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Investigations on Tightness of Polymer-Metal Hybrids in Environments with Thermal, Media, and Mechanical Loads

With polymer-metal hybrids becoming more commonly used as structural components it was investigated how they perform in complex environments with combined thermal, media, and mechanical loads. Special attention was put on media tightness under said loads. This paper sums up the activities of the polymer technology research group of the University of Kassel on hybrids produced by overmolding metal inserts. Investigations concerning joint strength and influence of (cyclic) temperature loads and chemical corrosion on media tightness of the joint were undertaken with different polymer-metal hybrid specimen geometries (simple and complex). In order to enhance adhesion and joint strength, different bonding agents and adhesives were used in the experiments. It could be shown that all joints of polymer-metal hybrids lost their tightness after being exposed to temperature ranges from 30 to +150 °C due to their highly different thermal expansion behavior. An elastomeric intermediate layer of certain minimum thickness in order to compensate the relative movement of plastic and metal and thus maintain integrity of the joint regardless of temperatures is proposed.

1 Introduction

Growing environmental awareness together with tightening CO_2 reduction policies (EU, 2005 and 2007) force the automotive industry among others to venture into uncharted waters and employ innovative lightweight construction strategies. As one of these strategies, multi-material design allows for the property profiles of all components to be used synergistically, especially in structural parts, while significantly reducing their overall weight (Heim, 2015). Thus, polymer-metal hybrids (PMH) become increasingly important for the automotive industry where weight, costs, and suitability for series production determine a technology's success or failure. Conventional structural PMH consist of thin metal sheets being reinforced by polymeric structures or of structures like the Erlanger Träger where the plastic component makes up the majority of the resulting hybrid part (Ehrenstein et al., 2003). They are typically used in or as car body components, like front-ends, but are less suitable for environments with higher and complex requirements concerning additional thermal loads, media tightness, and chemical corrosion resistance. For applications in vehicle powertrains, parts must meet additional requirements, such as

- controlled load introduction and distribution while maintaining overall media-tightness, particularly for connecting elements,
- chemical resistance to polymer-corroding fluids like oils, coolants, and salt water,
- tightness and mechanical stability under pressure and temperature ranges and gradients inside/outside from –40 to 150 °C (Gleich, 2010).

Object of these investigations are PMH that are to fulfil these abovementioned requirements for vehicle powertrains in contrast to conventional PMH which have already been investigated more thoroughly. They consist of a solid load bearing, e. g. die-casted, metal structure that is subsequently back- or overmolded with a thermoplastic, e. g. polyamide, through injection-molding (Paul et al., 2015). Possible applications for these performing PMH with solid load bearing metal structure are electric motors, (gear) housings, flanges, or similar parts in vehicle powertrains.

Relative movement in the joint zone, owed to different thermal expansion behaviors of polymer, and metal and thermoplastic's proneness to swelling in certain media, poses a major challenge for media tightness of these performance PMH, especially under combined thermal, mechanical, and media loads as occurring in powertrains or under the hood applications with direct contact to fluids like coolants or lubricants. The highly different thermal expansion coefficients of polymers and metals, reflected in high $\Delta\alpha$ values (Fig. 1), has restricted the use of PMH to environments with only modest temperature ranges from about –40 to +80 °C, as thermally induced strain itself can cause leakages or even failure of the joint. Fibre-filled materials with their anisotropic shrinkage are particularly prone to leakages (Fedler, 2016). Thus, parts of vehicle powertrains are still exclusively made of metals (Al, Fe, Mg etc.) which the present investigations seek to change.

Current state of the art joining methods for structural polymer-metal hybrid components is the use of mechanical fasten-

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ing, adhesive bonding, welding processes, and overmolding of metallic parts by injection-molding (Amancio-Filho, 2009; Paul et al., 2015). Overmolding can be split into form fit, force fit, and adhesive bonding. In this context, efforts were made and a patent was issued for making electric components, such as connectors, media tight and preventing the formation of gaps between the thermoplastic and the wire. This is achieved using form fit by coating the wire with an elastomeric polymer and then overmolding it with the thermoplastic in the standard injection-molding process (Fedler, 2016; Otto and Rauchmaul, 1983). Another way is also using form fit, only differing by a sealing strip that is beforehand applied to the metal component and subsequently overmolded by the thermoplastic. PMH of both approaches only hold together because form fit used and are made media tight by compacting the sealing to a certain degree during the injection-molding process so that it can afterwards compensate for the thermoplastic's shrinkage by re-expansion to a limited degree. This mechanism is being used in a recent patent (Rauchschwalbe et al., 2014).

In this case, for more evenly distributed forces in the joint, being able to forgo a form fitting geometry, and enabling a later integration into the injection-molding process as part of an in-mold assembly approach, an adhesive joint is desired. Form fit and adhesive bonds for conventional PMH have already been investigated (Paul and Luke, 2010; Paul et al., 2012). The state of the art for enhancing adhesive joints is the use of bonding agents, applied as a thin layer on a micro level before injection-molding (Amancio-Filho, 2009). They increase wettability and/or provide suitable functional groups on the substrate's surface allowing for a stronger chemical bond where otherwise there would be minimum to no adhesion (Habenicht, 2009). The most frequently used primers are silanes with their amino and vinyl functional groups promoting adhesion between inorganic and organic materials (Grujicic et al., 2008). However, there is no sufficient data available concerning strength and media tightness of these adhesive joints after exposition to abovementioned environments, i. e. cyclic thermomechanical loads under exposition to media. For this reason, a study was undertaken considering bonding agents as well as adhesives for the investigation. Most parts of the study are subject to confidentiality as it was carried out within a project with an industrial partner, which means that unfortunately several details like names and grades of materials cannot be included in this manuscript. However, findings are included to the extent possible and in a manner which ensures that the general message is still understandable and of interest to the reader.

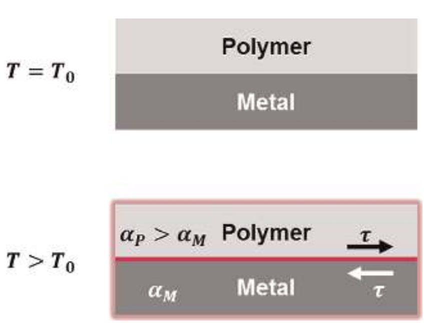

Fig. 1. Critical shear forces induced by different thermal expansion coefficients

2 Methodology

To overcome the present restrictions for the application of PMH components in the powertrain, each component of the hybrid, polymer and metal, as well as their combination was investigated. Injection-molding processes were run by previously determined internal optimum parameters or manufacturer specifications were used. Process parameter variations were not part of the investigations at this point.

The following aspects were taken into account and investigated regarding the factors defining, influencing, and disturbing permanent joint strength and media-tightness.

2.1 Material's Reaction to Media

In order to determine the selected materials' resistance to media, tensile test samples of three industrially relevant technical polymers (polyamide 6.6, polyphenylene sulfide, and polyphthalamide) were produced according to DIN EN ISO 527-2, Fig. 2, and notched Charpy test samples in accordance with DIN EN ISO 179/leA, Fig. 3, by injection-molding. After being aged in gear oils at 150 °C for 21 days, the samples underwent mechanical testing. There were three different gear oils, samples were only exposed to the most aggressive oil for a later comparison of the different effects.

Fig. 2. Injection-molded tensile test specimen acc. to DIN EN ISO 3167 for mechanical examination of basic material properties after media exposition

Fig. 3. Charpy test specimen notched acc. to DIN EN ISO 179-1, type 1-B for mechanical examination of basic material properties after media exposition

2.2 Basic Investigations with Simple Hybrid Specimens

Simple hybrid specimens were used for investigations concerning influence of different surface structures, ageing, and different bonding agents or adhesives on joint strength and media tightness, Fig. 4.

The aluminium metal inserts were produced by milling aluminium sheets and then partially shot-blasted in order to obtain a statistical, die-cast-like surface, Fig. 5.

These shot blasted metal inserts were manually cleaned with ethyl alcohol, each batch coated with a different bonding agent and subsequently partly overmolded, Fig. 6. The simple hybrid specimens were investigated with respect to their tensile strength as well as their ability to ensure lasting adhesion and tightness after exposition to media and temperatures of 150 °C.

To investigate media tightness, a luminescent additive was added to the corrosive media. After short-term media exposition for 96 h, these hybrid specimens underwent tensile testing in a Zwick Z010 following DIN EN ISO 527-2 under standard climate (23 °C and 50 % humidity acc. to DIN EN ISO 291:1997) and were afterwards examined under black light for a grayscale analysis to determine tightness. Elongation could not be sufficiently measured by the testing machine's traverse as the multisens extensometer could not be used due to the non-standard joint. Before testing, all media-contaminated specimen were stored in a desiccator for several days.

Only tensile forces could be documented due to the elliptic geometry of the hybrid specimen.

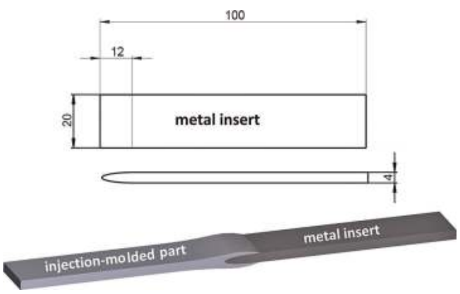

Fig. 4. Geometry of simple hybrid specimen with elliptic joint zone

Fig. 5. Shot-blasted metal insert for simple hybrid specimen

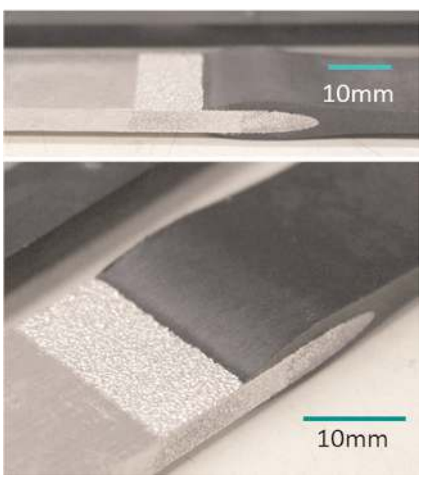

Fig. 6. Simple hybrid specimen

2.3 Triangular Specimen: Media Tightness and Residual Stress

A different approach was employed for the examination of a more complex hybrid specimen with triangular shape resembling possible later hybrid structures, see Fig. 7 for an overview and Fig. 8 for the joint zone.

The parts were produced by first coating the manually cleaned (ethyl alcohol) metal insert with the respective bonding agent or adhesive and subsequently overmolded in the injection-molding machine. The bonding agents were selected by taking the products yielding best results in the investigations with simple hybrid specimen. After the injection-molding process, the different combinations were tested with respect to the ability of the bonding agents to ensure lasting adhesion and tightness after exposition to media and temperatures ranging from –30 to +150 °C (as our test equipment did not allow us to go down to 40 °C). For this, the triangular specimens were exposed to the most aggressive gear oil at 150 °C for 504 h while a small extra batch was exposed for 200 h. Three specimens per matrix-adhesive combination were directly tested for media tightness while other three specimens per combination underwent further ageing by temperature ramps ranging from –30 to +80 °C and were afterwards also tested for media tightness by the same routine as the other specimens.

For tightness testing, a specially designed experimental setup was employed, Fig. 9. The specimen was fixed onto an airtight mount with airflow meter and the top cavity additionally

Fig. 7. Triangular shaped specimen

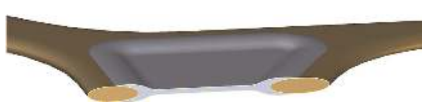

Fig. 8. Elliptic joint zone of triangular shaped specimen (CAD model)

filled with water to visually indicate the exact areas of leakage by rising bubbles, Fig. 10. During testing, air was introduced into the system with specified pressure. Airflow was measured after 60 s to include possible enlargement of leakage areas. Pressurisation was constant, maximum measurable flow rate was 250 cm^3/min.

Representative specimens, i. e. highly leaking or mostly tight samples, were additionally tested by Digital Image Correlation (DIC) for local delamination by tracking and measuring relative movement of the thermoplastic and the metal component to each other during temperature ramps.

2.4 Demonstrator

In addition to the specimens designed for specific testing requirements, a demonstrator was devised in cooperation with a vehicle manufacturer by modifying a mass-produced gear housing produced by die-casting. The hybrid demonstrator was designed by substituting lightly loaded areas of the gear cover with a polymer, Fig. 11.

First demonstrators were produced by rapid prototyping the plastic part and gluing it onto the metal component, Fig. 12. Final demonstrators were overmolded in a process similar to that of the abovementioned specimens, Fig. 13 and Geminger et al. (2011).

The two most promising intermediate layer materials from prior tests with triangular specimens were used for making the

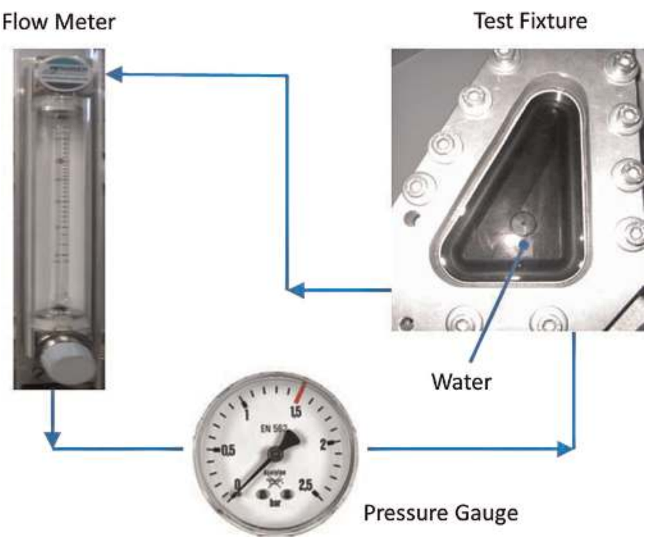

Fig. 9. Tightness testing: schematic sketch

Fig. 10. Experimental setup for tightness testing

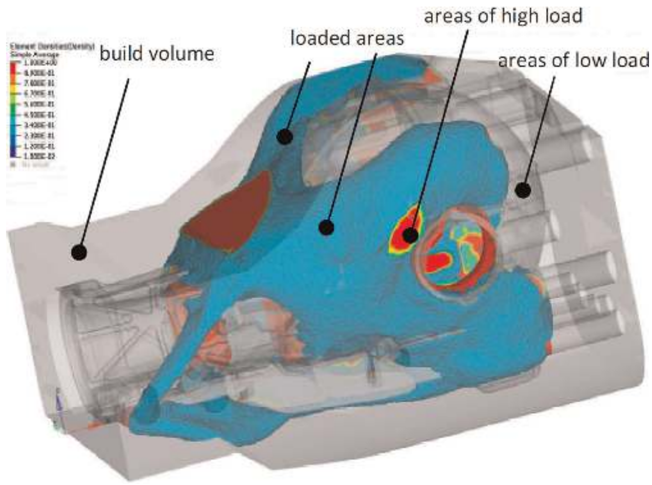

Fig. 11. Load distribution of the gear housing (Geminger et al., 2011)

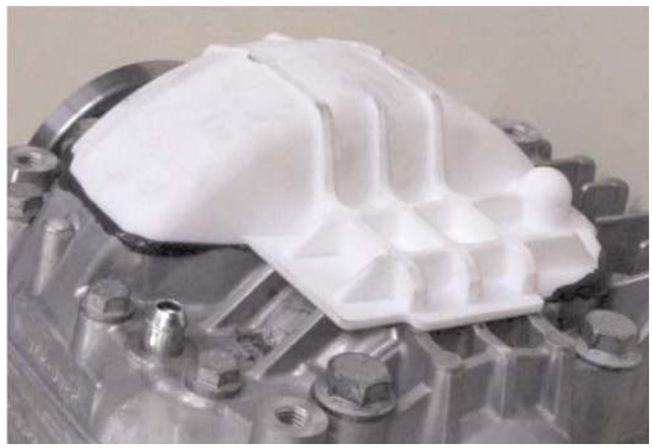

Fig. 12. First demonstrator with rapid prototyping polymer component (Geminger et al., 2011)

Fig. 13. Final hybrid gear housing demonstrator

final demonstrators. Due to a confidentiality agreement the materials cannot be specified, only that they are industrial one- and two-component adhesives and not conventional bonding agents. As manufacture of the demonstrator itself was demanding and the process could not be optimised at that stage, only basic tightness testing was undertaken by filling the demonstrators with the most aggressive gear oil and subjecting them for 7 days to the same temperature ramps as one half of the triangular specimens (–30 to +80 °C) and measuring the flowed through amount gravimetrically.

3 Materials

The following **polymers** were used:

- polyamide 6.6 with 30 % glass fibres,
- polyphthalamide with 35 % glass fibres, and
- polyphenylene sulphide with 20 % glass fibres.

The **metal** part of the test specimen was made of milled aluminium sheets (AlMgSi1).

The **Adhesives** used range from commercial primers, bonding agents, and 1- and 2-component adhesives even to non-standard materials for completely different applications as there was only a limited number of commercially available products on the market that met the abovementioned requirements (high temperatures, chemical resistance etc.):

1. high temperature high performance epoxy with good strength and corrosion resistance.
2. ultra-high temperature high performance epoxy for particularly high adhesion strength.
3. 1-component epoxy, hot-setting, unfilled: high strength, good thermal and chemical resistance.
4. 1-component epoxy, hot-setting, Al-filled, impact-resistant, thixotropic.
5. 2-component epoxy, high strength, thixotropic.
6. phenolic resin, rubber-metal bonding agent.
7. polymer-metal adhesion promoter for hybrid components.
8. 1-component ceramic-based inorganic phosphate bound sealing agent, alumina-filled, ultra-high temperature and high chemical resistance.
9. 2-component polyurethane structural adhesive for dynamically loaded applications, permanently elastic, high viscosity, high chemical and temperature resistance.
10. 2-component methyl methacrylate structural adhesive, impact-resistant, retaining flexibility after curing, high chemical and temperature resistance.
11. solvent-based synthetic resin primer.

4 Results

The findings are enumerated corresponding to the aspects listed in the Methodology section. All results are presented in relation to reference values as specific values cannot be disclosed due to the confidentiality agreement.

4.1 Material's Reaction to Media

The changes in tensile strength are visualised in Fig. 14, indicating a strong increase for PA 6.6 and only slight changes for PPA and PPS. All values from exposed specimens are compared to in-house measured values of dried specimens, not the manufacturer specification.

Results for impact strength are visualised in Fig. 15, deviating from the findings for tensile strength as only PA 6.6 shows an increase in notched impact strength whereas PPA and PPS show a slight to strong decrease in this discipline.

As means of a quick verification, whether the behavior of the investigated PA 6.6 may apply to other PA 6.6 types, another PA 6.6 type with glass fibre reinforcement was tested by the same routine. The second material yielded quite different results as tensile strength deteriorated, especially with gear oil 1, after long-term exposure at 150 °C. This is in contrast to the results with the first material showing significant improvement of mechanical properties after the same procedure, Fig. 16. The first PA 6.6 was used for all following experiments. Valid for all materials, gear oil 1 could be confirmed as the most aggressive lubricant and was therefore used for all subsequent tests.

4.2 Basic Investigations with Simple Hybrid Specimen

Tensile forces varied up to almost 4 kN for Polyamide with a bonding agent especially designed for hybrid applications, expectedly yielding highest results, no. 7 in Fig. 17. This was followed by an adhesive usually used for metal-rubber applications (no. 6) and a non-standard 1-component material (no. 8).

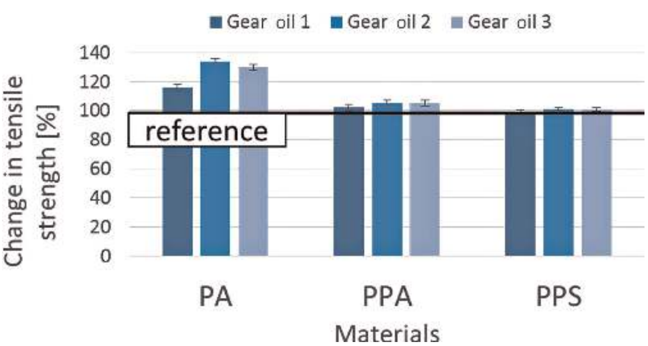

Fig. 14. Materials: Change of tensile strength after ageing (exposure to media) for 96 h

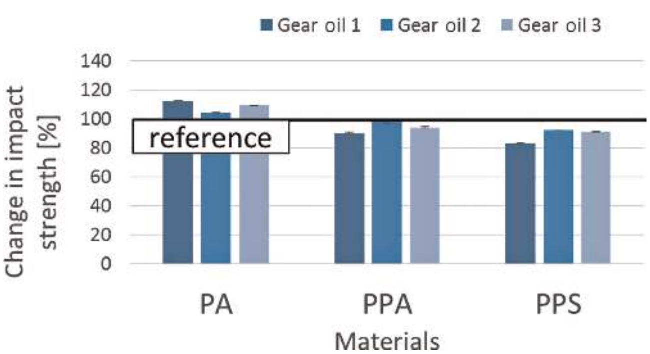

Fig. 15. Materials: Alteration of notched impact strength after ageing for 96 h

The order of results remains the same for media tightness testing by means of grayscale analysis. Joining zones of all specimens exhibit contamination with luminescent material, Fig. 18, showing that media tightness could not be achieved with these material combinations (polymer – bonding agent – aluminium), even after only 4 days of exposure to gear oil 1.

4.3 Triangular Specimen: Media Tightness and Residual Stress

Most samples showed significant leakage rates above the maximum measurable flow rate of 250 cm^3/min. with only two products being able to allow for a good bond, but even these samples were not entirely media tight. It was found that tightness highly depended on the duration of media exposure as the samples with only 200 h of thermal stress and media exposure showed significantly lower leakage rates. This shows how leakages were delayed, but are ultimately inevitable for these hybrid parts that have to meet the abovementioned standards, even by employing a geometry with form fit. Moreover, it could be shown that leakages were statistically distributed across the material seam without areas of leakage accumulation, Fig. 19, with two specimens showing wide leakages alongside one of the sides of the triangular geometry.

Digital Image Correlation analysis during temperature cycles proved to be problematic due to different air temperatures causing significant amounts of additional noise in the obtained images. Workarounds, such as pre-heating samples, taking them out of the oven and then observing the relative movement while cooling, are presently tested.

4.4 Demonstrator

With the first demonstrators based on rapid prototyping it could be shown that they could withstand combined mechanical loads and media exposition under internal pressure on an industrial end of line test stand, though media tightness was not achieved.

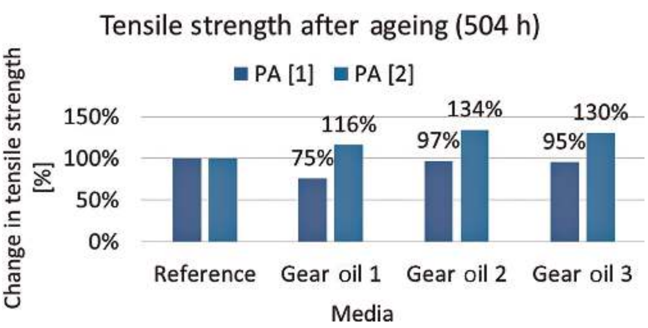

Fig. 16. Different ageing reaction of two PAs

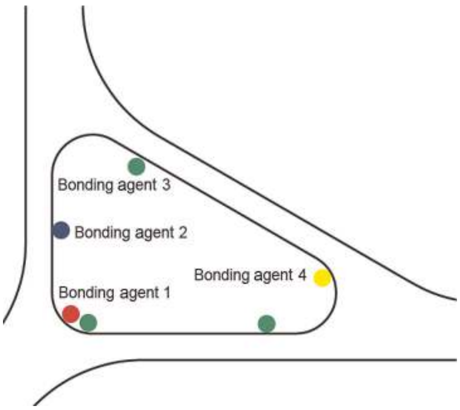

Fig. 19. Examples of leakage positions

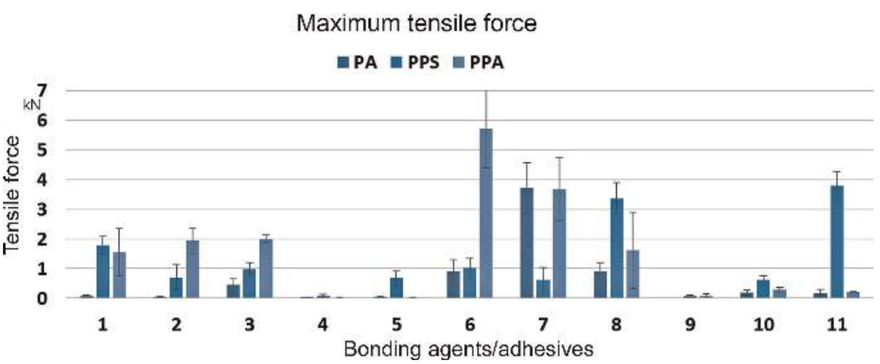

Fig. 17. Tensile forces of simple hybrid specimen

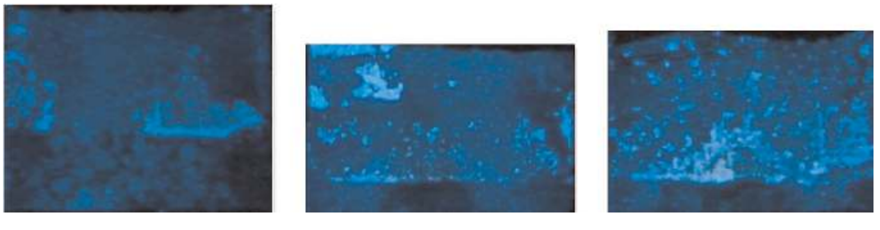

Fig. 18. Contamination of the joint with luminescent material under black light

Tightness testing with final demonstrators was basic, in this regard it could only be indicated that the demonstrators with the two-component adhesive leaked twice as much as those with the one-component product. Thus, neither adhesive was able to ensure lasting media tightness under given circumstances of combined thermal and media loads at this point.

5 Discussion

Before focus is put on hybrid joints, the fact that different glass-fibre reinforced polyamide materials exhibited different reactions to media exposure after a given time shall be mentioned as it shows that there can be significantly different reactions of the same polymer type depending on its specific composition.

Concerning hybrid specimens, it was confirmed that certain primers or adhesives do enable better adhesion and achieve higher joint strengths, but ultimately cannot ensure a media-tight joint after fatigue testing through combined media and thermal exposure. The weak point of the joint thereby is the interface of the injection-molded thermoplastic onto the respective adhesive which was visible as the bonding agents still stuck to the metal insert after tensile tests. Adhesion of the injection-molded thermoplastic onto the already cured adhesive is disadvantageous compared to the adhesive which was conventionally applied onto cleaned metal inserts. The most important insight here, however, is that the joints were ultimately destroyed by relative movement of plastic and metal component during temperature cycles, caused by the different expansion of both materials.

Based on this insight, a more advanced approach considering the different thermal expansion coefficients is required. At the University of Kassel, an approach with equalising intermediate layer between polymer and metal component is currently being pursued. This middle layer is of a polymer featuring elastomeric behavior and certain minimum thickness to be able to equalise all thermal strain-induced relative movement of plastic and metal component. Media tightness shall be thus maintained throughout the hybrid component's entire lifetime. Correspondingly, suitable manufacturing technology for the economic production of these abovementioned PMH components with intermediate layer is currently under development at University of Kassel. The target process is designed to be suited for high-quality series production together with high levels of automation, productivity, flexibility, and gapless quality assurance, i.e., to be competitive for replacing metal components that could not be replaced until now.

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