Review - Characterization of modified Elastomer Surfaces by wetting

1. Introduction: importance of wetting
An important example for wetting of superhydrophobic surfaces is the lotus effect that can be attributed to the surface microstructuring and hydrophobic properties of epicuticular waxes.[1-2] This effect is also found in other plants, e.g. lady’s mantle (Alchemilla mollis, see Fig. 1) and nasturtium (Nasturtium officinale). [3] The design and surface structures are an important factor in the development of dirt-repellent surfaces. Important technical applications of hydrophobic surfaces are self-cleaning roofing tiles, textile surfaces, paintings [4-5], hoses, seals and profiles [6] as well as icephobic polydimethylsiloxane (PDMS) coatings for the prevention of ice accumulation on wind turbines, aircrafts and heat pumps. [7-9] Unlike artificially produced surfaces, the lotus leaf surface has the property of self-regeneration. Its functionality remains after wetting. This serves as a protection from microorganisms or pathogens such as fungus spores or algae growth. [10]

2. Modified elastomer surfaces
Many elastomer products, for instance seals, profiles and windscreen wipers, often have undesirable surface properties with respect to their application or further processing [6]. Therefore, after treatment or modification is required in order to clean and functionalize the surface. In this way, it is possible to influence the adhesion behavior, to change the wetting properties of the polymer surface and finally to reduce the sliding friction value, stick-slip-behaviour and wear. Avoiding wear leads to a higher longevity of the elastomer products.

It has been shown that especially varnished elastomer composites [11-15], elastomer surfaces modified by gas-phase fluorination [15-16] and nanoparticle modified elastomers [15-17] are well-suited to influence wetting and to reduce friction. There has been very little research on the plasma treatment and plasma coating of elastomer surfaces in the literature so far. In particular, the activation of the elastomer surface and the usage of precursors (e.g. HMDOS and TEOS) to form a plasma polymer layer might be promising for reducing friction and stick-slip behavior. [18] Advantages are offered by those plasma processes, which operate at atmospheric pressure and thus require no complex and expensive vacuum technology. Furthermore, such atmospheric pressure plasma reactors can be operated continuously. This enables simple process control and ensures an efficient surface modification process. [6, 16] There are examples for the plasma treatment of elastomer surfaces, which are described briefly in the following.

High friction coefficients can be evidently reduced by plasma polymerization. Furthermore, it was shown that stick-slip behavior has vanished at high velocities. [18] Plasma polymerization with vinyl compounds on nitrile rubber alters the surface and reduces friction compared to untreated elastomers. [19] Martinez et al. have investigated the influence of different plasma treatments on the wettability of NBR and HNBR by means of sessile drop and XPS experiments. [20] Targeted chemical functionalization by plasma treatment on elasto-

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mers leads to an improvement of the wettability and the bonding by polar substances implies increased adhesive-ness. [6] For instance, the modification of natural rubber by plasma treatment leads to a concomitant decrease in surface roughness. [21] Deposited acetylene films on natural rubber by plasma polymerization are suitable primers to allow a rubber-to-steel compound. [22] Romero-Sanchez et al. have shown that the ethylene glycol contact angles on SBR surfaces were reduced by corona treatment improving the wettability of the elastomer surface. [23] The release force using a PUR adhesive could be increased concerning the bonding of two EPDM sheets. [6] The permeation properties of coated elastomers can be optimized, whereby the passage time could be delayed by 50 %. [6] Plasma-coated silicone rubbers overcome the disadvantages of contact lenses made of silicone rubber and do not affect the properties, such as flexibility of the lens; in this case the hydrophobic rubber is hydrophilized. [24] Recently, it has been shown that highly functionalized black silicone/elastomer composite surfaces exhibit either the lotus effect or the rose petal effect as a function of the mechanical strain in order to manipulate water droplets. The stretched or relaxed surface reveals extreme superhydrophobicity having a low sliding angle (see lotus effect). Thus, the apparent contact angle of a droplet on the composite surface can be adjusted between 170° and 110° upon mechanical stretching. This enables a wide range of hydrophobic surface wettabilities. [25]

3. Wetting: fundamentals and terminology
Contact angle measurements are carried out in order to characterize the wettability of solid technical surfaces. Due to its simplicity, relatively low-cost instruments and a long history, this method appears to be easy in its application. Despite the long experience of contact angle investigations, the measurement and interpretation suffers from insufficient experimental and theoretical protocols. Furthermore, the misuses of wetting terminology lead to misinterpretation of experimental contact angles. Contact angle measurements are the most surface sensitive of any common analysis technique having an analysis depth of ca. 0.5-1 nm. [26-28] Hence, contact angles are sensitive to many factors, e. g. surface geometry, roughness, contamination and deformation of polymer surfaces. [29-30] As a result, contact angle data are lacking for common materials which can serve as reference source. Contact angles which are measured for an observed system cannot be regarded as unique values. [30-31] The use of the contact angle concept in different fields (e. g. mechanical engineering, material science and electrical engineering) and the miniaturisation of various systems have led to confusing results. [29-31]

In the following common terms for different types of surfaces and contact angles used in wetting science are described. [29, 32]

**Ideal surface** – A flat, perfectly smooth, rigid and chemically homogeneous surface which does not chemically interact with the probe liquid. It shows zero contact angle hysteresis. In practice, an ideal surface is rarely encountered.

**Real surface** – A solid surface that is not ideal, regardless of type(s) of its deviation from the ideality of surface. The majority of surfaces that are used and tested are real surfaces.

**Contact angle** – Experimentally observed angle on the liquid side between the tangent to the solid surface and the tangent to the liquid-gaseous interface at the contact line among the three phases. The point of intersection between tangent lines is denoted as the contact point (see Fig. 2).

**Young contact angle** – This contact angle is a thermodynamic property of the three-phase system that corresponds to the lowest state of the energy for the system. In the year 1805 Young was able to show that the contour of a liquid droplet on an ideal solid, if one neglects its rheological properties, is determined only by the gravitational force and the interfacial tension. [33] If the droplet interacts with a solid, surface energy of the solid determines the contact angle of the drop. In the presence of a fluid phase in the form of a droplet, a pressure difference exists between the droplet interior and the gas phase, which can be quantified by Young-Laplace’s equation. [34] The Young equation is (see Eq. 1):

$$\cos \theta = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}}$$  \hspace{1cm} (1)
The letters S, L and V indicate the phases of the solid, the liquid and the gas phase, respectively. However, it is assumed that the drop has an ideal size [36]. In the case of small drops, the line tension may have to be considered since the contact angle increases as the ratio of length to surface of the droplet increases. This effect is negligible for drops larger than 1 μm. [37]

The interfacial tension can be considered as the reversible work, which is required under isothermal and isobaric conditions to increase the surface boundary by one cm². For following unit is used: \[
\gamma = \frac{J}{m^2} = \frac{N}{m}.
\]

For liquids, N/m whereas for solids or polymers J/m² is used. The order of magnitude of the surface tension of liquids is in the range between 10 and 100 mN/m. [38] The surface energies for untreated polymers have values ranging from ca. 16 J/m² (PTFE) to ca. 41 J/m² (polymide 66). Higher values can be achieved by chemical modification. For high-energy surfaces such as metals, values in the range of 100 to 5000 J/m² are observed. [38]

**Ideal contact angle** — The ideal contact angle is the contact angle on an ideal surface. For drops with radii of curvature larger than nanometric size, this contact angle equals the Young contact angle and represents the single equilibrium state that a drop may have on an ideal solid. For drops with smaller radii of curvature, a correction term that is related to the concept of ‘line tension’ needs to be applied. [29] The ideal contact angle is not accessible experimentally due to difficulties associated with the preparation of an ideal solid surface. Furthermore it is difficult to maintain equilibrium conditions during measurements. [39-42]

**Actual or local contact angle** — The contact angle existing locally at any point along the contact line is denoted as actual contact angle. It was theoretically proven that the actual contact angle is equal to the ideal contact angle at equilibrium. [43] However, the actual or local contact angle cannot be easily measured. Bhattarai et al. have introduced the surface roughness of a composite interface via an array of spherical nanoparticles with controlled wettability. They have found that the liquid interface is flat and its location relative to the solid substrate is determined by the particle size and the local contact angle. [38]

**Apparent or global contact angle** — The contact angle measured experimentally on the macroscopic scale is the only one that can be routinely measured. It is termed the apparent contact angle. This contact angle describes an ‘average’ contact angle for the entire three-phase contact line. There are a few types of apparent contact angles that are related in different ways to the Young contact angle, depending on the specific nature of the real solid surface. Apparent contact angles may represent either metastable equilibrium states of the system (local minimum in the Gibbs energy curve) or a stable equilibrium state (lowest minimum in the Gibbs energy curve, see Fig. 3). [36] The various kinds of the apparent contact angles are described in the following.

**Most stable contact angle** — The apparent contact angle associated with the state of the lowest Gibbs energy for a system representing the global minimum (see Figure 3) is denoted as most stable contact angle. In a few studies, the vibration of the solid surface has been applied by Della Volpe et al. [44] However, this contact angle has not been measured exactly so far. The most stable apparent (measured) contact angle on a rough but chemically homogeneous solid surface is predicted by the Wenzel equation. [45] This equation is valid if the liquid completely penetrates into the grooves of a rough surface and if the drop is sufficiently large compared to the roughness scale of the surface. Additionally, the drop must be axisymmetric. [46] The most stable contact angle on a chemically heterogeneous but smooth solid surface is predicted by the Cassie equation [47], if the drop is sufficiently large compared to the heterogeneity scale. [48] An extended version of the Wenzel and Cassie equations exist for cases that deal with wetting of a rough surface, when the liquid incompletely penetrates (or does not penetrate at all) into the roughness grooves. As such, the surface is ‘seen’ by the liquid as a rough and heterogeneous surface that is composed of the solid and ‘air’. This case is covered by the Cassie-Baxter equation. [47]

**Advancing contact angle** — The highest metastable apparent contact angle that can be measured (e.g. by increasing the volume of the drop, see Fig. 3).

**Receding contact angle** — The lowest metastable contact angle that can be measured (e.g. by decreasing the volume of the drop, see Fig. 3). The values of advancing and receding contact angles may vary depending on the method of measurement [49] and on the parameters of the system. Their measurements with a sessile-drop method are described in detail [50]. For example, in the case of a system that consists of a drop on a solid surface, these contact angles may depend on the drop volume. [51-52] Regardless of the experimental method, the values of advancing and receding contact angles may be affected by random noise — for example, vibrations of a building. [53]

**Contact angle hysteresis** — The difference of advancing and receding contact angle is the contact angle hysteresis which cannot be correlated with the ideal contact angle based on current knowledge. For example, using the Wenzel equation for the advancing or receding angle is misleading. However, the measurement of these angles is extremely important since contact angle hysteresis is a measure of the non-ideality of the solid surface. Also, contact angle hystere-
sis may be thought of as a rough indication of the degree of drop adhesion onto a solid surface, since in many cases the larger the contact angle hysteresis, the stronger is drop adhesion. It was demonstrated that nanometric holes in a monolayer can be detected through measurements of contact angle hysteresis. [54] In addition, a common misconception needs to be clarified. It is quite common to call the advancing and receding contact angles ‘dynamic’. It is true that the transition between metastable contact angles is indeed a dynamic process; however, these contact angles by themselves represent equilibrium states (although they are metastable).

The dynamic contact angle is a contact angle measured under dynamic flow conditions that is affected by the velocity of the flow due to viscous effects. Thus, it cannot characterise the equilibrium wettability. The deviation of the dynamic contact angle from the equilibrium contact angles depends on the capillary number. [55]

Static (sessile) contact angle – This is a term that refers to the measurement of the contact angle when the drop lands on the solid surface. To determine contact angles, the elastomer surface has to be prepared properly and pure liquids have to be used. There are also other factors which are important. The results depend on the experience of the operator. Furthermore, the measurement of a single static contact angle is not really adequate, because there is no single equilibrium contact angle. [55] As far as the static contact angle measurement is concerned, inhomogeneities and changes in wetting over time can be detected. [37]

Smooth surface
Hydrophilic surface – This surface is characterised by the Young contact angle for water being smaller than 90 °. [44]

Hydrophobic surface – This surface is characterised by the Young contact angle for water that is larger than or equal to 90 °. [44]

Rough surface
In practice, however, only very rarely smooth and chemically homogeneous surfaces are encountered, which are necessary in order to determine the contact angle according to Young for ideal surfaces. Contact angles of real surfaces are described on the one hand by the roughness of the surface, which can be explained by means of a Wenzel model (see Eq. 2) or the Wenzel factor. [45] The Wenzel factor \( r \) denotes the roughness of the surface. It indicates the ratio of the actual surface to the corresponding geometrically projected surface. For \( r = 1 \) the Young equation (ideal surface) is obtained. It represents the apparent, i.e., the macroscopically visible and measured contact angle, which is referred to the actual contact angle, i.e. the local contact angle due to the roughness, but which is not accessible experimentally. [56]

\[
r = \frac{\cos \theta_w}{\cos \theta_Y}
\]

Kamusewitz et al. derived a relationship between the contact angle hysteresis and Wenzel’s contact angle [67, 98]. If the droplet is larger than the roughness scale by two to three orders of magnitude, the Wenzel equation applies, as shown by Marmur. [57]

Whereas for the Wenzel equation the state of homogeneous wetting, in which the wetting liquid penetrates completely into the depressions of the rough surface, the state in which air cavities are present in the depressions of the topography is referred to heterogeneous wetting. In this case, due to the surface tension of the solvent and the roughness, the surface cannot be fully wetted. In the case of heterogeneous wetting of a rough and chemically homogeneous surface, the following equation was formulated by Cassie and Baxter (see Eq. 3), [47]:

\[
\cos \theta_{CB} = f_\text{r} \cos \theta_Y - (1 - f_\text{r})
\]

Considering \( f_\text{r} \) is the proportion of the projected wetted surface with respect to the total projected area, then \( f_\text{r} \) represents the roughness factor of the wetted portion of the surface. Assuming the values for \( f_\text{r} \) become very small, the most stable contact angle tends to 180 °. The resulting contact angle is greater than in the case of the Wenzel model since the interface between the two substances is smaller. These types of rough surfaces have the property of trapping air in their deeper layers, which is not displaced by the liquid during wetting showing the lotus effect. [2] Up to now, it is not fully understood how physical roughness and chemical heterogeneity affect the contact angle which is the decisive quantity to calculate the surface energy. [58] As shown, the knowledge of surface energy allows estimating the compatibility of fillers with rubbers. [59] To obtain the interfacial energy per unit area (work of adhesion) of two solid surfaces in contact, the substrate and the coating material, the surface energies of both are needed [60]. In contrast to ideal surfaces, real surfaces cannot be characterized by a single stable macroscopic contact angle, which is denoted as apparent contact angle. As a result there are different macroscopic contact angles. [32] These angles, described by metastable states (see Fig. 3), are due to the locally varying slope of the topography and thus correspond to multiple local minima of the free enthalpy of a liquid droplet on a solid surface (see Fig. 3). Energy barriers are present between these minima. In energetic equilibrium, where the Gibbs energy has the lowest value, the system is in the most stable state. The corresponding most stable macroscopic contact angle is called \( \theta_\text{eq} \) (see also Fig. 3). It is calculated from the arithmetic mean of the advance and receding contact angles. [32, 61] As a prerequisite for measuring the contact angle according to Marmur, a ratio between drop diameter and lateral extent of the roughness structures of at least three orders of magnitude is necessary. [32] As mentioned earlier, two regimes of wetting exist on rough surfaces: the liquid either completely or partially penetrates into the grooves of a rough surface. In the former case, the Wenzel equation predicts that the most stable contact angle on a roughened hydrophilic surface is lower than the corresponding ideal contact angle. On roughened hydrophobic surfaces, this equation predicts that the most stable contact angle is higher than on the ideal one. In the case of partial penetration, the most stable contact angle may further increase, since part of the surface that is in contact with the liquid consists of air. This, however, may reduce hysteresis and enable easy roll-off of a drop from the solid surface. The following definitions help to distinguish clearly between these states. More details are described in [29, 62].

Only little work has been devoted to correlate the contact angle hysteresis of a surface with roughness parameters, such as fractal dimension and height profile data. [56, 63] Only the mean roughness index has been used to characterize the surface roughness of a material with respect to changing the
contact angle. [64] Different lacquers coated on elastomers were considered in order to investigate the influence of roughness and surface composition on friction and surface energy. [61] Recent studies indicate that, in addition to these two models, there are so-called mixed-roughness-heterogeneous surfaces, based on 2-dimensional simulation calculations, from which the two borderline cases can be derived. [65, 66] Recent studies suggest that in addition to these two models of homogeneous and heterogeneous wetting, so-called mixed-roughness-heterogeneous surfaces based on 2-dimensional simulation calculations exist, from which the two limiting cases can be derived. [65, 67] In contrast to ideal surfaces, real surfaces cannot be characterized by a single stable macroscopic contact angle, which is also referred to as the apparent contact angle (measured contact angle). Instead, there are different macroscopic contact angles. [32] These angles, which are described by metastable states, are due to the locally varying slope of the topography and thus correspond to multiple local minima of the Gibbs energy of a liquid droplet on a solid surface (see Fig. 3). Energy barriers are present between these minima. In the energetic equilibrium (global minimum), where the Gibbs energy has the lowest value, the system is in the most stable state. The corresponding most stable macroscopic contact angle $\theta_m$ is calculated from the arithmetic mean value of the advancing and receding contact angles which are obtained from experimental investigations. [32, 59]

4. Work of adhesion

The contact angle between a liquid and a solid is a measure of the energetic interaction between the solid and the liquid and hence a measure of the wetting behavior. In order to measure the contact angle, the surface tension of the liquids used must be greater than the surface energy of the solid or the sample, respectively. If the surface tension of the liquids and the surface energy of the sample are the same, complete wetting takes place. This means that the contact angle becomes equal to $0^\circ$. According to the Young equation (see Eq. 1), the interfacial tension is also equal to $0^\circ$. In the case of complete spreading, this means complete wetting of the sample surface, consequently $\cos \theta = 1$ and $\theta = 0^\circ$. Spreading occurs when $\gamma_{lv} \leq \gamma_{sn}$. This behavior is a characteristic of the spreading pressure $p_s$ (see Eq. 4):

$$\gamma_{lc} - (\gamma_{ll} + \gamma_{sl}) \equiv p_{sp} > 0$$  (4)

For contact angles $\theta < 30^\circ$, good to sufficient wetting conditions are present. Complete non-wettability is $\theta = 180^\circ$, but this value is not achieved in practice. The highest reached value is about $160^\circ$ (superhydrophobic surfaces). [68] Adhesion is caused by the contact between the components. The adhesion is characterized by the so-called adhesion work, which is described by the Dupré equation (s. Eq. 5):

$$W_{ad} = \gamma_{lv} + \gamma_{sn} - \gamma_{sv}$$  (5)

The work of adhesion assumes the highest value when the surface tension of both components is the same; it is necessary to separate two partners. The higher $W_{ad}$, the higher is the adhesion. This is due to intermolecular forces along the interface. [55]

5. Contact angle hysteresis of elastomer surfaces

The contact angle hysteresis $\Delta \theta$ is the difference between the advancing and receding contact angle. Usually the values for $\Delta \theta$ vary between $5^\circ$ and $20^\circ$, but there can be also significantly larger values. [34] In the case of peroxide crosslinked natural rubber surfaces and water as wetting medium, values between $37^\circ$ and $66^\circ$ are found depending on the degree of crosslinking. The differences are even larger for water on BR (butyl rubber). The range is from $22^\circ$ to $69^\circ$. The removal of peroxide residues implies a decrease in the contact angle hysteresis. With the same chemical environment and roughness of the elastomer surface, the following changes can be observed: as the degree of crosslinking increases, the modulus of elasticity increases, the elastomers become harder and the advancing contact angle decreases, whereas the receding contact angle increases. Consequently, a decrease in the contact angle hysteresis is observed in the case of NR. Regarding the influence of the polarity of different solvents, no clear trend was observed. [69] On the basis of another model system, which consists of thin NBR films (raw rubber) on glass plates, it was shown that in the case of water as a solvent for the very smooth samples with increasing ACN content on the surface and inside (bulk) the hysteresis increases significantly [70]. The contact angle hysteresis of polymer surfaces, in particular with respect to the influence of different solvents on the hysteresis of elastomers, has not been investigated in detail. [69-71]

There are several reasons for the occurrence of hysteresis. [35, 72-73] A distinction is made between kinetic and thermodynamic hysteresis. [74-75] In kinetic hysteresis, changes occur, such as swelling, on the surface of the solid. [75] Roughness and chemical heterogeneity influence thermodynamic hysteresis. [74]

The physical surface roughness has the most important influence. Whenever a drop hits an elevation, it will jump to a position where the same contact angle is reached as before. In this way, the drop is prevented from further spreading until it is so great that it can overcome the elevation and spread further. The increase in contact angle hysteresis with increasing roughness is called a barrier effect. [71] Another reason is the chemical heterogeneity of the surface. [76] When a droplet spreads on a surface with a different environment, the so-called three-phase contact line is fixed (“pinning”) by lyophobic, i.e. liquid-repellent areas, and the contact line of lyophilic areas is retained when the droplets become smaller. A cause for the occurrence of hysteresis is the potential impurities of the measuring solution, which accumulate on the three-phase contact line. In this way, these substances hinder or facilitate the spreading or withdrawal of the liquid. This can be substantially reduced with the aid of solvents which do not swell the surface of the polymer. Soft surfaces, e.g. polymers, have the property that forces occur on the three-phase contact line which are so strong that the underlying layer is mechanically deformed. This also leads to a measurable contact angle hysteresis. [77-78] Furthermore, the adsorption and desorption of molecules during dissemination and withdrawal of the liquid is associated with the dissipation of energy, which manifests itself in the occurrence of hysteresis. In many cases combinations of these effects occur. A heterogeneity of the roughness of surfaces can lead to the pinning effect at certain points in the so-called three-phase contact line. This results in a contact line which runs in a zigzag manner. The order of magnitude and topography of the roughness is particularly important because it affects the wetting pro-
properties most strongly. On the basis of simulations, it was recently confirmed that the hysteresis on randomly rough, self-affine surfaces depends mainly on the value of the Wenzel factor r. In addition to this, it was shown that only the roughness in the μm range exhibits a hysteresis, but not in the nanoscale range. [79]

6. Methods for investigating the wetting of surfaces

The surface tension of liquids is determined by direct measurements. [34, 80] The well-known methods are the ring method according to de Nouy, the pendant-drop method and the Wilhelmy method. For solids, on the other hand, only indirect measuring methods can be used to determine the surface energy. The majority of available measuring methods are dynamic, such as the powder contact angle method, the single-fiber Wilhelmy method, the needle-in method, the tilting plate method, and the modified Wilhelmy balance technique. One differentiates between static and dynamic measurement methods in the investigation of solid surfaces. The method of the sessile drop can be used in both static and dynamic mode. In dynamic mode, it is also referred to as a „needle-in method“. In this article, the sessile drop method for static (see Chapter 6.1) and the modified Wilhelmy balance technique (see Chapter 6.2) were used for dynamic investigations.

6.1 Determination of contact angle using (static) sessile drop method

Static contact angle investigations can be used to characterize smooth surfaces [6, 74]. The static sessile-drop method was used in this review to determine the contact angle at room temperature (23°C). The procedure is shown in Fig. 4. A droplet of defined volume (2 μl) is carefully deposited on the surface to be examined and a drop contour image (“snapshot”) is recorded within 2 seconds by the CCD camera. [17, 64] In the scope of these contact angle investigations, 8 drops of each testing liquid (water, ethylene glycol and diiodomethane) on five different specimens of each sample were considered. The OCA 20 apparatus (Data Physics Instruments GmbH) was used for performing sessile drop experiments.

The static contact angle is determined by the drop contour analysis. In the first step, the drop image is subjected to a gray scale analysis, in which the calculation of the difference of the brightness of one image point to the neighboring image point is performed for the entire image. The drop outline and the baseline, i.e. the contact line with the surface, are obtained from the position of the maximum differences in brightness. The maximum contrast is calculated from the zero point of the 2nd derivative of the brightness profile from which the strongest change in brightness is obtained. To calculate the contact angle, the contour of the drop is adapted to a mathematical model. For this adjustment, there are different approaches depending on accuracy and computational complexity, including elliptical, circular and Young Laplace fitting. Depending on the method used, the entire drop contour, a part of the drop contours or only the area of the three-phase contact point, is evaluated. In the course of this work, the drop contour is automatically detected. Here, the contact angle determination was carried out according to the ellipse-fitting method, which proved to be particularly suitable for asymmetrical drop contours. [17-18] In the ellipse method, a line of the shape of an ellipse is fitted to the drop outline. This method is well-suited for contact angles between 10° and 100°. [81] The contact angle is determined as the slope of the contour line in the three-phase contact point on the left and right sides of the drop. [82]

According to Marmur, contact angle investigations using the sessile drop method on rough surfaces are only useful if the axissymmetry of the drop is ensured and the droplet diameter is 3 orders of magnitude larger than the scale of the arithmetic average roughness value (R̴). In the context of these studies, acetone and isopropanol were used in order to remove blooming residues such as accelerators (e.g. CBS and MBT) and their fission products from the elastomer surface [18] before the contact angle measurements. This plays an important role with respect to the technical application of polymers, since they contain not only the fission products of accelerators, but also nonpolar Anti-Sun Check Waxes and anti-oxidants.

6.2 Determination of dynamic contact angles (advancing and receding contact angles) using the modified Wilhelmy balance technique

Concerning the (dynamic) modified Wilhelmy balance technique or method, advancing and receding contact angles can be determined on solid samples with defined geometry. This method has several advantages compared to conventional optical methods like the sessile drop method. The measurement of a contact angle is reduced to measuring weight and length of a specimen, which is achieved by high accuracy and reproduducibility. [74, 85-87] Furthermore the measured force (see Eq. 6 and 7) concerning any given depth of immersion is already an averaged value. This does auto-
matically give a more accurate contact angle value showing the property of the entire sample [74, 83, 88], the roughness and chemical heterogeneity, respectively. Additionally the graphs of the Wilhelmy balance method are useful to study contact angle hysteresis at different wetting speeds. [74, 85] Stick-slip effects, which are shown for example in the needle-in method, are avoided [89]. In previous studies, only a few examples of surface modified polymers and elastomer composites have been investigated so far. [13, 18, 59, 74, 80, 90, 91]

The conventional Wilhelmy method, by which the surface tension of the liquids is determined, has been modified (see Fig. 5) in a way that a test specimen with defined dimensions was used instead of a DIN-standardized and roughened platinum plate. [55] Before dipping the sample in a test liquid, the surface tension of the solvents had to be determined with the Wilhelmy Pt-Ir-Plate. The DCAT 11 (Data Physics Instruments GmbH) was used for performing wetting experiments.

After balancing the weight force (mg = 0), the test specimen is immersed in the particular test liquid and emerged. The forces $F_{adv}$ and $F_{rec}$ (s. Eqs. 6 and 7) are measured as a function of the immersion depth $h$. $V = hbd$ is the volume and $l = 2(b+d)$ is the wetted length of the test specimen, and $\gamma$ designates the surface tension and $\rho_v$ the density of the solvent.

$$F_{adv} = \gamma_{lv} \cos \theta_{adv} - V \rho_v g + mg \quad (6)$$

$$F_{rec} = \gamma_{lv} \cos \theta_{rec} - V \rho_v g + mg \quad (7)$$

By linear regression to the immersion depth zero, the buoyancy force $F_a = \rho_v V g$ can be eliminated from the recorded force-distance diagrams. If the sum of buoyancy and weight force is equal to zero, the resulting force corresponds to the wetting force. Hence, the corresponding measured forces $F_{adv}$ and $F_{rec}$, from which the contact angles $\theta_{adv}$ and $\theta_{rec}$ can be calculated are obtained separately for the extrapolation of $h$ to 0 (i.e. $V=0$), [93]

$$\theta_{adv/rec} = \arccos \left( \frac{F_{adv/rec} (h = 0)}{\gamma_{lv}} \right) \quad (8)$$

Fig. 6 shows a plot from immersion and emerging a sample and the calculation of the mean contact angle. [11, 61] The samples have to be cleaned with isopropanol before use. The preparation of the samples is explained elsewhere. [61]

**7. Sample preparation**

### 7.1 Fabrication of samples used for sessile drop experiments

#### Preparation of elastomers

Two elastomers were studied in this work for the wetting investigations: EPDM and NBR. The EPDM sample composition is made of 100 phr (“per hundred rubber”) Keltan 4450 D, 5 phr ZnO, 1 phr stearic acid, 1.8 phr sulphur, 0.6 phr N-cyclohexyl-2-benzthiazylsulphenamide (CBS), 0.6 phr Mercaptobenzthiazole (MBT), zinc dibenzyl dithiocarbamate (ZBEC) as accelerators, zinc dicyanato diamine as cross-linking activator, 50 phr carbon black N 550 and 40 phr of an aliphatic plasticizer. Filled samples were prepared in an industrial type mixer. As far as the NBR samples are concerned, the type Perbunan NT 3445 was used. The NBR sample composition is made of 100 phr rubber, 5 phr ZnO, 1 phr stearic acid, 2 phr sulphur, 1.5 phr N-cyclohexyl-2-benzthiazylsulphenamide (CBS), 20 phr plasticizer alkylsulfonic phenyl ester (Mesamoll II) and 50 phr carbon black N 550.

#### Activation of the elastomer surface

For the activation of the elastomer surface by the Atmospheric Plasma-Plasma-Enhanced Chemical Vapor Deposition (AP-PECVD), a plasma jet (or plasma nozzle) was used (see Fig. 7), which is inexpensive to purchase. To operate a plasma
nozzle, a high-voltage power supply is needed, which is essential for igniting the plasma. An ionization gas (compressed air was used here), which is swirled, passes through the nozzle at 2000 L/h and is thereby put into the plasma state by the high-energy input of the high voltage. The stainless steel housing and the nozzle head are grounded, so that the potential-free plasma meets the surface to be treated.

**Plasma polymerization**

Additionally, a precursor is required for the coating, which is conveyed as a liquid via a pump in an evaporator, so that it can enter the gas phase. The carrier gas (nitrogen) transports the gaseous precursor into the plasma nozzle, where the ignited plasma fragments the precursor. Due to the flow of the ionization gas, the plasma flame with the fragmented precursor flows out of the nozzle and reacts on the surface to be coated. On the substrate, a highly crosslinked nanoscale plasma polymer is formed. The plasma polymer influences the friction behavior, whereas the bulk properties of the coated elastomer remain unchanged. In order to realize the goal of friction minimization between elastomers and the glass surface, the organosilicon precursors hexamethyldisiloxane (HMDSO) and tetraethyl orthosilicate (TEOS) were used to feed the plasma nozzle. The precursor density was configured manually and automatically checked by a balance through which the software recognizes deviations in precursor weight and adjust the pumping power to obtain the desired precursor flow. A peristaltic pump delivered the liquid precursor automatically into the evaporator where temperatures above the boiling point of the precursor prevail. Thus, the gas phase of the precursor is reached in the evaporator and passed through the carrier gas nitrogen into the nozzle. The process parameters related to the plasma jet treatment were not varied.

Since deposits of steel plates, fingerprints, blooming etc. are on the surfaces after vulcanization, it is important to first clean them with a lint-free cloth, acetone and isopropanol to ensure a clean surface on each substrate. Subsequently, the cleaned elastomers were placed at a distance of 10 mm below the plasma nozzle and activated with compressed air without inflow of the precursor, so that the last impurities of the surface are removed and the applied plasma polymer layer adheres to the substrate in the second step. The activation causes an increase in the surface energy and hydrophilizes the elastomer surface, which otherwise has low surface energies.

The plasma nozzle scans the substrate in the dimensions that are given to the system. This allows local surface treatment without masking. After the elastomer surfaces are activated, the actual coating process can take place in a second step. A big advantage of this method lies in its potential to be used as an inline process, which does not require interruption of production.

### 7.2 Samples used for the modified Wilhelmy balance technique

**Preparation of elastomers**

The samples were prepared according to the following procedure: S-SBR (VSL-2525-0) and EPDM (Keltan 512) either unfilled or filled with 50 phr of carbon black N 339 and N 550, respectively, were prepared via a conventional sulphur vulcanization system. During vulcanization, samples were produced with extremely smooth (through smooth vulcanization plates) as well as with defined rough (through rough vulcanization plates) surfaces. [13-14]

**Fig. 7:** Survey about the fabrication process of the plasma modification of elastomer surfaces using HMDSO (hexamethyldisiloxane) and TEOS tetraethyl orthosilicate as precursors [18].

**Fig. 8:** Contact angle measurements on EPDM samples: water on untreated surface (a), water on activated surface (b), diiodomethane on untreated surface (c), diiodomethane on activated surface (d).
Preparation of the coated elastomer composites

Varnished elastomers of EPDM and SBR have been investigated with respect to their friction properties on model substrates of steel, car glass and varnished sheets in previous studies. It has been demonstrated that the friction coefficient of elastomers coated with certain sliding lacquer systems can be reduced significantly compared to the uncoated equivalents. [13-14] To improve the adhesion of the lacquers to the corresponding elastomers, a suitable pretreatment of the elastomer surface had to be taken into account. Cleaned with isopropanol and fluorinated, the smooth and rough SBR samples (2 mm thickness) were coated entirely with the four different varnish systems and heated to 120-140°C for 2-5 minutes. [13-14, 61]

- 1-component PUR lacquer with PTFE particles (PTFE)
- 1-component polyurethane varnish without particles (TPU)
- 2-component PUR varnish (PU) with crosslinker
- PUR lacquer with polysiloxane, PTFE particles and crosslinker (PDMS)

The different lacquer layer thicknesses of 5 to 40 μm were achieved with varying the solids content of the lacquers. [13-14]

Characterization of the coated composites

Digital microscopy and SEM were applied to determine the coating thickness and the topography of the elastomer composites. The composition of the lacquers was analyzed by ATR-IR and EDX mapping. [13]

8. Results and discussion

8.1 Wetting of elastomer composites using the sessile drop method

In the following EPDM and NBR composites have been investigated by the static sessile drop method. Two out of three liquids were considered for the investigations (water and diiodomethane). The fabrication of the samples is described in section 7.1. The samples were always cleaned with acetone and isopropanol to remove blooming residues (e. g. accelerators) from the surface before the measurement (see section 6.1). The results of the untreated surfaces are revealed in Fig. 9 and 11a and c. In the next step the elastomer surface was activated with air (see Fig. 9 and 11 b and d). To reduce friction and stick-slip, the activated surfaces were treated with two precursors (HMDSO and TEOS) on both elastomers to form a plasma polymer layer (results see Fig. 9 and 11 e-h). The results of the sessile drop measurements of EPDM are shown in Fig. 8 and 9 and the results of NBR are reflected in Fig. 10 and 11.

As far as the EPDM samples are concerned, the arithmetic mean water contact angle on the activated surface decreases significantly compared to the untreated sample. This is due to the fact that the number of polar groups are increased by the incorporation of oxygen and nitrogen in the elastomer surface (see Fig. 8 and Fig. 9 a and b). The activated EPDM surface which was plasma polymerized in the presence of the precur-
sor HMDSO exhibits a higher contact angle compared to the activated surface. The reason for this lies in the fact that this surface is less polar. Using the precursor TEOS, the EPDM surface shows a contact angle of ca. 60° (see Fig. 9 e-h). The surface treated with HMDSO is less polar compared to one with TEOS.

The arithmetic mean contact angle of the NBR sample, which was activated by atmospheric plasma reveals also a significant decrease in comparison with the untreated NBR surface (see Fig. 10 and Fig. 11 a and b). This means that there are more polar groups in the surface of the activated NBR sample. Using HMDSO as precursor, a higher arithmetic mean contact angle compared to the activated surface is obtained. In contrast to this, the activated NBR surface which was plasma polymerized in the presence of the precursor TEOS reflects a higher contact angle in comparison with the surface which was only activated (see Fig. 11 b, e-h).

The samples of both elastomers which were plasma polymerized in the presence of the precursor HMDSO exhibit a higher contact angle than the samples which were processed using TEOS as precursor.

8.2 Wetting of elastomer composites using the modified Wilhelmy balance technique

It has been shown in previous studies that rough elastomer surfaces can be characterized very well by means of contact angle hysteresis, which is calculated from the difference of advancing and receding contact angle. Dynamically measured contact angles are relevant for the calculation of equilibrium contact angle values and surface energies. [11, 59, 61, 94] Previous studies have shown that contact angle hysteresis values, which represent a measure of the roughness and chemical heterogeneity of a surface [35, 65, 59], correlate well with roughness factors using differently smooth and rough coated elastomers. Ra, Rq, and Rz values are mainly used for the quantitative characterization of the roughness of smooth surfaces [64]. For many surfaces, particularly for rough specimens, it is necessary to use contact angle hysteresis values or fractal surface descriptors to describe surfaces and their morphology. [11, 96-97] For this purpose, contact angle hysteresis values of surface modified elastomers were compared for the first time with roughness values obtained from white light interferometry and stylus instrument measurements which correlate well with various roughness parameters. [11, 13, 90] We used the equilibrium contact angle as an arithmetic means of advancing and receding contact angles since no accepted analytical method is known [59, 98]. Three different samples for each solvent with respect to one varnish were consid-
ered. By using the modified Wilhelmy balance method, the advancing and receding contact angles could be reproduced well for solvents of different polarity. A set of different test liquids over a wide range of polarity was used to obtain the contact angles. Three samples with the same coating were needed to calculate advancing and receding contact angles for each of the seven solvents. [11, 13] The advantage of using the modified Wilhelmy balance technique for the determination of dynamic contact angles compared to the sessile drop method is that a large area is taken into account during the measurement [19], a good reproducibility is achieved and a method with very strong surface sensitivities is used. [11, 61, 74, 76, 88, 99] As an example, the following immersion and emerging cycles of the smooth and rough SBR samples are shown (see Fig. 13).

Water is used as probe liquid. It is a preferred liquid for contact angle measurements, because it has the highest surface tension (ca. 72.5 mJ/m² at 298 K). Hence, it has measurable contact angles on most polymorphic materials. [63, 74] As it is accepted, water has both non-dispersive and dispersive character. In contrast to this, hexadecane for instance has the lowest surface tension of ca. 27.3 mJ/m² resulting in near-zero contact angles on many polymers, but is useful for either fluorinated surfaces or when oleophobicity needs to be examined. Further details are explained elsewhere. [63, 74]

Roughening the SBR surface leads to a significant increase of the contact angle hysteresis from ca. 21° (smooth SBR surface) to ca. 41° (rough SBR surface). The smoothness of the curve indicates that the solid sample is heterogeneous.

By means of white light measurements, by which the surface is scanned without contact by a light beam, standard deviations σ from histograms of the z height values of the samples are obtained by fitting a Gaussian distribution function (see Eq. 9) to the measured data (s. Fig. 7). Here, A and B denote fit parameters and \( z_0 \) represents the mean value of the corresponding distribution.

\[
\Phi(z) = A + Be^{-(z-z_0)^2/\sigma^2}
\]

For the evaluation of the white light interferometry height data, a Gaussian fit was used. As shown in Fig. 13, the fit curve describes the data points quite well.

The parameter σ representing the standard deviation of the Gaussian fit (see Fig. 13) is regarded as a parameter for the roughness of a surface. Advancing and receding contact angles of the four different varnishes on smooth and rough SBR were measured by the modified Wilhelmy balance technique [11, 13]. Contact angle hysteresis values correlate quite well with the \( \sigma \)-values as it is revealed in Fig. 14. In addition to this, \( \sigma \) values are also in good accordance with values of the arithmetic average roughness value \( R_a \) measured by a stylus instrument. [11, 13] As expected, \( \Delta \theta \)-values for the very smooth SBR surface (reference) are very low in contrast to the varnished samples and rough SBR (see Fig. 14).

Usually, hysteresis values of about 10° or more were verified in experimental studies. Even values above 50° are measured. [63, 74] In the case of the uncoated rough sample, the value of \( \Delta \theta \) is

Fig. 13: Histogram of the height differences versus the z-height and the Gaussian fit curve for a rough SBR sample coated with PTFE varnish. [11, 13]

Fig. 14: Dependency of the contact angle hysteresis from the roughness parameter obtained from white light interferometry measurements. The contact angle measurements were carried out by the modified Wilhelmy balance technique.
about 20° higher compared to the smooth sample. This is due to air inclusions between the rough sample and the water, as shown by numerical simulations. [100]. The hysteresis values and the roughness parameters increase for all except all SBR samples with the applied varnishes. Compared to the rough reference sample, the hysteresis values of the rough varnished samples are 4 - 10° higher. The standard deviations of the advancing and retracting angles are between 0.5° and 2.3°. This is within the scope of measurement inaccuracy and can be classified as very well-reproducible. [63, 92] Therefore the varnishes level the unevenness of the rough surface only partially. Since even unevenness in the nm range can contribute to the contact angle hysteresis, there are no general criteria how smooth a surface must be, so that the surface roughness has no influence on the contact angle. [101-102]

As expected, the hysteresis values for the rough samples of the TPU and PU varnishes are significantly higher than for the two remaining varnishes, which both contain PTFE particles. The island-like structures of the PU coated sample are significantly rougher compared to the uncoated elastomer samples and it requires a larger area, as taken into account in the Wilhelmy measurements to capture the few, but significantly larger count in the Wilhelmy measurements to the uncoated elastomer samples and it contains PTFE particles. The island-like structures of the PU coated sample are significantly rougher compared to the uncoated elastomer samples and it requires a larger area, as taken into account in the Wilhelmy measurements to capture the few, but significantly larger areas. [11, 13]

9. Conclusion and outlook
Coated and plasma modified elastomer composites were characterized by the sessile drop and the modified Wilhelmy balance method. The sessile drop measurement is well suited to qualitatively assess smooth and plasma modified surfaces of elastomers easily. However, rough samples with irregularities, such as varnishes on rough elastomer surfaces, have to be analyzed by methods such as the modified Wilhelmy balance method. This method has several advantages compared to the sessile drop method. The measurement of a contact angle is reduced to measuring weight and length of a specimen, which is achieved by high accuracy and reproducibility. [74, 85-87] Furthermore the measured force concerning any given depth of immersion is already an averaged value. This does automatically give a more accurate contact angle value showing the property of the entire sample [74, 83, 88, 103-105], the roughness and chemical heterogeneity, respectively. It was shown that contact angle hysteresis values correlate with the roughness parameters obtained from white light measurements. Further investigations are necessary to characterize surfaces in order to compare, for example, surface descriptors (cut-off lengths and fractal dimensions) with hysteresis values and to obtain a better insight into the wettability of, in particular, rough specimens. Furthermore the characterization of samples with varied roughness and chemical heterogeneity is of particular interest to get a better understanding of wetting processes of elastomer surfaces. Also the investigation of the polymer-liquid interaction is important.

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References
[27] W. A. Zisman, J. Paint Tech. 44 (1972) 42.