

# Comparison study

Plasma surface treatment: contact angle makes it visible

Plasma treatment of polymer surfaces is widely used to improve the adhesion on the surface of work pieces. Surface treatment effects can be characterised by determination of surface energy either with the test ink method or with contact angle measurements. Application experts from DataPhysics Instruments have determined surface energy of four different polymers before and after surface treatment. The values were obtained by both test ink evaluation and optical contact angle measurements; the latter using the optical contact angle and drop contour analysis system OCA with corresponding software SCA, both designed and conceived by DataPhysics Instruments. Divergences in obtained results and subjectivity of the test ink method showed that it does not always give a comprehensive picture of surface energy of polymers. The contact angle measurement method has certain advantages, which are described in the report below.

Nowadays plastics are present in many different fields of application. Due to their high elasticity, temperature and deformation resistance they are produced for packaging as well as for complex and long-lasting technical components. Fields such as automotive industry, mechanical engineering, optics or medical goods require special polymer-based materials. Work pieces and blocks made out of these materials are often glued, coloured or coated before being processed. By doing so, the knowledge of surface characteristics of polymers is crucial for good wetting properties of the surfaces with the liquid components.

Surface activation of the polymer is therefore necessary as these materials are usually difficult to wet due to their low surface energy. The most effective surface treatment methods are low pressure plasma treatment, corona treatment, fluorination or flame activation [1]. All these treatment methods improve the liquid component adhesion to the solid due to an increase of surface energy of the solid, or specifically its polar components.

In order to control surface treatment results, international standards have been set up based on two different methods:

Firstly, optical contact angle measurements based on the testing of liquid droplet behaviours on the solid surface and further calculation of surface energy with its polar and dispersive parts. This method is defined, e.g. in the standard measurement procedure DIN 55660-2:2011-12 for inks and varnishes or in DIN EN 828:2013-04 for glues.

Secondly, the test ink method for which a standard procedure is given by ISO 8296 describing how a selection of inks with known surface tensions can be used in order to find the one which will wet the solid surface completely. The value of surface tension of this ink can be translated as the value of surface energy of the solid sample.

Experiments have shown that plasma treatment of polybutylene terephthalate increases the polar part of a materials surface energy which correlates directly with the durability of adhesion in the gluing process [2]. Therefore, the polar part of the surface energy allows the most exact forecast about adhesion properties of the surface. Test inks are not able to discriminate polar and dispersive molecular interactions between polymer and liquid and therefore might not give the most comprehensive picture of the substrate.

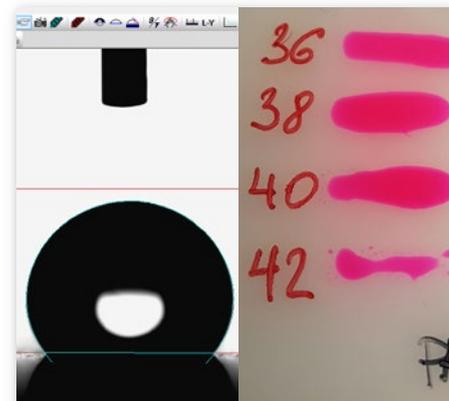


Figure 1: Contact angle measurement vs. test ink method

## Methods

### Polymers

The study involves the use of the polymers shown in Table 1. Polymers were divided into four groups according to the treatment type: control group, fluorination, treatment with propane-butane flame and Pyrosil® treatment.

### Surface treatment

The control group samples were cleaned with isopropanol then air-dried.

The fluorinated samples were provided by the company INNOVENT, Jena, Germany, immediately after fluorination and were measured without any previous cleaning. During the fluorination process polymer samples are incubated in fluorine saturated atmosphere. Thanks to their high reactivity fluorine atoms partially substitute hydrogen atoms on the polymer surface and lead to the increase of surface energy value and its polar part. Fluorination of a polymer is irreversible and allows for a long lasting effect on its treated surface.

Flame treatment (propane-butane and Pyrosil® gas) is especially efficient for applications in industry due to its little manpower needs. During the treatment process the “burning head” goes over the treated surface for a certain period of time and with a defined distance to the surface. The surface is thereby oxidized and its polar parts are increased [3].

The PYROSIL® method is based on the deposition of amorphous silicon oxide on the polymer surface. Precursor PYROSIL® is dosed into the flame and

Abbreviation	Complete denomination
PMMA	polymethyl methacrylate, acrylic or acrylic glass
PA-6	polyamide 6
silicone	polysiloxane
LD-PE	low density polyethylene

Table 1: Studied polymers

creates a thin (5-100 nm) durable layer on the polymer surface. The short flame exposure allows a non-destructive treatment.

Prior to the flame treatment the samples have been cleaned with isopropanol then air-dried.

Flame treatment was carried out with a portable device GVE 2 HB from Sura Instruments, Jena, Germany. During pyrolysis cartridges with either a pure gas mixture propane-butane or with additional precursor PYROSIL® were used. The burning head has been moved over the sample surface at a distance of 15-20 mm. Every surface was treated once. Further measurements were done once the sample cooled down to room temperature.

### Test inks

There are different test ink sets available with different toxicities and compositions. A non-toxic series of inks was chosen with a surface tension range of 28 to 60 mN/m given in discrete steps of 2 mN/m. Inks were brushed over the samples surface immediately after treatment. The ink with the surface tension closest to the assumed surface energy has been used first. If the edges of the stroke stay stable during at least two seconds, one can assume that the surface energy of the solid is equal to the value of surface tension of the tested ink. If the edges of the stroke contract, the ink does not wet the surface and one should pass on to the next ink with a lower surface tension.

### Optical contact angle measurement method

The optical method for contact angle measurement and further calculation of surface energy is based on the contour analysis of a liquid drop placed on the solid surface.

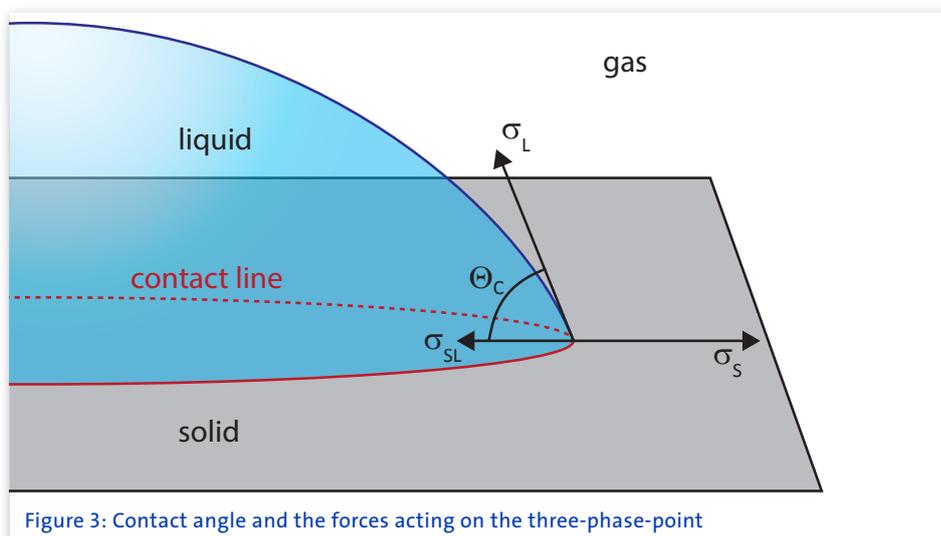


Figure 3: Contact angle and the forces acting on the three-phase-point

A line tangential to the liquid drop's surface is set in the point where the drop touches the solid surface (three-phase-point) (Figure 2). The angle between the samples' surface and the tangent line to the drop surface is called contact angle (CA). Small values of CA indicate good surface wettability.

Surface energy (SE) can be calculated according to the Young equation (Eq. 1) when the drop does not spread (static drop) and the force equilibrium is achieved in the three-phase-point (Figure 3).

$$\sigma_L \cos \Theta_C = \sigma_S - \sigma_{SL} \quad (\text{Eq. 1})$$

- $\sigma_L$  surface tension of the liquid [mN/m]
- $\sigma_S$  surface energy of the solid [mN/m]
- $\sigma_{SL}$  interfacial tension between the liquid and the solid [mN/m]
- $\Theta_C$  contact angle [°]

Knowing the values of polar and dispersive parts of SE allows for a more detailed picture of the wetting phenomena.

The polar part is responsible for the surface activity which is one of the most important parameters during gluing or coating processes. Hence, the pre-treatment methods focus on increasing this parameter.

The calculation of SE using the optical method is mostly carried out according to the Owens-Wendt (OWRK) theory, which states that the total SE is the sum of polar and dispersive parts [4]. Values needed for this calculation are CA values of at least two different test liquids on the solid surface, as well as the surface tension (SFT) of these liquids including their polar and dispersive parts.

The OWRK theory assumes that the solid surface is free of any structures, smooth and chemically and physically homogeneous. It is also important that it does not react with the test liquids. The Young equation together with OWRK model yield a second equation (Eq. 2), which allows the determination of polar and dispersive parts of the surface energy by linear regression based on CA values.

Furthermore the regression coefficient RQ can be calculated. According to Dataphysic's recommendation of using at least three test liquids the RQ value will be an indication of how well the assumptions of OWRK model reflects reality or if the test liquids are suitable for the solid surface properties (RQ value ~ 1).

$$\frac{\sigma_L (1 + \cos \Theta_C)}{2\sqrt{\sigma_L^d}} = \sqrt{\sigma_S^p} \cdot \sqrt{\frac{\sigma_L^p}{\sigma_L^d}} + \sqrt{\sigma_S^d} \quad (\text{Eq. 2})$$

- $\sigma_L^d$  dispersive part of liquid surface tension [mN/m]
- $\sigma_L^p$  polar part of liquid surface tension [mN/m]
- $\sigma_S^d$  dispersive part of solid surface energy [mN/m]
- $\sigma_S^p$  polar part of solid surface energy [mN/m]

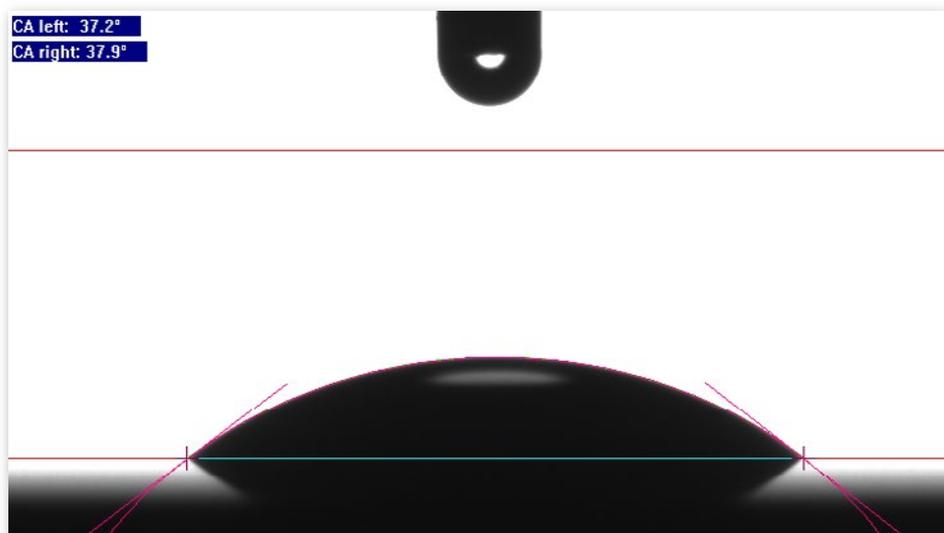


Figure 2: Drop profile in SCA software

Diiodomethane, ethylene glycol and thiodiglycol have been used in this study as test liquids. These test liquids have different polarities; they are non-volatile, mostly non-toxic and pure. The value of their SFT is high enough to form a contact angle easy to measure. The experiments have been carried out with an optical contact angle measuring and contour analysis system OCA 200, DataPhysics Instruments GmbH, Filderstadt, Germany (Figure 4).

## Results and Discussion

The SE values obtained with the test ink method and with the optical method are presented in Table 2.

Result comparison of SE values obtained with both measurement methods and for different surface treatments is presented for each polymer in the diagram below (Diagram 1). There are no SE values for untreated surfaces of silicone and LD-PE obtained with the test ink method because even the ink with the lowest SFT in the set (28 mN/m) did not generate a stable stroke.

A closer look on the diagrams of PMMA and PA6 shows that the best conformity in results between both measurement methods has been observed for the untreated surfaces. Untreated polymer surfaces are rather non-polar and have low SE due to their material characteristics. In case of treated surfaces the test ink method shows lower SE values than the values achieved with the optical method for these polymers.

The test ink method is based on the statement that SE of the solid surface is roughly equal to the SFT value of the liquid ( $\sigma_l = \sigma_s$ ) if it spreads completely on



Figure 4: Optical contact angle measuring and contour analysis system OCA 200

this solid surface. In this case the contact angle of this liquid will be equal to zero and its cosine equal to one. Using the Young model for the test ink method the equation remains valid only if the vector of intermolecular forces ( $\sigma_{sl}$ ) is equal to zero (see Figure 3, Eq. 1).

But the schematic (Figure 3) shows that even if the vectors of SE and SFT are equal, the contact angle value between them can have a value between  $0^\circ$  and almost  $180^\circ$ . Whereby the  $\sigma_{sl}$  vector of intermolecular forces between solid and liquid can be zero in case of a complete wetting or it can have a value different from zero if the wetting occurs partially.

It demonstrates that the test ink method does not take into consideration the vector of intermolecular forces that act between a liquid and a solid.

Forces between atoms and molecules that define the SE depend on the interactions of different nature (polar and non-polar). The interactions induced by a temporary load fluctuation of an atom/molecule are defined as non-polar or so called Van-der-Waals forces. Polar interactions are Coulomb's forces that act between constant and induced dipoles. The value of SE and of SFT is the sum of these two parts according to OWRK theory.

Polymer	Treatment	SE inks [mN/m]	SE CA [mN/m]	polar part [mN/m]	dispersive part [mN/m]	RQ
PMMA	untreated	40	37.76	4.35	33.41	0.99
	fluorination	42	45.35	5.27	40.07	0.94
	propane - butane	46	53.02	5.82	47.19	0.99
	PYROSIL®	46	48.71	9.98	38.74	0.99
PA-6	untreated	46	47.89	5.08	42.81	0.98
	fluorination	40	54.33	8.14	46.18	0.91
	propane - butane	46	59.87	26.52	33.43	0.8
	PYROSIL®	54	56	5.9	50.11	0.99
silicone	untreated	< 30	8.93	1.46	7.47	0.9
	fluorination	< 30	21.43	1.27	20.16	0.98
	propane - butane	46	43.07	14.21	28.86	0.75
	PYROSIL®	46	56	5.9	50.11	0.99
LD-PE	untreated	< 30	24.62	0.96	23.66	0.97
	fluorination	46	53.64	8.03	45.62	0.86
	propane - butane	48	47.5	9.38	38.12	0.97
	PYROSIL®	46	54.15	6.94	47.21	1

Table 2: Surface energy measurement with different methods

Intermolecular force between a liquid drop and a solid surface depends on the correlation between polar and dispersive parts of SE and SFT. If the affinity is high the possibility of molecular interactions between two phases is also high, which results in better adhesion and wettability (Figure 5).

In the scheme of figure 5 the values of SE and SFT are equal ( $\sigma_1 = \sigma_2$ ). In the left schematic one may observe a complete match between polar and dispersive parts that determine the maximum force of molecular interaction on the phase boundary. Interfacial tension tends to vanish which results in CA equalling to zero (complete wetting).

In the right schematic the polar and the dispersive parts of SE and SFT are different. The intermolecular force is weaker and the interfacial tension is higher. It results in positive CA values and in worse wettability and lower adhesion.

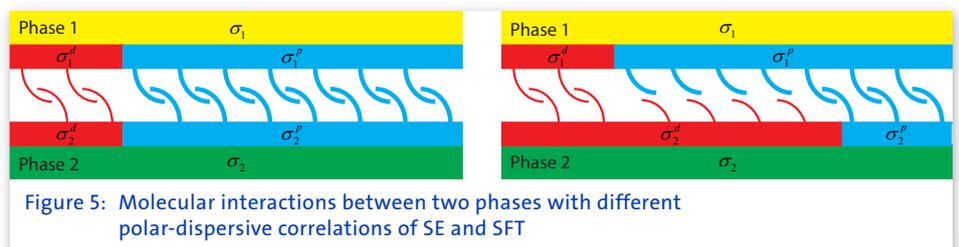


Figure 5: Molecular interactions between two phases with different polar-dispersive correlations of SE and SFT

## Conclusion

Test ink measurements provide correct and accurate results only if the correlation between polar and disperse parts of SE of a solid and SFT of the ink are congruent. The information about ink polarity and the exact composition of inks is not indicated by manufacturers so this correlation cannot always be assumed. This can clearly be observed in the results achieved in this study.

One may usually state that liquids with low SFT values have low absolute polar parts. This fact explains that the best correlation of SE values determined with the ink method and the optical method

is achieved with untreated polymers which are almost completely disperse due to their chemical composition.

Flame activation of a polymer surface enlarges its SE mostly by increase of polar parts which are impossible to determine with the test ink method. The optical method is better suited to define the differences between the various treatment methods and their resulting effects.

Comparative analysis shows that the SE measurement results obtained with test inks are not always congruent with SE values of a solid surface determined by optical contact angle measurements. The latter allows to define the value of SE with polar and disperse parts which are crucial to know in painting or coating applications. Furthermore an estimation of adhesion behaviour is possible.

Some test inks are toxic or volatile and there is a high risk of contamination while repetitively using the same brush for different surfaces. This contamination may change the ink composition and ink SFT which would highly influence the measurement results. Furthermore the result depends on the operator's interpretation of the brush stroke.

In comparison, the optical contact angle method allows an objective interpretation, reproducible results and allows measurements with pure and non-toxic test liquids.

One additional advantage of the optical contact angle method is the ability to work with small sample sizes: while the ink method requires enough space for several strokes as wide as the brush, the optical method requires only a few square millimetres for several small drops. It is possible to generate drops of several picoliter volume and thus a sample area of about 0.01 mm<sup>2</sup> will suffice.

Both methods are widely used but the optical contact angle method provides more information with regards to surface properties and is free from the limitations of the test ink method.

## Literature

- [1] A. Pfuch, A. Heft, M. Ertel, S. Schiemann, A. Schimanski „Effizienz der Vorbehandlung“, Kunststoffe 3/2006 P. 147-150
- [2] H. Gleich „Zusammenhang zwischen Oberflächenenergie und Adhäsionsvermögen von Polymerwerkstoffen am Beispiel von PP und PBT und deren Beeinflussung durch die Niederdruck-Plasmatechnologie“, Dissertation Universität Duisburg-Essen, 2004, P. 74
- [3] G. Habenicht „Kleben – erfolgreich und fehlerfrei“, Springer Verlag, 2016, P. 134
- [4] Owens, D. K.; Wendt, R. C. (1969). “Estimation of the surface free energy of polymers”, J. Apply. Polym. Sci. 13 (8): 1741–1747.

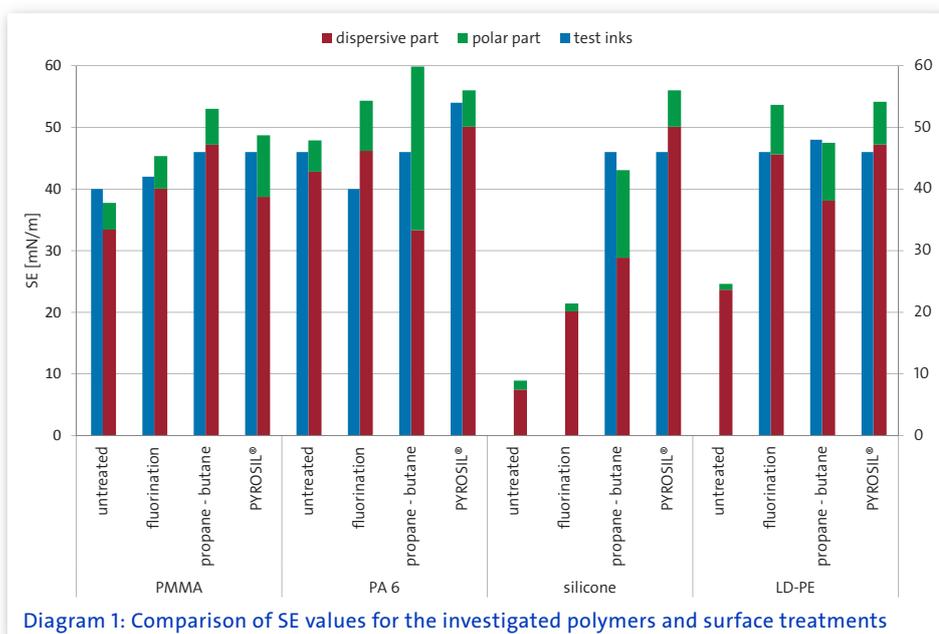


Diagram 1: Comparison of SE values for the investigated polymers and surface treatments