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Importance of surface tension for physical paint properties

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Abstract: Surface tension is a parameter of decisive importance for characterizing painted and unpainted surfaces related to wetting and adhesion phenomena. This article presents measurements of the surface tension of solids by means of an automatic contact angle measurement device. The evaluation of the surface tension is based on a separation into polar and disperse components. In addition, this paper briefly touches on other, more far-reaching approaches (acid/base) and discusses a method for the determination of dynamic surface tension of liquids.

1 Introduction

The wettability of a solid surface is a function of the relative surface tensions of the paint and the solid surface. In order to ensure good wetting of the substrate, the surface tension of the substrate must be as high as possible. If the substrate surface is contaminated with substances featuring a low surface tension or in case of materials with a rather low surface tension (e.g. many plastics, especially polyolefins), wetting and adhesion problems may occur.

While there are relatively simple methods for the determination of the surface tension of liquids (e.g. ring method), the surface tension of a solid is determined by measuring the contact angles of several test liquids with a known surface tension and polarity (see e.g. (1)).

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2 Theoretical background

In the literature, the basic equation to describe the interaction of the surface tensions of a liquid and a solid is called Young equation (2):

$$\gamma_s = \gamma_{sl} + \gamma_l \cos\theta \qquad (1)$$

with γ_s and γ_l representing the surface tensions of the solid and liquid phases (against the vapour) and γ_{sl} representing the interfacial tension between the solid and the liquid. The contact angle θ represents the angle that forms when a liquid comes into contact with a solid. Here, we will not go into detail with regard to the *spreading pressure* π_e *(difference between* γ_s *in the vacuum and* γ_s *against liquid* vapour) and refer to the literature on the subject. In general, it is being discussed that π_e is small or can be neglected in the case of low-energy surfaces, like polymers.

In the more far-reaching theoretical approaches which deal with the problems of interfaces, the surface tension of each phase is separated into components considering only the dispersion forces on the one hand and those components comprising all polar interactions ($\gamma = \gamma^d + \gamma^p$; with d representing the disperse and p representing the polar component) on the other. On the basis of this approach, *Owens and Wendt* (3) and *Kaelble* (4, 5) developed a relation enabling to link the contact angle with the polar and disperse components of the surface tensions of liquid and solid

$$\gamma_l\,(1 + \cos\theta)/2 = (\gamma_s^d\,\gamma_l^d)^{1/2} + (\gamma_s^p\,\gamma_l^p)^{1/2} \qquad (2)$$

After conversion of this equation to a general linear equation, a simple graphic analysis after measurement of the contact angles of various test liquids enables the determination of the solid surface tension.

The separation of the surface tension of a solid into polar and disperse components permits conclusions with regard to the type of forces active on the surface. So many pretreatment methods particularly increase the polar component of the surface tension by integrating polar groups (e.g. hydroxyl, carbonyl and carboxyl groups (6-11)) in the surface.

The measurements of the surface tension of the various samples, which are usually very time-consuming, were carried out using an automated contact angle measuring unit (AURAM) which has already been described at length in another article (12). It is a device for fully-automated proportioning and measuring of liquid drops on solid surfaces. The test liquids are twice distilled water, formamide, glycerol and ethylene glycol. The surface tension values of these liquids are listed e.g. in Ref. (1).

2.1 Example: Elastified polypropylene (PP-EPDM)

Good paintability of the plastic surface requires high surface tension values. Here, the polar component of the surface tension is particularly important (13, 14). In the literature, a large number of pretreatment methods are being discussed (flame-treatment, plasma, etc. as e.g. (6, 15-20)) which increase the surface tension of the plastics and thus improve the wettability and adhesion of the paint to the surface.

The surface tension values of untreated PP-EPDM materials are between 21 and 23 mN/m (total) with a low polar component of 2 to 3 mN/m. Surface tension measurements of flame-treated PP-EPDM plates were carried out using the AURAM automatic contact angle measuring device. After flame-treatment, the total surface tension increases and the polar component is strongly enhanced. After the third flame-treatment procedure, surface tension and polarity no longer change (Fig. 1).

The increase of the surface tension is due almost exclusively to the increase of the polar component of the surface tension. This increase of the polar component can be explained by the integration of polar groups into the surface. In the process, acidic and basic groups can occur in the surface (21-23). These groups can be determined e.g. by means of ESCA measurements (electron spectroscopy for chemical analysis).

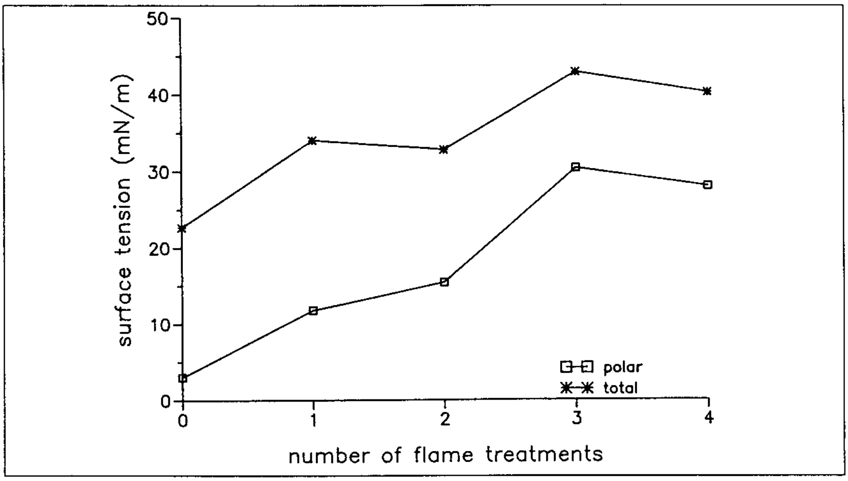

Fig. 1: Total surface tension and polar component of a PP-EPDM sample for different numbers of flame-treatments

Flame-treatment may lead to local inhomogeneities in the substrate surface. Fig. 2 shows the water contact angles of samples flamed once or twice. The measurements were carried out at right angles to the flame-treatment direction. Only in case of the sample flamed twice is a relatively homogeneous flame-treatment of the surface discernible. In addition, the quality of flame-treatment also depends on the materials used.

Fig. 3 shows the development of the total surface tension and the polar component of plasma-treated samples (oxygen discharge) over a period of approx. 5 weeks. Over an extended period of time, the surface tension values remain almost constant before decreasing slightly after approx. 3 weeks. It must be mentioned that faster decreases may occur depending on the material examined.

A visual impression of the pretreatment effect may be provided by SEM images (scanning electron microscope), showing that the plasma process does not entail an increase in surface roughness (20, 21).

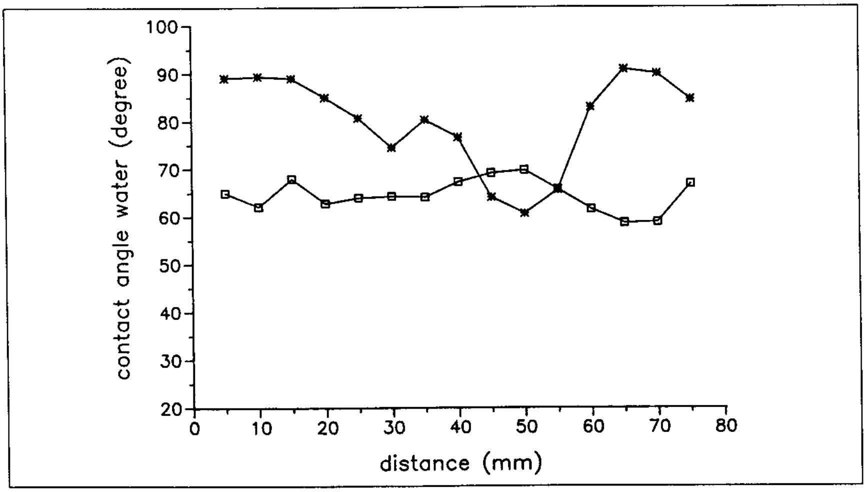

Fig. 2: Water contact angle of flame-treated PP-EPDM samples
(✱ 1 x flamed, ☐ 2 x flamed)

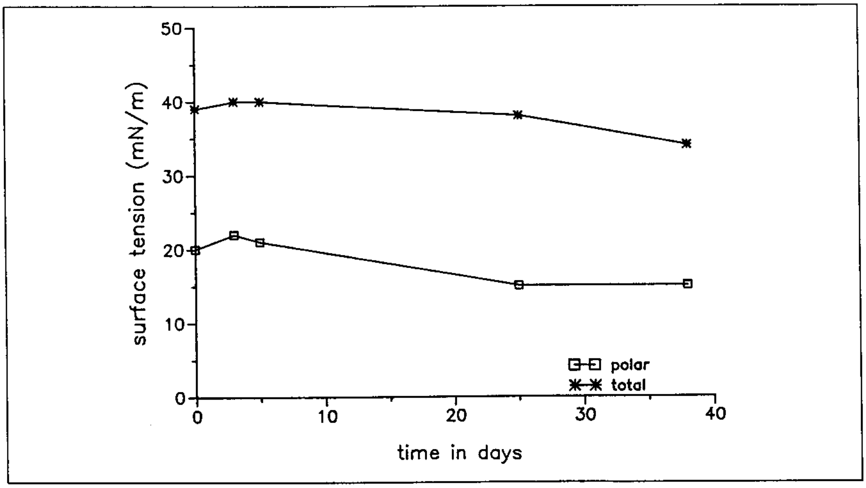

Fig. 3: Development of the surface tension of a plasma-treated PP-EPDM sample in the course of time

3 Theory according to *van Oss/Good/Chaudhury*

The theory presented in chapter 2, which separates the surface tension into polar and disperse components, has lead to some difficulties with regard to the interpretation of wetting and adhesion phenomena in recent years. This encouraged an examination of the practical applicability of other theories, particularly according to *van Oss et al.* (24).

Here, the surface tension is separated into two components:

$$\gamma = \gamma^{LW} + \gamma^{AB} \qquad (3)$$

γ^{LW} represents apolar components resulting from so-called "Lifshitz-van der Waals" interactions. γ^{AB} represents the component resulting from acid-base interactions (Lewis acid, Lewis base). This component is again separated into γ^{+} (acid parameter) and γ^{-} (base parameter), with

$$\gamma^{AB} = 2(\gamma^{+}\gamma^{-})^{1/2} \qquad (4)$$

The determination of γ^{LW} and the components γ_S^{+} and γ_S^{-} of the solid surface tension is carried out by measuring the contact angles θ of at least three test liquids, of which at least one is apolar (e.g. α-bromonaphthalene) and at least two are polar (see Table 1: test liquids), whose acid and base parameters are known. The following relation applies to a liquid:

$$\gamma_l (1 + \cos\theta) - 2(\gamma_S^{LW}\gamma_l^{LW})^{1/2} = 2(\gamma_S^{+}\gamma_l^{-})^{1/2} + 2(\gamma_S^{-}\gamma_l^{+})^{1/2} \qquad (5)$$

A corresponding system of equations is given for several liquids, the solution of which is described in (25). For the analysis of acid and base parameters, *Good* (25) suggests measurement with pairs of liquids. Suitable pairs of liquids are e.g.: water/formamide, water/ethylene glycol, water/glycerol.

The corresponding values (in mN/m) are found in (25), too:

Liquid	γ	γ^{LW}	γ^{+}	γ^{-}
Water	72.8	21.8	25.5	25.5
Formamide	58.0	39.0	2.28	39.6
Ethylene glycol	48.0	29.0	1.92	47.0
Glycerol	64.0	34.0	3.92	57.4
α-Bromonaphthalene	44.4	43.5	≈ 0	≈ 0
Diiodomethane	50.8	50.8	≈ 0	≈ 0

Table 1: Test liquids

3.1 Example: Wettability of basecoats

In the paint industry, the wettability of basecoats is an important technical property relative to clearcoat application. In the process, the liquid clearcoat is applied to the pre-dried basecoat layer. Wettability is gauged by coat thickness to be applied in order to achieve a closed clearcoat film; high values are indicative of poor wetting.

Fig. 4 shows the surface tension values γ^{LW} of the various dried basecoats as a function of clearcoat wetting. It is obvious that high values of γ^{LW} provide for better clearcoat wetting (transition at approx. 14 µm). In comparison to that, an evaluation of the acid/base parameters or according to *Kaelble* did not result in clear correlations. The liquid surface tension of the clearcoat was approx. 28 mN/m (sprayed).

Table 2 shows some typical paint materials and pre-treated plastics and their respective surface tension values. It is striking that the analysis according to *van Oss et al.* always shows a high γ^{-} component.

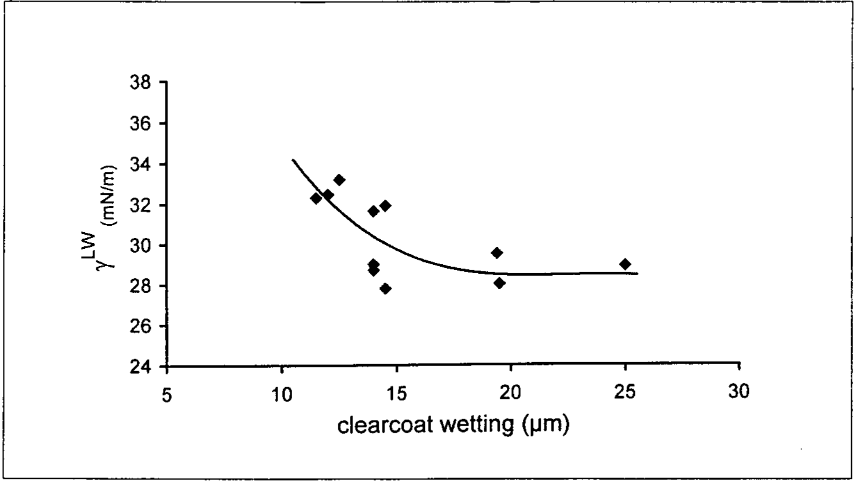

Fig. 4: Surface tension values γ^{LW} of various dried basecoats as a function of clearcoat wetting

Sample	***Kaelble***			***van Oss et al.***			
	γ	γ^d	γ^p	γ	γ^{LW}	γ^+	γ^-
PP-EPDM flame-treatm.	39.5	20.3	19.2	46.0	38.8	0.5	26.1
PPE modified fluorination	38.5	10.8	27.7	44.8	35.2	0.5	22.5
Electro coat 1	34.4	26.4	8.0	43.5	43.5	0.0	8.5
Electro coat 2	28.6	13.2	15.4	54.5	43.5	0.7	16.2
Primer-surfacer	21.3	5.9	15.4	48.6	37.1	2.2	15.1
Top coat	21.5	18.5	3.0	29.5	28.5	0.1	2.7

Table 2: Some typical paint materials and pre-treated plastics and their various components of surface tension (values in mN/m)

4 Dynamic surface tension of liquids

The bubble pressure tensiometer BP2 (Krüss) allows the determination of the dynamic surface tension of liquids according to the method of maximum bubble pressure. In contrast to static methods (ring and plate method), the bubble pressure method takes into account that substances lowering the interfacial tension (additives, tensides) in liquids need time to diffuse to the interface. Some additives diffuse and find their way to newly built interfaces faster than others and reduce the surface tension faster, too. In some cases, these processes occur in a split second.

In the bubble pressure tensiometer, gas bubbles are generated in the liquid to be examined at a defined bubble formation rate (26). The measuring device measures the maximum pressure occurring during the bubble formation process which is directly proportional to the surface tension. The tensiometer automatically increases the bubble formation frequency by between 1 and 10 bubbles per second. The time for the formation of a new interface is automatically reduced from 1 s to 0.1 s.

4.1 Example: Waterborne basecoat

The surface tension of the waterborne basecoats examined increases with a growing bubble formation rate, in an unsprayed state, however, only a minor decrease of the surface tension is found with increasing additive concentration (Fig. 5). In contrast, dramatic differences occur when sprayed material is measured (i.e. captured after spraying, Fig. 6). In the application test, the material featuring the lowest dynamic surface tension (highest additive concentration, lowest increase) has the best wetting properties with regard to the substrate.

The bubble pressure tensiometer suggests itself as the measuring tool of choice for all wetting phenomena related to "optimum use of additives".

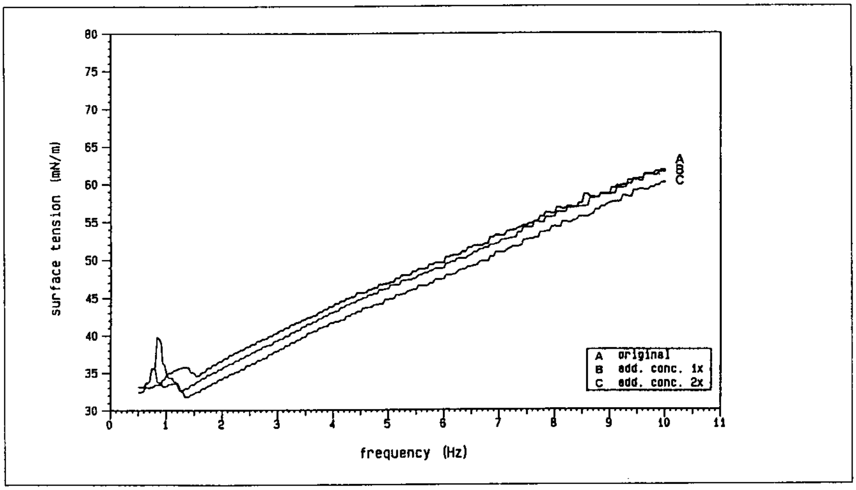

Fig. 5: Waterborne basecoats with various additive concentrations (unsprayed)

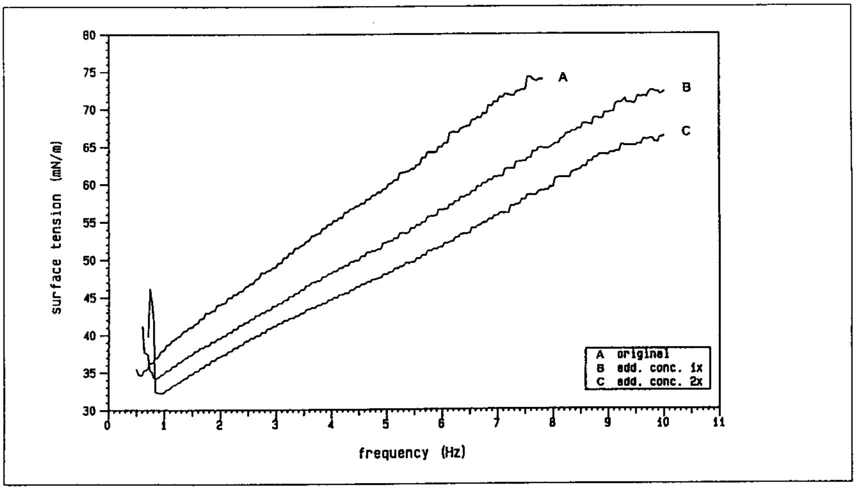

Fig. 6: Waterborne basecoats with various additive concentrations (sprayed)

5 Summary

The importance of the surface tension as a parameter for the description of wetting and adhesion phenomena in the paint industry was described with practical examples. For this purpose, various theories, particularly on the surface tension of solids were briefly introduced (*Kaelble*, *van Oss*) and applied to current problems. The examples presented dealt with problems from the fields of "pre-treatment of plastics" and "wettability/wetting of waterborne basecoats". Altogether, the interpretation of test results using these theories is not always successful and requires further statistical proof supported by practical application results.

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