

The effect of surface treatment on the shear properties of aluminium-polypropylene joints manufactured by laser beam

Tamas Temesi^a, Tibor Czigany^{a,b,*}

^a Department of Polymer Engineering, Faculty of Mechanical Engineering, Budapest University of Technology and Economics, Muegyetem rkp. 3, H-1111, Budapest, Hungary

^b ELKH-BME Research Group for Composite Science and Technology, Muegyetem rkp. 3, H-1111, Budapest, Hungary

ARTICLE INFO

Keywords:

Aluminium
Polypropylene
Laser joining
Shear strength
Surface treatment

ABSTRACT

In this article, we evaluated the mechanical response of laser-joined EN AW-6082 aluminium alloy and polypropylene (PP) specimens under quasi-static and cyclic shear loading. In order to increase the strength of the joints, we formed grooves in the aluminium with laser ablation. We determined the effect of PP melt viscosity and heat generated during the joining process on the shear strength of the joints using three types of PP with different melt viscosities. In order to influence the adhesion between the apolar polypropylene and the aluminium, we also treated some PP specimens with maleic anhydride (MA) prior to joint formation. We found that by doing so, the quasi-static shear strength of the joints increased by 50% on average. Furthermore, when we engraved many grooves in the aluminium and treated the PP specimens with MA, the average failure cycle number of specimens could be increased by an order of magnitude.

1. Introduction

In today's energy crisis, low-density materials (such as plastics and aluminium alloys) are used more frequently in the industry, as these materials require less energy to produce and use compared to conventional industrial raw materials (steel and other metal alloys). The spread of components and structural elements made from low-density materials increased the need for joining techniques, with which same-material and so-called hybrid joints (made from materials with a dissimilar chemical structure, such as metal-polymer joints) can be formed [1,2]. One such process that is well suited for industrial applications is the laser joining method, in which the metal component is heated by a laser beam. The metal component then transfers part of the heat generated to the polymer material, which melts and wets the aluminium surface, and a material-made joint is formed between the metal and polymer components when the polymer solidifies [3]. In most related publications, the applicability of laser-joined structural materials used in the automotive, aerospace, or medical industries was evaluated [4,5]. In the modern automotive industry, efforts are made to standardise manufacturing processes and to use the fewest materials types possible in order to achieve a high degree of recyclability at the end of the vehicle's life cycle. One of the most common polymer materials used today is

polypropylene, certain properties of which can be tailor-made to suit industrial needs, therefore it is widely used in the automotive industry [6].

The proper preparation and treatment (cleaning, structuring) of the joining surfaces has a significant influence on the strength and load-bearing capacity of joints, regardless of the material used. When creating metal-polymer bonds by laser joining, only the polymer material is melted, thus adhesion (similarly to adhesion bonding) forms the joint at the metal-polymer interface [2]. There are several reasons why the surface of metals is usually prepared or treated and the surface structure is altered before a joint is created: by roughening the surface, adhesion, and thus the strength of the joint can be increased according to the theory of mechanical connection; by removing contaminants and water vapour, the molecular composition and structure of the joining surface can be adjusted, a stable oxide layer can be created; and the surface tension (wettability of the surface) can be changed [7]. Laser surface machining (or laser ablation) is widely used in industry to create micro- or even macroscale surface features on the metal surface into which the polymer material can flow or cling after solidification, forming a joint that is both shape-locked and material-made [8–10].

Hino et al. [11] have demonstrated that by structuring and preparing (using an alkaline mixture and then in nitric acid) the surface of EN

* Corresponding author. Department of Polymer Engineering, Faculty of Mechanical Engineering, Budapest University of Technology and Economics, Muegyetem rkp. 3, H-1111, Budapest, Hungary.

E-mail address: czigany@eik.bme.hu (T. Czigany).

<https://doi.org/10.1016/j.polymeresting.2022.107882>

Received 23 August 2022; Received in revised form 4 November 2022; Accepted 23 November 2022

Available online 25 November 2022

0142-9418/© 2022 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

AW-1050A aluminium, the strength of Al-PP bonds can be significantly increased. This is caused by the fact that mechanical roughening increases the size of the surface where shape-locked joints can form, while chemical preparation allows the formation of –COOH functional groups on the aluminium surface to which the PP base material can bond with hydrogen bonds. Heckert et al. [12] have demonstrated that by preparing the surface of EN AW-1050A aluminium with laser surface treatment, narrow but deep trenches can be formed. Joints made using the treated aluminium and PP had high strength and were gas tight, which made them suitable for packaging applications.

In the case of polymers, it is common practice to clean and degrease the surfaces to be joined, while the aim of surface treatments is to increase the surface area and the number of polar functional groups, thus the surface energy of the polymer. A simple and industrially applicable treatment method is to modify the chemical structure and composition of the polymer (for example with the addition of adhesion-promoting substances or molecules to the monomer) [13]. A widely used additive for modifying the properties of low surface energy polymers such as polyethylene and polypropylene is maleic anhydride (MA). Its positive effect on joint strength has been demonstrated in several publications for adhesive bonded [14,15], and hot-pressed aluminium-PP bonds [16,17], but its applicability and usefulness in laser-joined Al-PP specimens has not yet been analysed.

From the point of view of the applicability of aluminium-PP joints in the automotive industry, it is of particular importance to investigate and analyse the mechanical response of laser-joined structures under quasi-static shear loading, and to determine the resistance and durability of the joints under cyclic loading conditions. In some recent publications, joints with different metal-polymer material combinations have been subjected to fatigue testing (e.g. Refs. [18,19]), but the aluminium-polypropylene material pairing, which is of particular importance for the automotive industry, has not yet been investigated. Therefore, we determined the response (load-bearing capacity, durability) of laser-joined aluminium-polypropylene specimens under quasi-static and cyclic shear loading. We also investigated how the load-bearing capacity of the joints is influenced by the melt viscosity of the PP material, and by the amount of heat generated in the aluminium during the joining process. We further investigated how the laser surface treatment of the aluminium, and the chemical treatment (with maleic anhydride solution) of the PP specimens affected the strength of the joints.

2. Materials and methods

In our work, we used the alloy EN AW-6082, which is widely used in the automotive industry and in construction as a material for load-bearing structures. This alloy contains about 1% magnesium and silicon alloying elements. For our experiments, we obtained 2 mm thick, rolled aluminium specimens 80 × 20 mm in size, formed from sheet metal by laser cutting.

We used three different types of PP materials, differing in their melt viscosities: these were random polypropylene copolymers named Tipplen R359A, R959A and R1059A made by MOL Petrolkémia Zrt (Tiszaújváros, Hungary). We chose these materials because they allowed us to analyse the effect of three different melt viscosities without changes in material composition on joint strength. We manufactured 2 mm thick sheet specimens 80 × 80 mm in dimension on an Arburg Allrounder 420C 1000-290 (Arburg Holding GmbH + Co. KG, Lossburg, Germany) injection moulding machine. We determined the shear strength of each PP material with a shear test according to ASTM D732-10, for which we cut specimens 40 × 40 mm in size from the injection moulded sheets.

We determined the thermal decomposition properties of the PP materials using a TA Instruments Q500 (New Castle, Delaware, USA) thermogravimetric analyser (TGA). We cut out samples of the injection moulded polymer materials with a weight of 3–6 mg, placed them in a platinum sample holder and heated them from room temperature to

600 °C at a heating rate of 10 °C min⁻¹. The decomposition temperature was the temperature corresponding to five percent mass loss according to the related standard (EN ISO 358:2014). During the measurements, we used both atmospheric air and nitrogen purge gas to test the decomposition properties of the samples. The values of the melt flow index (MFI), shear strength and decomposition temperature of the PP materials are shown in Table 1.

The preparation or treatment of the aluminium surface has a significant influence on the load-bearing capacity of the aluminium-polymer joints. In order to investigate the effect of surface preparation, we structured the aluminium by laser engraving grooves into its surface using an SPI G4 (Trumpf GmbH & Co. KG, Germany) pulsed Nd:YAG laser with a wavelength of 1064 nm. We used a constant average laser power of 10 W, a pulse repetition frequency of 20 kHz, ten repetitions of the engraving process and an engraving speed of 5 mm s⁻¹ to manufacture the grooves. The values were determined based on results shown in one of our previous publications [20].

In order to determine the structure of these grooves, we performed optical measurements using a Keyence VHX-5000 optical microscope (Keyence Corporation, Osaka, Japan) on cross-sections of aluminium specimens that were polished on a Struers LaboPol type grinding machine. We also used a scanning electron microscope (SEM) (Jeol JSM 6380LA, Jeol Ltd., Tokyo, Japan) and an energy dispersive spectrometer (EDS) coupled to the SEM machine to investigate the cross-sections of aluminium-PP joints.

We used a Trumpf TruDiode 151 (Trumpf GmbH & Co. KG, Germany) diode laser with a maximum power of 150 W and a continuous wave laser beam to create the aluminium-polymer joints. We manufactured the joints with a simple line joining procedure, whereby the assembled specimens were moved under the laser beam at a specified speed (in a speed range of 0.75–3.00 mm s⁻¹, with 0.25 mm s⁻¹ steps). We placed the 80 × 80 × 2 mm polymer and the 80 × 20 × 2 mm aluminium specimens (Fig. 1) into a clamping fixture we designed ourselves, which was fixed onto a computer-controlled moving table. Prior to joining, we cleaned the surfaces of all specimens by placing them into an ultrasonic vibration bath filled with 99.5% pure methanol (Merck KGaA, Darmstadt, Germany) for 1 min.

We loaded the joints until failure with a quasi-static shear test according to EN ISO 4587. We performed the tests on a Zwick Z005 universal testing machine (UTM) at a shear rate of 2 mm min⁻¹ and a gripping distance of 30 mm. We mounted the specimens into a vise gripper suitable for testing overlapped joints mounted on the UTM, with its gripping jaws offset in order to match the shape and thickness of the overlapped joints, to avoid bending stresses on the overlapped joints during gripping. For the shear tests, we created 5 parallel specimens with each parameter combination. We calculated the strength of the joints as the ratio of the maximum shear force (load-bearing capacity) and the nominal joint area (20 × 20 = 400 mm²).

In addition to the quasi-static mechanical tests, we also performed cyclic (fatigue) shear tests on an Instron 8872 hydraulic material testing unit, with 5-5 test runs per parameter combination. In these tests, the specimens were loaded to failure using a test speed of 20 mm min⁻¹ (corresponding to a test frequency of 0.83 Hz) and a triangular displacement load with an amplitude of 0.2 mm (Fig. 2). This way, the shear force applied to the test specimens did not exceed 70% of the shear

Table 1

Certain mechanical and thermal properties of PP materials used in our experiments.

Type of PP	MFI (210 °C, 2.16 kg) [g cm ⁻³]	Decomposition temperature [°C]	Shear strength (according to ASTM D732-10) [MPa]
R359A	10.32 ± 0.27	251	5.30 ± 0.14
R959A	30.84 ± 3.05	245	4.74 ± 0.19
R1059A	44.61 ± 6.96	244	4.32 ± 0.20

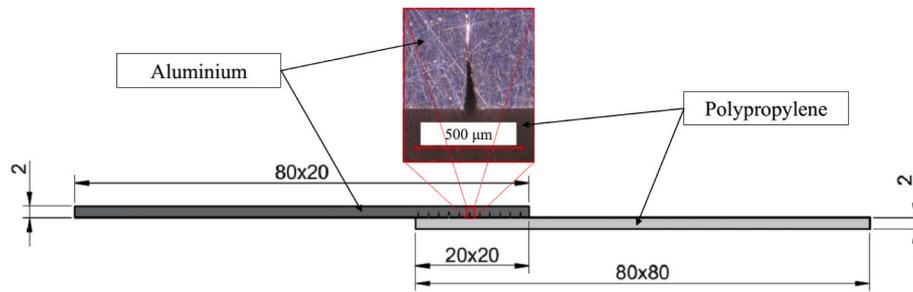


Fig. 1. Arrangement of aluminium and polymer specimens prior to joining, and the shape of grooves manufactured with laser engraving.

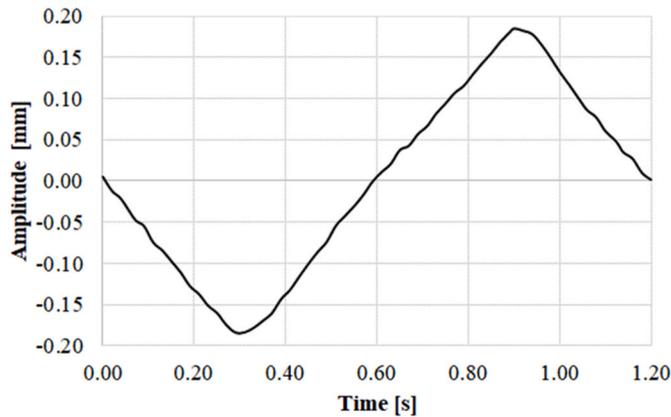


Fig. 2. Shape, amplitude and cycle time of the triangular displacement load function used in fatigue tests.

force that would cause failure of the joint with the lowest strength in quasi-static tests. We determined the mechanical response, and the effect of surface treatment under cyclic loading from the change in failure cycle number values.

3. Results and discussion

When starting our experiments, we assumed that the melt viscosity of the polymer material had a significant effect on the load-bearing capacity of the aluminium-polymer joints. For the experiments, we created 4 grooves (5 mm apart) on the surface of the aluminium specimens (the exact values were chosen based on results detailed in our previous publication [20]). The melt viscosity of polymer materials is also significantly affected by temperature. We determined the path of the laser beam so that it irradiated the aluminium specimen along a 14 mm long line, repeating the path five times. Since the length of the path (70 mm) was thus given, we were able to influence the temperature of the aluminium by varying the bonding speed (the irradiation time). In order to avoid degradation of the PP (which reduces the strength of the joints), we measured the temperature of the aluminium at different joining speeds. For this purpose, we used a K-type thermocouple assembly, with the sensor attached to the edge of the aluminium specimen, close to the region where the laser beam passed along the line path (trajectory) (Fig. 3).

The temperature values measured using different joining speed values are plotted as a function of time in Fig. 4. The measured values showed a periodic increase and then decrease regardless of joining speed. This was caused by the laser beam moving closer and then moving away from the spot where the temperature was measured, which resulted in wave peaks and valleys in the measurement curves. Furthermore, the maximum of the temperature values appeared later during the measurements, and also became higher as the joining speed decreased (and thus the irradiation time increased).

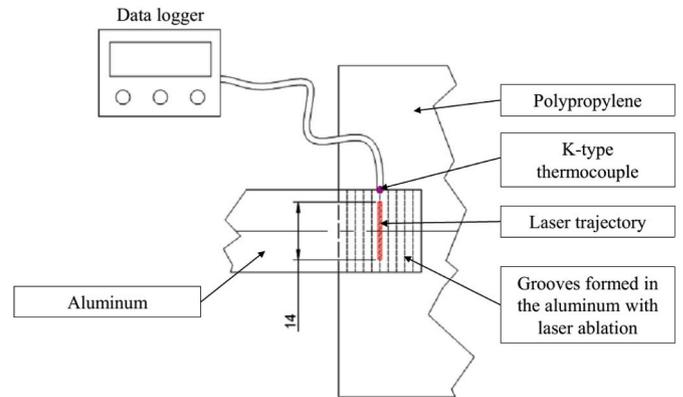


Fig. 3. Schematic of the measurement setup used to determine the temperature of aluminium. The temperature was measured at the point marked by the purple circle with a K-type thermocouple, with the laser beam heating the aluminium specimen along the red line, repeating the trajectory five times. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

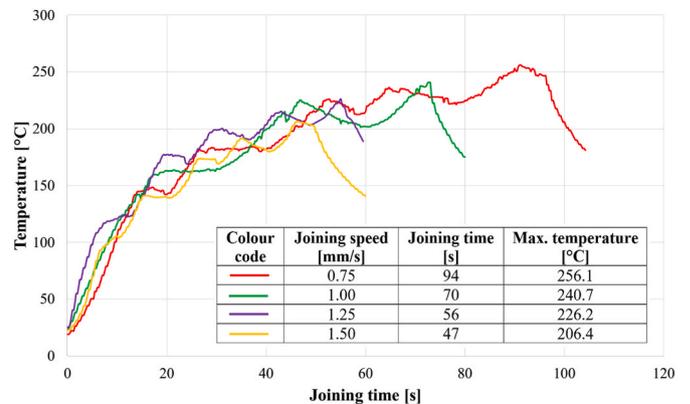


Fig. 4. The temperature variation of the aluminium specimen as a result of using different joining speed values, plotted as a function of joining time.

We determined the minimum joining speed value (leading to the highest heat formation in the aluminium) at which the “R1059A” PP, which has the highest melt flow rate (and is most susceptible to thermal degradation in terms of loss of mechanical properties) does not yet degrade. We determined the degradation properties of the chosen PP on a TGA apparatus at a heating rate of 10 °C min⁻¹ in air atmosphere. We chose atmospheric air as the test medium for these measurements because the Al-PP joints were formed in free air under ambient atmospheric conditions, thus the oxygen content of air may also play a role in the degradation of the PP material. According to the measurements (Fig. 5), the “R1059A”-type PP starts to degrade in air at around 240 °C.

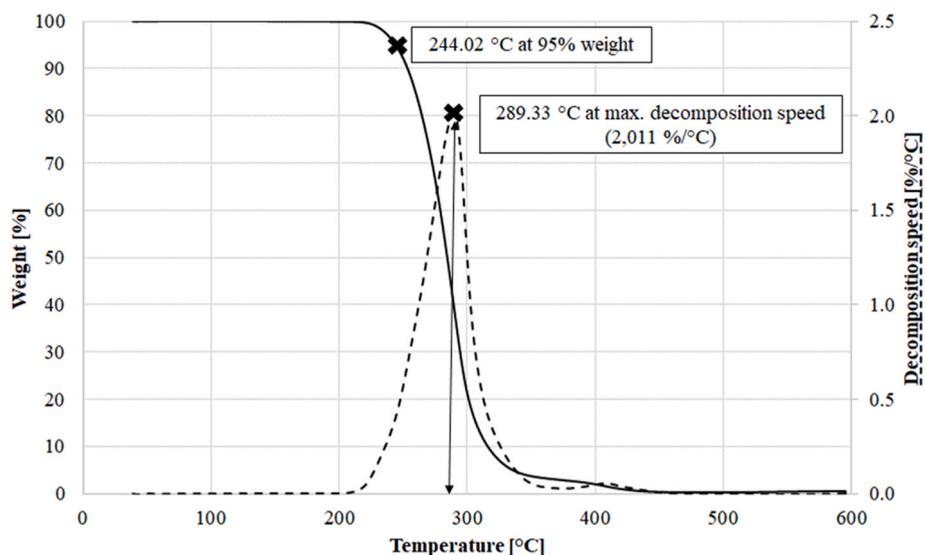


Fig. 5. Weight decrease and decomposition speed of „R1059A“-type PP measured in atmospheric air with TGA (heating rate: $10\text{ }^{\circ}\text{C min}^{-1}$).

Comparing this value with Fig. 4, it can be seen that at the joining speed of 0.75 mm s^{-1} the maximum temperature of the aluminium specimen exceeds $240\text{ }^{\circ}\text{C}$, so it is possible that the PP would degrade during joining at this joining speed. This was verified by TGA measurements on PP specimens cut from the joining surface of Al-PP joints (the heating rate was $10\text{ }^{\circ}\text{C min}^{-1}$). For these measurements, we used nitrogen as purge gas so that the degradation caused by heating the polymer under an atmosphere containing oxygen would not influence the results. This way, we were able to determine the thermal history of PP and the extent of its degradation. Fig. 6 clearly shows that the weight loss of the specimen cut from the Al-PP joints made with a joining speed of 0.75 mm s^{-1} starts at a temperature about $50\text{ }^{\circ}\text{C}$ lower compared to other samples cut out from specimens manufactured with a higher joining speed value. The maximum decomposition rate (the maximum value of the derivative weight change curve) is also at a lower value and presents at lower temperatures compared to other measured samples.

Based on these results, we determined that a joining speed higher than 0.75 mm s^{-1} is required to avoid degradation of the PP material when forming Al-R1059A PP joints. With this in mind, we carried out further experiments in which we created 4 grooves (5 mm apart) in the aluminium with laser surface treatment, as this was an ideal value in terms of the load-bearing capacity achievable, the time required for surface treatment, and the failure mode (cohesive fracture of PP) of joints, based on the results presented in our previous publication [20].

To form the joints between surface-treated aluminium and “R359A”, “R959A” and “R1059A”-type PP specimens, we started at a joining speed value of 0.75 mm s^{-1} and gradually increased it to 3.00 mm s^{-1} with 0.25 mm s^{-1} step intervals. We did not investigate the effect of higher joining speed values, as the load-bearing capacity of the joints made with all PP types was reduced to below 50% of the measured maximum load-bearing capacity.

In Fig. 7, the load-bearing capacity of the joints is plotted as a function of joining speed. The results show that both the melt flow index (MFI) and the temperature affect the strength of the joints. With the “R1059A”-type PP, the highest joint strength was obtained using a joining speed of 1.75 mm s^{-1} . At joining speeds lower than 1.00 mm s^{-1} , the decrease of joint strength was caused by thermal degradation of the material. At joining speeds higher than 1.75 mm s^{-1} , the melted material is less able to wet the aluminium surface due to the reduced heat input. In the latter case, it is logical to assume that there is also less flow of the melted material into the grooves. To verify this, we made images and EDS mapping with an electron microscope on cross-sections of specimens joined at different joining speed values.

We performed the EDS mappings by determining the type, percentage and distribution of atoms near the grooves and their immediate surroundings on specimens cut out from Al-PP joints. From the images and analyses obtained, we were able to deduce where the PP material was located on the surface. The SEM-EDS images (Fig. 8) showed that the melted PP filled the grooves well when the joining speed value was in the $0.75\text{--}2.00\text{ mm s}^{-1}$ range (Fig. 8a and b), but in many cases, we found bubbles (an example is shown in Fig. 8c) in the grooves next to the PP material in the $2.00\text{--}3.00\text{ mm s}^{-1}$ joining speed range. The reason for this was that the melted material was too viscous because of the high joining speed, and consequently the low heat input.

We obtained the highest joint strength for joints manufactured with the “R359A” and “R959A” PP types at a joining speed of 1.25 mm s^{-1} . The joint strength decreased at joining speeds higher than 1.25 mm s^{-1} , as the melted material was too viscous to properly wet the surface of the aluminium due to low temperature (low heat input) and low melt flow index (high viscosity). The rate of strength decrease was greater for the “R359A”-type PP (which has the highest melt viscosity of the three materials used in this study) than for the “R959A”-type PP: with “R359A”, a solid joint could no longer be formed at a joining speed of 3 mm s^{-1} and the strength decreased by more than 50% from the maximum value at a joining speed of 2.50 mm s^{-1} . With “R959A”, the average joint strength did not decrease significantly up to a joining speed of 2.25 mm s^{-1} , and above this speed the standard deviation of the

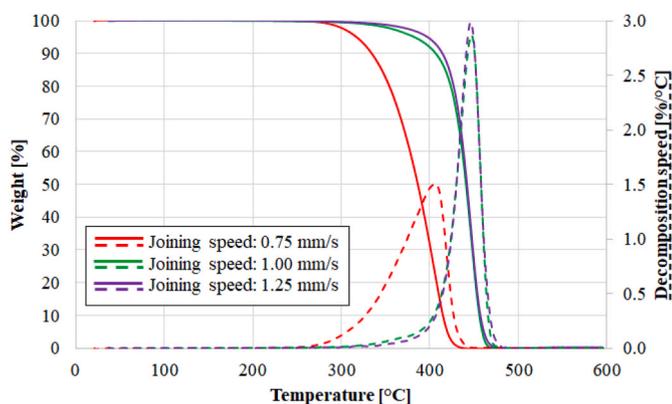


Fig. 6. Weight change (solid curves) and decomposition speed (dashed curves) of PP samples cut from the joining zone of Al-PP specimens manufactured at different joining speed values as a function of temperature.

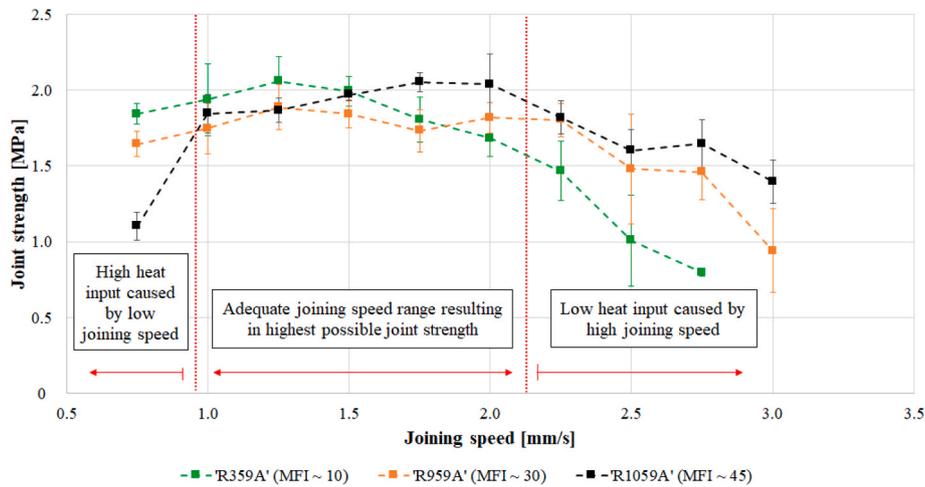


Fig. 7. Strength of Al-PP joints formed with PP materials of different melt flow index (MFI values in g cm^{-3}) as a function of joining speed. For the R1059A material, the large deviation of the first measurement point was caused by degradation of the PP due to high heat input.

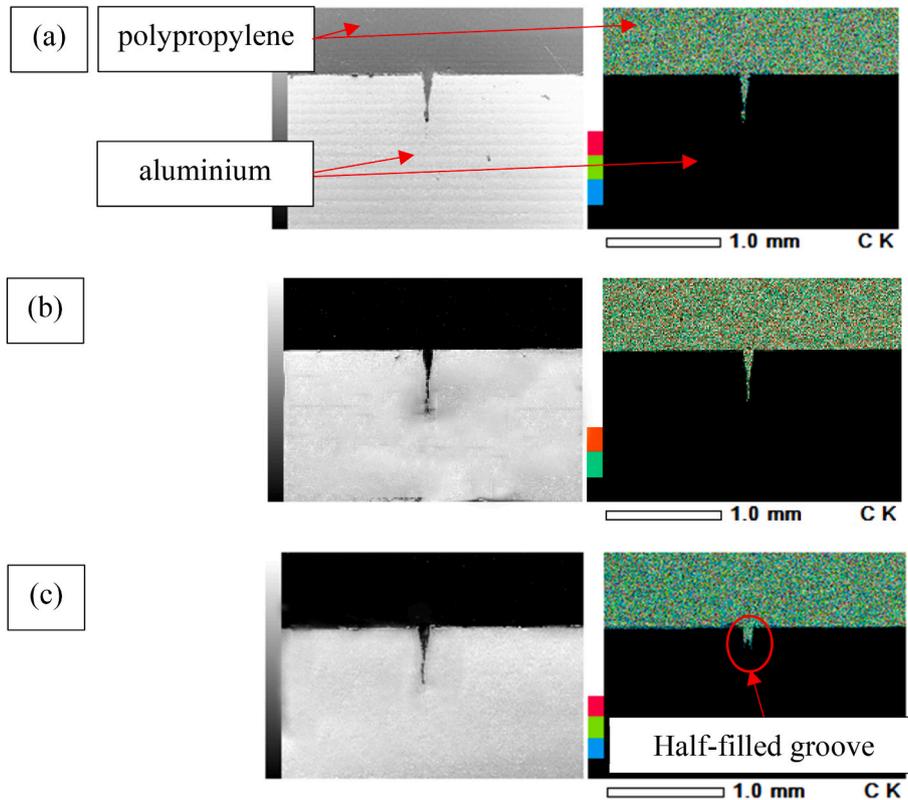


Fig. 8. SEM images and EDS maps of cross-sections of joints formed at different joining speeds ((a): 0.75 mm s^{-1} , (b): 1.75 mm s^{-1} , (c): 2.75 mm s^{-1}). On the left is an electron micrograph of the surface under investigation, and on the right is the distribution of carbon atoms on the same surface.

measured data values makes it difficult to evaluate and determine trends.

The shear strength of the joints formed did not exceed 2.1 MPa in any case, regardless of the type of PP used. Thus, the joining efficiency rate (JER) of the highest strength joints (calculated by dividing the measured joint strength values by the shear strength of the base material determined according to the ASTM D732-10 standard shear test, see Table 1) varied between 30 and 40%. One reason for this may be that during the shear test of the joints, the low stiffness PP specimen deforms under load, moving out of the shear loading plane. The joint zone is then subjected to additional bending and torsional loads, which causes the joints to fail under small load. The effect of this can be influenced and

reduced by modifying the shape of the specimens and the joining zone and the method of gripping during loading. Another possible reason for the low joining efficiency rate is the apolar nature of PP, which prevents the van der Waals interaction between aluminium and PP. This can be influenced by optimising the parameters of laser surface treatment in order to increase patterning of the surface and form more structures into which the melted material can flow (thus forming more shape-locked sites) and by mixing adhesion promoting additives (e.g. maleic anhydride) into the polymer.

Based on our experiments, we have shown that the melt flow index (melt viscosity) of the PP material does not significantly affect joint strength when the appropriate joining speed range (heat input range) is

chosen, and the grooves created in the aluminium can be filled by the melted polymer. Thus the joining process can be sped up (to further suit industrial needs) by using a material with higher flow rate (a lower average molecular weight), provided that this does not significantly affect the strength and mechanical properties of the PP base material (and thus the Al-PP joint).

3.1. The effect of surface treatment of PP with maleic anhydride on the strength of Al-PP joints

Based on our experiments so far, we have shown that it is fairly easy to create Al-PP joints by laser joining: by choosing the joining parameters right, joints with acceptable strength can be formed, without the need to compress the parts together during the joining process, or any post-joining treatment steps. However, in order to obtain a high strength joint, the surface of the aluminium must be treated (for example by engraving a large amount of grooves on the surface), because the strength of the joint manufactured with apolar PP in itself can only be influenced by increasing the amount of shape-locking sites into which the melted PP can flow. This is necessary because PP macromolecules do not contain atoms of high electronegativity that can form high strength, chemical adhesion-based bonds (van der Waals or dipole-dipole interactions) with molecules in the polar oxide layer of aluminium.

There are a number of methods and processes that can be used to increase the adhesion between the joined parts, and thus the strength and load-bearing capacity of the material-made joints. One such method is the use of compatibilizers, which can be dispersed in the polymer material during the manufacture of components or applied to the surface in the form of a solution or suspension before the joint is formed. Several publications have already demonstrated that maleic anhydride (MA) is a compatibilizer that is excellent for thermoplastic polymers and for coating fibre reinforcement materials, with a significant effect on the fibre-matrix adhesion (e.g. Refs. [21,22]). This is because MA is a highly reactive polar compound due to its chemical structure, with a total of six non-bonding electron pairs of three high electronegativity oxygen atoms (see Fig. 9), which can form strong secondary interactions or even primary chemical bonds. MA can, under the right conditions, attach to the functional groups of polymers by primary chemical bonding or can even be incorporated as a functional group on the molecular chain by grafting.

We investigated how the treatment of PP with maleic anhydride affects the strength of Al-PP joints. Since a PP grafted with MA of the make and type used in our previous experiments was not available, we decided to treat the surface of the PP sheets with a MA solution. For this purpose, a saturated solution was prepared by dissolving MA in acetone on a heated magnetic stirrer. We chose the "R359A"-type PP for these experiments, as it had the highest melt viscosity and produced the Al-PP joint with the highest strength. We also laser engraved grooves in the aluminium specimen, with different groove numbers and spacing (0

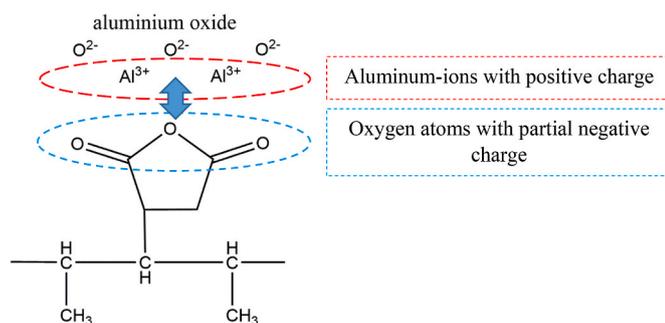


Fig. 9. A possible attachment of the maleic anhydride molecule to the PP chain and the formation of an ion-dipole bond between the highly polar oxygen atoms of MA and the aluminium ions in the aluminium surface oxide layer.

trench, 4 trenches 5 mm apart, 5 trenches 2 mm apart, 11 trenches 2 mm apart) in order to study the effect of these surface treatment parameters. Before joining, the aluminium and PP specimens were degreased in an ultrasonic vibration bath, by immersing them in methanol for 1 min, and then the MA solution was applied to the PP specimens using a brush, leaving 0.10 ± 0.02 g MA on the surface after the evaporation of the solvent. As a reference, we also created joints where the PP sheet was not treated with MA prior to the formation of the joint. The joints were formed at a joining speed of 1.25 mm s^{-1} , as we produced the joints with the highest average strength with this speed value in our previous measurements (Fig. 7).

When the polypropylene and the MA applied onto its surface are in the melt state, the MA molecule can bond with a tertiary carbon atom of the PP chain by opening up the unsaturated double bond in the MA ring. In doing so, the spatial position of the MA molecule is locked so that the oxygen atoms with high electronegativity are facing outwards from the main chain of the PP. If such a molecule is formed, a strong dipole interaction between the aluminium oxide layer (which most often contains Al_2O_3 and $\text{AlO}(\text{OH})$ molecules) and the PP-MA compound can be created (see Fig. 9). We found that treating the surface with MA increases the strength of the joints by at least 50% (compared to the reference joints not treated with MA, Fig. 10), regardless of the surface texture (number and distance of grooves in the aluminium).

Liu et al. [23] compounded different amounts of MA into isotactic PP and joined the PP-MA compounds with aluminium foils using direct melt bonding. They found the same strength amplification phenomenon when a certain amount of MA was used. Based on the three dimensional reconstruction of the joint interface, they concluded that the phenomenon is caused by a change in the molecular structure of the PP-MA compound, as they observed a "soft layer" with decreased crystallinity and molecular weight near the joint interface. They also theorised that carboxylic acid ($-\text{COOH}$) groups can also form as a result of interfacial chemical interactions between the oxide layer of the aluminium and MA

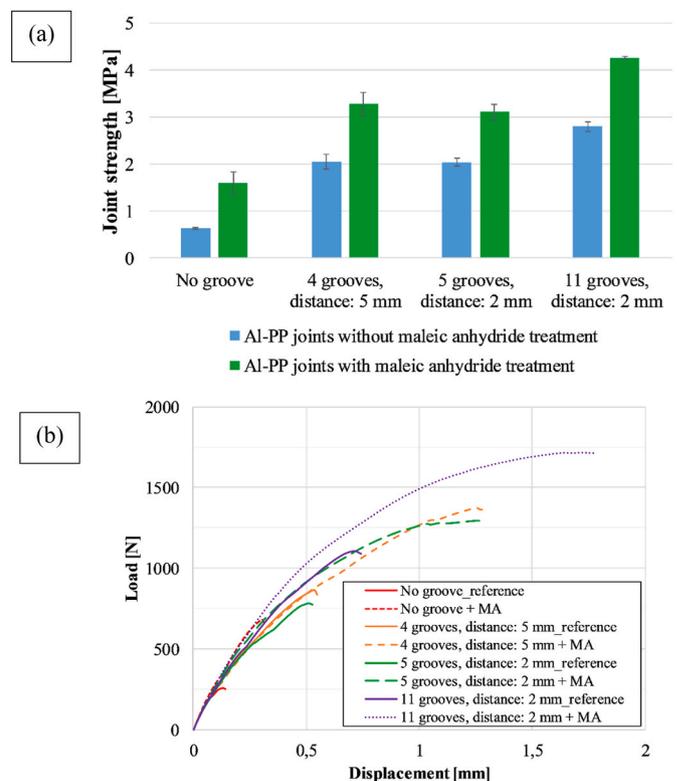


Fig. 10. The effect of surface treatment of PP with maleic anhydride on the strength of Al-„R359A” PP joints (a), and a typical load-displacement curve for all joint types (b).

molecules. As the molecular weight and crystallinity of polymers determine their toughness, and thus their mechanical behaviour, they concluded that chemical bonding (between -COOH groups and the aluminium oxide) is not the primary reason for the strength amplification effect.

We found that joint strength was higher in all cases when MA was applied, regardless of aluminium surface structuring. The samples without MA treatment and those treated with MA showed a similar trend (see Fig. 10), with MA only affecting the magnitude of the measured values: a slight decrease in strength is observed in both cases when we switched to a groove spacing of 2 mm. In our opinion, this is due to the fact that for grooves close to each other (spaced 2 mm or less from each other), the stress accumulation effect of the grooves is amplified, while for a groove spacing greater than 2 mm, this effect is gradually reduced and can be counteracted by increasing the number of grooves.

The rate of strength increase was highest when no surface structures were engraved in the aluminium. This may be caused by the fact that there are less sudden changes in surface topology in the aluminium specimens that could influence the formation, parameters and behaviour of the interfacial “soft layer”, and thus its strength amplification effect. However, the maximum joining efficiency rate could be obtained with aluminium specimens containing 11 grooves spaced 2 mm apart, and is about 80%. This is an extremely high value based on measurements and our literature review, and about one and a half times higher than the JER of joints made from the same materials without MA treatment. This shows that joint strength can also be increased by promoting mechanical interlocking through the formation of shape-locked joining regions, even though it counteracts part of the effect of the interfacial soft layer. It is also important to note that even with the manual application of MA, a sufficient number of PP-MA recombinations could form *in-situ* during the joining procedure to allow the joint strength between aluminium and PP to be significantly affected. This is a promising aspect, as compounding MA into the bulk material may be contra productive industrially, as it takes time and energy, and may also adversely affect the properties of the bulk material itself.

During our experiments, we found that the failure of the MA treated samples occurred by failure of the interface between the aluminium and

polypropylene sheets. In contrast, failure of non-treated specimens with more than five grooves was always caused by cohesive failure inside the PP sheet (as shown in our previous publication [20]). This phenomenon can also be caused by the formation of the tough interfacial layer, which is able to withstand higher loads and deformation without failure, compared to reference samples. We also evaluated the interfaces before loading (using cross-sectional images, Fig. 11a and b) and after failure (using images made of the aluminium specimens’ surfaces) with optical microscopy. We found no significant difference between reference (Fig. 11a and c) and MA-treated samples (Fig. 11b and d).

3.2. Cyclic shear tests of Al-PP joints

The analysis of the mechanical response of aluminium-polymer joints to cyclic shear loading is of particular importance for their industrial applicability, since, for example, a vehicle component containing a joint may be subjected to a number of complex loads of different frequencies. The investigation of overlapped aluminium-polymer joints under cyclic loads is still understudied in the literature and further studies are needed to ensure the industrial uptake of hybrid joints.

We devised experiments, in which we modelled the effects of cyclic shear loading on aluminium-“R359A” PP joints using a shear load speed of 20 mm min^{-1} . The results presented in the previous chapter showed that the treatment of the polypropylene surface with maleic anhydride significantly affected the mechanical properties of the joints under quasi-static shear loading. To verify the effect of MA on the mechanical properties of the joints under cyclic shear stress, we used PP sheets both with and without surface treatment with MA to form the joints. In addition to investigating the effect of MA surface treatment, we also varied the number and spacing of the grooves created in the aluminium using the configurations described in the previous chapter (4 trenches spaced 5 mm apart, 5 trenches spaced 2 mm apart, and 11 trenches spaced 2 mm apart). This allowed us to investigate the effect of the aluminium surface preparation on the behaviour and mechanical properties of the joints under cyclic shear loading.

The MA-treated PP specimens were prepared as described in the

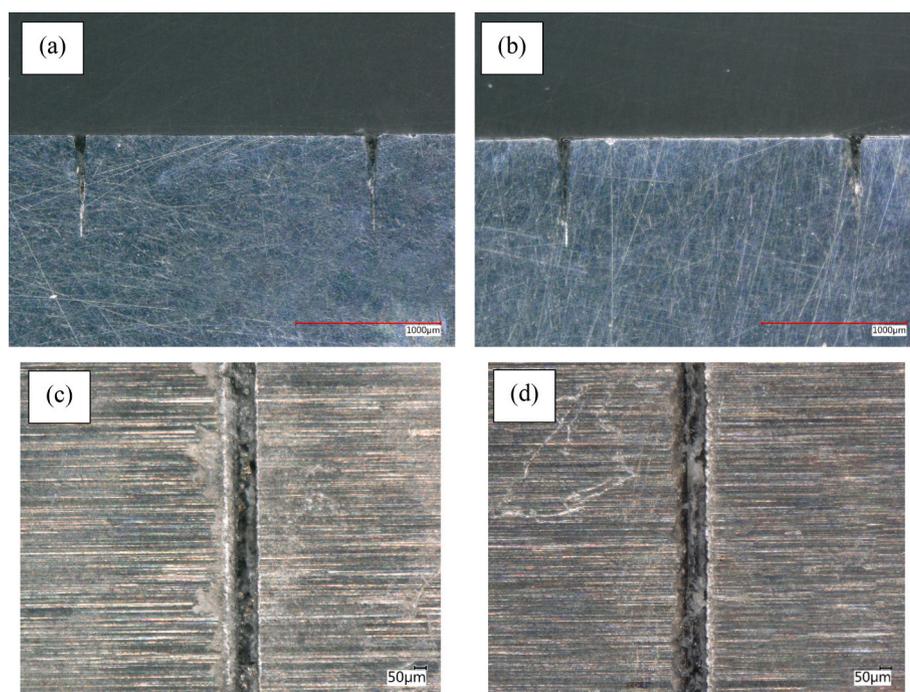


Fig. 11. Cross-sections of reference sample (a) and sample treated with MA (b) before shear loading and surface of aluminium specimens ((c) marks the reference, while (d) marks the sample treated with MA) after failure of specimens.

previous chapter: after degreasing in methanol, a brush was used to apply the MA solution to the joining surface of the PP specimens, leaving 0.10 ± 0.02 g MA on the surface after the evaporation of the solvent. The aluminium and PP sheets were joined with a joining speed of 1.25 mm s^{-1} , as this produced the maximum bond strength for joints manufactured with “R359A”-type PP based on our previous studies (Fig. 7).

The measurements were performed on an Instron 8872 computer-controlled hydraulic materials testing machine using a triangular displacement load with an amplitude of 0.2 mm. During the tests, the equipment compressed the grips by 0.2 mm from the initial gripping distance in each cycle and then expanded them by 0.2 mm from the initial gripping distance, resulting in a total deformation of 0.4 mm of the specimens in the grips (a typical load cycle is shown in Fig. 2). In the measurements, the Al-PP samples were loaded until failure, thus we were able to determine the number of cycles to failure of the joints created with specimens with a given surface treatment (different numbers and spacing of grooves in the aluminium, MA treated and untreated PP) (Table 2).

As shown in Table 2, similarly to the quasi-static shear rate tests, varying the number and spacing of the grooves in the aluminium and the surface treatment with maleic anhydride both affected the fatigue resistance (average failure cycle number) and durability of the joints. Based on our measurements, both the formation of a larger number of grooves and the surface treatment of PP sheets with MA can increase the failure cycle number. By reducing the spacing in-between the grooves (from four trenches spaced 5 mm apart to five trenches spaced 2 mm apart), the failure cycle number was also reduced. This effect could be counteracted by increasing the number of grooves (from five to eleven, without changing the 2 mm distance between the grooves) and by treating the surface of the PP sheets with MA, furthermore by creating eleven grooves, the fatigue resistance of the joints could be increased by an order of magnitude on average. This phenomenon is analogous to the reduction in strength observed in quasi-static shear tests due to a reduction in grooves spacing (see Fig. 10).

4. Summary

In the experiments described in this paper, we manufactured aluminium-polypropylene (Al-PP) joints with laser joining in order to investigate the effect of polymer melt viscosity, peak temperature of the aluminium and different surface treatment methods (laser engraving of the aluminium, depositing maleic anhydride between the aluminium and PP before joining) on the strength of these joints.

Using a K-type thermocouple, we measured the peak temperature of the aluminium specimen at different joining speed values ($0.75\text{--}3.00 \text{ mm s}^{-1}$). We found that if during joining, the peak temperature of the aluminium is higher – even if only for a short period of time – than the decomposition temperature of the PP, thermal degradation of the PP occurs, which consequently decreases its mechanical properties and also the load-bearing capacity of Al-PP joints. With quasi-static shear testing of Al-PP joints prepared with joining speed values from this range, we found that the average joint strength was roughly the same in a relatively wide joining speed range ($1.00\text{--}2.00 \text{ mm s}^{-1}$) and that the melt viscosity of the polymer does not significantly affect the maximum joint strength value that can be achieved.

We also investigated whether using a compatibilizer material, namely maleic anhydride (MA), can influence the strength of laser-joined Al-PP specimens. We deposited (on average) 0.1 g of MA onto the surface of PP specimens before joining. We found that even this small amount of MA significantly increases both quasi-static joint strength (by 50%) and the fatigue properties of the joints under cyclic shear loading (the average failure cycle number was increased by an order of magnitude) and also influences the failure mode of the joints.

Table 2

Surface treatment dependent average failure cycle numbers based on cyclic shear tests of Al-PP joints.

Type of specimen (type of surface treatment)	Average failure cycle numbers and their standard deviation
4 grooves, distance: 5 mm	370 ± 26
4 grooves, distance: 5 mm + MA	575 ± 31
5 grooves, distance: 2 mm	351 ± 32
5 grooves, distance: 2 mm + MA	630 ± 28
11 grooves, distance: 2 mm	3144 ± 172
11 grooves, distance: 2 mm + MA	7287 ± 215

Author contributions based on CRediT roles

Tamas Temesi: Conceptualisation, Methodology, Investigation, Writing – Original Draft, Writing – Review & Editing, Visualization. Tibor Czigany: Conceptualisation, Methodology, Resources, Supervision, Writing – Review & Editing, Funding Acquisition.

Statements

We confirm that this submission is the authors' original work and has not been submitted or published elsewhere before. We also confirm that all co-authors and responsible authorities involved at the institute where the work was carried out approve the submission of this manuscript.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgements

The research reported in this paper and carried out at BME has been supported by the NRD Fund (TKP2020 NC, Grant No. BME-NCS) based on the charter of bolster issued by the NRD Office under the auspices of the Ministry for Innovation and Technology. This work was also supported by the Hungarian National Research, Development and Innovation Office (NKFIH), through grant OTKA K 138472.

References

- [1] T. Temesi, T. Czigany, Integrated structures from dissimilar materials: the future belongs to aluminum-polymer joints, *Adv. Eng. Mater.* 22 (2020), 2000007, <https://doi.org/10.1002/adem.202000007>.
- [2] S.T. Amancio-Filho, L. Blaga, *Joining of Polymer-Metal Hybrid Structures - Principles and Applications*, John Wiley & Sons, Inc., Hoboken, New Jersey, United States of America, 2018, <https://doi.org/10.1002/9781119429807>.
- [3] A. Fortunato, G. Cuccolini, A. Ascari, L. Orazi, G. Campana, G. Tani, Hybrid metal-plastic joining by means of laser, *Int. J. Material Form.* 3 (2010) 1131–1134, <https://doi.org/10.1007/s12289-010-0971-1>.
- [4] A. Bauernhuber, T. Markovits, Laser assisted joining of metal pins and thin plastic sheets, *Phys. Procedia* 39 (2012) 108–116, <https://doi.org/10.1016/j.phpro.2012.10.020>.
- [5] J. Jiao, Q. Wang, F. Wang, S. Zan, W. Zhang, Numerical and experimental investigation on joining CFRTP and stainless steel using fiber lasers, *J. Mater. Process. Technol.* 240 (2017) 362–369, <https://doi.org/10.1016/j.jmatprotec.2016.10.013>.
- [6] P. Krawczak, Automotive plastics: what future is there for polymers in tomorrow's electric and autonomous vehicles? *Express Polym. Lett.* 15 (2021) 288, <https://doi.org/10.3144/expresspolymlett.2021.25>, 288.
- [7] A. Pizzi, K.L. Mittal, *Handbook of Adhesive Technology*, Marcel Dekker, Inc., New York, NY, USA, 2003.
- [8] J. Byskov-Nielsen, P. Balling, Laser structuring of metal surfaces: micro-mechanical interlocking, *Appl. Surf. Sci.* 255 (2009) 5591–5594, <https://doi.org/10.1016/j.apsusc.2008.07.118>.

- [9] J.J. Narbon, C. Moreno-Díaz, J.M. Arenas, Influence of surface treatment on the surface energy of an aluminium substrate, *Colloids Surf. A Physicochem. Eng. Asp.* 560 (2019) 323–329, <https://doi.org/10.1016/j.colsurfa.2018.09.010>.
- [10] S.G. Kim, A. Suzuki, N. Takata, M. Kobashi, Control of surface micro-structure for Al alloy/polymer joining fabricated by laser process using Al–Ti–C powders: effect of powder composition, *J. Adv. Join. Process.* 4 (2021), <https://doi.org/10.1016/j.jajp.2021.100068>.
- [11] M. Hino, Y. Mitooka, K. Murakami, K. Urakami, H. Nagase, T. Kanadani, Effect of aluminum surface state on laser joining between 1050 aluminum sheet and polypropylene resin sheet using insert materials, *Mater. Trans.* 52 (2011) 1041–1047, <https://doi.org/10.2320/matertrans.L-M2011804>.
- [12] A. Heckert, C. Singer, M.F. Zaeh, R. Daub, T. Zeilinger, Gas-tight thermally joined metal-thermoplastic connections by pulsed laser surface pre-treatment, *Phys. Procedia* 83 (2016) 1083–1093, <https://doi.org/10.1016/j.phpro.2016.08.114>.
- [13] M. Grujicic, V. Sellappan, M.A. Omar, N. Seyr, A. Obieglo, M. Erdmann, J. Holzleitner, An overview of the polymer-to-metal direct-adhesion hybrid technologies for load-bearing automotive components, *J. Mater. Process. Technol.* 197 (2008) 363–373, <https://doi.org/10.1016/j.jmatprotec.2007.06.058>.
- [14] M.-A. Chen, H.-Z. Li, X.-M. Zhang, Improvement of shear strength of aluminium-polypropylene lap joints by grafting maleic anhydride onto polypropylene, *Int. J. Adhesion Adhes.* 27 (2007) 175–187, <https://doi.org/10.1016/j.ijadhadh.2006.01.008>.
- [15] J. Chen, K. Du, X. Chen, Y. Li, J. Huang, Y. Wu, C. Yang, X. Xia, Influence of surface microstructure on bonding strength of modified polypropylene/aluminum alloy direct adhesion, *Appl. Surf. Sci.* 489 (2019) 392–402, <https://doi.org/10.1016/j.apsusc.2019.05.270>.
- [16] C.-S. Liang, Z.-F. Lv, Y. Bo, J.-Y. Cui, S.-A. Xu, Effect of modified polypropylene on the interfacial bonding of polymer–aluminum laminated films, *Mater. Des.* 81 (2015) 141–148, <https://doi.org/10.1016/j.matdes.2015.05.021>.
- [17] X. Chen, C. Shen, X. Xia, S. Xu, Surface treatment and adhesion strength of aluminum foil for lithium-ion battery package, *Surf. Interface Anal.* 53 (2021) 559–568, <https://doi.org/10.1002/sia.6943>.
- [18] Y.J. Chen, T.M. Yue, Z.N. Guo, Fatigue behaviour of titanium/PET joints formed by ultrasound-aided laser welding, *J. Manuf. Process.* 31 (2018) 356–363, <https://doi.org/10.1016/j.jmapro.2017.11.027>.
- [19] J. Jiao, Q. Zou, Y. Ye, Z. Xu, L. Sheng, Carbon fiber reinforced thermoplastic composites and TC4 alloy laser assisted joining with the metal surface laser plastic-covered method, *Compos. B Eng.* 213 (2021), <https://doi.org/10.1016/j.compositesb.2021.108738>.
- [20] T. Temesi, T. Czigany, *Laser Joined Aluminum-PP Sheets: the Effect of the Surface Preparation of Aluminum. The International Journal of Advanced Manufacturing Technology*, under Editorial Review after Major Revision, 2022.
- [21] L.D.P. Fajardo Cabrera de Lima, R.M.C. Santana, C.D. Chamorro Rodriguez, Influence of coupling agent in mechanical, physical and thermal properties of polypropylene/bamboo fiber composites: under natural outdoor aging, *Polymers* 12 (2020), <https://doi.org/10.3390/polym12040929>.
- [22] M.E. González-López, J.R. Robledo-Ortiz, R. Manríquez-González, J.A. Silva-Guzmán, A.A. Pérez-Fonseca, Poly(lactic acid) functionalization with maleic anhydride and its use as coupling agent in natural fiber biocomposites: a review, *Compos. Interfac.* 25 (2018) 515–538, <https://doi.org/10.1080/09276440.2018.1439622>.
- [23] Y. Liu, Y. Shigemoto, T. Hanada, T. Miyamae, K. Kawasaki, S. Horiuchi, Role of chemical functionality in the adhesion of aluminium and isotactic polypropylene, *ACS Appl. Mater. Interfaces* 13 (2021) 11497–11506, <https://doi.org/10.1021/acsami.0c22988>.