

## OPTIMIZATION OF ADHESIVELY JOINED LASER-SINTERED PARTS

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### Abstract

As additive manufacturing technologies are advancing in quality and economic feasibility, joining and assembly is becoming increasingly important for industrial users. In this study, the performance of four adhesives for polyamide 12 specimens is analyzed. Testing of bonding relevant factors, such as the surface energy of the solid substrates, is conducted. Tensile shear tests of plain polyamide 12 specimens glued together, show an early adhesive failure of the joint. To increase the polar bonding forces and the surface energy of the solid substrate, pretreatments such as atmospheric plasma, chemical, corona and flame treatment are applied. An increase up to 81% of the original binding strength can be achieved with flame treatment. As an alternative to increase the bonding strength of the joints, the effects of design changes of the bonding area are looked at. The research shows that micro tubes on the surface of a substrate can increase the bonding strength up to 49%. A summary of the impact of all pretreatments and design changes is given and the suitability of each application is assessed.

**Meta Tags:** Additive Manufacturing, Laser Sintering, Adhesives, Bonding Agent, Assembly, Norms and Standards

### Introduction

*Additive Manufacturing* (AM) technologies, such as *Laser Sintering* (LS), are on the way to getting established as full-fledged manufacturing technologies [1]. Yet only a few applications have made it into industrial serial production. The reasons for this are manifold. Today, most additive manufacturing technologies are on the cusp of being economically viable, thus almost all users are trying to realize first small batch serial parts [2]. The inefficiency of AM technologies is the predominant drawback at the moment, however most professional operators seem to believe in an increasing efficiency and cost breakdown [3]. Heavy capital investments of worldwide leading companies into AM technologies show the trust in future profitability of these manufacturing systems [4], [5]. The manufacturing technologies themselves and the poor quality of the manufactured parts used to be in the focus of international research for many years and were considered as a big disadvantage of AM [6]. Many machine improvements have been implemented in the last years, such as optical thermography, new heat management systems, better oxygen sensors, or software updates. These developments have demonstrably enhanced the quality of the manufactured parts and led to a general acceptance of AM parts for serial production [7], [8].

An often overlooked barrier for forward vertical integration of the AM technologies into the manufacturing industry is the lack of reliable AM norms and standards which match with industrial standards. Overall, implemented quality standards in industries such as the

automotive sector are extremely high. For example, regulations for passenger safety or avoidance of part failure are crucial and must be taken into account at all times. As a result, the need for internal testing and detailed standards is immense.

Currently most requirements for norms and standards in the field of AM are coming from the aeronautical and the medical industries [9]. The requirements for the automotive industry differ in several ways. One example is the joining and assembly of AM parts. It has not been researched before and standards for these techniques are non-existent as of now. When looking at interior automotive parts for example, the majority of components are put into place by using an adhesive. Scientific literature on the examination of the performance of adhesively-bonded joints of laser-sintered parts is missing.

The aim of this research is to identify an adhesive suitable for joining polyamide 12 (PA12) specimens. Afterwards, it is analyzed how the performance of the bonded joint improves by changing the design of the overlapping area or by pretreating the specimens. In this research, conglutinated specimens will be examined to detect the main factors impacting on the bonding performance of laser-sintered parts, such as the surface roughness or the surface energy. Furthermore, the bonding of injection-molded Acrylnitril-Butadien-Styrol (ABS) to laser-sintered PA12 parts will be compared to PA12 to PA12 connections. The joint performance will be tested by tensile shear tests according to DIN-EN 1465 with an overlapping distance of 10 mm. A failure analysis will complete the validation process.

### **Material Characterization:**

Laser-sintered PA12 specimen have been studied for several years in literature [10]–[12]. The surface roughness and structure of PA12 is well known [12], [13]. Authors such as Wudy et al. and Mielicki emphasize the importance of the surface tension as a vital parameter during the solidifying process of the powder bonding during the laser sintering process [14], [15]. However, adhesive relevant facts such as the combination of the surface energy, the surface tension of the solid material and an exact topology mapping of PA12 have not been looked at together. Hence, a characterization especially for adhesive relevant factors is undertaken in this paper.

A *Scanning Electron Microscope* (SEM) (Zeiss / Leo 1455VPSE) is used to analyze the surface morphology (Figure 1) at first. In addition to that, confocal microscopic pictures ( $\mu$ Surf / Nanofocus) are taken to further portrait the surface structure and analyze the surface roughness of the samples (Figure 2).

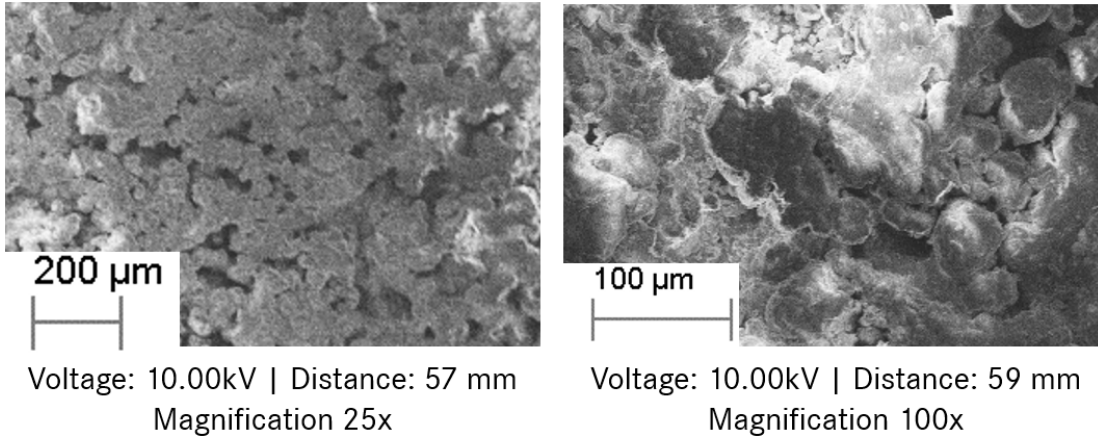


Figure 1: Scanning electron microscopic pictures of shear tensile specimens of PA12 at 25 and 100 magnification.

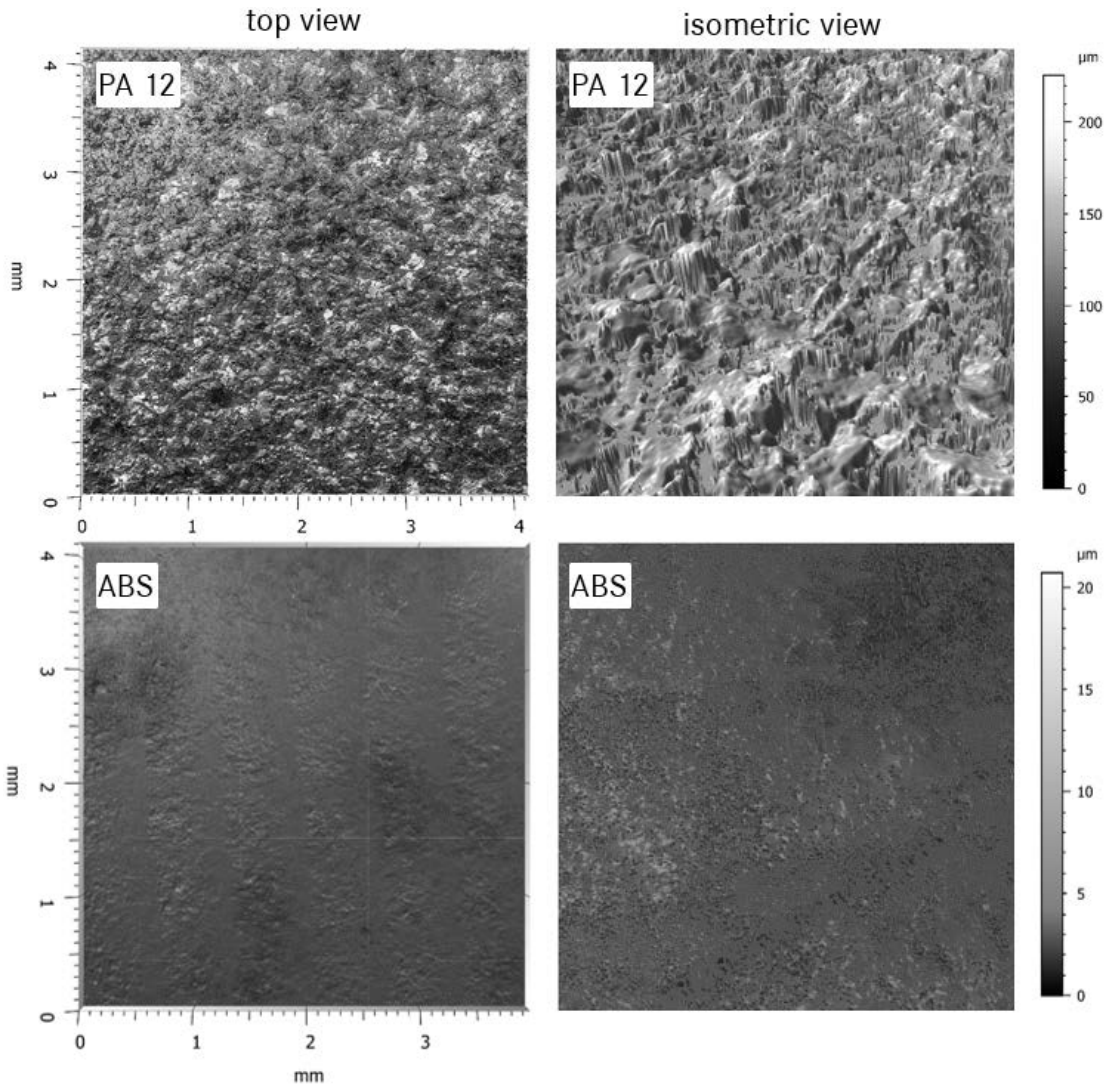


Figure 2: Surface mapping of ABS and PA12 specimens with confocal microscopy

The manufactured specimens were built with an EOS P760 and a volume energy of 0.4 J/mm<sup>3</sup>. The used parameters deposit about 30% more energy than the original standard parameters [16], [17]. This can theoretically result in additional partly-fused or sintered particles on the surface. However, the surface morphology of parts manufactured with standard parameters did not differ. The pictures of the SEM show specimens with evenly spread spherical particles at the surface. The size of the adherent particles varies from 2 μm to 50 μm. Some powder particles are sinter-bonded onto the surface. A two-dimensional simplified sketch of the surface is displayed in Figure 3. The surface appears to have rounded peaks instead of spiky and sharp tips.

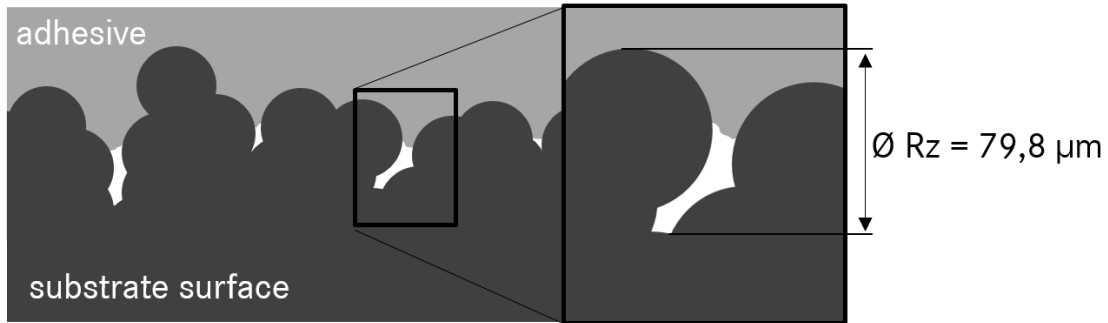


Figure 3: Oversimplified sketch of the surface of a laser-sintered PA12 samples

The confocal microscopic surface characterization of PA12 shows an average surface roughness value Ra of 10.7 μm (ISO 4287) and a Sa value of 12.4 μm (ISO 25178) which is close to the values of Grimm et al.'s and Vetterli et al.'s studies of Ra and Sa of 10 μm ± 3 μm [18], [19]. But more interesting is the peak-to-valley height, as it affects the selection of the adhesive. Since the roughness depth Rz of 79.8 μm is relatively high compared to the ABS's of 1.1 μm, suitable pastes need to have a high rate of dissemination and a low viscosity to cover as much surface area as possible (Table 1). The sketch in Figure 3 depicts the Rz dimension and indicates that the surface tension of the adhesive has to be low so that it can fill deep holes.

Material	Ra	Rz	Sa	Sz
PA12	10.7 μm	79,8 μm	12.4 μm	226 μm
ABS	0.16 μm	1.10 μm	0.19 μm	3.92 μm

Table 1: Surface roughness of the characterized materials

Another important aspect for selecting a suitable adhesive is the surface energy or surface tension of the substrates. The higher the surface energy of the solid substrate and the surface energy of the liquid bonding agent is, the stronger the bonding will be. Secondary valence forces at the molecular level keep the substances connected. Polar groups of the top and boundary layer are involved in this process primarily. This physical effect is called adhesive bonding [20]. A formula for the surface energy  $\gamma$  can be derived from Gibbs Free Energy  $g$ , which is the function of the Temperature  $T$ , the pressure  $p$ , the amount of substance  $n$  and the surface area  $A$  [21].

$$\gamma = \left. \frac{\delta g}{\delta A} \right|_{T,p,n_i} \quad (1)$$

$$dg = -sdT + vdp + \sum \mu_i dn_i + \gamma dA \quad (2)$$

A well-known method to measure the surface energy of a liquid is the sessile drop method. The contact angle of a test liquid is being measured to identify the surface energy and determine the disperse and polar forces [22]. In this research the surface energy is measured with the Owens, Wendt, Rabel and Kaelble method (Machine MSA / Kruss, static measurement, drop volume 2  $\mu\text{l}$ , climate 23/50, waiting time 5 s, deriving method test liquids water and diiodomethane). Habenicht compiles the surface energies of various polymers [23]. Table 2 compares the surface energies of ABS and polyamides from the literature with the measurements of the laser-sintered PA12 and injection-molded ABS specimens of this research.

<b>Materials</b>	<b>Surface Energy <math>\sigma</math></b>
Acrylnitril-Butadien-Styrol (* Habenicht)	35 ... 44 $\text{mJm}^{-2}$
Polyamids (* Habenicht)	49 ... 57 $\text{mJm}^{-2}$
ABS (injection-molded)	72 $\text{mNm}^{-1}$ (normally 40 $\text{mNm}^{-1}$ )
PA12 (laser-sintered)	47 $\text{mNm}^{-1}$

\* Literature information [23]

Table 2: Surface energies of ABS and PA12 derived from contact angle measurement and literature

#### Adhesives:

Four adhesives have been selected for evaluation as suitable bonding agent for PA12 parts (Köratac HF300, Turboflex 4in1, Scotch-Weld DP 8005 and Scotch-Weld DP 8805). To assess the performance of each adhesive (ABS to ABS and ABS to PA12), tensile shear specimens are cleaned, joined together and then pulled apart after hardening (according to DIN-EN 1465). Figure 4 displays the specimen dimensions and the two typical fracture behaviors. Each bonding was tested five times for statistical reliability. The bonding of PA12 to ABS specimens withstands about 40 % less shear tension than the bonding of ABS to ABS specimens (Table 3). This is due to an early delamination of the adhesive from the PA12 sample. Consequently, pretreatments will be applied onto the PA 12 specimens to increase the surface energy of the substrate and raise the adhesive strength of the bonding agent. The agent Scotch Weld DP 8005 has been chosen for an additional optimization and a more detailed analysis of the failure, because it showed the highest average shear strength of ABS and PA12.

<b>Bonding agent</b>	<b>Material Combination</b>	<b>Max. Shear Tension</b>	<b>Type of failure</b>
Köratac HF300*	ABS/ABS	6.5 MPa	Substrate fracture
Scotch Weld DP 8005	PA12/ABS	5.6 MPa	Adhesive delamination (PA12)
Scotch Weld DP 8005*	ABS/ABS	8.7 MPa	Substrate fracture
Scotch Weld DP 8805	PA12/ABS	4.5 MPa	Adhesive delamination (PA12)
Scotch Weld DP 8805*	ABS/ABS	8.8 MPa	Substrate fracture
Turboflex 4 in 1	PA12/ABS	0.3 MPa	Adhesive delamination (ABS)

\* Reference to conventional assemblies (ABS to ABS)

Table 3: Results of the tensile shear test of joints bonded with different agents

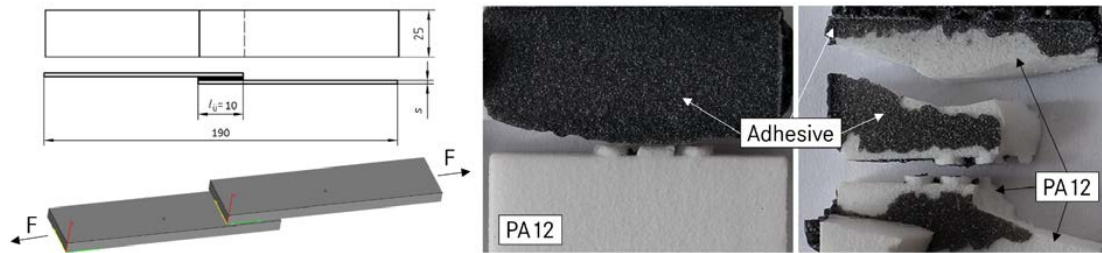


Figure 4: Tensile shear specimen dimensions (left), adhesive delamination of the adhesive (center), substrate fracture (right)

## Experimental

### Surface activation:

The aim of the surface pretreatments is, as described above, to increase the surface energy of the solid PA12 samples to enhance the adhesive bonding. The PA12 samples will be activated chemically with corona, with atmospheric plasma and through flame treatment. Table 4 gives an overview of the parameters of the pretreatments and a short description of the processes.

#### **Flame treatment**

##### **Description:**

The substrate is exposed to a gas flame (1700°C). The depth of the treatment varies by substrate. Polarized forces on the surface of the substrate are created by the treatment [22].

##### **Parameters:**

- Machine: Hill Flame Impingement 20-1
- Burner: T24-150
- Length: 1000 mm
- Distance: 100 mm
- Air/Gas Ratio: 25/1 propane

#### **Corona treatment**

##### **Description:**

Corona is an electric process which uses ionized air to increase the surface energy of substrates and typically transforms the substrate surface from a disperse state to a polar state [22].

##### **Parameters:**

- Machine: Tantec LabTEC
- Generator: HV-X02
- Power: 120W
- Spheroid electrode
- Distance to substrate: 15 mm

#### **Atmospheric plasma treatment**

##### **Description:**

Substrates are treated with highly accelerated air plasma, which is created by an electric arc at atmospheric pressure. Polar groups are transferred into the substrate [22].

##### **Parameters:**

- Machine: Tigres Plasma-Blaster MEF 4
- Power: 600W
- Distance to substrate: 35 mm
- Treatment duration: 4 s

#### **Chemical treatment (DIN EN 13887)**

##### **Description:**

Etching solutions are applied onto the surface of the substrate to activate or oxidize the surface.

##### **Parameters:**

- Chemicals:
  - Ethyl acetate (91 ± 1 %)
  - Resorcinol (9 ± 1 %)

Table 4: Description and parameters of the pretreatments of the PA12 specimens

Figure 5 shows the surface energy after the pretreatments. Especially the amount of polar forces is essential for a good bonding [22]. Therefore the focus should be on the ratio of disperse to polar surface forces. Printed PA12 parts have a very low amount of polar surface forces of  $< 1 \text{ mNm}^{-1}$ . This is the main reason for a very early adhesive failure of the regular joints (without any pretreatment). Parts exposed to atmospheric plasma have a polar share of  $2 \text{ mNm}^{-1}$ . A flame impingement increases the polar forces up to  $7 \text{ mNm}^{-1}$ , corona treatment up to  $21 \text{ mNm}^{-1}$ , and chemical treatment up to  $35 \text{ mNm}^{-1}$ . The chemical modification results in the highest polar forces, and corona treatment adds up to the highest surface energy over all.

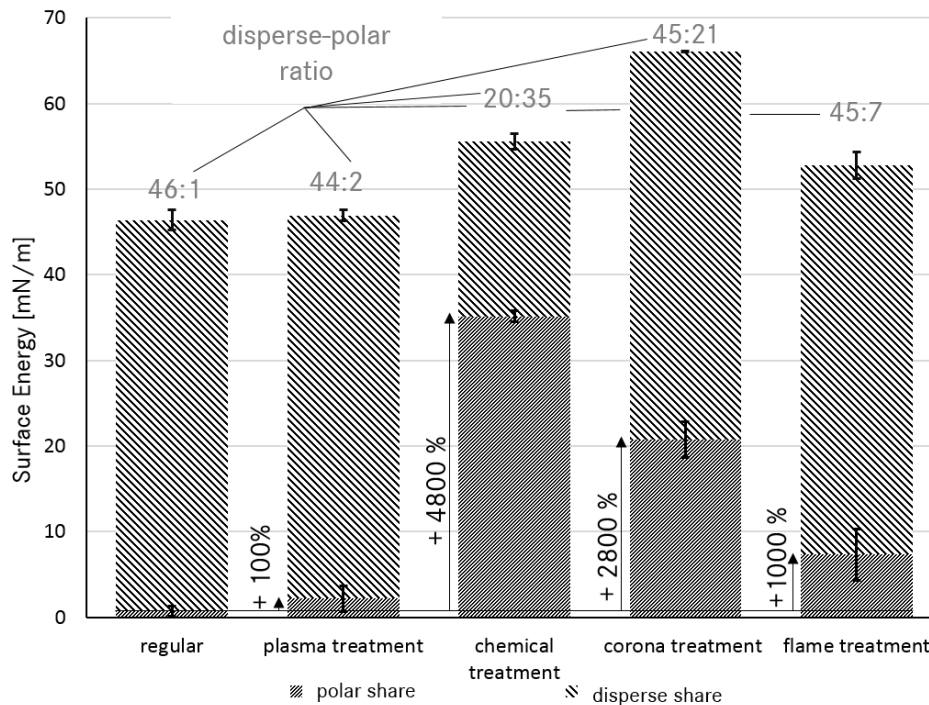


Figure 5: Surface energy, disperse and polar forces of the PA12 specimens before and after the activation processes

The tensile shear strength of the PA12 specimens before and after the treatments is displayed in Figure 6. The graph depicts that high surface energies create an improved overall adhesive bonding, but there is no direct correlation between the quantity of the polar share and the tensile shear strength. This can be explained by looking at the failure type of the joints. The fracture behavior of parts with corona, chemical and flame treatment has changed from adhesive to cohesive, or to a complete part rupture. If the polar share is at a minimum of  $7 \text{ mNm}^{-1}$ , the behavior at rupture is related to the material properties of the hardened bonding agent, the gap height of the connection, and the material properties of the substrate. Overall, there is a strong influence of the joining parameters such as the gap height between the substrates, the surface roughness and the amount of bonding agent between the samples. Therefore the tensile shear forces can vary strongly.

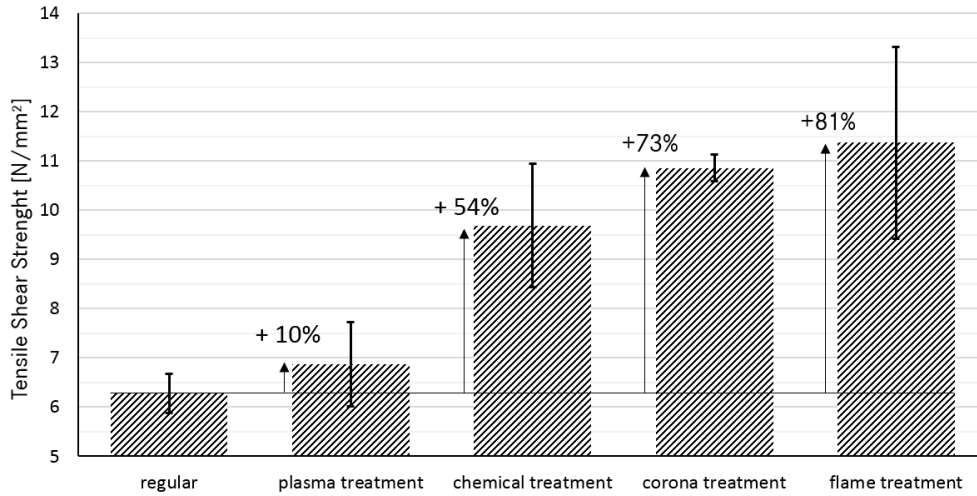


Figure 6: Tensile shear strength of the PA12 specimens at different activation methods

#### Design changes to the adhesive surface:

Another method to increase the adhesive strength of a substrate is to change the design of the substrate surface. Four design changes are being looked at for this research: a design to (A) increase the surface area, (B) create an undercut for the agent, (C) adjust the gap height and (D) create mechanical catching structures (Figure 7).

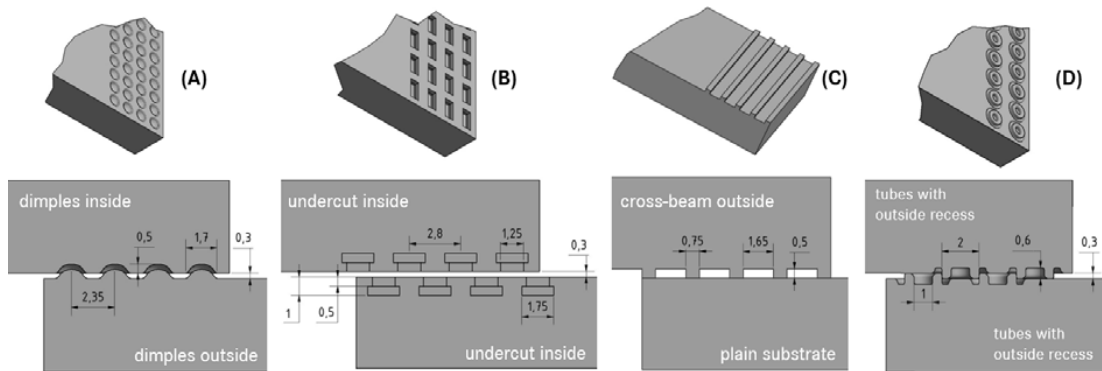


Figure 7: Design changes of the substrates and the geometrical dimensions: (A) dimples inside and outside, (B) inside undercut, (C) cross-beam structure, (D) tubes with outside recess

Starting with the design with the lowest impact on the adhesive strength, the cross-beam design did improve the adhesive bonding by about 4%. The idea of the cross-beam design is to manually adjust the gap between substrates. Rasche mentioned in his research that an increase of the bonding gap affects the bonding performance negatively [24]. The substrate without cross-beams caused an early adhesive failure. The undercut design is meant to increase the surface of the substrate and prevent an adhesive slip off. The shape of the structured area of the specimens was not accurate enough to allow the bonding agent to interlock with the substrate, the bonding strength did only increase by 6%. The dimples design did increase the surface area by 44%, therefore a significant performance increase can be seen. The tubes design did not only increase the surface area, but it also allowed to manually adjust the gap between the samples and created a mechanical interlocking of the solid substrates. Therefore the tensile shear



strength increased by 49 %. A summary of the bonding performance of the specimens with the new designs is given in Table 5.

	<b>Applied Changes</b>	<b>Tensile Shear Strength</b>	<b>Stand. Dev</b>	<b>Delta</b>
	Original LS PA12 specimen*	6.27 N/mm <sup>2</sup>	0.4 N/mm <sup>2</sup>	0
Design change	# Cross-beam design (C)	6.54 N/mm <sup>2</sup>	0.96 N/mm <sup>2</sup>	+ 4 %
	# Undercut design (B)	6.64 N/mm <sup>2</sup>	0.35 N/mm <sup>2</sup>	+ 6 %
	# Dimples design (A)	9.01 N/mm <sup>2</sup>	1.38 N/mm <sup>2</sup>	+ 44 %
	# Tubes design (D)	9.33 N/mm <sup>2</sup>	0.45 N/mm <sup>2</sup>	+ 49 %
Pretreatments	~ Plasma treatment	6.87 N/mm <sup>2</sup>	0,86 N/mm <sup>2</sup>	+ 10 %
	~ Chemical treatment	9.67 N/mm <sup>2</sup>	1.26 N/mm <sup>2</sup>	+ 54 %
	~ Corona treatment	10.85 N/mm <sup>2</sup>	0.27 N/mm <sup>2</sup>	+ 73 %
	~ Flame impingement	11.37 N/mm <sup>2</sup>	1.95 N/mm <sup>2</sup>	+ 81 %

\*Reference sample

Table 5: Overview of effects on the tensile shear strength of PA12 specimens

### Conclusion

As indicated in the literature, the low polar forces of PA12 compared to ABS make an adhesive bonding especially challenging. To meet the high safety and quality standards of most industries, the bonding strength should be increased by using one of the introduced pretreatments or by applying design changes. Both processes, pretreating the specimens or changing the design of the bonding area, improve the bonding strength in a satisfactory way.

Pretreatments can be applied relatively fast and cheap, however the parts have to be joined together shortly after the treatment. Today, primers or other pre-processing steps are common in the manufacturing industry. Thus it should be easy to incorporate chemical or corona treatment into modern manufacturing processes for AM parts on site.

Changing the surface design of the PA12 specimens can also result in a higher bonding strength and new designs can be applied fairly easy to the parts. Some designs can even reduce the manufacturing costs of the printed parts because less material is being used. Even if new designs can increase the bonding strength, further research on chosen surface designs is necessary as some designs could increase the internal stress of the samples and cause an early part failure.

Further testing and validation of assembly technologies, such as adhesives joining, is required for future industrial use of AM parts. Norms and standards should be created to advise users and to simplify the application of AM technologies.

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