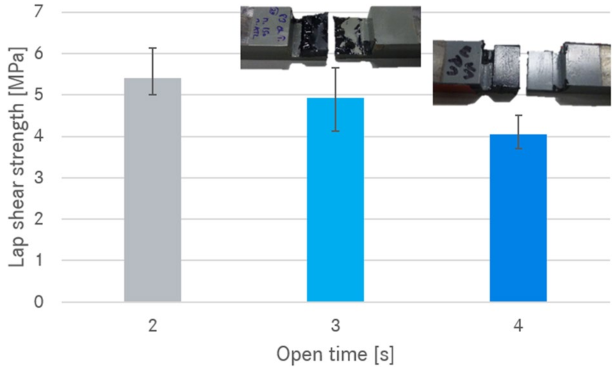

Fig. 6 Lap shear strength as a function of time before contact with adherend

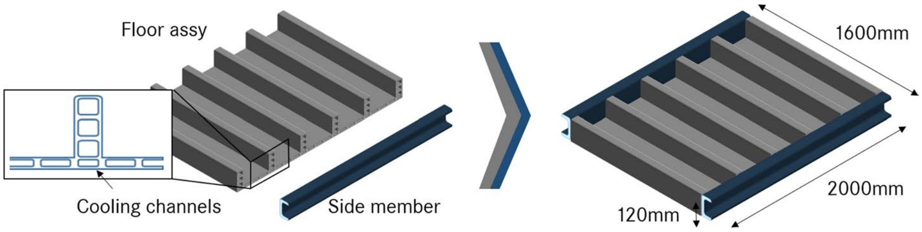

Fig. 7 Joining of battery housing

It is generally possible to confirm that, the longer it takes for an already cross-linking adhesive to reach the surface of the adherend, the lower the adhesive forces will be. This tendency is, of course, less critical if a generally less reactive adhesive system is used. Especially with the 2C PUR 2 material used here, this behavior must be taken into account.

Case study

The fast injection bonding process can potentially be used, for example, for the currently much-discussed battery housings of electric vehicles. One of the difficulties lies in realizing a joining seam that is over two meters in length. It is necessary for two side members to be connected to the floor assembly in a sealed and crash-proof manner (Fig. 7). “Sealed” refers in particular to the interface to the cooling medium glycol. The glycol flows through the cooling channels integrated in the extrusion direction of the floor assembly. Compared to deep-drawn battery housings with internal or external cooling channels, the variant with integrated channels has clear advantages in terms of heat management. At present, the side members are joined by welding, although this leads to problems with welding distortion and leak tightness [18].

For bonding, the side member and the floor assembly are positioned at a defined gap from each other. Next, the adhesive is injected into the gap through a nozzle. Due to the low viscosity of the polyurethane and the corresponding orientation of the components with respect to gravity, the gap fills according to the form shown in Fig. 8. The spread of the polyurethane is limited by the side member, the floor assembly and seals.

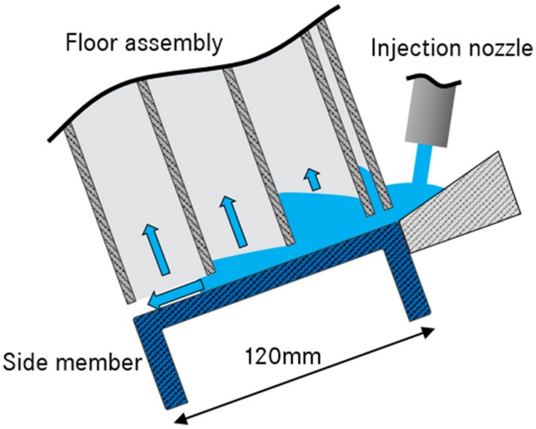

Fig. 8 Cross section of side member and floor assembly

The low-viscosity flow behavior of the polyurethane allows the PU material to rise into the cooling channels and cavities of the floor assembly, thereby increasing the available adhesion area. Another side effect of the rise of the PUR material is that the cooling channels are securely sealed, which dispenses with the need for sealing plugs.

Thanks to the highly reactive 2C PUR material, the seals shown in orange in Fig. 8 can be removed soon after application of the adhesive. The 2C polyurethane is injected by a mixing head mounted on the robot head. During application, the robot moves along the bonding gap to allow complete filling of the bonding gap along the entire length of the battery box. The bonded components can be further processed immediately. Knowing the behavior of the viscosity over time in dependence on the temperature helps a lot developing the application process to a reproducible level.

Conclusion and outlook

The highly reactive 2C PUR system offers many advantages for the joining of large structural components. The material is elastic enough to compensate for elongation and stiff enough after just a few seconds to allow immediate further processing. This paper identified and assessed the new challenges of injection bonding with fast-curing 2C PUR systems with regard to rheology and adhesion. The results showed that the rheological behavior of the material is extremely temperature dependent and the property to build adhesion with the surface is dependent on the time the material takes to hit the surface. In future, it would be of great interest also to simulate the injection bonding process. The planned flow paths could be validated at an early stage, with adherend geometries being adapted even before the first prototypes are produced.

Authors' contributions

GC carried out the experiments on rheology and adhesion, drafted the manuscript and KD supported with his expertise on adhesion. Both authors read and approved the final manuscript.

Author details

[1] Daimler AG, HPC F150, 71059 Sindelfingen, Germany. [2] Institut für Füge- und Schweißtechnik, Technische Universität Braunschweig, Langer Kamp 8, 38106 Brunswick, Germany.

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Competing interests
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