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Investigation of the curing behaviour of bio-based adhesives and the application in automotive industry

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Kurzfassung

Derzeit werden in der Automobilindustrie erdöl-basierte, meist lösemittelhaltige Klebstoffe eingesetzt, die in der Herstellung, Lagerung, Handling und Arbeitssicherheit umwelt- und gesundheitsbedenklich sind. Zusätzlich entsteht bei der Verarbeitung dieser Produkte CO_2, welches im Zusammenhang mit der Klimaerwärmung diskutiert wird. Der Mobilitätssektor verantwortet 29 % des gesamten CO_2-Ausstoßes in Europa, wodurch die Automobilindustrie gefordert ist Maßnahmen zu ergreifen, um die CO_2-Bilanz eines Fahrzeuges über den gesamten Lebenszyklus zu verbessern. Mögliche Ansatzpunkte sind, neben Energieeffizienzmaßnahmen und der Einbindung von erneuerbarer Energie im Fertigungsprozess, der Einsatz von bio-basierte Materialien. Lignin, das zweithäufigste Biopolymer der Erde, welches als Nebenprodukt in der Papier- und Zellstoffproduktion in Form von Lignosulfonat anfällt, eignet sich als potentielles Rohmaterial für die Herstellung von Klebstoffen, Bindemitteln oder Carbonfasern, welche auch in der Automobilindustrie eingesetzt werden können. Die vorliegende Arbeit untersucht den Einsatz von enzymatisch polymerisierten Lignosulfonaten (epLS) als Klebstoff in der Automobilindustrie. Basierend auf dem Stand der Technik zu Klebstoffen im Fahrzeugbau, wurde ein methodischer Ansatz zur Evaluierung des industriellen Einsatzes von neuartigen Klebstoffen entwickelt. Im ersten Teil der Arbeit wurden standardisierte Testmethoden für Klebstoffanwendungen nach DIN Norm, unter anderem mit verschiedenen Substraten untersucht, wobei sich der zweite Teil mit der Ermittlung der Materialeigenschaften von dem epLS-Klebstoff beschäftigt. Es hat sich gezeigt, dass eine Viskosität zwischen 9 und 10 Pa·s, ein Trockensubstanzgehalt von 30 m% und ein Anteil Lignosulfonat : Glyzerin von 2:1 die besten Eigenschaften hinsichtlich Aushärteverhalten, Applikation, Adhäsion und Lagerung besitzen. Der epLS-Klebstoff ist resistent gegen polare und nicht polare Lösemittel und hält den klimatischen Bedingungen, welche im Fahrzeuginnenraum herrschen, sowie Temperaturen bis 75 °C stand. Klebeversuche mit Stahl, Aluminium, carbonfaserverstärktem Kunststoff und Polypropylen zeigten geringe Adhäsion, wohingegen die Zug-, Scherversuche mit Leder eine Scherfestigkeit von 0.2 MPa erzielten und die geforderten Festigkeitsanforderungen von 0.02 MPa erreichten. Auf Basis der Ergebnisse wurde im dritten Teil der Arbeit die Anwendung in der Sitzfertigung an der bestehenden Fertigungslinie und unter realen Bedingungen erfolgreich getestet. Im Vergleich zum derzeit verwendeten Klebstoff konnte eine Reduktion der Aushärtetemperatur von 135 °C auf 35 °C, sowie eine vergleichbare Klebe- und Oberflächenqualität der Leder-Verklebung erzielt werden. Die Ergebnisse dieser Arbeit zeigen daher, dass ein Ersatz von fossil-basierten Klebstoffen durch bio-basierte Klebstoffe möglich ist. Weitere industrielle Anwendungen für Innenraumverkleidungen oder das Fügen von anderen bio-basierten Materialien im Fahrzeugbau sind in der längerfristigen Betrachtung potentielle Anwendungen des epLS-Klebstoffes.

Abstract

Currently used adhesives in automotive industry are fossil-based and mostly contain organic solvents, which are harmful in terms of production, storage, handling and safety at work. Additionally, the utilization of these materials forms CO_2 which is discussed in the global warming debate. A significant agent in this debate is the mobility sector which generates 29 % of the total CO_2-emissions in Europe. Therefore, the automobile industry is forced to realize measures to improve the CO_2-balance during the whole life cycle of a car. Beside energy saving measures and the implementation of renewable energy in the car manufacturing process, the application of sustainable products, for example bio-based materials, is a possible approach to reduce the CO_2-emissions. Lignin, the second most abundant biopolymer on Earth, which forms lignosulfonates as by-product during the sulfite pulping process, serves as a promising raw material for the production of carbon-rich products, for example adhesives, binders or carbon fibers which can be applied in automotive industry. The present work aims at the implementation of enzymatically polymerized lignosulfonates (epLS) as a potential adhesive in automotive industry, especially in car seat manufacturing. Based on the state-of-the-art-technology of adhesives in car design, a methodical approach was developed to evaluate an industrial application of novel adhesives. The first part of the work deals with test methods according to DIN EN standards and adhesion tests with different substrates. In the second part the characterization of the epLS-adhesive was determined. The epLS had the best properties regarding curing behaviour, application, wettability and storage at a viscosity between 9 and 10 Pa·s, a dry substance content of 30 wt% and a proportion of lignosulfonates : glycerine of 2:1. The epLS is resistant against polar and nonpolar solvents and withstands climate conditions prevailing in interiors, as well as temperatures up to 75 °C. Initial screening tests of epLS with materials like steel, alumina, carbon fiber reinforced plastic or polypropylene showed a low bonding ability, whereas the lap shear tests with leather resulted in a shear strength of 0.2 MPa and thus met the strength requirements of 0.02 MPa. Based on these outcomes, in the third part of the work the epLS-adhesive was applied on existing equipment and in real conditions in the car seat manufacturing. The adhesive bonding of leather-viscose had promising and energy-saving curing properties, while a reduction of the curing temperature from 135 °C to 35 °C was achieved. Compared to the commercial adhesive a sufficient bonding and surface quality of the leather were achieved. The results obtained in this work demonstrate the possibility to replace fossil-based adhesives by bio-based adhesives. In a broader sense, the epLS can be used for applications other than seat manufacturing, such as paneling interior components with leather, cotton or other fabrics or serving as new bonding technology for bio-based materials and composites.

Table of content

1 Introduction

During the last decade the demand for renewable resources has been increasing, driven by the motivation to reduce the emissions of CO_2, a greenhouse gas, formed by the utilization of fossil-based resources. Meanwhile renewable energy technologies, such as hydropower, wind or solar power are incorporated in modern energy concepts and even numerous countries in the world legislate the limitations of CO_2-emissions. One major role in terms of greenhouse gases is the mobility sector, which consumes more than half of the annually produced oil and is with 29 % of the total CO_2-emssions in Europe, beside the energy generation sector with 42 %, the second largest emitter. [1] [2]

Germany for example, is limiting the CO_2-emission of cars with combustion engines to 95 gram per kilometre in 2020. Forecasts expect further intensifications and therefore the automotive industry contributes significantly in terms of greenhouse gas emissions. The global warming debate, driven by regulations, consumers, non-governmental organizations (NGO's) and media, pressure the car manufacturer to invent new strategies to hold its position on the market. [1] [3] [4] [5]

In regards to the reduction of CO_2-emissions many activities have been done in automotive industry, e.g. improvement of combustion and emission characteristics of the powertrain technology or reduction of the fuel demand due to lightweight design. As an example, reducing the weight of a car by 10 wt. % decreases the consumption of fuel in l/100 km by 6.8 vol. %. Another approach is the implementation of biofuels for combustion engines or the investigation of other driving technologies, e.g. hydrogen or electricity. [6] [7]

Beside the mentioned activities, additional measures have been undertaken to improve the CO_2-balance of a car. The original equipment manufacturer (OEM's) consider the whole life cycle of a car, for example the demand of materials and energy, the emissions during the manufacturing, its impact during the usage and finally the disposal. Under consideration of the safety and construction standards, a continuous replacement of declining or fossil-based materials are potential ways to reduce the overall CO_2-footprint. Renewable materials or bio-based composites may replace fossil based fabrics, adhesives, reinforcement fibres, polymers, and other conventional materials. [8]

However, modern materials in car design, e.g. bio-based composites, need new joining technologies. Adhesive bonding has been raised as promising alternative to welding or riveting. Adhesives provide the assembling of different material types, have less requirements in terms of construction and contribute to new, challenging designs. Compared to other joining technologies, adhesive have no thermal or structural impacts on the material’s structure and are available in a broad variety in terms of their application and demand of the consumer. Further, they enable the realization of lightweight design in cars to reduce fuel consumption. [9]

So far the adhesive applied in automotive industry are of synthetic origin and consist of fossil based carbon compounds with hydrogen, oxygen, nitrogen, sulphur and chloride. Some adhesives are critical in terms of environment, health and safety. To reduce the environmental impact, fossil-based adhesives can be replaced by renewables. There are a few natural based adhesive, e.g. starch or protein, but due to low bonding strength to components made of metal and due to the physical properties, like thermal resistance or water solubility, they are not used in automotive industry so far. [10]

It is known that technical lignin, one of the major components of lignocellulosic biomass, might be suitable as adhesive, as this is the task that lignin has in wood. So far, technical lignin has not been sufficient properties for adhesive application. A broad molecular weight distribution and the irregular structure of technical lignin worsen the mechanical properties, as well as flow and dispersion behaviour and hence industrial application is limited. [11]

Huber et al. [12] investigated the improvement of lignosulfonate and Kraft lignin properties by enzymatic polymerization with laccase *Myceliophthora thermophila* (MtL). It was found that the wetting properties of lignosulfonates were dramatically enhanced. This might be a great opportunity to replace fossil based adhesives by enzymatic polymerized lignosulfonate.

2 Objectives

The goal of the present thesis is the investigation of enzymatically polymerized lignosulfonates (epLS) as a potential adhesive for the application in automotive industry, especially in car seat manufacturing and interior panelling. The first part of the thesis deals with the theoretical background of adhesives in car design, defines the requirements and considers the state-of-the-art technologies of adhesives. The experimental part is divided into the standard test methods for adhesives in automotive application and into the determination of the material properties of the used lignin-adhesive. Third part of the thesis summarizes the adjustment of the adhesive and the substrates in order to achieve the most promising adhesive-substrate combination. The results are then applied in a real production environment in the car seat manufacturing and finally, a future outlook of the application of the bio-based adhesive is prepared.

3 Theoretical background

3.1 Historical development of adhesives

Adhesive bonding as joining technology was popular even in the Stone Age. Resins were extracted from different wood types, like birch and pine, and used for the manufacturing of weapons. The technology was improved in the old Egypt where proteins from animals or plants were used to extract the components with adhesive properties. Just before the 2^{nd} World War bio-based adhesives, like protein, starch or carbon hydrates were produced.

Since 1950 adhesives with natural origin has been replaced by synthetic fossil-based polymers. They turned out to be much cheaper and were modified chemically to fulfil demanding application requirements, like water resistance, UV resistance or curing behaviour. Phenolic adhesives were one of the first inventions in 1909 and the production of synthetic adhesives was driven by an abundance of new synthetic products. [13]

Meanwhile, the application of adhesives has been established in industrial application. Historically, the first adhesives were used in aerospace design, followed by the automotive industry. In the meantime adhesives find their application in mechanical engineering, electronic and mechatronic sector. There is a broad variety of adhesives and their application differ in respect to their chemically properties and the requirements of the application.

Recent trends show, that the amount of adhesives in automotive industry is continuously increasing. For instance, in 2001, about 10 meters of adhesives were used for the body of the BMW 7 series, today about 150 meters are used, which equals approximately 18 kg. [5]

3.2 Definitions and terms

Adhesive joining (adhesive bonding) is defined as the process of joining parts using a non-metallic substance (adhesive) which undergoes a physical or chemical hardening reaction (curing) causing the parts to bond together through surface interaction (adhesion) and internal strength (cohesion). Further definitions exist in accordance to DIN 8593-8, DIN EN 923, DIN EN 13887 and VDI/VDE 2251. [10]

Adhesion is defined as the force acting between the adhesive and the substrate. Adhesion is the result of the mechanical interlocking between the adhesive and the surface of the material as well as physical and/or chemical interaction between the adhesive and the material. However, processes related to adhesion are difficult to describe because not all interactions are known. [14]

Cohesion is the strength of the adhesive itself. This is due to the mechanical trapping and interlocking of the adhesive molecules and their physical and/or chemical affinity for each other. However, the molecular interaction is more important for a sufficient bonding than the mechanical interlocking. [14]

A necessary condition for a sufficient bonding is the ability of the adhesive to wet the surface of the substrate and to interact with it. This is represented by the contact angle α between the liquid and the interface of the solid. The contact angle is usually quantified by the Young equation, which defines that at a given temperature and pressure a certain contact angle can be determined. The model mainly concentrate on ideal smooth and homogenous surfaces where models like Wenzel or Cassie-Baxter even consider rough and heterogeneous surfaces of the substrates. The wetting is optimal if the contact angle α is lower than 35°, as depicted in Fig. 3-1. A proper wetting is achieved when the surface tension of the substrate is higher than the surface tension of the adhesive. A suitable surface treatment of the joining parts improves the wetting behaviour. Additionally, an appropriate viscosity of the adhesive optimizes the penetration behaviour and enhance the interaction between the adhesive and substrate molecules. [10] [15] [13]

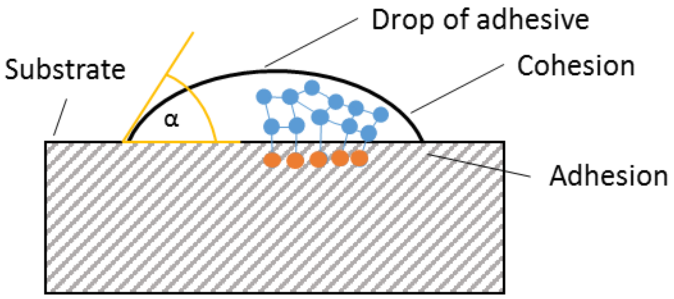

Fig. 3-1: Definition and terms: A drop of adhesive on the substrate. The blue spheres indicate the cohesive bonding inside the adhesive matrix (cohesion), the orange spheres indicate the bonding between the adhesive and the substrate (adhesion). The contact angle α is the angle between the surface of the substrate and the adhesive drop.

The optimum distance between the adhesive and the substrate surface should be ≤ 1 nm (see Fig. 3-2). Due to impurities, e.g. abrasive residues from manufacturing process or oil from conservation, the distance between the adhesive and the substrate may be larger. In some cases the substrate material is treated abrasively or chemically to remove impurities and to increase the surface roughness. This enables proper penetration of the adhesive molecules into the substrate material, where the adhesive molecules can attach to connection points of the substrate, i.e. edges. However, if the roughness of the substrate is too high, the distance between the molecules is increased and they cannot attach each other. Therefore the average surface roughness Rz of the surface should be between 30 and 70 µm. If the adhesive layer is very thin (≤ 25 nm), the cohesive bonding is weakened and thermal or mechanical effects cannot be compensated. Oppositely, if the adhesive layer is too thick, it tends to creep. [14] [16] [13]

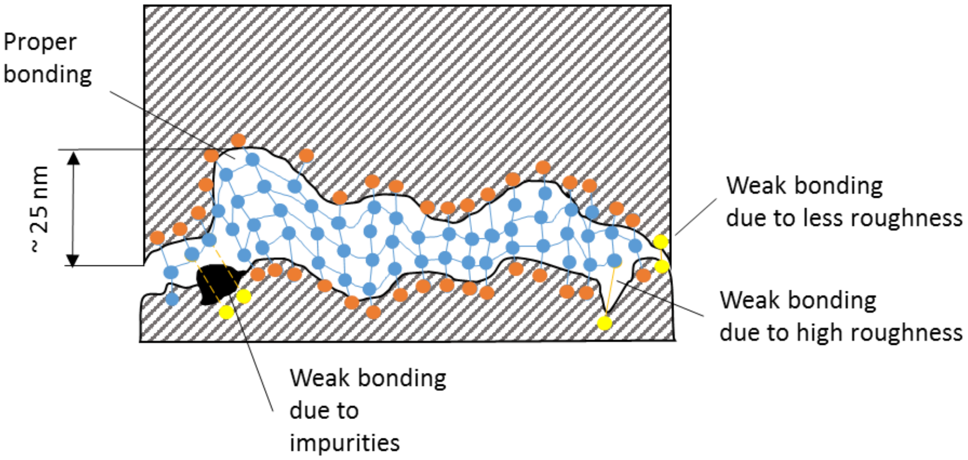

Fig. 3-2: Influence of certain parameters on the bonding ability of adhesives: The blue spheres indicate the cohesive bonding inside the adhesive matrix (cohesion), the orange spheres indicate proper bonding between the adhesive and the substrate (adhesion), the yellow spheres indicate weak or no bonding between the adhesive and the substrate molecules.

3.3 Adhesive in automotive industry

According to Growney et al. [17], in the year 2010 over 2 million tonnes of pressure sensitive adhesive, i.e. tapes were produced where the production volume of adhesives for automotive industry was 230.000 tones. Beside the electronic and aerospace industry, the highest priced adhesives belong to the automotive sector. Exemplarily, an automotive mounting and reparation adhesive for steel/alumina bonding costs 423 €/kg [18], compared to conventional wood adhesive which costs 71 €/kg [19]. The higher costs are reasonable if the requirements for adhesives in automotive application are considered. A large number of adhesives with different strength and deformation behaviour, handling and curing properties are available in automotive industry. The application ranges from structural adhesive with high requirements in terms of strength and durability to assembly adhesives which have, beside the adhesive properties, also some sealing effects.

As mentioned before, the driving force for the application of adhesives in automotive industry is the requirement do reduce weight leading to a decreased fuel consumption. As a consequence, lightweight design concepts by combining different materials, i.e. multi materials or “Material-Mix” are developed. The new design principles require alternative joining technologies, where adhesives play an essential role. [10] [20]

3.3.1 Common joining technologies in automotive area

Depending on the application different joining technologies are used in cars, which incorporate a combination of adhesive bonding and other joining technologies, like riveting, flanging and folding. The concept enables the fixation of parts or even the increase in energy absorption or force transformation. Besides adhesive bonding, common joining technologies in automotive area are:

- Welding (arc welding, laser welding)
- Spot welding
- Clinching
- Riveting
- Flanging and folding

The common bonding opportunities are state-of-the-art technolgoies which provide high-strength and long-lasting joints. [10] [9] [21] [22]

3.3.2 Categorization of adhesives in terms of their application

In the following section the field of application is explained to demonstrate the attractive properties of adhesives in car manufacturing, as well as the advantages and disadvantages. The large variety of adhesives on the market arises from the broad industrial use. Areas of adhesives are joining of different materials, vibration dampening, replacement of spot welding, attachment of exterior panels or structural bonding. To generalize this variety of products, a simple categorization is done which is shown in Fig. 3-3. This categorization has the aim to show the complexity of the adhesive applications. [10]

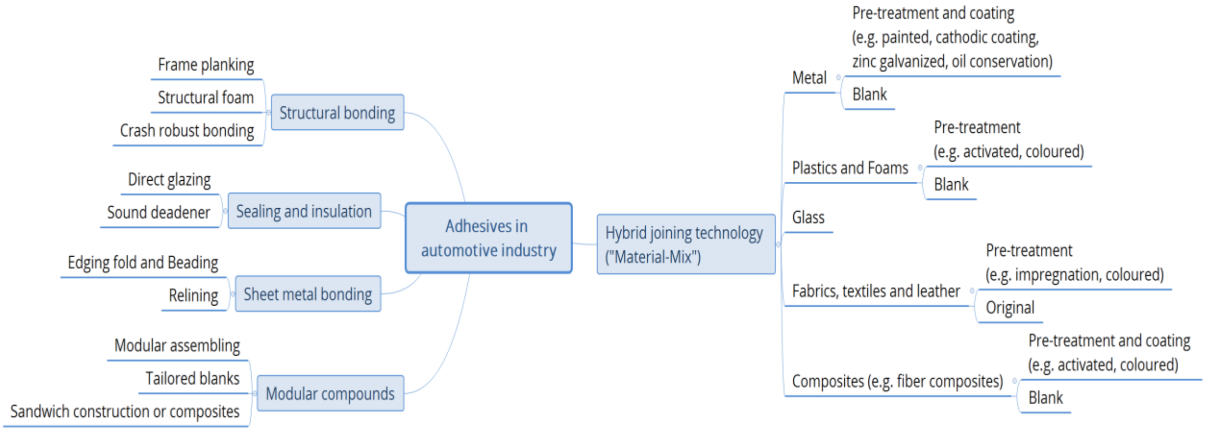

Fig. 3-3: Fields of adhesive application in automotive industry. [10]

3.3.2.1 Material combinations used in car design

Common materials in automotive design are metals, like alloyed steel or alumina, plastic and plastic foams, glass, rubber products, textiles, fabrics, leather and partially composites, e.g. based on carbon fibre or even bio-based. With the variety of materials used for car manufacturing the challenges in joining technologies increase. Fig. 3-4 exemplarily illustrates some possible material combinations in a car. Some of these are an integral part of the body, like the purple marked A- or B-pillar or are used as hang-on parts that consist of a combination of steel/alumina sheets, like side panels or the hood. Depending on the strength requirements the components of a car are pre-treated, e.g. cold formed, warm formed, alloyed or surface treated. [23] [20] [10]

Not only structure relevant components are bonded adhesively. Even interior parts, for example seats, consist of multiple materials. For example, the leather cover for seats is first upholstered with a polyurethane foam or viscose layer to increase the seat comfort and the stability of leather. Therefore, the upholstering is bonded adhesively to the leather (or cotton) before covering the seat shell as it can be seen in Fig. 3-5.

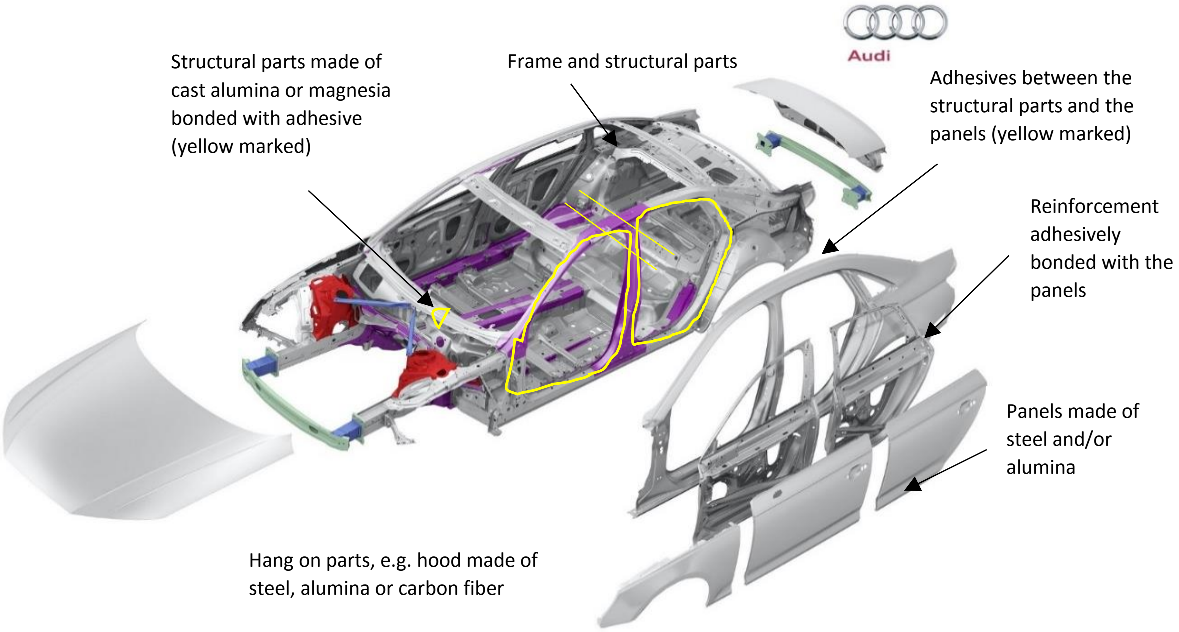

Fig. 3-4: “Material-Mix” in modern cars: Possible combinations of alumina and steel in the Audi A4. Exemplarily, the yellow marked line indicate adhesive strips which bond structural parts with panels. The adhesive has the task to bond the components and to insulate, adapted from [23].

Fig. 3-5: Construction of a seat: Adhesive are applied for bonding cotton, fabric or leather to the upholstering or shell, adapted from [81].

The material combinations in automotive sectors, which are exemplary shown in Fig. 3-4 and Fig. 3-5, are:

- Alumina/steel bonding: Panels of alumina and the structural frame of steel are bonded together.
- Carbon-fibre-reinforced polymer (CFRP)/metal bonding: Roof, doors and closures are bonded with the frame made of steel or alumina.
- Magnesia/alumina/steel: structural parts in frame or power train.
- Fibre/leather/cotton with organic and/or inorganic materials: seats, dashboard, interior door panels.

Some other combinations are:

- Plastic/glass bonding: The rear panel made of fibre reinforced polypropylene is bonded with the rear window.
- Plastic/metal bonding: A complex part made of plastic acts as additional structural part by absorbing energy and is bonded to metal parts.

3.3.2.2 Structural Bonding

Frame design incorporates the joining of sheets and panels and enables flexible design concepts and even better strength performance of the car’s structure. As depicted in Fig. 3-4, the metal sheets for panelling are bonded with reinforcement components. This concept has beneficial effects, like an even force transformation and better surface quality compared to arising spot deformation due to punch riveting or spot-welding.

Foaming in the cockpit of the car is applied for sound compensation or as reinforcement for the structure. In both cases the substance is applied un-foamed on the metal sheet or in the cavities of profiles. During further process steps, like during the cathodic dip painting or during drying processes of the coating, the substance expands and bonds to the surface of the metal.

3.3.2.3 Sealing and insulation

Direct glazing is a suitable method to bond car windows with the structure. The adhesive is applied on the flanges of the coated car structure and the window is positioned. In contrast to rubber as insulation material, the adhesive has high torsion and roof stiffness and transforms the force smoothly from the car structure to the car window. A positive side effect is the improved sealing properties of adhesives and therefore the possibility to modify the body shape to reduce the drag force of a car.

In terms of sound compensation adhesives have beneficial effects, like noise and vibration reduction. Noise generated from the power train or from wheels during driving are transferred into the cockpit.

The so called sound deadener made of viscoelastic polymers, like polyvinyl acetate or polyvinylchloride, reduce the sound waves. Besides sound reduction the temperature resistance is a relevant key factor of the adhesive, since the vibration energy absorbed by the polymeric adhesive is transformed to heat.

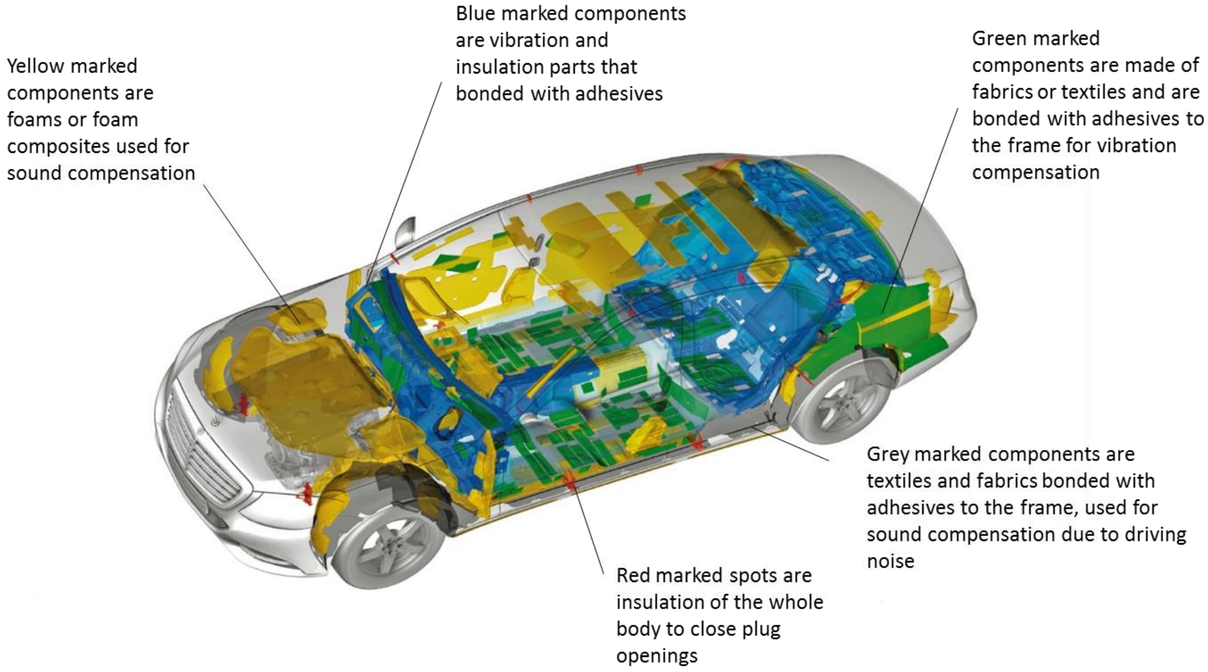

Fig. 3-6: Sealing and insulation in a Mercedes Benz W222 series adapted from [82].

3.3.2.4 Sheet metal bonding

Edging fold and beading is applied for bonding metal sheets, e.g. doors, closures and sliding roofs. Two thin metal sheets are bonded adhesively by overlapping the outer sheet around the inner sheet (see Fig. 3-7). Compared to spot-welding the planar bonding area enables a smoother force transformation and therefore an increase in stiffness. Additionally, as mentioned before, adhesive bonding has beneficial effects in sealing and therefore an increase in corrosion protection. A great benefit in regards to the manufacturing time is the omission of further manual treatment to smoothen the deformations on the surface. This is usually necessary after spot-welding or other punctual bonding technologies that cause undesired pressure spots.

Relining adhesives find their application in placing the reinforcement profiles and the structure to the outer metal sheets, e.g. behind closures and roofs. The benefit is the high capability for gap compensation since the adhesive expand to fill a gap up to 5 mm. Further advantages are good vibration properties, as well as enhanced stiffness. [10] [22]

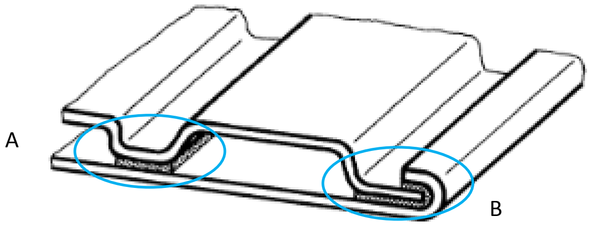

Fig. 3-7: Adhesives for sheet metal bonding: (A) relining bonding, (B) edging fold bonding. [10]

3.3.2.5 Modular compounds

Recent manufacturing concepts incorporate a modular assembling of parts which are provided as one component. This concept enhance simplicity in car manufacturing and reduces handling and operation costs. Some beneficial effects of adhesives are, besides the joining opportunities of the single parts, once more the sealing properties beneath the modular parts.

Other applications of adhesives in modular design are tailored blanks which are multiple layered sheets bonded adhesively and then pressed together or shaped. Fig. 3-8 shows a honeycomb structure bonded adhesively with sheets. Those modules are used for regions where high tensions are located, e.g. beams, wheel arches or base plates and are bonded with the frame or other parts by welding. A similar application is found in sandwich construction where base and coating layers are bonded adhesively. The concept, where plastic materials such as polystyrol or polyurethane and wood panels, alumina, CFRC or stainless steel are layered, has improved insulation and sound compensation properties. In terms of lightweight design this concept has further potential for passenger car design where lighter fibre materials, even bio-based, are bonded with high strength components like steel or alumina.

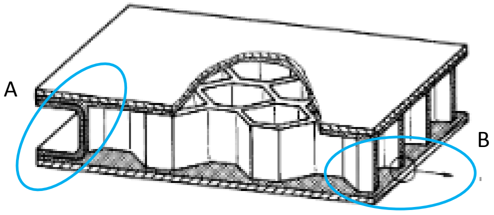

Fig. 3-8: Modular design/tailored blanks with adhesive bonding (blue marked): (A) profiles, (B) honeycomb structure. [10]

3.3.3 Advantages and disadvantages of adhesives

To conclude, considering the high performance in crash and deformation behaviour, the adhesive joining technology serves as a long lasting bonding of stiff materials with an elastic and high strength bonding. Additionally, adhesives have some other beneficial effects, like insulation properties or sound compensation. Nevertheless, each joining technology and even adhesive bonding has some drawbacks which need to be considered in terms of the requirements and applications and even in development of novel adhesives. Tab. 3-1 summarizes the advantages and disadvantages of adhesives as joining technology. [10], [21], [22]

Tab. 3-1: Advantages and disadvantages of adhesives as joining technology in car design.

Parameter	Advantages	Disadvantages/ Drawbacks
Strength properties	Load on bonded parts is distributed uniformly to the load direction	Low peeling strength
	High strength bonding in combination with other joining technologies	Depending on curing process and layer thickness, the adhesive tends to creep
	High fatigue and elastic strength	Low adhesive layer strength has to be compensated with a large joining area
	Material properties of the substrate are not influenced	Strength calculation and simulation is challenging since of the variety of adhesive types and influences of various parameters
Application	Simple tools for application, e.g. brush, air syringe, cartridge	High influences of time and process parameters, e.g. climate condition, curing time and temperature, on the curing and strength properties, which have to be controlled.
	It is a lightweight joining technology compared to welding, riveting or screwing and enables weight reduction of a car	Depending on the viscosity, the adhesive has to be pre-heated to reduce the viscosity and to make the adhesive applicable.
	Material-Mix is applicable and therefore new design concepts are possible	Form stability during application has to be guaranteed and depends on the viscosity and curing behaviour

Impact on substrate	No thermal impact on the material since adhesive bonding is a "cold joining technology", meaning that the microstructure of the substrate is not affected.	The bonding strength is reached after the adhesive cures out and that takes longer than welding or riveting. However, it can be integrated in the process, for example where structural adhesives cure simultaneously with the coating in an oven
	Heat-sensitive materials and parts with thin wall thickness can be joined since the adhesive bonding has no thermal impact on the materials.	Combination of adhesive bonding and “hot joining technologies”, e.g. welding, is critical since the thermal stability of the adhesive is limited and causes degradation of the adhesive.
	Adhesive bonding is distortion-free whereas in comparison to welding, no expansion/contraction takes place and in comparison to spot welding or clinching, no punctual deformation occur	High influence of the substrate's surface condition on the adhesive bonding. Therefore, parameters, e.g. maximum oil load, roughness, impurities, coating or primer have to be considered.
Side effects	Materials with different electrochemical properties can be jointed since adhesive have insulation properties	Possible aging due to of UV-light, vibration and temperature fluctuations which causes worsen in adhesive properties and bonding strength
	Good vibration absorption enables application as sound deadener	Depending on the formulation, some adhesives are flammable, hazardous and have a high solvent-content and are critical in terms of production, handling, storage and safety at work
	Adhesives have gap filling and tolerance compensating properties	Colour and Odour of adhesive might be relevant for visible surfaces and interiors

3.4 Categorization of adhesives

Adhesives are usually categorized in dependence of their chemical modification. Fig. 3-9 shows the classification into organic and inorganic adhesives and demonstrates the possible components of the adhesvies. Organic adhesives are further distinguished into synthetic or natural origin. As mentioned in section 3.1 natural adhesive, like proteins, have not find their application in automotive industry. Synthetic organic adhesive have, in regards to the bonding strength and ageing resistances, better performances than natural ones. Organic and inorganic adhesives differ in terms of the application temperature and thermal resistance. Organic adhesives can be applied at lower temperature, whereas inorganic adhesives have a higher thermal resistance. A combination of organic and inorganic compounds is Silicone. [10]

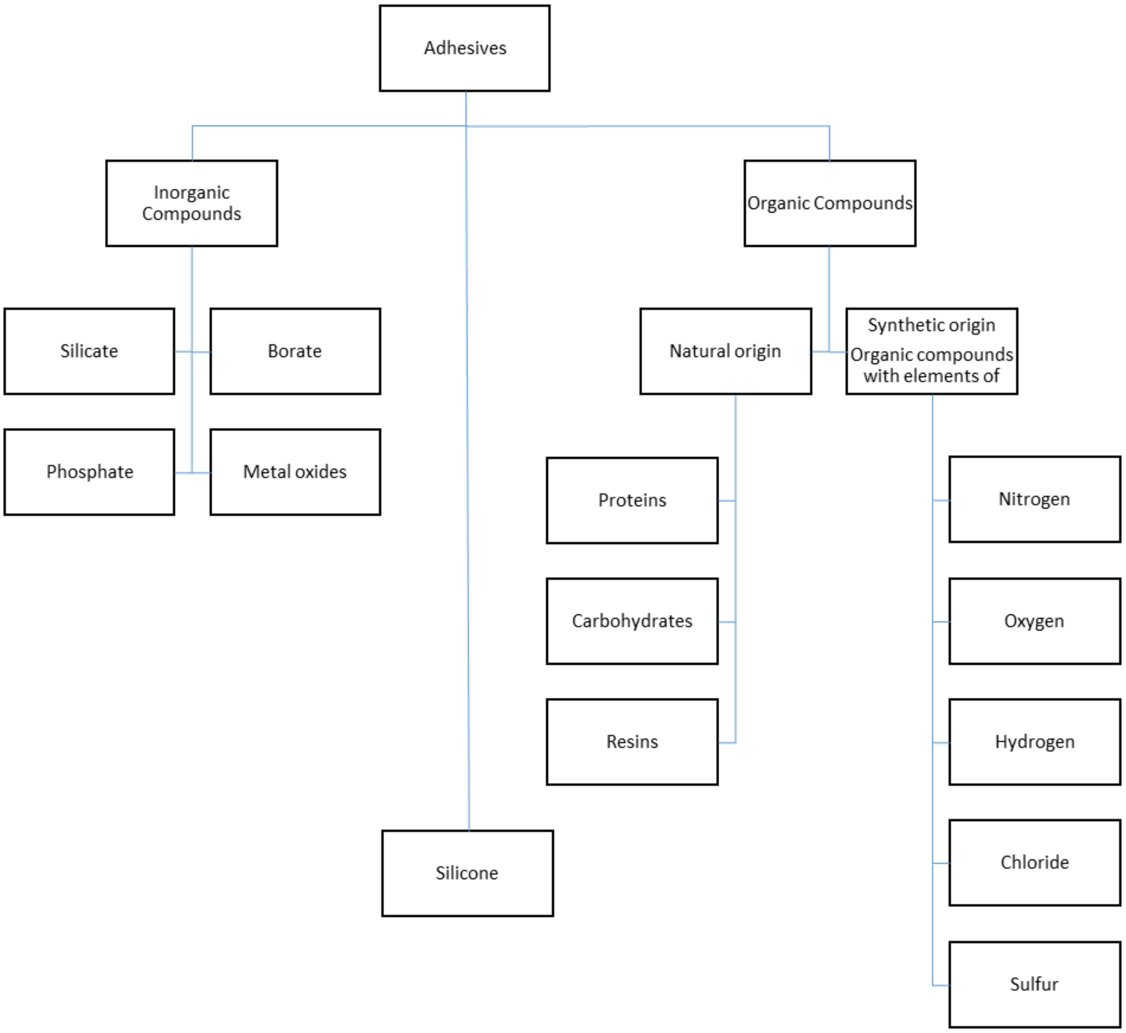

Fig. 3-9: Categorization of adhesives in terms of their compounds: In general, adhesive are categorized into inorganic and organic ones. The natural ones are not applied in automotive industry.

Fig. 3-10 demonstrates a further categorization depending on the curing behaviour of the adhesives. For the industrial application, a variety of adhesives were developed in order to fulfil the individual requirements related to handling, application and curing temperature and time. The categorization is based on the number of reactants where the term “one-component or two-component adhesive” is defined. In dependence on the adhesive type heat, pressure or humidity initialize the polymerization and therefore the curing process.

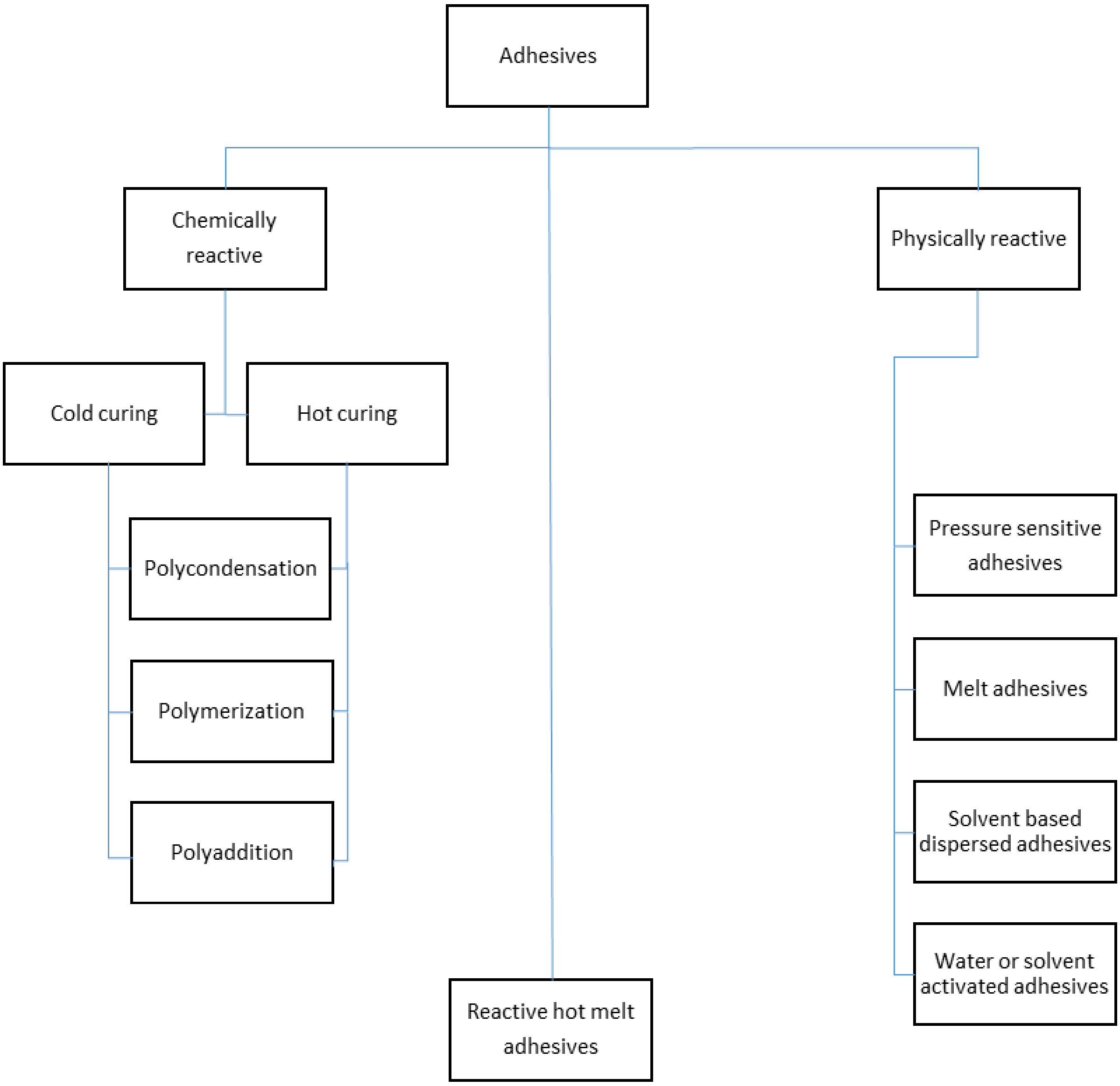

Fig. 3-10: Categorization of adhesives in terms of their curing behaviour.

Chemically reactive adhesives consist of reactive monomers or pre-polymers which polymerize in dependence on the time and/or temperature. To initiate the polymerization some pressure is added and often held constant until the process is finished and the adhesive is cured. This is done by fixation the joining parts with clinches or clips or putting on some weight. The chemically reactive adhesives consist of two or more reactants and are so called “two-component adhesives”. The second reactant is added to the major component before application or it is present on the surface of the substrate (e.g. humidity). After adding the second component the polymerization starts. Water activated adhesives cure in presence of humidity, at least at 40 % r.H.

Physically reactive adhesives consist of one single polymer which is dispersed in a solvent. This system is a so called one-component adhesive and is often added with non-reactive components, like softener, pigments or stabilizer. To start the polymerization some heat is applied to evaporate the solvent or even pressure is added. Fixing the joining parts with clinches or clips supports the penetration of the adhesive into the gaps and surface of the substrate. In comparison to chemically reactive adhesives no chemical reaction takes place.

Reactive hot meld adhesives are a combination of both polymerization mechanism. Hot meld adhesives usually have a very high viscosity (1200 Pa·s) and are heated in order to decrease the viscosity and to start the reaction as well as to enable the application via cartridge. Common adhesives in automotive industry are epoxy resins or polyurethanes. [10][24]

In respect to the regulations in terms of use and emission of volatile organic compounds (VOC) a new categorization for adhesives arose. VOC`s are highly relevant for automotive industry where solvent containing coatings, solvent-containing cleaning and maintenance materials and even adhesive are used. These substances are problematic for health, safety and environment and are regulated by the European Regulation 1999/13/EG or DIN 55 469. The solvent content induced a new categorization where adhesives are distinguished into solvent, low-solvent and solvent-free systems. In discussion are terms like “water-based” instead of low-solvent adhesives, because in general these systems contain a certain amount of organic-solvents which cause emissions and hazardous effects. Therefore, new requirements in terms of safety at work, e.g. dust fan, breathing mask, or safety, e.g. explosion protection in storage areas and environment, e.g. disposal as hazardous waste, have been arising. [25]

3.5 Requirements for adhesives in terms of application

This chapter summarizes the high impact of the curing behaviour on the strength and duration properties, as well as, on the handling and application. The automotive industry uses a wide range of adhesives which have plenty of advantageous properties. But, as already described in section 3.3.3, adhesives are sensitive in regards to the process conditions. To ensure the durability of the adhesive bonding some requirements have to be fulfilled. Further, the quality and safety standards in automotive sector need to be met. Certain standards, e.g. ASTM, DIN ISO or EN define the relevant criteria. This section includes the minimum requirements for adhesives in automotive industry and refers to physical properties, handling, curing and aging behaviour and describes the testing methods to evaluate this key parameter. [10] [26]

In general the following characteristics has to be considered in terms of adhesive application in automotive applications:

- Reproducibility and guarantee of a constant quality
- Constant bonding quality for strength calculation and simulation
- Simple handling, like automatic or manual application, storage durability, environmental, health and safety issues
- Practical knowledge and experience with the joining system and know-how in the application
- Adaption, meaning the possibility to integrate the technology in the existing car manufacturing process
- Guarantee of an ecological and economic useful concept , for example where material and manufacturing costs has to be considered

These requirements need further knowledge in terms of:

- Physical properties of the adhesive: a new adhesive shall be similar to a presently used material and safety data sheet, viscosity, density, degradation temperature has to be known
- Appropriate design principles of the adhesive joining technology, for example:
  - Geometry of the joining parts
  - Substrate combination and properties
  - Type of adhesive

  - Stress direction: adhesives are sensitive for shear stress and peel off stress

- Properties of substrates in regard to adhesive bonding ability, e.g. reactivity forces for an adhesive bonding, surface properties of the substrate, roughness, impurities and oil load

- Strength and deformation properties of the adhesive and the adhesive bonding, e.g. elastic behaviour

- Durability in terms of climate conditions, UV-light or chemicals

- Practical application:

  - Curing behaviour has to be defined to ensure sufficient bonding strength

  - Adhesive layer thickness/amount has to be known to avoid creeping or weak bonding

  - Storing, handling and preparation of adhesive has to be in order to the instruction of supplier

- Possibility to evaluate the quality of the technology and provide constant process parameter, as well appropriate testing methods

Since the application of adhesives in automotive area is broad, the requirements vary significantly. For example, the degradation temperature of structural adhesives or sealing needs to withstand temperatures up to 200 °C. The requirement arises since the car body is running through the coating process where the coating is finally dried in an oven at around 180 °C. In other cases, the adhesive has to have high a resistance against UV-light or temperature fluctuations, like in case near the gear or power train, or at the car window. For application in interior, like seating, the adhesive and the seat material have to be elastic and flexible but needs to have UV-light resistance and heat durability since the temperature inside the passenger cell can rise dramatically during summer time. To define the required properties for a certain adhesive technology, the application of the adhesive and the surrounding conditions have to be identified.

To conclude the mentioned key issues and requirements described in this section, Fig. 3-11 summarizes the parameter to guarantee a sufficient bonding ability. Additionally, these principles are the basis for the evaluation of the bio-based adhesive discussed in the experimental part 4.

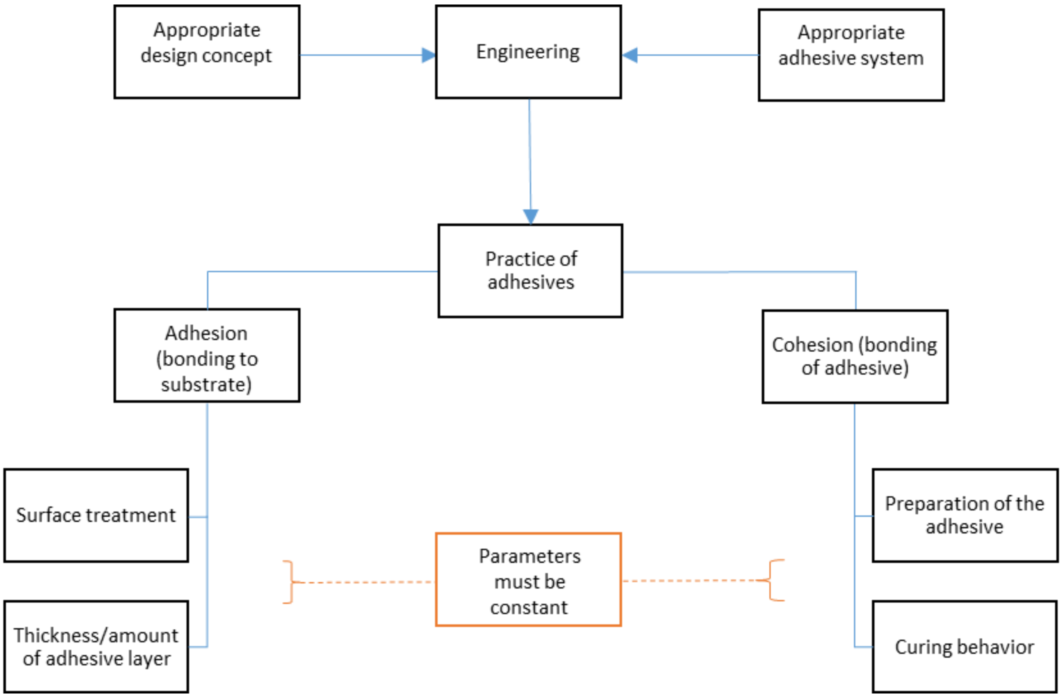

Fig. 3-11: Overview of adhesive requirements for industrial application. To guarantee a sufficient bonding ability of the adhesive, the parameters have to be considered.

3.6 Utilization of lignin for bio-based adhesives and bio-materials

In order to reduce the overall CO_2 balance of a product and the intention to improve environment, health and safety standards, bio-based materials are a part of many research activities worldwide.

Wood or wooden biomass is the most important resource for the utilization of bio-based materials. Wood consists of cellulose, hemicellulose, lignin and extractives. Besides the usage for heating and building, it is used for pulp and paper production. The chemical compositions of wood depends on the species and contributes to the product properties. In spruce for example cellulose is present with 39.5 wt%, the lignin content is approximately 27.5 wt%, hemicellulose contribute with 27.6 wt% and the residual extractives have an amount of 2.1 wt%. [27]

Cellulose is the major component of the fibre cell wall and is extract from wood for pulp and paper production. The by-product lignin, the second most abundant biopolymer on Earth, is of special interest not only because of its high heating value, as well because of its abundance and the potential to serve as replacement for fossil-based resources. Lignin is an amorphous polymer consisting of different phenyl alcohol structures and is a by-product in the pulping process. For the production of pulp, the lignin is dissolved from wood and hence the cellulose is removed from the pulp liquor. There are different methods for the cellulose digestion as well as for the following pulp bleaching, e.g. the sulphite or sulphate process. Since the pulping process is energy demanding lignin is utilized for combustion. The lignosulfonates derived from the sulphite process have a higher molecular weight compared to Kraft lignin, further the lignosulfonates are in comparison to Kraft lignin over the whole pH-range water soluble, whereas Kraft-lignin precipitates at pH values <10. Handling of lignosulfonates in terms of upgrade into other products is therefore easier. [28][29] [30]

At present, the pulp and paper industry focus on the isolation of lignin to enable value-added utilization. The present work deals with lignosulfonates, respectively with enzymatically polymerized lignosulfonates, which have to be isolated from the liquor containing also hemicellulose and pulping chemicals. The liquor is first separated from the pulp by filtration, followed by ultrafiltration to increase the lignosulfonates in solution. To obtain the lignosulfonates in dry form the solution is then evaporated and the residue is dried. [30] [31]

Commercial use of isolated lignin is, besides the utilization as bio-fuel for heat generation, the production of synthetic vanillin, dimethylsulphoxide (DMSO), dispersants, emulsifiers and binders. Even platform chemicals like phenol, benzene, toluene and xylene are a possible utilization of lignin. These platform chemicals can be reacted further to produce value-added chemicals. Therefore, the lignin extraction plays an important role in pulp production and needs the cooperation with other industrial sectors, like the chemical industry. It is chemically challenging to cleave the highly branched and resistant Lignin molecules to obtain smaller molecules that can be further synthesized for platform chemicals. However, for adhesives and resins production those lignin is suitable since the base material for those substances are usually mixtures of different aromatic compounds. Lignin for adhesive production is a promising option, since the application of adhesives enables weight reduction of a car, as it was described in section 3.3.1. As already mentioned, the so-called lightweight design decreases the consumption of fuel and therefore reduces greenhouse gas emissions. An additional approach to reduce the CO_2-emission is the implementation of bio-based materials, where lignocellulosic materials play an important role. [28][29] [30]

According to report of the Centre of Automotive Research [32], there are several ways to implement bio-based materials. Beyond traditional uses, like wood trim, leather or cotton textiles, they are used as reinforcement or filler. In today’s cars a number of bio-based components, e.g. made of flax, sisal or hemp, are used for interiors or floor panels or even for foams in seats. In the BMW 7 series the content of sisal for the door panel is about 70 wt%, the headrests in Ford Focus and Ford Fiesta are 13 to 16 wt% sisal-based. [32]

There are several approaches in automotive industry to increase the proportion of bio-based materials, e.g. using lignocellulosic fibres as filler or reinforcement or as additive to polyurethane foams. Since lignin mainly contains functional groups, e.g. hydroxyl or phenols it can be used as monomer for polymers. Alonso et al. [33] investigated the application of lignosulfonates for phenol-formaldehyde adhesives whereas softwood ammonium lignosulfonates had the best results in terms of reactivity. Budin et al. [34] found that ultra-filtrated lignosulfonates are suitable for combining at with phenol-formaldehyde. The phenol-formaldehyde adhesive containing lignosulfonates in a range from 10 to 30 wt% had appropriate technical properties and turned out to be suitable for industrial application for insulation boards made of mineral wool. [34]

In regards of carbon fibre reinforced components (CFRC) lignin was considered to replace the petroleum-based prefiber polyacrylonitrile (PAN). The high availability, the lower price compared to PAN and the theoretical high carbon content motivates researcher to investigate the application of lignin as pre-curser for CFRC production. Challenging is the inhomogeneous and random structure of lignin that impairs the mechanical properties. [35] [36]

It is known that technical Lignin is suitable as adhesive but the properties, e.g. mechanical belongings or flow and dispersion behaviour have been not sufficient for industrial application. The limitations of technical lignin in regards to adhesive application are due to their polymer structure and due to the broad molecular weight distribution. [11]

A modification of the lignin structure would widen the application range of technical lignin. T Saito et al. [37] reported, that a more homogenous network structure and the change in molecular mass weight distribution increases the properties of lignin as a blend for thermoplastics. [37]

Therefore it is part of research to improve the properties of lignin by modification of the molecular structure and increasing the molecular weight. Williams et al. [16] stated that the increase in cross-linking improves the adhesive bonding strength and durability. [16] [12]

Huber et al. [12] investigated the improvement of the lignosulfonate and Kraft lignin properties by enzymatic polymerization with laccase *Myceliophthora thermophila* (MtL). The phenols of the lignosulfonates are oxidized through laccase and oxygen radicals are formed. Those radicals then polymerize and change the molecular structure where C-C, aryl-aryl, ether or aryl-alkyl linkages are formed. Additional to the main research in enzymatic polymerization they found that the adhesive properties of lignosulfonates were dramatically enhanced. [12] [38]

It has to be mentioned, that the structure of lignosulfonates is complex and has different side chains formed during the pulping process, where even chiral centres in dependence of the process conditions are generated. Fig. 3-12 depicts the theoretical structure of magnesium lignosulfonates and highlights some possible groups and side chains. The yellow marked circle indicate the hydroxyl-groups, which may be attached by the enzyme laccase to initiate the radical polymerization. [39] [40]

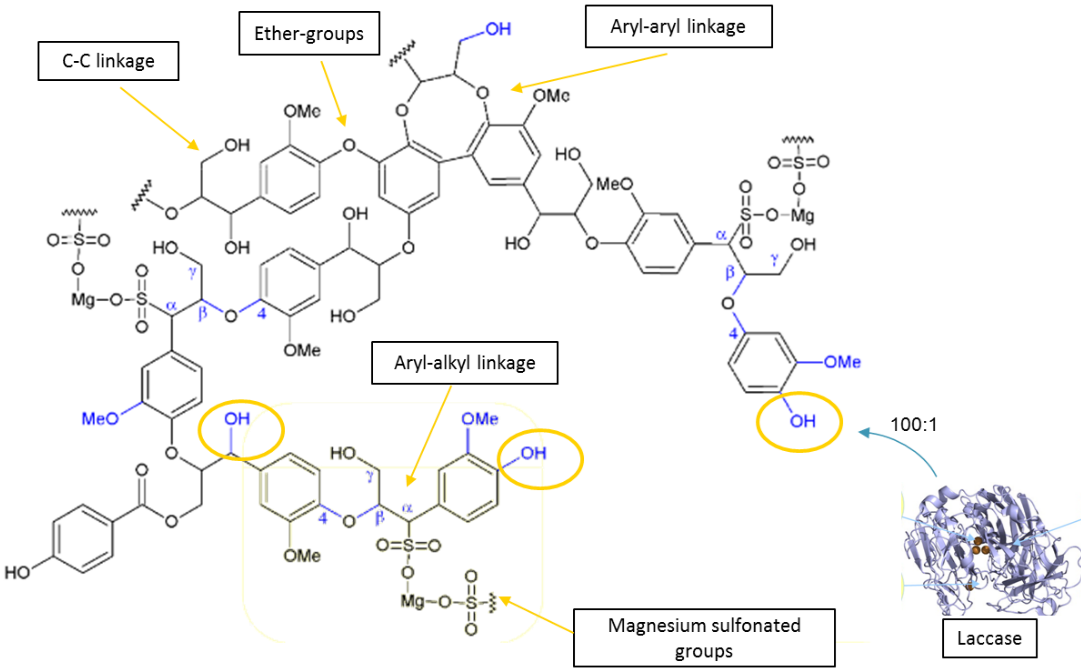

Fig. 3-12: Suggested structure of magnesium lignosulfonate. The yellow circles highlight the OH-groups, where the enzyme laccase *Myceliophthora thermophile* probably attach. Other functional groups and side chains are explained in the figure, adapted from [11] [38] [40] [83].

4 Experimental approach and discussion

4.1 Experimental approach

The present work investigates the application of enzymatically polymerized lignosulfonates (epLS) as adhesive, using different material parings relevant for the automotive application and a variation of the composition of epLS. To focus on the most promising combination(s) between adhesive and substrate, an initial adhesion test was applied, which is described in section 4.2.4. Based on that these results standard tests in terms of adhesives for automotive industry were carried out to evaluate the applicability. The required data respectively properties of the standard test methods were extracted from internal and external standards and discussed with the Department of Quality, Engineering and Production at Magna Steyr Fahrzeugtechnik (Graz, Austria) to define a clear working approach. Finally, the material data of the epLS-adhesive were determined and the industrial application for car seat manufacturing was investigated.

For an efficient and methodical approach a guideline was prepared which is meant to identify the optimum combination of epLS-type/substrate pairing. The workflow of the experimental approach is depicted in Fig. 4-1.

The experimental section is divided into four parts, where the first part describes the preparation of epLS, especially the pre-polymerization and previous investigations which are made to identify the optimum epLS-type and material combination(s). The second part includes the evaluation of the epLS-adhesive with standard test methods and the third part deals with the determination of the material data. To evaluate a commercial application of the epLS-adhesive, the last part describes a case study where the epLS-adhesive is tested in car seat manufacturing.

The material data, like density, water content, solubility, as well as the thermogravimetric analysis were investigated in cooperation with the Institute of Chemical Engineering and Environmental Technology, whereas the viscosity and the contact angle were determined in cooperation with the Institute of Pulp, Paper and Fibre Technology at Graz, University of Technology (Graz, Austria). Standard test methods, like initial adhesion, lap shear tests or alternating climate test were carried out by the Department of Department of Material Testing at Magna Steyr Fahrzeugtechnik (Graz, Austria).

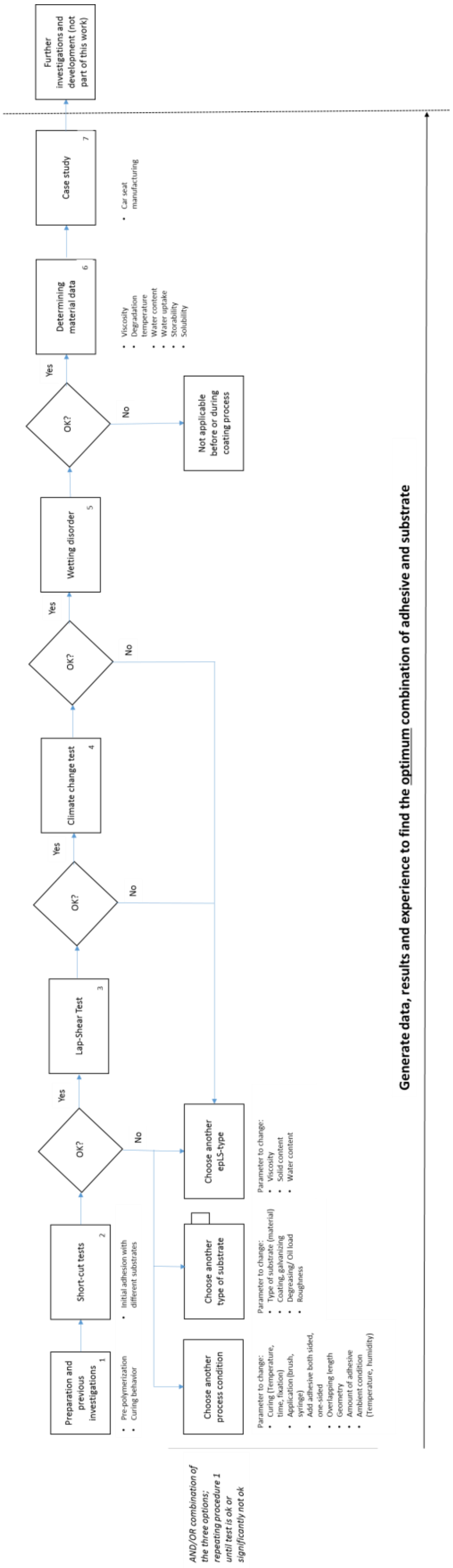

Fig. 4-1: Experimental approach: The guideline serves as a systemic approach to investigate novel adhesives, such as the epLS-adhesives, in terms of a commercial application for automotive industry.

4.2 Preparation of epLS and previous investigations

4.2.1 Materials

Enzymatically polymerized Lignosulfonates (epLS) were provided by the Institute of Environmental Biotechnology of the University of Natural Resources and Life Sciences, Vienna, Austria (BOKU). The epLS consists of ultra-filtrated Magnesium (Mg)-lignosulfonate (LS) derived from a local pulp and paper plant, glycerine and enzymes and were provided in different compositions. The enzymes were Laccase from *Myceliophthora thermophila* (MtL). [12]

In order to optimize the adhesive composition in terms of applicability different ratios of LS to MtL/Glycerol/AKD (alkyl ketene dimer) as well as different dry substance content of LS were investigated. The ratio of the ingredients, the batch index I, denoting the composition of the epLS, and the total dry substance content (% TDS) are as summarized in Tab. 4-1.

Tab. 4-1: Types of enzymatically polymerized lignosulfonates in dependence of their compositions.

Indication	**TDS (wt%)**	**LS : Glycerine (-)**	**AKD (w/v%)**	**LS : MtL (-)**
epLS_15/2/0	15	2:1	0	100:1
epLS_30/2/0	30	2:1	0	100:1
epLS_30/0/0	30	1:0	0	100:1
epLS_21/2/5	21	2:1	5	100:1

The materials for adhesive testing from different manufacturer and were provided by Magna Steyr Fahrzeugtechnik, Graz, Austria. Those materials were zinc galvanized steel, alodine coated alumina, polypropylene (PP ST6008), carbon fibre reinforced plastic (CFRP, P16_30 142 Hexion EPFC LCM-278), leather and viscose.

The solvents used for the solubility tests were

- Isopropanol (70 %): Carl Roth
- Isohexane (96 %): Carl Roth
- HCl (32%): Sigma Aldrich
- NaOH (26%): Sigma Aldrich
- Aqua regia: nitric acid (65 %) and hydrochloric acid (35 %) in a molar ration of 1:4

4.2.2 Pre-Polymerization

Different degree of polymerization were investigated by carrying out the polymerization until a certain progress and categorizing it according to the viscosity. Tab. 4-2 explains the categorization and defines the degree of polymerization by the viscosity.

Tab. 4-2: Categorization of the different polymerized epLS in dependency of their viscosity.

Categorization	Abbreviation	Description	η (Pa*s)
Original	original-epLS	as delivered by BOKU, described in Tab. 4-1	< 0.1
Hydrogel	hydrogel-epLS	pre-polymerization was exceeding the optimum viscosity point	> 10
Optimum	pre-epLS	the epLS was pre-polymerized until the optimum viscosity was reached	9 - 10
Cured	cured-epLS	the epLS was applied on a substrate (e.g. leather) and cured	undefined, solid
Dried	dried-epLS	As described in 4.4.4 the epLS was dried in an oven to remove the water to achieve a solid content of 100 wt%	undefined, solid

The pre-polymerization of epLS increases the viscosity and improves the application properties. Fig. 4-2 shows how the procedure was carried out. The pre-polymerization was performed by heating and stirring the original-epLS in a beaker on a temperature controlled magnetic stirrer (IKA RET control/t) until a desired viscosity was reached that enables an appropriate application. The application and bonding behaviour was best right before hydrogel formation. Therefore, the pre-polymerization was stopped before a hydrogel was formed by removing the beaker from the heating plate. The epLS with this optimum viscosity can be applied on the substrate with a brush, spatula or syringe.

The parameter range for the pre-polymerization of epLS with a dry substance content of 30 wt% and the epLS with 21 wt% TDS leading to sufficient viscosity were T = 50 °C – 57 °C and t = 1.5 h – 2 h, whereas the pre-polymerization of epLS with a dry substance content of 15 wt% was carried out at the same temperature in 8 h. Due to the long polymerization time of the epLS with 15 wt% TDS, the epLS with 30 wt% TDS was used for further investigations. The temperature was chosen since the enzymes have their activity maximum between 45 °C – 50 °C [41]. It was observed that a bulk temperature of T = 20 – 25 °C decreases the polymerization ability and therefore increases the reaction time for epLS_30/2/0 up 8 h. For a homogenous consistency the magnetic stirrer was adjusted to 750 rpm. During the experiment it was observed that a too high stirrer speed inhibits the polymerization, whereas slower stirring worsens the homogeneity of the substance and therefore the application and adhesive properties.

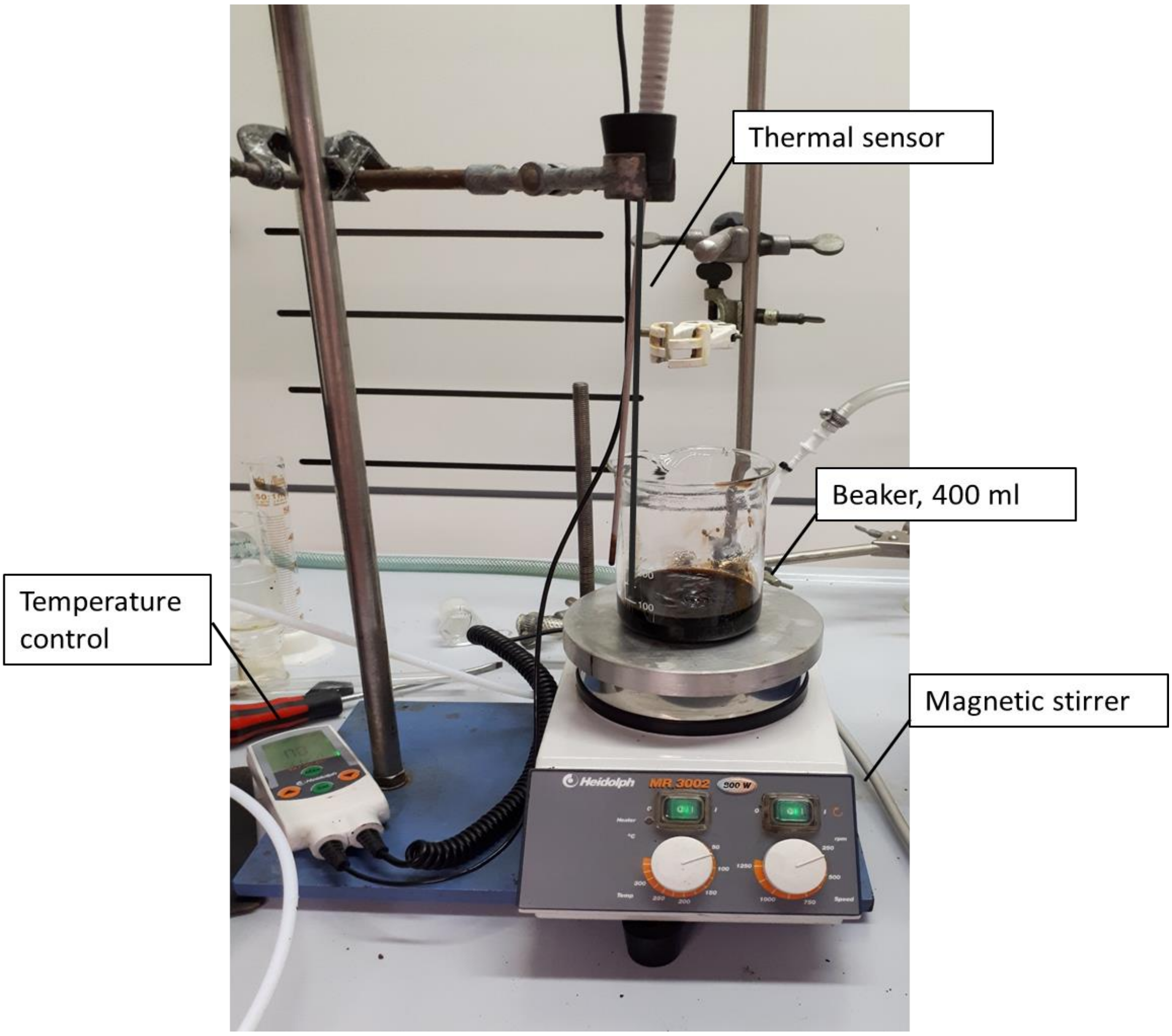

Fig. 4-2: Experimental set-up for pre-polymerization of epLS_30/2/0: The parameter were T = 50 °C – 57 °C and t = 1.5 h – 2 h, with a stirrer speed of 750 rpm. The pre-polymerization was proceeded until the optimum viscosity was reached. The optimum viscosity was η = 9 to 10 Pa·s and was determined according to section 4.4.2.

4.2.3 Curing behaviour

As described in section 3.5, the curing behaviour is influenced by the temperature and humidity and the curing influences the bonding ability of the adhesive. Therefore the parameters of the optimum curing condition had to be defined and kept constant for all material pairings.

The curing behaviour of pre_epLS_30/2/0 was investigated qualitatively. The epLS was applied on polypropylene (PP). PP was chosen instead of leather or other porous materials to avoid any penetration. An adhesive strip of 1 cm x 10 cm size was applied with a syringe onto the PP and cured in different ways. Tab. 4-3 summarizes the curing condition chosen for the investigations.

The sample was once placed in an oven at different temperature regimes T = 40°C, 60°C and 100 °C and secondly cured at ambient conditions in two different laboratory rooms, where the temperature and humidity was measured.

Tab. 4-3: Different parameters for investigation of the curing behaviour of pre-epLS. The relative humidity in the drying oven was not measured.

T (°C)	**r.H. (%)**	**t (min)**	**Curing method**	**Sufficient curing?**
40	-	20	Oven	Yes
40	-	45	Oven	Yes
60	-	20	Oven	Yes
60	-	45	Oven	Yes
100	-	10	Oven	No
24	58	20	Ambient climate condition in laboratory room	No
24	58	90	Ambient climate condition in laboratory room	Yes
23	35	20	Ambient climate condition in laboratory room	No
23	35	60	Ambient climate condition in laboratory room	Yes

Fig. 4-3 shows a sample of epLS on PP before and after curing. The curing process was considered as finished as soon as the adhesive strip could be peeled off without any cohesive fracture. Cohesive fracture indicates insufficient cross-linking of the molecules due to unfinished polymerization, related to too short curing time or due to degradation of the substance, related to too hot temperature.

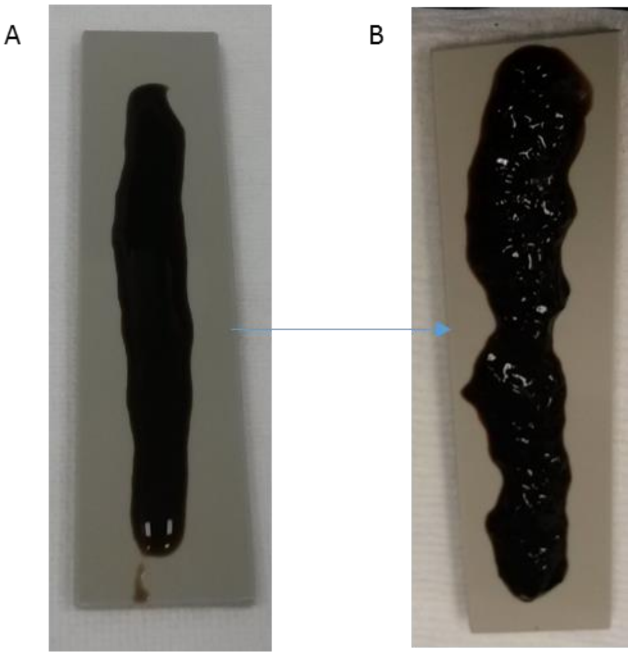

Fig. 4-3: epLS on PP: (A): before curing, (B): after curing at T = 23 °C, 35 % r.H. for 60 min).

Sufficient bonding ability was even reached at ambient conditions in the laboratory rooms within a curing time of t ≤ 90 min. If the time was t ≤ 60 min, the curing process was not completed and the adhesive showed cohesive fracture after peeling off. For T = 23 °C, 35 % r.H., no cohesive fracture was detected after t = 60 min, for T = 24 °C, 58 % r.H. no cohesive fracture was observed after t = 90 min. Since the adhesive bonding of different material pairings was carried out in different laboratory rooms where the climate conditions were not constant, a temperature and humidity range was defined. The range of proper curing conditions were defined to be between T = 23 – 25 °C, 35 - 43 % r.H and a curing time of t = 60 min or T = 24 – 26 °C, 58 – 66 % r.H, and a curing time of t = 90 min. For each bonding test, especially for curing the adhesive on the substrate, the conditions were measured to verify the temperature and humidity.

An increase in temperature from 23 °C to 40 °C or 60 °C by placing the sample in an oven reduces the curing time from 60 min to 20 min, which means that the polymerization is accelerated. At an oven temperature T > 100 °C some sections with burned adhesive were identified, which indicated degradation of the adhesive. Therefore the curing behaviour respectively the degradation behaviours was investigated in the thermogravimetric analysis and will be discussed in 4.3.5. [42] [12]

4.2.4 Initial adhesion

4.2.4.1 Experimental approach

While adhesives are durable at normal stresses, i.e. tensile and compression stress, they are very sensitive in terms of shear stress. To expose the adhesive to the worst-case conditions, the peel off testing was applied. During this test, the highest impact of the shear stress takes place. If the peel off testing showed proper results regarding cohesive and adhesive fracture, the bonding was considered as sufficient enough for lower loading stresses, e.g. tensile stress. This is justified by the fact that other stresses, like tensile or compression stress or a combination of tensile and shear stress, have less mechanical impact on the bonding than peel off stress. [43] [44]

The initial adhesion test is a manual peel off test, where the adhesive strip is pulled at an angle of 90 ° normal to the substrates plane. The test was applied for screening the adhesive bonding strength between epLS and the substrate. The investigated substrates were alodine coated alumina, zinc galvanized steel, polypropylene, leather and CFRP. The used adhesive type was pre-epLS_30/2/0, whereby original-epLS_30/2/0 and hydrogel-epLS_30/2/0 were used as reference.

The testing was carried out in accordance to the Magna-internal instruction AAQ54209 where a strip of pre-epLS (1 cm x 10 cm) was applied on the investigated materials and cured at 24 °C, 58 % r.H. and for 60 min. After curing, the strip was removed by continuously pulling one end by hand while the bonding was cut with a knife. Fig. 4-4 shows the experimental set up and the fracture pattern which was evaluated referring to DIN EN ISO 10365. [45]

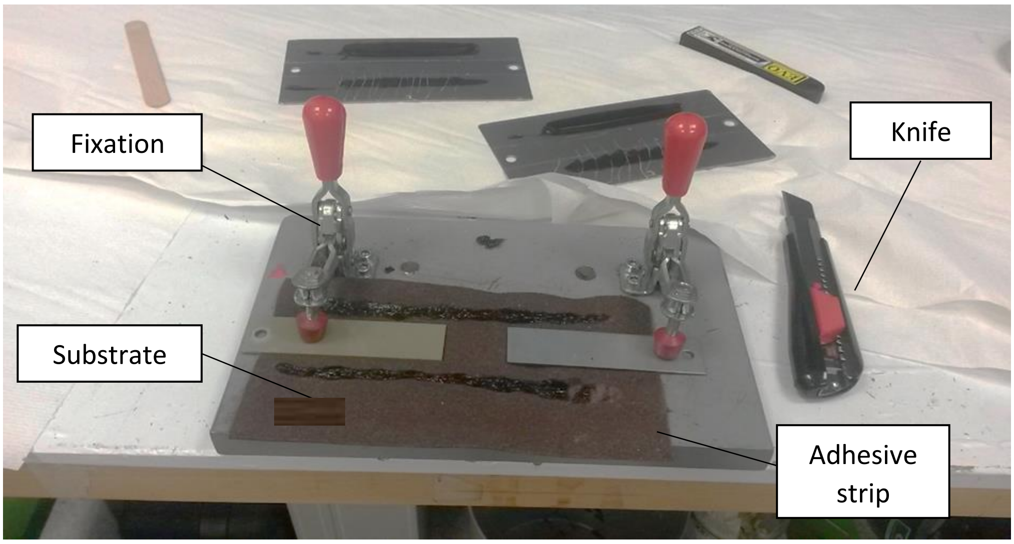

Fig. 4-4: Experimental set up for the initial adhesion test: The adhesive strip was applied onto leather and cured at 24 °C, 58 % r.H. for 60 min. After putting the leather sample in the fixation, the adhesive strip was removed with a knife.

After the peel off test, the adhesive remaining on the substrate was analysed. If the adhesive residue is distributed evenly among the surfaces, the fracture was cohesive which means the adhesive matrix itself broke. If no adhesive residues were found on the substrate surface an adhesive fracture occurred. Usually the fracture pattern shows a combination of both cases. According to Bode E. et al. [43] for adhesive applications generally an adhesive fracture is preferred over the cohesive fracture. Substrate fracture before adhesive fracture is not useful in terms of lap shear testing since the substrate breaks earlier than the adhesive. This information helps choosing the appropriate parameter like the displacement rate for later lap shear testing. The sample with the best fracture pattern was chosen for further investigations. Fig. 4-5 illustrates the peel off test and two possibly occurring fracture patterns. [43] [46]

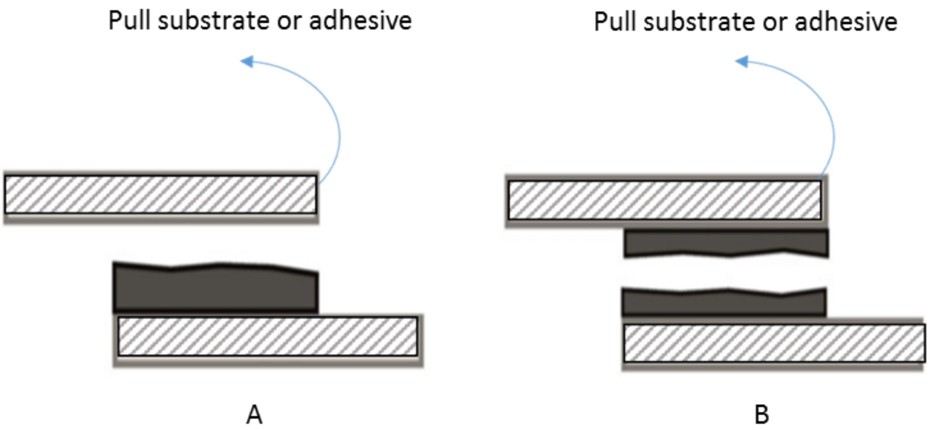

Fig. 4-5: Fracture pattern after peel off test: (A): adhesive fracture, where the adhesive remains on the substrate, (B): cohesive fracture, where the adhesive matrix breaks.

4.2.4.2 Results

The initial adhesion test showed that the pre-epLS_30/2/0, applied onto leather, had the best fracture pattern. Region (A) in Fig. 4-6 depicts the fracture pattern of hydrogel-epLS_30/2/0 and region (B) depicts pre-epLS_30/2/0. First the pre-epLS was applied, then the hydrogel-epLS was applied with a syringe. The fracture pattern analysis showed mainly substrate fracture for the region (B), where pre-epLS was applied, meaning that some fibres of leather were torn out. This indicates firstly that the cohesive bonding of the adhesive is sufficient and secondly that the adhesive bonding strength between the substrate and the adhesive was even stronger than the strength of the leather itself. In terms of lap shear testing, described in section 4.3.1, a substrate fracture before adhesive fracture is not useful since the substrate breaks earlier than the adhesive. However, this information helps choosing the appropriate parameter like the displacement rate for the later lap shear testing. [43]

Region (A) in Fig. 4-6 shows hydrogel-epLS. The application with a syringe was difficult since the outlet was often plugged or the adhesive spread out uncontrolled which is caused by the inhomogeneous consistency of the hydrogel-epLS. Further, the adhesive bonding was not sufficient, neither before, nor after curing. The reason for that might be the high viscosity; the substance was not able to penetrate into the pores of the leather and no interaction between hydrogel-epLS and leather took place. This resulted in an insufficient cohesive and adhesive bonding strength.

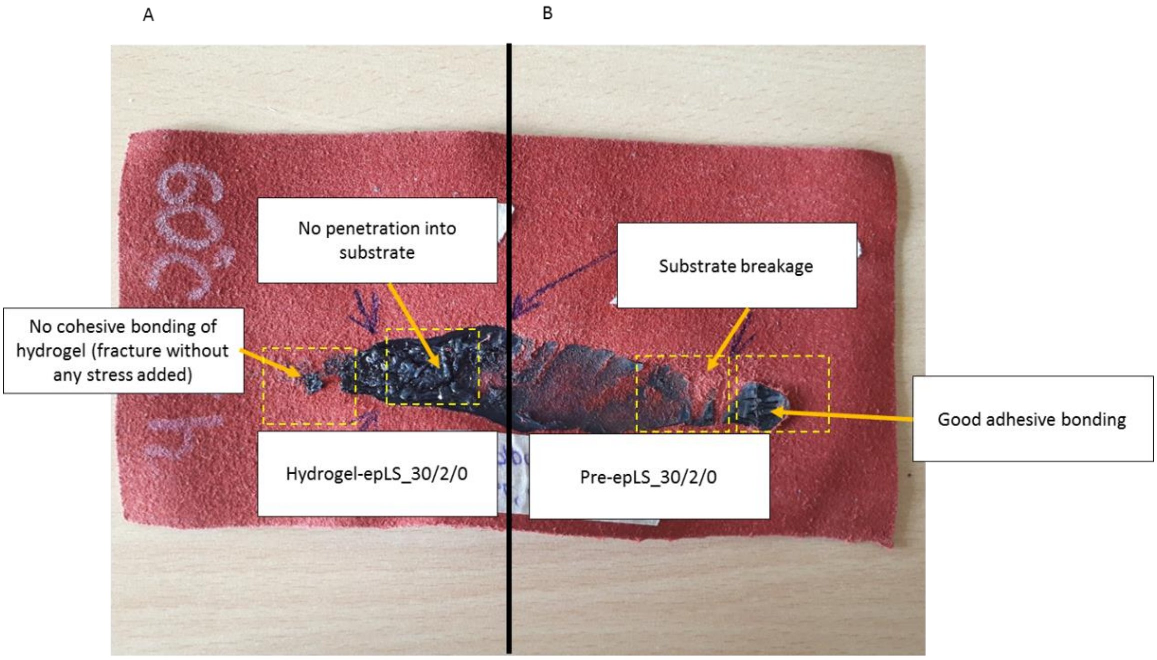

Fig. 4-6: Fracture pattern of the initial adhesion test: (A) is the region where first hydrogel-epLS was applied, (B) is the region where then pre-epLS was applied. With a syringe. The areas marked in yellow demonstrate the fracture pattern.

The test with original-epLS_30/2/0 showed good adhesive bonding but insufficient application behaviour. Due to the lower viscosity of original-epLS_30/2/0 compared to pre-epLS_30/2/0, the adhesive penetrated easier into the leather pores and bonded there adhesively, but also was highly fluent and lead to unstable behaviour on the leather meaning that the adhesive was very thin and was distributed in all directions. In terms of adhesive consumption and contamination of the substrate and the working place the viscosity needs to be higher to ensure that the adhesive remains on the substrate and keeps its form stability.

Even more unsatisfying results were gained with the original-epLS with the dry substance content of 15 wt% which was highly fluent and showed bad application, curing and adhesive properties Fig. 4-7 illustrates this characteristic, where the epLS_15/2/0 was applied on leather. Pre-polymerized epLS_15/2/0 had sufficient bonding and application properties, however the pre-polymerization of epLS_15/2/0 was carried out in 8 h compared to the pre-polymerization of epLS_30/2/0 which was carried out within 2 h. Therefore the epLS with a dry substance content of 15 wt% was not investigated further.

The evaluation with the substrates alumina, steel, PP and CFRP showed insufficient bonding ability. Comparable with a sticker, the cured adhesive could be peeled off easily. The fracture pattern showed no cohesive fracture and even no residues of adhesive on the substrate's surface. This indicates that no interaction took place and therefore the epLS-adhesive could not bind to the substrate. Based on the results, these substrates were not investigated for further experiments. Fig. 4-7 demonstrates this result, exemplary for zinc galvanized steel.

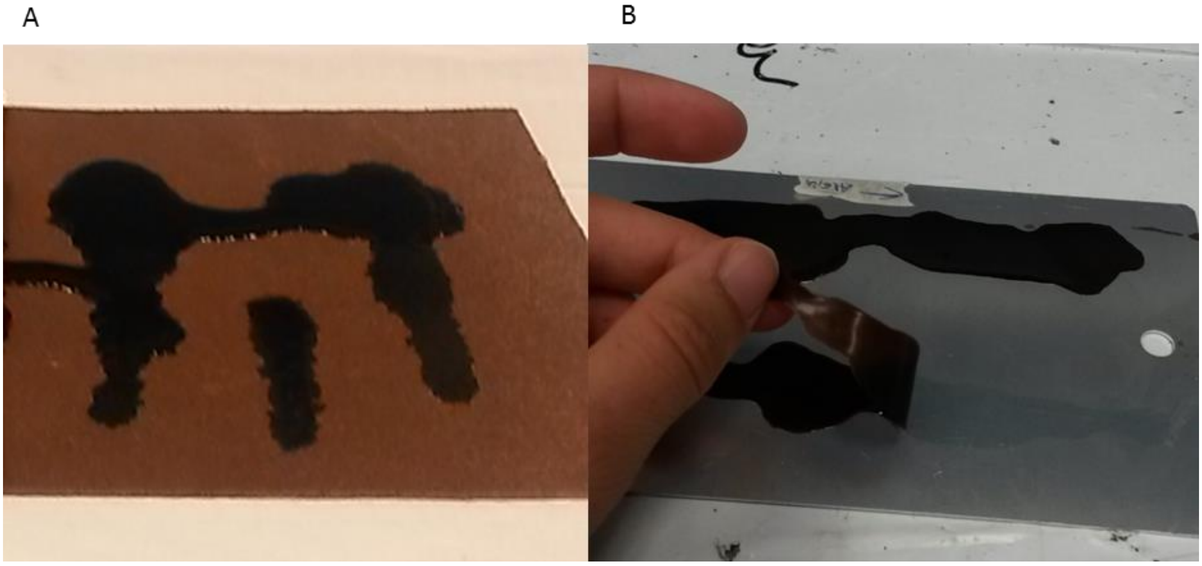

Fig. 4-7: Initial adhesion tests: (A): epLS_15/2/0 applied on leather; because of the low viscosity it had bad application and stability properties; (B): pre-polymerized epLS_30/2/0 on zinc galvanized steel; no adhesive bonding took place.

Based on this screening it was found that pre-epLS_30/2/0 had the best performance in terms of pre-polymerization, application with a syringe or brush and regarding to the adhesion strength. Williams et al. [16] stated that an optimum penetration of the adhesive into the substrate's pores is crucial to enable a proper adhesive and cohesive bonding and the results show that the viscosity is an important factor. Therefore only pre-epLS_30/2/0 was used for further investigations.

4.3 Standard test methods for automotive application

This chapter summarizes the standard test methods for adhesives which were applied to the epLS adhesive. The standard test methods were carried out in cooperation with the Department of Quality, Engineering and Production at Magna Steyr Fahrzeugtechnik (Graz, Austria).

4.3.1 Shear strength

4.3.1.1 Experimental approach

The shear strength is investigated with the lap shear test performed with Z050, TestXpert II (ZWICK, Germany) in accordance to DIN EN 1465 [47]. The fracture pattern was evaluated in reference to DIN EN ISO 10365 [45].

For the test 1 a leather-leather combination was tested and prepared with pre-epLS_30/2/0 and pre-epLS_30/0/0 which does not contain glycerine. The lot size of the prepared samples was n = 3. Additionally, one sample was prepared for adjusting the parameters on the lap shear testing machine.

For test 2, leather and viscose were bonded with pre-epLS_30/2/0. To investigate a possible improvement of the shear strength a leather-viscose bonding with pre-epLS_21/2/5, which contains AKD, was also prepared. The samples were prepared twice to compare the results of the lap shear test before and after the alternating climate test. The results are summarized in section 4.3.3.2. The lot size was n = 5, additionally, one sample was prepared for adjustment of the parameters on the lap shear testing machine.

The amount of adhesive for each sample was between 0.18 and 0.21 g/cm² and was applied one-sided with a spatula. A wooden roller was used for an initial bonding and for smoothing the surface of the leather. The sample were cured at T=23 °C, 35 % r.H for 60 min. The overlapping area was 50 mm x 35 mm, clamping length was 100 mm, the displacement rate of the jaws was 10 mm/min. Fig. 4-8 shows the prepared samples and dimensions for the lap shear testing of pre-epLS_30/2/0. Fig. 4-9 shows the experimental set up of pre-epLS_30/0/0 and pre-epLS_21/2/5. The figure shows that especially the AKD-epLS penetrates through the viscose layer and appears on the other side.

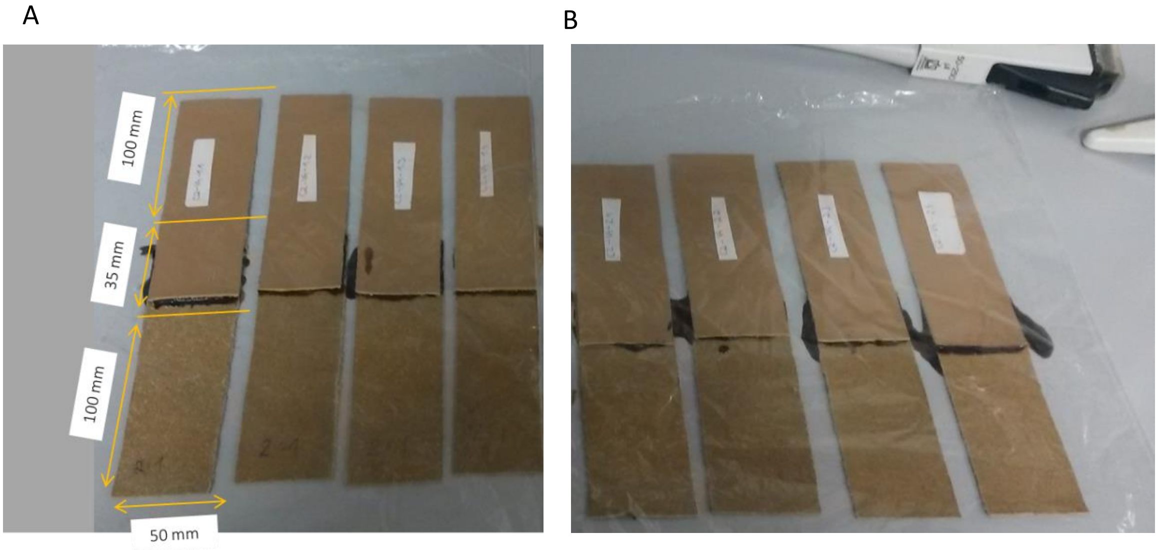

Fig. 4-8: Prepared samples for the lap shear test 1: The overlapping area was 50 mm x 35 mm, clamping length was 100 mm, the displacement rate of the jaws was 10 mm/min. (A) leather-leather with pre-epLS_30/2/0, (B) leather-leather bonded with pre-epLS_30/0/0. The dimension are depicted once in (A).

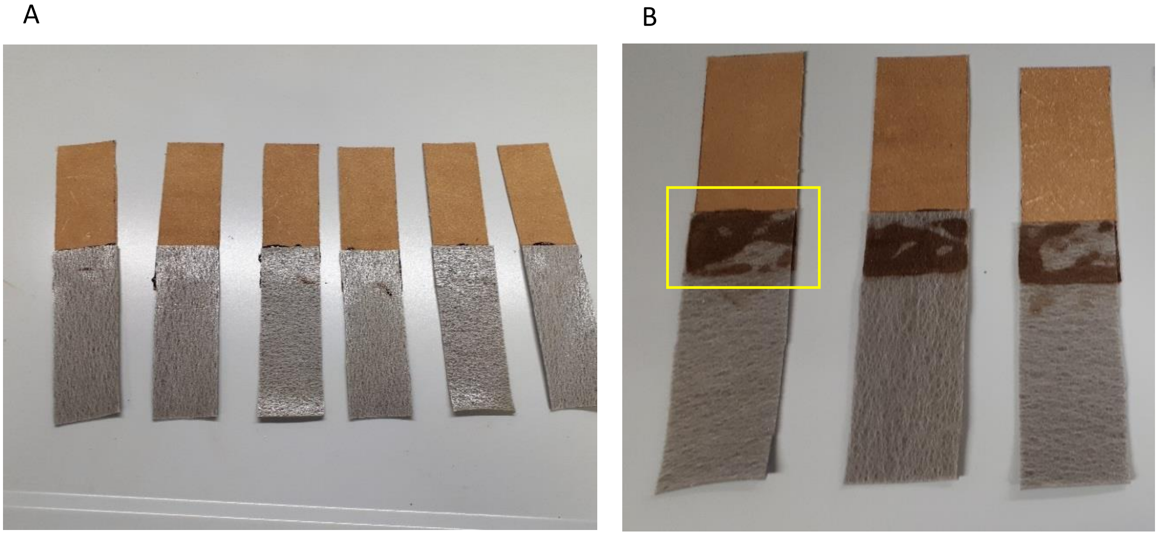

Fig. 4-9: Prepared samples for the lap shear test 2: The overlapping area was 50 mm x 35 mm, clamping length was 100 mm, the displacement rate of the jaws was 10 mm/min. (A) leather-viscose with pre-epLS_30/2/0, (B) leather-viscose bonded with pre-epLS_21/2/5. The area marked yellow demonstrates the epLS-adhesive with AKD which penetrates through the viscose.

The results of the lap shear test can be interpreted in multiple ways. A graph is generated where the force in dependence on the elongation of the substrate is depicted, which give information about the maximum force that can be hold by the adhesive until the fracture occurs ($\mathrm{F_{max}}$). The shape of the force curve gives information about the adhesive fracture, e.g. the flatter the curve the higher the elasticity of the sample. It has to be mentioned, that the lap shear test not only depends on the adhesive properties, but also on the substrate. [43]

The maximum shear strength is calculated by dividing the maximum load, which is the outcome of the lap shear test, by the bonding area (where A = 50 mm x 35 mm):

$$\tau_{\max} = \frac{F_{\max}}{A}\ [\mathrm{MPa}]$$

Equ. 4-1

$\tau_{\max}$…maximum shear strength until fracture (MPa)

$F_{\max}$…maximum load until fracture (N)

A…adhesive bonding area (m²)

4.3.1.2 Results of the leather-leather bonding

Fig. 4-10 displays the stress/elongation diagram of test 1, where a leather-leather bonding with pre-epLS_30/2/0 was investigated. The colour of the curves indicates the sample (number 1 to 4), whereas sample 4 is used for adjustment of the testing machine. The mean value of the maximum load was 364.7 N, where the averaged shear strength was 0.2 MPa. The maximum load was 553 N where the sample broke at 40.2 mm. The curve of sample 2 and 3 has a long, flat shape which indicates elastic behaviour. According to Bode et al [43], the minimum shear strength of the adhesive has to be higher than the substrate. For the application in car seat manufacturing the shear strength has to be at least 0.02 MPa, respectively 12.5 N, since this is shear strength of the weakest material in the pairing, namely viscose. The maximum shear strength of the viscose was determined in 4.3.1.3. Tab. 4-4 summarizes the results of test 1, whereas the original data can be found in the appendix in chapter 11. [43]

According to Jankauskaitė et al. [48] the nature of the leather has an influence on the stress distribution of an adhesive bonding. Even when the same leather batch was used for the preparation of the sample it might be that the strength properties vary due to their natural origin of leather. Therefore it has to be considered that the leather has elastic properties and might support the high elongation, as well as leading to different lap shear results, as it is also seen for the lap shear test 2 with pre-epLS_30/0/0. [49]

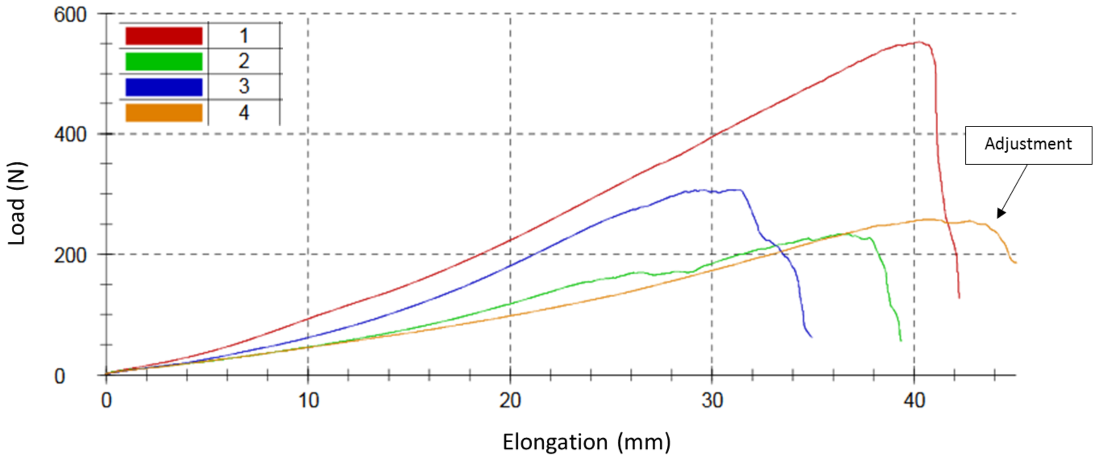

Fig. 4-10: Load/elongation diagram of test 1 with pre-epLS_30/2/0 and leather: The colour of the curves indicates the sample number 1 to 4, whereas number 4 was prepared for adjustment of the parameters on the lap shear testing machine and is not taken into account.

Tab. 4-4: Results of the test 1: Maximum load until fracture of the sample with pre-epLS_30/2/0 and leather.

Sample number	**Maximum shear strength (MPa)**	**Elongation at fracture (mm)**	**Maximum load (N)**	**Elongation at maximum load (mm)**
1	0.3	42.2	553.0	40.2
2	0.1	39.3	234.0	36.3
3	0.2	34.9	307.0	30.9
mean value	0.2	38.8	364.7	35.8
standard deviation	0.1	3.7	167.1	4.7

Fig. 4-11 demonstrates the fracture pattern of all 3 samples and shows mainly cohesive fracture of the adhesive. Exemplarily, some regions are marked to explain the pattern. The yellow circles are regions where leather fibres were partially torn out which aligned to a substrate fracture. The blue areas indicate cohesive fracture, which indicates that the matrix of the epLS-adhesive broke, but the adhesive bonding to the leather was sufficient. At the edges, some adhesive fracture was detected (marked in green), where the adhesive was applied imprecisely.

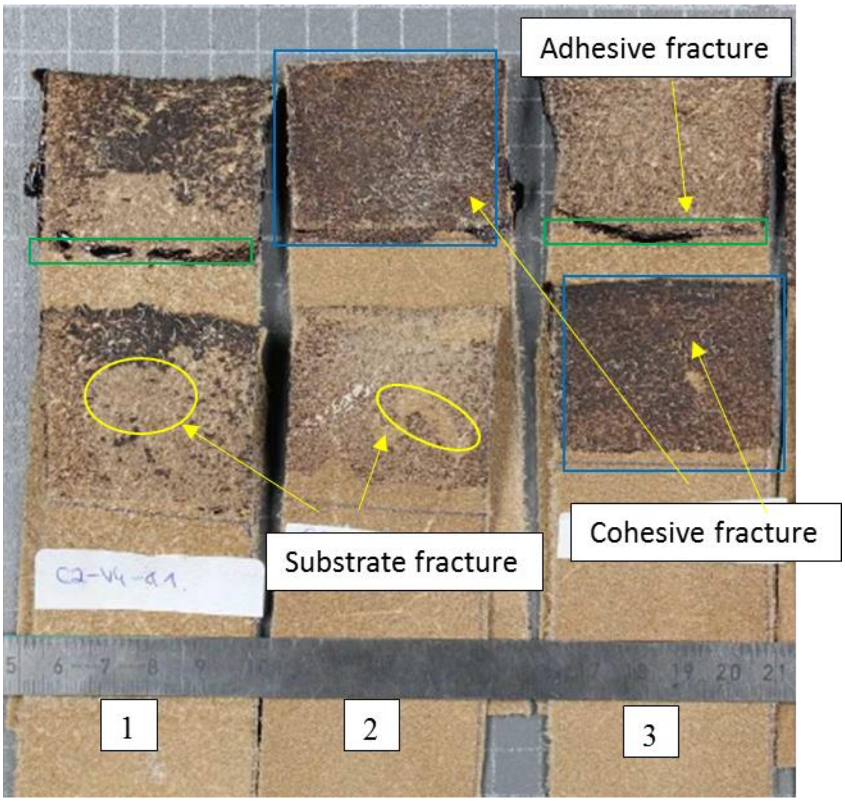

Fig. 4-11: Fracture pattern of test 1: Leather-leather bonding with pre-epLS_30/2/0. The yellow circles show regions where substrate fracture took place. The blue areas indicate cohesive fracture.

In comparison to the samples examined in test 1, the samples with pre-epLS_30/0/0 in the test 2, led to different results. The maximum averaged load of pre-epLS_30/0/0 in test 2 was 342 N and therefore smaller than the averaged load of pre-epLS_30/2/0 in test 1. However, the epLS_30/0/0 also met the minimum shear strength of 0.02 MPa, respectively 12.5 N, but the elongation length, which indicates an elastic behaviour, was smaller than the elongations length of epLS_30/2/0. Pre-epLS_30/2/0 had an elongation length of 35.9 mm, whereas pre-epLS_30/0/0 broke at an elongation length of 27.9 mm. Tab. 4-5 summarizes the results of test 2, whereas the original data can be found in the appendix in chapter 11.

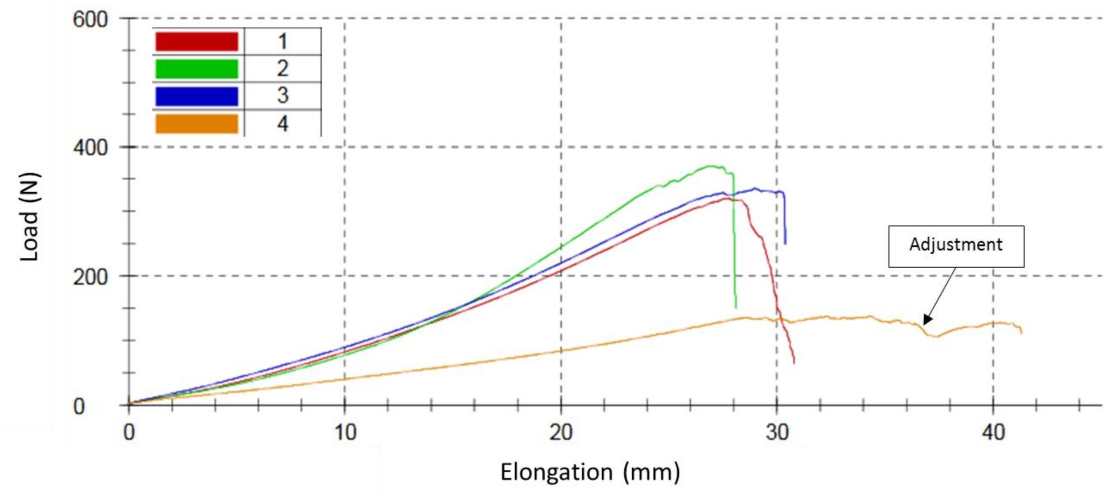

Fig. 4-12: Load/elongation diagram of test 2 with pre-epLS_30/0/0 and leather: The colour of the curves indicates the sample number 1 to 4, whereas number 4 was prepared for adjustment of the parameters on the lap shear testing machine and is not taken into account.

Tab. 4-5: Results of the test 2: Maximum load until fracture of the sample with pre-epLS_30/0/0 and leather

Sample number	**Maximum shear strength (MPa)**	**Elongation at fracture (mm)**	**Maximum load (N)**	**Elongation at maximum load (mm)**
1	0.2	30.8	320.0	27.7
2	0.2	28.1	371.0	26.9
3	0.2	30.4	335.0	29.0
mean value	0.2	29.8	342.0	27.9
standard deviation	0.0	1.5	26.2	1.1

Fig. 4-13 depicts the fracture pattern of the 3 samples tested in test 2, where epLS_30/0/0 was investigated. The fracture pattern show mainly cohesive fracture with partially adhesive fracture Compared to the samples in test 1, where epLS_30/2/0 was used, substrate fracture was not identified which indicates that the bonding of the epLS_30/0/0, which was without glycerine, was not as strong as the bonding of epLS_30/2/0 with glycerine.

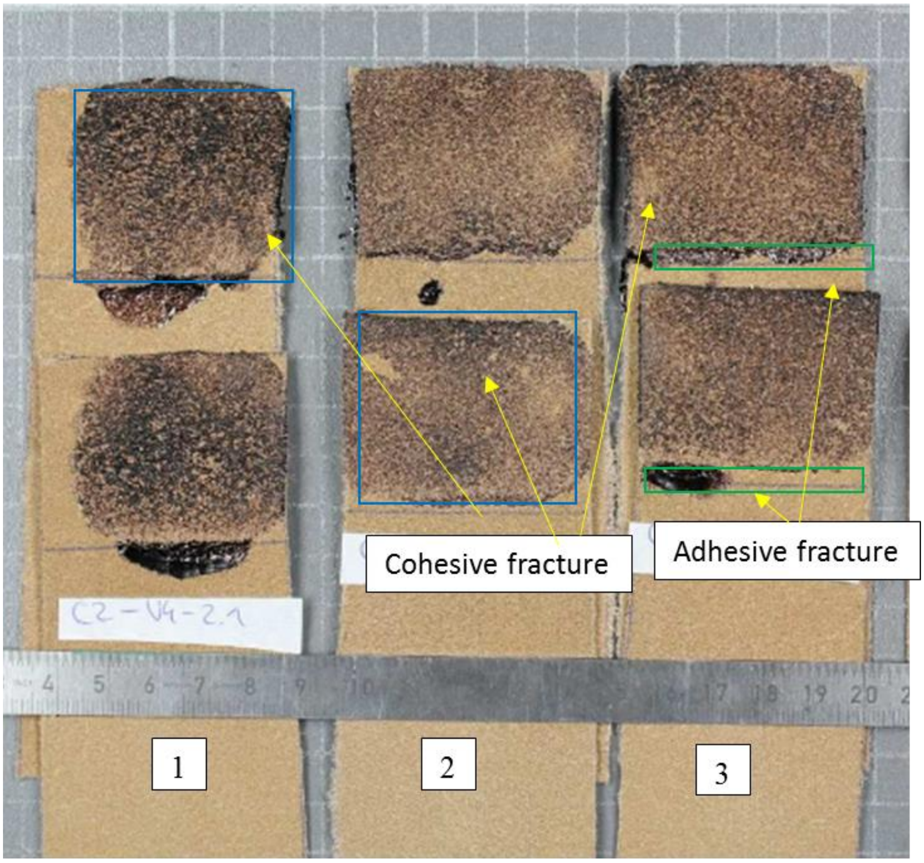

Fig. 4-13: Fracture pattern of test 2 with a leather-leather bonding with pre-epLS_30/0/0: The areas marked in blue indicate cohesive fracture, whereas the areas marked in green demonstrate adhesive fracture.

The better shear stress performance of the samples in test 1, where epLS_30/2/0 was tested, is explained by the fact that a certain amount of glycerine added to the epLS results in an increase of the elastic behaviour. Glycerine or other softener added to adhesives do not influence the polymerization but they are embedded in the molecular network and hence influence the flexibility of the molecules and therefore the deformation ability which improves the adhesive and cohesive strength. [46] [10]

Based on the results of the lap shear test it can be stated that the pre-epLS_30/2/0, which contained glycerine, showed the better results regarding shear strength and elastic behaviour. Nevertheless, the lap shear test is a fast method that is applied for a simple comparison of different substrates or adhesives. A precise interpretation of the curve can be done by investigating the material properties of leather, which were not available, and applying other tests where the elastic behaviour can be compared, like dynamic test methods or with a 90 ° peel test. These investigations were not carried out in this work. [50]

4.3.1.3 Results of the leather-viscose bonding

Since the leather-leather bonding with epLS_30/2/0 showed promising results, a leather-viscose bonding was carried out to investigate further material-pairing. Instead of pure epLS_30/0/0, a leather-viscose bonding with epLS_21/2/5, with AKD, was tested to examine an improvement or worsening of the strength performance. The preparation of the samples was carried out twice, once for a lap shear test before and once for a lap shear test after the alternating climate test. This section demonstrates the results of the lap shear test before the alternating climate test, whereas the results after the alternating climate change test are presented in section 4.3.3.2.

The lap shear test was not successful since the viscose broke before the epLS-adhesive showed fracture. The viscose had a low shear strength, meaning a fracture occurs at F_{max} = 12.5 N, compared to leather/epLS-adhesive which broke at $F_{max} \geq 250$ N. Even reinforcements with alumina strips did not yield useful results, where the sample broke at 43.7 N. The results are demonstrated in Fig. 4-14, where sample 2 is reinforced with alumina strips. Based on these results a manual shear testing was carried out and the fracture pattern was then analysed in accordance to DIN EN ISO 10365 [45], whereas the viscose was peeled off manually, as it was described in section 4.2.4

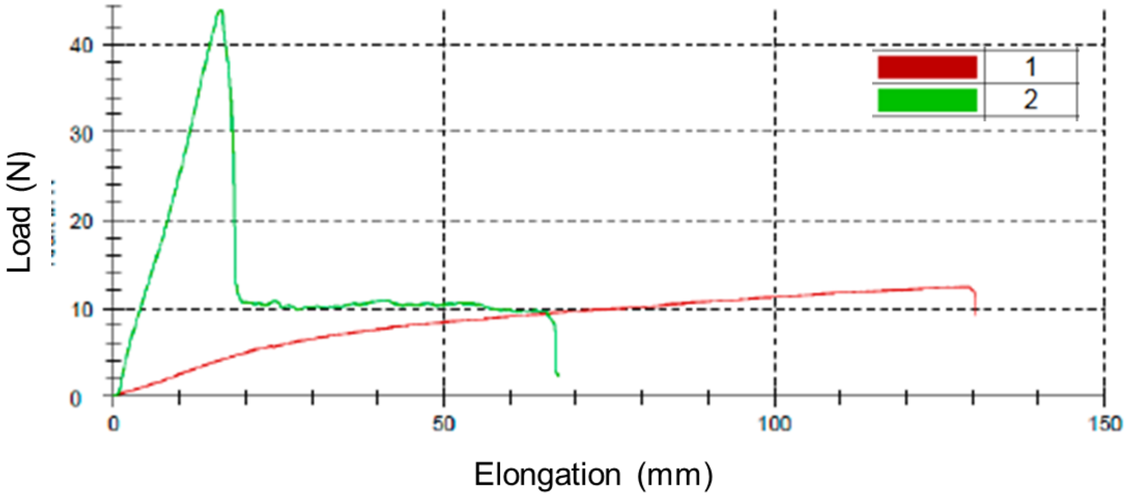

Fig. 4-14: Load/Elongation diagram of test 3 with pre-epLS_30/2/0 and leather-viscose: The viscose broke before the epLS-adhesive. The colour of the curves indicates the sample number 1 to 2, whereas number 2 was reinforced with alumina strips which also did not lead to a useful result.

According to the report of the lap shear testing, indicated by the Magna-internal number WT61565, the fracture pattern of the pre-epLS_30/2/0 showed mainly substrate fracture, see Fig. 4-15, whereas the fracture pattern of the AKD-pre-epLS_21/2/5 showed both, adhesive and cohesive fracture. This indicates that the latter one is weaker in terms of inner bonding strength and bonding to the substrate.

Further, as noticed in the preparation of the samples with AKD-epLS and shown in (B) of the Fig. 4-15, the adhesive penetrates through the viscose material which leads to adhesive loss.

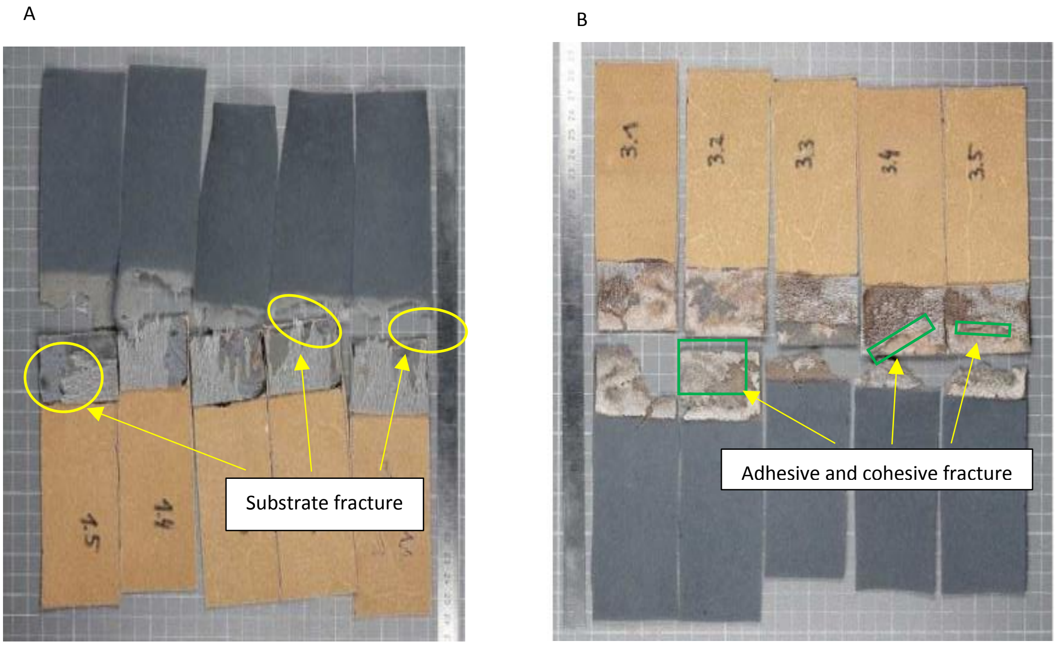

Fig. 4-15: Fracture pattern of the leather-viscose samples: (A) epLS_30/2/0, (B) epLS_30/2/5. (A) shows the fracture pattern of pre-epLS_30/2/0 which had substrate fracture, whereas the green areas in (B) indicate adhesive and cohesive fracture of epLS_21/2/5. (B) also depicts the penetration of the epLS-adhesive through the viscose, whereas no penetration is observed in (A).

4.3.1.4 Potential use of epLS as structural adhesive in comparison with commercial adhesives

To discuss a potential use of epLS-adhesive for structural application, where a high load is applied, the epLS is compared to commercial adhesive used in automotive application. The maximum shear strength of an alumina-alumina bonding with a 1-component epoxy hybrid adhesive is 30 MPa [24], compared to the shear strength of epLS was 0.2 MPa, which is seen in Tab. 4-4. In regards to the application of epLS as structural adhesive, the epLS does not meet the strength requirements of 30 MPa. Additionally, no sufficient alumina bonding was achieved with epLS-adhesive as described in section 4.2.4., which limits the application for structural components, like steel, alumina or CFRP.

However, the performance of the epLS-adhesive in comparison to Dow Slow cure from Bob Smith Industries, a 2-component epoxy adhesive, which was applied for a steel-steel bonding, is comparable. Fig. 4-16 shows an example which was prepared in a previous study at Wayne State University, Michigan, USA. The bonding area of the steel sample was 25.4 x 25.4 mm and the rate of displacement was 1 mm/min. As expected, the commercial adhesive bonding had a sharp curve and showed less elastic behaviour which is common for structural adhesive used in automotive industry. The curve of those adhesives is much steeper than for the epLS-adhesive indicating a high strength of the adhesive but a lower elasticity. The 2-component epoxy adhesive cures during 6 -8 hours at ambient conditions and is used for metal, glass or wood. In comparison, the epLS-adhesive cured during t = 60 min and had still promising strength and elastic performance. Under the consideration that the origin of the epLS-adhesive is bio-based, whereas the commercial adhesive is synthetically produced, the performance of epLS_30/2/0 is promising. [51]

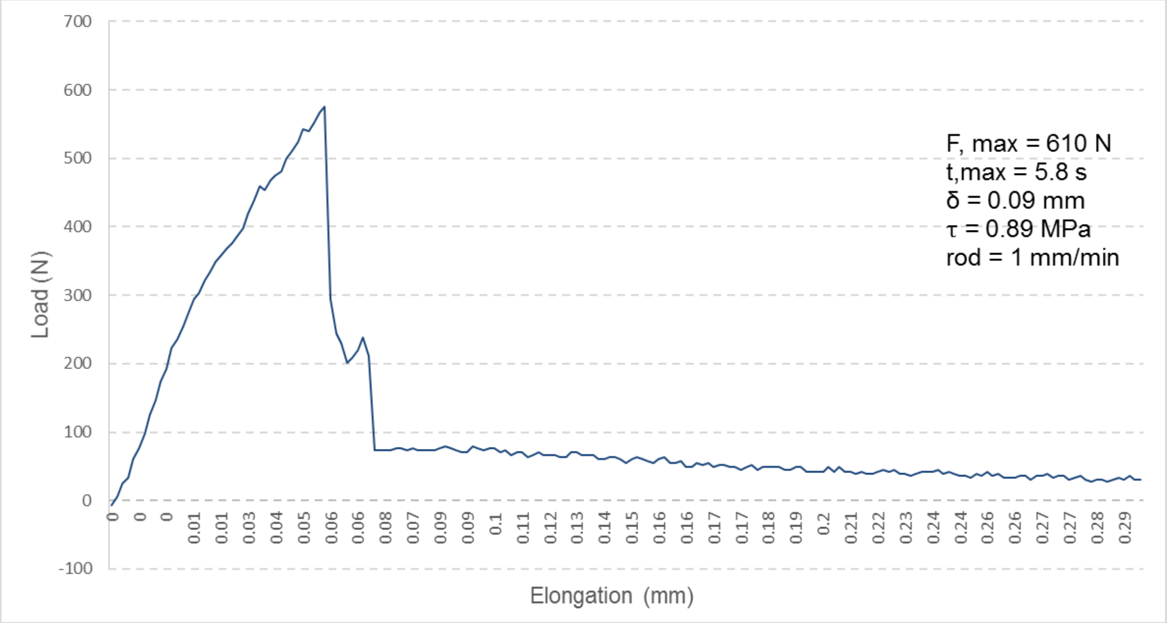

Fig. 4-16: Load/Elongation diagram of a 2-component epoxy adhesive applied on steel: The bonding area of the steel sample was 25.4 x 25.4 mm and the rate of displacement was 1 mm/min. Compared to the epLS-adhesive applied on leather, the curve is much steeper, but the maximum load is comparable to the epLS_30/2/0, which had an averaged F,max = 364.7 N, summarized in Tab. 4-4.

4.3.2 Water resistance

4.3.2.1 Experimental approach

During sulfite pulping the lignin is sulfonated and becomes hydrophilic. In terms of automotive application it is of high interest to investigate the solubility of the epLS-adhesive. It has to be guaranteed that the adhesive does not degenerate if it is exposed to humidity or water either due to spilling liquids on interior components or humid climate conditions. [52] [53]

The water absorption or desorption ability was investigated gravimetrically. The investigated substances were original-epLS_30/2/0, pre- epLS_30/2/0 prepared in accordance to 0, dried-epLS_30/2/0 as prepared in section 4.4.4 and hydrogel-epLS _30/2/0 prepared according to 4.2.2, but running the pre-polymerization procedure for 3 h. Approximately 4 – 5 g of the substance were transferred into a petri dish (see Fig. 4-17) and exposed to 3 different conditions for 8 hours. The samples were placed in 2 different laboratory rooms with ambient conditions and once outside, where the temperature and humidity were monitored. The conditions inside were T=24 °C, 35 % r.H. and T=20 °C, 54 % r.H. and the ambient conditions outside were T=6 °C, 78 % r.H. The change of mass was monitored by weighting the mass on a precision scale at time intervals of 15 min. The results are summarized Tab. 4-6.

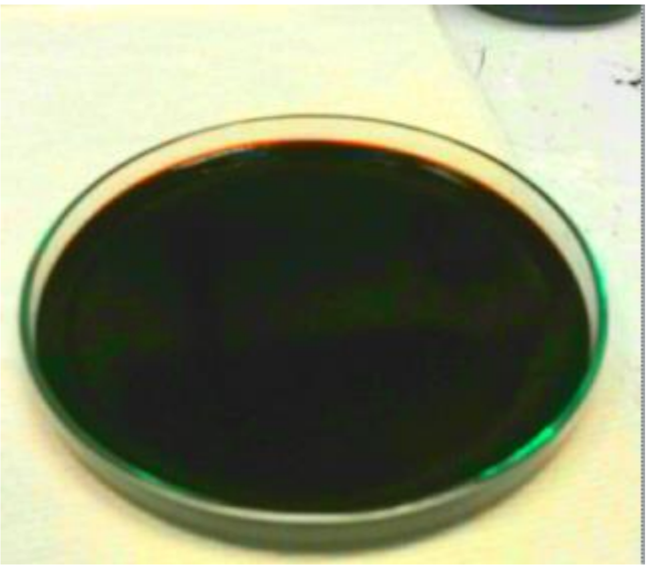

Fig. 4-17: Experimental set-up for the water absorption/release ability: The sample was transferred in a petri dishes and exposed to ambient climate conditions for 8 h.

The water resistance of the cured epLS-adhesive was investigated in accordance to D2 DIN ISO 204 [54]. For that a leather-leather and a leather-viscose sample were prepared with pre-epLS_30/2/0, cured in accordance to 4.2.3 and put separately into two beakers with demineralized water for 3 h. The change of mass was monitored by weighting the mass before and after the experiment. The temperature of the water was 20 °C and was monitored with a thermometer. To verify how much water is taken up by the leather, a previous test with leather exposed to water was done in accordance to DIN 4843 T2 [55]. A leather and viscose sample with 40 cm x 40 cm was prepared and exposed to water for 8 h. The weight was measured before and after the test. Since a degradation of the cured-epLS results in a dilution of the bonding strength, the bonding ability was evaluated by manual peel testing and fracture pattern analysis in accordance to DIN EN ISO 10365 [45]. Fig. 4-18 shows the respective samples, exposed to demineralized water.

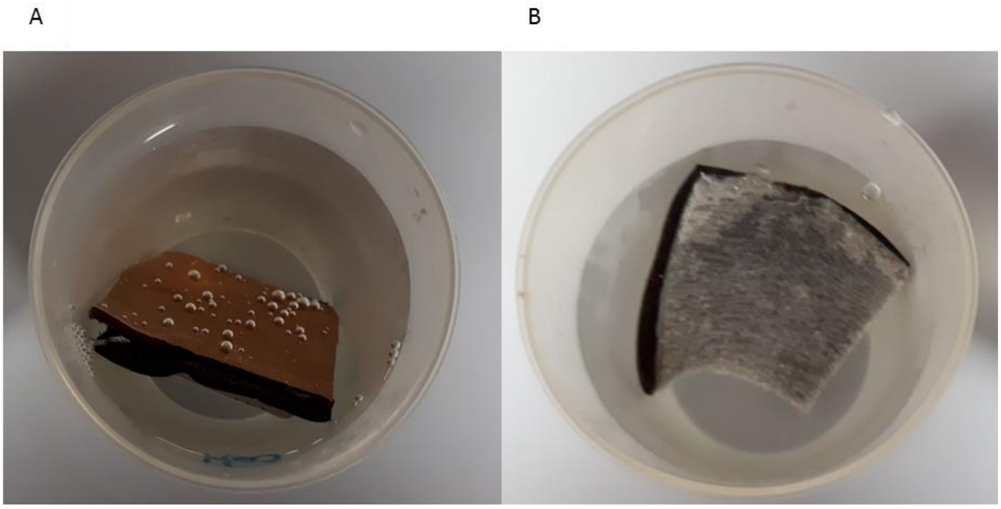

Fig. 4-18: Water resistance test: (A) cured-epLS_30/2/0 in a leather-leather bonding. (B) cured epLS_30/2/0 in a leather-viscose bonding. The samples were fully covered with water and exposed for 8 h.

4.3.2.2 Results

Tab. 4-6 summarizes the results of the water uptake/ release behaviour of different epLS-types. The negative sign indicates release of water, whereas the positive values indicates water uptake. The term "n.r." refers to not relevant, since the standard DIN ISO 204 D2 prescribe the testing with cured adhesive on a substrate. [54]

Tab. 4-6: Water uptake or release during t = 8 h. The samples were exposed to ambient climate conditions and to demineralized water according. The change in mass during the time was monitored.

Conditions	Original-epLS	Pre-epLS	Cured-epLS on leather	Dried-epLS	Hydrogel-epLS
T=24 °C, 35 % r.H	-78 %	-23 %	0 %	0 %	-73 %
T=20 °C, 54 % r.H.	-74 %	-5 %	0 %	3 %	-51 %
T=6 °C, 78 % r.H	-37 %	0 %	0 %	4 %	-43 %
T = 20 °C, in water	n.r.	n.r.	53 %	n.r.	n.r.

Compared to the other epLS-samples the original-epLS had the highest water loss at T=24 °C, 35 % r.H. This is explained by the curing process, where the enzymes in presence of oxygen cleave the phenolic groups and initiate the polymerization where water is formed as by-product, which then evaporates. [12]

For all epLS-samples, the loss of water is higher at 24 °C and 35 % r.H. This was expected, since this testing condition was related to the highest temperature and the lowest humidity [56]. The lower the temperature and the higher the relative humidity, the lower is the water release, which is confirmed for all epLS-samples. The tendency that the water uptake decreases with decreasing temperature and increasing humidity is also confirmed.

Pre-epLS also showed some significant amount of water desorption, especially at T=24 °C, 35 % r.H, which is reasonable since the polymerization process has not been finished. The polymerization was in process and therefore water split off and evaporated. The trend, the higher the humidity in the atmosphere, the less water is released, is confirmed again.

A promising result is that the cured-epLS did not take up any water when exposed to the atmosphere. In terms of application it is required that the cured epLS-adhesive does not take up any water and hence this requirement was met.

The evaluation in accordance to D2 DIN ISO 204 [54], where a leather-leather and a leather-viscose sample were exposed to water, caused degradation of the epLS-adhesive. This test was meant to be an initial screening to get first hints in regards to the water resistance. In terms of application for interiors the exposure of water for 8 h, which means that the passenger cell is totally floated, is very unlikely and therefore the test is not representative for interior application. Therefore, an alternating climate test for interior components was carried out and is described in 4.3.3.

Different to the cured-epLS, the dried-epLS showed a water uptake of up to 5 wt%. The reason for this behaviour might be the different pore structure after the epLS is dried or cured. Since of the drying process was carried out in accordance to section 4.4.4, at T = 40 °C, p = 400 mbar, the water inside the pores of the structure may evaporates quicker than during the curing process at ambient climate conditions. The polymerization process, which is still continuing during drying, is accelerated and therefore the structure is consequently not as homogeneous as the structure generated during the polymerization process of the cured-epLS. In the dried-epLS the pores remained and took up water when getting in contact with the humid atmosphere. This phenomena was also observed during the determination of the water content described in 0, where the mass of the dried-epLS sample increased rapidly after a few minutes at ambient conditions of T = 24 °C and 35 % r.H.

For a comparison, the water uptake/release was investigated for the hydrogel as well. The water loss of hydrogel was similar to the original-epLS. It was observed that the substance got brittle and lost its shape and elasticity. The characteristic of hydrogels is their water uptake ability which makes them, depending on their properties, attractive as e.g. medicine or hygiene product or even as ion exchange matrix, but they tend to drain rapidly if exposed to dry conditions. Beside that hydrogel-epLS has no adhesive properties, they cannot be applied for automotive industry since they degrade at even moderate ambient climate conditions like it was for T = 24 °C, 35 % r.H. or T = 20 °C, 54 % r.H. [57] [58]. Fig. 4-19 illustrates the loss in shape and verifies the necessity to avoid hydrogel formation of epLS.

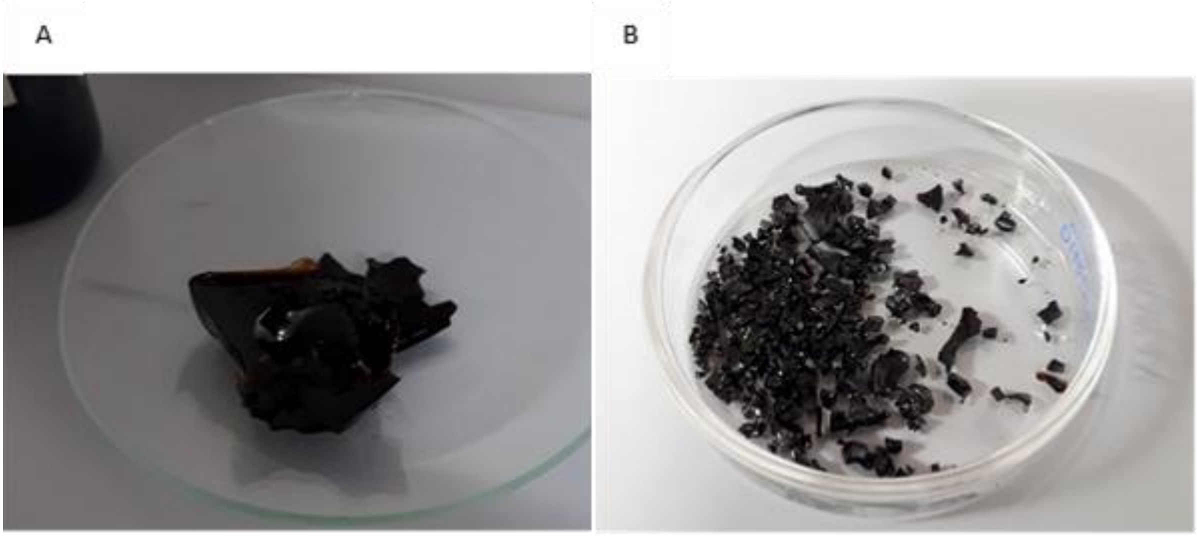

Fig. 4-19: Loss of mass and shape of hydrogel after 8 h: (A) hydrogel-epLS_30/2/0 at the beginning and (B) after exposure to the ambient climate conditions of T = 24 °C, 35 % r.H. where the hydrogel-epLS had a mass loss of 73 wt.%.

4.3.3 Alternating climate test

4.3.3.1 Experimental approach

The alternating climate testing was carried out in accordance to the internal standards of Magna for interior components. The sample is placed in a climate chamber where temperature, humidity and salts were adjusted. Each cycle of the climate test was running with different temperature and humidity programs, the top-condition was at 80 °C and 80 % r.H., the low-condition was at – 30 °C and 0 % r.H., and the intermediate condition was at 23 °C and 20 % r.H. In total the alternating climate test was running 10 days, the duration of one cycle was 12 h and each cycle was repeated 20 times. After the alternating climate test was finished the bonding strength was tested with the lap shear test, see 4.3.1 [45].

4.3.3.2 Results

The leather-viscose sample prepared with epLS-adhesive showed promising results in terms of the climate change test. As depicted in Fig. 4-20 the epLS_30/2/0 showed mainly substrate fracture, whereas the epLS_21/2/5, with AKD, had cohesive and partially adhesive fracture. Further, the epLS_21/2/5 caused discoloration and minor deformation of the viscose after the climate change test which is not sufficient in regards of visual quality. The strength properties of the epLS_30/2/0 were sufficient, before and after the climate change test. According to the test report, no weakening of the bonding was noticed. Therefore, it can be concluded, that the addition of AKD does not meet the requirements for interior adhesives in regards to strength and climate condition.

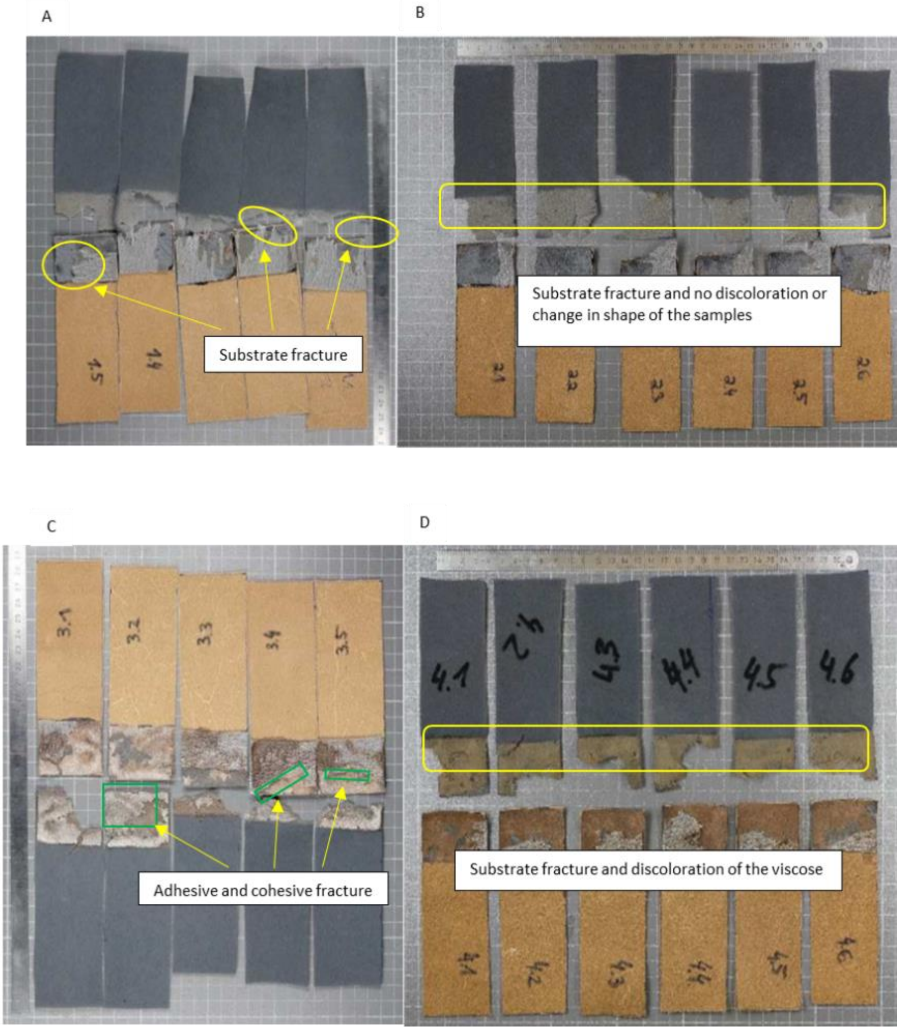

Fig. 4-20: Fracture pattern of the lap shear test of leather-viscose samples before and after the alternating climate test: (A) pre-epLS_30/2/0 before and (B) after alternating climate test and (C) pre-epLS_21/2/5 before and (D) after alternating climate test.

4.3.4 Storability

4.3.4.1 Experimental approach

The storability the epLS-adhesive is a relevant factor in terms of handling and industrial application. It has to be possible that the epLS-adhesive can be prepared in a bulk by pre-polymerization and can be stored until the adhesive is applied. Therefore the application behaviour and the strength behaviour for pre-epLS_30/2/0 were investigated.

In terms of the application behaviour it was found, that hydrogel-epLS is worse to apply than pre-epLS. Therefore a hydrogel formation, which is also continuing after the pre-polymerization due to the presence of oxygen and active enzymes, is undesired und needs to be prevented. According to Huber et al. [12] the enzymes are thermophilic and have their maximum activity between 45 - 50 °C [41] where they polymerize the lignosulfonates in presence of oxygen. Therefore it was expected that the pre-epLS can be stored in an airtight container at low temperatures. To verify this assumption the application behaviour of pre-epLS was investigated after storage at three temperatures, 23.5 °C, 8 °C and -3 °C. The pre-epLS was stored in an airtight PP-tube for 1h, 2h, 24 h and 72 h, where samples were taken for the application test. The investigation was carried out visually by applying the adhesive with a brush on a leather surface. If the adhesive was still spreadable and had adhesive properties, the stability was defined as sufficient. If the adhesive polymerized to a hydrogel and was not spreadable, the stability was defined as insufficient.

To investigate a decrease of the bonding strength, the pre-epLS_30/2/0 was stored in an airtight PP-tube at 8 °C for 7 days, thereafter it was applied for a leather-leather bonding, as described in section 4.3.1 and tested with the lap shear machine.

4.3.4.2 Results

It was observed that the pre-epLS was still spreadable after 1 h, 2 h, 24 h and 72 h when stored at 8 °C. Compared to that the pre-epLS stored at 23.5 °C, polymerized to hydrogel after 2 h and was brittle after 72 h. It is assumed that even during storage, some oxygen is incorporated into the epLS bulk during the stirring. At moderate temperature the enzymes still catalyse the polymerization process. Therefore the pre-epLS has to be stored at low temperatures in an airtight container. Another option is to handle the epLS-adhesive as two-component adhesive, where the lignosulfonates and the enzymes are stored separately, followed by adding the enzyme and initiating the pre-polymerization just before the application.

In regards of the shear strength, the epLS-adhesive, stored for 7 days at 8 °C, had a strength performance comparable to the pre-epLS, applied on leather directly after pre-polymerization. The results indicate that the storage of the pre-epLS is possible under this condition. Fig. 4-21 presents the load vs. elongation diagram where the mean value of the maximum load was 313 N. Compared to the lap shear test, carried out in accordance to 4.3.1, the mean value of the maximum load of the pre-epLS, directly applied after pre-polymerization, was 337.8 N which refers to a decrease of 8 %. The averaged shear strength for both epLS-adhesives, before and after storage, was 0.2 MPa. Tab. 4-7 summarizes the results of the lap shear test, whereas the original data can be found in Appendix 11. Compared to sample 1 to 3, the sample 4 had a flat curve which demonstrates the difference of elastic properties due to the natural origin of leather.

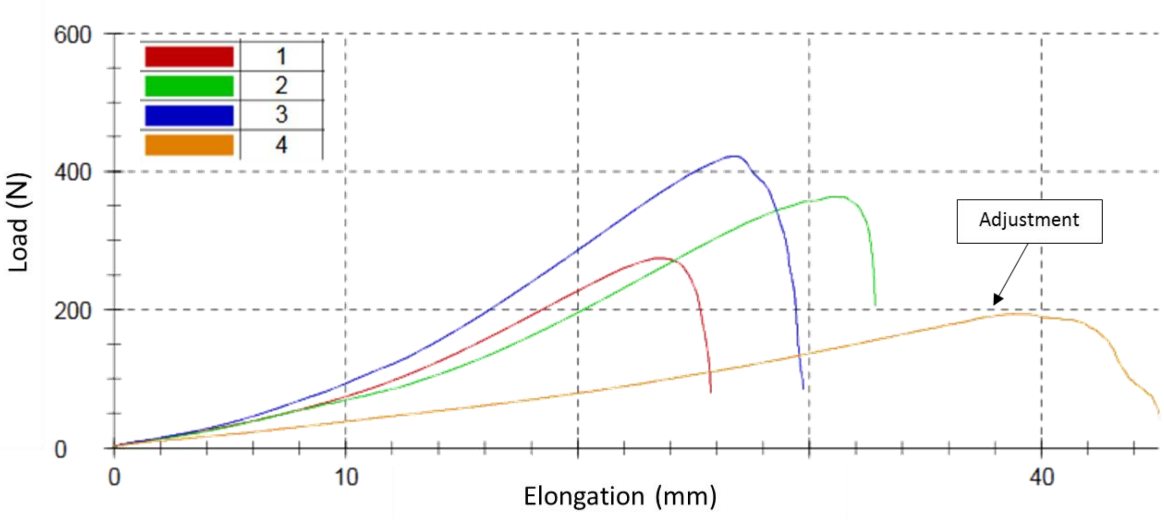

Fig. 4-21: Load/elongation diagram of the storability test with pre-epLS_30/2/0, stored for 7 days in an airtight PP-tube at 8 °C: The colour of the curves indicates the sample number 1 to 4, whereas number 4 was prepared for the adjustment of the lap shear test.

Tab. 4-7: Results of the storability: Maximum load until fracture of the sample with pre-epLS_30/2/0, stored for 7 days in an airtight PP-tube at 8 °C.

Sample number	**Maximum shear strength (MPa)**	**Elongation at fracture (mm)**	**Maximum load (N)**	**Elongation at maximum load (mm)**
1	0.2	25.7	274.0	23.6
2	0.2	32.8	363.0	31.0
3	0.2	29.7	421.0	26.9
mean value	0.2	29.4	352.7	27.2
standard deviation	0.0	3.6	74.0	3.7

4.3.5 Degradation temperature

4.3.5.1 Experimental approach

The temperature resistance and degradation temperature were investigated in a simultaneous thermal analysis device (STA). The STA was carried out using the ST449C Jupiter, Netzsch apparatus. The material of the sample container was Al_2O_3. To avoid measurement errors due to possible impurities of the containers they were first added to aqua regia and then put into the STA apparatus to run a simple temperature profile. The cleaning mode used a temperature gradient of 30 K/min, up to an oven temperature of 350°C, where the temperature was kept constant for 20 min to remove any residues of other substances in the container. For the analysis two containers were used. One container was filled with the sample and the other was the reference container for the DSC signal. Around 50 mg of the test substance were transferred to the sample container which was then placed in front of the reference container. Fig. 4-22 shows the arrangement of the sample container in the STA sample carrier.

The analysis was run using a temperature profile starting at an oven temperature of 20 °C; heating up to 220 ° C with a heating rate of 20 K/min. The maximum temperature was defined with 220 °C, as temperatures of max. 180°C are currently used in drying ovens for the coating of a car. However as the epLS-adhesive is water based even lower curing and drying temperatures are expected. The analysis was carried out with pre-epLS_30/2/0, prepared according to section 0 and with epLS_30/2 /0, dried in oven according to section 0.

According to Rusche et al. [59] the degradation behaviour of epLS should be investigated by running the STA with 2 different gas settings to examine the decomposition process in regards to thermal oxidation or other processes, e.g. a chemical reaction. Therefore the STA was first performed with a mixture of 80 vol.% synthetic air and 20 vol.% nitrogen to examine the combustion process and then with pure nitrogen atmosphere.

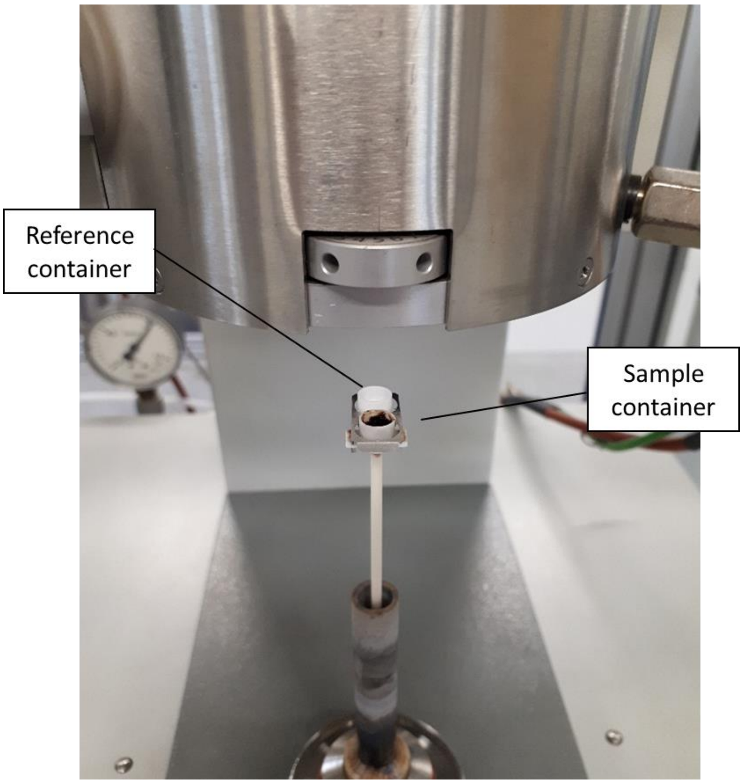

Fig. 4-22: Experimental set-up of the STA: The epLS-samples, once pre-epLS and once dried-epLS, were placed in the sample container. A second container was used as reference. The temperature profile was starting at an oven temperature of 20 °C; to the final temperature 220 ° C, with a heating rate of 20 K/min. Two different gas settings were defined.

4.3.5.2 Results

The STA delivers, beside the weight loss of the sample, a signal that correlates to the consumed or released energy. An exothermic signal has a peak in the negative direction of the ordinate while an endothermic signal has a positive peak. An exothermic signal mostly indicates a combustion reaction or a chemical reaction, e.g. a polymerization, whereas an endothermic signal indicates a phase change, e.g. melting or evaporation. Since no detailed data of the polymerization process and the macromolecular structure of the epLS were available, some assumptions, which are based on the known composition of the epLS are done and evaluated with the results.

The pre-epLS contains a significant amount of water, embedded in the pores of the polymeric structure of the epLS. As expected it evaporates and release an endothermic signal which indicates the phase change of the water to vapour. In Fig. 4-23, line (A), shows a sharp drop, combined with an endothermic peak detected after 45 min at an oven temperature of 57 °C. This phenomena was expected at a temperature around 100 °C, where water usually evaporates. In consideration of the polymerization process of epLS, it can be assumed, that the reaction was still in progress and therefore water was split of which then evaporates. This is reasonable since the reaction temperature for the pre-polymerization is between 50 °C and 57 °C and, according to the instruction of the STA apparatus, an evaporation of water far below the normal boiling point takes places at the beginning of the experiments, if open sample containers are used.

The last significant peak occurs between the line B and line C, where the maximum of the oven temperature is reached. The high temperature level caused full degradation where only char remained in the container, as depicted in comparison to the other epLS-samples at the end of this section in Fig. 4-26. Fig. 4-23 displays the procedure of the STA where the mass loss of the pre-epLS, the temperature profile and the energy signal in dependence of the time are shown.

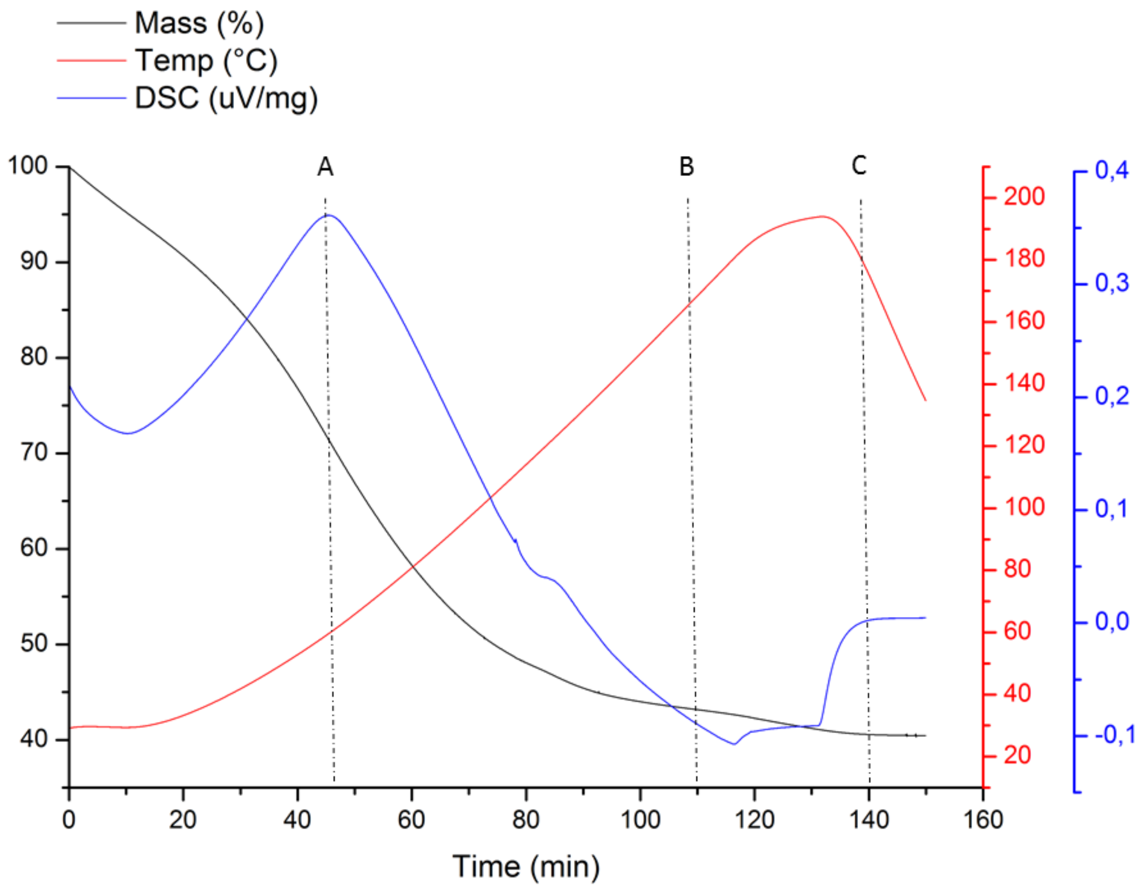

Fig. 4-23: STA of pre-epLS_30/2/0: The diagram shows the mass loss of the sample, the oven temperature and the energy signals during the analysis. An exothermic signal has a peak in negative direction of the ordinate while an endothermic signal has a positive peak. The gas setting was 80 vol. % synthetic air, 20 vol. % N2. (A): indicates an evaporation of water at 57 °C. Line (B) and (C) highlight the region, where degradation of the sample took place.

For the industrial application the degradation behaviours of the cured-epLS, cured on a substrate, is crucial. As it was seen in the first analysis, the main proportion of mass loss originates from the water. The cured-epLS is free of water and besides the evaporation process of water, a more precise investigation can be done regarding to the polymerization and decompositions process. As expected, compared to the pre-epLS, the dried-epLS has a lower mass loss. Fig. 4-23 shows the results of the STA of cured-epLS_30/2/0. Line (A) highlights that the decomposition starts after 60 min and a temperature of T = 75°C. This decomposition product might be water which is formed during the proceeding polymerization process of epLS. That the polymerization process is continuing at higher temperatures was approved by Johannsson et al [60], who investigated a coating based on a an aqueous dispersion of lignosulfonate, clay, latex and starch, which were radical coupled with laccase. Johannsson et al [60] observed that the enzyme activity still remained after drying the sample at T =100 °C.

A significant exothermic signal was detected after 115 min and 180 °C, indicating most probably a combustion process. To evaluate if the peak at 180°C corresponds to a combustion process, the same analysis was carried out in the absence of oxygen [59]. Fig. 4-25 summarizes the data for this analysis.

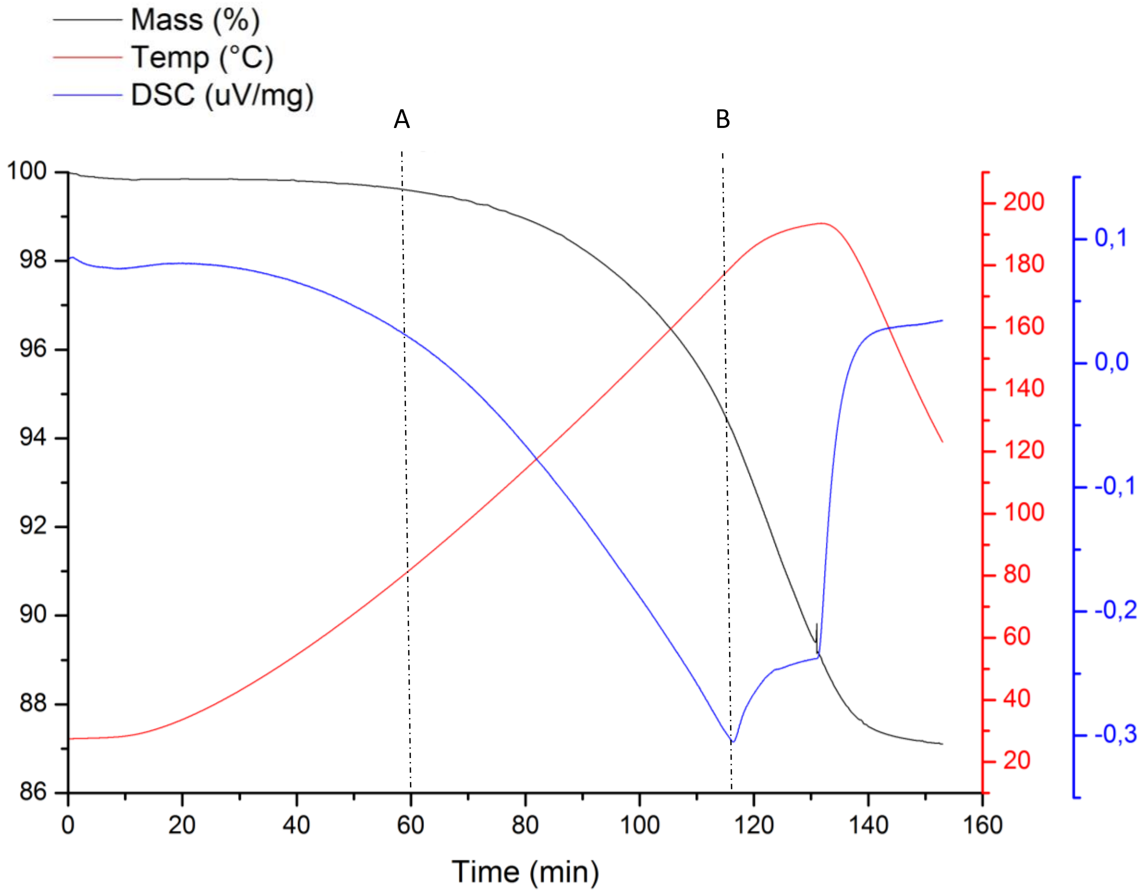

Fig. 4-24: STA of cured-epLS_30/2/0: The diagram shows the mass loss of the sample, the oven temperature and the energy signals during the analysis. An exothermic signal has a peak in negative direction of the ordinate while an endothermic signal has a positive peak. The gas setting was 80 vol.% synthetic air, 20 vol.% nitrogen. (A) indicates where the decompositions procedure is initiated. Line (B) highlights a decomposition due to thermal oxidation, i.e. combustions.

According to Fig. 4-25, the mass loss of the sample was 0.3 wt% compared to Fig. 4-24, where the mass loss of the sample during the STA with synthetic air was 13 wt%. These results indicate that the presence of oxygen accelerates the degradation procedure due to oxidation; therefore the peak in Fig. 4-24, line (B), refers to a combustion process. Nevertheless, Fig. 4-25, line (A), highlights the minor mass loss of 0.3 wt% after t = 115 min, which signalizes that also some degradation of the sample was initiated. The residue of the epLS-sample after the STA is depicted in Fig. 4-26, part (C), where the char-like residue of the sample is seen. This is in agreement with Brebu et al [61], who determined a degradation of lignin starting at 180 °C and is further confirmed by Ismail et al. [62] who reported a char-like substance, formed during the STA of an ester-type cross-linked epoxy resin derived from lignosulfonates and glycerine in the presence of nitrogen. [61] [62]

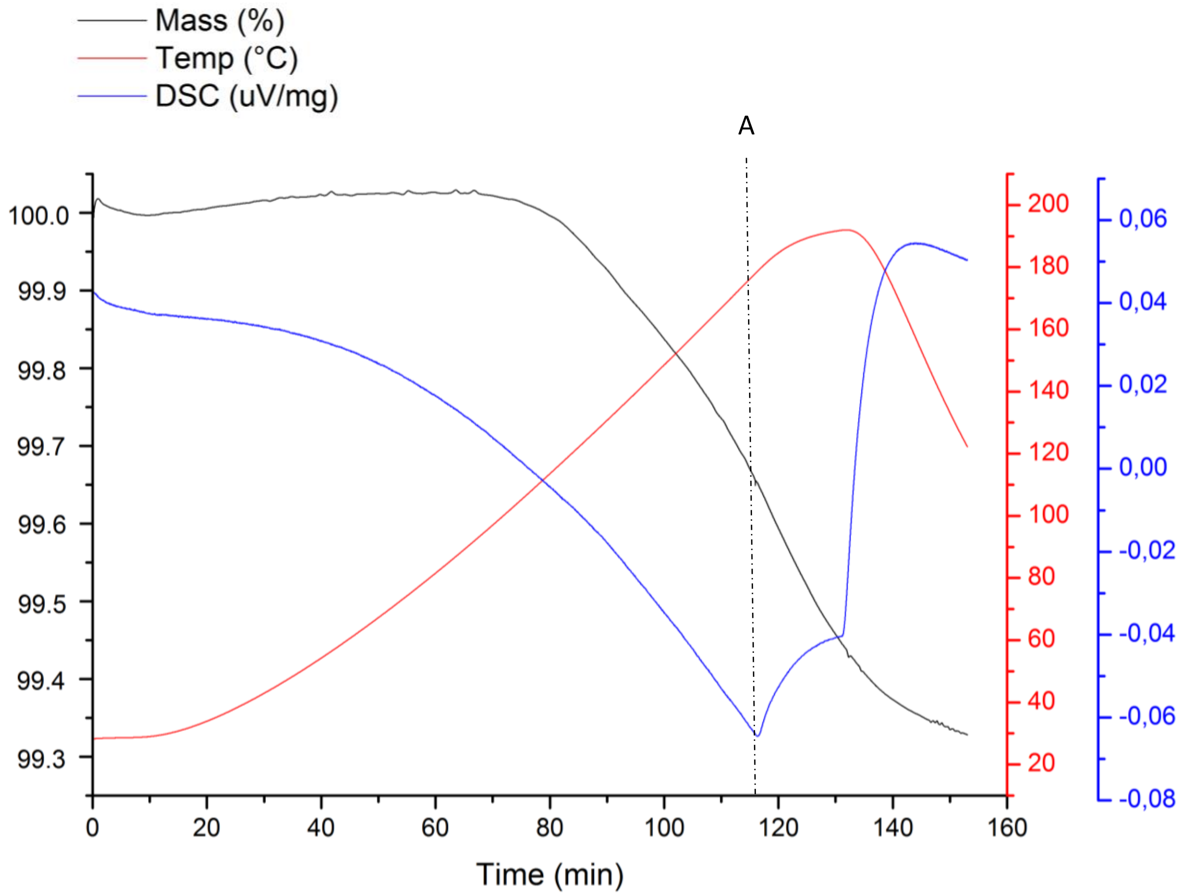

Fig. 4-25: STA of cured-epLS_30/2/0: The diagram shows the mass loss of the sample, the oven temperature and the energy signals during the analysis. An exothermic signal has a peak in negative direction of the ordinate while an endothermic signal has a positive peak. The gas setting was 100 vol.% of nitrogen. (A) highlights the minor mass loss of 0.3 wt% of the sample

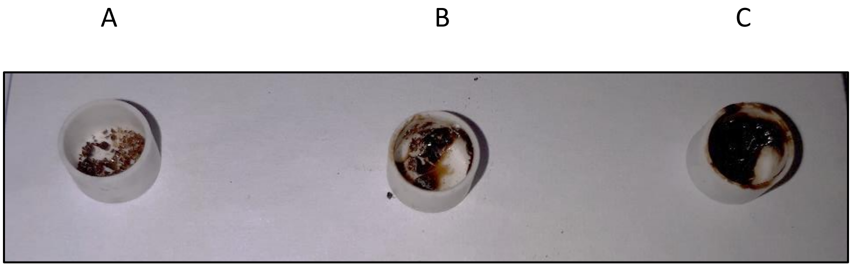

Fig. 4-26: Residues of the epLS-samples after the STA: (A): refers to pre-epLS after the STA with 80 vol.% synthetic air and 20 vol.% nitrogen, where the highest loss in mass was determined, (B) refers to dried-epLS after STA with 80 vol.% synthetic air and 20 vol.% nitrogen, (C): refers to dried-epLS after STA with pure nitrogen atmosphere where a char-like substance was formed.

4.3.5.3 Decomposition products

In terms of environment, health and safety standards it has to be ensured, that no hazardous substances are formed during the degradation procedure. Since the structure of lignosulfonates is complex and detailed data about the molecules which are formed during the enzymatic polymerization is not available, some assumptions have to be made to identify the products which may decompose during the STA. [63]. Fig. 3-11 in the chapter 3.6 illustrates the theoretical structure of magnesium lignosulfonate.

A coupling of the thermogravimetrical analysis with a mass spectrometry or a chromatography, enables a detailed study of the volatile products, however, those methods were not available during the performed work and therefore some comparable sources were consulted~~.~~ [39]

Lima et al. [61] investigated the degradation behaviour of lignosulfonates Kraft lignin and reported a slight weight loss of lignosulfonates until 100 °C, as it was also observed in the STA depicted in Fig. 4-23. They attributed the weight loss to the evaporation of water. In presence of oxygen, some degradation products, like carbon dioxide and carbon monoxide were formed above 100 °C. This might be represented in the STA of dried-epLS with synthetic air in Fig. 4-24. The present work did not investigate the decomposition of epLS between 200 °C and 400 °C where the main degradation of lignin is expected. In this range carbonyl, benzylic and phenolic hydroxyl groups are formed and above 400 °C the aromatic rings of the lignin structure decompose and condensate. However, in terms of application it can be stated, that the present work verifies data from the literature that mainly water is released up to 75°C and hence no hazardous components are released. Temperatures above 75 °C lead to degradation and the higher the temperature the more hazardous components may be formed. In technical applications this leads to the restriction that the epLS-adhesive must not be exposed to temperatures higher than 75°C.

4.3.6 Paint wetting impairment

4.3.6.1 Experimental approach

Substance which are applied in automotive industry needs to be tested for paint wetting impairment, especially if the substance is applied in a paintshop for coating cars. The test is carried out in accordance to the Magna-internal standard AAQ54095 (“Überprüfung auf Lackverträglichkeit”) which is based on the VDMI standard of testing for paint wetting impairments [64] where an alodine coated alumina sheet, 10 cm x 20 cm, was chosen as reference material. The wettability was evaluated by coating the half of the alumina sheet with a 1 component white base coat, half of the alumina sheet with a 1-component clear coat, then applying drops of epLS-adhesive with a syringe on the coated surface, followed by drying on air. If no wettability paint impairment is detected, e.g. spots of the paint, the epLS is confirmed that the epLS does not lead to wetting impairment.

4.3.6.2 Results

No wetting impairment was detected and therefore the epLS would be compatible with the used coating materials in automotive application. The test report can be found in the appendix chapter 11 (WT60953).

4.4 Material data

Based on the first experimental part, the epLS_30/2/0, which was pre-polymerized according to 4.2.2, was found to be the most promising epLS-type in regards to application and strength properties. Some data were already available, whereas some characteristic material properties are still missing. For industrial application properties, like the degradation temperature, density, viscosity and colour have to be determined. Therefore some additional data are determined to characterize the epLS-adhesive and to earn further informations in terms of handling, application and future application of the adhesive.

4.4.1 Density

4.4.1.1 Experimental approach

The density of epLS was measured gravimetrically using a volumetric flask with a volume of 100 ml. The sample was transferred into the flask and the mass was weighted on a precision scale at T = 23.5 °C. The lot size was n = 5. The density was calculated in accordance to Equ. 4-2:

$$\rho = \frac{\mathrm{m_{epLS}}}{\mathrm{V_{epLS}}}$$

Equ. 4-2

ρ…Density of epLS sample (kg/m^3)

$\mathrm{m_{epLS}}$…Mass of epLS sample (kg)

$\mathrm{V_{epLS}}$…Volume of epLS sample (m^3)

4.4.1.2 Results

The density of original epLS is 1.0914 kg/dm^3 and was determined gravimetrically. The determination with a densimeter was not possible since the epLS polymerizes and hence plugs the tubes. It was also not possible to measure the density of pre-epLS since the density strongly depends on the porosity and structure of the substance, as it is for hydrogels [65]. The approach determining the density in a cumulative way can not be done as the particular composition of the pre-epLS is not known. Therefore it is assumed, that the density of pre-epLS is higher than that of the original-epLS since the viscosity increases with proceeding polymerization.

4.4.2 Viscosity

4.4.2.1 Experimental approach

During the polymerization in accordance to 4.2.2 the viscosity increases up to a certain point where a hydrogel is formed. Based on this observation the viscosity η of pre-epLS_30/2/0 was monitored in dependence on the polymerization time and the shear rate γ, where the temperature in the bulk was kept constant. The viscosity of epLS was determined with a rheometer (SN7940, Physica MCR 301 from Anton Paar, Austria), using the plate to plate method with 50 mm diameter and a gap of 1 mm. The ambient temperature was 25°C. The epLS was prepared in accordance to 0. To investigate the change of viscosity with ongoing polymerization, after a certain time 5 ml of the sample were transferred into the measurement device. The shear rate was set to increase from 1 to 1000 1/s. The gained data was analysed with the program RHEOPLUS by Anton Paar.

4.4.2.2 Results

Fig. 4-27 summarizes the results, where the viscosity increases with proceeding polymerization. The red line indicates sample 1 of the pre-epLS_30/2/0 at the beginning of the polymerization procedure, where the black line shows the viscosity of the same sample at the end of the pre-polymerization.

If no shear rate was applied, the initial viscosity was 0.0077 Pa·s which continuously increased with ongoing polymerization. After 105 min, the viscosity of sample 6 suddenly raised up to 10 Pa·s which might indicate a maximum of the polymerization rate. It is assumed that the concentration of the radicals was high and the molecules interacted with each other more frequently. Therefore the polymerization process is accelerated and this leads to an increase of the polymer length which further resulted in an increase of the cross-linking and viscosity. [66]

At shear rates $\gamma < 1000$ 1/s the viscosity remained mainly constant which indicates a viscoelastic behaviour of the epLS [67]. For the samples 1 to 5 which had a viscosity $\eta \leq 1$ Pa·s the viscosity first decreases slightly with increasing shear rate until the shear rate is $\gamma > 1250$ 1/s, where the viscosity drops rapidly. Line (A) in Fig. 4-27, highlights this behaviour which corresponds to a typical shear thinning behaviour of polymers. [68]–[72]. The higher viscous sample 6 did not show this significant characteristics.

Fig. 4-27 (line B) signalizes that the viscosity of the less polymerized samples (1 to 5) increased again above a shear rate of $\gamma > 4000$ 1/s, which might be due to the rearrangement of the molecular structure. On the contrary, the higher polymerized epLS with $\eta = 10$ Pa·s remained shear thinning. This is attributed to the highly cross-linked structure, which prevent a rearrangement of the molecules in its original position. [73] [74]

Beside the identification of the optimum pre-polymerization point, which is at a viscosity of η = 9 – 10 Pa·s, also the shear thinning behaviour of epLS is beneficial for industrial application, since the epLS-adhesive is spreadable by adding shear stress via brush or other tools.

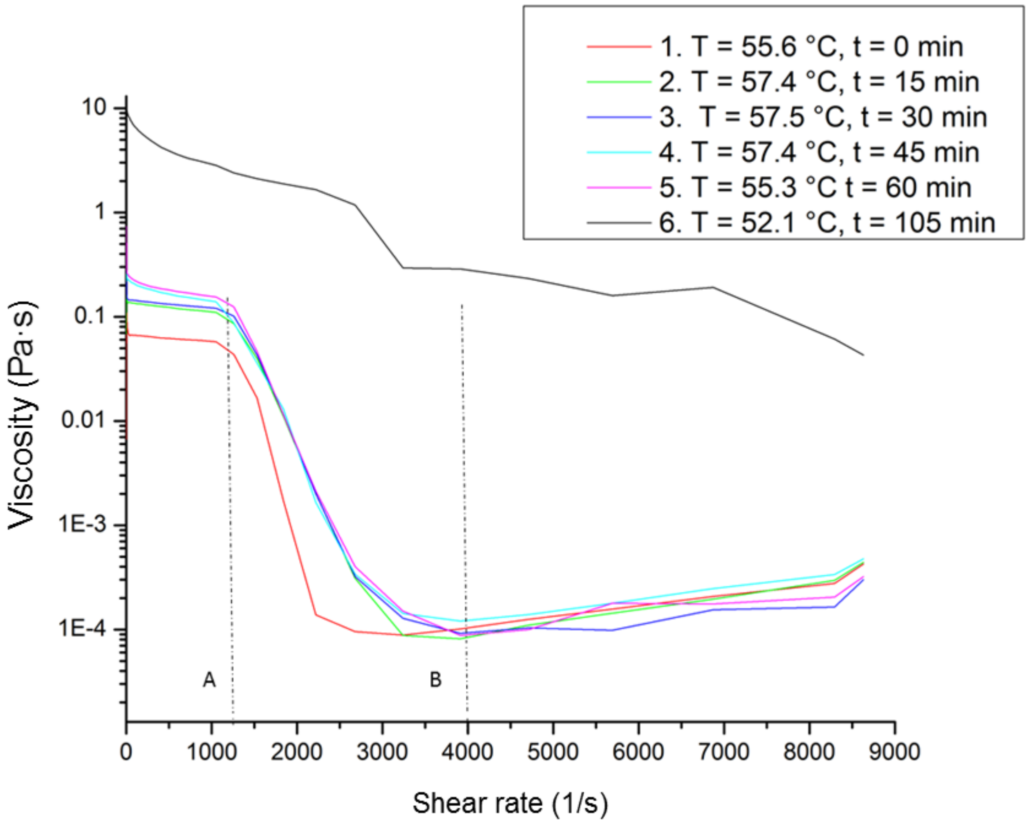

Fig. 4-27: Viscosity of epLS_30/2/0 in dependence of the polymerization time and shear rate: The epLS was polymerized for 105 min and every 15 minutes a sample was taken. Line (A) and (B) indicate a characteristic change in the viscosity of epLS in dependency of the shear rate.

4.4.3 Solubility

4.4.3.1 Experimental approach

The solubility was investigated by adding 10 ml of the solvents described in 4.2.1 to 4 g of each epLS-type. The pre-epLS and hydrogel-epLS were prepared in accordance to 4.2.2, the cured-epLS was prepared in accordance to 4.2.3 and the dried-epLS was prepared in accordance to 4.4.4. The testing was carried out in a beaker while stirring by hand with a spatula. The temperature of the solvent was 23 °C and was kept constant by using a temperature controlled heating plate (IKA RET control/t). For an initial screening, the solubility was evaluated visually, i.e. in dependency of the turbidity of the solvent.

4.4.3.2 Results

It was found, that the solubility in polar solvents, e.g. water, depends on the grade of polymerization. The higher the polymerization respectively the curing process, the less soluble is the epLS. This observation corresponds to the fact that the solubility of polymers generally decrease with increasing degree of polymerization. Additionally, Ortner et al. [75] observed an improved water repellence ability after enzymatic polymerization, which results in an increase of the molecular weight. This is in line with results from Kudange et al. [38] who reported an improved water resistance of lignosulfonates with higher cross-linking. [16]

Further, Williams et al. [16] found, that an increase of the adhesive insolubility correlates to the strength of the adhesive bonding. This is reasonable since the bonding strength increases with proceeding polymerization respectively curing process, whereby the higher degree of polymerization further increases the solubility. This characteristic was also observed during the preparation of the samples for the lap shear test, described in 4.3.1.1. The leather samples bonded with pre-epLS_30/2/0 could be manually rearranged and adjusted within 10 min after application, meaning that the polymerization process is not finished and therefore has a low bonding strength. It was also observed, that the working place polluted with residues of pre-epLS could be cleaned with water, meaning that the adhesive is soluble in polar solvents. Beside the initial adhesion test described in 4.2.4, the solubility test can be also used as convenient screening test for adhesives.

Tab. 4-8 presents the results of the solubility test. Lignosulfonates are originally hydrophilic [63], but in a polymerized form the solubility in polar solvents decreases. The reason for that might be that during the polymerization process water is split off and other hydrophobic components are formed, e.g. C-C, aryl-aryl, ether or alyl-alkyl linkages. Therefore, the polarity respectively the hydrophilicity is reduced which furthermore reduces the miscibility with water. None of the tested lignosulfonates were soluble in organic respectively nonpolar solvents, like isopropanol or hexane. It is expected that with increasing chain length of the side groups of the phenolic ring, the solubility of the lignosulfonates remains the same. The solubility of epLS in aqua regia remains the same, independently of the degree of polymerization. This refers to the characteristic, that aqua regia is highly corrosive and degrades all organic substance and even metals, like gold, platinum, and palladium.

Tab. 4-8: Results of the solubility test in dependence of the different polymerized epLS. The pre-epLS and hydrogel-epLS was prepared according to 4.2.2, the cured-epLS was prepared according to 4.2.3 and the dried-epLS was prepared according to 4.4.4.

epLS-type	Original-epLS	Pre-epLS	Hydrogel-epLS	Cured-epLS (on leather)	Dried-epLS (in oven)
Isopropanol	insoluble	insoluble	insoluble	insoluble	insoluble
Isohexane	insoluble	insoluble	insoluble	insoluble	insoluble
H_2O	soluble	soluble	soluble	slightly soluble	insoluble
HCl, 32 %	slightly soluble	slightly soluble	slightly soluble	slightly soluble	insoluble
NaOH, 26%	slightly soluble	slightly soluble	insoluble	slightly soluble	insoluble
Aqua regia	soluble	soluble	soluble	soluble	soluble

4.4.4 Water content

4.4.4.1 Experimental approach

The water content of pre-epLS, where 5 batches were prepared in accordance to 4.2, was investigated with a ceramic crucible dried for 2 h at 105 °C before chilling it at ambient temperature in a desiccator. The tare was noted and around 1.2 g of pre-epLS sample were transferred into the crucible. The crucible was then placed in the vacuum oven and the sample was dried at 40 °C and 200 mbar for 5 hours until the weight remained constant. After chilling the crucible in the desiccator to ambient conditions T =23 °C, the final mass was weighted and the loss of water was determined in accordance to Equ. 4-3:

$$\mathrm{WC}\ [\%] = 1 - \frac{\mathrm{m_O} - \mathrm{m_{dried}}}{\mathrm{m_O} * 100\ \%}$$

Equ. 4-3

WC...water content of epLS (wt%)

$\mathrm{m_O}$...mass of epLS sample before drying (g)

$\mathrm{m_{dried}}$... mass of epLS sample after drying (g)

4.4.4.2 Results

As it can be seen in Tab. 4-6, the dry weight of the pre-epLS after drying the substance in the oven was in average 60 % of the initial weight. That means, that the pre-epLS consists of 40 wt% water even after the pre-polymerization. It was expected, that the water content of pre-epLS is much lower since the viscosity of pre-epLS is 100 times higher than the original-epLS. This might be explained by Ortner et al. [75], who reported an increased water retention ability after the lignosulfonates were enzymatically polymerized, which may explain that pre-epLS still incorporates water. Apart from that, compared to the investigation of the water resistance in 4.3.2, it is observed that the water uptake/release capability is not reversible. As described in 4.3.2, the dried-epLS did not take up water and even solubility tests, as described in 4.4.2.2, showed no degradation in water. The theory that the molecular structure changes during the enzymatic polymerization and therefore influence the interaction with water, explains this phenomenon.

Tab. 4-9: Water content of 5 different pre-epLS-batches, dried at 40 °C, 200 mbar, until no mass change was detected (5 h in average)

Batch number	Water content (wt%)
1	40
2	40
3	33
4	41
5	44

4.4.5 Contact angle

4.4.5.1 Experimental approach

The contact angle measurement was carried out with an OCA 200 DDE4/x ESR-N (DataPhysics, Germany) by placing a droplet with a volume of 2 µl of the epLS-sample on the surface of the substrate. The measurement is based on the Young model and the contact angle is determined in accordance to DIN EN 828. An image of the drop in profile is taken as soon as the droplet remains stable at the surface, and the angle between the drop and the substrate surface is determined with the software SCA 20 (DataPhysics, Germany). The substances measured were original-epLS_30/2/0 and pre-epLS_30/2/0, prepared according to 4.2.2. The goal was to investigate the difference of the contact angle in dependence of the viscosity. The climate condition in the laboratory was T = 25°C, 50 % r.H. The substrates tested were alodine coated alumina, galvanized steel, polypropylene, leather and CFRP as described in 4.2.1. To remove the impurities the substrates were cleaned with isopropanol.

4.4.5.2 Results

The results of the contact angle measurement are summarized in Fig. 4-28 to Fig. 4-31, where the difference between original-epLS and pre-epLS are depicted. The figures of (A) depict the results of the original-epLS, where the figures of (B) present the pre-epLS. A snapshot was taken after the drop was placed on the substrate and remained stable which means that the shape did not change significantly. The contact angle vs. the drop age is plotted in a curve.

The contact angle of pre-epLS compared to the original epLS is smaller for all substrates, which indicates that the enzymatic polymerization of lignosulfonates improves the wettability. As mentioned in the theoretical part 3.2 a sufficient wettability of the adhesive requires a contact angle smaller than 35°.

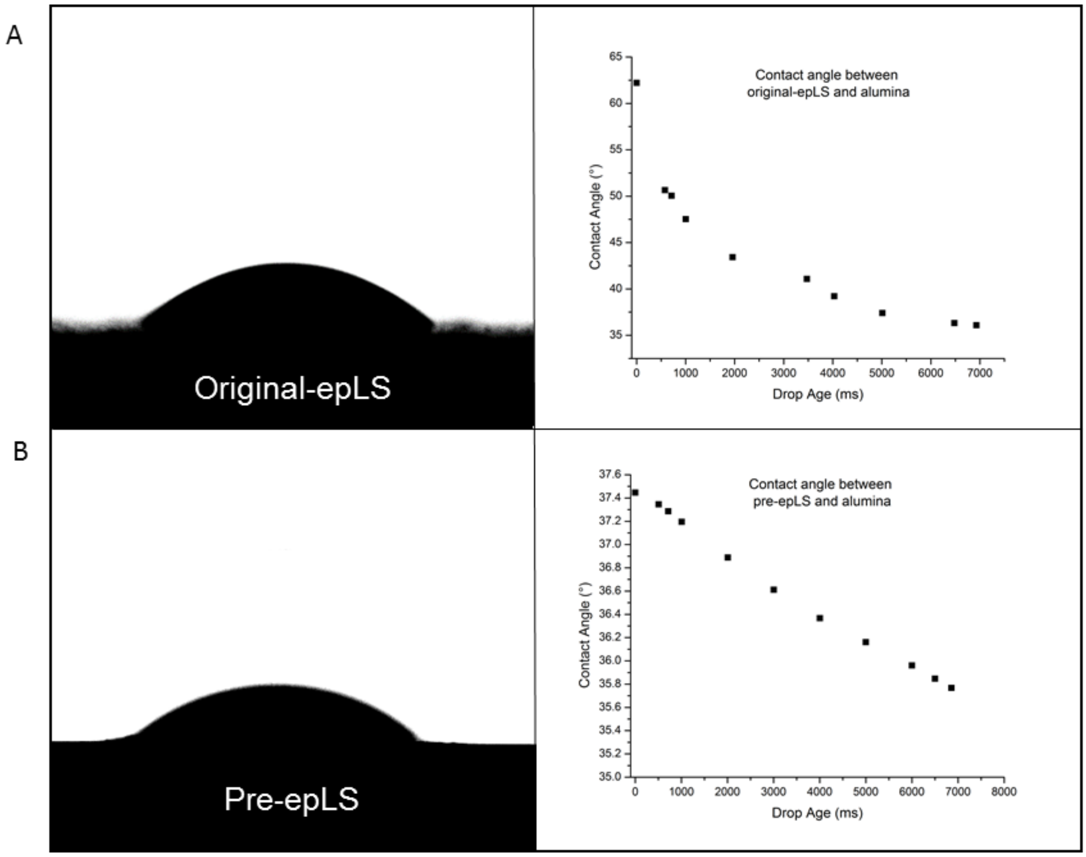

Fig. 4-28: Drop pictures and contact angle as a function of time for alumina: (A) depicts the drop of the original-epLS and the contact angle vs. drop age, (B) depicts the drop of pre-epLS and the contact angle vs. drop age.

Fig. 4-28 shows the contact angle of the epLS to alumina which is close to 35°. Good adhesion was expected, but this has not been confirmed with the initial adhesion test. Experiments of Huntsberger et.al [76] showed that even if the contact angle has an optimum value, the adhesion is not always sufficient. Goldschmidt et al. [15] explained this phenomena with the fact that Van-der-Waals forces and hydrogen bridging bond forces, as well as the surface roughness and the viscosity influence the adhesion ability. Further, differences in the wettability of the same adhesive and substrate may occur, if the temperature or humidity change. Those parameters influence the viscosity and therefore the penetration behaviour and cause a change of the boundary forces due to water absorption.

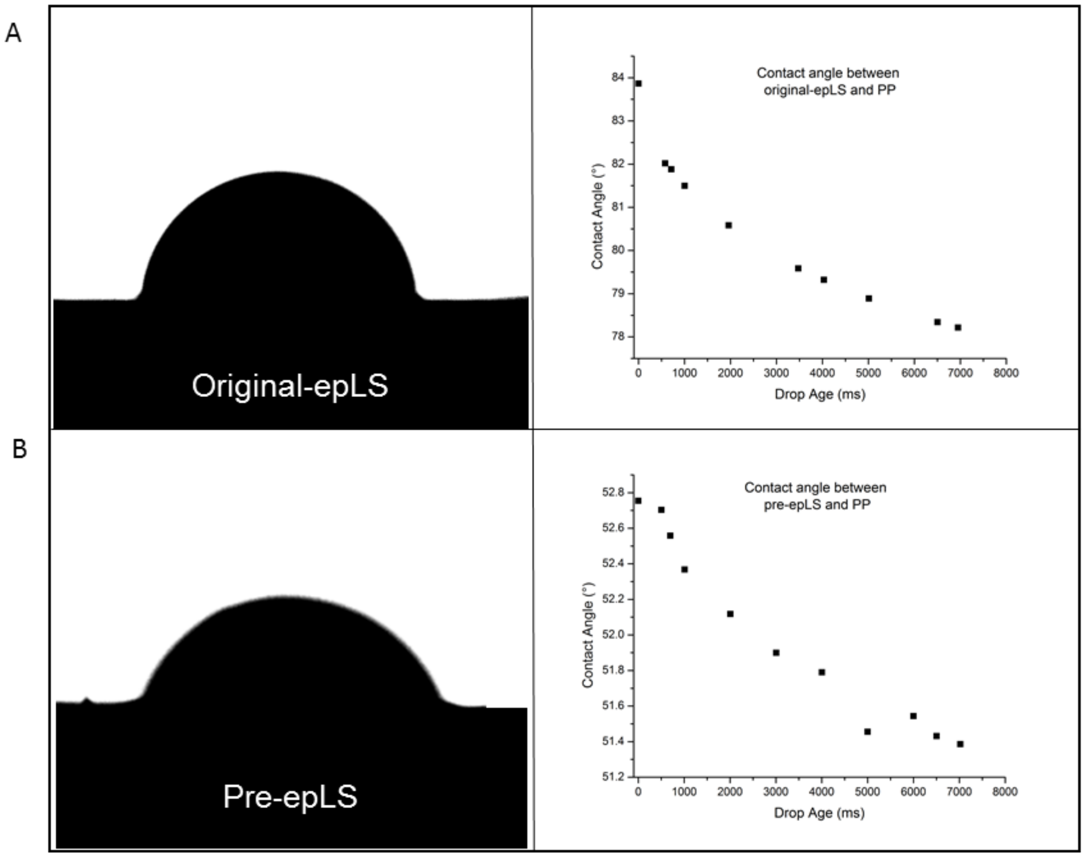

Fig. 4-29: Drop pictures and contact angle as a function of time for PP. (A) depicts the drop of the original-epLS and the contact angle vs. drop age, (B) depicts the drop of pre-epLS and the contact angle vs. drop age.

As expected, the contact angle between epLS and PP is higher than 35° and is shown in Fig. 4-29. This originates from the characteristic that those materials have a lower surface energy compared to steel or alumina. As mentioned in the theoretical part 3.2 the surface tension of the substrate has to be higher than the surface tension of the adhesive or coating material. Exemplarily, stainless steel has a surface energy of 1000 mN/m, whereas PP has a surface energy of 30 mN/m. As reference, epoxy resins, which are mainly applied in structural joining, have a surface energy of 47 mN/m which may explain why they are suitable for steel-alumina bonding. As known from coating industry, it is not possible to achieve good adhesives coating of those materials without any polarizing or other surface activating pre-treatments. [15]

Same as for PP, Fig. 4-30 shows that the contact angle measurement with zinc galvanized steel resulted in a higher contact angle than 35 °. It has to be mentioned that the contact angle for steel might be smaller if the surface is not treated with zinc or phosphate coating. The galvanic coating decreases the surface tension from 1000 mN/m to 47 mN/m and requires some additional primer to increase the wettability of the painting. The same occurs at a high oil load or other impurities, which have to be removed before coating. [15]

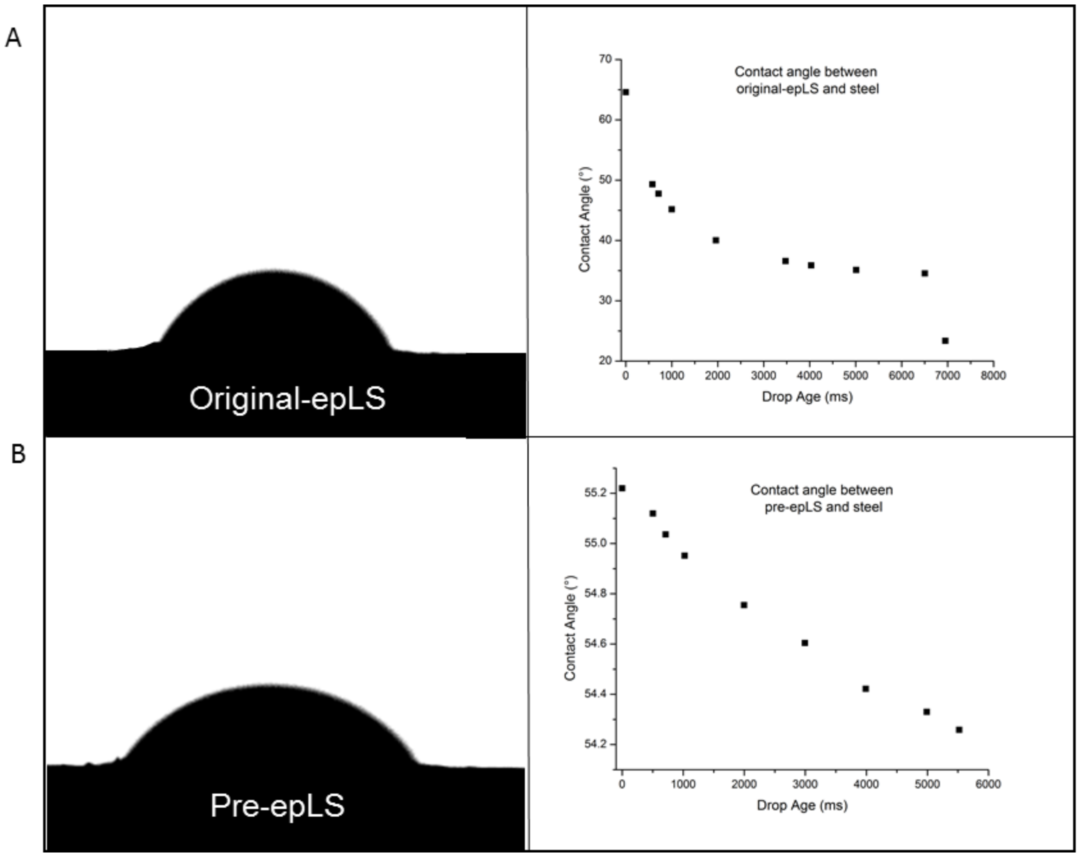

Fig. 4-30: Drop pictures and contact angle as a function of time for zinc galvanized steel: (A) depicts the drop of the original-epLS and the contact angle vs. drop age, (B) depicts the drop of pre-epLS and the contact angle vs. drop age.

Fig. 4-31 illustrates the contact angle between original-epLS and CFRP which is close to 65°. The contact angle between the original-epLS in and CFRP, shown in (A) decreases rapidly, but remains stable after the drop age of $t_{,drop}$ = 3500 ms. As shown in (B) the wettability of the epLS-adhesive is improved after pre-polymerization, resulting in a contact angle smaller than 44.6°.

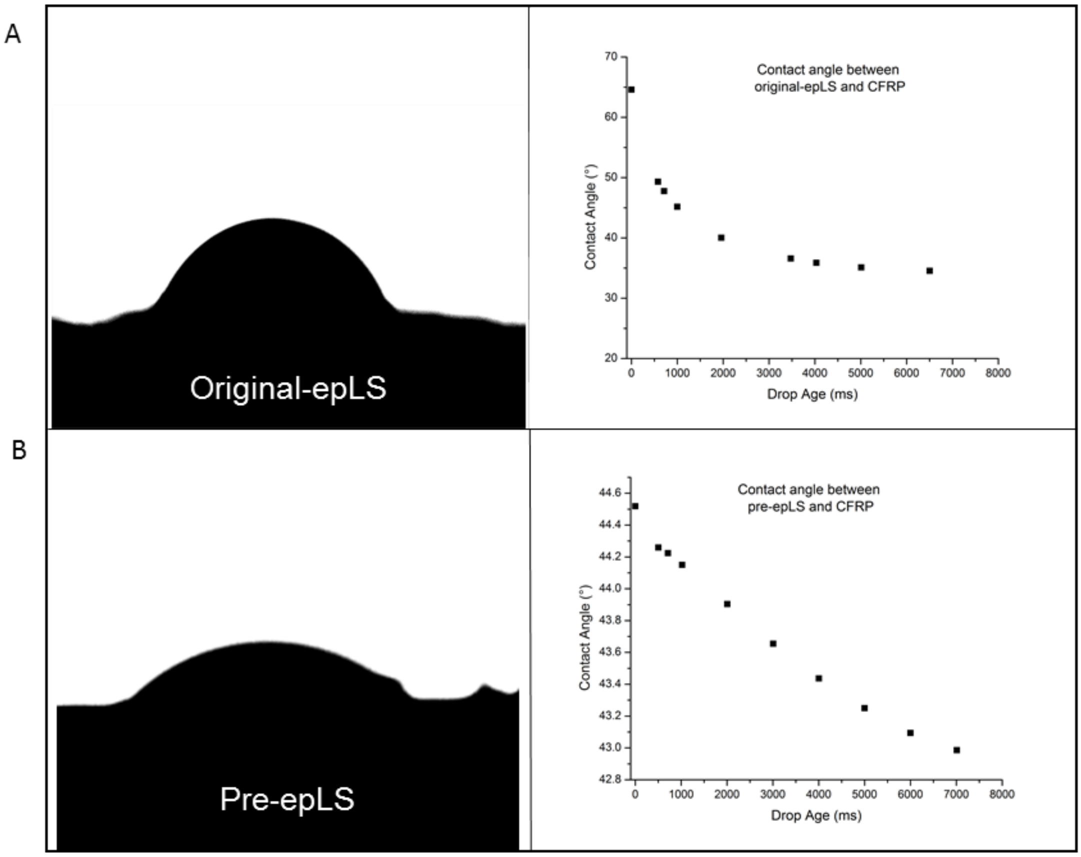

Fig. 4-31: Drop pictures and contact angle as a function of time for CFRP: (A) depicts the drop of the original-epLS and the contact angle vs. drop age, (B) depicts the drop of pre-epLS and the contact angle vs. drop age. Note that the contact angle in (A) decreases rapidly, but remains stable after 3500 ms.

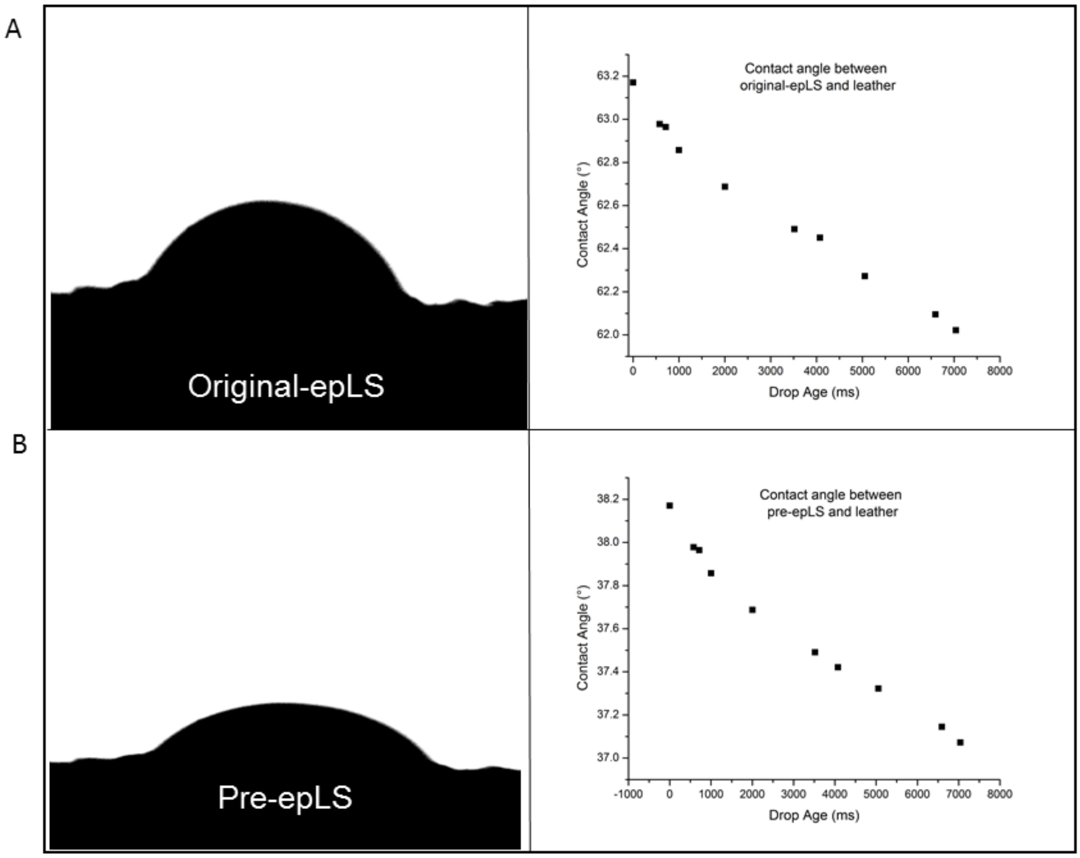

Fig. 4-32: Drop pictures and contact angle as a function of time for leather: (A) depicts the drop of the original-epLS and the contact angle vs. drop age, (B) depicts the drop of pre-epLS and the contact angle vs. drop age.

The contact angle of leather, which was so far the most promising substrate for an adhesive bonding with epLS, has a slightly higher contact angle than steel, as depicted in Fig. 4-32. This is explained by the model used for this contact angle determination, which is based on Young. The Young model is designed for ideal, smooth surfaces, which is not appropriate for the rough leather surface and therefore, the contact angle appears to be higher [77] [78]. To investigate the contact angle between epLS and leather, models of Wenzel or Cassie-Baxter are more accurate. These models consider rough and heterogeneous surfaces of solids, as explained in Fig. 4-33. As typical for application of adhesives, the wettability is improved by spreading the adhesive over the substrate. Therefore it is reasonable, that after distributing the epLS-adhesive with a brush the preconditions for a sufficient adhesion are given.

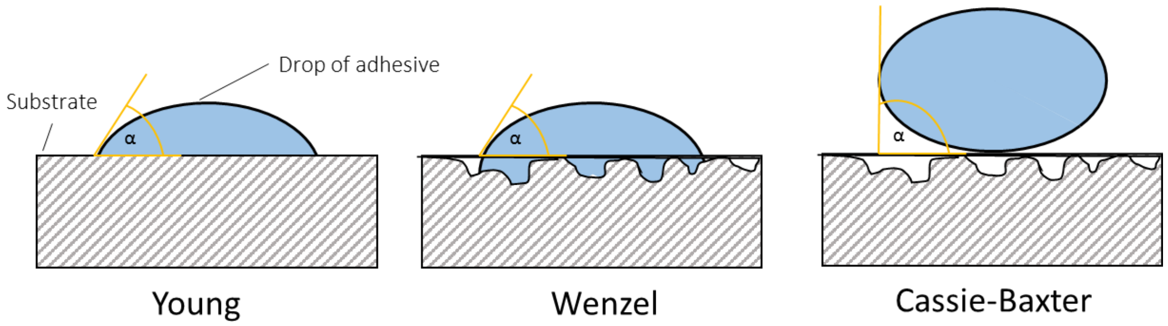

Fig. 4-33: Models for the determination of the contact angle and surface energy according to Young, Wenzel or Cassie-Baxter. [77] [78]

However, the wettability of epLS on leather was improved after polymerization and can be explained by the polarity of the substrate and the epLS-adhesive. During the tanning process of leather, the collagen fibres are chemically treated to increase the water and temperature resistance. This results in an increase of the hydrophobicity. Similarly, the proportion of polar groups of epLS was reduced during the enzymatic polymerization, thus the hydrophobicity of the adhesive increases and this further results in a better wettability.

To conclude, for all substrates the contact angle decreases with the drop age, which is related to the penetration and therefore spreading of the epLS-adhesive. It is also observed that the decline of the contact angle with the drop age is less distinct for pre-epLS compared to the original-epLS. This can be explained by the increase of the viscosity which consequently improves the stability of the drop. [79]

4.4.6 Summary of the material data

The most important material properties and data of pre-epLS_30/2/0 are summarized in Tab. 4-10.

Tab. 4-10: Material data of pre-epLS, which was prepared according to section 4.2.2.

Properties	**pre-epLS**
Substance	Enzymatically polymerized magnesium lignosulfonate with a total dry substance content of 30 wt% with glycerine (volume ration of 2:1) and laccase *Myceliophthora thermophile* (volume ratio of 100:1)
Colour	brown
Storage	at 8°C, in absence of oxygen, 7 days
Viscosity	9 - 10 Pas at T = 50.0 - 55.6 °C
Density before pre-polymerization	1.09 kg/m³ at 23.5°C
Degradation temperature	75 °C
Solubility in water after curing	soluble in water, if exposed for 8 h
Chemicals resistance after curing	resistant against polar solvents, e.g. water HCl, NaOH; resistant against nonpolar solvents, e.g isopropanol, isohexane
Curing	60 min, at T=23 °C, 35 % r.H, no contact pressure needed
Bonding ability to	Leather, viscose
Shear strength	0.2 MPa
Contact angle to leather (defined with Young)	37.0 – 38.2°
Paint wetting impairment	No

4.5 Application in car seat manufacturing

A final, but major step in the investigation of the epLS for automotive industry, was the examination under industrial conditions, especially for car seat manufacturing. Attention was paid not only to the adhesive bonding ability, but also to the handling properties, curing behaviour and optical appearance of the bonding.

As described in the theoretical part in chapter 3.3 one application in automotive industry is the use of adhesives for seat manufacturing. A car seat made of leather consists of different parts which are upholstered with viscose or foam and then sewed together to form a seat cover. The seat cover is then put on the seating shell which is the form donating component of the seat. The upholstering is adhesively bonded to the inner rough side of the leather.

Since initial adhesion test with pre-epLS_30/2/0 and leather turned out to be promising, a viscose-leather bonding for seat components was tested. The adhesives was applied with a brush onto the inner rough surface of the leather and then bonded with the viscose part, as depicted in Fig. 4-34. The samples were then cured in a laminating machine, FX Diamond CFL from Veit Kannegiesser, located in the seat manufacturing hall at Magna Steyr Fahrzeugtechnik in Graz, Austria. The machine was equipped with two heated drums to achieve a certain temperature and contact pressure. Fig. 4-35 shows the machine and the prepared leather-viscose samples. The test was carried out applying different temperature and pressure profiles to meet the optimum conditions for the epLS-adhesive. The exact conditions and the results are summarized in Tab. 4-11. The samples were transported with a conveyer belt into the heating zone of the laminating machine (v_{Belt} = 2.3 m/min). To avoid impurities of the drums due to excess of epLS-adhesive, the samples were covered with heat resistant paper.

Fig. 4-34: Dimension of the leather-viscose components which used in the car seat manufacturing and were bonded on a laminating machine

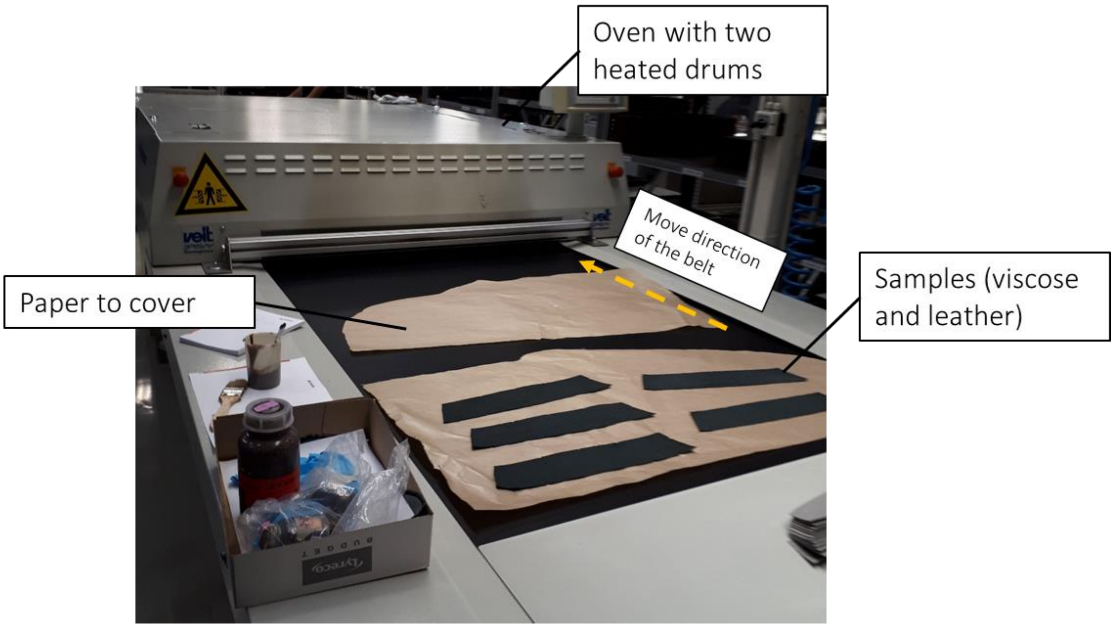

Fig. 4-35: Laminating machine with leather-viscose samples located in the seat manufacturing hall. The samples were transferred on a conveyer belt in the oven zone, where two heated drums apply a contact pressure.

Tab. 4-11 summarize the process parameter in the oven and the visual evaluation of the bonding material. The evaluation is carried out in cooperation with the team leader of cutting zone/seat manufacturing who focused on the bonding ability and the visual appearance of the leather-viscose bonding. The results of the evaluation were defined with green (optimum), yellow (improvement necessary) and red (not sufficient). The reference condition for the same leather-viscose bonding with a commercial dispersion adhesive for leather, fabrics and other textiles, were T_1 = 85 °C, T_2 = 135 °C, p = 3 bar, v = 2.3 m/min. T_1 and T_2 indicate the temperature at the two drums in the oven.

Tab. 4-11 shows that the process conditions 1 to 4 were not sufficient for the epLS-adhesive. With decreasing temperature and pressure the bonding ability increased and was as comparable to the commercially used adhesive. At constant throughput time, which corresponds to the conveyer belt velocity v_{Belt} = 2.3 m/min, the best results were achieved at a temperature $T_{1,}$ T_2 = 35 °C and a contact pressure of p = 2.0 bar. As obtained from the STA, degradation was expected at a temperature $T \geq 75$ °C and was observed at process conditions 1 and 2. Therefore the tests were carried out at lower temperatures, as summarized in Tab. 4-11. The optimum pressure was p = 2 bar, below that warping occurred (see Fig. 4-36), whereas a penetration of the epLS through viscose was detected if the pressure was higher than 2 bar (see Fig. 4-37). The test at a pressure $p \geq 3.5$ bar was even more challenging, since the epLS-adhesive was pressed out of the layered substrates and led to impurities on the drums. As a result, no adhesive remained on the substrate and therefore no adhesive bonding ability was given.

Tab. 4-11: Parameters for the car seat manufacturing with pre-epLS_30/2/0 and leather-viscose.

i	T_1 (°C)	T_2 (°C)	p (bar)	v_{Belt} (m/min)	Evaluation	Sufficient quality?
1	85	135	3.5	2.3	no adhesive bonding; warping of the leather-viscose component; degradation of the epLS was observed;	Red
2	68	78	3.5	2.3	epLS was pressed out and even penetrated through the viscose; no residue of epLS on the substrates; no adhesive bonding, degradation of the epLS was observed	Red
3	55	62	3.0	2.3	some residue of epLS on the substrate; epLS was partially pressed out; good adhesive bonding	Yellow
4	35	35	1.5	2.3	no penetration; epLS remained on substrates; weaker adhesive bonding; warping and surface quality of leather were not acceptable	Yellow
5	35	35	2.0	2.3	excellent adhesive bonding; minor loss in surface quality	Green

The experiment with lower pressure (p = 1.5 bar) caused thermal warping of the leather (see Fig. 4-36). Even the surface of the leather lost its smooth appearance. Obviously, a minimum pressure is needed in order to straighten the leather, if the pressure is too low the fibres become brittle and shrink, where humidity accelerates this process. Comparable to ironing, an increase of the contact pressure counteracted this behaviour. To improve the quality of the leather surface the contact pressure was therefore increased to p = 2.0 bar and the evaporation of water was avoided by ensuring an optimum pre-epLS viscosity of η = 9 - 12 Pa·s. [80]

Fig. 4-36: Warping and deformation of the leather-viscose sample due to contact pressure p < 2 bar

Another observation was the high absorption ability of the viscose, even though the epLS-adhesive was first applied onto the leather layer. A pressure of p ≥ 3 bar and a viscosity of η ≤ 9 Pa·s causes the epLS-adhesive to penetration through the viscose and to appear on the outer surface (Fig. 4-37). The viscosity is an important key factor, especially for bonding of porous materials. This aligns with Williams et al. [16], who stated, that the penetration into the substrate depends on the viscosity of the adhesive and influences the adhesion behaviour. Too much or too less penetration of the adhesive into the substrate results in a decrease of the adhesion.

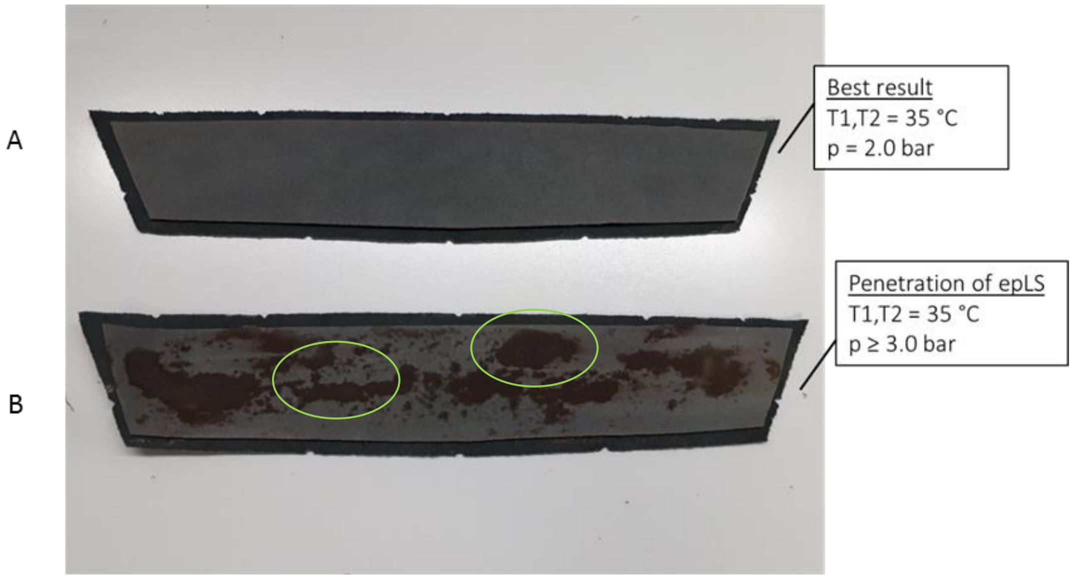

Fig. 4-37: Comparison of two leather-viscose samples, bonded with epLS-adhesive on the laminating machine: (A) showed the best result, (B) shows penetration of the epLS at p ≥ 3 bar

Fig. 4-38 shows the comparison of the commercial adhesive to the epLS adhesive. Some residues of the epLS were recognized at the edge of the viscose, highlighted in (A) with the green circle. (A) points out areas which are defined as “nonvisible areas”, meaning that the customer regularly can not see these regions and therefore the quality requirements are not as strict, as for “visible areas”, where high standards in terms of surface quality and appearance have to be met. To improve the results, pre-epLS can be applied more precicsle by adjusting the viscosity. However, the results are promising since the application experiment showed that the appearance of the leather surface was improved by optimizing the pressure and temperature in the oven. To reduce the contact pressure is not recommended otherwisee leather tends to deform again.

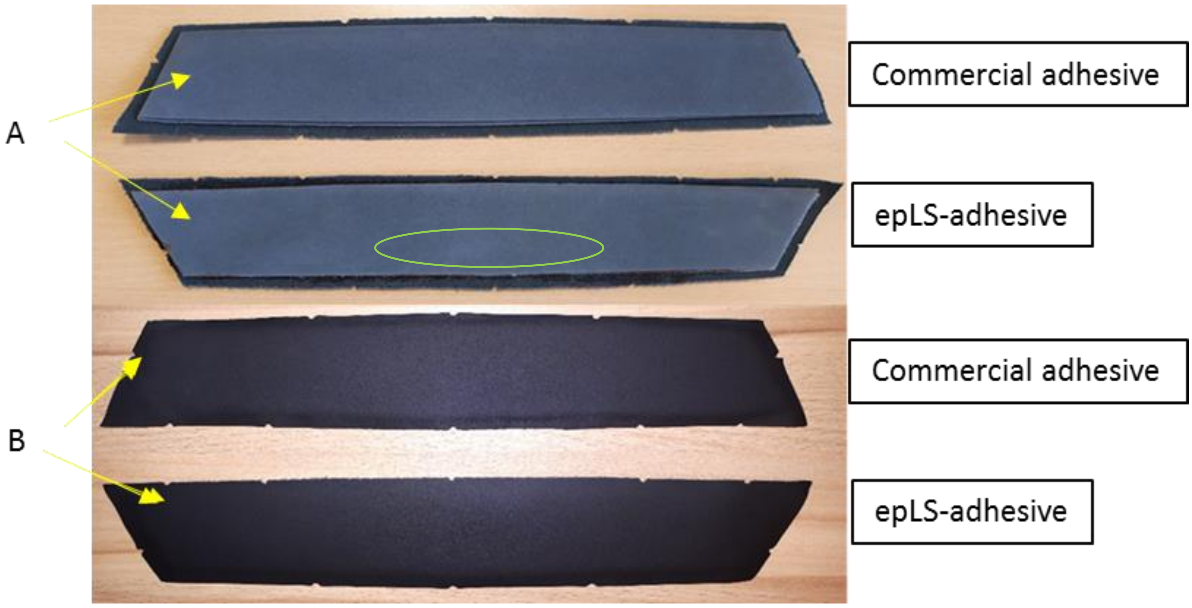

Fig. 4-38: Comparison of the currently used adhesive and the epLS-adhesive. (A) highlights non visible areas, where some residues of adhesive were detected (marked green), (B) highlights visible areas where the surface has to meet the quality standards

5 Conclusion and outlook

Currently used adhesives in automotive industry are fossil-based and usually contain organic solvents or other hazardous substances, which have harmful properties in terms of environment, health and safety. The global warming debate motivates recent research and industry to reduce the CO_2 emissions formed by the utilization of fossil-based resources. One major role in this discussion is the transport sector, which consumes more than half of the annually produced oil and is beside the energy generation sector, the second largest emitter of CO_2-emssions [2]. Regulations, consumers, non-governmental organizations, like NGO's and media pressure the automotive industry to invent new strategies to hold its position on the market. In order to reduce the CO_2-footprint of a car different topics need to be undertaken, where one approach is the use of bio-based materials in car manufacturing. The present work investigates the application of bio-based adhesives in automotive industry, which is a possible pathway to replace fossil-based adhesives and to improve the overall CO_2-balance of a car. The investigated bio-based adhesives are enzymatically polymerized lignosulfonates in different compositions (epLS) which may serve as promising alternative to commercially used adhesives in car manufacturing. [3] [11]

Lignin, the main component of the investigated bio-based adhesives, represents 30 wt. % of all nonfossil-based carbon sources and since of their abundance the utilization of technical lignin is of high interested. Lignosulfonates (LS), which are generated from the sulfite pulping process, provide a high potential for a commercial application in industry, like adhesives, binders or stabilizers. [52]

In the first part of this work the epLS was examined in terms of the bonding strength to different substrates, degradation due to temperature and humidity and further, in terms of storability, handling and industrial applicability for car seat manufacturing. Initial screening tests of different epLS-types showed that the adhesive bonding of leather and viscose lead to promising results, whereas materials like steel, alumina, CFRP or PP has less or even no bonding ability. Based on the lap shear experiments, epLS_30/2/0 with a glycerine proportion of 2:1 in respect to LS, showed the highest shear strength, with an average of 0.2 MPa and a maximum load of 364.7 N. These results meet the strength requirements of leather-viscose bonding in seat manufacturing of at least 0.02 MPa and 12.5 N. The load/elongation curve indicated elastic, but durable behaviour of the adhesive. The epLS without glycerine and with AKD resulted in worse strength performance, especially in terms of the elongation length and fracture pattern, which showed even cohesive fracture. Therefore epLS_30/2/0 was chosen for the investigation of the materials properties, such as viscosity, contact angle or solubility in polar and nonpolar solvents, which was carried out in the second part of this work, followed by the examination of the industrial applicability, which is summarized in the third and last part.

It was found, that with proceeding polymerization of the epLS, which refers to an increase in a molecular weight and higher cross-linking of the polymeric structure [11], the adhesion, cohesion and application properties were improved and further, the solubility in water, polar and nonpolar solvents was decreased. Based on these observations a pre-polymerization of epLS (pre-epLS) was carried out to reach sufficient application and adhesion properties. An improvement of the wettability properties with proceeding polymerization was also observed during the contact angle measurement where the contact angle of pre-epLS and the investigated substrate was smaller compared to the original-epLS. The contact angle determined with the Young model of epLS to leather was between 37.0 – 38.2°. The optimum pre-polymerization point was reached at a viscosity η between 9 and 10 Pa·s and must not go beyond, where then hydrogel with insufficient adhesion and application properties is formed. The pre-polymerized epLS showed shear thinning behavior for shear rates $\gamma > 1200$ 1/s, which is beneficial for industrial application since the epLS-adhesive is spreadable by adding shear stress via an application tool, like a brush.

The water resistance of epLS carried out with an exposure to water for 8 hours, resulted in a dissolution of the adhesive, thus the application for exteriors or structural components is not suitable. In regards to moderate climate conditions, as prevailing in the interior of a car, the epLS showed great durability. Under an ambient climate conditions, neither water uptake nor water release was detected. During the thermogravimetric analysis it was found that no decomposition takes place at $T \leq 75$ °C. Based on these observations the application of epLS in seat manufacturing, was chosen, where no tough conditions occur, but a high elasticity is required.

In the third part of this work a leather-viscose bonding was examined in regards to industrial processing and evaluated in terms of bonding strength and visible appearance. Compared to the commercial adhesive, which has to be cured at $T = 85$°C/ 135°C, the oven temperature could be reduced to $T = 35$ °C within the same throughput time of $v_{Belt} = 2.3.$ m/min and comparable quality of the leather-viscose bonding. The curing behaviour is beneficial in terms of energy consumption and is attributed to the enzymatic polymerization which takes place due to a radical coupling of the phenolic-groups of lignosulfonates in the presence of oxygen and is not initialized due to heat or pressure. [9] [11]

To conclude, the epLS-adhesives can be a sustainable alternative to common fossil-based adhesives used in automotive industry, where the field of application is mainly the adhesive bonding of interior components. Further investigations of the molecular structure are essential to determine possible hazardous products formed during degradation at a temperature higher than 75 °C. The investigation of the cross-linking arrangement and the functional groups are crucial to optimize the adhesion bonding ability to other substrates, like metals or plastic. This could improve the wetting and bonding behavior and enlarges the application for interior applications, other than seat manufacturing, like paneling of inner structural components with leather, cotton or other fabrics. In terms of lightweight design, the epLS-adhesive serves as a promising bonding technology for future design concepts, for example the use of bio-based composites or wooden panels. This concept enables further reduction in weight, a better recyclability and an improved overall CO_2-footprint of cars.

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7 Abbreviations

7.1 General

AKD	Alkyl ketene dimer
CFRP	Carbon fiber reinforced plastic
epLS	Enzymatic polymerized lignosulfonates
HCl	Hydrogen chloride
LS	Lignosulfonate
MtL	Laccase Myceliophthora thermophila
n.r.	Not relevant
N_2	Nitrogen
NaOH	Sodiumhydroxide
PP	Polypropylene
pre-epLS	Pre-polymerized epLS
DS	Dry substance content in percent [%]

7.2 Symbols

α	[°]	Contact angle
A	[m²]	Adhesive bonding area
F_{max}	[N]	Maximum load/force until fracture
m_O	[g]	Mass of epLS sample before drying
m_{dried}	[g]	Mass of epLS sample after drying
m_{epLS}	[g]	Mass of epLS sample

η	[Pa*s]	Viscosity
ρ	[kg/m³]	Density of epLS sample
p	[bar]	Pressure (contact pressure)
R_z	µm	Averaged surface roughness
τ_{max}	[MPa]	Maximum shear strength until fracture
t	[h], [min]	Time for polymerization respectively curing
$t_{,drop}$	[ms]	Drop age
T	[°C]	Temperature
V_{epLS}	[m³]	Volume of epLS sample
v_{Belt}	[m/s]	Conveyer belt velocity of the laminating machine
WC	[%]	Water content of epLS in percent

8 Image index

9 Table index

10 Equation index

11 Appendix

The results of the water uptake measurement, described in 4.3.2 are given in the table Tab. 11-1 and Tab. 11-2.

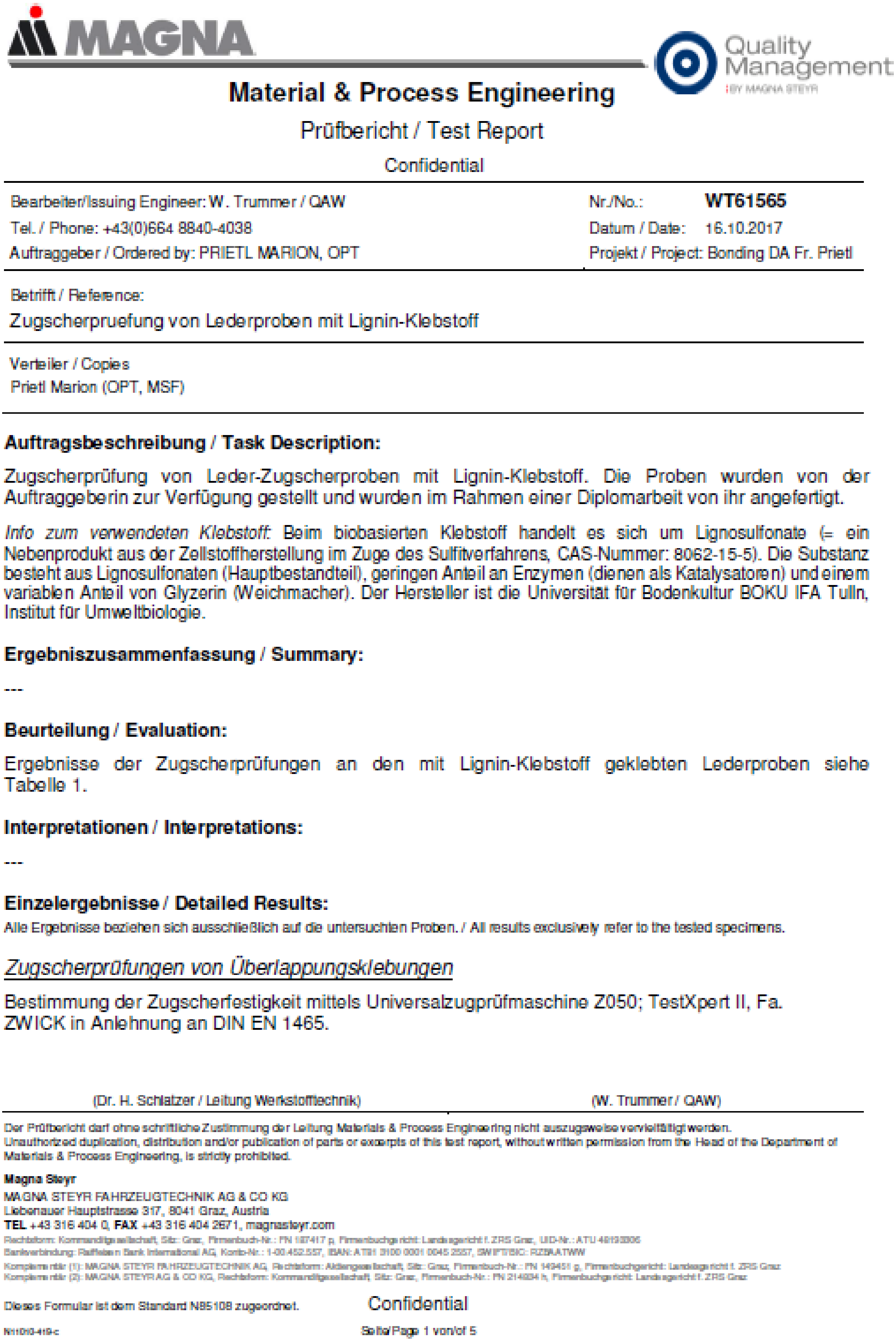
Tab. 11-1: Water uptake and release measurement, carried out in according to 4.3.2 (part 1)

t = 8:00 h	**Original-epLS**			**Pre-epLS**		
Conditions (T, r.H.)	**m,0 (g)**	**m,t (g)**	**dm/dt (%)**	**m,0 (g)**	**m,t (g)**	**dm/dt (%)**
T=23 °C, 35 % r.H	3.95	-3.0	-78	3.95	-0.9	-23
T=20 °C, 54 % r.H.	3.95	-2.91	-74	3.93	-0.2	-5
T=6 °C, 78 % r.H	3.94	-1.45	-37	3.96	0	0

Tab. 11-2: Water uptake and release measurement, carried out in according to 4.3.2.5 (part 2)

t = 8:00 h	**epLS-cured**			**epLS-dried**			**Hydrogel-epLS**		
Conditions (T, r.H.)	**m,0 (g)**	**m,t (g)**	**dm/dt (%)**	**m,0 (g)**	**m,t (g)**	**dm/dt (%)**	**m,0 (g)**	**m,t (g)**	**dm/dt (%)**
T=23 °C, 35 % r.H	0.42	0.42	0	0.5061	0	0	3.95	-2.9	-73
T=20 °C, 54 % r.H.	0.41	0.41	0	0.5051	0.0147	3	3.95	-2.01	-51
T=6 °C, 78 % r.H	0.39	0.39	0	0.5042	0.021	4	3.95	-1.7	-43

The results of the lap shear are given in WT61565 (page 95) and WT63013 (lap shear testing including climate change test, page 100). Note, the samples with index 1 to 4 and 5 to 8 are pre-epLS_30/2/0, the samples with the index 9 to 12 are pre-epLS without glycerine, epLS_30/0/0. The results are discussed in 4.3.1.2. Sample with index 5 – 8 were used for storability test discussed in 4.3.3.2.



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Quality Management
BY MAGNA STEYR

Material & Process Engineering

Prüfbericht / Test Report

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Bearbeiter/Issuing Engineer: W. Trummer / QAW
Tel. / Phone: +43(0)664 8840-4038
Auftraggeber / Ordered by: PRIETL MARION, OPT

Nr./No.: **WT61565**
Datum / Date: 16.10.2017
Projekt / Project: Bonding DA Fr. Prietl

Betrifft / Reference:
Zugscherpruefung von Lederproben mit Lignin-Klebstoff

Verteiler / Copies
Prietl Marion (OPT, MSF)

Auftragsbeschreibung / Task Description:

Zugscherprüfung von Leder-Zugscherproben mit Lignin-Klebstoff. Die Proben wurden von der Auftraggeberin zur Verfügung gestellt und wurden im Rahmen einer Diplomarbeit von ihr angefertigt.

Info zum verwendeten Klebstoff: Beim biobasierten Klebstoff handelt es sich um Lignosulfonate (= ein Nebenprodukt aus der Zellstoffherstellung im Zuge des Sulfitverfahrens, CAS-Nummer: 8062-15-5). Die Substanz besteht aus Lignosulfonaten (Hauptbestandteil), geringen Anteil an Enzymen (dienen als Katalysatoren) und einem variablen Anteil von Glyzerin (Weichmacher). Der Hersteller ist die Universität für Bodenkultur BOKU IFA Tulln, Institut für Umweltbiologie.

Ergebniszusammenfassung / Summary:

Beurteilung / Evaluation:

Ergebnisse der Zugscherprüfungen an den mit Lignin-Klebstoff geklebten Lederproben siehe Tabelle 1.

Interpretationen / Interpretations:

Einzelergebnisse / Detailed Results:

Alle Ergebnisse beziehen sich ausschließlich auf die untersuchten Proben. / All results exclusively refer to the tested specimens.

Zugscherprüfungen von Überlappungsklebungen

Bestimmung der Zugscherfestigkeit mittels Universalzugprüfmaschine Z050; TestXpert II, Fa. ZWICK in Anlehnung an DIN EN 1465.

(Dr. H. Schlatzer / Leitung Werkstofftechnik) (W. Trummer / QAW)

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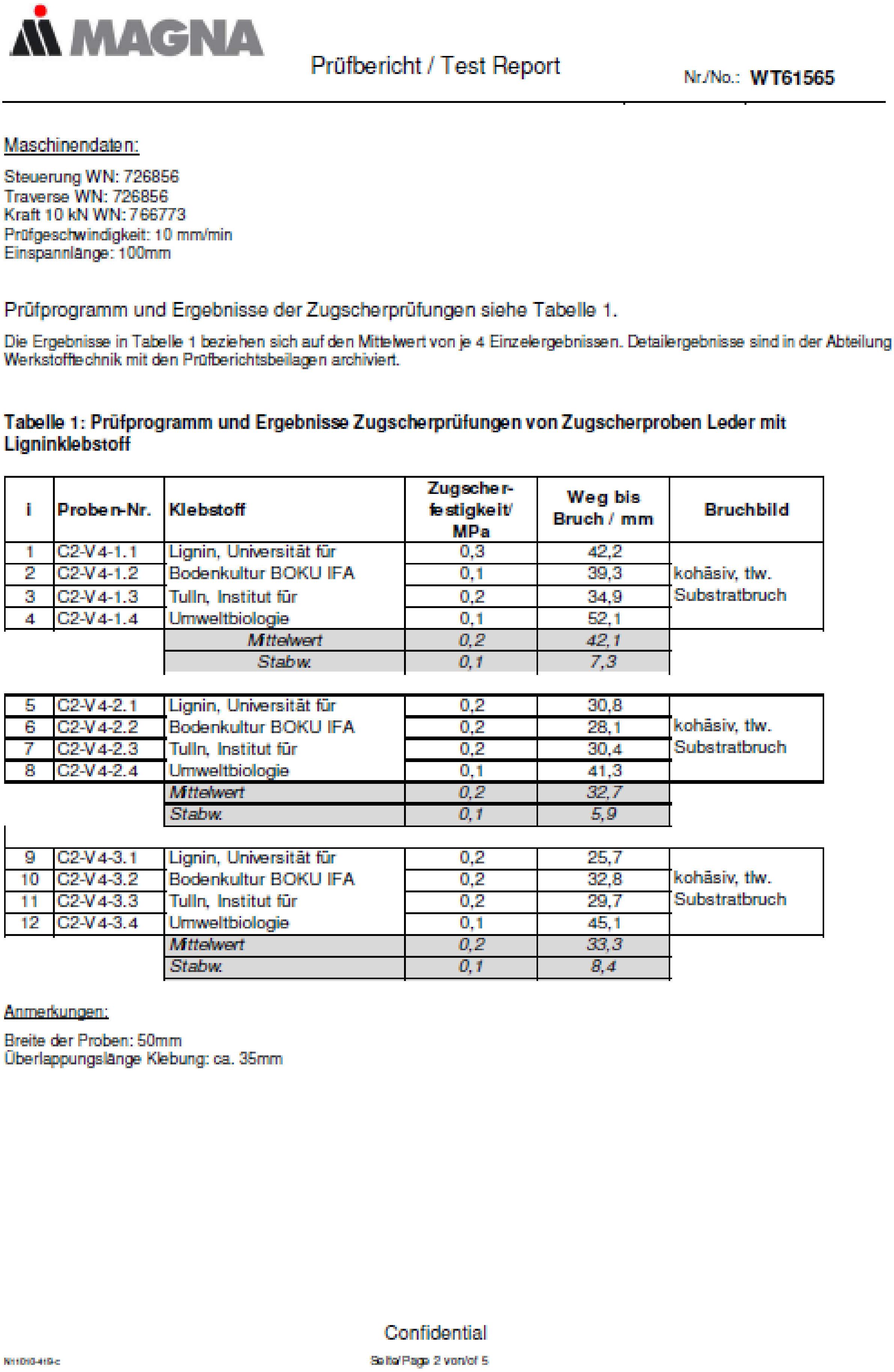

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Prüfbericht / Test Report

Nr./No.: **WT61565**

Maschinendaten:

Steuerung WN: 726856
Traverse WN: 726856
Kraft 10 kN WN: 766773
Prüfgeschwindigkeit: 10 mm/min
Einspannlänge: 100mm

Prüfprogramm und Ergebnisse der Zugscherprüfungen siehe Tabelle 1.

Die Ergebnisse in Tabelle 1 beziehen sich auf den Mittelwert von je 4 Einzelergebnissen. Detailergebnisse sind in der Abteilung Werkstofftechnik mit den Prüfberichtsbeilagen archiviert.

Tabelle 1: Prüfprogramm und Ergebnisse Zugscherprüfungen von Zugscherproben Leder mit Ligninklebstoff

i	Proben-Nr.	Klebstoff	Zugscherfestigkeit/ MPa	Weg bis Bruch / mm	Bruchbild
1	C2-V4-1.1	Lignin, Universität für Bodenkultur BOKU IFA Tulln, Institut für Umweltbiologie	0,3	42,2	kohäsiv, tlw. Substratbruch
2	C2-V4-1.2		0,1	39,3	
3	C2-V4-1.3		0,2	34,9	
4	C2-V4-1.4		0,1	52,1	
		Mittelwert	*0,2*	*42,1*	
		Stabw.	*0,1*	*7,3*	
5	C2-V4-2.1	Lignin, Universität für Bodenkultur BOKU IFA Tulln, Institut für Umweltbiologie	0,2	30,8	kohäsiv, tlw. Substratbruch
6	C2-V4-2.2		0,2	28,1	
7	C2-V4-2.3		0,2	30,4	
8	C2-V4-2.4		0,1	41,3	
		Mittelwert	*0,2*	*32,7*	
		Stabw.	*0,1*	*5,9*	
9	C2-V4-3.1	Lignin, Universität für Bodenkultur BOKU IFA Tulln, Institut für Umweltbiologie	0,2	25,7	kohäsiv, tlw. Substratbruch
10	C2-V4-3.2		0,2	32,8	
11	C2-V4-3.3		0,2	29,7	
12	C2-V4-3.4		0,1	45,1	
		Mittelwert	*0,2*	*33,3*	
		Stabw.	*0,1*	*8,4*	

Anmerkungen:

Breite der Proben: 50mm
Überlappungslänge Klebung: ca. 35mm

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Seite/Page 2 von/of 5

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Prüfbericht / Test Report

Nr./No.: **WT61565**

FOTODOKUMENTATION

Abbildung 1: C2-V4-1. 1-4

Abbildung 2: C2-V4-2. 1-4

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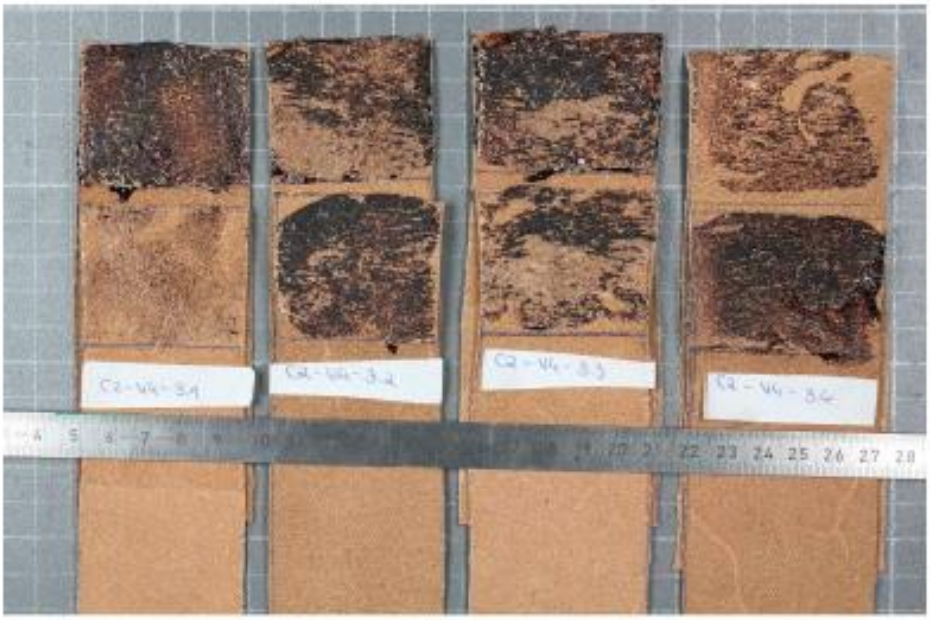
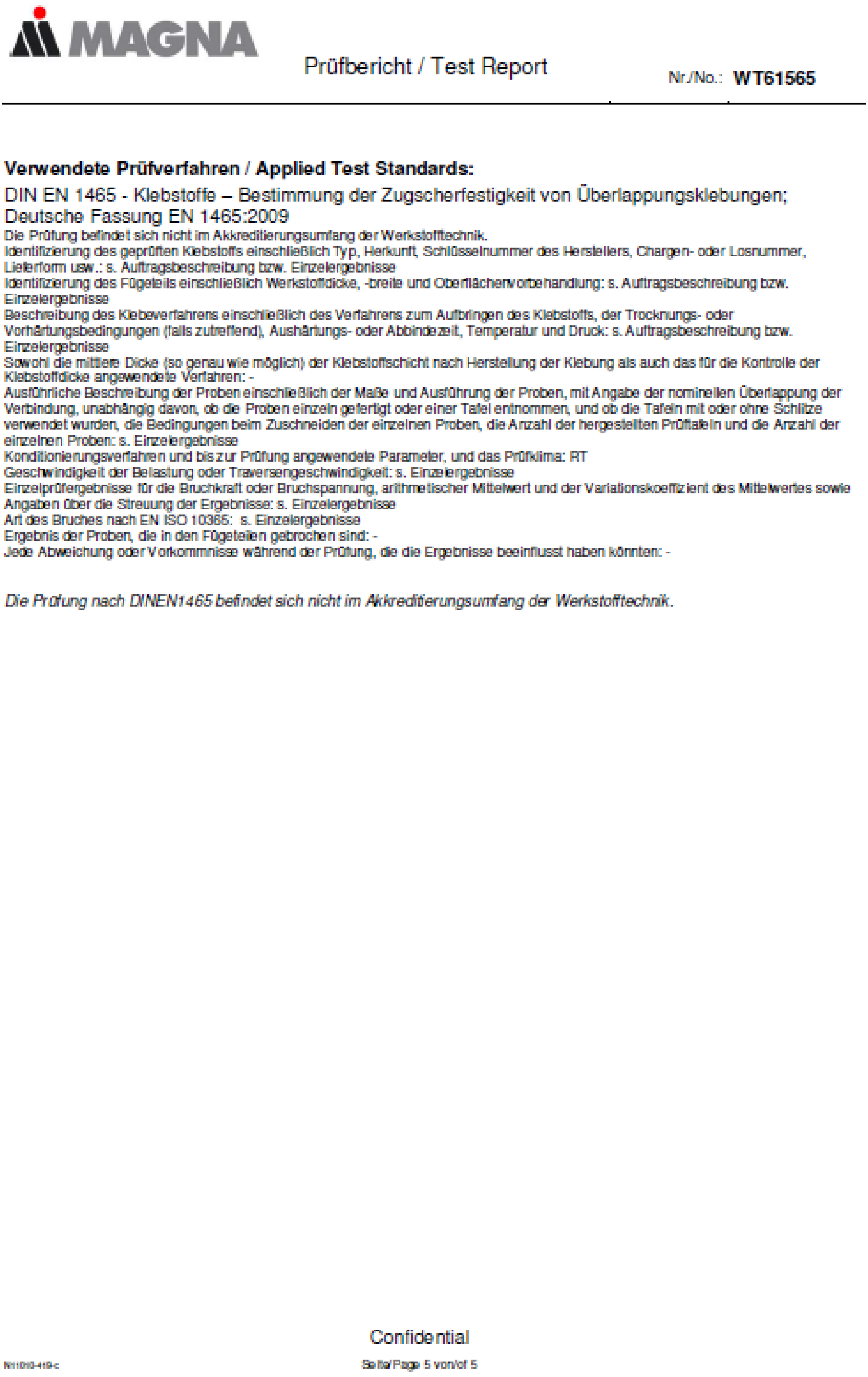


Abbildung 3: C2-V4-3. 1-4



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Prüfbericht / Test Report

Nr./No.: **WT61565**

Verwendete Prüfverfahren / Applied Test Standards:

DIN EN 1465 - Klebstoffe – Bestimmung der Zugscherfestigkeit von Überlappungsklebungen; Deutsche Fassung EN 1465:2009

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Identifizierung des geprüften Klebstoffs einschließlich Typ, Herkunft, Schlüsselnummer des Herstellers, Chargen- oder Losnummer, Lieferform usw.: s. Auftragsbeschreibung bzw. Einzelergebnisse
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Beschreibung des Klebeverfahrens einschließlich des Verfahrens zum Aufbringen des Klebstoffs, der Trocknungs- oder Vorhärtungsbedingungen (falls zutreffend), Aushärtungs- oder Abbindezeit, Temperatur und Druck: s. Auftragsbeschreibung bzw. Einzelergebnisse
Sowohl die mittlere Dicke (so genau wie möglich) der Klebstoffschicht nach Herstellung der Klebung als auch das für die Kontrolle der Klebstoffdicke angewendete Verfahren: -
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Konditionierungsverfahren und bis zur Prüfung angewendete Parameter, und das Prüfklima: RT
Geschwindigkeit der Belastung oder Traversengeschwindigkeit: s. Einzelergebnisse
Einzelprüfergebnisse für die Bruchkraft oder Bruchspannung, arithmetischer Mittelwert und der Variationskoeffizient des Mittelwertes sowie Angaben über die Streuung der Ergebnisse: s. Einzelergebnisse
Art des Bruches nach EN ISO 10365: s. Einzelergebnisse
Ergebnis der Proben, die in den Fügeteilen gebrochen sind: -
Jede Abweichung oder Vorkommnisse während der Prüfung, die die Ergebnisse beeinflusst haben könnten: -

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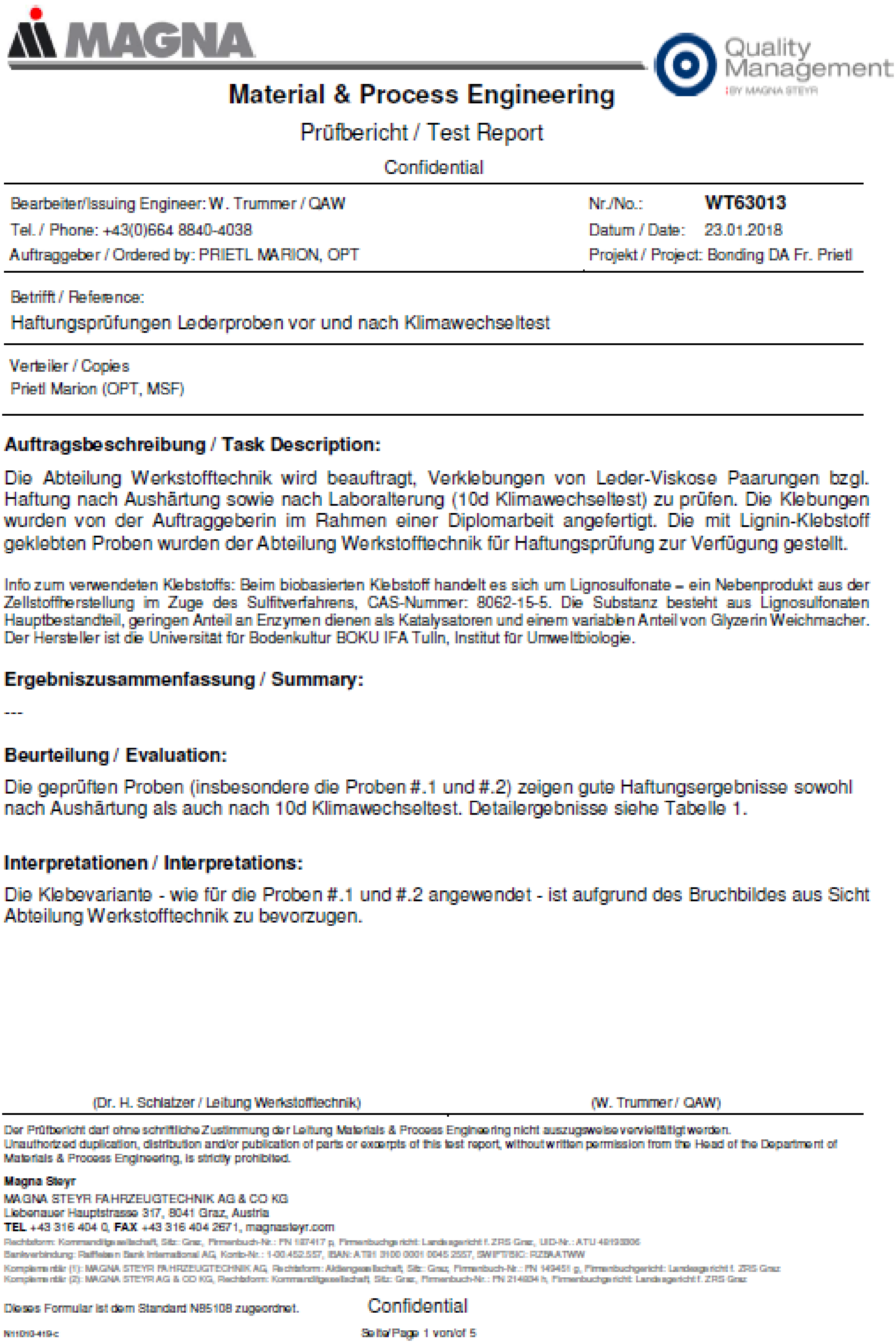

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Quality Management
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Material & Process Engineering

Prüfbericht / Test Report

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Bearbeiter/Issuing Engineer: W. Trummer / QAW		Nr./No.:	**WT63013**
Tel. / Phone: +43(0)664 8840-4038		Datum / Date:	23.01.2018
Auftraggeber / Ordered by: PRIETL MARION, OPT		Projekt / Project:	Bonding DA Fr. Prietl

Betrifft / Reference:
Haftungsprüfungen Lederproben vor und nach Klimawechseltest

Verteiler / Copies
Prietl Marion (OPT, MSF)

Auftragsbeschreibung / Task Description:

Die Abteilung Werkstofftechnik wird beauftragt, Verklebungen von Leder-Viskose Paarungen bzgl. Haftung nach Aushärtung sowie nach Laboralterung (10d Klimawechseltest) zu prüfen. Die Klebungen wurden von der Auftraggeberin im Rahmen einer Diplomarbeit angefertigt. Die mit Lignin-Klebstoff geklebten Proben wurden der Abteilung Werkstofftechnik für Haftungsprüfung zur Verfügung gestellt.

Info zum verwendeten Klebstoffs: Beim biobasierten Klebstoff handelt es sich um Lignosulfonate – ein Nebenprodukt aus der Zellstoffherstellung im Zuge des Sulfitverfahrens, CAS-Nummer: 8062-15-5. Die Substanz besteht aus Lignosulfonaten Hauptbestandteil, geringen Anteil an Enzymen dienen als Katalysatoren und einem variablen Anteil von Glyzerin Weichmacher. Der Hersteller ist die Universität für Bodenkultur BOKU IFA Tulln, Institut für Umweltbiologie.

Ergebniszusammenfassung / Summary:

Beurteilung / Evaluation:

Die geprüften Proben (insbesondere die Proben #.1 und #.2) zeigen gute Haftungsergebnisse sowohl nach Aushärtung als auch nach 10d Klimawechseltest. Detailergebnisse siehe Tabelle 1.

Interpretationen / Interpretations:

Die Klebevariante - wie für die Proben #.1 und #.2 angewendet - ist aufgrund des Bruchbildes aus Sicht Abteilung Werkstofftechnik zu bevorzugen.

(Dr. H. Schlatzer / Leitung Werkstofftechnik) (W. Trummer / QAW)

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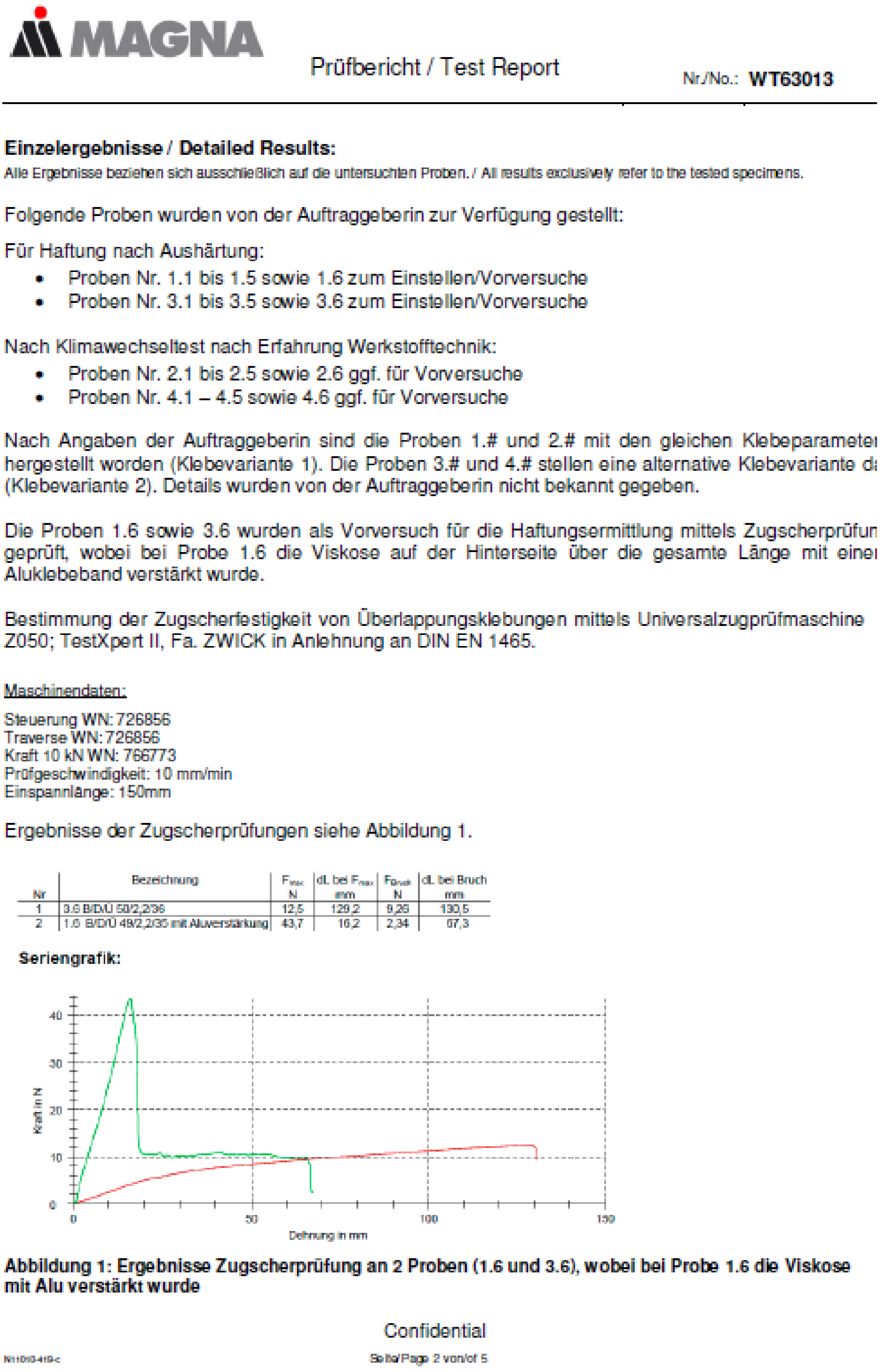

MAGNA Prüfbericht / Test Report Nr./No.: **WT63013**

Einzelergebnisse / Detailed Results:

Alle Ergebnisse beziehen sich ausschließlich auf die untersuchten Proben. / All results exclusively refer to the tested specimens.

Folgende Proben wurden von der Auftraggeberin zur Verfügung gestellt:

Für Haftung nach Aushärtung:

- Proben Nr. 1.1 bis 1.5 sowie 1.6 zum Einstellen/Vorversuche
- Proben Nr. 3.1 bis 3.5 sowie 3.6 zum Einstellen/Vorversuche

Nach Klimawechseltest nach Erfahrung Werkstofftechnik:

- Proben Nr. 2.1 bis 2.5 sowie 2.6 ggf. für Vorversuche
- Proben Nr. 4.1 – 4.5 sowie 4.6 ggf. für Vorversuche

Nach Angaben der Auftraggeberin sind die Proben 1.# und 2.# mit den gleichen Klebeparamete hergestellt worden (Klebevariante 1). Die Proben 3.# und 4.# stellen eine alternative Klebevariante d (Klebevariante 2). Details wurden von der Auftraggeberin nicht bekannt gegeben.

Die Proben 1.6 sowie 3.6 wurden als Vorversuch für die Haftungsermittlung mittels Zugscherprüfun geprüft, wobei bei Probe 1.6 die Viskose auf der Hinterseite über die gesamte Länge mit eine Aluklebeband verstärkt wurde.

Bestimmung der Zugscherfestigkeit von Überlappungsklebungen mittels Universalzugprüfmaschine Z050; TestXpert II, Fa. ZWICK in Anlehnung an DIN EN 1465.

Maschinendaten:

Steuerung WN: 726856
Traverse WN: 726856
Kraft 10 kN WN: 766773
Prüfgeschwindigkeit: 10 mm/min
Einspannlänge: 150mm

Ergebnisse der Zugscherprüfungen siehe Abbildung 1.

Nr	Bezeichnung	F_{max} N	dL bei F_{max} mm	F_{Bruch} N	dL bei Bruch mm
1	3.6 B/D/Ü 50/2,2/36	12,5	129,2	9,28	130,5
2	1.6 B/D/Ü 49/2,2/35 mit Aluverstärkung	43,7	16,2	2,34	67,3

Seriengrafik:

Abbildung 1: Ergebnisse Zugscherprüfung an 2 Proben (1.6 und 3.6), wobei bei Probe 1.6 die Viskose mit Alu verstärkt wurde

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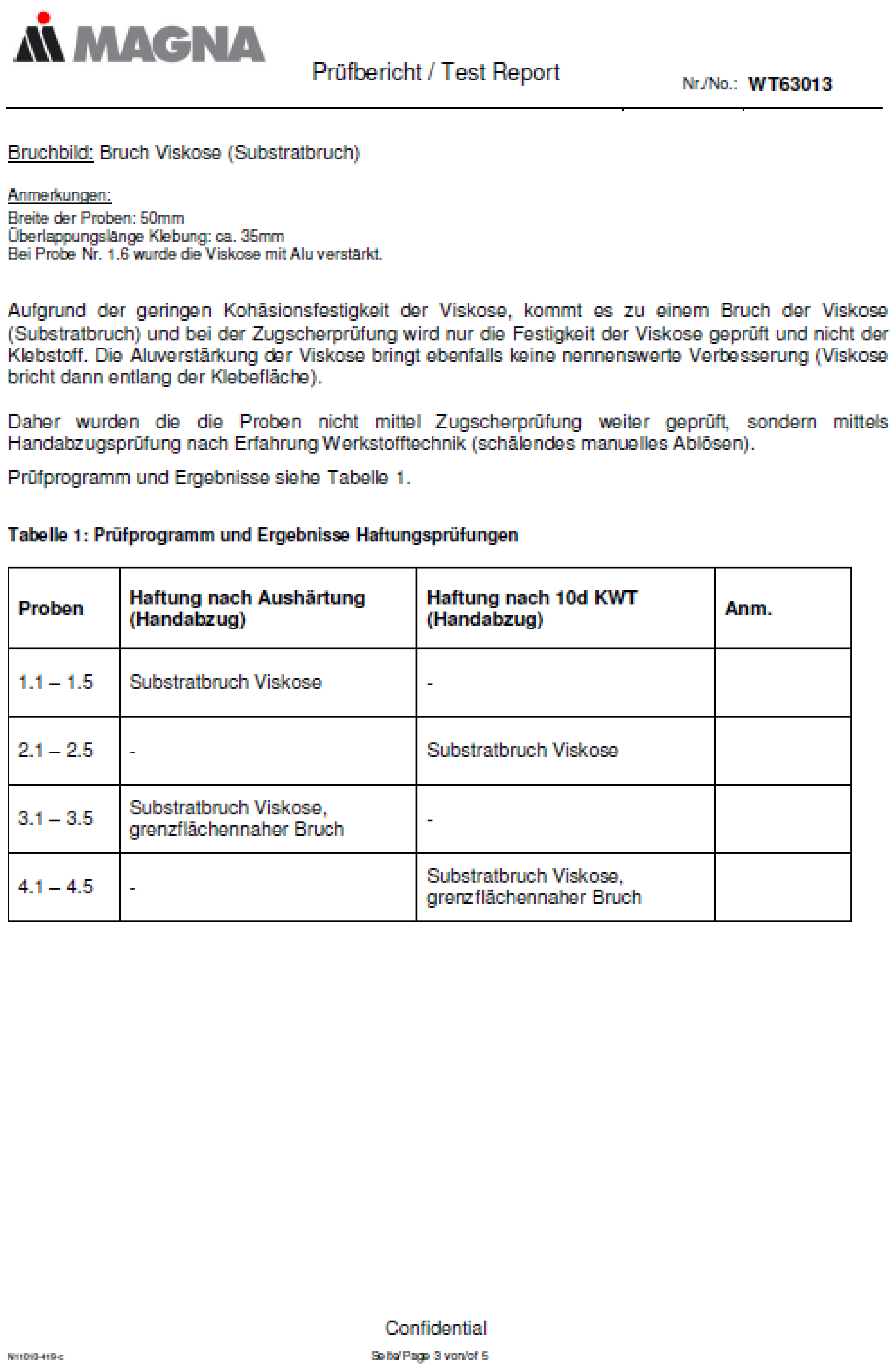

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Nr./No.: **WT63013**

Bruchbild: Bruch Viskose (Substratbruch)

Anmerkungen:
Breite der Proben: 50mm
Überlappungslänge Klebung: ca. 35mm
Bei Probe Nr. 1.6 wurde die Viskose mit Alu verstärkt.

Aufgrund der geringen Kohäsionsfestigkeit der Viskose, kommt es zu einem Bruch der Viskose (Substratbruch) und bei der Zugscherprüfung wird nur die Festigkeit der Viskose geprüft und nicht der Klebstoff. Die Aluverstärkung der Viskose bringt ebenfalls keine nennenswerte Verbesserung (Viskose bricht dann entlang der Klebefläche).

Daher wurden die die Proben nicht mittel Zugscherprüfung weiter geprüft, sondern mittels Handabzugsprüfung nach Erfahrung Werkstofftechnik (schälendes manuelles Ablösen).

Prüfprogramm und Ergebnisse siehe Tabelle 1.

Tabelle 1: Prüfprogramm und Ergebnisse Haftungsprüfungen

Proben	**Haftung nach Aushärtung (Handabzug)**	**Haftung nach 10d KWT (Handabzug)**	**Anm.**
1.1 – 1.5	Substratbruch Viskose	-	
2.1 – 2.5	-	Substratbruch Viskose	
3.1 – 3.5	Substratbruch Viskose, grenzflächennaher Bruch	-	
4.1 – 4.5	-	Substratbruch Viskose, grenzflächennaher Bruch	

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FOTODOKUMENTATION

Abbildung 2: 1.1-1.5

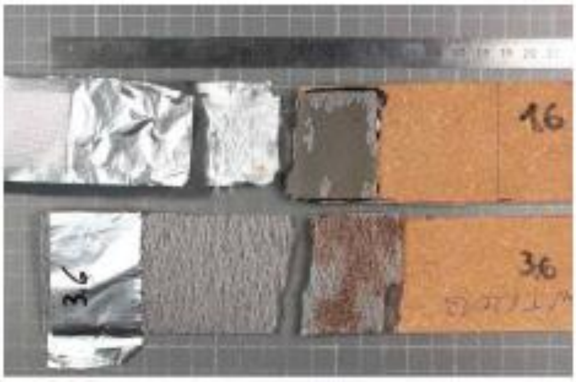

Abbildung 3: 1.6 und 3.6

Abbildung 6: 2.1-2-6

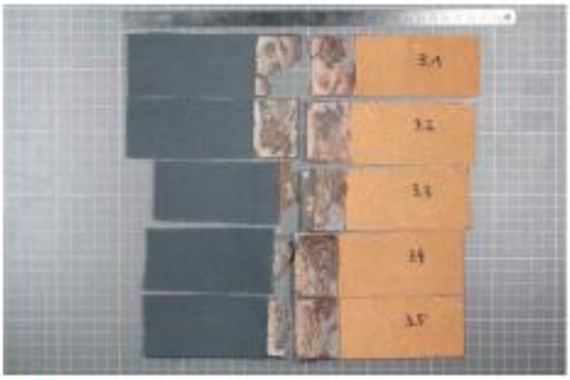

Abbildung 4: 3.1-3.5

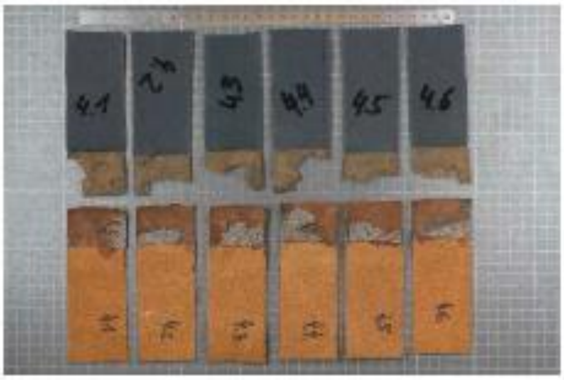

Abbildung 5: 4.1-4.6

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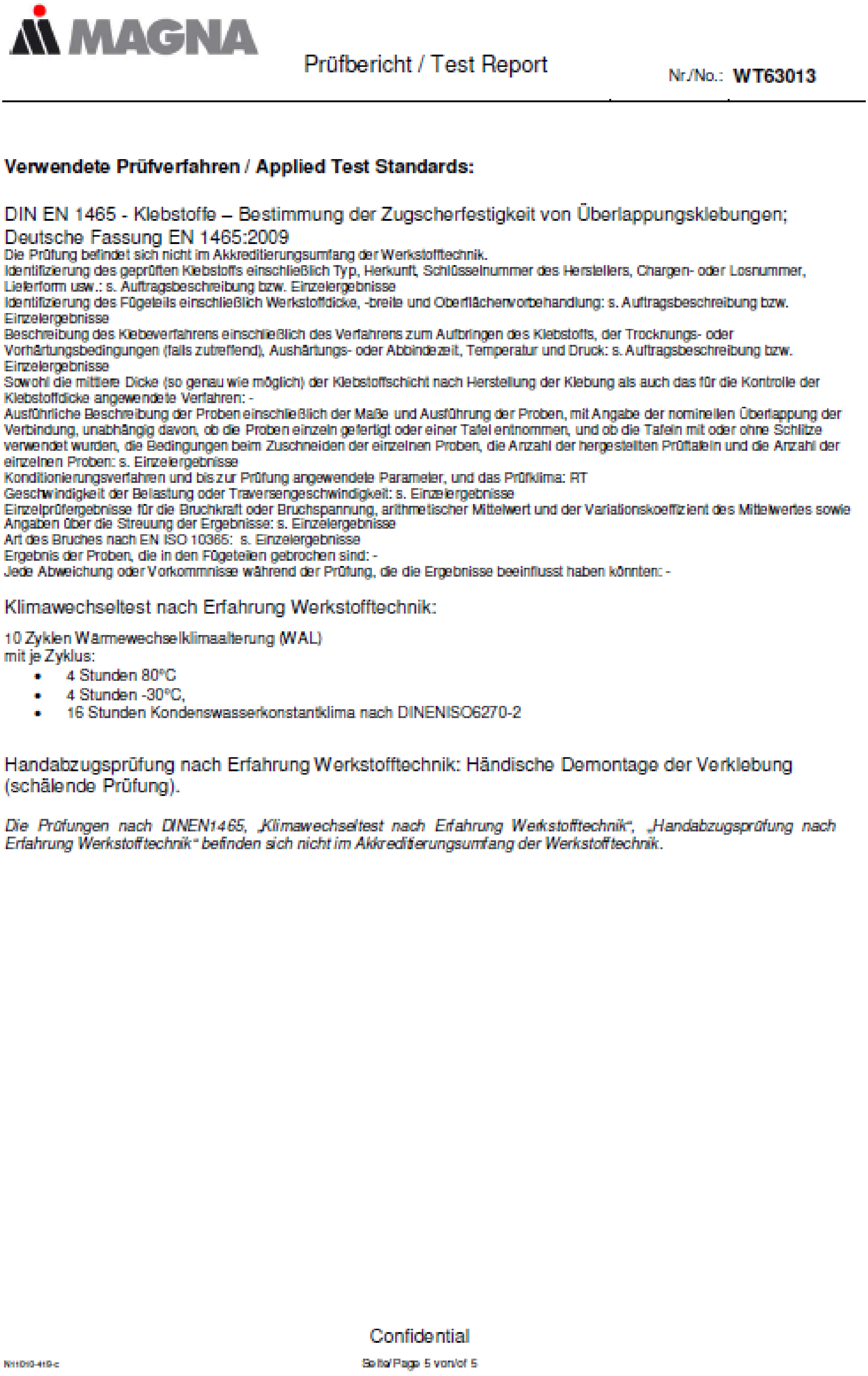

Prüfbericht / Test Report

Nr./No.: **WT63013**

Verwendete Prüfverfahren / Applied Test Standards:

DIN EN 1465 - Klebstoffe – Bestimmung der Zugscherfestigkeit von Überlappungsklebungen; Deutsche Fassung EN 1465:2009

Die Prüfung befindet sich nicht im Akkreditierungsumfang der Werkstofftechnik.
Identifizierung des geprüften Klebstoffs einschließlich Typ, Herkunft, Schlüsselnummer des Herstellers, Chargen- oder Losnummer, Lieferform usw.: s. Auftragsbeschreibung bzw. Einzelergebnisse
Identifizierung des Fügeteils einschließlich Werkstoffdicke, -breite und Oberflächenvorbehandlung: s. Auftragsbeschreibung bzw. Einzelergebnisse
Beschreibung des Klebeverfahrens einschließlich des Verfahrens zum Aufbringen des Klebstoffs, der Trocknungs- oder Vorhärtungsbedingungen (falls zutreffend), Aushärtungs- oder Abbindezeit, Temperatur und Druck: s. Auftragsbeschreibung bzw. Einzelergebnisse
Sowohl die mittlere Dicke (so genau wie möglich) der Klebstoffschicht nach Herstellung der Klebung als auch das für die Kontrolle der Klebstoffdicke angewendete Verfahren: -
Ausführliche Beschreibung der Proben einschließlich der Maße und Ausführung der Proben, mit Angabe der nominellen Überlappung der Verbindung, unabhängig davon, ob die Proben einzeln gefertigt oder einer Tafel entnommen, und ob die Tafeln mit oder ohne Schlitze verwendet wurden, die Bedingungen beim Zuschneiden der einzelnen Proben, die Anzahl der hergestellten Prüftafeln und die Anzahl der einzelnen Proben: s. Einzelergebnisse
Konditionierungsverfahren und bis zur Prüfung angewendete Parameter, und das Prüfklima: RT
Geschwindigkeit der Belastung oder Traversengeschwindigkeit: s. Einzelergebnisse
Einzelprüfergebnisse für die Bruchkraft oder Bruchspannung, arithmetischer Mittelwert und der Variationskoeffizient des Mittelwertes sowie Angaben über die Streuung der Ergebnisse: s. Einzelergebnisse
Art des Bruches nach EN ISO 10365: s. Einzelergebnisse
Ergebnis der Proben, die in den Fügeteilen gebrochen sind: -
Jede Abweichung oder Vorkommnisse während der Prüfung, die die Ergebnisse beeinflusst haben könnten: -

T

Klimawechseltest nach Erfahrung Werkstofftechnik:

10 Zyklen Wärmewechselklimaalterung (WAL)
mit je Zyklus:

- 4 Stunden 80°C
- 4 Stunden -30°C,
- 16 Stunden Kondenswasserkonstantklima nach DINENISO6270-2

Handabzugsprüfung nach Erfahrung Werkstofftechnik: Händische Demontage der Verklebung (schälende Prüfung).

Die Prüfungen nach DINEN1465, „Klimawechseltest nach Erfahrung Werkstofftechnik“, „Handabzugsprüfung nach Erfahrung Werkstofftechnik“ befinden sich nicht im Akkreditierungsumfang der Werkstofftechnik.

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The results of the paint wetting impairment test is given in WT60953:

Material & Process Engineering

Prüfbericht / Test Report

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Bearbeiter/Issuing Engineer: W. Trummer / QAW	Nr./No.: **WT60953**
Tel. / Phone: +43(0)664 8840-4038	Datum / Date: 21.09.2017
Auftraggeber / Ordered by: KAUFMANN STEFAN, DIPL.-ING., ZL	Projekt / Project: MBD

Betrifft / Reference:
Lackverträglichkeitsprüfung eines ligninbasierten Klebstoffs

Verteiler / Copies
Prietl Marion (OPT, MSF)

Auftragsbeschreibung / Task Description:

Lackverträglichkeitsprüfung ligninbasierter Klebstoff. Möglicher Einsatz als Klebstoff in der Montage. Diplomarbeit Fr. Prietl.

Abbildung 1: Angelieferte bzw. untersuchte Probe

Ergebniszusammenfassung / Summary:

-

Beurteilung / Evaluation:

Der ligninbasierte Klebstoff ist nicht lackstörend.

Interpretationen / Interpretations:

Das Material ist somit für den Einsatz im Betrieb geeignet.
Bei Einsatz als Rohbau-Klebstoff ist zusätzlich eine Emissionsprüfung bei 190°C/30min erforderlich.

(Dr. H. Schlatzer / Leitung Werkstofftechnik) (W. Trummer / QAW)

Der Prüfbericht darf ohne schriftliche Zustimmung der Leitung Materials & Process Engineering nicht auszugsweise vervielfältigt werden.
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