Application Report

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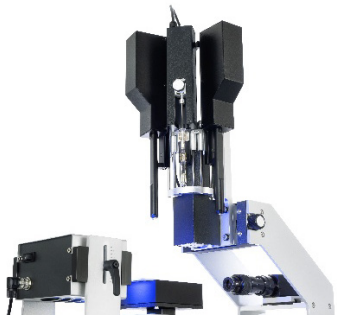


DSA30 with Stood-up Drop dosing unit

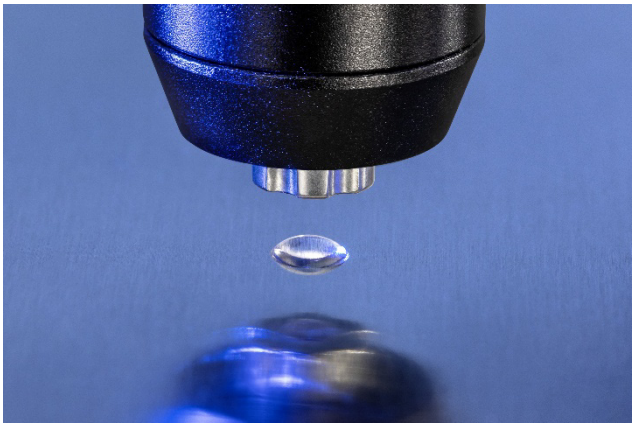
This Application Report is based on the published work of the ISF – Welding and Joining Institute at RWTH Aachen University. [1] We at KRÜSS would like to thank our partners for sharing their insights and results.

Receding Contact Angles with the Stood-up Drop® to Predict Adhesion Performance

Why dewetting-sensitive contact angle measurements outperform wettability metrics based on wetting when predicting adhesion properties

Polypropylene-based glass fiber reinforced polymers (PP-GFRP) are increasingly used in cost- and weight-critical structures, including hydrogen infrastructure. Adhesive bonding of such materials requires surface activation to enable reproducible bond strength. In industrial practice, contact angle measurements are widely applied to qualify activated surfaces prior to bonding.

This Application Report summarizes and contextualizes results from one of the first peer-reviewed academic studies demonstrating that the receded contact angle (CA), measured using the Stood-up Drop® (SUD) technique, shows, for the investigated system, a higher sensitivity to adhesion-relevant surface states than conventional advancing or advanced contact angle. The data originate from lap-shear joint testing and surface analysis of plasma-activated PP-GFRP, as published by Heym et al [1].



Background

Wetting and dewetting

Wetting describes liquid spreading on a solid surface and is commonly characterized by the *advanced contact angle*, i.e. the angle measured after wetting is finished. This is also often referred to as the *static contact angle*, a term that does not take the "history" of a drop into account and is therefore somewhat vague. Therefore, in this study the term advanced

contact angle (CA) is used throughout when measuring wetting.

These values are widely used to detect major changes in surface free energy and/or structure after activation, as well as to assess wettability. The receding CA, by contrast, describes dewetting, i.e. liquid retraction. Dewetting studies had been experimentally more challenging until the launch of the KRÜSS Stood-up Drop and were therefore less frequently used to analyze surface properties. As shown in KRÜSS Application Report AR301 [2], wetting and dewetting are not symmetrical processes and parameters derived from dewetting are often more sensitive to interfacial instabilities relevant for adhesion.

Advanced wetting vs. receded dewetting in adhesion control

In adhesion processes, equilibrium wetting alone is insufficient to describe interfacial performance during adhesive application, squeeze-flow, and curing. Advanced CAs mainly reflect the thermodynamic tendency of a liquid to spread, whereas dewetting-sensitive parameters probe the resistance of the interface against liquid withdrawal. The Stood-up Drop technique induces rapid spreading followed by controlled retraction of a thin liquid lamella into a defined drop, enabling reproducible measurement of receded CAs without complex dynamic protocols. [3] This concept forms the methodological basis for correlating receded CAs with mechanical adhesion performance in the present report.

Experimental section

All experimental preparations and testing procedures were carried out by Heym et al at the Welding and Joining Institute (ISF) – RWTH Aachen University. A detailed description of all methods and conditions is provided in the original publication. [1]

Materials and surface activation

Single-layer polypropylene-based GFRP tapes (PP-GF, glass fiber content 70wt%) were surface-activated using piezoelectric direct discharge plasma treatment with varied treatment intensity, controlled by pretreatment speed. Untreated, plasma-treated and subsequently water-washed surfaces were investigated. After pretreatment, the GFRP specimens were bonded in a single-lap joint configuration using a two-component epoxy adhesive.

Contact angle measurements

Advanced water CAs were measured using a conventional sessile drop method according to DIN EN 828. The first equilibrium image frame after droplet deposition was used for CA evaluation. These values were used to describe wetting behavior and, in the publication [1], to calculate surface free energy via the Owens-Wendt-Rabel-Kaelble (OWRK) model [4], [5], [6].

Receding CAs were measured using a KRÜSS DSA30 Drop Shape Analyzer equipped with a Stood-up Drop dosing unit.

Joint preparation and mechanical characterization

The joints were prepared from a uniaxial PP-GFRP laminate (CELSTRAN® CFR-TP PP GF70-13, Celanese) and a two-component epoxy adhesive (3M Germany). The PP-GF tape was cut in horizontal fiber direction, pretreated, and placed in a fixture device. Then the adhesive was applied, and the counterpart specimen was placed with an overlap of 12.5 mm fixed with a weight of 1 kg. After curing at 100 °C for 2 h, the joint performance was quantified using lap-shear testing according to DIN EN 1465. Lap-shear strength and fracture modes (adhesive, mixed, substrate failure) served as the reference dataset for correlating surface characterization results with mechanical performance.

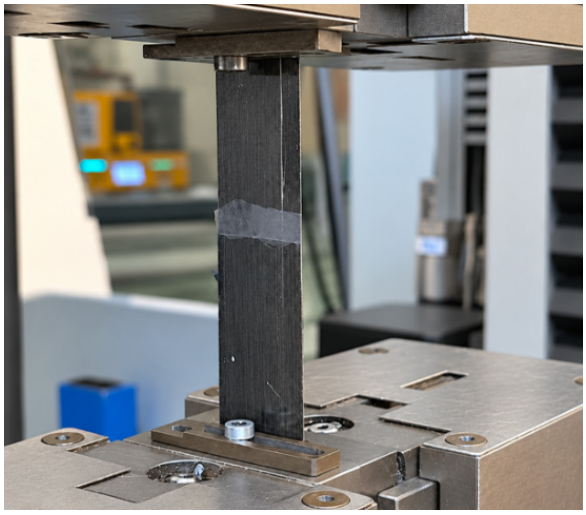


Fig. 1: Example of a lap-shear strength measurement

Results

Effect of plasma activation intensity on wetting and dewetting behavior

Piezoelectric direct discharge plasma activation varied by changing the treatment speed, with lower speeds corresponding to higher activation intensity. For non-washed surfaces, both advanced and receded CA measurements showed a consistent trend: decreasing treatment speed resulted in lower contact angles, corresponding with increased surface activation. This trend indicates improved wettability and increased resistance to liquid withdrawal for more intensely activated surfaces. Fig. 2 presents the CA values as a function of plasma treatment speed for the non-washed surface comparing advanced and receded (SUD) CAs.

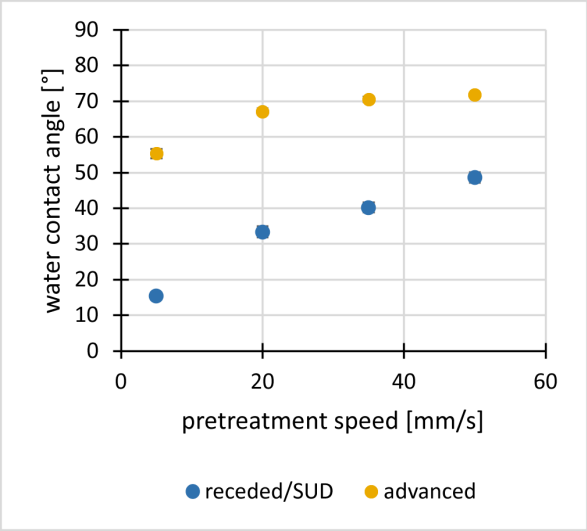


Fig. 2: Water CAs as a function the pretreatment speed for the non-washed surfaces.

Over the range of plasma intensities investigated, the receded CA values span a wider absolute range (15.5° to 48.6°) than the advanced CAs (55.3° to 71.8°). This larger dynamic range enables finer differentiation between activation states, particularly in regimes where small differences in surface chemistry or structure are present.

Surface structure modification and formation of low-molecular-weight oxidized material

Microscopic analysis reported in the peer-reviewed study [1] revealed that intensive plasma activation leads to pronounced surface restructuring. At low treatment speeds, plasma exposure resulted in the formation of heterogeneous surface regions identified as low-molecular-weight oxidized material (LMWOM), generated by chain scission and oxidation reactions at the polymer surface.

Post washing surface analysis

After washing the plasma-treated surfaces with deionized water, clear differences between advanced and receded CA became apparent. Advanced CAs had increased for all non-washed surfaces (s. Fig. 2), indicating the decreasing occurrence of LMWOMs as the treatment speed increases (and intensity decreases). However, after washing, advanced CA values no longer vary with plasma activation intensity: surfaces treated at different speeds exhibited similar advanced CAs despite different activation histories. In contrast, receded CA measurements still correlated with activation intensity even after washing. Lower plasma treatment speeds continued to result in lower receded CAs, demonstrating that dewetting behavior remained sensitive to the underlying degree of surface activation. Fig. 3 shows the CA data as a function of the pretreatment after washing.

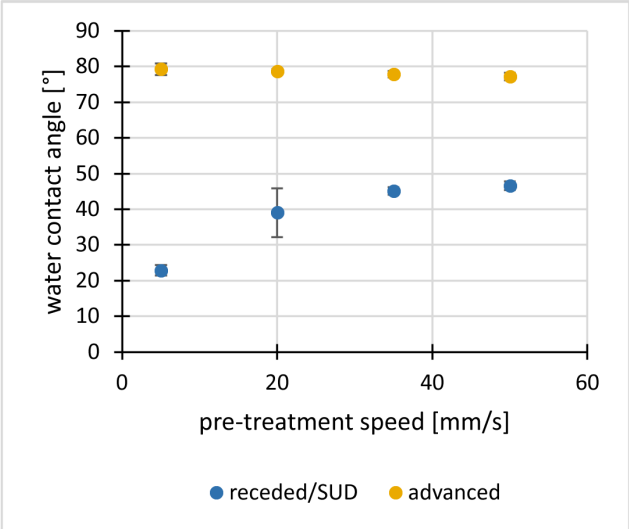


Fig. 3: Water CAs as a function of the pretreatment speed for the washed surface.

This highlights that receded CA captures activation-related surface characteristics that are masked in advanced wetting measurements after removal of easily soluble surface.

These highly oxidized surface layers exhibit strong wettability and are water-soluble. Their removal during washing explains the observed increase in advanced CAs and the loss of correlation between

advanced CA and plasma activation intensity. Only receded CA measurements remained sensitive to the plasma-induced structural modification of the underlying polymer surface and therefore continued to reflect activation differences even after LMWOM removal.

Correlation of wetting parameters with lap-shear strength

Fig. 4 summarizes the lap-shear strengths obtained after plasma activation at different treatment speeds. Above a range of 10 MPa to 12 MPa a transition to substrate failure occurs, which limits further differentiation of joint strength between highly activated samples.

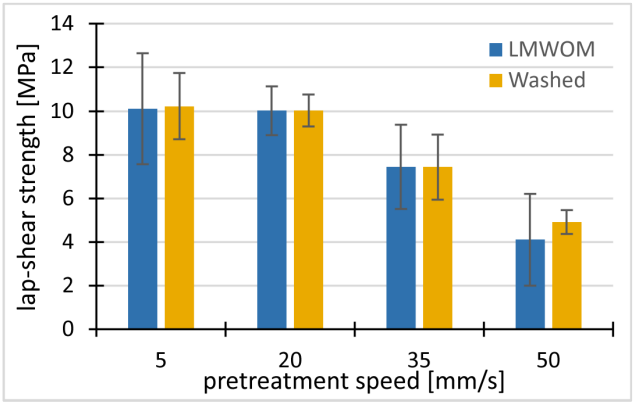


Fig. 4: Lap-shear strength depending on pre-treatment speed for washed and non-washed surfaces.

Figs. 5 and 6 correlate the mechanical lap-shear results with the corresponding CA measurements, revealing clear differences between advanced and receded CAs in their ability to reflect adhesion-relevant surface states. For LMWOM-covered surfaces, advanced contact angles show only minimal incremental changes between different activation levels up to the transition to substrate failure in lap-shear testing. In contrast, receded CA exhibits larger step changes, providing improved sensitivity to differences in activation. While the washed surfaces show virtually no differences in advanced CA, receded CA still allows a sound distinction between low and high activation states.

Beyond the transition to substrate failure, further increase in activation states can still be detected by contact angle measurements, but no further correlation with the joint strength can be established.

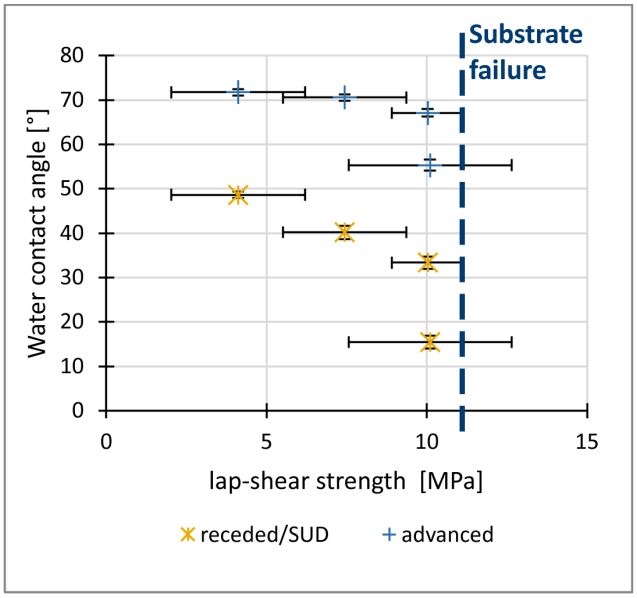


Fig. 5: Correlation of water CA measurements and lap-shear strength for the LMWOM surfaces.

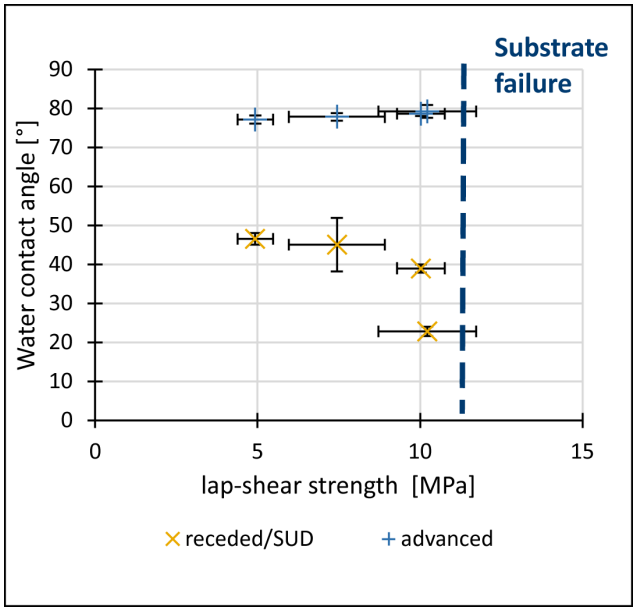


Fig. 6: Correlation of water CA measurements and lap-shear strength for the washed surfaces.

Overall, this refined correlation highlights that the receded CA (SUD) provides a significantly better method to monitor surface activation and thus predict adhesion performance than the so far often used advanced contact angles.

Summary

The presented findings are based on one of the first peer-reviewed academic studies directly comparing advanced contact angle, receded contact angle (Stood-up Drop®), and mechanical bond strength for plasma-activated polymer composites. Advanced contact angles describe wetting but show limited to no correlation with lap-shear strength for activated PP-GF surfaces. Receded contact angles, measured with the KRÜSS Stood-up Drop method, correlate systematically with lap-shear strength and fracture mode. Thus, receded contact angle provides an adhesion-relevant metric for prequalification of polymer surfaces prior to adhesive bonding.

Literature

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