Development of Joining Methods for Highly Filled Graphite/PP Composite Based Bipolar Plates for Fuel Cells: Adhesive Joining and Welding

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Abstract: Novel material solutions for bipolar plates in fuel cells require adapted ways of joining and sealing technologies. Safe and life time enduring leak-tight contacts must be achieved by automatic processes using reasonable joint forces. A proper sealing should manage such challenges as good ageing properties, excellent leak-tightness, high thermal conductivity and low gas permeability. Hence in this work, adhesive bonding and welding are considered as suitable methods, which can fulfill the requirements mentioned above. Adhesive systems seem to be more easy to apply than conventional sealing (hand layed-up rubber gaskets), e.g. with automatic dispensers. Additionally, the properties of an adhesive joint can be enhanced by a process-specific surface pre-treatment. This work focuses on the characterization of adhesive systems and their joints with highly filled graphite composites. Mechanical properties of the joints were characterized through lap-shear tests. The influence of ageing caused by humidity or acidic solvent at increased temperature on the bond line properties as well as neat adhesive was examined. The thermal conductivities of neat adhesives and through the entire joint were examined. In order to improve above conductivities, roughening, substrate pre-heating, post-curing and various contact pressure weights were applied. Plasma treatment was chosen as surface pre-treatment method for improving substrate's surface energy. An alternative to bonding is plastic welding, which does not require the use of sealants and adhesives. Based on former study of influences of filler content on the welding process using ultrasonic, hot plate or infrared welding, a welding method for joining the graphite compounds was derived.

INTRODUCTION

One of the major problems by assembling fuel cell stacks is ensuring tight sealing between both bipolar plates and preventing leakage of media from the inside of the cell. A proper sealing/joint of bipolar plates should exhibit sufficient mechanical properties, low gas permeability, resistance to humidity and increased temperature and provide high tightness. So far, O-rings or profile gaskets are mostly used for sealing in fuel cells, which require time-consuming hand lay-up and certain contact pressure for necessary tightness, which can be problematic for brittle, graphite-based bipolar plates. In those conventional sealing, gas feeding channels in the bipolar plates are still exposed to leakage [1, 2]. Therefore, there is a need to find a better sealing method in fuel cell stacks. Adhesive joining or welding seem to be suitable methods due to the possibility of automated processing and high tightness of the bonding between both components. Except of sealing, joints with good mechanical properties can be provided, so that the fuel cell stack can be assembled without necessary compression forces on bipolar plates, as it is needed in case of O-rings or gaskets.

Polypropylene (PP)/graphite-based composites seem to be promising materials for bipolar plates and are successfully applied in industry. However, PP is considered as a polymer with very poor adhesiveness due to its nonpolar properties. Therefore, a proper surface pre-treatment of every PP surface before joining is necessary. Plasma treatment was found as most effective method for improving polarity and adhesion of PP materials [3].

The production of material-locking plate joints using a plastic welding method offers the advantage that the assembly process is greatly simplified and the number of mounting elements and additional materials (sealing material or adhesives) can be reduced. In extensive welding tests, the welding behavior of conductive graphite compounds was analyzed using the ultrasonic, infrared, and heating element welding methods [4,5]. The welding quality of highly filled plastic composites is significantly influenced by the graphite content in the material as increasing graphite content reduces the polymer part available for welding. In addition, mechanical damping increases as well as the thermal diffusivity which all affects the weld formation. Thereby, the ultrasonic welding method is restricted by process limitations when joining composites highly filled with graphite. A major challenge for infrared and hot plate welding methods is the thermal conductivity of the composite materials. In order to establish a material-locking joint during the welding process, a defined melting of the material in the joining area is decisive. Due to of the heat flow into the parts to be joined, however, the needed welding temperature level is difficult to reach and to retain. Due to volumetric heating the entire joining part is heated up, which leads to deformation of the joined part wall when applying a joining force [4,5].

This work focuses on the development of bonding and welding methods, which will be suitable for an assembly of PP composite materials filled with high graphite contents used for bipolar plates in fuel cells, redox-flow batteries or housings in heat exchangers. The following properties of epoxy- and PUR based adhesive systems as well as adhesive joints were examined: mechanical properties (lap-shear test), thermal conductivity, gas permeability, and resistance to humidity and acidic solvents at increased temperature. Possible improvement of the properties of adhesive joints through surface pre-treatment (plasma, roughening, pre-heating of the surface) was preliminary tested. New idea of welding method for joining of graphite compounds will be presented.

EXPERIMENTAL PART

Materials

Three kinds of graphite based composites made based on PP/EPDM (70/30) blends with 65 wt.% (G65) or 80 wt.% (G80_1) expanded graphite Sigratherm® GFG600 and 80 wt.% (G80_2) synthetic graphite Timcal Timrex® KS300-1250/KS150 were used. The composites based on polypropylene (PP, Sabic PP579S) were melt mixed using the lab scale co-rotating twin-screw extruder Typ ZSK26Mc (Coperion) using a screw with a L/D ratio of 45. Compounding was performed at 200°C, a throughput of 10 kg/h and a rotation speed of 150 min^{-1} and compression molded to model bipolar plates with 200 x 220 x 3 mm^3. For lap-shear tests of adhesive joints aluminum samples (alloy 2024) were used.

Commercially available adhesive systems were selected based on requirements for fuel cell's and heat exchanger's working conditions:

- EP1 – 2K epoxy-based, filled with glass micro spheres
- EP2 – 2K epoxy-based, filled with glass micro spheres
- EP3 – 2K epoxy-based, in form of cast resin
- EP4 – 1K epoxy-based, filled with aluminum powder, thermal curing
- EP5 – 2K epoxy-based, low viscous
- PUR – 2K polyurethane-based.

In order to carry out welding tests, type 1BA tensile test rods were injection molded from a test compound consisting of the matrix material PP and the synthetic graphite (70 wt.%). Rectangular samples with the dimensions 15 x 10 x 4 mm^3 were prepared.

Test Methods

Lap-shear tests of single lap adhesive joints were carried out with the universal testing machine Zwick Roell 20 kN in accordance with DIN EN 1465. The samples were prepared with dimensions 100 x 25 x 3 mm^3 (graphite composites) and 100 x 25 x 1.6 mm^3 (aluminum) and stuck together with an overlapping length of 12.5 mm and a bondline thickness of 0.2~0.3 mm.

Thermal conductivity (TC, through-plane) was determined with the laser flash method on the device Netzsch LFA 447 at 25°C for neat adhesive resins and through the adhesive joints. Samples were pressed to cylindrical shape with diameter of 12.7 mm and thickness of 2 mm. Post-curing process was carried out at 70°C / 5hrs.

Dynamic contact angles were measured on the Data Physics OCA 35 XL device with two fluids: water, 1,5-pentanediol and diiodomethane. Surface tension was calculated based on the obtained contact angles using Owens, Wendt, Rabel and Kalble model.

Ageing of single lap joints (aluminum substrate) was carried out in 100% relative humidity at 60°C over 10 days. Ageing of neat adhesives (same cylindrical samples as in thermal conductivity measurement) was performed in 25%-sulfuric acid solution at 60°C over 48hrs.

Graphite composite surfaces were either treated with the vacuum plasma device TePla 440-G (O_2, 10 cm^3/min, 60 sec, 0.23 mbar) or roughened with sandpaper P150, or annealed at 50°C / 5hrs.

FTIR spectroscopy of the cured adhesive surfaces was carried out with the FTIR microscope Hyperion 2000 with Vertex 7 and Raman spectroscopy on Raman Microscope WITec alpha 300R.

RESULTS

The results of the lap-shear tests with the aluminum substrate are shown in Fig. 1. Depending on the kind of adhesive, an increase or decrease of the lap-shear strength after ageing was observed. Almost all lap-joints fractured adhesively, except of EP1, where without ageing mixed fracture (partially adhesively, partially cohesively within adhesive layer) and after ageing adhesive fracture were observed. The adhesive EP5 exhibit no resistance against humidity at increased temperature and lost his mechanical properties after ageing. EP3 and EP5 have limited resistance against ageing and the decrease of lap-shear strength is around -25%. EP1 and EP4 seem to withstand conditions approximated to those in fuel cells with satisfying results, e.g. changes of lap-shear strength < ±10%. The increase of lap-shear strength of EP1 and EP2 could be caused by post-curing or softening of the adhesive during ageing process. Lap-shear tests conducted with graphite composite materials with EP1 show without and after ageing the same strength results namely fracture within the substrate material due to the tensile and bending load. Hence, the adhesive joint exhibit higher strength than strength of substrate material and would be suitable for joining these graphite composites.

As summarized in Table 1, according to expectations neat adhesives exhibit low thermal conductivity (TC) in the range of 0.24 - 0.57 W/(m·K). The highest thermal conductivity has the adhesive EP4 (0.57 W/(m·K)) due to incorporated aluminum powder. The influence of post-curing on thermal conductivity of two adhesives (EP1 and EP3) was examined and only slight improvement was observed (+ 5-6%). Thermal conductivities measured through adhesive joints with graphite filled composites and several adhesives are also shown in Table 1. It was observed, that the thermal conductivities through the joint have values between the thermal conductivities of substrate and neat adhesive. Generally, higher thermal conductivity through the joint can be reached with adhesives having higher conductivity. The differences in thermal conductivity through the joints between adhesives EP3 and EP4 with the composite substrates G80_1 and G80_2 can be explained through the thicker adhesive layer when using the adhesive EP4. When increasing the pressing weight during the curing phase of the joints, the thermal conductivity through the joint improved as shown on the sample of G65. Joints made of adhesives with higher thermal conductivity and substrates with lower conductivity result in higher conductivity through the joint than joints made of adhesives with lower conductivity and substrates with higher conductivity.

The influence of roughening or pre-heating or both of the substrate surfaces on thermal conductivity was examined with the composite materials G65 and G80_2 combined with the adhesive EP3. When using G65 no improvement of thermal conductivity through the joint was observed after these treatments. This could be caused by the relatively high porosity of the composite substrate surface, so that roughening has not much contribution to the aimed increase of the contact surface area between the adhesive and the substrate. Roughening of the surface of the G80_2 composite indicated an improvement of thermal conductivity through the joint by 22%.

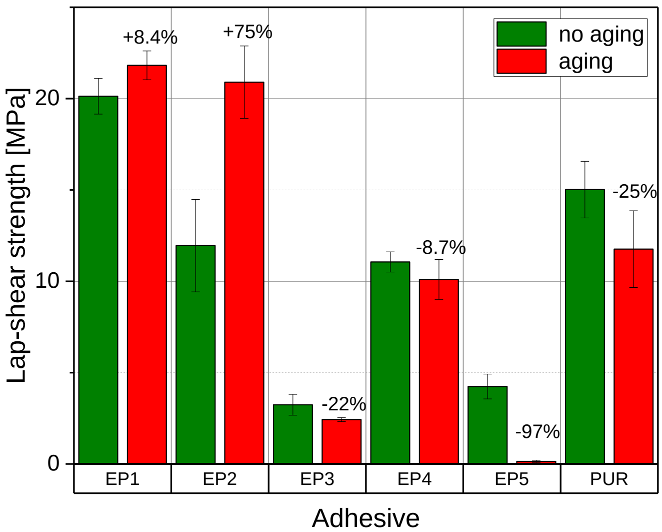

FIGURE 1. Results of lap-shear test with aluminum substrate without and after ageing (100% rel. humidity at 60°C, 10 days) [IPF].

In order to evaluate the changes on the composite materials by plasma treatment, dynamic contact angle measurements were performed on the untreated and plasma-treated surfaces of all graphite composites. Based on the contact angles, surface tensions and their polar and dispersive component were calculated (Table 2) A significant increase of surface tension can be seen with increased filler content in comparison with neat polypropylene, but all materials still exhibit non-polar surface properties. Vacuum plasma treatment was found as an good method to increase surface tensions of all materials, what is important for wetting properties. Interesting fact is that composites with high filler content could be activated more effective than the neat polypropylene, i.e. much higher increase of polar components of the surface tensions (see Table 2). Higher polarity of the surface can be crucial for adhesion between substrate and adhesive layer and significantly improve ageing properties of an adhesive joint.

The chemical resistance of the neat adhesive against 25%-sulfuric acid solution was tested. The adhesives EP1, EP2, and EP5 exhibit not sufficient chemical resistance. Significant changes on the sample surface (etching), in color, weight and dimensions of the samples after ageing have been observed.

TABLE 1. Thermal conductivity (TC) of neat adhesives, substrate materials, substrate/adhesive/substrate (s/a/s) and pressing weight [IPF].

Material	Adhesive	Pressing weight [g]	Adhesive layer thickness [mm]	TC adhesive [W/(m·K)]	TC substrate [W/(m·K)]	TC through joint (s/a/s) [W/(m·K)]
G65	EP3	360	0.3	0.42	8.7	3.2 ±0.7
		750	0.2			4.4 ±0.3
		1200	0.2			2.5 ±1.1
G80_1		600	0.2		16.4	6.7 ±0.2
G80_2		600	0.2		15.7	6.3 ±0.5
G80_1	EP1	600	0.4	0.24	16.4	2.2 ±0.4
G80_2		600	0.4		15.7	2.3 ±0.4
G65	EP4	600	0.4	0.57	8.7	3.5 ±0.2
G80_1		600	0.4		16.4	4.3 ±0.5
G80_2		600	0.45		15.7	5.2 ±1.7

In the corresponding FTIR-spectra of these samples, distinct difference before and after chemical ageing occurred, which indicate decomposition or strong oxidation of the adhesives. Adhesive EP4 seems to withstand the chemical attack and EP3 and PUR exhibit limited resistance against sulfuric acid. In this case, no changes in weight or dimensions were found, but EP3 and PUR exhibited some color changes of the sample after ageing. In the FTIR spectra of EP3 and PUR bands indicating oxidation were observed. When using EP4, the FTIR-spectrum of the surfaces indicated somehow lower oxidation of this adhesive. In Raman spectroscopy of EP4, the spectrum of aluminum sulfate was found on the sample surface, which was created through the contact of aluminum powder with sulfuric acid.

TABLE 2. Surface tensions of the graphite materials with polar and dispersive components [IPF].

Material	Surface tension [mN/m]		Polar component [mN/m]		Dispersive component [mN/m]	
	untreated	plasma-treated	untreated	plasma-treated	untreated	plasma-treated
PP SABIC 579S	29.8	37.5	1.4	8.9	28.4	28.5
G65	47.4	55.6	0	20.7	47.4	34.9
G80_1	44.5	52.8	0.1	16.4	44.4	36.4
G80_2	51.3	50.9	1.8	17.1	49.5	33.8

Based on the results of the practical welding tests and material analyses, a concept for hot pressing of the highly filled graphite compounds at the IKV was derived and validated in an initial feasibility study. The thermal properties of the material can be used specifically for heat input by heating the joining area completely through contact with a heating element (see Fig. 2). At the same time, a joining force is applied so that the heating and joining phase do not run separately from each other as in infrared or hot plate welding method. The graphite filler prevents the melt from sticking to the heating element.

A constructive encapsulation of the melt is used to prevent undesired flow of the melt. As a further decisive process parameter compared to hot plate or infrared welding, the joining force can be significantly increased. Initial tests with graphite based polypropylene composite with 70 wt.% of synthetic graphite have shown promising results, although the fracture does not run along the joint interface in the case of mechanical failure.

This indicates that the base material strength is reached. Further tests are required in order to be able to evaluate the hot pressing process. In this context, a vario-thermally temperature-controlled joining tool is developed, which allows controlled cooling of the melt after a certain joining time.

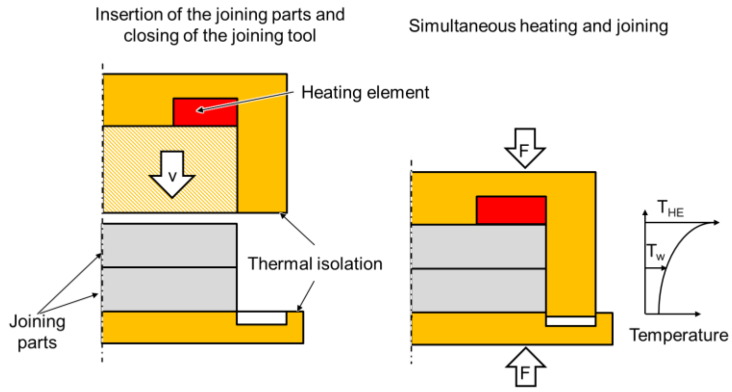

FIGURE 2. Schematic illustration of the welding of highly filled graphite compounds [IKV]

SUMMARY

Commercially available epoxy and PUR based adhesive systems were tested regarding the operating conditions in fuel cells, redox-flow batteries and heat exchangers. Depending on the material class of the adhesives, incorporated fillers and curing conditions, the adhesives exhibit different properties and can withstand differently the conditions in the named applications. Adhesive EP4 seems to fulfill all the application requirements due to sufficient mechanical properties and good resistance against humidity and chemicals at increased temperature. EP1 seems to be suitable for sealing and joining of bipolar plates in fuel cells and heat exchanger housings, where the durability in humid environment at increased temperature is required. The PUR based adhesive exhibits limited resistance against operating conditions in all applications and thus could be also considered as a suitable adhesive. Further investigation of all adhesives is needed.

Adhesives filled with conductive fillers (EP4) exhibit higher thermal conductivity than unfilled adhesive systems. The thermal conductivity through the joint is much lower than that of the substrate materials but significantly higher than that of neat adhesives. Joints with thicker adhesive layer show the tendency to lower thermal conductivity through the joint. It appears that the adhesive layer has a higher contribution to the thermal conductivity through the joint than the substrate material, taking into consideration the fact, that the adhesive layers have only thicknesses of 0.2~0.4 mm and the substrates of ~0.85 mm on each side of the joint. When increasing the pressing weight during the curing phase of the adhesive or roughening of the substrate surface, the thermal conductivity of the joints can be improved.

Plasma treatment of the substrate surfaces, which represents a fast and efficient method, was shown to improve wettability and polarity of the surfaces of the composites with high graphite contents, which is crucial for high quality adhesive joints.

Due to the high thermal conductivity of highly filled graphite composites, joining by means of conventional plastic welding methods is a major challenge. A material-adapted joining process seems to be promising in order to realize a high-quality weld seam. In order to assess the suitability, further investigations are necessary. For this purpose, a suitable test piece is used, which allows leak tests and bursting pressure tests. In order to optimize the process control, a variothermal temperature control system is integrated into the joining tool.

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