

## Description of the analytical method for characterizing the surface energy and polarity of liquid and solid contact adhesives

### 1.) Basics

Contact adhesives represent a complicated mixture of polymeric components, by which adhesion, cohesion, aging resistance and other properties can be controlled within wide limits. For the process of glueing, the knowledge of the surface energy of both adhering components and their polarities is of particular importance to avoid mis-matchings when selecting an adhesive. As an introduction to the problems involved, the interface-physical basics of wetting are represented here as one of the essential conditions for adhesion.

#### Interfacial tension

The interfacial tension can be introduced by means of thermodynamics. If a condensed phase forms an interface with another phase or the vacuum, then the physical properties of the interface must be incorporated in the description of the energetic behaviour of the phase.

The value  $\gamma$  (or  $\sigma$ ) is called the interfacial (or surface) tension and equals the reversible work that must be done to increase the interface. Its dimension is N/m, which is formally equivalent to the interfacial energy (J/m<sup>2</sup>). Both terms are often equated, which, strictly spoken, is only true under isothermal conditions and is permitted for solid bodies when the mechanical energy for structural changes is negligible.

In the following chapters, with an interface between two condensed phases,  $\sigma$  is called the interfacial tension, with an interface between a condensed and a gas phase or the vacuum it is called surface tension.

The interfacial tensions are a direct consequence of the intermolecular forces of interaction.

The surface or interfacial tensions of liquids can be directly measured with the known tensiometric methods or the pendant-drop method described below.

Surface tensions of solids, however, can only be determined indirectly. The most frequently applied method to determine the surface tension of solids with low surface energy (such as plastics) is the determination from the wetting angle data.

#### Contact angle

The wetting angle (also known as contact angle) between a drop of a liquid with a known surface tension and a solid surface (see Fig. 1) depends on the relation between the adhesive forces, which would make the drop spread on the surface, and the cohesive forces of the liquid, which would contract the drop to a sphere with a minimum surface. If a drop of liquid lies on an ideally level,

homogeneous surface, an equilibrium contact angle  $\theta$  forms between liquid and solid surface at any point of the three-phase line, where the solid, the liquid and the vapour phase meet.

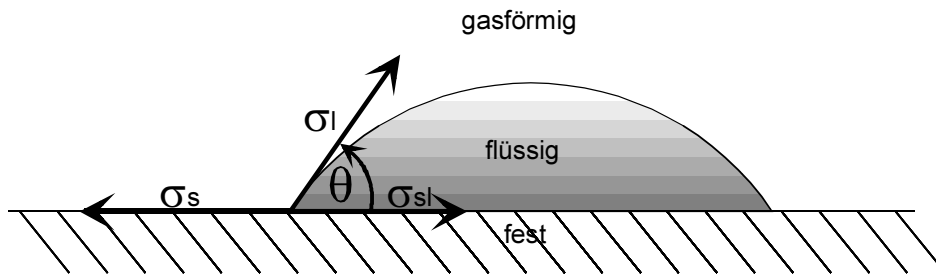


Figure 1: Contact angle  $\theta$  and wetting.

When the drop expands, as a rule there will be a somewhat greater contact angle (advancing contact angle) than when the drop gets smaller (receding contact angle). The contact angle hysteresis as the difference between the advancing and the receding contact angle is interpreted as a sequence of geometric and surface-energetical non-homogeneities of the solid. The wetting angle of the liquid on the solid adjust itself so that the sum of the forces equals zero. This interrelationship for the state of equilibrium is described by Young's equation:

$$\sigma_s = \sigma_{sl} + \sigma_l \cdot \cos \theta \quad (1.1)$$

If the drop was to be removed from the surface again, the amount of energy would have to be expended that is required to newly create the same portions each of liquid surface and of solid surface. At the same time, the energy is released that was stored in the interface between liquid and solid. The work to be done is therefore:

$$W = \sigma_s + \sigma_l - \sigma_{sl} \quad (1.2)$$

By comparison to equation (1.1) the result for this work, also called adhesion work, is:

$$W = \sigma_l (1 + \cos \theta) \quad (1.3)$$

From equation (1.3) it can be seen that work has to be done every time that a wetting process is to be undone. It can further be seen that contact angles are predictable, when the adhesion work  $W$  can be calculated from the known substance properties of the liquid and of the solid.

The solid-gaseous interface can, especially with highly energetic interfaces, be covered by a film of liquid molecules adsorbed from the gas phase, which reduces  $\sigma_s$ . In this case, the film pressure  $\pi$  is accounted for in equation (1.1) by replacing  $\sigma_s$  by  $\sigma_s - \pi$ . On plastics, the adsorption energy is small because of their low surface tension, so that the film pressure is negligible.

Measurable values of Young's equation are the wetting angle  $\theta$  and the liquid surface tension  $\sigma_l$ ; the interfacial tension  $\sigma_{sl}$  between the solid and the liquid phase cannot be measured. Hence, only the wetting tension  $\sigma_s - \sigma_{sl}$  can be exactly determined from measured data. For determining  $\sigma_s$  or  $\sigma_{sl}$  one has to assume one of the two values, generally  $\sigma_{sl}$ , because mostly  $\sigma_s$  is the required value.

To describe the value  $\sigma_{sl}$ , a series of models was developed by which it can be determined from the surface tensions  $\sigma_s$  and  $\sigma_l$  of the phases involved.

Some idea of the multitude of possible formulations is given in Section 3 in connection with the description of the calculation method according to Owens, Wendt, Kaelble and Rabel.

## 2.) Measuring method to determine contact angles, surface and interfacial tensions

To calculate the surface energy of a contact adhesive, in case of a change of phase within the temperature range to be measured, several measuring methods are necessary. In the temperature range where the contact adhesive is in a solid state, the calculation of the surface energies is made on the basis of contact angle measurements with 3 liquids of different polarities on adhesive layers prepared from the molten mass.

In the upper temperature range, where the contact adhesive is in a liquid state, for the calculation of the disperse and the polar portions of the surface energies, measurements of the surface tensions directly on the molten contact adhesive are made with the lamella method and measurements of the interfacial tension of the molten contact adhesive against a purely disperse solvent with the pendant-drop method.

### Measurement of contact angles with the sessile-drop method

In the past and still today, contact angles are mostly determined by means of optical methods in a transmitted light set-up. For this purpose, a resting drop is exposed to diffused light from one side and observed from the other side. In the most simple set-up this measurement is made by means of a protractor eyepiece, in which case the result may be influenced by the subjective perception of the experimenter and the results are therefore hardly reproducible. This is why recently, video-supported systems are increasingly used. This is enabled not least by the availability of high-performance image processing cards and reasonably priced powerful computers.

In these systems, the eyepiece is mostly replaced by a CCD camera. In order to determine the contact angle, the image processing software has to perform the following tasks, which are schematically shown in Fig. 2:

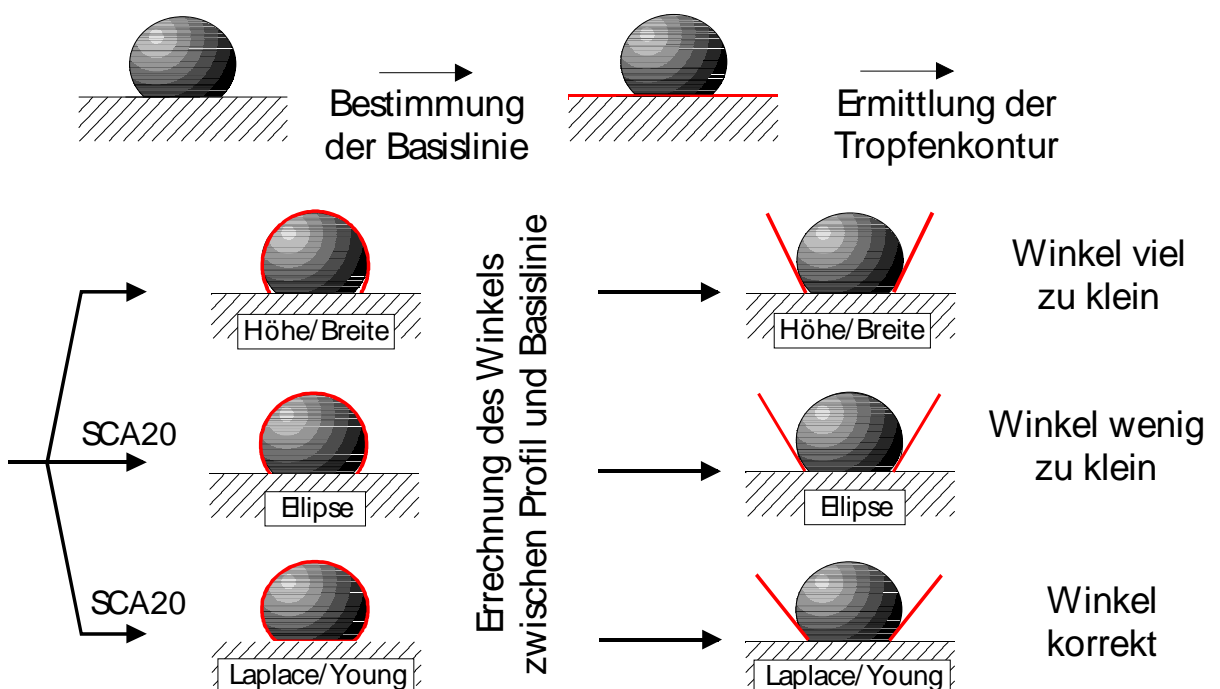


Figure 2: Schematic illustration of the measuring process of contact angles

- determination of the base line at the phase boundary solid/liquid
- determination of the drop contour
- measurement of the contact angle
- First, by means of the CCD camera a digital image of the drop on the surface is recorded. The position of the base line and also that of the drop contour is determined by calculating the difference of the brightness of one image spot to the adjacent image spot. The drop contour and the base line then result from the position of the maximum differences between brightnesses, i.e. of the maximum contrast.
- Before determining a contact angle, the drop contour line must be matched to the measured drop outline. Various methods are applied for this, which differ considerably in their accuracy, but also in the amount of calculation they require.
- In the height/width method, a segment of a circle is matched to the drop outline. Especially with larger drops, this method leads to considerable errors, because due to gravity, the drop shape greatly differs from that of a spherical segment.
- In the ellipse method, a line of elliptical shape is matched to the drop outline. Here, the deviations from the actual shape of the drop are a few percent.
- In the Young-Laplace method, a curve is matched that exactly follows the drop outline. The drop shape is determined by the force equilibrium between surface tension and gravity. In the Young-Laplace method, the corresponding equation is solved numerically, with the solution being adapted to the previously determined drop outline by means of a parameter.
- A comparison of the various methods shows that only the ellipse and the Young-Laplace method yield satisfying accuracies in determining the contact angle. The ellipse method has the advantage of supplying a result within fractions of a second, whereas the Young-Laplace method, depending on the computer used, requires 1-2 seconds. For rapid absorption processes, this method is therefore only useful up to a point.

To determine the surface energy of a solid with its polar and disperse portions, the contact angle is measured with a number of test liquids and evaluated with a suitable, pre-defined method. In the video-supported contact angle measuring instrument OCA 20 of Dataphysics, which is to be described below, the evaluation method according to Fowkes, Owens-Wendt, Wu, Neumann, the extended Fowkes method and the option to evaluate after the Brönstedt-Lowry theory are integrated in the software and are (after selection) performed fully automatically by the computer. For the case of pure polymer materials, the method according to Wu has proven useful, because - as known from literature - especially with low-energetical systems (as represented by polymers) it leads to better reproducible results than other methods. For the case of multi-component plastic systems, the determination of the solid surface tension after the Owens-Wendt method has

proven useful. The method according to Wu requires the use of at least two, the method according to Owens-Wendt of at least two, better three suitable test liquids, and each additional liquid increases the accuracy of the calculated result. The choice of the test liquids has a crucial influence on the accuracy of the values obtained, the selection of suitable test liquids, however, can sometimes be difficult. On the one hand, an influence of the test liquid on the surface by partial etching or dissolving must be excluded. On the other hand, the surface tension of the test liquid must not be altered by possibly existing soluble substances on the surface. If one or both of the described processes are found, this shows in a wide variation of the measured contact angles in spite of a visually homogeneous surface, and in a bad reproducibility of the results. As a rule, water is also used as a test liquid. This has to be ruled out, however, if for instance in the treatment of plastics, water-soluble groups form on the surface, on which water molecules settle down and which therefore falsify the measurement. Alternatively, in such cases ethylene glycol, diiodomethane, dimethyl sulphoxide (DMSO) and formamide are used.

In the case of contact angle measurements on the contact adhesives in their solid state, the selection of solvents has been specified in so far as diiodomethane or p-cymene are used as disperse liquids. Decisive for the selection of these particular solvents as reference liquids, beside chemical considerations, were their thermal stability as well as their pure dispersivity (with diiodomethane) and their varying polar portions (for ethylene glycol and thiodiglycol) with total surface tensions of a similar order of magnitude. Hence, the demand for great polarity differences of the test liquids as one of the pre-conditions for determining solid surface energies from wetting angle measurements is fulfilled.

After having optimized these marginal conditions, the experimental procedure of contact angle measurement is reduced to an exact dosing of the liquid (by means of a manual or automatic dosing system) and the generation of a drop suited for evaluation as well as the exact optical recording (in a possibly optimal bright-dark contrast if recorded as a digital image by means of a CCD camera) and the evaluation of the drop contour by means of the software. An example for an evaluable contour of a sessile drop is given in Fig. 3.



Figure 3: Contour of a sessile drop

## The pendant-drop method

The method of the pendant drop is based on the generation of a well-formed drop and the optical recording and evaluation of its contour.

If the drop is in contact with the surrounding gas space, the surface tension of the liquid generating the drop can be determined. If the adjacent phase is formed by a second liquid, the interfacial tension existing between the two liquids can be found by determining the drop profile. The knowledge of the surface tension of the liquid phase in relation to the surface tension of the solid is - as already considered in the introduction - a necessary criterion for making predictions regarding wetting processes. A very crucial criterion (especially for adhesion, too) are the polar and the disperse portions of the surface or interfacial tension of the liquid (or of the non-setting contact adhesives, which are regarded as high-viscosity liquids also at room temperature, where a sufficiently great molecular mobility can be assumed). If the adhesive and the surface to be glued have the same or very similar overall surface tensions, good glueing properties may be expected only if the polarity is nearly the same. The knowledge of the polarity becomes less important when the overall surface tensions differ considerably.

Hot-setting contact adhesives were taken as an example to find, on the basis of pendant-drop measurements, the interfacial tension between the hot-setting contact adhesives and a purely disperse solvent and to determine the polar and disperse portions of the surface tension of the contact adhesives by means of a calculation method to be explained below (see Section 3). For this purpose, a drop of the liquid to be investigated is generated at the bottom end of a capillary with a manual or automatic dosing system. In the case of a liquid as the surrounding medium, the liquid with the higher density should be placed in a cuvet, and the liquid with the lower density should form the drop within this phase. With a CCD camera, the contour of the drop (Fig. 4) is recorded.

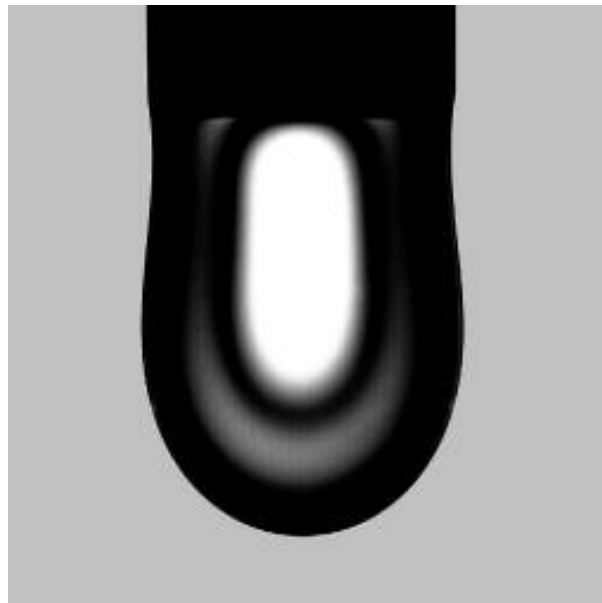


Figure 4: Contour of a pendant drop.

The outer shape of the drop is determined by two forces. For one thing, the weight acts on the length of the drop in vertical direction, for the other, the surface tension strives to keep the drop in spherical shape to minimize its surface. Characteristic of the state of equilibrium is the change of the curvature along the drop contour. This equilibrium of forces is described in a mathematically exact way by the Young-Laplace equation. If the contour of the drop is known, the surface or interfacial tension can be determined by solving this equation. The disperse or the non-polar portion of the surface tension can be calculated by

measuring the interfacial tension of the test liquid against a completely non-polar liquid. The polar portion then results from the difference between the overall surface tension and the disperse portion.

For hot-setting contact adhesives it is shown how by means of the contact angle measuring instrument OCA20 the polar and disperse portions of their surface tension can be easily determined on the basis of the pendant-drop method. As a purely disperse liquid for the required interfacial tensions, FC70 was chosen. The presented method is of fundamental interest and can be applied to any liquid whose wetting properties are to be characterized.

The surface tension  $\sigma_1$  of the contact adhesive is determined with the OCA20 and the SCA22 software in air. To calculate the non-polar portion, the interfacial tension  $\sigma_{1/2}$  is measured against FC 70 (perfluorotripropylamine). The FC 70 as a purely disperse liquid was chosen because the contact adhesives are practically insoluble in it, whereas by many other disperse liquids, depending on the temperature they are more or less strongly etched or completely dissolved.

According to Owens & Wendt, the following applies for the interfacial tension  $\sigma_{1/2}$ :

$$\sigma_{1/2} = \sigma_1 + \sigma_2 - 2 \left( \sqrt{\sigma_1^d \cdot \sigma_2^d} + \sqrt{\sigma_1^p \cdot \sigma_2^p} \right) \quad (1.4)$$

Where  $\sigma_1^d$  and  $\sigma_1^p$  mean the disperse and the polar portion of the investigated PSAs, whereas  $\sigma_2^d$  and  $\sigma_2^p$  represent the respective portions of the non-polar surrounding medium, in this case FC 70. Hence  $\sigma_2^d = \sigma_2$ , because  $\sigma_2^p = 0$ . Therefore the disperse portion is determined by transposing the equation (1.4):

$$\sigma_1^d = \frac{(\sigma_2 + \sigma_1 - \sigma_{1/2})^2}{4\sigma_2} \quad (1.5)$$

The polar portion is calculated according to:

$$\sigma_1^p = \sigma_1 - \sigma_1^d \quad (1.6)$$

A problem may occur if the interfacial tension of the contact adhesive against the purely disperse liquid is lower than the surface tension of the disperse liquid. In this case the calculation of the disperse and the polar portions of the surface energy of the contact adhesive using the Owens-Wendt equation to be explained below becomes problematic. It would then have to be checked whether a different method - like for instance the evaluation according to Wu - should be applied.

Summing up, it can be said that with the contact angle measuring instrument OCA 20 and the pertaining software SCA 22 on the basis of the pendant-drop method there exists a very precise and rapid way to characterize a liquid in general and contact adhesives in particular regarding their wetting properties. The surface tension is directly accessible, and the polar and disperse portions can be calculated relatively easily after having determined the interfacial tension against a non-polar liquid.

From the knowledge of the polar and disperse portions of the surface tension of the contact adhesives unknown so far, predictions regarding wetting and adhesion processes are possible.

## Method with the DataPhysics OCA 20

### Lamella method

The lamella method developed by DataPhysics represents a new method of determining the surface tension at increased temperatures. The determination of the surface tension of molten polymers or contact adhesives so far was only possible with considerable experimental efforts. The lamella method permits a rapid and precise measurement of the surface tension with a considerably reduced experimental effort compared to conventional methods, even at temperatures up to 350°C.

Traditional methods of determining the surface tension with gravimetric tensiometers are mostly restricted to a temperature range up to max. 100°C. In suitable temperature control devices, the contour analysis of pendant drops (pendant-drop method) is also possible at higher temperatures. What is problematic is the handling of high-viscosity molten polymers. The dosing by means of heated syringes is troublesome, and especially their cleaning is difficult and time-intensive. Moreover, problems frequently occur from the formation of gas bubbles in the syringe, which make the dosing of drops of a defined size difficult or even impossible. The newly developed lamella method avoids these difficulties, because only easy to clean components come into contact with the molten polymer, and the sample container is open so that gas inclusions cannot occur.

Like the method of the pendant drop, the lamella method is based on the equilibrium between the weight and the surface tension. As schematically shown in Fig. 5, a liquid lamella will form if a vertical test body is brought into contact with a liquid. With contact angles between 0° and 90°, the lamella is curved upward, whereas for contact angles between 90° and 180° it is curved downward.

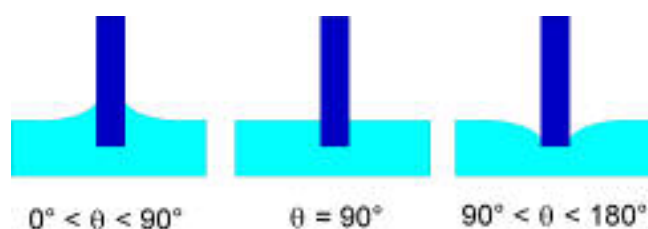


Figure 5. Schematic representation of the formation of a lamella

If the contact angle is exactly 90°, then there is no curvature of the liquid.

The lamella develops from the tendency of the liquid to wet the test body. In this process, the effect of the surface tension strives to keep the newly generated surface as small as possible. At the same time, the weight wants to minimize the volume of a rising lamella. At equilibrium, the effect of the surface tension and that of the weight just counterbalance each other. When the weight is known, the surface tension of the liquid can be calculated from the exact knowledge of the lamella contour. The underlying equation of the state of equilibrium is the differential Young-Laplace equation, for which there is no closed analytical solution with these marginal conditions. By means of quick PC systems and accordingly optimized solution algorithms, however, it is possible to work out the surface tension exactly numerically within fractions of a second. From Fig. 5 it becomes clear that with a contact angle of 90° and a straight cylindrical test body, no lamella can be generated. If, however, instead of a



cylindrical body a sphere is used, then a lamella will also form at a contact angle of  $90^\circ$ , because the curved spherical surface does not assume a constant  $90^\circ$  angle towards the horizontal.

The experimental procedure for the lamella method can be classified as follows. In a specially shaped sample container, the polymer or the contact adhesive is molten. For this purpose, the electrically heated temperature control device TEC 350 is used, which in this case replaces the sample stage of the optical contact angle measuring instrument OCA 20. Into the molten sample, the spherical test body is immersed, so that its end is completely wetted. With the CCD camera a digital image of the lamella at the required temperature is recorded and saved. To calculate the surface tension, the software must work out the weight of the lamella. For this it is necessary to enter the density of the molten material and to determine the enlargement ratio of the recorded image. The density is entered by the experimenter, whereas the enlargement ratio is worked out by means of the geometry of the test body. After the measurement, the test body as well as the sample container can be easily cleaned mechanically, for instance in an ultrasonic bath.

By the example of a viscous contact adhesive, below the lamella method is compared to that of the pendant drop. For this purpose, Fig. 6 shows the image of a pendant drop of the contact adhesive at  $120^\circ\text{C}$ . Because of its rectangular format, the CCD camera was moved by  $90^\circ$  from the horizontal to achieve the best possible image filling.



Fig. 6: Pendant drop of a contact adhesive at  $120^\circ\text{C}$ .

From this image, a surface tension of  $35,16 \pm 0,04 \text{ mN/m}$  was determined. A density of  $1,0518 \text{ g/cm}^3$  was assumed.

The lamella method was applied to the same material. The corresponding image is shown in Fig. 7. The lamella and the spherical test body are clearly visible.



Fig. 7: Lamella of the contact adhesive at  $120^\circ\text{C}$

From this image, a surface tension of  $34,81 \pm 0,35$  mN/m for the same density as in Fig. 6 was determined. Hence the two values agree within an error of 1% of the lamella method.

### 3.) Evaluation of the disperse and polar portions of the surface energy

At an interface, a particle experiences attractions from its own and from the adjacent phase. A mechanical consideration therefore supplies, for the interfacial tension, the difference between the surface energies of both phases. This is expressed in the interfacial tension model of Antonow. On non-polar substances, the predictions from the Antonow model agree well with the experimental data. A similar train of thought forms the basis of Zisman's surface critical energy  $\sigma^{crit}$ : a liquid will completely wet a solid, when the forces of attraction of the solid phase acting on the liquid molecules are greater than those of the liquid phase. A solid has precisely the surface tension of the measuring liquid, when its surface tension is just small enough to wet the solid completely.

Fowkes suggested to divide the interfacial tensions between two condensed phases into additive components orienting themselves on the individual intermolecular forces of interaction. He separated the disperse portion  $\sigma_{sl}^d$  containing London's dispersion interactions, from the polar portion  $\sigma_{sl}^{pol}$  containing the Keesom (dipole-dipole), the Debye (dipole-induced dipole) and the hydrogen bridge forces of interaction:

$$\sigma_{sl} = \sigma_{sl}^d + \sigma_{sl}^{pol} \quad (3.1)$$

From the Good-Girifalco equation, Owens and Wendt, considering the division of the interfacial tension to equation (3.1), developed a method with which the disperse and the polar surface tension portion of solid surfaces can be determined from wetting angle measurements with measuring liquids of different polarities. Wu replaced the geometric mean in the equations by the harmonic mean, which he explained. Apart from this, his method corresponds to that of Owens and Wendt, which is to be considered more thoroughly here, because it forms the basis for the calculation of the surface energies of the solid contact adhesives.

#### The method according to Owens, Wendt, Rabel and Kaelble

Owens, Wendt, Rabel and Kaelble based their method on the assumption that the interfacial energy can be split up between the molecules according to the forces of interaction. They distinguish between disperse interactions and polar interactions. Polar interactions include the Coulomb interactions between permanent dipoles and those between permanent and induced dipoles. The interaction due to fluctuations over time in the load distribution within the molecules is called disperse interaction. Polar and disperse contribution to the surface energy or surface tension are combined by addition. Hence it applies:

$$\sigma_l = \sigma_l^d + \sigma_l^p \quad \sigma_s = \sigma_s^d + \sigma_s^p \quad (3.2)$$

Where  $\sigma_l^d$  and  $\sigma_l^p$  are the disperse and polar portions of the liquid, whereas  $\sigma_s^d$  and  $\sigma_s^p$  mean the respective portions of the solid. According to Owens, Wendt, Rabel and Kaelble, the interfacial energy can be calculated from the portions of the liquid and of the solid by forming the geometric mean.

It results for  $\sigma_{sl}$

$$\sigma_{sl} = \sigma_s + \sigma_l - 2 \left( \sqrt{\sigma_s^d \cdot \sigma_l^d} + \sqrt{\sigma_s^p \cdot \sigma_l^p} \right) \quad (3.3)$$

If this expression is entered in equation (3.2) for  $\sigma_{sl}$  and transposed towards the unknown values, the result is a straight line equation of the form

$$y = a \cdot x + b \quad (3.4)$$

where

$$y = \frac{1 + \cos\theta}{2} \cdot \frac{\sigma_l}{\sqrt{\sigma_l^d}} \quad x = \sqrt{\frac{\sigma_l^p}{\sigma_l^d}}$$

$$a = \sqrt{\sigma_s^p} \quad b = \sqrt{\sigma_s^d} \quad (3.5)$$

Hence, by plotting y against x,  $\sigma_l^p$  can be calculated from the gradient of a compensation straight line and  $\sigma_l^d$  from the axial section. For this purpose, the contact angle of at least two liquid drops is measured on the unknown surface.

If suitable computer software is available, the solution is calculated after entering the measured contact angles and the surface tension data of the liquids used within fractions of a second. By using suitable data bases with stored data on liquids over the temperature, the process is further simplified. A typical evaluation using a computer is shown in Fig. 8.

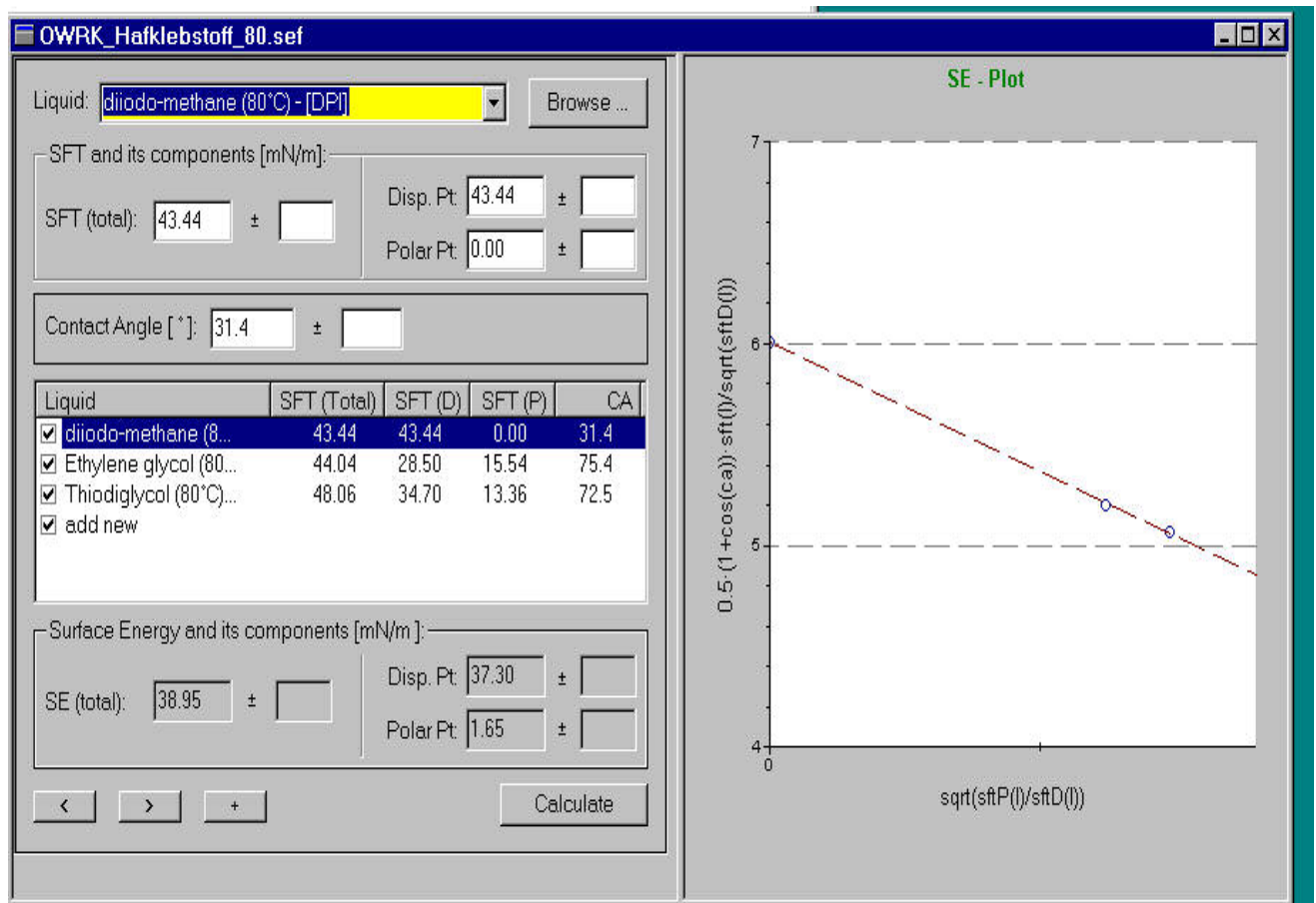


Fig. 8: Evaluation according to OWRK, determination of the polar and disperse components of the surface energy

#### 4.) Experiment set-up, handling, measuring instruments

The measurement of the static contact angles or of the dynamic advancing angles according to the sessile-drop method as well as the measurement of the surface or interfacial tensions according to the lamella or pendant-drop method were all made with the video-supported contact angle measuring instrument OCA 20, in dependence on the temperature. Below follows therefore a short description of the instrument. In Fig. 9, a schematic picture of the instrument is shown.

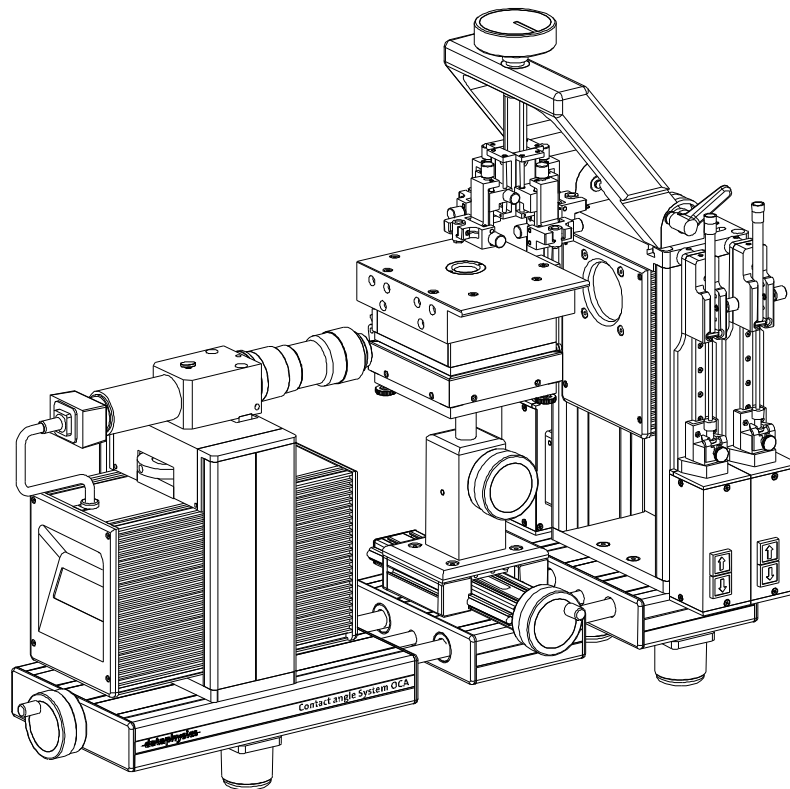


Figure 9: OCA 20 with multiple dosing system, electronic syringe modules, measuring stage and video camera

The OCA 20 measuring system consists of the following elements:

- CCD video camera with a resolution of 768x576 pixels and an image frequency of up to 50 frames per second
- Integrated temperature measurement and indication in the range of - 40 ..400°C
- Up to four manually or motor-driven and software-controlled dosing units or, alternatively, one direct dosing unit with a manual or electrical syringe

The measuring stage serves for holding the solid samples and keeping them level. Additionally, instead of the standard sample stage, a temperature control device can be adapted, either as a liquid temperature control chamber TFC 100 or as an electrically temperature-controlled measuring chamber TEC 350. Both temperature control chambers have connectors permitting work in an inert gas atmosphere.

For dosing the liquid drop - either as a sessile or as a pendant drop - the manually or electronically software-controlled syringes are available to generate a drop of a pre-defined volume. The selection of the tube diameter depends on the drop size required for the respective measuring method. For generating sessile drops of very small volumes, as they were used for the contact angle measurements on the contact adhesives (with a drop volume of 2  $\mu\text{l}$ ), tubes with a small diameter (0.2 to 0.3 mm diameter) are preferable. If drops with large volumes and diameters are preferred, as they are possible for instance for the measurement of the surface tension of liquids by means of the sessile-drop method and the Laplace-Young evaluation (on the condition that the contact angle between liquid and solid should be at least 120°), then also tubes with a diameter of up to 2 mm may be used.

For measurements with the pendant-drop method, it is of particular importance to minimize the calibration error. This calibration which forms a basis for the surface tension calculation to be made on

the drop profile, is performed by the software integrated in the OCA 20 by means of the outer tube diameter independently determined prior to measuring (and which was previously entered in the evaluation software as a reference value). For liquids with surface tensions up to 30 mN/m, tubes with a diameter in the range from 1 to 2 mm, for liquid surface tensions in the order of magnitude of the water value, tube diameters in the range from 1.5 to 3 mm should be used. The recording and evaluation of the drop contour are automatically performed by the SCA 22 software.

As another required value to be entered in advance, the density of the liquid with which the wetting angle measurements are made, as well as its surface tension with the polar and disperse portions at the respective measuring temperature must be known. If interfacial tension measurements are made with the pendant-drop method, the knowledge of the densities of both liquids and their surface tensions at the respective measuring temperature is required. For selected liquids, this information is included in the integrated software of the OCA 20 in the form of a data base, which can be expanded at any time.

Finally here are some remarks on handling the hot-setting contact adhesives.

The measurement of the contact angles on the contact adhesives in their solid state according to the sessile-drop method was directly made on the adhesive layers prepared from the molten mass by determining the dynamic advancing angle. For this purpose, a piece of contact adhesive was removed from the respective compact material mechanically and under heat and then by means of a sliding process directly molten onto a glass slide as evenly as possible. It is important to make this molten layer as even as possible and without the inclusion of air. The glass slide with the molten layer to be measured was fixed in the liquid temperature control chamber TFC 100 or, from 50°C on, in the electrically temperature-controlled chamber TEC 350 and the temperature in the gas space surrounding the drop was determined. It has proven indispensable to work under dry nitrogen in the temperature control chamber, because the contact adhesive layers molten onto the glass slide tend to attract water very quickly.

As liquids of different polarities, ethylene glycol, thiodiglycol and diiodomethane were used. Diiodomethane as a purely disperse solvent turned out to not be suited for all kinds of hot-setting adhesives due to the etching effect visible on some contact adhesives. For certain contact adhesives, therefore, the contact angle measurements were additionally made with p-cymene as a disperse solvent and the resulting contact angle data incorporated in the calculation of the surface energies. The samples, however, also show etching effects with the polar liquids ethylene glycol and, even more, with thiodiglycol. Some contact adhesives obviously containing tensides showed these etching effects even at low temperatures. Due to the lacking constancy of the contact angle values, this made the determination of the surface energy more difficult. Therefore, in the course of the measuring procedure it was decided to determine static contact angles in the phase of the first wetting of the molten layer. A practical replacement by other polar solvents not etching the contact adhesives with a surface tension in a similar order of magnitude and the corresponding temperature stability seems impossible at present.

The evaluation of the surface energies of the contact adhesives in their liquid state by direct measurement of their surface tensions was made on the OCA 20 with the lamella method by optically measuring the curve contour of the lamella generated from the freshly molten contact adhesive (three-phase contact line) over the temperature.

The respective contact adhesive sample was mechanically removed from its compact material, molten in a specially made metal cuvet and then fixed in the electrically temperature-controlled chamber TEC 350. The temperature in the gas space surrounding the molten mass was determined. It is recommended to work under dry nitrogen. By means of a rotationally symmetrical sample body (whose diameter must be determined prior to the measurement by means of a micrometer screw), a lamella is generated from this molten mass above the contact adhesive reservoir and - as described - optically measured and evaluated. The results of the automatic contour evaluation were average values of the measured surface tensions for the respective hot-setting adhesive over the temperature.

For the lamella method, in addition to the diameter of the test body (on which the molten lamella is drawn from the reservoir), also the density of the molten mass at the respective measuring temperature must be known.

The interfacial tension measurements required for the determination of the disperse and the polar portions of the surface tension were made with the pendant-drop method on the OCA 20. Here, too, the respective contact adhesive sample was freshly molten. By taking the molten mass into a special tube and then pressing it out again, a drop was generated from this molten adhesive, whose contour in contact with the purely disperse liquid FC70 was then optically measured with the CCD camera and evaluated with the SCA 22 software. Here, too, the change of the curvature along the drop contour representing the interface between contact adhesive and FC 70 is characteristic of the state of equilibrium. By evaluating this drop contour according to the Laplace-Young method integrated in the software, this interfacial tension between contact adhesive and FC70 can be calculated, when the densities of the drop liquid (molten mass) and of the disperse liquid are known.

The surface tension values for FC70 over the temperature were determined by DataPhysics by means of own measurements made earlier.

The measurements were, however, considerably complicated by the high viscosity of the contact adhesives. Some experimental skill is needed for generating a drop with a suitable contour and holding this drop on the tube over the entire temperature measuring range. The manual dosing of the hot-setting adhesive drop is recommended here.

In spite of these difficulties, significant results were achieved for the examined contact adhesives in the determination of the total surface energies as well as of their polar and disperse portions.

## **5.) Summary of the liquid parameters (density, SFE - incl. FC70)**

For performing the contact angle, surface tension and interfacial tension measurements on the contact adhesives, the knowledge of certain liquid parameters against the temperature is required. For the liquids used as polar or disperse reference liquids, these data are available from DataPhysics Instruments GmbH, Filderstadt, on request.