

Highlighting Thermal Post-Treatment for Improving Long-Term Media-Tightness of Polymer-Metal Hybrids



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Abstract

Polymer-metal hybrids are increasingly used in the conductor industry, where long-term stable tightness against aggressive and/or corrosive media must be ensured even under variable environmental conditions. Two bonding principles are available for this purpose, which can generate the required full-faced contact at the interface between metal and polymer. Regardless of whether full-faced micromechanical interlocking or full-faced bonding is used, a sufficiently high contact temperature must be reached at least once before the hybrid is used in order to completely infiltrate the undercuts with polymer melt or ensure the reactivity of the incorporated adhesion promoter. In this paper, a thermal post-treatment is proposed that not only offers technical and economic advantages, but at the same time uses a third bonding principle to realize full-faced contact between the two dissimilar materials. The hybrids produced by assembly injection molding were investigated before and after temperature cycling test with the differential pressure test and, in a more specific observation, in the helium vacuum test for their tightness properties and with pull-out tests for their adhesion properties as a function of the metal pretreatment and thermal post-treatment. In addition to thermally post-treated polypropylene/aluminum hybrids, those made of glass fiber-reinforced polyamide and copper also showed promising results - even without incorporated adhesion promoter or metal pretreatment. Condensation moisture, which led to water absorption during the temperature cycling test in the case of the thermally post-treated polyamide/metal composites due to the hygroscopic nature of the polyamide, appears to be a major cause of failure compared to the different thermal expansion coefficients of polyamide and metal.

Keywords: Polymer-metal hybrids; Media-tightness; Bonding principle; Thermal fatigue resistance; Thermal post-treatment

Introduction

The increasing electrification of private motorized transport increases the demand for electrical conductor materials. Metals such as aluminum, which has the highest density-specific electrical conductivity among the engineering metals, are suitable for this purpose. Regardless of whether the focus is on signal or power transmission, the corresponding components must be electrically insulated as well as protected against environmental influences. Polymers are indispensable in this field due to their excellent insulating properties as well as their chemical resistance. To ensure electrical conductivity while providing insulation, an increasing use of polymer-metal hybrids (PMHs) can be expected. Whereas metals and polymers are often in a competitive situation in traditional engineering practice, hybrid technology combines the advantages of both materials with the corresponding processing and machining technology and thus allows the targeted use of synergy effects. These have already been

successfully used in the past for load-bearing hybrid structures [1]. Transferability with regard to electrical conductor materials should also be ensured in the future. However, the media-tightness of these systems is becoming increasingly important, since the migration of media, such as water, into the interface can cause the conductor to corrode and thus malfunction [2]. In order to exclude these malfunctions during the service life, full-faced contact of the polymer with the metal surface is crucial and thus a major challenge for the developer. Essentially, there are two fundamental principles of contacting the two dissimilar materials with regard to media tightness [3]. Rough metal surfaces can cause the solidifying polymer to become mechanically interlocked as it penetrates microstructures, creating a full-faced micromechanical interlocking [4]. The undercuts in the micro or sub-micro scale [5] required for this can be achieved by abrasive blasting [6], laser structuring [7], wet-chemical [5] or electrochemical pretreatment

[8]. According to [9], the undercuts must be infiltrated as deeply as possible with molten polymer, otherwise microleakage will occur. While this approach eliminates the need for an adhesion promoter, there is a need for metal pretreatment of a mechanical, thermo-mechanical, chemical or electro-chemical nature. In [10], Emrich et al. give a detailed overview of polymer-metal combinations joined according to this bonding principle with respect to the temperature change-induced decrease in maximum shear strength. Whereas only for joints of a thermoplastic elastomer with aluminum and copper a long-term stable helium tightness (helium leakage rate $< 10^{-5}$ mbar·l·s⁻¹ [10]) is attested, no values are given for the remaining material combinations.

The use of previously mentioned adhesion promoters, which must be adapted to the respective polymer, represents the second principle for creating a full-faced bonding between metal and polymer. In [11], Eltermann and Wilde succeeded in improving the tightness of a near-series lead frame demonstrator by means of a two-stage curing acrylic-based adhesion promoter. Besides the work of Heinle et al. [12], this paper is one of the few that actively deals with thermal fatigue resistance of media-tight PMHs. Due to the coefficients of thermal expansion (CTE) of metal and polymer, which can differ by up to one order of magnitude, different relative movements of the materials cause internal shear stresses, which can lead to delamination and subsequent gap formation and thus to leakage [12-14]. Therefore, ensuring sufficient thermal fatigue resistance plays an essential role in the development of media-tight PMHs. Hallak et al. [14] realized the approach, which was already discussed by Geck et al. [13], of integrating a viscous intermediate layer on a two-stage curing acrylate base into the interface between a glass fiber reinforced polyamide and a copper alloy, which expands during temperature exposure above its glass transition and thus allows micro gaps to be closed.

According to our literature research, another bonding principle exists that can possibly lead to long-term, full faced contact between polymer and metal. Some polymers have organic functional groups in their native molecular structure, which can form physicochemical or even chemical bonds with the likewise reactive oxide or hydroxide layers of copper or aluminum resulting in strong intermolecular forces [15-18]. In addition to hydrogen bonds [19,20] and other acid-base interactions, in which electrons are withdrawn from an oxidized aluminum surface (donor) in the direction of the functional groups of the polymer (acceptor) and covalent bonds are formed as a result [21], also covalent C-O-Al bonds between polymer amide groups and hydroxide aluminum groups are reported [22]. In our opinion, this bonding principle could be used especially in the conductor industry to avoid costs for time consuming metal pretreatments or often-expensive adhesion promoters.

However, regardless of the chosen bonding principle, there is an overriding difficulty in contacting the two dissimilar materials. Specifically, the contact temperature when the viscous polymer

melt meets the solid metal surface is the primary influencing factor with regard to the resulting bond properties [1,6]. Low contact temperatures result in either insufficient infiltration of undercuts on the metal surface [6,23] or in reduced reactivity of incorporated adhesion promoters [24]. In order to achieve short cycle times due to economic considerations, the mold temperatures and thus also the associated contact temperatures in the manufacturing of media-tight PMHs from bulk and engineering thermoplastics are 80°C maximum. A look at the literature offers the following approaches to tackling this problem:

- a. Insert metals are heated either directly in the mold or in an upstream process step [1,3,6,8,9,23,25].
- b. The mold temperatures are increased to high temperatures that are irresponsible from an economic point of view [5,26].

While the disadvantages of the latter are obvious, upstream heating of the inserts has the disadvantage that, on the one hand, the temperature drops rapidly during transfer to the cavity as a result of heat transfer to the ambient and, on the other hand, after insertion as a result of the high thermal conductivities of the metals in contact [23]. In addition, the heating parameters must be adapted to the often-varying ambient conditions. Whereas in the case of direct heating in the mold, complex mold engineering is to be expected, in both cases the additional heat introduced into the mold must be dissipated again. The discussed disadvantages of the previous approaches prove the need for development with regard to smart process.

In addition, our literature review showed that there are only a few studies on long-term properties of media-tight PMHs and that there is still a considerable need for research in this area. Therefore, the present work deals, on the one hand, with the application of different bonding principles under the aspect of media-tightness of hybrid PMHs before and after temperature cycling. On the other hand, a cost-saving thermal post-treatment process is presented which can be easily integrated into the existing PMH manufacturing process chain and with which the long-term properties of media-tight PMHs in the conductor industry can be significantly improved.

Experimental Part

This chapter presents the test materials, the material-dependent processes for manufacturing, and the selected test methods for investigating the resulting tightness and adhesion properties of the various PMHs.

Materials

The investigated insert materials, which were provided by the company Wieland-Werke AG (Ulm, Germany), were pure aluminum type EN AW-1050A according to EN 573-3:2019 (D) and deoxidized copper with low residual phosphorus content type Cu-PHC according to CEN/TS 13388:2020 + AC:2020 (D).

In the following, the aluminum type will be abbreviated as “Al” and the copper type as “Cu”. Both metal types are characterized by excellent electrical conductivity and are therefore preferred as conductor materials [27]. Both commercially available, black-colored polyamide 6 (PA6) type Durethan B30S and a 30 percent by weight short glass fiber-reinforced, black-colored polyamide 6 (PA6-GF30) type Durethan BKV130 from LANXESS Deutschland GmbH (Cologne, Germany) were used as joining partners to the presented metals. While both materials exhibit sufficient insulation properties up to elevated temperatures, the glass fiber-reinforced variants are increasingly manifesting themselves in the conductor industry due to their increased stiffness, lower moisture absorption and reduced thermal expansion in the longitudinal direction of the fibers [28]. Prior to assembly injection molding, the PA6 raw materials in form of pellets were dried at 80°C for 6 h according to the manufacturer specifications using dry air dryer type DR202 MT from Bierther GmbH (Bad Kreuznach, Germany).

Additional PMHs were manufactured from a commercially available natural color, homopolymeric polypropylene (PP) grade 100-GA12 from Ineos Holdings Ltd. (London, United Kingdom), with a melt flow rate (MFR) of 12 g/10 min at 230°C and 2.16 kg loading. In order to generate adhesion between the polymer and the metal surface, 0.2 wt.% of maleic anhydride (MAH), which acts as an adhesion promoter [17,21,24,29], was added to the neat PP in the form of PP grafted with MAH (PP-g-MAH). The MFR value of the PP-g-MAH grade AT3115E provided by Mitsui Chemicals Europe GmbH (Duesseldorf, Germany) was 28 g/10 min at 230°C and 2.16 kg loading. In the following, the copolymer “PP + PP-g-MAH” resulting from the addition will be referred to only as “PP”. PP is coming into focus primarily due to its electrolyte resistance [29] as well as its considerable cost advantage compared to polyamides and is therefore included in the present study. General properties of the conductor and insulation materials examined are summarized in Table 1.

Table 1: General properties of the investigated conductor and insulation materials at 23°C.

Property	Polymers			Metals		
	Unit	PP	PA6	PA6-GF30	Cu	Al
Young's Modulus	[MPa]	1300	3200/1000 ¹⁾	9300/5200 ¹⁾	127·10 ³	69·10 ³
CTE	[10 ⁻⁶ ·K ⁻¹]	80/100 ²⁾	100/110 ²⁾	20/100 ²⁾	17.7	23.5
Density	[g/cm ³]	0.91	1.14	1.37	8.94	2.7
Resistivity	[Ω·m]	10 ¹⁶	10 ¹² /2·10 ⁹ ¹⁾	3·10 ¹² /10 ¹⁰ ¹⁾	1.72·10 ⁻⁸	2.64·10 ⁻⁸

¹⁾dry/conditioned

²⁾longitudinal/transverse.

Test specimen geometry

In this study, hybrid circular disc specimens with a diameter of 30 mm and a wall thickness of 1.2 mm were investigated, Figure 1. The lateral outer dimensions of the rectangular metal insert show 25·8 mm² at a metal sheet thickness of 0.8 mm (aspect ratio 10:1). Consequently, the contact area between polymer and metal in case of the hybrid specimens without thermal post-treatment counts 21.12 mm². The total path length (z-direction) between polymer and metal, within a possible leakage can occur, equals the wall thickness of 1.2 mm of the test specimen.

Insert pretreatment

The copper and aluminum inserts were punched from rolled sheet and subsequently cleaned and degreased with propan-2-ol in an ultrasonic bath type Elmasonic S 10 H from Elma Schmidbauer GmbH (Singen, Germany) at a constant water temperature of 40°C in about three successive five-minute cleaning cycles. Apart from the cleaning procedure in the ultrasonic bath, subsequent treatment steps were carried out in a 300 ml beaker filled with 180 ml of the appropriate medium. Using a specially manufactured holder, 20 metal inserts could be treated simultaneously. The metal inserts were immersed approx. 19 mm vertically in the medium.

Copper pretreatment

In order to minimize the punching burr of the copper inserts to prevent possible stress concentrations in the polymer at the corner areas of the insert [12], the copper inserts were pickled in nitric acid (HNO₃) with a concentration of 65 vol.%, which also causes partial material removal and thus roughening of the surface structure [15]. Various studies have already shown that this effect is only of secondary importance with regard to the resulting bond properties [19,20,25], which is why it is not addressed again in this study. All pretreatment steps can be taken from Table 2 below.

Aluminum pretreatment

In addition to the objective of the aluminum pretreatment to minimize the punching burr, the formation of nanostructures on the surface, which enables full-faced microscale interlocking of the polymer in these very structures, is still desired. For this purpose, a so-called hot water treatment (HWT), as already successfully used in a similar way by Zhao et al. [5] for injection molded direct joining (IMDJ) of a 30 percent by weight glass fiber reinforced polybutylene terephthalate (PBT-GF30) and aluminum, was applied. After the natural oxide layer of the aluminum was removed by sodium hydroxide (NaOH) with a concentration of 10 wt.% in a first process step, the inserts were placed in a tempered water

bath with a constant temperature of 65°C for 300 s. Water bath temperature and treatment time correspond to the parameters optimized by Zhao et al. [5] as the authors attest the optimum between achievable depth and number of nanostructures. More detailed information on pretreatment can be found in Table 3. All of the inserts were rinsed with deionized water (DI water) after the respective pickling processes and dried in the final step in

an exicator at room temperature (23°C ± 2°C) and stored until removal. Specimens manufactured with pretreated inserts are referred to as “Pretreated” in the following. In order to be able to specifically evaluate the influence of pretreatment on thermal fatigue resistance, only inserts freed from surface contaminations (Table 3) serve as a reference. Specimens manufactured with such inserts are subsequently referred to as “Untreated”.

Table 2: Pretreatment conditions for copper.

Step	Process	Medium	Concentration [vol.%]	Temperature [°C]	Time [s]
1	Cleaning & Degreasing	Propan-2-ol	100	40	900
2	Pickling	H ₂ SO ₄	10	23	60
3	Pickling	HNO ₃	65	23	5
4	Rinsing	DI water	100	18	180
5	Drying	Air	-	23	-

Table 3: Pretreatment conditions for aluminum.

Step	Process	Medium	Concentration [wt.%]	Temperature [°C]	Time [s]
1	Cleaning & Degreasing	Propan-2-ol	100	40	900
2	Pickling	NaOH	10	65	60
3	Rinsing	DI water	100	18	180
4	Drying	Air	-	23	-
5	HWT	DI water	100	65	300
6	Drying	Air	-	23	-

Assembly injection molding

The hybrid specimens were manufactured by assembly injection molding employing an injection molding machine type 220 S Allrounder 150-30 from Arburg GmbH & Co. KG (Lossburg, Germany) with a screw diameter of 15 mm using a single-cavity mold with spot gating. The injection molding processing

conditions are shown in Table 4. The metal inserts were inserted by hand with nitrile gloves, and after overmolding with the respective polymer the finished molded part was also removed manually. The specimens were stored on perforated plates at standard atmosphere (23°C and 50% humidity) until removal.

Table 4: Injection molding processing conditions for the manufacturing of the investigated test specimens.

Parameter	Unit	PP	PA6	PA6-GF30
Nozzle temperature	[°C]	240	265	265
Mold temperature	[°C]	60	100	100
Injection speed	[cm ³ /s]	30	12	12
Switchover melt pressure	[bar]	700	550	750
Holding pressure	[bar]	500	500	500
Holding pressure time	[s]	7.5	9	9
Cycle time	[s]	28.9	43.6	41.3

Thermal post-treatment

In order to generate full-faced contact between metal and polymer while at the same time ensuring economical process conditions, it is possible to make targeted use of the thermal conductivity and eddy current loss of the metal to inductively

heat an injection-molded PMH specifically at the interface and thus subsequently achieve a high contact temperature between the two materials. In this process, the respective polymer was partially heated 55°C ± 5°C at a heating rate of about 1000 K*min⁻¹ above the corresponding crystallite melting temperature at the interfacial region. Here, the subsequent temperature input into

the interface is used on the one hand to increase the reaction rate between organic functional groups and to allow rapid conformational changes of the polymer chains towards the metal surface [20,22] to support the formation of hydrogen bonds as one possible form of interaction [19,20]. On the other hand, in the case of full-faced micromechanical interlocking, the infiltration depth of the undercuts can be multiplied without having to adapt the process conditions during overmolding. Thermal post-treatment was carried out immediately after the injection molding process

by means of a mobile induction heating system of the type Minac 6/10 from EFD Induction GmbH (Freiburg in Breisgau, Germany) with a maximum output power of 10 kW at a frequency range of 10 kHz to 40 kHz. During the heating process, the temperature of the metal insert was monitored by a miniature sheath thermocouple from TC Mess- & Regeltechnik GmbH (Moenchengladbach, Germany) and the temperature of the polymer component by an infrared camera from Optris GmbH (Berlin, Germany), and the temperature profile over time was digitally recorded.

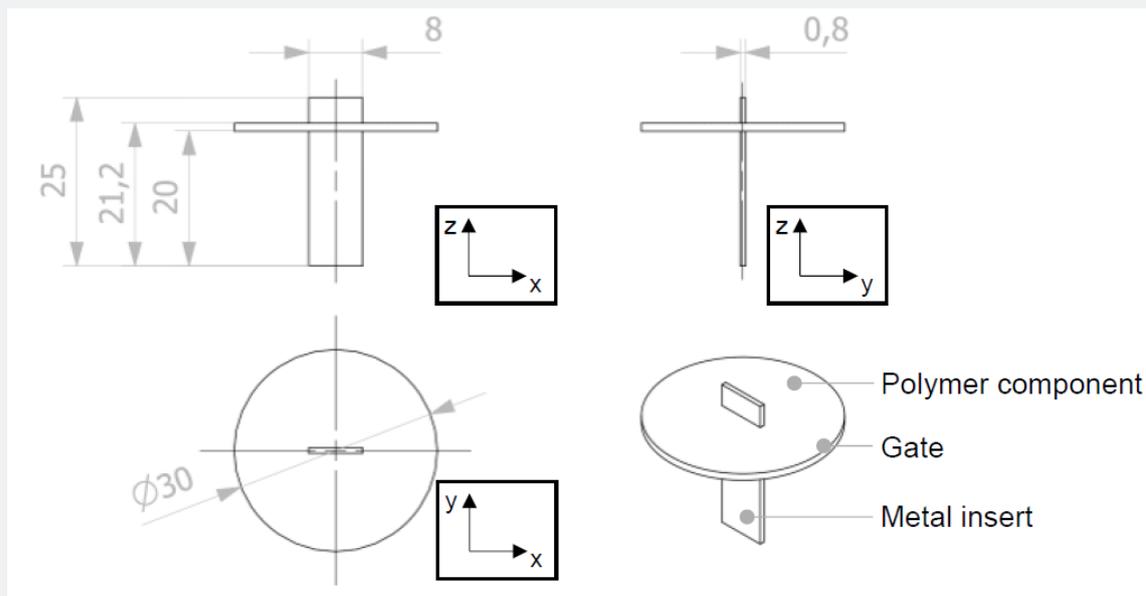


Figure 1: Investigated test specimen (polymer-metal hybrid demonstrator) in different drawing views.

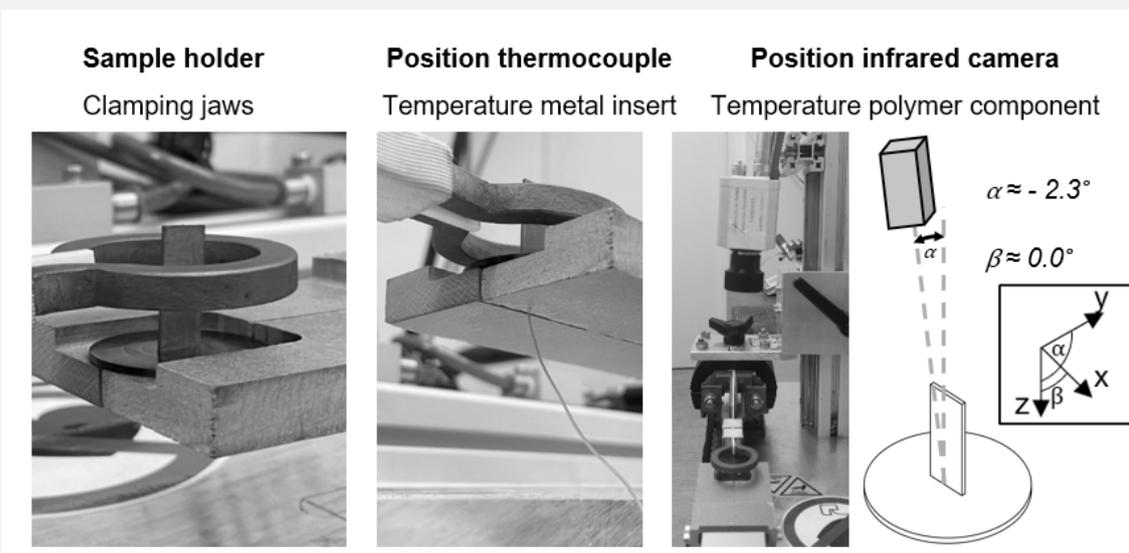


Figure 2: Overview of the equipment for thermal post-treatment.

In order to ensure high reproducibility, the test specimens were placed and aligned in a sample holder manufactured

for this purpose, consisting of two clamping jaws, Figure 2. The pneumatically actuated clamping jaws were made of

Kelutherm 800M from KELUX Hochleistungswerkstoffe GmbH (Olfen, Germany), which has a thermal conductivity of $0.26 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$. After thermal post-treatment, the specimens were again stored on perforated plates at standard atmosphere until removal for tightness testing. Thermally post-treated specimens are subsequently referred to as "Thermally post-treated". To determine the emission coefficient of the investigated materials, measurements were carried out under a defined oven atmosphere. PP, PA6 and PA6-GF30 samples were placed in a convection oven type UT 5060 EK from Heraeus Deutschland GmbH & Co. KG (Hanau, Germany) and kept at 40°C for 20 minutes before measurement. The infrared camera was also placed in the oven to ensure a constant temperature during the measurement. In addition to the temperature sensor integrated in the oven, a Ni-Cr-Ni temperature sensor was placed in close proximity to the sample to determine the actual prevailing temperatures. The lowest temperature deviation between the infrared camera and the temperature sensors used was achieved with an emission coefficient of 0.96.

Temperature cycling test

In order to be able to specifically investigate the influence of the material parameters, the metal insert pretreatment as well as the thermal post-treatment on thermal fatigue resistance, temperature cycling test were carried out in accordance with DIN EN 60068. The PMHs were transferred on metal grids into a climatic chamber type CTC256 provided by Memmert GmbH & Co. KG (Schwabach, Germany). The PMHs passed through the temperature program shown in Figure 3 one hundred times, leading to a total duration of 361 h. There was no relative humidity control, which means that condensation is to be expected, which may affect the experimental results [10], especially in the case of the polyamide/metal hybrids due to the hygroscopic nature [30] of the polyamide and the associated tendency to swell (even at the interface [18]) as a result of water absorption. At the end of the test cycles, the specimens remained at room temperature for two hours to achieve temperature equilibration before starting the tightness tests.

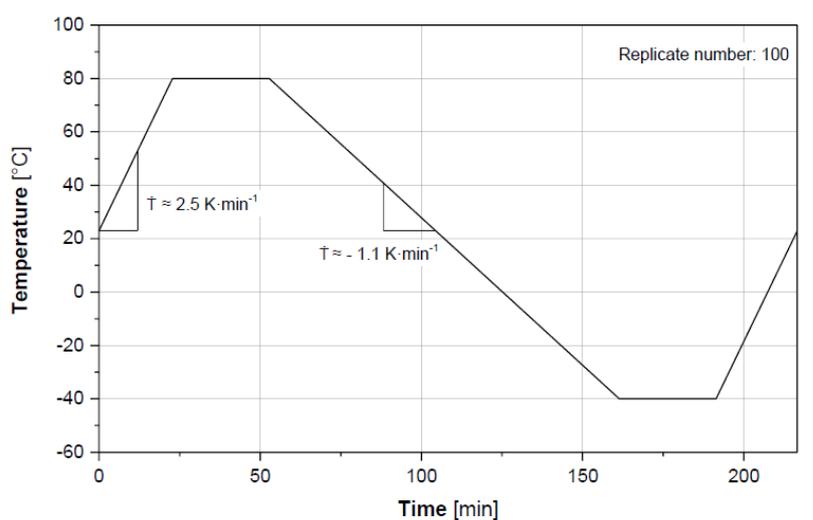


Figure 3: Temperature program applied in the temperature cycling test in order to study thermal fatigue resistance of various PMH samples.

Tightness tests of polymer-metal boundary zone

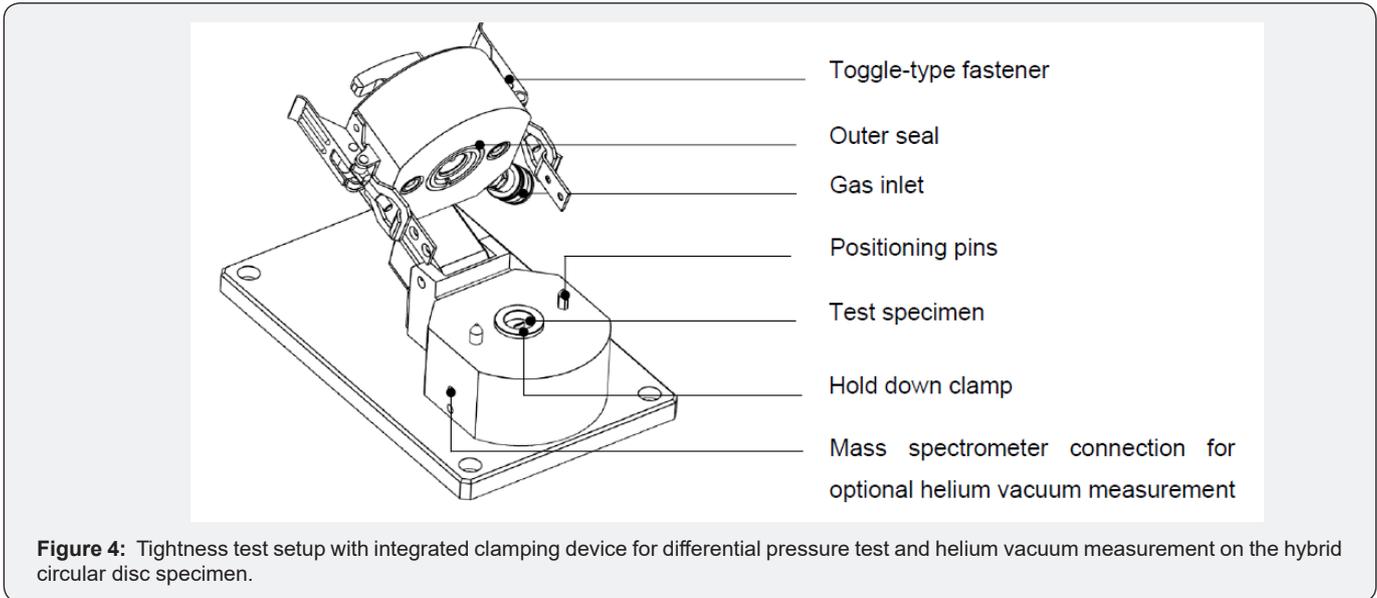
Tightness of the test specimens was measured by means of a differential pressure leakage tester type Integra DD6 from Dr. Wiesner Steuerungstechnik GmbH (Remshalden, Germany) with a pressure resolution limit of 10^{-4} mbar in combination with a suitable clamping device at standard atmosphere, Figure 4. Here, the test specimen, which is pressed reproducibly against the inner seal via two toggle-type fasteners, and a tight reference volume are subjected to an overpressure of 1 bar for 10 s in the so-called filling phase. After a subsequent settling time of 10 s, which is intended to ensure temperature compensation between the pressurized surface of the sample and the compressed air,

the actual 5 s measurement of the relative pressure change with respect to the reference volume is carried out. Calibration with a test leak made it possible to determine the total test volume of 71.2 ml, which is made up of the volumes of the pressurized chamber, the air hose and the test device itself. Thus, the relative pressure change could be converted to an equivalent leakage rate in $\text{mbar}\cdot\text{l}\cdot\text{s}^{-1}$.

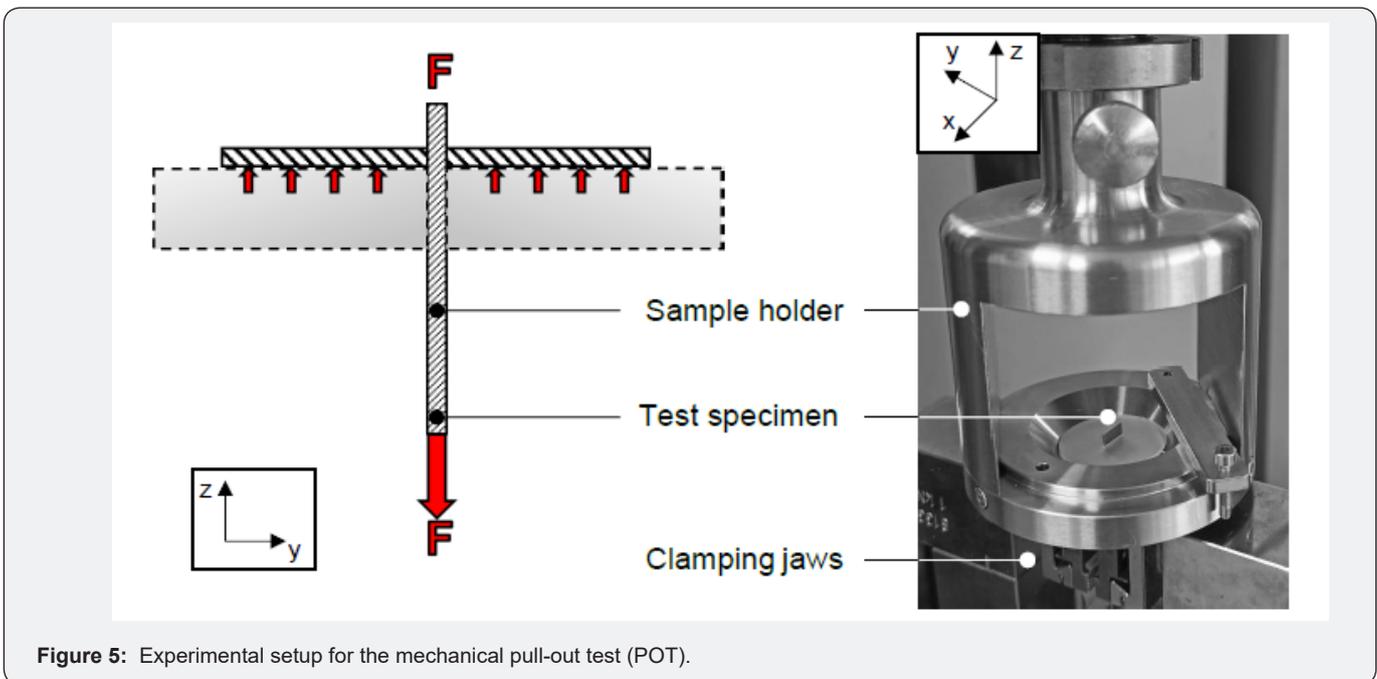
A nitrile butadiene rubber (NBR) O-ring with a durometer hardness of 72 Shore A was used as an inner seal, with an inner diameter of 22 mm and a cord thickness of 2.5 mm. For statistical validation of the collected results, five samples per setting were measured before and after the temperature cycling

test, respectively. This involved multiple determinations of each sample with a replicate number of five in order to exclude measurement errors due to a faulty clamping. In the following, only the mean values of the leakage rate from the results of the five measured samples including their standard deviation are presented for discussion. The test facility has been designed so that the compressed air supply at the gas inlet can be replaced by a helium supply via quick-release fastener. Additionally, a mass spectrometer can be connected, which allows a helium vacuum measurement according to DIN EN 1779: 1999 B2.1. Since the

same test facility could be used, the comparability of results of the helium vacuum measurements and the differential pressure tests is sufficiently ensured due to identical clamping conditions. To ensure complete filling with test gas, the test facility is evacuated by means of a built-in suction pump before the helium test gas with a purity of 99.996 vol.% is introduced at a pressure of $1 \text{ bar} \pm 50 \text{ mbar}$. Five specimens were measured once per setting to statistically validate the results collected. In the following, the averaged leakage rates and their time-dependent progressions including their standard deviation are presented for discussion.



Pull-out test (POT) of metal insert from PMH



For studying on the achieved mechanical bond strengths of differently manufactured PMHs and their possible decrease as a result of thermal cycling, pull-out tests were carried out before and after the temperature cycling test by means of a universal tensile testing machine type Zwick Roell Z005 from Zwick GmbH & Co. KG (Ulm, Germany) with a load measuring cell of 5 kN. In this test the metal insert is pulled out of the polymer component and the necessary pull-out force versus pulling distance recorded, while the hybrid sample is kept in a special designed sample holder and the metal insert is pulled by means of clamping jaws at an initial clamping distance of 5 mm, Figure 5. The hybrids were tested at a constant testing speed of 1 mm/min until rupture at room temperature. The maximal measured pull-out force was used to characterize the bond strength of attested sample. For statistical approach, a set of five samples was tested and for each set of samples the average of the maximum pull-out force and the respective standard deviation were evaluated.

Thermogravimetric analysis (TGA)

TGA measurements were performed employing a thermogravimetric analysis device type 3+ from Mettler-Toledo GmbH (Greifensee, Switzerland) on untreated copper and aluminum as well as on differently treated aluminum inserts in a temperature range from 30°C to 300°C in order to be able to detect volatile constituents of the respective surface, which could migrate into the interfacial regions between polymer and metal when thermal post-treatment is applied. With identical sample

volumes, the initial sample masses varied from 19.2 mg to 57.3 mg due to the different densities of copper and aluminum (Table 1). All samples were heated in 70 μ l alumina crucibles at a constant heating rate of 20 K \cdot min⁻¹ under oxygen atmosphere with a purge gas flow of 50 ml \cdot min⁻¹.

Differential scanning calorimetry (DSC)

In order to characterize the possible catalytic effect of copper on the PP in the case of the thermally post-treated PP/Cu hybrids, dynamic oxidation induction temperature (OIT) measurements were performed employing a differential scanning calorimeter type 3+ from Mettler-Toledo GmbH (Greifensee, Switzerland) on samples taken near the interface as well as from the polymer component with an initial sample mass of 5.0 \pm 0.1 mg from thermally post-treated PP/Cu hybrids. Measurements in 40 μ l aluminum crucibles with perforated lids were conducted in the temperature range from 30°C to 230°C at heating and cooling rates of 20 K \cdot min⁻¹, respectively, using nitrogen as purge gas (N₂) in the first heating and cooling, and oxygen (O₂) for the second heating, each with a flow rate of 60 ml \cdot min⁻¹.

Results & Discussion

In the following, the results of the metal insert pretreatment, on the one hand, and the investigated results on the tightness as well as the adhesion properties of differently manufactured hybrid specimens in the initial state and after the temperature cycling test, on the other hand, are presented for discussion.

Insert Pretreatment

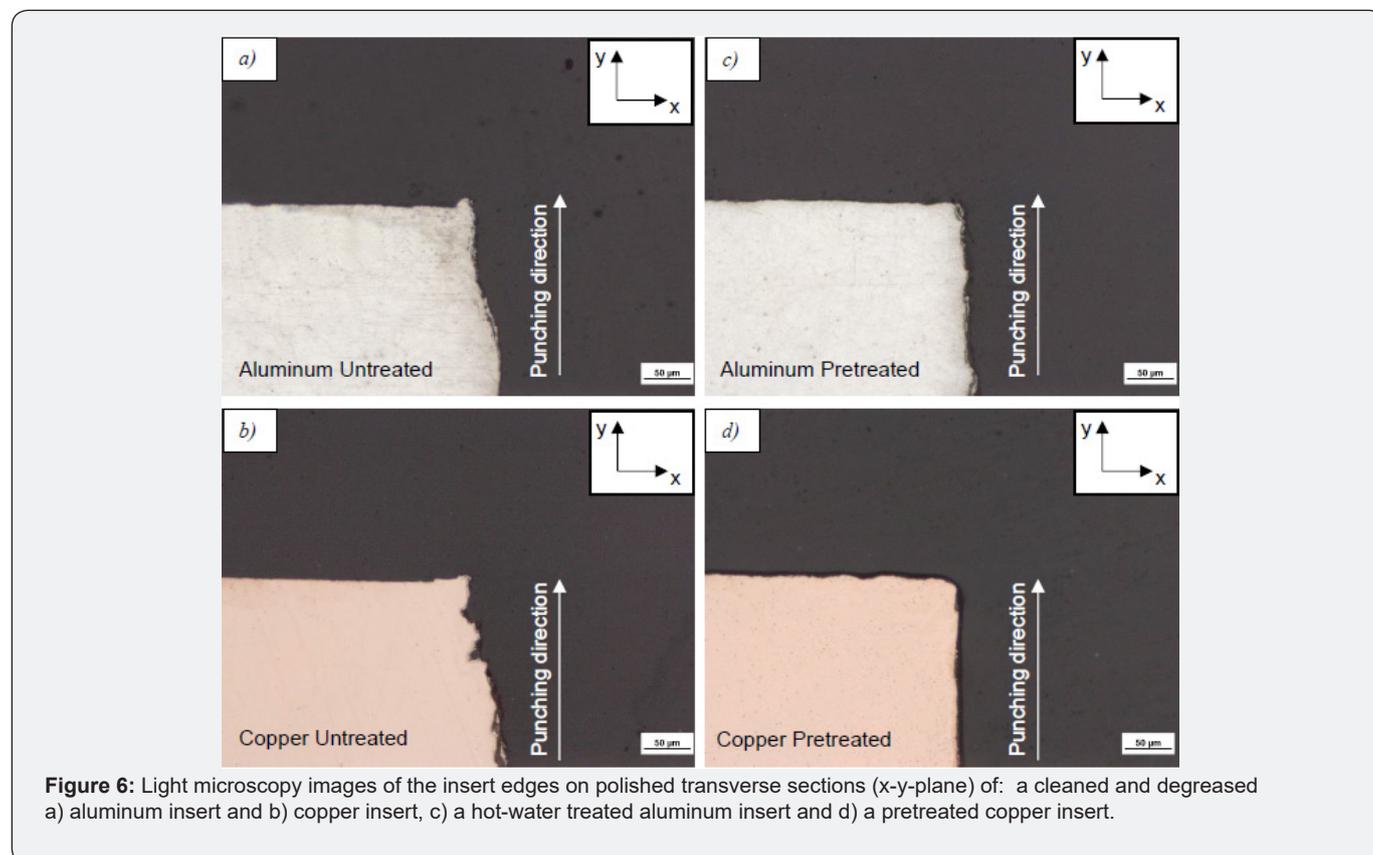


Figure 6: Light microscopy images of the insert edges on polished transverse sections (x-y-plane) of: a) cleaned and degreased a) aluminum insert and b) copper insert, c) a hot-water treated aluminum insert and d) a pretreated copper insert.

Figure 6 shows the punching edges of pretreated aluminum and copper inserts compared to the punching edges of untreated variants (step 1 only, Table 2 & Table 3). Regardless of the metal, a significant rounding of the edges can be observed as a result of the pretreatment, which can minimize stress concentrations in the polymer through a sharp metal burr interaction during thermal cycling and thus probably prevents crack-induced leakage [12]. The selected pretreatment procedures are therefore suitable for increasing thermal fatigue resistance. Figure 7 shows scanning

electron beam microscopy (SEM) images of an untreated aluminum insert and an aluminum insert pretreated by the HWT procedure, Table 3. While the orientation in rolling direction can still be seen on the untreated aluminum surface, the formation of plate-like nanostructures from reactive $\text{Al}(\text{OH})_3$ and AlOOH molecules as a result of the water-aluminum reaction, can be observed on the surface treated with HWT [5]. Consequently, it should be possible to realize micromechanical interlocks with these inserts, which can ensure full-faced contact between aluminum and polymer.

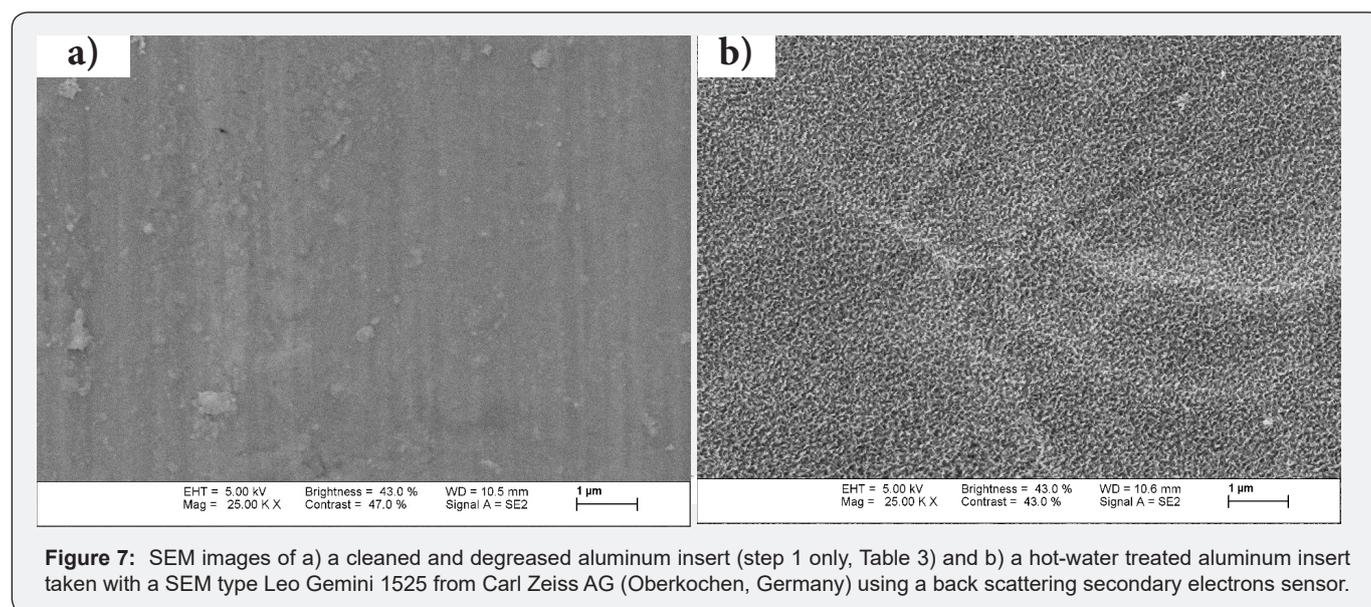


Figure 7: SEM images of a) a cleaned and degreased aluminum insert (step 1 only, Table 3) and b) a hot-water treated aluminum insert taken with a SEM type Leo Gemini 1525 from Carl Zeiss AG (Oberkochen, Germany) using a back scattering secondary electrons sensor.

Tightness & Adhesion of PMH

Initial state

Figure 8 compares the leakage rates of the different polymer-metal combinations that were combined in assembly injection molding. In addition, the influence of metal pretreatment and thermal post-treatment of PMH samples on the tightness is shown. Considering the standard deviation, it was not possible to produce watertight [8] PMHs without pretreatment of the metal inserts. When considering the maximum pull-out forces, it becomes apparent that overmolding untreated metal inserts under process parameters similar to those used in series production does not result in any adhesion between the two materials. The low measured pull-out forces result from a poor bonding of these hybrids and present probably mainly the friction force between polymer and metal acting during the pullout of the insert. The reason for poor bonding is the insufficient contact temperature of the melt when it reaches the metal surface during the injection molding process [1,6]. Nevertheless, considerable differences in leakage rates of about one decade between PA6/metal hybrids and PA6-GF30/metal hybrids can be observed, where the PA6-GF30/metal hybrids exhibit the comparatively higher leakage rates. Since in the case of the glass fiber reinforced variant can be assumed to have a more elastic deformation and recovery behavior at identically applied testing pressure and thus the

elasticity-related compensation of the pressure change caused by leakage during the measurement phase of the differential pressure test should be comparatively higher, these differences are almost certainly the result of the glass-fiber additive. Another indicator of this is that the differences in leakage rates occur despite an equal lack of adhesion between the two material combinations, Figure 9.

Navoor [31] investigated the existing test specimen geometry under identical process parameters on both polymers experimentally as well as numerically and found that the glass fiber content leads to a negative shrinkage in the cross-flow direction of the PA6-GF30 from the metal insert and thus to a gap formation, while the unreinforced PA6 shrinks onto the metal insert. In this case, the origin of gap formation in the glass fiber-reinforced variant is explained by the lack of bulging as a result of the strong restraint to shrinkage in the direction of flow. The leakage rate results obtained in Figure 8 seem to confirm these findings. With regard to the untreated variants, a reduction in the leakage rate can only be observed for the pretreated PA6/Al and PA6-GF30/Al hybrids, Figure 8. In the case of the pretreated PA6/Al hybrids, the leakage rates are below $8.33 \cdot 10^{-3} \text{ mbar} \cdot \text{l} \cdot \text{s}^{-1}$ and 0.5 ml/min respectively, making them watertight compared with the demanding conventional maximum permissible air leakage rates according to [8]. If this effect were due to the nanostructures

shown in Figure 7, a similar effect should be detectable with the pretreated PP/Al hybrids. While the maximum pull-out force increases by a factor of 5.5 for pretreated PA6/Al hybrids and even by a factor of 23 for the pretreated PA6-GF30/Al hybrids, it remains constant for the pretreated PP/Al hybrids. Based on these observations, it could be inferred that the nanostructures

of the aluminum in the case of the PP/Al hybrids were not sufficiently filled with melt during the injection process. However, the higher switchover melt pressure of PA6-GF30 (Table 4) during processing indicates a comparatively faster increase in viscosity as a result of nucleation accelerated by the glass fibers [32].

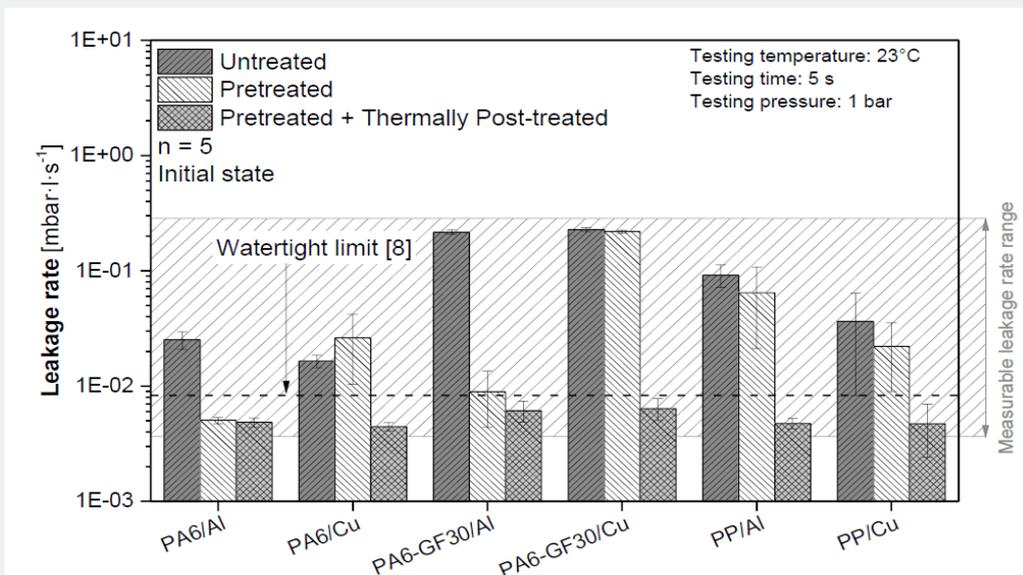


Figure 8: Leakage rates of various polymer-metal combinations measured with the differential pressure test in the initial state before temperature cycling test; mean values from five measurements including their standard deviation.

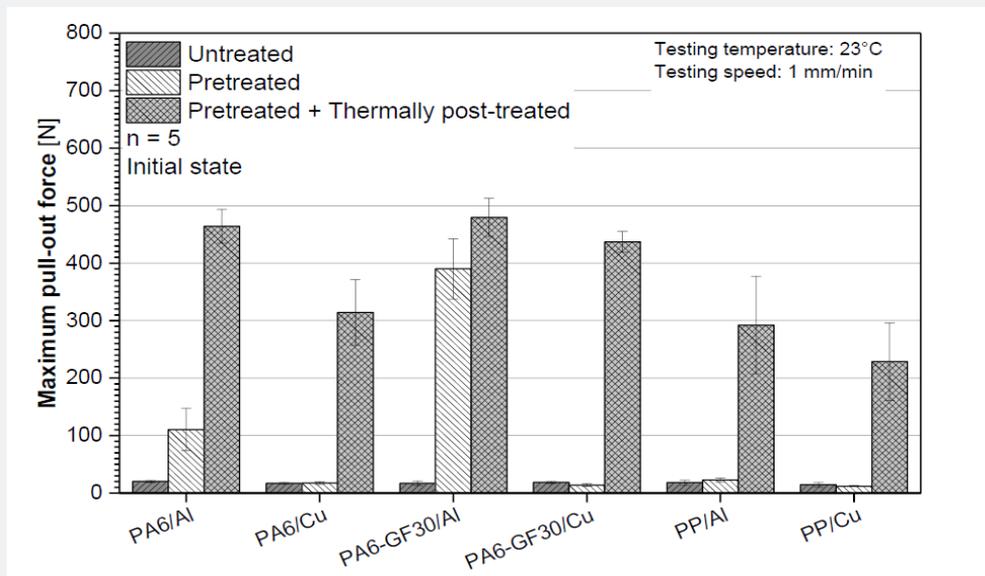


Figure 9: Maximum pull-out force of various polymer-metal combinations in the initial state before temperature cycling test; mean values from five measurements including their standard deviation.

Therefore, it should be possible to realize at least identical penetration depths in the nanostructures produced and thus comparable tightness or adhesion when using PP for overmolding. While the authors in [5] use the nanostructures generated by HWT for micromechanical interlocking between aluminum

and PBT-GF30 at a mold temperature of 130°C, the generated structures should be questioned with respect to their suitability for micromechanical interlocking, at least from the aspect of near-series processing. Due to the increased pull-out forces as well as the improved tightness properties of the pretreated polyamide/

aluminum hybrids, it must be assumed that these effects are due to chemical [22] or physicochemical bonding, for instance formation of hydrogen bonds as one possible form of interaction [19,20]. The types of interactions just mentioned are also possible in principle due to the anhydride functional groups and the -COOH groups in the adhesion-modified PP [21]. In previous studies [21,24,29], the adhesion-modified olefins are always treated in the minute range at temperatures above 190°C. This ensures reactivity and furthermore migration of the MAH towards the metal surface [24]. Since a high cooling rate and thus a low contact temperature can be assumed for the injection molding under the given molding conditions, it is highly probable that only a few of these functional groups with sufficient reactivity are located in the interfacial region between PP and Al.

The remarkable increase in the maximum pull-out force of the pretreated PA6-GF30/Al hybrids compared to the unreinforced variant was already observed by Amend et al. [33] and could suggest additional interactions between organic functional groups from the glass fiber surface [28] and the aluminum surface. According to Lucchetta et al. [9], a mechanical anchoring of the glass fibers may also contribute to this effect.

All injection molded polymer/copper hybrids exhibit gross leakage as well as lack of adhesion in the interface. Although hydrogen bonds between the amide groups and the oxidized copper surface are possible due to the reactive oxide layer present in the case of untreated specimens, these reactions probably occur preferentially with hydroxide layers [22]. In addition, it is conceivable that the contact temperature at the interface is even lower compared to the polyamide/aluminum hybrids due to the higher thermal conductivity of the copper. The results presented in Figure 8 & Figure 9 indicate that full-faced contact between metal and polymer can also be achieved with the aid of intrinsic functional groups of polymers and, in some cases even native, oxide or hydroxide layers on the metals. In addition to full-faced micromechanical interlocking and full-faced bonding, this is a third bonding principle for achieving high media-tightness which is likely to be of particular interest in the conductor industry.

With regard to the results obtained from the thermally post-treated PMHs, a significant improvement in tightness and adhesion properties can be observed for all material combinations except polyamide/aluminum, for which the interfacial bonding potential has already been improved as a result of HWT and has obviously improved a maximum. While the subsequent partial melting of the interfacial region in the case of the PP/metal hybrids causes a chemical reaction of the functional groups from the MAH with the metal surfaces, namely with the oxide layer on the copper surface or the hydroxide layer on the aluminum respectively, in the case of the polyamide/metal hybrids the formation of further physicochemical [16] and/or chemical bonds can be assumed [22]. Since the nano structuring of the inserts by means of HWT only showed a positive effect on tightness and adhesion

properties in the case of the polyamide/aluminum composites, which moreover cannot be attributed with sufficient certainty to the micromechanical interlocking, it can be tentatively concluded that the thermal post-treatment is highly effective and more universally applicable in terms of manufacturing watertight [8] PMHs, so that time-consuming and sometimes health-endangering metal pretreatments may not be necessary in the future. In the following, the hybrids are examined with respect to their thermal fatigue resistance to verify this.

After temperature cycling test

Figure 10 & Figure 11 show the results for the leakage rate and the maximum pull-out force after temperature cycling test. For the time being only those variants of PMH were tested which exhibited acceptable performance regarding tightness and pull-out force in the initial state. In the case of the exclusively pretreated PA6/Al and PA6-GF30/Al hybrids, a significant decrease in adhesion and an associated increase in leakage rate can be seen. This effect is much more pronounced in the case of the unreinforced variant, which initially seems to be due to the comparatively higher thermal expansion differences between aluminum and PA6, Table 1. The same phenomenon was observed in the comparison of the thermally post-treated PA6/Al and PA6-GF30/Al hybrids, where in the case of the unreinforced variant an increased number of gaps visible to the naked eye were found between the metal insert and the polymer. However, with regard to the thermally post-treated PA6-GF30/Cu hybrids, which continue to be watertight with regard to most demanding requirements [8], the theory of a causal relationship between the thermal expansion differences of the polymer/metal combination and the failure after temperature cycling fails. Since the CTE of copper is approx. 25% smaller than that of aluminum (Table 1), the post-treated PA6-GF30/Cu hybrids should therefore fail similarly to the post-treated PA6-GF30/Al hybrids. Consequently, the respective thermal expansion difference of the polymer used to the respective metal cannot be the only sensitive parameter which leads to delamination and thus to leakage after temperature cycling. Emrich et al. [10], Brockmann [18] and Emrich [34] already reported on interfacial defects due to water diffusion.

One explanation for the cause of failure of the thermally post-treated polyamide/aluminum hybrids can possibly be found in the hydroxide layer on the aluminum surface created by HWT. Figure 12 shows the results from TGA measurements on an aluminum insert treated with HWT and an aluminum insert pickled with NaOH (until step 3, Table 3), as well as on copper and aluminum inserts cleaned with propan-2-ol only. At about 50°C, a mass constancy up to elevated temperatures for the copper and only a slight loss of mass for the aluminum sample treated with NaOH can be observed. This confirms that no water volatilizes in the case of the copper due to dehydration and only a small amount in the case of the pickled aluminum, whereas the HWT treated aluminum sample exhibits an ongoing mass loss due to

water release from the surface. In contrast, the untreated as well as the HWT treated aluminum samples exhibit a mass loss up to elevated temperatures of 300°C (Figure 12) which suggests a dehydration of the surface layers, the native (untreated) one as well as the specifically generated hydroxide layer (HWT). The temperature range discussed here correlates well with the values for the dehydration of Al(OH)₃, reported by Digne et al. [35]. Consequently, this dehydration may also occur during thermal

post-treatment, which in the case of the polyamide may lead to adsorption of the water diffused from the hydroxide layer due to its hygroscopic nature and subsequent hydrolysis reactions in the interface [30]. This explanation is plausible, since the discussed failure characteristics cannot be seen with regard to thermally post-treated PP/Al hybrids after temperature cycling due to the hydrophobic nature of polypropylene [21].

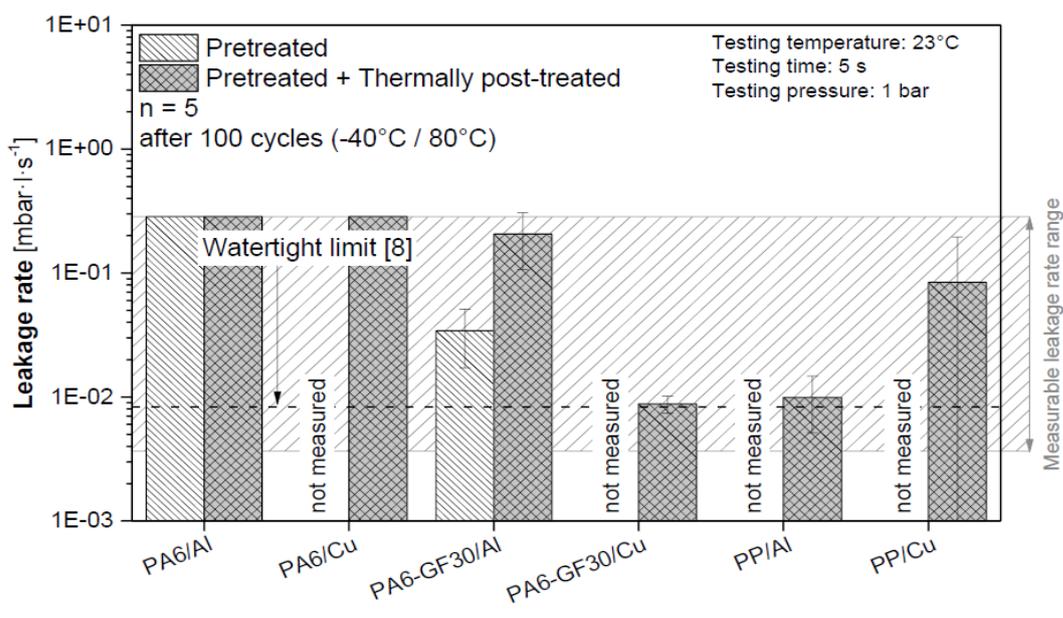


Figure 10: Leakage rates of various polymer-metal combinations measured with the differential pressure test after temperature cycling test (100 cycles from -40°C to 80°C); mean values from five measurements including their standard deviation.

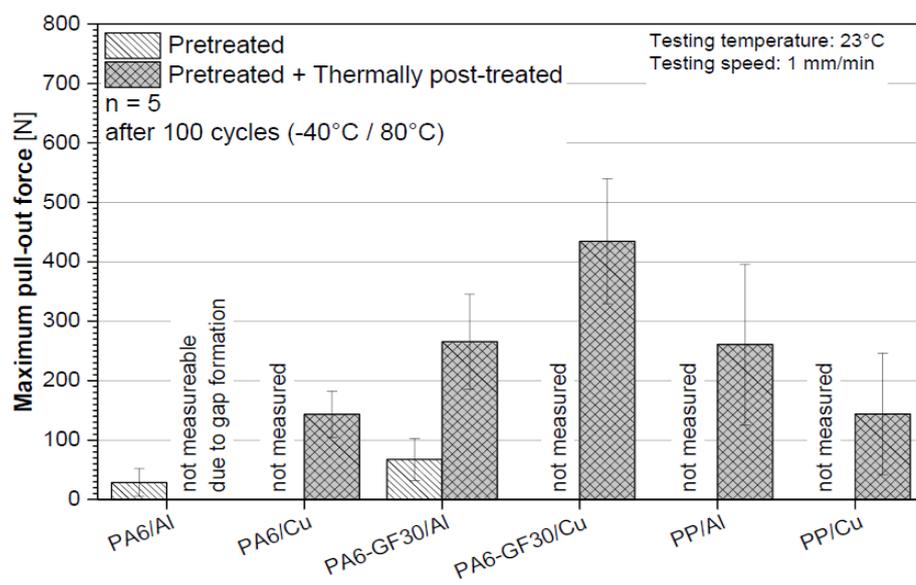


Figure 11: Maximum pull-out force of various polymer-metal combinations after temperature cycling test (100 cycles from -40 °C to 80 °C); mean values from five measurements including their standard deviation.

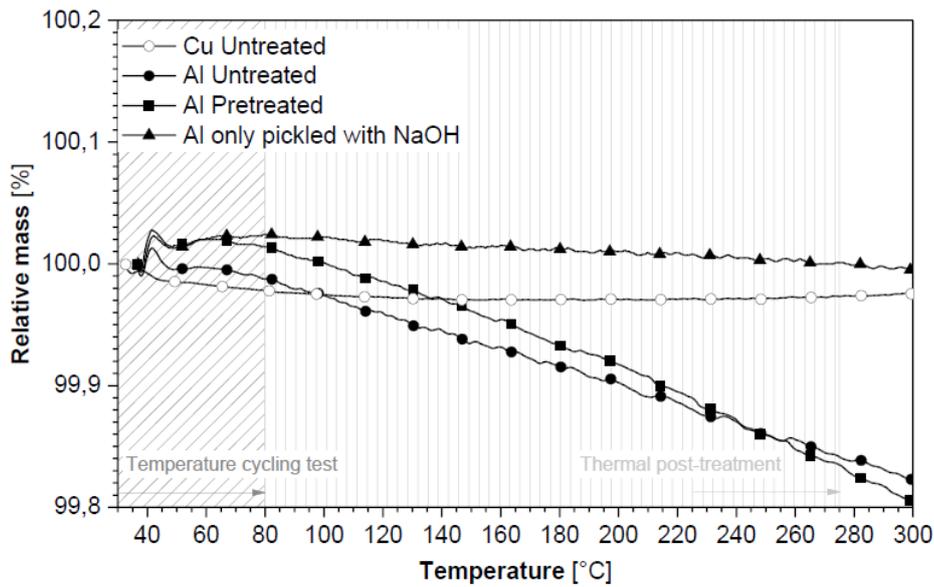


Figure 12: TGA thermogram of various metal inserts heated at 20 K·min⁻¹ in oxygen atmosphere.

Another explanation represents the irreversible damage caused by the competitive adsorption of water from the environment, which on the one hand substitutes the hydrogen bonds formed with the reactive aluminum surface, causing a physical weakening of the interface [34]. On the other hand, the native hydrogen bonds between the backbone chains of the polyamide itself are also substituted [36] by deposition of water molecules, resulting in a reduction of the entanglement [30] and thus an increase in volume [28,36]. The volume increase, often referred to as the swelling process, results in additional material movement at the interface during temperature cycling [34]. It can be assumed that both effects lead to delamination of the polymer and thus to leakage. However, the latter seems to play a primary role, since thermally post-treated PA6/Cu hybrids also fail

after temperature cycling test, although no thermodynamically unstable hydroxide layers are present here. While this is due to absorbed condensation moisture in the temperature cycling test, the glass fiber reinforcement in the case of thermally posttreated PA6-GF30/Cu hybrids prevents failure of this type due to the comparatively lower water absorption [28].

Figure 13 & Figure 14 show the leakage rate and the maximum pull-out force after thermal fatigue of the interfacial layer for various PMHs, normalized to their respective values in the initial state (Figure 8 & Figure 9). The normalized leakage rate and the normalized maximum pull-out force are calculated as follows:

$$q_{Norm} = \frac{q_{Cycling}}{q_{Initial}} \quad (1)$$

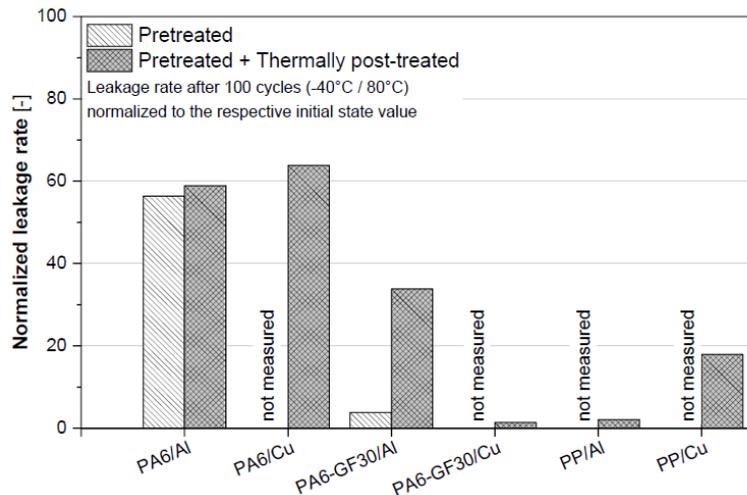


Figure 13: Leakage rate of various polymer-metal combinations after temperature cycling test (100 cycles from -40°C to 80°C) normalized to the respective initial value (Figure 8); only mean values were used for the required calculation variables.

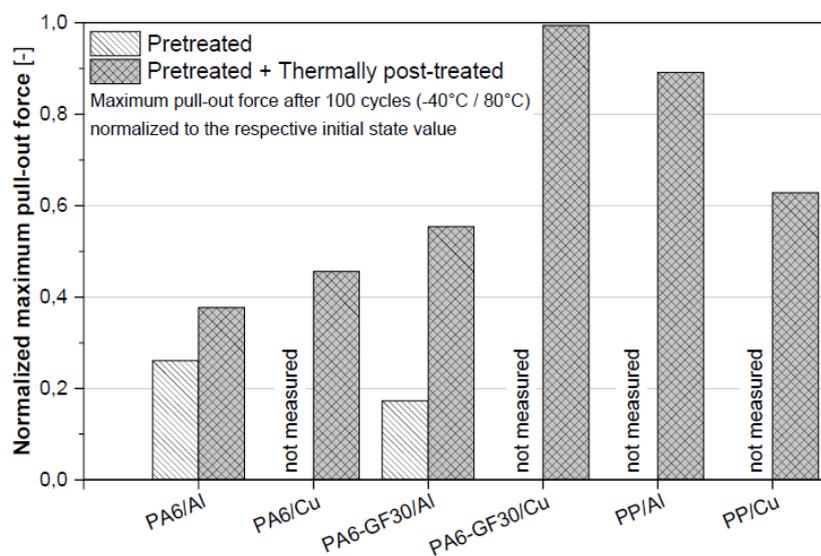


Figure 14: Maximum pull-out force of various polymer-metal combinations after temperature cycling test (100 cycles from -40°C to 80°C) normalized to the respective initial value (Figure 9); only mean values were used for the required calculation variables.

In the equation \dot{q}_{Norm} is the normalized leakage rate, $\dot{q}_{Cycling}$ the leakage rate after temperature cycling test, and $\dot{q}_{Initial}$ the leakage rate in the initial state. A high value of \dot{q}_{Norm} implies a considerable increase in the leakage rate due to thermal cycling and suggests poor long-term durability of the interface under consideration.

$$F_{Norm} = \frac{F_{Cycling}}{F_{Initial}} \quad (2)$$

In the equation F_{Norm} is the normalized maximum pull-out force, $F_{Cycling}$ the maximum pull-out force after temperature cycling test, and $F_{Initial}$ the maximum pull-out force in the initial state. A low value of F_{Norm} implies a considerable decrease in the maximum pull-out force due to thermal cycling and suggests poor long-term durability of the interface under consideration.

While the normalized leakage rate of the thermally post-treated PP/Cu hybrids is about 17.9 after the temperature cycling test, this value is only 2.1 for the thermally post-treated PP/Al hybrids. Similarly, the normalized maximum pull-out force for the thermally post-treated PP/Al hybrids is still 0.89 while the value for the thermally post-treated PP/Cu hybrids is only 0.63. Both parameters demonstrate the comparatively poorer long-term properties in the case of the thermally post-treated PP/Cu hybrids, which are very likely the result of catalytic degradation to the polypropylene in the presence of copper [37]. The results from DSC measurements under oxygen atmosphere on thermally post-treated PP/Al and PP/Cu hybrids shown in Figure 15 confirm the assumption of catalytic degradation to the polypropylene in the presence of copper during thermal post-treatment. In the case of the thermally post-treated PP/Al hybrids, a decrease in the oxidation induction temperature (OIT) of 2.7% can be observed on the sample taken near the interfacial region compared to the

sample taken from the polymer component. Similarly, this value drops by 8.6% for the thermally post-treated PP/Cu hybrids. In the present case, a reduction in OIT may be due to the catalytic effect of the copper on PP, but according to Frick and Stern [32], a change in the effect of the incorporated aging protection is also a possibility. Since the PP raw material sample has an identical OIT of 205°C as the near-interfacial sample of the thermally post-treated PP/Al sample, an altered or deteriorated mechanism of action of the aging protection due to the thermal post-treatment is unlikely. Thus, the reduced OIT of 194°C observed in the case of the thermally post-treated PP/Cu sample, both near the interface and in the polymer component, can be attributed to the catalytic effect of copper on PP. Since the OITs of all samples are below the processing temperature of the thermal post-treatment, it could be assumed that thermal oxidative aging already occurs during the thermal post-treatment. However, the OITs are assumed to be higher under atmospheric air, so degradation due to thermal post-treatment can be excluded.

In order to investigate the tightness properties of the promising thermally post-treated PA6-GF30/Cu variant once again with another measuring system, the test facility shown in Figure 4 was connected to a helium mass spectrometer type ASM340 from Pfeiffer Vacuum GmbH (Aslar, Germany). The results of the subsequently performed helium vacuum measurements are shown in Figure 16. Both the pretreated and untreated hybrids show values below a helium leakage rate of 10^{-6} mbar·l·s⁻¹ after temperature cycling test. Even if the testing time were extrapolated up to ten years, the measured leakage rate would still remain below the threshold value of 10^{-5} mbar·l·s⁻¹, which certifies long-term stable helium tightness [10], provided there are no noticeable aging effects in the polyamide. In addition,

no significant differences between the two variants can be found in the standard deviations. This could mean that the time-intensive and environmentally critical metal pretreatment is no longer necessary, if thermal post-treatment of the interfacial region is performed and only the thermal shock resistance of these post-

treated hybrids is considered. However, the standard deviation of the pretreated variant is slightly smaller, which could indicate a more uniform interface formation during thermal post-treatment due to a more uniform edge geometry of the pretreated copper insert.

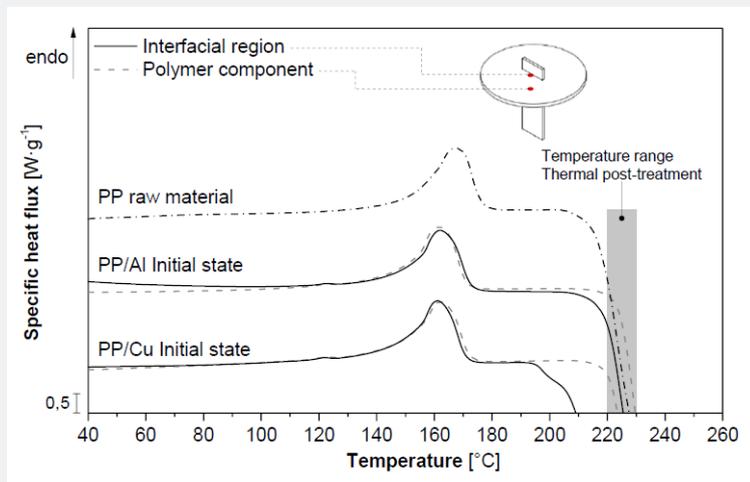


Figure 15: Degradation behavior of thermally post-treated PP/Al and PP/Cu hybrids at the interfacial region (solid line) and in the polymer component (dashed line) compared to the PP raw material (dash-dot line).

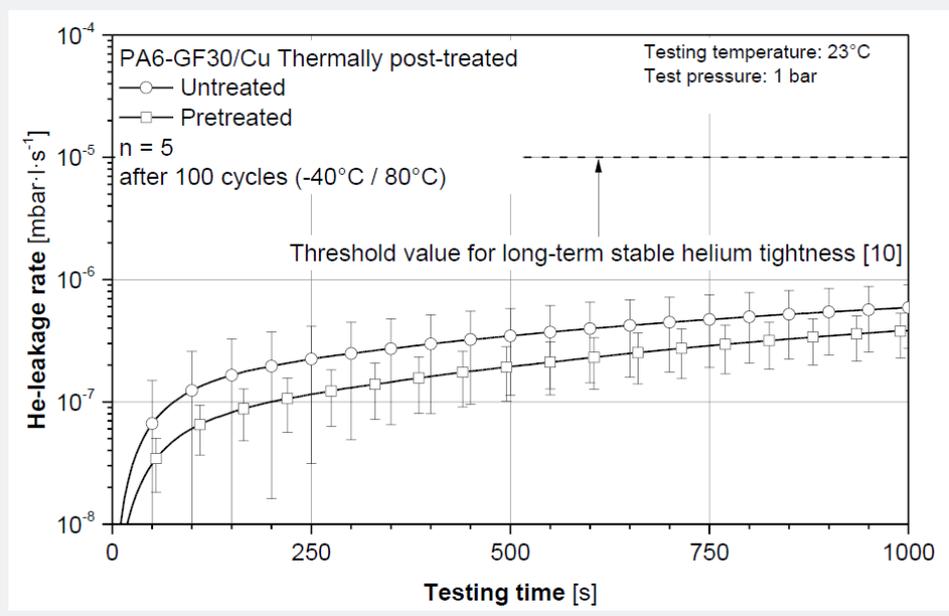


Figure 16: Influence of metal pretreatment on the measured He-leakage rate of thermally post-treated PA6-GF30/Cu hybrids after temperature cycling test (100 cycles from -40°C to 80°C); mean values from five measurements respectively including their standard deviation.

Conclusion

In the present work, a thermal post-treatment process has been investigated, which has been applied to PMHs made of technically relevant materials by means of assembly injection molding. The focus here was on improving media tightness with regard to temperature cycling, as also occurs in the later use of

such components. At the same time, a further bonding principle based on physicochemical and/or chemical bonds between reactive metal surfaces and organic functional polymer groups was investigated with regard to its suitability for ensuring long-term stable media-tightness. While the hybrids were characterized in their initial state and after temperature cycling

test by means of classical pull-out tests, the media-tightness was investigated analogously by means of differential pressure tests and, in a more specific consideration, also by means of the helium vacuum leakage measurement. The most important results of the study are listed below:

a. Thermal post-treatment of PMHs is suitable for improving their long-term stable media-tightness, but only under consideration of the selected bonding principle as well as material-specific parameters, such as the hygroscopic character in the case of polyamide or the copper-induced catalytic degradation behavior of polypropylene. Thermally post-treated PA6-GF30/Cu and PP/Al hybrids showed the most promising results. Comparative helium vacuum leakage measurements after temperature cycling test on thermally post-treated PA6-GF30/Cu hybrids with and without edge rounding at the inserts showed that there is the potential here to dispense with the insert pretreatment. From an ecological point of view, this would be a further advantage of thermal post-treatment in addition to the elimination of insert pre- or in-mold-heating. While the leakage rate of the PA6-GF30/Cu hybrids as well as the PP/Al hybrids after temperature cycling is only at the lower threshold value with respect to the maximum permissible air leakage rate for watertightness [8], long-term stable helium tightness (He-leakage rate $< 10^{-5}$ mbar·l·s⁻¹ [10]) could be demonstrated at least for thermally post-treated PA6-GF30/Cu hybrids. Since helium is the comparatively more critical medium with regard to leakage, the measurement resolution of the differential pressure tester and/or the threshold values found in the literature should be seriously questioned.

b. Condensation moisture from the environment plays a major role with regard to the long-term properties of thermally post-treated polyamide/metal hybrids after temperature cycling test. If the hybrids are thermally post-treated in the dried state, there is a demonstrable risk of subsequent moisture absorption up to the equilibrium water content. The results of the present study support the theory already reported by Emrich et al. [10], Brockmann [18] and Emrich [34] that moisture penetrates into the amorphous part of the polymer structure and beyond that (at least partially) into the interface. This results in swelling induced material movement, which eventually leads to pronounced gap formation (transverse flow direction) and the associated leakage. It was observed that a gap formation visible to the naked eye occurred in the thermally post-treated, unreinforced polyamide/metal hybrids, while this damage feature could only be detected once in the thermally post-treated, glass fiber-reinforced polyamide/metal hybrids. Since the glass fiber-reinforced variant exhibits a similar CTE in the transverse flow direction as the unreinforced variant, it can be concluded that moisture from the environment has a dominant influence in terms of media-tightness after temperature cycling. The results of the thermogravimetric investigations on aluminum inserts also indicate that the dehydration of native hydroxide layers or those produced by means of HWT already starts at temperatures

of approx. 55°C. This could explain the unexpected failure of thermally post-treated PA6-GF30/Al hybrids after temperature cycling test.

From a fundamental scientific point of view, further investigations should focus on the bonding principle that has been proven effective in terms of thermal fatigue resistance. It is still not possible to make a clear statement about the types and quantities of bonds produced and their different contributions to the overall behavior. We suggest that the metal inserts of the thermally post-treated PA6-GF30/Cu hybrids pulled in the pull-out tests should be investigated using the spectroscopic methods which were used in [19,20,22] alone in each case. This could provide at least a rudimentary differentiation between hydrogen bonds and covalent bonds. Further applied research in the near future could address process parameter influences such as heating rate, temperature and protective atmosphere, on the property spectrum of thermally post-treated PMHs. In the long term, the integrability of the thermal post-treatment process into existing assembly injection molding processes should be studied and the transferability of the results obtained to more complex molded part geometries with a large number of metal inserts should be investigated.

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