

Static solvent contact angle measurements, surface free energy and wettability determination of various self-assembled monolayers on silicon dioxide

Dimitri Janssen ^{a,b}, Randy De Palma ^{a,b}, Stijn Verlaak ^b, Paul Heremans ^{b,*}, Wim Dehaen ^a

^a Department of Chemistry, KULeuven, Leuven, Belgium

^b Imec vzw, Leuven, Belgium

Received 14 November 2005; received in revised form 5 April 2006; accepted 5 April 2006

Available online 30 May 2006

Abstract

In many fields and applications, a good knowledge of the wetting behaviour of solvents on a surface is crucial. Self-assembled monolayers (SAMs) have enabled improved control over surface properties, while more recent fields such as organic electronics gave rise to new applications and requirements regarding solvent–substrate interactions. However, most reported wettability studies are limited to practically less relevant solvents such as water, diiodomethane or hexadecane. Herein we report static contact angle measurements of various, typical SAM-modified surfaces, characterizing these surfaces' wettabilities over a wide range of practically relevant solvents. Surface energies, both the polar and the disperse component, of these SAM-modified surfaces are extracted with various methods from the contact angle data. Reliable methods for surface energy extraction, such as the Owens–Wendt–Rabel–Kaelble method and the method after Wu, yield values which could be expected from the chemical structure and nature of the self-assembled molecules and which correspond well to the few reported literature values. We also determined wetting envelopes for the various surfaces which allow easy prediction of the surfaces' wettability for a certain solvent and which ensure relevance for current and future solvents.

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Keywords: Monolayer; Surface energy; Wetting; Organic semiconductor

1. Introduction

Knowledge of the wetting behaviour of solvents on surfaces is notably important in the interest of basic physics, but also for many industrial processes and applications such as cleaning, coating, printing, paints, textiles, etc. Self-assembled monolayer (SAM) films have provided new and easier ways to control the physical and chemical properties of surfaces [1]. For example, organosilane compounds are known to form robust, chemisorbed SAMs on a wide variety of surfaces such as glass, quartz, metal oxides [1] and even polymers [2], and are used in biological interfaces and sensors [3,4], in micro-electromechanical systems [5], in organic electronics [6–9] and so on.

In the field of organic electronics, local modification of surface properties, such as the surface energy, has been used to print self-aligned source-drain contacts [10], to steer pentacene crystal growth [11], or more generally applied to improve adhesion of photoresists and developers in lithographic processes [12].

Knowledge of the wetting behaviour and surface energy of such monolayer films with widely used, typical processing solvents can be valuable both for technological and for more fundamental purposes.

In this paper we examine, by means of static contact angle measurements, the wettability of a wide range of practically relevant solvents on silicon dioxide substrates modified with various, commercially available organosilane self-assembled monolayers. From these data, surface energies and wetting envelopes are extracted which allow for a well-considered choice of the appropriate solvent and/or surface properties (by modification with a self-assembled monolayer film) in many applications and fields.

* Corresponding author. Imec vzw, Kapeldreef 75, B-3001 Leuven, Belgium.
Tel.: +32 16281521; fax: +32 16281501.

E-mail address: Paul.Heremans@imec.be (P. Heremans).

2. Experimental section

2.1. Substrate and SAM film preparation

All self-assembled monolayers were deposited at room temperature on n-doped (100) silicon wafers (Wacker) with a layer of 100 nm thermal silicon dioxide. Prior to deposition, these substrates were cleaned with ‘Piranha solution’ (3:7H₂O₂:H₂SO₄), followed by a ‘standard clean 1’ (1:1:5 H₂O₂:NH₄OH:H₂O) and stored in high-purity water until use.

Films of octadecyltrichlorosilane (OTS, from Aldrich, >90%), 11-cyanoundecyltrichlorosilane (CUTS, from Gelest Inc.), phenylethyltrichlorosilane (PETS, from ABCR, 97%), 1H,1H,2H,2H-perfluorodecyltrichlorosilane (FDTS, from ABCR, 97%), 11-bromoundecyltrichlorosilane (BUTS, from Gelest Inc., 95%), 10-undecenyltrichlorosilane (UETS, from Gelest Inc., 97%) and 2-phenyltrichlorosilane (PTS, from ABCR, 97%) were deposited from the vapor phase. The cleaned substrates were placed together with 7.5 µl of the silane in a vacuum oven at 140 °C for 30 to 60 min.

Films of 2-[methoxy(polyethyleneoxy)propyl]trimethoxysilane (PEG6/9, from ABCR, 90%) were deposited overnight from toluene (Acros, spectrophotometric grade 99+%) with a trace of diluted HCl and 0.5% (v/v) silane. [13] The silane is left to hydrolyse for 5 min prior to substrate immersion. After deposition, samples are thoroughly rinsed with toluene, CCl₄, acetone, methanol and water and baked for 15 min at 110 °C under nitrogen. For films of 11-(triethoxysilyl)undecanal (TESU, from Gelest Inc., 97%), the same procedure was used except for the deposition duration which was shortened to 3 h as this yields less polymerization.

Films of 3-aminopropyltriethoxysilane (APTES, from ABCR, 97%) and 3-mercaptopropyltriethoxysilane (MPTES, from ABCR, 95%) were deposited according to the procedure provided by the supplier from a 2.0% (v/v) solution in 95:5 ethanol–water. For MPTES a trace of acetic acid is added. The silane is left to hydrolyse for 5 min prior to substrate immersion. After 30 min the substrates are rinsed thoroughly with ethanol, dried under N₂ and baked for 15 min at 110 °C under nitrogen.

Under the conditions used, the resulting SAMs showed a maximal contact angle value that corresponds well to known literature values (see Section 3.1) while maintaining a minimal roughness (verified by atomic force microscopy, data not shown).

A carboxyl-terminated monolayer (oxUETS) was obtained by ozonolysis of an UETS monolayer in an ozone-enriched chamber for 5 min [14]. The conversion of the terminal alkene-group to a carboxylic acid is estimated to be 50–60% based on the assumption that the overall surface energy is a linear combination of the surface energies of the different, functional groups at the surface (Fig. 1) [15].

2.2. Contact angle measurements

Solvents were used as received: acetone (Air Products Electronic Chemicals), *n*-heptane (GR for analysis, Merck), isopropanol (Air Products, SULSI), chlorobenzene (Aldrich, ReagentPlus™ 99%), *p*-xylene (Aldrich, anhydrous 99+%), dichloromethane (JT

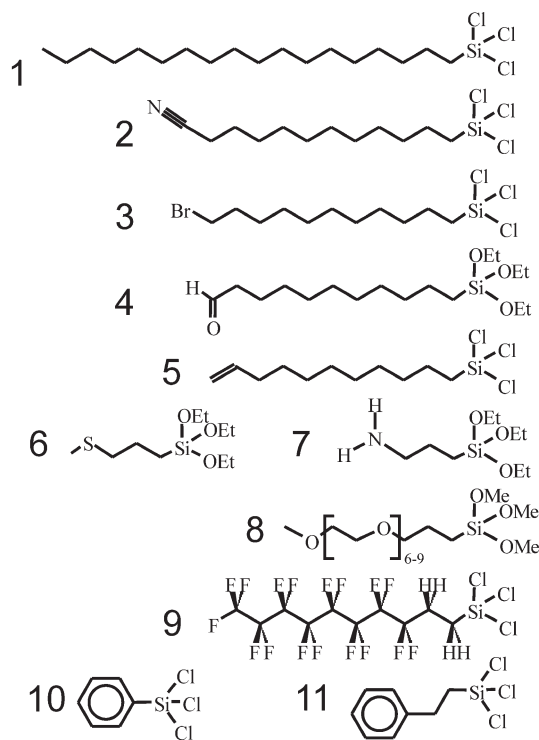


Fig. 1. Self-assembled monolayers of octadecyltrichlorosilane (OTS, 1), 11-cyanoundecyltrichlorosilane (CUTS, 2), 11-bromoundecyltrichlorosilane (BUTS, 3), 11-(triethoxysilyl)undecanal (TESU, 4), 10-undecenyltrichlorosilane (UETS, 5), 3-mercaptopropyltriethoxysilane (MPTES, 6), 3-aminopropyltriethoxysilane (APTES, 7), 2-[methoxy(polyethyleneoxy)propyl]trimethoxysilane (PEG6/9, 8), 1H,1H,2H,2H-perfluorodecyltrichlorosilane (FDTS, 9), phenyltrichlorosilane (PTS, 10) and 2-phenylethyltrichlorosilane (PETS, 11) were deposited on silicon dioxide substrates.

Baker, Baker analyzed), ethylacetate (Merck, GR for analysis), toluene (Acros, spectrophotometric grade 99+%), tetrahydrofuran (Merck, Seccosolv®), dimethylsulfoxide (DMSO, Aldrich, anhydrous 99.9%), acetonitrile (Acros, PA), *N*-methylpyrrolidone (NMP, Acros, PA), Fluorinert FC-3283 (3M), anisole (Acros, PA), 1,2-dichlorobenzene (Aldrich, anhydrous 99%), 1,2,3,4-tetrahydronaphthalene (tetralin, Aldrich, reagent grade 97%), 1,4-dioxane (Acros, extra dry with molecular sieves), methanol (Ashland, VLSI), *N,N*-dimethylformamide (DMF, Aldrich, anhydrous 99.9%), chloroform (Merck, GR for analysis). Water is ultrapure and deionized (resistivity > 18.2 MΩ 1 cm).

Static contact angle measurements with the sessile drop method were recorded and analyzed at room temperature on a OCA-20 contact angle meter from DataPhysics Instruments GmbH with SCA20 software (version 3.4.6 build 79). Reported contact angles are the average of at least 3 measurements. Contact angles below 10° could not always be fitted and determined by the software and in this case, are designated with “<10”. Surface energies and wetting envelopes were obtained with this software using the available methods described further.

3. Results and discussion

3.1. Contact angle measurements

The contact angle values of the various solvents for the different self-assembled monolayers are summarized in Table 1.

Table 1
Overview of the measured contact angles of the solvents for the different SAMs

	OTS	CUTS	PETS	FDTs	BUTS	SiO ₂	UETS	PTS	TESU	APTES	oxUETS	MPTES	PEG/9
Water	98.2±0.3	68.1±0.6	87.9±2.2	109.6±0.4	91.1±1.5	<10	94.7±1.4	73.9±0.8	69.7±2.2	58.4±1.7	66.3±0.9	40.3±0.3	35.8±1.0
Acetone	9.5±0.2	<10	<10	50.5±1.3	<10	<10	<10	<10	<10	<10	<10	<10	<10
<i>n</i> -Heptane	<10	<10	<10	62.7±0.3	<10	<10	<10	<10	4.0±0.4	<10	4.3±0.8	<10	<10
Isopropanol	<10	<10	<10	45.2±2.0	<10	<10	4.9±0.7	<10	6.1±0.4	<10	6.3±0.4	6.7±0.9	6.4±0.5
Chlorobenzene	31.8±0.1	<10	<10	76.0±1.3	<10	<10	23.5±0.9	<10	<10	<10	5.9±1.1	12.2±0.5	4.9±0.6
<i>p</i> -Xylene	23.8±0.5	<10	<10	73.7±0.3	<10	<10	13.1±1.3	<10	5.2±0.6	6.2±0.6	5.5±0.1	<10	5.4±0.3
Dichloromethane	27.3±0.9	14.3±0.6	12.8±0.9	69.4±1.1	13.4±0.2	14.4±0.5	21.5±1.6	14.1±1.1	13.2±0.4	12.8±0.3	12.5±0.4	12.9±0.2	13.4±0.1
Ethylacetate	20.5±0.8	10.5±0.4	10.4±0.9	52.9±0.8	10.4±0.8	10.5±0.6	16.6±1.3	9.9±0.4	<10	<10	5.5±0.7	<10	<10
Toluene	24.8±0.5	<10	6.2±0.3	74.5±0.6	6.5±0.5	5.3±0.4	23.3±1.4	5.7±0.2	4.6±1.0	6.4±0.5	5.4±0.3	6.0±0.6	4.8±1.2
Tetrahydrofuran	23.2±0.5	<10	6.2±0.6	60.2±0.6	5.8±0.9	5.4±0.9	15.1±1.5	6.2±0.7	5.9±0.5	6.5±0.3	6.2±0.1	7.0±0.6	6.1±0.5
Dimethylsulfoxide	62.8±0.4	19.4±1.3	28.9±1.5	84.6±1.1	45.5±1.3	<10	55.0±3.0	27.1±2.2	15.6±2.5	28.9±2.4	17.3±1.6	9.0±4.3	16.3±1.4
Acetonitrile	44.0±0.2	<10	15.4±1.2	73.0±0.8	17.8±1.7	<10	29.2±0.3	9.7±2.3	<10	10.7±0.6	<10	5.9±0.2	<10
<i>N</i> -methylpyrrolidone	55.0±1.0	<10	14.7±0.4	80.5±0.6	35.2±1.6	<10	44.6±0.3	19.7±3.1	<10	17.8±1.5	5.7±1.0	4.7±1.3	<10
Fluorinert FC-3283	<10	3.9±0.2	<10	21.6±1.0	4.6±0.9	<10	4.4±0.7	4.2±0.9	<10	<10	3.7±0.2	4.6±0.3	4.4±0.2
anisole	49.5±0.5	7.0±0.5	7.1±0.3	79.8±0.2	12.8±0.8	6.5±0.7	29.8±0.7	10.4±1.2	4.7±0.9	10.2±0.5	19.3±2.0	8.7±0.4	4.6±0.1
1,2-Dichlorobenzene	42.7±0.6	<10	9.4±0.6	80.5±0.3	13.2±1.8	<10	30.4±0.6	13.8±0.9	<10	13.2±0.2	21.5±0.3	14.6±0.1	5.6±0.3
Tetralin	35.9±1.0	9.0±1.0	7.1±0.7	82.9±0.8	<10	5.7±0.1	21.2±0.7	6.4±2.4	4.5±0.2	10.6±0.2	15.0±0.7	11.7±0.1	5.1±0.4
1,4-Dioxane	48.2±0.9	5.2±0.8	<10	77.8±0.4	6.0±0.8	5.9±0.3	25.7±0.6	7.6±0.8	5.4±1.6	9.7±0.5	11.8±1.3	7.6±0.9	6.9±0.2
Methanol	31.5±0.8	<10	<10	58.2±0.8	<10	<10	<10	<10	<10	<10	<10	<10	<10
DMF	57.1±0.5	<10	8.1±2.1	79.2±0.8	20.4±0.6	<10	22.9±0.8	7.5±0.5	<10	11.6±1.1	13.5±3.8	6.6±0.4	<10
Chloroform	30.0±1.4	6.7±0.8	7.3±0.7	68.8±1.2	6.3±0.7	<10	22.9±0.8	7.5±0.5	7.6±0.1	7.3±0.4	6.5±0.9	6.5±0.7	7.6±0.7

Table 1 serves as a guideline for the wettability of typical processing solvents on various substrates or indicates which surface modification can be applied to improve solvent wetting. A few general trends can be quickly noticed: first, all of the studied solvents wet the clean silicon dioxide substrate, indicating that this substrate has a very high surface energy. An FDTs-modified substrate on the other hand is hardly wetted by any of the solvents, not even by the perfluorinated alkane Fluorinert® which is indicative of an extremely low surface energy. Other silane films showing little wetting are OTS and to a slightly lesser extent UETS. Such low wettability surfaces can be problematic, e.g. when a polymer is to be spin-coated on top from solution. For example, poly-3-hexylthiophene (P3HT) is a semiconducting polymer that is widely used in the field of organic electronics in thin-film transistors [16] and solar cells [17], and it is usually spin-coated from solution to obtain thin films. However a P3HT solution in chlorobenzene does not wet an OTS-modified surface, yielding inhomogenous thin films. Based on Table 1, we improved surface wetting and film formation by using a PTS-SAM instead of an OTS-SAM as surface treatment or alternatively by choosing toluene as solvent instead of chlorobenzene.

The de-wetting of water and DMSO on most modified surfaces clearly demonstrates the rather apolar nature of most films and the strong polar nature of these solvents. For water contact angles, values for silane-modified surfaces on oxides can be found in literature and compare reasonably well to our results as can be seen in Table 2. This also means that our SAMs are qualitatively representative despite the use of (slightly) different procedures in the cited literature in Table 2.

Contact angle data for solvents other than water (e.g. hexadecane, diiodomethane and bicyclohexyl) can be found in the literature [18,19,34]. These solvents are typically used for the calculation of surface energies but were not used in this study as they are of less interest from technological (e.g. processing) point of view. In this paper we focus on the wettability of more practically relevant solvents which, to our knowledge, has not been studied before.

3.2. Surface energy determination

Contact angle measurements can be related to surface tensions or energies via Young's equation [35]:

$$\gamma_{sv} = \gamma_{sl} + \gamma_{lv} \cos \theta \quad (1)$$

where θ is the measured contact angle and γ is the surface energy of the solid–vapor (sv), solid–liquid (sl) and liquid–vapor (lv) interface. Depending on the model which is used, an expression for γ_{sl} can be combined with Eq. (1) and results in a relation between the contact angle and the liquid's surface tension from which the solid's surface energy can be extracted. As an interaction between two phases can be split into different components (e.g. polar, dispersive, hydrogen-bonding, ...), some models, like the Owens–Wendt–Rabel–Kaelble method (OWRK) [36,37], distinguish a polar and a disperse fraction of the surface energy. In this study we have extracted surface energies of the various SAM-modified substrates from the collected contact angle data

Table 2
Comparison of measured static contact angles (CA) with reported literature values

	Zisman	Fowkes	Owens, Wendt, Rabel, Kaelble			Wu			EOS
	γ_{crit}	Disp	SE	Disp	Polar	SE	Disp	Polar	SE
FDTS	-1.37 ± 0.03	15.11 ± 0.16	13.50 ± 0.12	11.22 ± 0.09	2.28 ± 0.07	16.14 ± 0.12	12.64 ± 0.07	3.49 ± 0.10	14.67 ± 0.54
OTS	20.03 ± 0.03	26.23 ± 0.16	23.50 ± 0.05	18.07 ± 0.05	5.43 ± 0.01	25.38 ± 0.12	22.57 ± 0.12	2.81 ± 0.02	23.97 ± 1.01
CUTS	26.26 ± 0.03	33.09 ± 0.33	41.33 ± 0.04	15.65 ± 0.04	25.68 ± 0.01	39.67 ± 0.04	24.08 ± 0.04	15.59 ± 0.01	31.79 ± 2.33
PETS	26.23 ± 0.03	31.90 ± 0.25	35.82 ± 0.05	16.17 ± 0.03	19.64 ± 0.04	32.71 ± 0.03	23.36 ± 0.02	6.35 ± 0.02	30.13 ± 1.97
BUTS	25.24 ± 0.03	30.87 ± 0.22	31.39 ± 0.03	17.34 ± 0.03	14.04 ± 0.01	30.77 ± 0.05	26.48 ± 0.04	4.29 ± 0.01	28.59 ± 1.63
SiO ₂	143.50 ± 0.73	34.14 ± 0.55	77.36 ± 0.02	9.23 ± 0.02	68.13 ± 0.01	71.91 ± 0.02	21.93 ± 0.02	49.98 ± 0.00	37.23 ± 3.92
UETS	23.32 ± 0.03	29.19 ± 0.19	28.15 ± 0.09	17.54 ± 0.08	10.61 ± 0.05	28.70 ± 0.12	25.20 ± 0.12	3.50 ± 0.01	26.85 ± 1.39
PTS	25.85 ± 0.03	32.59 ± 0.31	37.64 ± 0.04	16.51 ± 0.03	21.14 ± 0.02	36.67 ± 0.02	24.37 ± 0.01	12.30 ± 0.02	30.86 ± 2.11
TESU	26.37 ± 0.03	33.05 ± 0.35	40.89 ± 0.03	15.77 ± 0.03	25.12 ± 0.00	39.03 ± 0.05	24.30 ± 0.05	14.73 ± 0.00	31.76 ± 2.32
APTES	25.11 ± 0.03	33.06 ± 0.40	45.25 ± 0.03	14.51 ± 0.03	30.73 ± 0.00	44.12 ± 0.05	22.89 ± 0.05	21.24 ± 0.01	32.01 ± 2.44
oxUETS	26.02 ± 0.03	33.06 ± 0.36	42.00 ± 0.03	15.46 ± 0.03	26.54 ± 0.01	40.52 ± 0.02	23.81 ± 0.02	16.71 ± 0.00	31.85 ± 2.36
MPTES	24.79 ± 0.03	33.77 ± 0.46	59.47 ± 0.05	11.83 ± 0.04	47.64 ± 0.03	55.78 ± 0.03	22.47 ± 0.03	33.31 ± 0.00	34.41 ± 3.10
PEG69	24.34 ± 0.03	33.83 ± 0.51	62.51 ± 0.02	11.31 ± 0.02	51.21 ± 0.00	58.50 ± 0.01	22.29 ± 0.01	36.21 ± 0.00	34.78 ± 3.21

based on several different models. Table 3 shows the calculated surface energies in mN/m after the Zisman [38], Fowkes [39], Owens–Wendt–Rabel–Kaelble [36,37], Wu [40] and Equation-of-State (EOS) models [41].

In the Zisman method [38], critical surface tensions (γ_{crit}) are derived from a plot of $\cos\theta$ versus γ_1 (the test liquid's surface tension) for the various test liquid. The linear regression extrapolated value of γ_1 at $\cos\theta = 1$ equals the critical surface tensions (γ_{crit}). This linear relationship between $\cos\theta$ and γ_1 is based on the (outdated) assumption of Antonow [42] and practically only applies for purely disperse liquid–solid systems rendering the Zisman method rather limited and inaccurate. For FDTS for instance, a negative value is obtained, which is unphysical. However when water as test liquid is omitted in the Zisman fit, the calculated critical surface tension is ~ 6 mN/m, which corresponds well to values reported in literature [38,43]. For OTS,

critical surface tension values of 20.2 mN/m [18] and 20.5 mN/m [43] compare well with the value we obtained (20.03 mN/m). When the Zisman method is applied to polar surfaces, like clean silicon dioxide, the obtained value ($\gamma_{\text{crit}} = 143.5$ mN/m) no longer compares to values from more accurate methods, e.g. 72.6 mN/m from dynamic contact angle hysteresis [44] or 71.9 mN/m from the method after Wu (Table 3). In general, the values obtained by the Zisman method indicate a clear difference between low-energy surfaces (like FDTS and OTS) and high-energy surfaces (like clean SiO₂). It also shows a trend in surface energies that corresponds to what can be expected based on the chemical nature (e.g. hydrophobic, dipolar, hydrophilic) of the modified surfaces.

The method after Fowkes [39] uses an expression for γ_{sl} in which only the disperse component of the interface interactions is specified. Therefore this method is only suited for determination of the disperse contribution to the surface energy. The obtained values show again a similar trend and differences in surface energies as the Zisman method although less extreme.

The method after Owens–Wendt–Rabel–Kaelble [36,37] discerns between a polar and a disperse component of the surface energy and uses a geometric mean of these in the expression for γ_{sl} . The calculated surface energies show the high- and low-energy properties of respectively silicon dioxide and FDTS/OTS surfaces and compare well to reported literature (OTS: 23–25 mN/m, SiO₂: 72 mN/m) [44]. Again the values also nicely correspond to the trend expected from the chemical nature of the surface.

When looking at the different components of the surface energy, it can be seen that the disperse component is quite similar for most surfaces. The differences in surface energy between the substrates seem to be largely due to differences in their polar components. If the dipole moments of the molecules' end groups are compared with the polar components of their respective surface energy, one can see some correlation: molecules with no or a very small dipole moment (like FDTS, OTS and UETS) have a small polar contribution to surface energy; polar groups or bonds like in CUTS, APTES or in silicon dioxide give rise to large polar surface energy components. This correlation however does not fit all molecules, e.g. BUTS has a

Table 3
Critical surface tension (γ_{crit}) and surface energies (SE) with their disperse (Disp) and polar component, in mN/m, for the different substrates calculated according to the methods after Zisman, Fowkes, Owens–Wendt–Rabel–Kaelble, Wu and Equation-of-State (EOS)

Substrate	Measured static CA (in °)	Literature data (in °)
OTS	98.2 ± 0.3	~ 100 [6], 111 (from solution) [18]; 104 (from vapor phase) [19]
CUTS	68.1 ± 0.6	72 ± 2 [20]
PETS	87.9 ± 2.2	80 (for polystyrene), 69 [21]; 86 (for phenylundecyltrichlorosilane) [22]
FDTS	109.6 ± 0.4	119 [23]
BUTS	91.1 ± 1.5	82 ± 1 [20]; 84 [24]
Clean SiO ₂	< 10	~ 10 [21]
UETS	94.7 ± 1.4	~ 100 [25]
PTS	73.9 ± 0.8	63 [21] 72 [26]
TESU	69.7 ± 2.2	65 ± 2 (aldehyde-terminated thiol SAM) [27]; 60–70 (oxidation of 3-glucidoxypolytri-methoxysilane) [28]
APTES	58.4 ± 1.7	52–56 (APTES on quartz) [29]; 63 ± 2 (reduction of CUTS) [20]
oxUETS	66.3 ± 0.9	35 [25]; 54.9 ± 1.6 [30]
MPTES	40.3 ± 0.3	52 [31]; 67 ± 4 (from vapor phase) [32]
PEG6/9	35.8 ± 1.0	36 ± 2 [13]; 33 ± 3 (PEG silane) [33]

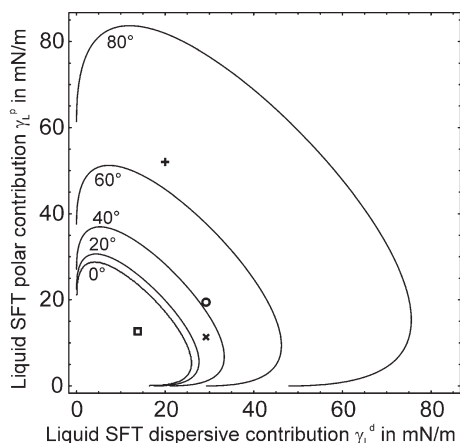


Fig. 2. Wetting envelope with 0°, 20°, 40°, 60° and 80° contours for a surface modified with phenyltrichlorosilane (PTS), polar and disperse surface tensions of valeronitrile (□; <10°), water (+; 73.9±0.8°), ethyleneglycol (O; 53.2±2.8°) and *N*-methylpyrrolidone (×; 19.7±3.1°) with the corresponding experimental contact angle values in brackets.

strong dipole but small polar component while PEG6/9 has a small dipole but strong polar component.

We conclude that the dipole moment of the end group alone cannot explain the polar component of the surface energy. Clearly, other factors like chain length, the influence of the silane group, the influence of the underlying, polar substrate, etc. must be involved. Maybe additional interactions like hydrogen-bonding and acid-base behaviour play a role in the wetting behaviour of solvents on functionalized surfaces.

The method after Wu [40] also discerns between a polar and a disperse component of the surface energy but uses a harmonic mean of these in the expression for γ_{sl} . The calculated values, trends and conclusions are very similar to those obtained using the OWRK method. On average the disperse component is slightly larger while the polar component is smaller. This might be attributed to the use of the harmonic mean which is a bit more accurate, especially for high-energy systems, than the geometric mean used in the OWRK method. Again the differences in surface energies for the various substrates are largely due to

differences in the polar components, while the disperse components are comparable.

Finally, the “Equation-of-State” method [41] is based on an empirical expression for γ_{sl} and only uses the total surface tension of the test liquid. In other words, this method does not discern the type of interaction, namely polar or disperse and is therefore practically less accurate and only applicable to mainly disperse systems. This is clear from our results: the obtained surface energy values compare reasonably well to the other methods except for substrates with higher surface energies, e.g. PEG6/9 or SiO₂.

3.3. Wetting envelope

Knowledge of a surface’s polar and disperse surface energy components allows the determination of the so-called wetting envelope of this surface. Now, the polar and disperse fractions of the liquid for which the contact angle is 0° ($\cos\theta=1$) are calculated with the same equations after OWRK or Wu. When this polar fraction is plotted against the disperse fraction, a closed contour for $\cos\theta=1$ is obtained which is called the wetting envelope. Similarly, contours for higher contact angles can be calculated and plotted. Knowledge of the wetting envelope allows easy wettability determination for current and future solvents as any liquid whose polar and disperse fraction lie within the contour for a certain contact angle, will wet the corresponding solid with the contact angle of this contour. This is illustrated in Fig. 2: the polar and disperse components of the surface tensions of valeronitrile (12.37 and 13.63 mN/m) [45], ethyleneglycol (19 mN/m and 29 mN/m) [46], *N*-methylpyrrolidone (11.58 mN/m and 29.21 mN/m after DataPhysics Instruments GmbH) and water (52.2 mN/m and 19.9 mN/m) [47] are plotted on the wetting envelope of a PTS-modified substrate. The point for water is lying between the 60° and 80° contour of the PTS wetting envelope which practically means that it will not wet a PTS-modified surface but rather show a contact angle between 60° and 80°. Experimentally we measured a contact angle for water of 73.9±0.8°. Valeronitrile is lying within the 0° contour indicating that this solvent will wet the PTS surface very well. This is confirmed

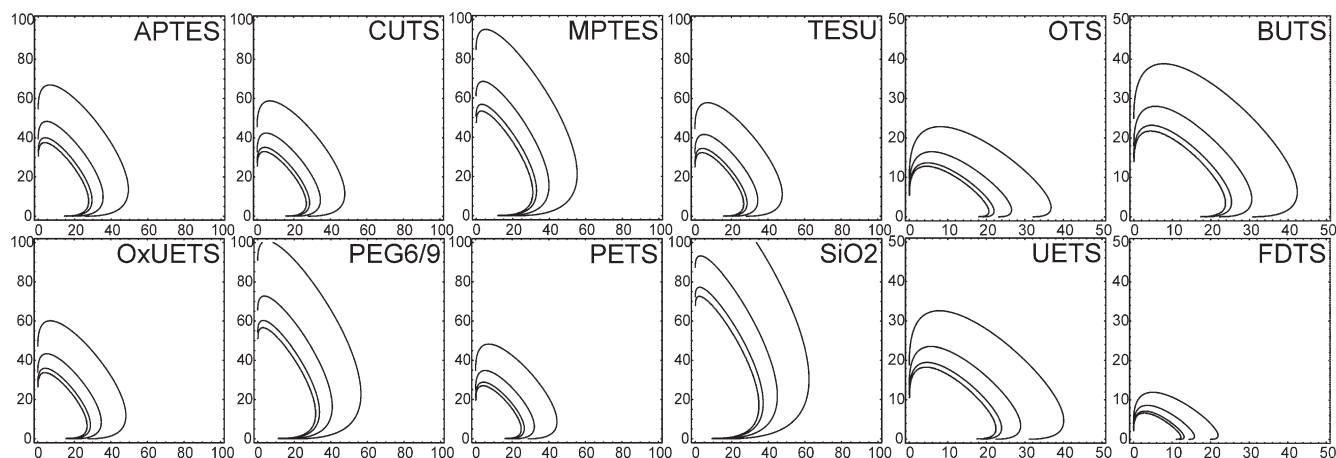


Fig. 3. Wetting envelopes with 0°, 20°, 40° and 60° contours and the dispersive and the polar surface tension in mN/m on the horizontal and the vertical axis. The scale is 0–100 mN/m except for OTS, BUTS, UETS and FDTS where it is 0–50 mN/m.

experimentally as the measured contact angle was too small to be accurately fitted by the software ($<10^\circ$). For NMP and ethyleneglycol, the wetting envelope predicts a contact angle between 20° and 40° and 40° and 60° . The measured values respectively are $19.7 \pm 3.1^\circ$ and $53.2 \pm 2.8^\circ$. Although the predicted contact angles are not exact, the example above clearly shows that wetting envelopes are more than accurate enough to practically obtain a good idea of the wetting behaviour of a solvent, even of solvents other than the ones studied herein. This ensures relevance of this study for current and future solvents. Wetting envelopes for the studied surfaces other than PTS are depicted in Fig. 3. All wetting envelopes were plotted based on the surface energy values obtained with the OWRK method.

4. Conclusion

In this paper we present an extensive study on the static contact angle of silicon dioxide surfaces modified by self-assembled monolayers with a wide range of practically relevant solvents, e.g. for spin-coating polymer solutions. These contact angle values give a direct indication of solvent wettability and allow the selection of the appropriate solvent or surface treatment to assure a good solvent wetting. From these data, we were also able to determine both the polar and the disperse component of the surface free energies of the modified surfaces with several models. In summary, surface energies extracted with the methods after Owens–Wendt–Rabel–Kaelble and Wu yield values which could be expected from the chemical structure and nature of the self-assembled molecules and which correspond well to the few reported literature values. For the different substrates, we plotted wetting envelopes and demonstrated their use as a more accessible way for determining wettability not only of the solvents used in this study but also for other and possibly relevant solvents now and in the future.

Acknowledgement

D.J. and R.D.P. gratefully thank IWT Vlaanderen for financial support. Part of this work has been supported financially by the European project NAIMO (IP500355).

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