Kraft *et al. Appl Adhes Sci (2017) 5:14*
DOI 10.1186/s40563-017-0093-9

Applied Adhesion Science

RESEARCH Open Access

Nondestructive testing of contaminated CFRP surfaces with the BonNDTinspect® system

André Kraft[1*], Kai Brune[2], Cristian Tornow[2], Gudrun Mühlhofer[3], Bernd Mayer[2] and Bernd Valeske[4]

*Correspondence:
andre.kraft@bmw.de
[1] BMW AG, Petuelring 130, 80788 Munich, Germany
Full list of author information is available at the end of the article

Abstract

Composite materials are already being used in the mass production of structural components in the automotive industry, particularly at the BMW Group. Adhesive bonding is generally considered to be the best technique for joining CFRP (carbon fiber reinforced plastic) light-weight structures. The conventional NDT (nondestructive testing) methods currently being used focus on the detection of material defects, e.g. debonding. These methods give little information about the surface properties or bond quality. A new ENDT (extended nondestructive testing) method is the BonNDTinspect system, based on a patent held by the Fraunhofer IFAM. An ultrasonic atomizer nozzle creates a water-aerosol and the small water droplets are sprayed onto the surface. Depending on the surface properties (surface energy or contamination state), the aerosol will form wide or narrow drops on the surface. We determined a test for certain contaminations, including release agents, oil, and fingerprints, the detection of which is critical to ensure the performance of adhesively joined CFRP structures. The BonNDTinspect system is an inline-capable NDT technique that is suitable for distinguishing surface states for adhesive bonding of CFRP. We verify this statement with destructive tests, including the single-lap shear test. It was found by using an extension of the evaluation criteria that it is possible to detect contamination such as water-soluble release agent, CFRP dust and fingerprints. The investigated contamination with hydraulic oil allows only a clear differentiation between cleaned and contaminated. A contamination with corundum is not detectable by the BonNDTinspect system alone.

Keywords: NDT, Release agent, Adhesive bonding, Inline detection, Aerosol-wetting test

Background

Continued growth of the world's population and the simultaneous scarcity of resources have led to a need for increased efficiency in almost all areas of life. Sustainability and environmental protection are also becoming increasingly important focal points and, with the pressing issue of climate change, the emission of pollutants has become a central issue. In addition to industry, the transportation sector is a main emitter of CO_2, contributing around 26% of overall CO_2 emissions within the EU, whereby passenger cars (12% of overall emissions) are responsible for almost half of this. According to EU regulations, the cap for CO_2 emissions from passenger cars is currently set at an average of 120 g CO_2/km and will be cut to under 95 g/km by 2020 [1]. Regarding the reduction of CO_2 emissions, one major factor is reducing the weight of the vehicle [2]; per 100 kg

reduction in vehicle weight, CO_2 emissions can be cut by up to 7.5–12.5 g/km [3, 4]. In order to fully utilize the potential of different light-weight materials as well as material combinations, adhesives have been used as a joining technology for the last 60 years. Initially, structural parts were bonded in the aviation industry [5, 6], but meanwhile, adhesives as joining technology are commonly used in all branches of industry [7]. This enables the production of highly complex parts and, subsequently, technological effort. These high standards lead to an equally high demand in terms of quality, which can only be met by defining and complying with measures for quality assurance [5, 6]. For this purpose, the recently introduced DIN 2304 is an application-oriented comprehensive standard for the quality assurance of adhesive materials [8].

Even though adhesion has various operating principles, the decisive factors [7] are in the angstrom to nanometer range (0.1–1 nm). The physical and chemical properties of adjacent phases should be coordinated in such a way that an interaction between the joining parts is possible [7, 9, 10, 11]. Therefore, the full adhesive strength of the physicochemical properties within the uppermost atomic layers of the surfaces is a decisive factor in order for surfaces to bond ([6];[12]). As a result, the interaction of the surfaces to be bonded as well as the adhesives themselves are decisive for the ultimate quality of the adhesive bond. The respective pre-treatments steps must be in place in order to have the respective reactive surfaces of the joining parts. A wide range of activating and purification procedures exist for this purpose and can be based on physical, chemical, or mechanical methods [7]. Since even the slightest variation in the total process can lead to adhesive failure, it is absolutely essential that robust production processes as well as the monitoring of surface conditions are used. Process variations can include a defective cleaning system that does not fully remove process contaminations, such as fingerprints, or similar non-compliance with quality assurance measures. In order to increase process reliability and the respective quality assurance, an (inline) process control of the surface conditions is required. Such inline control measures help to detect defects at an early stage and thus reduce costs incurred due to excess work or rejected parts. Such an assessment system must meet the high standards of speed, sensitivity, and process suitability of the existing production system.

Over the last few years, carbon fiber reinforced plastics components (CFRP) have become increasingly important in the automobile industry, among others. Their use has become necessary in response to the increasing demands placed on the complexity of parts and the importance of lightweight design. Subsequently, adhesive technology is absolutely essential in order to fully exploit the potential of lightweight design. The use of release agents is still necessary in the process of producing CFRP components; however, any release agent residue can have an impact on the adhesive behavior of the surfaces. In this case, residues less than a mono layer in thickness can lead to the failure of the adhesive ([13–18]; [19]). Figure 1 shows CFRP shear tensile specimens. The left sample shows an adhesive fracture pattern in the shear tensile test. In contrast to the right sample, it was contaminated with release agent. This clarifies the need for a corresponding pre-treatment or cleaning of a surface to be glued.

Fiber reinforced plastics or carbon fiber reinforced plastics (CFRP) are used on a large scale at the BMW Group. In order to ensure a smooth operation within production, it is necessary to establish inline measurement systems to assess surface conditions in a quick

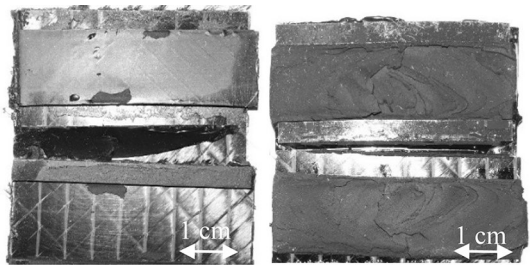


Fig. 1 Adhesive failure (*left*) cohesive failure (*right*)

and safe manner. Thanks to the BonNDTinspect system, it is possible to check and assess the wetting properties of surfaces both inline as well as in the industrial field. It is important for such a system that all the common process contaminations can be detected. In this context, particularly critical contaminations were assessed in an assessment matrix using samples with defined contaminations of release agents, hydraulic oil, corundum, and CFRP dust. These samples were subsequently assessed using the BonNDTinspect system and then tested in a single-lap shear test. Since the BonNDTinspect system is a comparative measuring method, a reference test of the surfaces is required. For film-type contamination, for example, high performance liquid chromatography can be used with mass spectroscopy coupling. Likewise, for example, the reference measurement by means of XPS is a standardized method for detecting activation of thermoplastic matrix systems. The combination of the assessment result of the BonNDTinspect system and the fracture pattern allows conclusions to be drawn regarding the adhesive behavior of the surfaces.

Materials and experimental methods

Materials

The epoxy resin system used in production was also applied during the tests. The resin component is a mixture of bisphenol-A-epichlorohydrin-resin and bisphenol-F-epichlorohydrin-resin. The hardener component is an amine hardener. In the described tests, the resin and hardening components were used in the mixing proportion secured for production of ±3% by weight. The individual components of the resin system as well as the release agents used are listed;

- Resin component: Hexion Epikote Resin PAT.
- Hardening component: Hexion Epikote Curing Agent PAT.
- Internal release agent: Hexion PAT 657 BW.
- External release agent: Hexion PAT 608 FP.

The following table shows the applied contaminations and the respective concentration rate; it depicts the mean value of the three measurements per condition (Table 1). The concentration levels of hydraulic oil, corundum, and carbon-fiber dust were assessed using high-precision scales. For the fingerprints, three different fingerprints with different sizes each from five people were used. The concentration level in this case was determined via the contaminated surface. The release agent contamination was

assessed with an HPLC–MS. The percentage values of the release agent are those with the subsequently described release agent solution. The condition Z0 corresponds to the clean sample that was not contaminated. The contamination was selected using a rating matrix, which assessed the contamination probability during the production process. The gradations of the concentrations were chosen such that Z1 represents the smallest contamination quantity and Z3 or Z6 the largest contamination quantity. The states Z2–Z5 for release agents or state Z2 corresponding to the other contaminations are selected between the extreme values of the contaminant quantities. For reasons of differentiability, a combination of contaminations was not carried out.

For the later single-lap shear tests, the cold-curing 2-K-adhesive Beta Force 2816S from Dow Automotive was used. The adhesive consists of the components polyol and isocyanate. The second joining part used in addition to the epoxy resin system was a 2.5-mm-thick steel sheet coated with cathodic dip paint.

Surface preparation

The starting materials used were off-tool parts of CFRP test plates that had been milled with a dry mill to the standardized sample dimensions. The test plates were run through a cleaning process to ensure that there was no further contamination apart from that purposefully applied. In order to define a starting condition, the test plates were analyzed using the BonNDTinspect system before every contamination procedure. The samples were then reproducibly contaminated with the respective contamination. Once they had been conditioned, the samples were again checked using the BonNDTinspect system. The adhesive was applied by a robot and the second "sample part" was applied manually. Conventional clamps were used to fix the position of the joining parts. Once they had been successfully joined, the samples were conditioned for 7 days at room temperature. After the conditioning had been completed, the samples were examined using a single-lap shear test machine. In order to obtain reproducible release agent samples, the dip-coat procedure on the one hand and the aerosol application on the other hand were tested. Beginning with the dip-coat procedure, the samples were dipped at a speed of 60 mm/min without stopping time into a 0.6% release-agent solution. Since this procedure lead to a non-homogenous contamination by the release agent (Fig. 2), for further release agent contaminations an aerosol application was selected.

Table 1 concentration level and contaminated surfaces

Contamination	Concentration						
	Z0	Z1	Z2	Z3	Z4	Z5	Z6
Release agent (µg/100 mm^2)	0	<30 (0.125%)	<30 (0.19%)	<30 (0.22%)	<30 (0.25%)	40 (0.60%)	50 (1.10%)
Hydraulic oil (µg/100 mm^2)	0	235.56	408.89	1740.22	4213.33		
Fingerprint (100 mm^2)	0	184.22	329.82	583.85	–		
Corundum (µg/100 mm^2)	0	253.33	493.33	680.00	–		
CFRP-dust (µg/100 mm^2)	0	244.44	471.11	915.56	–		

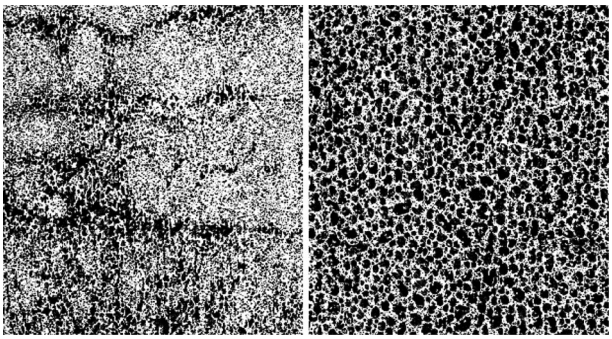


Fig. 2 Release agent application: dip-coated surface (*left*), after aerosol application (*right*)

Hereby, the samples were fixed to a traversing table while the spray gun was fixed so that it always had the same distance to the traversing table and thus the samples. The traversing table was set up so that the samples passed the spraying range at a speed of 100 mm/s (Fig. 3). To ensure that the same spray dosage was applied to all samples, the spraying process was started before the samples were set in motion and the process was only stopped once the samples had left the spraying range. The contaminated samples were then dried at room temperature in a sample holder.

The contamination by the hydraulic oil was carried out with a syringe; a drop was placed on the sample and was subsequently wiped off with a conventional lint-free cloth. This procedure was repeated until no residues were visible to the naked eye and only an oil film remained. In order to have different levels of concentration, two different methods of wiping the oil off were applied, based on scenarios likely to be encountered during production. In the first method, the oil was wiped off with a little pressure, and in the other method, the pressure applied to the cloth was increased.

In order to have a reproducible, homogenous application of the CFRP dust, it needed to be atomized. For this purpose, a hole was cut into the lid of a bucket, which was then fitted with a filter consisting of various layers of plastic netting. In addition, the bottom of the bucket was cut off and a balloon was placed over the bucket, creating the ability to produce a blast of air to atomize the CFRP dust contained in the bucket. This generated a homogenous application to the surface. The necessary reproducibility was generated via the defined amount of CFRP dust that was put into the bucket.

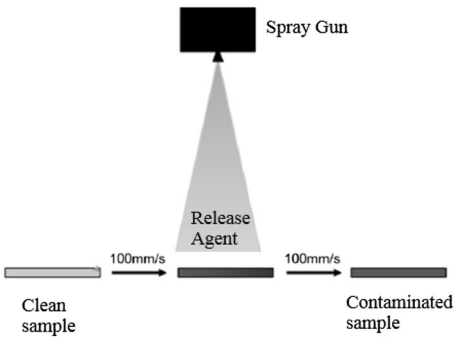


Fig. 3 Spraying process of the release agent

The corundum was applied manually and as homogenously as possible to the surface. To ensure reproducibility of the application amount, the part was placed onto the scales and contaminated in that position.

Analytical tools

BonNDTinspect system

The BonNDTinspect system is a method for the surface characterization of wetting properties based on the aerosol wetting test procedure developed at Fraunhofer IFAM [20].

The reason for the development of this method was the limited significance value of contact angle measurements and the water break test. Depending on the surface energy, the behavior of the sprayed drops varies. This behavior is analogous to the behavior of a water droplet during contact angle measurement. Thereby, a defined amount of water in one single drop shows a direct connection to the recorded contact angle measurement. Compared to the contact angle measurement, the BonNDTinspect method offers the advantage that several thousand drops are applied to, for example, an area of 2 cm by 3 cm. Originally, the criteria for evaluating the wettability were limited to the average drop size, number of drops. For the evaluation of the quality of the measurement, the fit was made to a Rosin–Rammler distribution. With these three criteria alone, a clear differentiation of the surface condition is possible only to a limited extent. For this reason, it is necessary to extend the range of evaluation criteria. For example, the roundness factor and the mode (droplets/cm^2) were determined as new criteria in empirical experiments as a meaningful extension. The number of drops with a mean value, the circularity distribution, and the droplet size distribution can be an indicator for the wettability of a given surface. For example, on a cleaned surface with low surface energy, small drops are formed. In the case of surface contamination, e.g. by a water-soluble release agent, large droplets are formed. This is also the case with increasing surface energy. Figure 4 shows schematically the process sequence of the wetting test using the BonNDTinspect system. Looking at this scheme from left to right according to the process sequence, for example, a CFRP surface contaminated with the release agent to be removed undergoes a pre-treatment step such as a cleaning process. Then a wetting test is done that can in principle be divided into two steps: an aerosol application and, on the other hand, an image is recorded and then an evaluation of the image. If the evaluation of a pre-determined limit is reached, a downstream process can be started. This can be, for example, the application of an adhesive or a varnishing process. Otherwise the pre-treatment process would have to be carried out again.

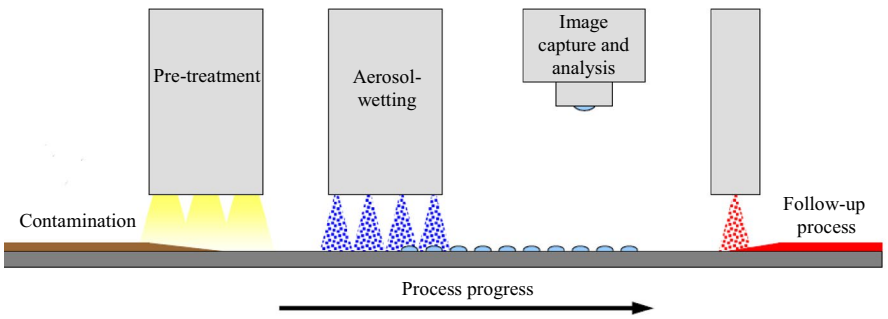


Fig. 4 Process diagram of an inline inspection

Figure 5 shows the basic experimental setup. For the BonNDTinspect method, an ultrasonic nozzle is used to generate a narrow droplet size distribution during ejection and a high-precision pump ensures a constant flow of water. The water drops emerging from the nozzle are directed via a constant flow of air onto the surface of the sample. The drops applied to the surface are digitally imaged by a camera. The following figure shows a process diagram of an inline inspection.

HPLC–MS

High-pressure liquid chromatography-mass spectroscopy, in short HPLC–MS, is a non-destructive test method in which the chromatographic separation of substances is linked to a spectroscopic analysis of materials. In the case of determining the surface component contamination, the surface is first rinsed with temperature-distilled water, then the rinsing solution is concentrated and fed to the HPLC–MS. HPLC chromatographically separates the components of the solution and transfers the substances found to undergo mass spectroscopy. This can then determine the mass and thus, with a known surface area, the contamination concentration. In the case of an examination into release agent contamination, a CFRP specimen of at least 100 cm^2 is first rinsed with 60 °C warm distilled water and the resulting solution is collected. The solution is evaporated in a drying oven at 110 °C, the residue is dissolved in 0.5 ml of MeOH/THF (1:1), and then filtered. The specific component of the release agent can then be determined via HPLC–MS using the amount of ethoxylated ricinolates.

The concentration is expressed in µg/ 100 cm^2.

Single-lap shear test

To examine the bonding properties, the junction in single shear was used in accordance with DIN EN 1465, as depicted in Fig. 6. The dimensions of the sample were a width of 45 mm (b), an overlapping length of 15 mm ($l_ü$), a sample thickness of 2.2 mm (t), a freely suspended length of the quasi-static load input of 100 mm (l_e), and an adhesive layer thickness of 1.5 ± 0.1 mm (d_k). The required bond line thickness spacers were made of self-adhesive hard rubber. The total indicative amount for $l_ü/t = 5 \ldots 10$ for the overlap ratio of bonded surface connections for fiber-reinforced plastics [21] complied with 15 mm/2.2 mm = 6.8 in the following experiments.

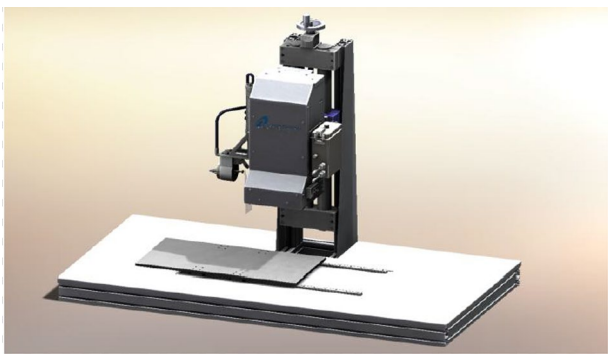


Fig. 5 The basic experimental setup of the BonNDTinspect system

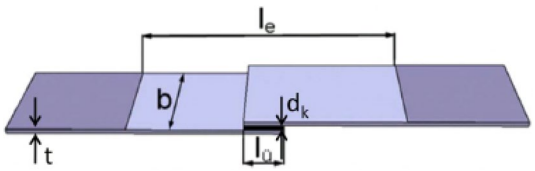


Fig. 6 Single-lap shear sample

To test the single-lap shear test samples, a material testing machine Z010 from Zwick was used. The testing machine is designed for quasistatic stress, with a single, stationary, dynamic, or varying profile. For the classification of fracture phenomena of the adhesive bonds according to DIN EN ISO 10365, the following designations from the table were used, whereby a distinction is made between adhesive failure, substrate-specific near cohesive failure, cohesive failure, and broken by delamination. With a test speed of $v = 20$ mm/min, the samples were loaded until failure and the force was recorded on the crosshead.

Failure modes were for DIN 10365, [22] (Table 2).

Results and discussion

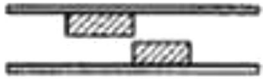
This chapter includes the results obtained from the wetting test and the fracture pattern, in addition to their discussion.

The following table lists the setting parameters of the BonNDTinspect system. The selection of the parameters was carried out empirically. The decisive factor was a constant wetting of the surface over several measurements. The choice regarding the amount of water was made so that there were mainly only a few drops on the surface. The choice of evaluation criteria was based on the best distinctness of contamination conditions. The resin system used for the tests has hygroscopic properties, so that a distortion of the results can be excluded when water is applied, reference tests were carried out. For this purpose, in addition to purified samples, samples were also glued, which were wetted with aerosol up to five times.

No difference could be identified between the non-wetted and wetted samples. This is due to the fact that, on the one hand, there is no contamination of the surface by the high-purity water and, on the other hand, the applied water evaporates without residue within 5 s (Table 3).

As described in "Materials and experimental methods", the contaminants CFRP dust (Fig. 7), corundum (Fig. 8), hydraulic oil (Fig. 9), and fingerprints (Fig. 10) were applied to the surfaces. In all contaminations excluding corundum (Fig. 8), the droplet size increased with the amount of contamination. A problem in the corundum contamination was that multiple individual corundum grains were contained within a droplet. This was due to the distribution of the grains lying below the size of the droplets on the sample. A mean drop size of 112 µm ± 5 µm was measured for reference samples Z0 of a CFRP dust contamination (Fig. 7), corundum (Fig. 8), hydraulic oil (Fig. 9), and fingerprints (Fig. 10). The deviation from the average is based on the technical surface of the test specimens and the associated slight change in the wetting properties. The BonNDTinspect system has a system-technical variance of ±2.5 µm.

Table 2 Classification of fracture phenomena of the adhesive bonds

AF	SCF	CF	DF
Adhesive failure	Substrate-specific near cohesive failure	Cohesive failure	Broken by delamination
			
			

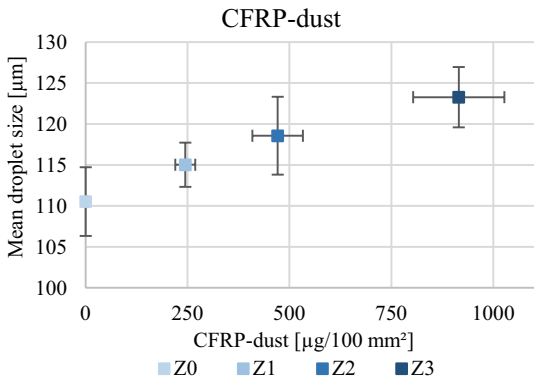


Fig. 7 Contamination state of CFRP-dust

Figure 7 shows an increase in the variation as CFRP dust loading increases over the surfaces. This is due to the fact that the dust particles are not within the droplet, as in the case of contamination with corundum, but rather that the drops are increasingly prevented from spreading. The strong variation in the area of the fingerprints is due to the fact that it was not possible to reproducibly produce the same contact pressure on the surface. This inhomogeneity has an area variation and thus a variation in droplet size as a result.

Table 3 Setting parameters of the BonNDTinspect system

Measurement System	BonNDTinspect
Aerosol-liquid	Ultrapure water
Volume flow	3.0 ml/min
Feed rate	100 mm/s
Airflow	60%
Test mode	Half-automated
Evaluation criteria 1	Wetting fraction
Evaluation criteria 2	Roundness
Evaluation criteria 3	Modus/cm^2
Evaluation criteria 4	Mean droplet size

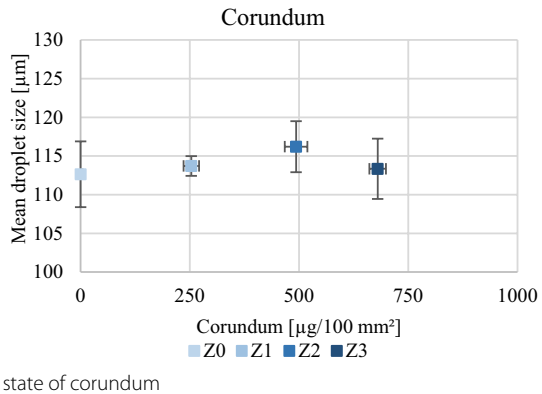


Fig. 8 Contamination state of corundum

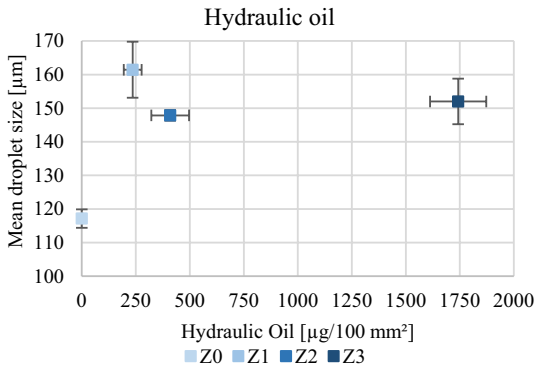


Fig. 9 Contamination state of hydraulic oil

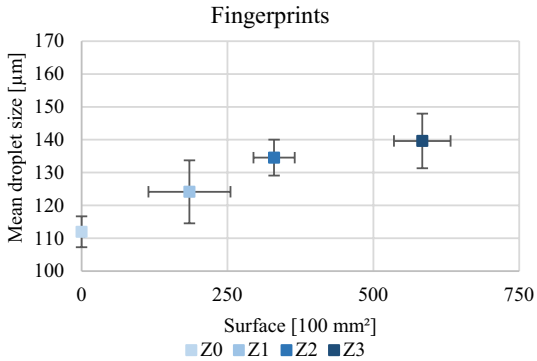


Fig. 10 Contamination state of fingerprints

Release agent

In the following, the results of the release agent analysis are presented. Figures 11, 12, 13 show, by way of example, the images taken by the BonNDTinspect system of CFRP samples with a release agent concentration of 0.25% (Fig. 11), 0.6% (Fig. 12) and 1.10% (Fig. 13). A magnification of the drop size (black inked) can be seen between the applied concentration of 0.25 and 0.6%. With a coated release agent concentration of 1.1%, the effect of spinodal dewetting occurs [23].

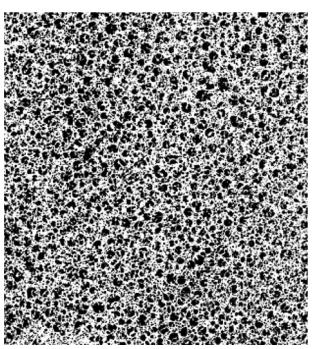


Fig. 11 Release agent contamination of 0.25%

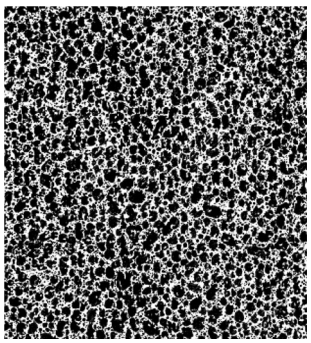


Fig. 12 Release agent contamination of 0.60%

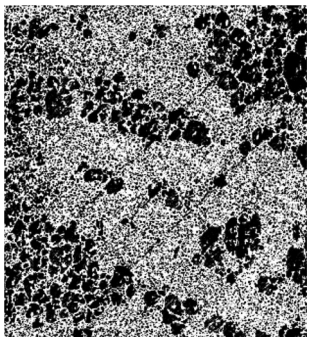


Fig. 13 Release agent contamination of 1.10%

For the investigation of the detectability of the water-soluble release agent, a new batch of the resin system had to be used. This is also shown in the measurement of the reference samples. As shown in Fig. 14, an average droplet diameter of reference samples (Z0) of 145 ± 5 µm has been determined. Such a variation of the initial states as compared to the previous batch clarifies the need for a reference study in a batch change. Accordingly, limits must be adjusted within the BonNDTinspect system. The property of spinodal dewetting shown in Fig. 13 cannot be determined solely by the mean droplet diameter (cf. Fig. 14). For this reason, the (droplets/cm^2) mode was introduced as a further criterion for evaluation.

The effect of spinodal dewetting is reflected in the increasing modus, thus there is a high standard deviation in the mean droplet sizes in the figure. Despite the high deviation, a conclusion can be drawn from the combination of the two evaluation criteria for the state of contamination.

Figure 15 shows the different concentration amounts of the release agent corresponding to the average droplet diameter and the associated fracture surface. The purified reference samples consistently showed a cohesive fracture pattern (samples 16–20). An adhesive failure was mainly observed for a release agent concentration higher than 0.22% (samples 1–5). Below 0.22%, a substrate-near cohesive fracture or a cohesive fracture was often observed (samples 6–15). The reference study HPLC–MS was unable to detect a release agent contamination of less than 0.25%. Here, the determined values

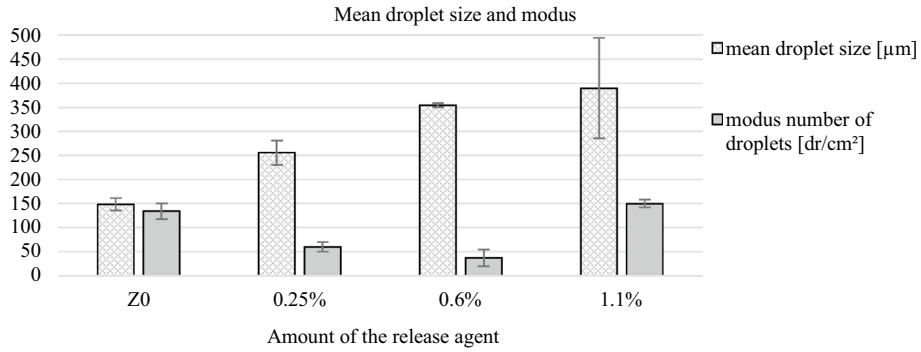


Fig. 14 Release agent; mean droplet size and modus

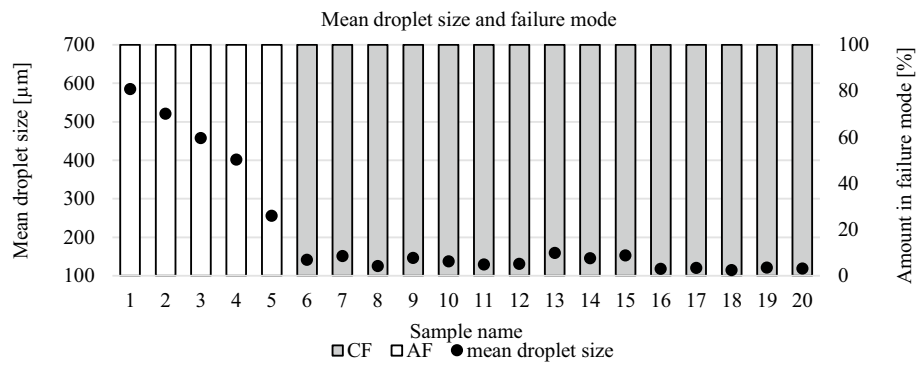


Fig. 15 Release agent; mean droplet size and failure mode

are all below the detection limit. The shear tensile stresses determined are minimum at 3.2 MPa for sample 1, sample 5 which still shows an adhesive failure reached 6 MPa. Samples 6–15 achieved a shear tension of approx. 9 MPa. As expected, the reference samples have the highest shear stress at 9.7 MPa.

The mean droplet diameter also enables a very good correlation between the droplet image and the fracture pattern. The results of the shear test are compared with those obtained using the BonNDTinspect method. The initial aim is to generate a correlation between fracture and drop image. For a droplet size of about 170 microns, cohesive failure was observed. This corresponds to a release agent contamination of about 0.22%. The above-mentioned detection limit of the HPLC–MS corresponds to a droplet size of about 300 microns.

The sample designation and the tested concentrations in Figs. 16 and 17 are analogous to Fig. 15. Based on the wetting ratio, a comparable behavior can be observed as well as the mean droplet size. The inhomogeneities in the range of samples 13–15 are also not traceable with an adjustment of the experiment. The boundary between predominantly adhesive and cohesive fracture behavior is at a roundness of 1.5. This corresponds to an applied release agent concentration of 0.22%. The detection limit of the HPLC–MS corresponds to a roundness of about 1.9. If the results of release agent detection are considered, a further evaluation criterion is necessary, especially with higher concentration

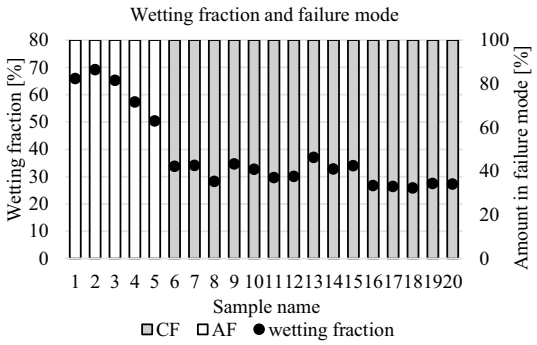


Fig. 16 Release agent; wetting fraction and failure mode

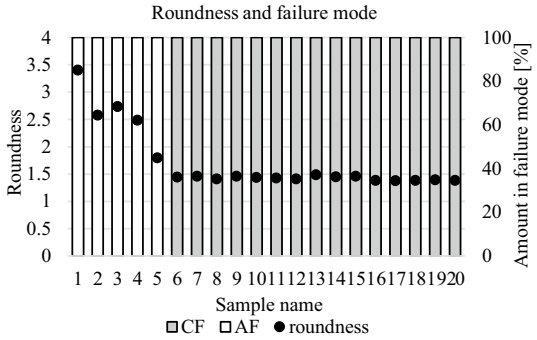


Fig. 17 Release agent; roundness and failure mode

amounts. Furthermore, it was found that the BonNDTinspect system has a higher sensitivity to detection of the release agent compared to HPLC–MS. Based on the detection of the release agent, a differentiation of the release agent contamination is possible via both the wetting component and also the mean value and the roundness.

Hydrologic oil

Based on Figs. 18, 19, 20, regarding the contamination by hydraulic oil a distinction can be made between the cleaned surface and the minimum contamination. The samples

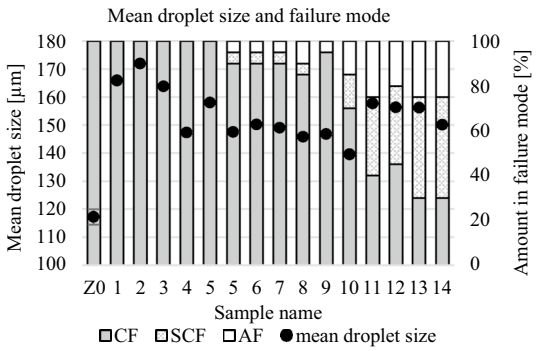


Fig. 18 Hydraulic oil; mean droplet size and failure mode

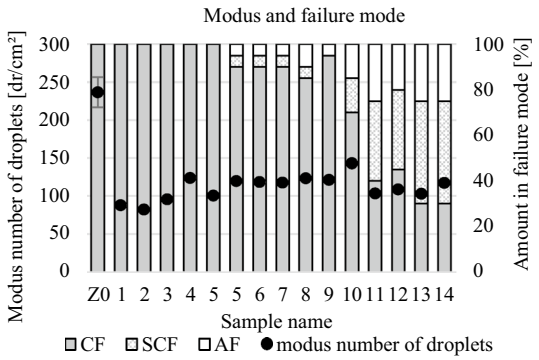


Fig. 19 Hydraulic oil; modus and failure mode

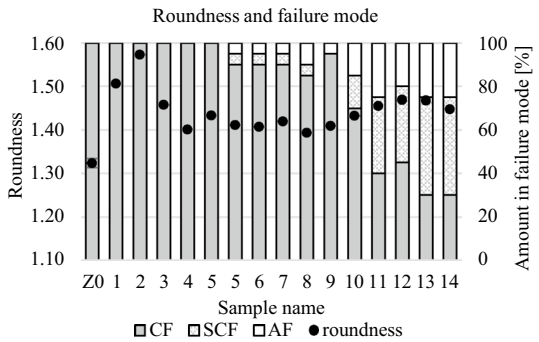


Fig. 20 Hydraulic oil; roundness and failure mode

with the designation 1–5 correspond to the state Z1, their shear tensile stress is 9.3 MPa, samples 6–10 correspond to state Z2 are, despite the adhesive fractions in the fracture pattern, at 9.1 MPa, as well as the samples 11–14 of the highest concentration quantity Z3 and a shear tensile stress of 8.7 MPa. The state Z0 corresponds to the purified, non-contaminated reference sample, also here a mean shear tensile stress of 9.7 MPa was measured. There is a small deviation in the difference between minimum contamination and maximum contamination. Here, the evaluation by means of criteria and mode and roundness is best suited. However, a more precise distinction between the states Z1 and Z3 cannot be made either by the average droplet size (Fig. 18), the mode (Fig. 19) or the roundness (Fig. 20).

Sample 14 corresponds to a coverage of about 1700 µg/100 mm^2. Such contamination can be detected by the naked eye on the basis of differences in the gloss of the surfaces. On the basis of the fracture pattern, a differentiation can be done between the contamination quantities. Thus, above a concentration Z2, an increase in the adhesive fracture pattern can be observed. A further increase in the adhesive fractions in the fraction pattern is shown in samples of state Z3. This leads to a determination about which the adhesive system can absorb a certain amount of hydraulic oil without causing any changes in its adhesiveness. The differentiation of the contamination quantities in conjunction with the adhesive properties are well-suited to detect early defects such as wear-resistant seals at an early stage without causing a failure of the adhesive bond.

Corundum

The detection of corundum on the surface is difficult, as mentioned earlier. This is because the corundum grains have a diameter smaller than that of the drops applied to the surface. The evaluation criteria examined were droplet diameter, mode, wetting percentage, and roundness and provided no conclusion about the contamination state.

Figure 21 shows the behavior of the droplets as an example, whereby the standard deviation is higher than the measured difference in the mean droplet size. The samples labeled 1–5 correspond to the state Z1, and their shear stress is 5.9 MPa at a low level. At 7.1 MPa, samples 6–10 (state Z2) have a higher stress level, despite the adhesive fractions in the fracture pattern and a higher corundum loading, similar shear tensile stresses are also achieved with Z3 state samples.

The disturbances of the boundary layer between the adhesive and the surface of the component due to corundum contamination are so large that only isolated adhesive bonds can be formed (see Fig. 21). This adhesive behavior and insufficient differentiation of the surface conditions using the BonNDTinspect system clarify the necessity of another testing method. By way of example, scattered light measurement is mentioned here, whereby it is possible to detect particles on the surface.

CFRP dust

Based on the detection of CFRP dust on the surface, it is possible to distinguish the contamination states based on the roundness (Fig. 22) and the mean droplet size (Fig. 23).

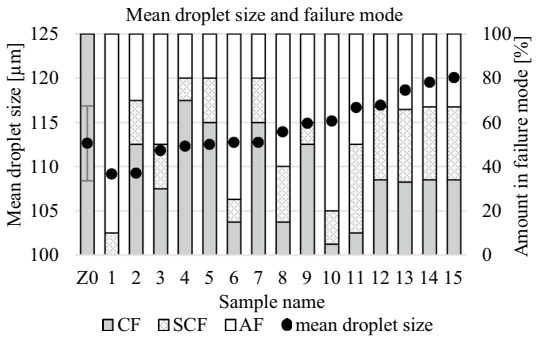


Fig. 21 Corundum; mean droplet size and failure mode

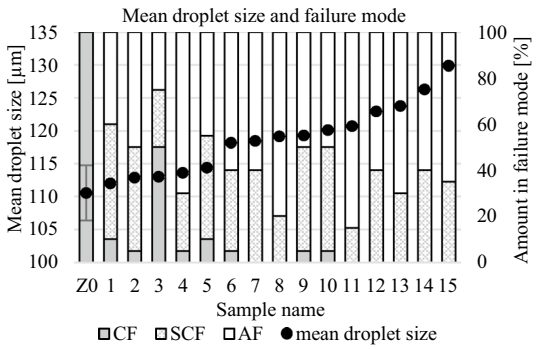


Fig. 22 CFRP dust; mean droplet size and failure mode

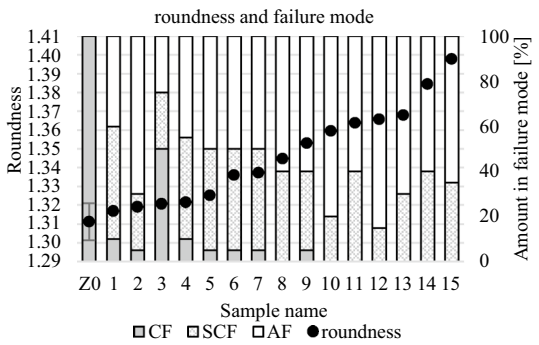


Fig. 23 CFRP dust; roundness and failure mode

The adhesive Beta Force 2816 s is very sensitive to contaminants such as dust or corundum. Therefore, already a small increase in contamination leads to adhesive failure. For this reason, regarding the contamination with dust there is currently no tolerance range within the evaluation criteria of roundness and mean droplet diameter.

However, because even small amounts of corundum obviously interfere with the adhesion, an alternative measuring method should be employed. This could be, for example, the scattered light method developed at the Fraunhofer IFAM, which is also a nondestructive examination that can be used to determine surface roughness.

Analogous to the critical fracture pattern, the shear tensile stresses are accompanied by the fact that, in the case of state Z1, corresponding to samples 1–5, an average of 6.3 MPa is achieved. Samples of the contamination state Z2 achieved a shear tensile stress of 5.6 MPa. The lowest shear tensile stress of 4.4 MPa was achieved for samples 11–15 of conditions Z3, this also mirrors in the mainly adhesive or near-substrate failure.

Fingerprints

Fingerprints are, aside from release agent residues and CFRP dust, the contaminants with the highest probability of being applied during the manufacturing process. As shown in the diagrams below, the evaluation criteria were average droplet diameter, wetting proportion, and mode; they are very well suited to detect fingerprints. They are to be viewed critically with respect to the adhesion behavior as seen below. They can be declared by the detection well as a defective surface.

In Fig. 24, a significant increase in the drop diameter can be seen with increasing contamination. The large fingerprints on the cleaned sample can be differentiated the best. The difference between the droplet size is 40 microns on average. A similar behavior is shown in Fig. 25. Here, the mode, depending on the contamination, was compared to the fracture pattern. As with the droplet diameter, the best distinction here is possible between the purified surface and the largest fingerprints. There is a difference between the two states 100 of dr/cm^2. The wetting portion as shown in Fig. 26 is approx. 25% and rises to a maximum of 33% with increasing contamination. This is based in the fact that the capillary lines of the fingerprints are completely wetted with water. The variations of individual evaluation criteria are due to different fingerprints and thereby based on the individuality of the capillary lines.

The amount of contaminants increases according to the size of the fingerprints. The specimen Z0 is characterized as the reference sample with a shear tensile stress of

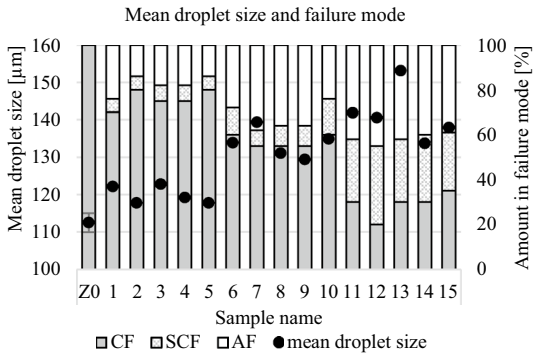


Fig. 24 Fingerprint; mean droplet size and failure mode

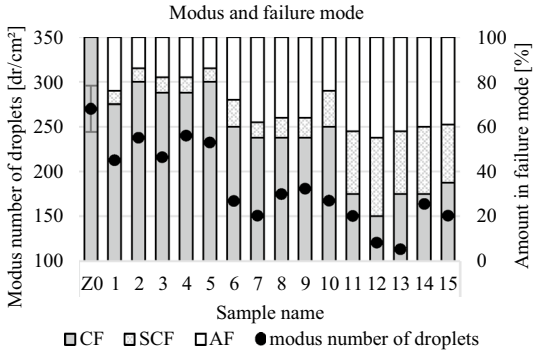


Fig. 25 Fingerprint; modus and failure mode

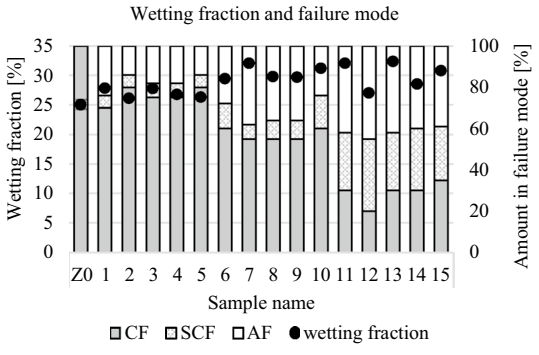


Fig. 26 Fingerprint; wetting fraction and failure mode

9.7 MPa and a completely adhesive fracture pattern. The samples of the state Z1 (samples 1–5) fail on average at 8.6 MPa, this drop in stress can also be seen in the fracture pattern with an increasing proportion of adhesive failure. The same behavior applies to states Z2 to Z3 and the corresponding shear tensile stresses of 7.1 or 6.5 MPa. Compared to the contamination, a fracture pattern shifted slightly in the direction of adhesive failure becomes clear. This is due to the fact that besides the skin grease, there is also still sweat on the fingerprints. In further investigations, it was found that both alkaline and acidic sweat solutions themselves lead to adhesive failure even in small quantities.

However, compared to the contamination by CFRP dust and release agents it is not possible to obtain a statement about the technical cleanliness of the surface based on roundness (Fig. 27). Although a distinction is possible between the extreme samples (cleaned and heavily contaminated), with a low contamination of the surface, only a minimum change in roundness is measurable. The reason is the ratio between large drops that are generated by the fingerprints and the small droplets of the clean surface.

Conclusions

The objectives of the experiments were to show whether it was possible to detect process contamination using the BonNDTinspect system as well as whether these contaminations can be differentiated with reference to their concentration and whether a conclusion can be drawn based on the result of wetting on the adhesiveness. The experiments carried out clarify that it is not possible to differentiate between the standard evaluation criteria such as the average droplet size, the wetting proportion, and the possibility of differentiating highly concentrated amounts of release agent. The effect of the spinodal dewetting of the release agent requires an extension of the evaluation criteria by the mode and the roundness. Furthermore, the experiments showed that a reference investigation with appropriate adaptation of the limit values is necessary in the case of a batch change of the resin system. The BonNDTinspect method can be used to detect surface contamination such as release agents, CFRP dust, and fingerprints. In the case of contamination with corundum, it is impossible to make a statement about the nature of the surface using the selected conditions. As can be seen from the evaluation criteria mean droplet diameter, the roundness, and the mode, the BonNDTinspect-system showed good sensitivity to all contaminations.

From a roundness of the droplets <1.5, a cohesive fracture behavior was shown in the experiments of the release agent. The same applies to samples with an average droplet diameter <190 µm and a mode/cm^2 >90. Apart from the clear differentiability, it has been found that by using the BonNDTinspect system, surface contamination by an external release agent can be clearly detected below the detection limit of HPLC–MS.

Contamination with hydraulic oil should be considered less critical because the adhesive Beta Force 2816s is very tolerant of oil on the surface. On the other hand, fingerprints are very problematic because even a minimal contamination results in adhesive failure. The same applies to a surface that has been contaminated with carbon dust. This

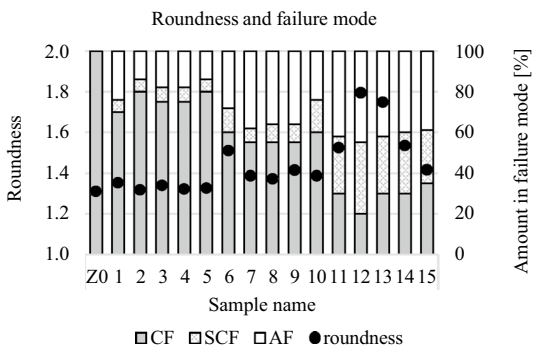


Fig. 27 Fingerprint; roundness and failure mode

leads to adhesive failure in the single-lap shear test once even minimal pollution has been applied.

For further consideration, it is possible to draw on the scattered light sensor analysis, developed at the Fraunhofer IFAM, at the same time. The advantage of a combination of these measuring systems is that not only the wettability of the surfaces but also the surface relief can be determined. Both systems are referred to as ENDT procedures.

Authors' contributions
The authors of the contribution are AK, KB, CT, GM, BV and BM. AK worked out sample preparation and measurements of the surface wettability. AK developed, performed and—with CT—evaluated the droplet images and set up relations between wettability and surface state. AK adapted evaluation model modus and set up relation between HPLC results. AK, CT, KB and GM took part in setting up the experiments and in analyzing and merging the obtained data. GM, KB, BV and BM contributed in the conceptual approach and in discussing the obtained data. AK and CT drafted the manuscript. All the authors contributed to perform the research work described in the article and they all agree with the submission. All authors read and approved the final manuscript.

Author details
[1] BMW AG, Petuelring 130, 80788 Munich, Germany. [2] Adhesive Bonding Technology and Surfaces, Fraunhofer Institute for Manufacturing Technology and Advanced Materials IFAM, Wiener Straße 12, 28359 Bremen, Germany. [3] BMW AG, Ohmstraße 2, 84030 Landshut, Germany. [4] Fraunhofer Institute for Nondestructive Testing IZFP, Campus E3 1, 66123 Saarbrücken, Germany.

Acknowledgements
The authors are grateful to Dr. Michael Noeske for fruitful discussions.

Competing interests
The authors declare that they have no competing interests.

Availability of data and materials
All relevant data of the article are presented in the manuscript (in tables or figures). The content of the manuscript has not been published, or submitted for publication elsewhere.

Ethics approval
The section ethics approval is not applicable for our contribution.

Funding
The section funding is not applicable for our contribution.

Publisher's Note

Received: 22 May 2017 Accepted: 22 July 2017
Published online: 01 August 2017

References

1. Ministry of Justice. Kraftfahrzeugsteuergesetz, 26th September 2002 (BGEl. IS. 3818), changed by Article 1 on 27th May 2010 (BGBl. IS. 668). Berlin: Federal Law Gazette; 2010.
2. Füssel U. Auswahl von Fügeverbindungen für den Leichtbau. Presentation. Technical University Dresden. 2000.
3. Heyn H. Fügetechnologien im Wettbewerb—Anforderungen der Automobilindustrie. Hannover: Fügetechnisches Gemeinschaftskolloquium; 2011.
4. Kelly G. Joining of carbon fibre reinforced plastics for automotive applications. Cumulative dissertation, Royal Institute of Technology, Sweden, Stockholm. 2004.
5. Hennemann OD, Brockmann W, Kolleck H. Handbuch Fertigungstechnologie Kleben—the results of research at BMFT-cooperative project. Munich: Hanser Verlag; 1992.
6. Heßland A, Hennemann OD. Qualitätssichernde Maßnahmen in der Klebetechnik. Adhäsion Kleben und Dichten. 1994;38:10ff.
7. Habenicht G. Kleben—Grundlagen, Technologien, Anwendungen. 5th ed. Berlin: Springer; 2005.
8. Groß A, Lohse H. Die neue DIN 2304 und ihr Nutzen für die Praxis Qualitätssicherung in der Klebtechnik. Adhäsion Kleben und Dichten. 2015;6:12–9.
9. Gleich H. Zusammenhang zwischen Oberflächennergie und Adhäsionsvermögen von Polymerwerkstoffen am Beispiel von PP und PBT und deren Beeinflussung durch die Niederdruck Plasmatechnologie. Dissertation. University Duisburg-Essen. 2004.
10. Possart W, editor. Adhesion, current research and applications. Weinheim: Wiley; 2005.
11. Starck F. Kleben von Kunststoffen, Kleben: Grundlagen, Forschungsergebnisse, Anwendungen. Conference Report. Otti-Kolleg, Regensburg. 2004.

12. Hauert R, Hug P. Adhäsion als Grenzflächenproblem. In: Schindel-Bidinelli, editor. Kleben—16th International Symposium Swissbonding, Rapperswill, Switzerland. 2002.
13. Czarnecki JV, Hayek-Boelingen MV, Gudladt HJ, Schenkel H. Kontaminationstolerantes Kleben—aktueller Stand der Entwicklung. Adhäsion Kleben und Dichten. 2004;4:36ff.
14. Davis GD. Contamination of surfaces: origin, detection and effect on adhesion. Surf Interface Anal. 1993;20:368–72. doi:10.1002/sia.740200507.
15. Fricke A. Untersuchung des Einflusses silizium-organischer Kontaminatonen auf die Adhäsionseigenschaften polymerer Werkstoffe. Dissertation, Technical University Claushthal. 2007.
16. Parker BM. Problems in bonding CFRP. In: Adhesives, sealants and encapsulants conference, conference report. 234ff. London, Great Britain. 1985.
17. Parker BM. Adhesive bonding of contaminated carbon fiber composites. In: International conference on structural adhesives, conference report. 123ff. London, Great Britain. 1986.
18. Parker BM. Bendability of carbon fiber composites. In: Bonding and repair of composites, conference report. 55ff. London, Great Britain. 1989.
19. Parker BM, Waghorne R. Testing epoxy composite surfaces for bondability. Surf Interface Anal. 1991;17:471ff. doi:10.1002/sia.740170710.
20. Wilken R, Markus S, Amkreutz M, Tornow C, Seiler A, Dieckhoff S, Meyer U. Method and device for testing a surface quality. EP1893974 B1. 2008.
21. Niemann G, Winter H, Höhn BR. Maschinenelemente. 4th ed. vol 1: Konstruktion und Berechnung von Verbindungen, Lagern, Wellen. Heidelberg: Springer; 2005.
22. DIN. Din 10365. Bezeichnung der wichtigsten Bruchbilder. 1995.
23. Jacobs K, Herminghaus S. Oberflächenphysik: Strukturbildung in dünnen Filmen: Wie perlt eine Flüssigkeit von einer Unterlage ab? Phys Bl. 1999;55:35–40. doi:10.1002/phbl.19990551211.