Quantitative Surface Free Energy with Micro-Colloid Probe Pairs

Ehtsham-Ul Haq[a]*, Yongliang Zhang[a], Noel O'Dowd[b], Ning Liu[a], Stanislav Leesment[c], Claude Becker[d], Edoardo M. Rossi[e], Marco Sebastiani[e], Syed A. M. Tofail[a] and Christophe Silien[a]*

* Ehtsham.U.Haq@ul.ie and Christophe.Silien@ul.ie

[a] Department of Physics and Bernal Institute, University of Limerick, V94 T9PX, Limerick, Ireland

[b]School of Engineering and Bernal Institute, University of Limerick, V94 T9PX, Limerick, Ireland

[c] Funcoats SA, Technoport 4B, rue du commerce Foetz, Luxembourg

*[d] Spectrum Instruments Ltd., Stewart House, National Technological Park, Limerick, Ireland*

[e] Engineering Department, Roma Tre University, Via della Vasca Navale 79, 00146 Rome, Italy

Supplementary information (tables and figures)

Table S1: Recorded contact angle wetting measurements on the five test surfaces, using three solvents. Total (T), polar (P), and dispersive (D) components of the SFE calculated using Owen-Wendt approach.

sample	contact angle (degrees)			SFE (T) (mJ/m^2) Owen-Wendt	SFE (P) (mJ/m^2) Owen-Wendt	SFE(D) (mJ/m^2) Owen-Wendt
	water	methylene iodide	formamide			
sh-Si	163±2	121±1	120±4	4±1	1±0.5	3±0.5
HOPG	65±2	46±2	63±1	42±5	12±2	30±3
silica/Si	62±2	50±1	44±1	46±1	13±1	33±1
Si	47±4	43±2	32±3	56±3	29±1	26±2
mica	20±3	48±1	6±2	68±2	37±1	32±1

Figure S2: (left) Second-order regression of F_{pull} on the CA-derived SFE values for the testing set with PS colloidal probe (regression coefficients computed on the training set). (center) Same with silica colloidal probe. (right) Same with PS and silica colloidal probes combined. The data for sh-Si are shown in black, HOPG in red, silica in green, silicon in blue, and mica in cyan.
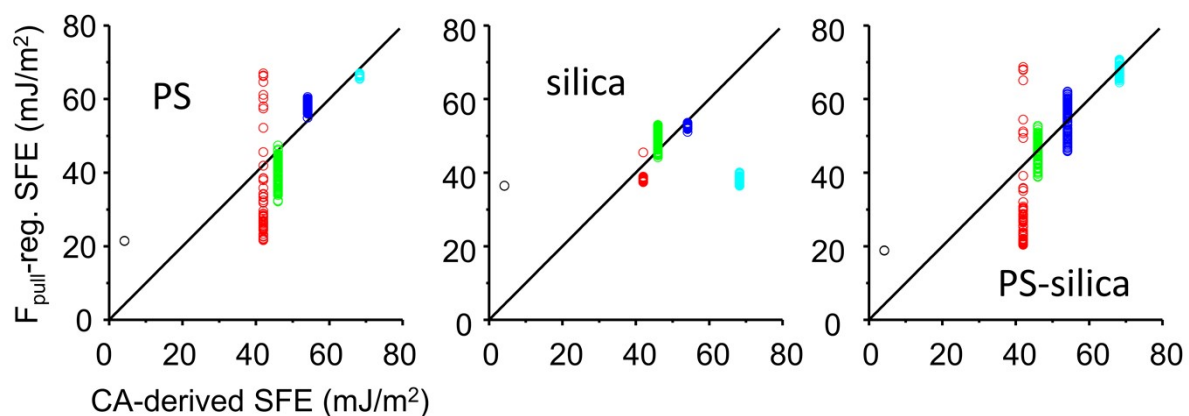
Figure S3: Table compiling the R-squared values obtained when fitting the metrics median of samples of 1, 5, 10, and 20 $F(d)$ curves onto the CA-derived SFE values. The values are shown for both training and test sets. From left to right: for PC analysis with the PS colloidal probe alone, silica probe alone, PS and silica combined, and for the fitting of median of the F_{pull} values with the PS colloidal probe alone, silica probe alone, PS and silica combined. (bottom): scatter plots of R-squared values extracted from the table (for the test sets only). R-squared >0.95 are found with samples of 10 curves and above when both colloidal probe data are combined.

sampling	PCA						Fpull					
	PS train	PS test	silica train	silica test	PS-silica train	PS-silica test	PS train	PS test	silica train	silica test	PS-silica train	PS-silica test
1	0.66971	0.64319	0.016462	-0.15695	0.69381	0.73907	0.18086	0.22439	-6.3056	-6.87	0.42288	0.39073
5	0.6708	0.66778	0.14409	0.081478	0.89886	0.90548	0.54283	0.55214	-7.2944	-7.2062	0.61941	0.59651
10	0.71749	0.71172	0.6448	0.71065	0.95393	0.94586	0.57038	0.59352	-7.1951	-6.8748	0.64845	0.66562
20	0.74323	0.74036	0.79779	0.81337	0.96459	0.96152	0.57836	0.58249	-7.1803	-6.8747	0.6441	0.62243
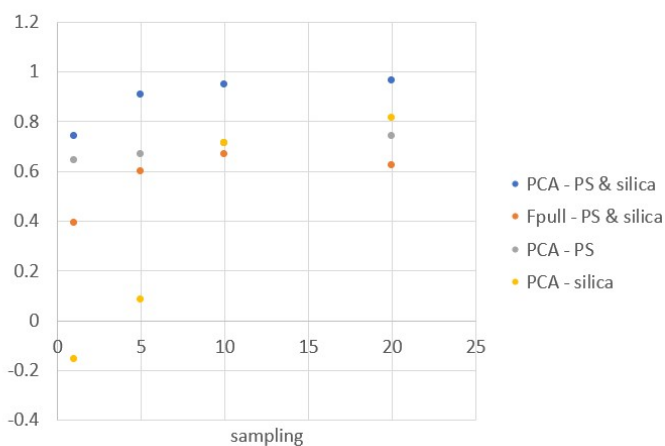
Figure S4: PC2 vs. PC1 scatter plots including ITO data. The reference surfaces sh-Si, HOPG, silica, silicon, and mica used to create the PC models are respectively plotted in red, green, blue, cyan, and magenta. The data for ITO are shown in yellow. The PCs for ITO were computed after establishing the transformation parameters from the five reference surfaces, used thus as the training set. The same five reference surfaces were used to fit the regression models, with the CA-derived SFEs used as targets. (a) PC model developed for the PS colloidal probe. (b) PC model developed for the combined PS and silica colloidal probes.
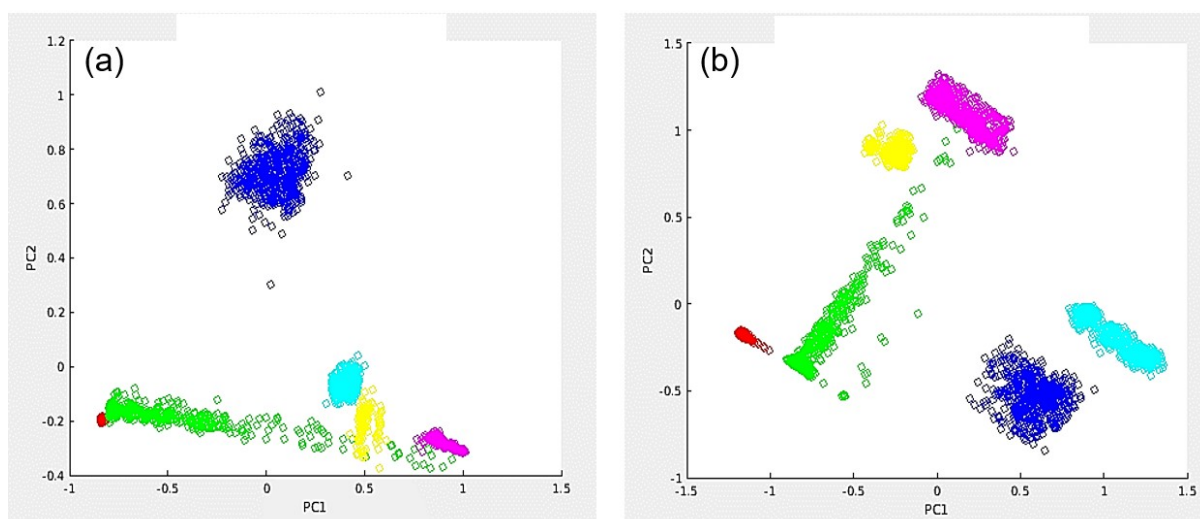
Figure S5: F(d) curves recorded on the mica reference surface using the PS colloidal probe: (a) with probe velocity of 100 nm/sec; (b) with tip velocity of 1000 nm/sec.