Effect of organosilicate application on thermo-pressure bonding of metals and composites with thermoplastic matrix

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Abstract: *The paper deals with application of organosilicate sol-gel to improve the adhesion of overlapped joints of metallic non-ferrous alloy thin sheets and continuous fibre reinforced composites by heat and pressure. The organosilicate layer showed a significant increase in adhesion of EN AW 6082 T6 and AZ91 alloys to glass fibre reinforced polypropylene matrix composite.*

Keywords*: METAL – COMPOSITE JOINING, THERMO-PRESSURE BONDING, ORGANOSILICATE*

1. Introduction

The joining of metal and composite materials plays a key role in modern lightweight automotive body design. This process allows the mechanical properties of metals, such as strength and ductility, to be combined with the low weight and specific properties of composites, such as corrosion resistance or the ability to absorb vibrations. This integration of materials allows automotive engineers to optimise the body structure in terms of safety, energy efficiency and durability, while also achieving reductions in overall vehicle weight and emissions. [1 - 4]

Joints of metals and composites in the manufacture of lightweight and durable vehicles have found their application in various body parts, e.g. as:

- Hybrid frame construction: some vehicles use metal frames combined with composite panels to achieve higher strength and lower weight. These joints are often made by bonding or mechanical joining.
- Doors and hoods: Composite materials, mainly carbon fibre reinforced, are often combined with metal parts to reduce the weight of the door or hood while maintaining its strength and impact resistance.
- Floor panels: Some electric vehicles use composite floor panels bonded to metal frames, improving stiffness while reducing the overall weight of the vehicle.

Composite materials in terms of applicability in lightweight body design will be either thermosoftening or thermoset matrix and in terms of the reinforcing phase, long continuous fibres, which have a much higher reinforcing effect compared to short fibres, will be used in particular. [5 - 6]

High-strength fibres are the most suitable lightweight materials for the transmission and absorption of forces. The directional orientation of the fibres in the composite and their complete consolidation with the thermoplastic polymer allows for high structural strength solutions. Components can therefore be designed with small wall thicknesses.

Thermoplastic composites are produced and processed in solvent-free processes and allow for complete recycling cycles. In this way, it contributes to a sustainable industry that is friendly to climate change and uses natural raw materials efficiently.

Innovative thermosoftening prepregs made from highly flexible composite materials, organosheets consist of continuous fibres in a matrix of various engineering thermoplastics - polypropylene, polyamide 6, polyamide 66, polyamide 12, polycarbonate, thermoplastic polyurethane and polyphenylene sulphide. The reinforcing fibres are glass, carbon, aramid or natural fibres such as cotton, flax, jute and others. This combination of fibers and matrix gives the flat organosheets excellent strength and stiffness combined with extremely low weight. As a result, even complex components can be manufactured efficiently. [7 - 9]

Depending on the material thickness of the combination of fibers and thermoplastic polymers, composites can provide material properties varying from high flexibility to high stiffness. Compared to the individual materials of which they are composed, thermoplastic composites achieve higher specific strain energy absorption rates and are an ideal solution for applications that require dynamic properties at reduced weight.

This article discusses the potential application of organosilicates for thermoplastic joining of metals and composites with thermosoftening matrix in order to improve the adhesive surface properties of the materials. This is studied in terms of selected parameters such as surface roughness of these joints, their load-bearing capacity and dissipated energy at joint failure.

2. Materials and methods

The following materials were used for the research:

Metals:

- Aluminium alloy EN AW 6082 T6 (AlSi1MgMn), 1 mm thick sheet (hereafter Al).
- Magnesium alloy AZ 91, 2 mm thick sheet (hereafter Mg).

Composites (Fig. 1):

- polypropylene matrix composite reinforced with glass fibre, 1.5 mm thick organosheet (hereafter GF)
- polypropylene matrix composite reinforced with carbon fibre, 1,5 mm thick organosheet (hereinafter CF)

The melting point of the polypropylene matrix is 165°C.


a) CF b) GF

Fig. 1 *Appearance of composite samples*

Methodology of joint formation

To determine the adhesive bond strength of the metal and composite, adhesive bonds were formed by pressure and heat only, without adhesive. The function of the adhesive in this application is fulfilled by the thermosoftening matrix of the composite. A schematic of this type of bond is shown in Fig. 2. The materials (metal and composite) were overlapped and preheated to a temperature >165°C and compressed with a force of 90 N. The pressure of the preheated materials lasted for 2 minutes in the case of the glass fibre composite and 2.5 minutes in the case of the carbon fibre composite.

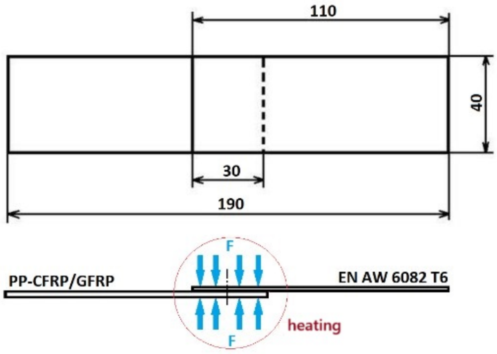


***Fig.** 2 Adhesive bond*

To strengthen the adhesion of the joint, an experimental organosilicate formulation was applied to the metallic materials (Al, Mg) to improve the adhesion between organic and inorganic materials. Using the formulation, it is assumed that the organic functional groups in the organosilicate will form a strong chemical bond with organic materials such as organic bonding agents in paints, adhesives or polymeric materials on the one hand, and on the other hand, by alkoxysilane linkages, they are able to bind firmly to materials of an inorganic nature (metals, alloys, minerals).

The technological procedure of organosilicate coating deposition was as follows: degreasing (alkaline degreaser, concentration 30g/l, 60°C, 10 min), rinsing, immersion in a solution of organosilicate preparation in demineralized water (concentration 250ml/l, 20°C, 10 min), hot air drying.

SEM and EDX analysis

Surfaces with the above layer were analysed using SEM. EDX analysis was performed to identify characteristic features on the surfaces.

Methodology of the roughness measurement

Roughness measurements were carried out according to EN ISO 21920-2:2021 before and after the application of the organosilicate layer with a Mitutoyo Surftest SJ-301 stylus profilometer (Mitutoyo, Japan). The following parameters were measured: Ra (arithmetical mean height of the assessed profile), Rz (maximum height of profile in the sampling length), RSm (mean profile element spacing) and the non-normalized parameter RPc (mean number of peaks per centimeter of sampling length). Five measurements of the above parameters were taken on each material, from which the average value was then calculated. The profilograms of each surface were also recorded with the Abbot-Firestone material ratio curve of the profile.

Methodology of testing the load-bearing capacity of joints

The material combinations tested were Al-CF, Al-GF, Mg-CF, Mg-GF, where the metal parts were in as-delivered condition, without any treatment or degreasing as well as with a layer of organosilicate (OS) to test the possible improvement of adhesion with the composite.

The load bearing capacity of the formed adhesive bonded joints was expressed in the form of maximum force at the moment of failure of the joint Fmax [N]. Forty joints of each material combination were formed and tested.

3. Results

EDX analysis of metal part surfaces

The surface of the Al material, its elemental EDX analysis in the original state and after the organosilicate layer deposition are shown in Fig. 3.

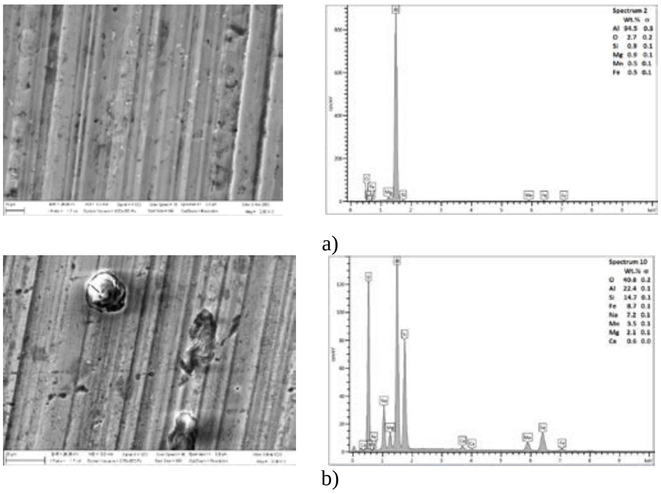


***Fig. 3** Surface Al (a) in initial state, (b) with organosilicate layer*

The surface of the Mg material, its elemental EDX analysis in the initial condition and with the organosilicate layer are shown in Fig.4.

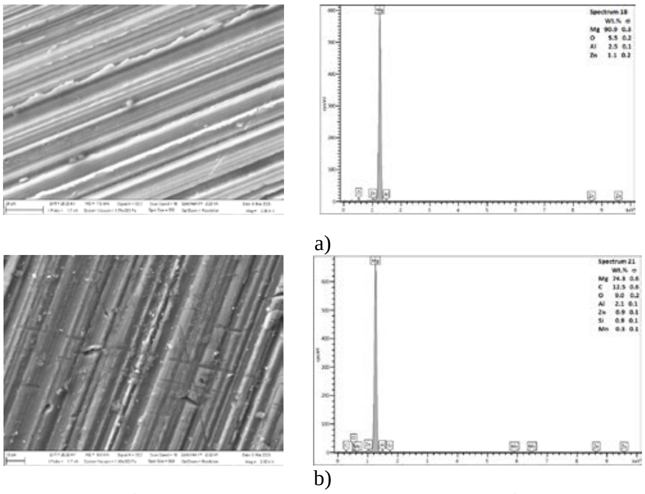


***Fig. 4** Mg surface (a) in initial state and (b) with a layer of organosilicate*

On the surface with deposited organosilicate layer for both Al alloy and Mg alloy, increased C and Si content appear in the EDX spectrum as evidence of the presence of an organosilicate layer of organic nature with organo-modified SiO_2 nanoparticles on the metal surface.

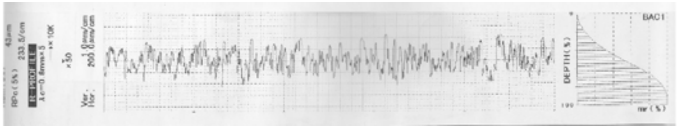
Surface roughness assessment

The resulting values of selected roughness parameters of metallic materials Al and Mg, determined by the stylus profilometer, are listed in Tab. 1 as the average of five measurements.

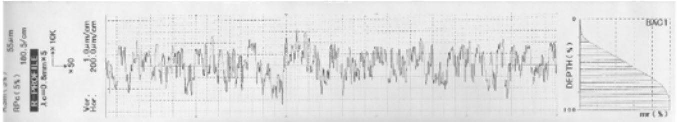
***Tab. 1** Average roughness parameters of Al and Mg*

	Ra [μm]	Rz [μm]	RSm [μm]	RPc [-/cm]
Al	0.38	2.20	43.6	231.98
Al OS	0.47	2.62	51.00	199.66
Mg	0.11	0.89	99.40	101.70
Mg OS	0.20	1.47	140.60	73.64

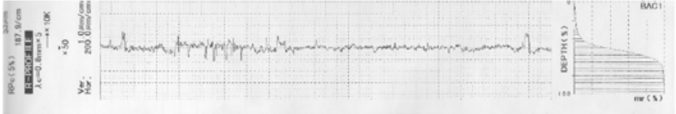
Fig. 5 shows the profilographs of the Al and Mg surfaces in original state and with the organosilicate layer applied.



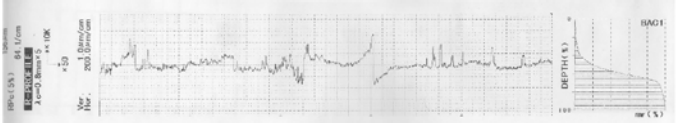
a) Al



b) Al OS



c) Mg



d) Mg OS

***Fig. 5** Surface profilographs*

Both materials were originally relatively smooth and roughness measurements confirmed this. The Mg surface showed less roughness Ra and Rz than Al. Tab. 1 shows the changes in surface roughness of each material when the organosilicate gel layer was applied. The vertical parameters of the initial roughness of both materials (Ra, Rz) increased slightly after the application of the organosilicate layer. The mean width of the profile elements RSm also increased slightly, analogously the number of peaks per centimeter of measured length decreased. This indicates that the gel layer of organosilicate filled in some of the valleys of the surface profile.

Load-bearing capacity of adhesive bonded joints

Tab. 2 shows the load-bearing capacity of adhesive joints of all material combinations, expressed in the form of the maximum force at the moment of failure of the joint Fmax [N] as an average of 40 measurements (joints) and the average value of the dissipated energy W [J] at the failure of the adhesive joints.

***Tab. 2** Load-bearing capacity and energy dissipated by joints*

	Fmax [N]	Standard deviation [-]	Coefficient of variation [%]	SW p-value [-]	W [J]
Al-CF	94	30.28	32	0.2815	0.01
Al-CF OS	83	25.25	30	0.3779	0.01
Al-GF	127	47.89	38	0.1294	0.02
Al-GF OS	4524	763.85	17	0.1020	1.39
Mg-CF	5001	1601.90	32	0.3782	1.16
Mg -CF OS	1982	630.52	32	0.2126	0.38
Mg -GF	1360	641.40	47	0.0550	0.22
Mg -GF OS	2432	718.71	30	0.1542	0.44

The above results lead to the following findings:

- Al-CF and Al-CF OS joints are not satisfactory, they were already breaking during clamping, even the application of organosilicate did not bring the expected improvement.

- The Al-GF joints are also not satisfactory, but the application of the organosilicate layer brought a significant improvement in adhesion and therefore also in load-bearing capacity with an average value of 4.5 kN (maximum up to 5.8 kN)

- The Mg-CF joints had the highest load capacity, up to 5 kN (maximum up to 8.5 kN), however, the application of organosilicate caused a drop in load capacity to 2 kN.

- The Mg-GF joints had a load capacity of 1.4 kN, with the organosilicate layer the load-bearing capacity increased to 2.4 kN.

The load-bearing capacity of the adhesive joints shows considerable variance within the tested set of 40 joints, despite the fact that the joints were formed under identical conditions, indicating the unstable nature of the adhesive bonding of the materials. The higher the maximum Fmax values were in each group of joints, the larger the variation range and standard deviation were in that group. The heterogeneity of the data can also be assessed by the coefficient of variation.

The coefficient of variation, also known as Pearson's coefficient of variation, is a statistical characteristic that informs about the relative dispersion of a set of data, that is, the degree of variability of values as a percentage of the arithmetic mean. It is calculated by dividing the standard deviation by the absolute value of the mean of the set and is usually expressed as a percentage for better understanding. If the coefficient of variation is <30%, we speak of a good variability characteristic; if it is more than 50%, the set under consideration is considerably heterogeneous. From this point of view, it can be stated that, except for Al-GF OS, the variability is significant for all other groups of joints, but does not exceed 50% and thus the data are not heterogeneous and can be further statistically processed.

Many statistical methods assume that the basic statistical population has a normal distribution (many real data sets do not have a normal distribution). If the normality assumption is not met, statistical method cannot be used. Normality tests, such as the Shapiro-Wilk test (SW test), are used to test whether a given population of data can be considered normal distribution. The Shapiro-Wilk normality test tests the validity of hypotheses:

H0: the data set has a normal distribution

H1: the data set does not have a normal distribution

The SW normality test was performed online, i.e. the data under consideration were copied and pasted into a commonly available online calculator. The result was a p-value, whereby the following applies:

- if $p < \alpha$, the null hypothesis is rejected at the α significance level in favour of the alternative hypothesis,

- if $p > \alpha$, the null hypothesis cannot be rejected.

In terms of p-value for the SW test, the results of the load-bearing capacity of all types of adhesive joints show normality at the significance level α=0.05.

Fig. 6 shows the appearance of the joint surfaces after failure.

Al-GF OS Mg-GF OS

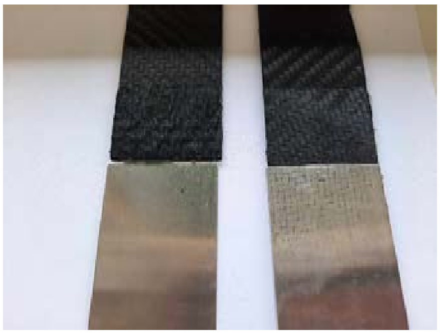


Fig. 6 *Appearance of adhesive joints after load-bearing capacity testing*

From Fig. 6 and actual observation of the joints after failure is clear that the failure of the joints was always adhesive. Only the impressions of the fiber orientation in the composite remained visible on the metal plates.

The results show that the organosilicate layer should only be used where it has been shown to improve the adhesion of the joints, i.e. in the case of joining both types of metal plates with the GF composite. The GF composite, due to the thickness of the glass fibres and their volume fill (47%,) contains a greater amount of free PP matrix which, when the heated composite is compressed, adheres better to the metal part. CF composite contains up to 51% fibers, so it has less free PP matrix to form the bond.

Conclusions

Based on the results obtained, the following information was found:

- The presence of organosilicate on the surface of both materials investigated, Al alloy and Mg alloy, was confirmed by EDX analysis by the increased C and Si content with organo-modified nanoparticles.

- The roughness after the deposition of the organosilicate layer on the surface of both materials reached an increased value for the parameters studied. This fact gives the assumption of an improved adhesion of the surfaces of the materials and thus the load carrying capacity in the application of the subsequently realized joints.

- Among the realized types of joints, the influence of the applied organosilicate resulted in an increase of adhesion in the case of joining metal plates with GF composite. For joints with CF composite, the application of an organosilicate layer is of no practical significance.

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