A novel colored talc filler: Preparation and surface properties determination using two distinct methods

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ABSTRACT: A better understanding of a filler's surface properties is critical for determining the most effective polymer reinforcement fillers. In this work, a colored talc filler (CTF) was prepared and its surface properties were comparatively studied to those of talc filler (TF), using inverse gas chromatography (IGC) and contact angle methods—Owens-Wendt-Kaelble (OWK), van Oss-Chaudhury-Good (vOCG) and Wu. The results indicated that the dispersive component (γ_s^D) for both samples contributed a major part (68-81%) of the total surface energy (γ_s^T), and displayed a decreasing trend with increasing surface coverage, meaning the fairly energetic surface heterogeneity for them. The γ_s^D values determined by the contact angle methods were consistent, although lower than those using IGC analysis. The specific

1 component (γ_s^{SP}) calculated by the contact angle methods were also consistent and
2 lower than those calculated using IGC. The specific Gibbs free energies of adsorption
3 (ΔG^{sp}) changed with surface coverages, further confirming the heterogeneous nature
4 of both samples. The significantly lower γ_s^T value for CTF could reduce filler
5 particle-particle interactions, allowing a better dispersion in matrix, and thus lead to
6 an improvement in mechanical performance of CTF/polymer composite.

7 **KEYWORDS:** Talc filler; surface properties; inverse gas chromatography; contact
8 angle; MATLAB toolbox

9

10 NOTATION

11 OWK Owens-Wendt-Kaelble

12 vOCG van Oss-Chaudhury-Good

13 IGC inverse gas chromatography

14 TF and CTF talc filler and colored talc filler

15 γ_s , γ_L and γ_{SL} surface free energies of solid, liquid and solid-liquid (mJ/m²),
16 respectively

17 θ contact angle (°)

18 W_A , W_C work of adhesion (mJ/m²) and cohesion (mJ/m²)

19 γ_s^{LW} , γ_s^{AB} Lifshitz-van der Waals and Lewis acid-base component of surface free
20 energy (mJ/m²)

21 γ_s^+ , γ_s^- Lewis acid and Lewis base parameter of surface free energy (mJ/m²)

22 γ_s^D dispersive component of surface free energy (mJ/m²)

23 γ_s^{SP} specific component of surface free energy (mJ/m²)

- 1 γ_s^T total surface free energy (mJ/m²)
- 2 γ_{50}^D and γ_{50}^{SP} mean value of dispersive and specific component (mJ/m²)
- 3 ΔG_{sp} specific Gibbs free energies of adsorption (kJ/mol)
- 4 iGC-SEA iGC Surface Energy Analyzer
- 5
- 6
- 7

8 **1. Introduction**

9 Talc is a plate-like layered structure magnesium silicate mineral, in which the
 10 octahedral brucite layer is sandwiched between two tetrahedral silica sheets[1,2].
 11 Many reports have indicated an improvement in performance after a polymer matrix
 12 was reinforced with talc filler[3-7]. However, it is well known that, the filler nature of
 13 talc influences its reinforcement ability depending on the surface activity, particle size,
 14 specific surface area and surface functional groups[8,9]. Among these properties,
 15 surface activity affects the reinforcement ability the most, as the chemical nature of a
 16 particle's surface determines filler-filler and filler-matrix interactions. These
 17 interactions in turn affect the filler's dispersion in matrix and thus the final
 18 performance of composite[10]. Therefore, a better understanding of a filler's surface
 19 properties is critical for determining the most effective polymer reinforcement fillers.

20 Contact angle measurement is one of the most commonly used techniques for the
 21 solid surface characterization. The surface free energy of a solid can be determined by
 22 measuring the contact angles of different test liquids (the amount needed depending
 23 on the calculation methods) on its surface according to the Young's equation[11].
 24 There are numerous methods, such as the Zisman plot[12-14], Fowkes[15],
 25 Owens-Wendt-Kaelble (OWK)[16,17], van Oss-Chaudhury-Good (vOCG)[18] and

1 Wu[19] for calculating the surface energy from equilibrium liquid contact angles.
2 However, this method usually involves difficult and time-consuming experiments, as
3 factors such as surface roughness, chemical heterogeneity and bulk penetration of the
4 wetting liquid could result in contact angle hysteresis[20,21]. As an alternative,
5 inverse gas chromatography (IGC) has proven to be a reliable technique for surface
6 characterization, offering advantages of independence from sample morphology and
7 accurate measurement over a wide range of temperatures. However, to the best of our
8 knowledge, there are sparse reports on the surface characterization of talc-derived
9 fillers. Thus, in this work, a colored talc filler (CTF) was prepared and its surface
10 properties were comparatively studied with those of talc filler (TF), using IGC and
11 contact angle measurement—OWK, vOCG and Wu. It aims at probing the CTF as a
12 candidate filler for the masterbatch industry.

13 **2. Basic theories**

14 **2.1 Contact angle methods**

15 The key equation used to determine the solid surface energy by contact angle
16 measurement is the Young's equation[22], which was derived from the equilibrium
17 condition of forces representing surface tensions at the contact point of three phases:
18 solid, liquid and gas.

$$19 \quad \gamma_L \cos \theta = \gamma_S - \gamma_{SL} \quad (1)$$

20 where γ_S , γ_L and γ_{SL} are the surface free energies of solid, liquid and solid-liquid
21 (mJ/m^2), respectively. θ is the contact angle between the solid surface and test liquid
22 ($^\circ$).

23 In the Young's equation, both θ and γ_L are measurable. In order to obtain γ_S
24 and γ_{SL} by solving this equation, an additional relationship between these quantities
25 has to be made. An understanding of the different methods requires an explanation of

1 work of adhesion (W_A). The equation for W_A can be written as:

2
$$W_A = \gamma_A + \gamma_B - \gamma_{AB} \quad (2)$$

3 where γ_A and γ_B represent the surface tensions of phases A and B; and γ_{AB}
4 represents the interfacial tension between the two phases. For the solid-liquid system,
5 the equation can be written as:

6
$$W_A = \gamma_S + \gamma_L - \gamma_{SL} \quad (3)$$

7 Combining it with the Young's equation yields:

8
$$W_A = \gamma_L(1 + \cos \theta) \quad (4)$$

9 In a similar way, the work of cohesion (W_C) of one substance (e.g., A) can be
10 defined as:

11
$$W_C = \gamma_A + \gamma_A - 0 = 2\gamma_A \quad (5)$$

12 Berthelot[23] stabilized the direction to surface energy calculations and assumed
13 that W_A between the solid and liquid equals the geometric mean of individual
14 cohesion work.

15
$$W_A = \sqrt{W_{SS}W_{LL}} \quad (6)$$

16 Combining it with Eqs. 4 and 5 yields:

17
$$W_A = \sqrt{W_{SS}W_{LL}} = 2\sqrt{\gamma_S\gamma_L} = \gamma_L(1 + \cos \theta) \quad (7)$$

18 **2.1.1 OWK method**

19 Owen and Wendt[17] extended Fowkes' idea[24,25] and proposed the following
20 form for W_A :

21
$$W_A = 2\sqrt{\gamma_S^D\gamma_L^D} + 2\sqrt{\gamma_S^{SP}\gamma_L^{SP}} \quad (8)$$

22 Combining it with the Young's equation leads to Eq. 9:

$$\gamma_L(1 + \cos \theta) = 2\sqrt{\gamma_S^D \gamma_L^D} + 2\sqrt{\gamma_S^{SP} \gamma_L^{SP}} \quad (9)$$

There are two unknowns γ_S^D and γ_S^{SP} in Eq. 9, thus at least two liquids with known dispersive and specific components are needed to solve it. In this work, the surface energy parameters for TF and CTF were determined using formamide and diiodomethane as the test liquids.

2.1.2 vOCG method

Van Oss et al.[26-28] followed Fowkes' theory and treated surface energy as a sum of Lifshitz-van der Waals component (γ_S^{LW}) and acid-base component (γ_S^{AB}). The interfacial tension was postulated for solid-liquid systems as:

$$\gamma_{SL} = \gamma_S + \gamma_L - 2[\sqrt{\gamma_S^{LW} \gamma_L^{LW}} + \sqrt{\gamma_S^+ \gamma_L^-} + \sqrt{\gamma_S^- \gamma_L^+}] \quad (10)$$

Combining it with the Young's equation, we can obtain:

$$\gamma_L(1 + \cos \theta) = 2\sqrt{\gamma_S^{LW} \gamma_L^{LW}} + 2\sqrt{\gamma_S^+ \gamma_L^-} + 2\sqrt{\gamma_S^- \gamma_L^+} \quad (11)$$

Since there are three unknowns γ_S^{LW} , γ_S^+ and γ_S^- in Eq. 11, at least three test liquids are needed to solve it. In this study, the distilled water, formamide and diiodomethane were used.

2.1.3 Wu method

In addition to the OWK method, the other two liquid method for considering the harmonic mean relationship was proposed by Wu[19,29]. He discerned between dispersive and specific components of the surface energy, but instead of using the geometric mean as in Eq. 9, he uses a harmonic mean in the expression for γ_{SL} .

$$\gamma_{SL} = \gamma_S + \gamma_L - 4\left[\frac{\gamma_S^D \gamma_L^D}{\gamma_S^D + \gamma_L^D} + \frac{\gamma_S^{SP} \gamma_L^{SP}}{\gamma_S^{SP} + \gamma_L^{SP}}\right] \quad (12)$$

1 In combination with the Young's equation, Wu's equation can be written as:

$$\gamma_L(1 + \cos \theta) = \frac{4\gamma_S^D \gamma_L^D}{\gamma_S^D + \gamma_L^D} + \frac{4\gamma_S^{SP} \gamma_L^{SP}}{\gamma_S^{SP} + \gamma_L^{SP}} \quad (13)$$

3 As in the OWK method, Wu's method also requires the use of at least two liquids;
4 thus the formamide and diiodomethane were applied.

5 **2.2 IGC method**

6 **2.2.1 Surface energy**

7 The basic theory of IGC is presented here and more details can be found
8 elsewhere[30,31]. In IGC, the term “inverse” indicates that the solids to be examined
9 are packed into the column and this material is probed by gas mixtures injected into
10 the column. The injection of known molecule probes, including both nonpolar and
11 polar probes, enables us to characterize the surface properties of the packed materials.
12 Stationary-phase characterization can be achieved by partitioning the sample between
13 the mobile phase and the stationary phase, indicated by the time taken to elute the
14 samples. In IGC analysis, the surface energy has traditionally been determined at
15 infinite dilution (ID-IGC), where probe concentrations were kept low to rule out
16 lateral probe-probe interactions and favor probe-stationary phase interactions only. In
17 this case, the injected gas probes interacted with only the highest energy sites.
18 However, in reality many real solid surfaces are heterogeneous and more likely to
19 have a distribution of differing surface energy sites. The probe molecules should
20 interact with both low- and high-energy sites, although the interactions should be
21 dominated by the high energy sites. To address this shortcoming, IGC analysis has
22 been extended to finite concentrations (FD-IGC), allowing the construction of
23 adsorption isotherms for full surface characterization. These isotherms, covering a
24 wider or even an entire adsorption range, can provide more in-depth information on

adsorbate-adsorbent interactions, complement the analysis at infinite concentrations, and determine the surface energy distributions.

A standard procedure of solid surface characterization is that the γ_s^D is first calculated using a series of *n*-alkanes as probes (in this case, hexane, heptane, octane, nonane and decane); then the acid-base parameters can be obtained by measuring the specific Gibbs free energies of adsorption (ΔG^{sp}) for various polar probes (in this case, dichloromethane (DCM), toluene and chloroform). Based on the vOCG approach[32] and applying the Della Volpe scale[33] for surface tension components of polar solvents, the γ_s^{sp} is subdivided into Lewis acid (γ_s^+) and Lewis base (γ_s^-) components.

2.2.2 Surface energy distribution

Surface energy heterogeneity is one of the most useful characteristics provided by IGC. It manifests with a distribution of various surface sites with different energy levels and constitutes an energetic map of the solid surface, allowing a prediction of the materials properties, in particular the formulation of composites, adhesives or blends. Such a heterogeneity profile can be represented by an energy distribution function. It is worth mentioning that, IGC is not the only mean of measuring surface energy heterogeneity and alternative techniques are considered. The problem is that, contact angle measurement requires macroscopic crystals in order to determine specific energy contributions. Such measurements on specific crystalline facets may neglect edge effects and defects, and reflect a bulk average surface energy for solids. Another approach is adhesion force measurement by atomic force microscopy[34], but there are theoretical and technical challenges to this methodology. IGC provides data over a wide range of probe surface coverages, yielding information about the

relative heterogeneity of the surface energy distribution of a material[35].

3. Experimental

3.1 Raw materials

Raw black talc was supplied by Guang Feng Tian Tu Chemical Co., Ltd., China. It was calcined at high temperature to remove the impurities and obtain the talc filler (TF). C.I. Direct Red 28 (DR 28) was provided by Yiwu Yu Fang Pigment Co., Ltd., China.

3.2 CTF preparation

The TF powder is mixed with DR 28, water and hexadecyltrimethylammonium bromide at a weight ratio of 20: 2: 8.5: 1. After vigorous stirring, the mixture was left standing for 24 h. Then it was filtered and the filter cake was dried. The dried cake was ground to obtain the colored talc filler (CTF).

3.3 Characterization and tests

The surface energy characterization of TF and CTF were carried out using an iGC Surface Energy Analyzer (iGC-SEA, Surface Measurement Systems, UK). Approximately 300 mg of the powders were packed into individual dimethyldichlorosilane treated glass columns. The samples were run at surface coverages of 0.5-10% with polar and nonpolar molecular probes. The sample column was preconditioned for 1 h at 343.15 K and 0% RH with 10 ml/min helium carrier gas, under the same conditions as in the experiment. The contact angles of TF and CTF for three test liquids (distilled water, formamide and diiodomethane) were measured using the sessile drop method. The surface tension and its components for test liquids are listed in **Table 1**. The contact angle measurement was carried out at 20 °C and the ambient humidity using a goniometer (DSA100, Krüss GmbH, Germany).

Insert Table 1

4. Results and discussion

4.1 Contact angle methods

The contact angles for TF and CTF determined using the sessile drop method are listed in **Table 2**. It can be observed that there were no significant differences between the contact angles of both samples. In addition, contact angles for the three liquids were all less than 90°, implying an amphiphilic character for both samples. This was consistent with the results in literatures, where the contact angles of talc for water, formamide and diiodomethane were reported as 79, 43 and 42°, respectively[36]. Douillard et al.[37] revealed advancing contact angles of 60, 42 and 38° for water, formamide and diiodomethane, respectively.

Insert Table 2

4.2 Surface energy parameters

4.2.1 OWK method

The surface energy parameters calculation using this method in combination with MATLAB function are displayed in APPENDIX 1. For TF, the $\sqrt{\gamma_s^D}=6.6500$ and $\sqrt{\gamma_s^{SP}}=3.7140$, and thus c^2 is calculated to obtain $\gamma_s^D=44.2$ and $\gamma_s^{SP}=13.8$. For CTF, the $\sqrt{\gamma_s^D}=6.6184$ and $\sqrt{\gamma_s^{SP}}=3.6263$, and thus the $\gamma_s^D=43.8$ and $\gamma_s^{SP}=13.2$.

4.2.2 vOCG method

The surface energy parameters calculation in combination with MATLAB function are displayed in APPENDIX 2. For TF, the $\sqrt{\gamma_s^{LW}}=6.6500$, $\sqrt{\gamma_s^+}=0.9713$ and $\sqrt{\gamma_s^-}=6.6735$, and thus c^2 is calculated to obtain $\gamma_s^{LW}=44.2$, $\gamma_s^+=0.9$ and γ_s^-

1 =44.5. For CTF, the $\sqrt{\gamma_s^{LW}}=6.6184$, $\sqrt{\gamma_s^+}=0.8663$ and $\sqrt{\gamma_s^-}=6.8578$, and thus the
2 $\gamma_s^{LW}=43.8$, $\gamma_s^+=0.8$ and $\gamma_s^-=47.0$.

3 **4.2.3 Wu method**

4 The surface energy parameters calculation using the Wu method in combination
5 with MATLAB function are displayed in APPENDIX 3. The γ_s^D and γ_s^{SP} can be
6 directly obtained, and for TF, the $\gamma_s^D=44.4$, $\gamma_s^{SP}=14.1$; for CTF, the $\gamma_s^D=44.0$, γ_s^{SP}
7 =13.5.

8 **4.3 IGC method**

9 **4.3.1 Surface energy and distributions**

10 The combined plot of γ_s^D , γ_s^{SP} and γ_s^T profiles of TF and CTF obtained from
11 iGC-SEA are displayed in **Fig. 1**. The profiles showed that the γ_s^D component of
12 both samples contributed a major part (68-81%) of γ_s^T . In addition, the surface
13 energy displayed a decreasing trend with increasing surface coverage and the highest
14 energy sites occupied approximately 0.5% of the fillers. The difference in the
15 measured absolute γ_s^D values at low and high coverages indicated heterogeneity
16 among surface energy sites. For TF, the calculated γ_s^D fell into the range of
17 121.6-170.6 mJ/m² across the surface coverages measured. As a comparison, the CTF
18 showed a lower range of 51.1-76.8 mJ/m², which might be ascribed to its more
19 uniform surface after loading with DR 28.

20 Compared to γ_s^D , the γ_s^{SP} component contributed less to γ_s^T , implying a lower
21 polarity for both samples. The calculated γ_s^{SP} fell into the range of 28.8-40.0 mJ/m²

for TF and 18.1-34.6 mJ/m² for CTF. The γ_s^{SP} at each surface coverage was calculated from the basic γ_s^- and acid γ_s^+ components of surface energy using the vOGC concept. As compared to the γ_s^+ component, the γ_s^- component decreased remarkably at lower surface coverages.

Insert Fig. 1

In order to represent the heterogeneity of both samples in a more illustrative manner, the surface energy distributions were obtained by a point-by-point integration of the surface energy profiles, resulting in the plots of γ_s^D , γ_s^{SP} and γ_s^T surface energy versus percentage of surfaces (area increment), as shown in **Fig. 2**. As expected, all energetically heterogeneous samples had wide variations of surface sites. TF exhibited a wider range of γ_s^D distribution, from 114.38 to 172.35 mJ/m², with a mean value (γ_{50}^D) of 125.20 mJ/m²; whereas CTF had less pronounced energetic heterogeneity, with its γ_s^D distribution ranging from 43.45 to 76.83 mJ/m² and a γ_{50}^D of 49.69 mJ/m². In the case of γ_s^{SP} distribution, CTF exhibited a range of 15.50-19.19 mJ/m² with a γ_{50}^{SP} of 35.26 mJ/m². TF showed a range for the γ_{50}^{SP} distribution, from 29.44 to 39.46 mJ/m², with a γ_{50}^{SP} of 32.22 mJ/m².

Insert Fig. 2

4.3.2 Specific free energy profiles

The surface properties of fillers also depend on the ability to participate in specific interactions resulting from the presence of polar functional groups on the surface of the material. The ΔG_{SP} profiles resulting from the interactions with three polar probes (DCM, toluene, chloroform) for TF and CTF are displayed in **Fig. 3**. The

ΔG_{SP} changed with surface coverages, confirming the heterogeneous nature of the samples. Both samples also showed strong degrees of interaction with all the polar probes, but predominantly interacted with DCM. The ranking for decreasing ΔG_{SP} interactions was: DCM (acidic probe) > toluene (neutral probe) > chloroform (acidic probe) for TF and DCM (acidic probe) > chloroform (acidic probe) > toluene (neutral probe) for CTF.

Insert Fig. 3

4.3.3 Total work of cohesion and adhesion profiles

Knowledge of the surface energies between filler particles would allow an objective decision to be made about the extent of filler-matrix interaction. The extent of the interaction between filler particles could be quantified by the W_C , which in turn can be determined by IGC. The plot of W_C for TF and CTF is shown in **Fig. 4**. The W_C between filler particles was determined as 300.8-421.2 mJ/m² for TF and 138.4-222.8 mJ/m² for CTF. The CTF showed a significantly lower W_C value compared to the TF, indicating weaker filler-filler interactions, which could lead to an increase in composite performance. The W_C profiles were similar to the γ_s^D profiles, as the W_C is equivalent to $2\gamma_s^T$, confirming that most of the γ_s^T can be attributed to the dispersive contribution. The W_A of water and dimethyl sulfoxide (DMSO) molecules on TF and CTF surfaces was also included in **Fig. 4**. It showed that, for both samples, the W_A of DMSO was larger than that for water across all surface coverages. The larger W_A values of DMSO indicated a relatively better dissolution property in DMSO and a more lipophilic nature for the material surfaces.

Insert Fig. 4

4.4 Surface energy comparsion

The surface energy calculated using IGC and three contact angle methods are included in **Table 2**. It can be observed that the γ_s^D determined by the OWK, vOCG and Wu method were consistent, but lower than those using IGC analysis. From a theoretical point of view, the results obtained from IGC and contact angle measurement are somewhat different. Ticehurst et al.[38] claimed that the γ_s^D results from the two methods cannot be identical, because of the distinction in their theoretical approaches. In the surface characterization of phenol-formaldehyde-lignin resin, Matsushita et al.[39] also observed a discrepancy between the absolute values of γ_s^{LW} calculated by the two methods. However, in the measurement of pharmaceutical powders, Planinšek et al.[40] found a good correlation between results obtained from the two methods. Thus, a satisfactory solution to this question would require further systematic study comparing data obtained from both methods. In fact, IGC analysis performed to determine γ_s^D is mostly carried out under infinitely dilute conditions, where minimal doses of molecular probes are used. Therefore, any information obtained from IGC under these conditions will mainly concern the most active sites of the solid surfaces, which may constitute only a small fraction of the surface examined. In addition, IGC evaluates mainly high energy sites, which is associated with preferential interactions of injected probes with these sites on the heterogeneous surface of stationary phase[41,42].

As for γ_s^{SP} , it fell into the range of 28.8-40.0 mJ/m² for TF and 18.1-34.6 mJ/m² for CTF, as determined by IGC. As a comparison, the γ_s^{SP} values calculated by the contact angle methods were also lower. A difference in γ_s^{SP} between the two methods was reported as well[43], a result that can be expected because an infinite IGC operates at zero surface coverage of the probe molecules, and predominantly

1 detects high energy sites[44]. Thus, the γ_S^{SP} values obtained by IGC will often be
2 larger than those obtained by contact angle methods, as the latter detect surface sites
3 of all energy levels and thus determine an average energy level for the solid surface.

4 The γ_S^T values determined by IGC were in the range of 150.4-210.6 mJ/m² for
5 TF and 69.2-111.4 mJ/m² for CTF. The values determined by OWK, vOCG and Wu
6 methods were consistent, but also lower than those determined by IGC. According to
7 Eq. 5, W_C equals $2\gamma_S^T$. Therefore, the CTF showed lower W_C as compared to TF,
8 which could reduce the filler particle-particle interactions, allowing its better
9 dispersion in a polymer matrix.

10 **5. Conclusion**

11 The γ_S^D component for TF and CTF contributed a major part of γ_S^T and
12 changed as a function of surface coverages, indicating the fairly energetic surface
13 heterogeneity for both samples. The values determined using the three contact angle
14 methods in combination with MATLAB function were consistent, although lower
15 than those obtained by IGC analysis. Compared to γ_S^D , the γ_S^{SP} component
16 contributed less to γ_S^T , implying a lower polarity for both samples. The values
17 calculated by the contact angle methods were consistent, and also lower than those
18 calculated using IGC. The ΔG^{sp} changed with surface coverages, further confirming
19 the heterogeneous nature of both samples. The lower γ_S^D and γ_S^{SP} values for CTF
20 added up to a lower γ_S^T value, which could reduce filler particle-particle interactions,
21 and thus lead to an increase in polymer composite performance.

23 **APPENDIX 1**

24 MATLAB function for the calculation using OWK method:

$$\begin{aligned}
1 \quad & a = [\gamma_{FL}^D \wedge 0.5 * 2 \quad \gamma_{FL}^{SP} \wedge 0.5 * 2; \quad \gamma_{DL}^D \wedge 0.5 * 2 \quad \gamma_{DL}^{SP} \wedge 0.5 * 2] \\
2 \quad & b = [\gamma_{FL} * (1 + \cos(\theta_F * \pi / 180)); \quad \gamma_{DL} * (1 + \cos(\theta_D * \pi / 180))] \\
3 \quad & c = a \backslash b
\end{aligned}$$

4 where γ_{FL}^D , γ_{FL}^{SP} and γ_{FL} represent the γ_L^D (39.0 mJ/m²), γ_L^{SP} (19.0 mJ/m²) and
5 γ_L (58.0 mJ/m²) of formamide (as seen in **Table 1**), respectively. θ_F represent the
6 contact angles of TF and CTF for formamide (8° for TF and 14° for CTF, as seen in
7 **Table 2**). Similarly, γ_{DL}^D , γ_{DL}^{SP} and γ_{DL} are the γ_L^D (50.8 mJ/m²), γ_L^{SP} (0 mJ/m²)
8 and γ_L (50.8 mJ/m²) of diiodomethane. θ_D is the contact angle of two samples for
9 diiodomethane (30° for TF and 31° for CTF). The result array c equals $\sqrt{\gamma_s^D}$ and
10 $\sqrt{\gamma_s^{SP}}$; thus c² need be further calculated to obtain γ_s^D and γ_s^{SP} .

11 The calculation for TF:

$$\begin{aligned}
12 \quad & \gg a = [39.0 \wedge 0.5 * 2 \quad 19.0 \wedge 0.5 * 2; \quad 50.8 \wedge 0.5 * 2 \quad 0 \wedge 0.5 * 2] \\
13 \quad & b = [58.0 * (1 + \cos(8 * \pi / 180)); \quad 50.8 * (1 + \cos(30 * \pi / 180))] \\
14 \quad & c = a \backslash b \\
15 \quad & a = \\
16 \quad & \quad 12.4900 \quad 8.7178 \\
17 \quad & \quad 14.2548 \quad 0 \\
18 \quad & b = \\
19 \quad & \quad 115.4355 \\
20 \quad & \quad 94.7941 \\
21 \quad & c = \\
22 \quad & \quad 6.6500 \\
23 \quad & \quad 3.7140
\end{aligned}$$

24 The calculation for CTF:

$$25 \quad \gg a = [39.0 \wedge 0.5 * 2 \quad 19.0 \wedge 0.5 * 2; \quad 50.8 \wedge 0.5 * 2 \quad 0 \wedge 0.5 * 2]$$


```

1      b=[58.0*(1+cos(14*pi/180)); 50.8*(1+cos(31*pi/180))]
2
3      c=a\b
4
5      a =
6
7      12.4900    8.7178
8
9      14.2548    0
10
11     b =
12
13     114.2772
14
15     94.3441
16
17     c =
18
19     6.6184
20
21     3.6263

```

APPENDIX 2

MATLAB function for the calculation using vOCG method:

```

14  a=[  $\gamma_{WL}^D$  ^0.5*2   $\gamma_W^-$  ^0.5*2   $\gamma_W^+$  ^0.5*2;  $\gamma_{FL}^D$  ^0.5*2   $\gamma_F^-$  ^0.5*2   $\gamma_F^+$  ^0.5*2;  $\gamma_{DL}^D$  ^0.5*2
15       $\gamma_D^-$  ^0.5*2   $\gamma_D^+$  ^0.5*2]

```

```

16  b=[  $\gamma_{WL}$  *(1+cos( $\theta_w$ *pi/180));  $\gamma_{FL}$  *(1+cos( $\theta_F$ *pi/180));  $\gamma_{DL}$  *(1+cos( $\theta_D$ *pi/180))]

```

```

17  c=a\b

```

where γ_{WL}^D , γ_W^- , γ_W^+ and γ_{WL} are the γ_L^D (21.8 mJ/m²), γ^- (25.5 mJ/m²), γ^+ (25.5 mJ/m²) and γ_L (72.8 mJ/m²) of water (as seen in **Table 1**), respectively. θ_w is the contact angles of TF and CTF for water (24° for TF and 23° for CTF, as seen in **Table 2**). Other symbols for ethylene glycol and diiodomethane are presented in a similar way. The result array c equals $\sqrt{\gamma_S^{LW}}$, $\sqrt{\gamma_S^+}$ and $\sqrt{\gamma_S^-}$, and c² also need be calculated to obtain the γ_S^{LW} , γ_S^+ and γ_S^- .

The calculation for TF:

```

25  >> a=[21.8^0.5*2  25.5^0.5*2  25.5^0.5*2; 39.0^0.5*2  39.6^0.5*2  2.28^0.5*2;

```

```

1  50.8^0.5*2 0^0.5*2 0^0.5*2]
2      b=[72.8*(1+cos(24*pi/180)); 58.0*(1+cos(8*pi/180)); 50.8*(1+cos(30*pi/180))]
3      c=a\b
4      a =
5          9.3381    10.0995    10.0995
6          12.4900    12.5857    3.0199
7          14.2548         0         0
8      b =
9          139.3061
10         115.4355
11         94.7941
12      c =
13         6.6500
14         0.9713
15         6.6735
16      The calculation for CTF:
17      >> a=[21.8^0.5*2 25.5^0.5*2 25.5^0.5*2; 39.0^0.5*2 39.6^0.5*2 2.28^0.5*2;
18  50.8^0.5*2 0^0.5*2 0^0.5*2]
19      b=[72.8*(1+cos(23*pi/180)); 58.0*(1+cos(14*pi/180)); 50.8*(1+cos(31*pi/180))]
20      c=a\b
21      a =
22          9.3381    10.0995    10.0995
23          12.4900    12.5857    3.0199
24          14.2548         0         0
25      b =
26          139.8128
27          114.2772
28          94.3441
29      c =

```

1 6.6184

2 0.8663

3 6.8578

4 **APPENDIX 3**

5 MATLAB function for the calculation using Wu method:

6 gamma_L=[γ_{FL} γ_{DL}];

7 theta=[θ_F θ_D];

8 y=gamma_L.*(1+cosd(theta));

9 gamma_{DL}=[γ_{FL}^D γ_{DL}^D];

10 gamma_{SPL}=[γ_{FL}^{SP} γ_{DL}^{SP}];

11 x=[gamma_{DL}

12 gamma_{SPL}];

13 f=@(a,x)(4*a(1)*x(1,:)/(a(1)+x(1,:))+4*a(2)*x(2,:)/(a(2)+x(2,:)));

14 [beta]=nlinfit(x,y,f,[20 20]);%

15 warning('off');

16 fprintf('gamma_{DS}=%f\n',beta(1));

17 fprintf('gamma_{SPS}=%f\n',beta(2))

18 where γ_{FL} , γ_{FL}^D and γ_{FL}^{SP} represent the γ_L (58.0 mJ/m²), γ_L^D (39.0 mJ/m²) and

19 γ_L^{SP} (19.0 mJ/m²) of formamide (as seen in **Table 1**), respectively. θ_F is the contact

20 angles of TF and CTF for formamide (8° for TF and 14° for CTF, as seen in **Table 2**).

21 Other symbols are presented in a similar way for diiodomethane. Not similar to the

22 OWK and vOCG method, the two unknowns γ_S^D and γ_S^{SP} can be directly obtained

23 using this method. The gamma_{DL}, gamma_{SPL}, gamma_{DS} and gamma_{SPS} represent γ_L^D ,

24 γ_L^{SP} , γ_S^D and γ_S^{SP} , respectively.

1 The calculation for TF:

```
2       >> gammaL=[58.0 50.8];
3       theta=[8 30];
4       y=gammaL.*(1+cosd(theta));
5       gammaDL=[39.0 50.8];
6       gammaSPL=[19.0 0];
7       x=[gammaDL
8         gammaSPL];
9       f=@(a,x)(4*a(1)*x(1,:)./(a(1)+x(1,:))+4*a(2)*x(2,:)./(a(2)+x(2,:)));
10      [beta]=nlinfit(x,y,f,[20 20]);%
11      warning('off');
12      fprintf('gammaDS=%f\n',beta(1));
13      fprintf('gammaSPS=%f\n',beta(2))
14      gammaDS=44.421377
15      gammaSPS=14.093834
```

16 The calculation for CTF:

```
17      >> gammaL=[58.0 50.8];
18      theta=[14 31];
19      y=gammaL.*(1+cosd(theta));
20      gammaDL=[39.0 50.8];
21      gammaSPL=[19.0 0];
22      x=[gammaDL
23         gammaSPL];
24      f=@(a,x)(4*a(1)*x(1,:)./(a(1)+x(1,:))+4*a(2)*x(2,:)./(a(2)+x(2,:)));
25      [beta]=nlinfit(x,y,f,[20 20]);%
26      warning('off');
27      fprintf('gammaDS=%f\n',beta(1));
28      fprintf('gammaSPS=%f\n',beta(2))
29      gammaDS=44.027748
```

gammaSPS=13.488760

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1 **Figure captions:**

2 Fig. 1. Surface energy profiles of TF and CTF as a function of surface coverages

3 Fig. 2. Surface energy distributions of TF and CTF

4 Fig. 3. Specific free energy profiles of different solvents for TF and CTF as a function
5 of surface coverages

6 Fig. 4. Total work of cohesion and adhesion profiles of TF and CTF as a function of
7 surface coverage

8

1

Fig. 1

1

Fig. 2

1

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Fig. 3

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2

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Fig. 4

Table 1. Surface tension and its components for the probe liquids

Surface energy parameters (mJ/m ²)	Water	Formamide	Diiodomethane
γ_L	72.8	58.0	50.8
γ_L^D	21.8	39.0	50.8
γ_L^{SP}	51.0	19.0	0
γ^+	25.5	2.28	0
γ^-	25.5	39.6	0

Table 2. Surface energy and its components for two samples obtained by contact angle measurement and IGC

Samples	Contact angles (°)			Surface energy parameters (mJ/m ²)															
				OWK			vOCG					Wu			IGC				
	Water	Formamide	Diiodomethane	γ_s^T	γ_s^D	γ_s^{SP}	γ_s^T	γ_s^{LW}	γ_s^{AB}	γ_s^+	γ_s^-	γ_s^T	γ_s^D	γ_s^{SP}	γ_s^T	γ_s^D	γ_s^{SP}	γ_s^+	γ_s^-
TF	24	8	30	58.0	44.2	13.8	56.9	44.2	12.7	0.9	44.5	58.5	44.4	14.1	150.4-210.6	121.6-170.6	28.8-40.0	18.4-19.5	11.1
CTF	23	14	31	57.0	43.8	13.2	56.1	43.8	12.3	0.8	47.0	57.5	44.0	13.5	69.2-111.4	51.1-76.8	18.1-34.6	10.1-18.7	8.1