Surface Tension of Polytrifluoropropylmethylsiloxane

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Synopsis

Surface tension studies of the most common fluorosilicone, poly(3,3,3-trifluoropropylmethyl-siloxane) (PTFPMS), give unexpected results. Compared to polydimethylsiloxane (PDMS) the liquid surface tension is higher, the critical surface tension of wetting similar, and the solid surface tension, determined by water and methylene iodide contact angles and the method of Owens and Wendt, considerably lower. As the outermost surface of the lowest energy materials are comprised of close-packed perfluoromethyl groups and as a flexible polymer backbone should aid in the adoption of the lowest surface energy configuration, fluorosilicones could in principle be the lowest surface energy polymers. In practice, other groups such as the ethylene link between the perfluoromethyl group and the siloxane backbone in PTFPMS are required to produce a stable material. This introduces factors such as bulkiness of side chains, unresolved fluorocarbon/hydrocarbon dipoles, and fluorine/silicon coordination effects. The results are discussed in these terms and compared with PDMS and two fluoropolymers, polytetrafluoroethy-lene (PTFE) and polychlorotrifluoroethylene (PCTFE). PTFE shows similar trends to PTFPMS whereas PCTFE behaves rather like PDMS.

INTRODUCTION

The simple notion of regarding polymer side chains or pendent groups as the primary surface active entities with the polymer backbone controlling the way in which these pendent groups are presented at a surface has proved useful in describing the surface properties of silicones, particularly the most common commercially available materials, the polydimethylsiloxanes (PDMS).[1] In this view, PDMS is seen as a particularly favored case of a very surface active (low surface energy) pendent group, the methyl group, arranged along the most flexible backbone, the siloxane chain, that thus allows the methyl groups to be presented to their best effect. This separation of the roles of pendent group and backbone is a gross simplification but is useful in explaining why PDMS has a critical surface tension of wetting similar to hydrocarbons whose surface consists of close-packed methyl groups. Because of the extreme localization of the fields of force in covalently bonded methyl groups, the pendent methyl groups on PDMS also behave as an array of close-packed methyl groups with little direct effect from the siloxane back-bone. These concepts of Zisman[2] are reflected in his critical surface tension of wetting tables where the lowest energy surfaces are those based on CF_3— and —CF_2— entities. Fluorosilicones, with such groups as the pendent groups on the siloxane backbone, should thus be the ultimate low surface energy poly-mer—the lowest surface energy entities arranged on the most flexible back-bone. Hence our interest in the surface activity of fluorosilicones.

Unfortunately, having aliphatic fluorocarbon side chains directly pendent to the siloxane backbone does not result in useful materials. Fluorinated substituents on the first and second carbon atom weaken the Si—C bond causing a tendency to eliminate fluorine from these positions 1 or 2 to silicon and form SiF bonds. This is particularly so with nucleophilic agents.[3] Consequently, hydrolytic stability of such materials is poor, especially under alkaline conditions. The thermal stability of 1- and 2-fluoroalkyl silicon compounds is also low, partly owing to the high affinity of fluorine for silicon. Practical interest has thus focussed on fluoroorganosilicones in which the fluorocarbon substituent is sufficiently far from the Si—C bond, usually on the third carbon atom. The most familiar fluorosilicone is the first of this series, poly(3,3,3-trifluoropropylmethylsiloxane) (PTFPMS). In surface energy terms the effects of the CF_3— and the —CH_2— groups are contradictory, the CF_3— group being intrinsically more surface active, i.e., lower surface energy, than CH_3— and the —CH_2— group being less surface active. In principle, either a lower or a higher surface tension for PTFPMS than PDMS could be rationalized. In practice, the liquid surface tension of PTFPMS is higher than PDMS while the critical surface tensions of wetting are very similar.[1] To shed further light on this situation, the solid surface tension of PTFPMS has been determined by the method of Owens and Wendt[4] using water and methylene iodide. A major advantage of this approach is that there is a considerable literature available for data comparison. The surfaces studied have been characterized by XPS (X-ray photoelectron spectroscopy).

EXPERIMENTAL

The contact angles were determined using a Ramé-Hart Inc., NRL model A-100 contact angle goniometer. Results quoted are the average of both sides, measured numerous times, of at least five drops in each case. No systematic changes in value with time were observed, and thus the reported values can be taken to be equilibrium values—the shortest drop ages were of the order of 20 s; the longest were about 10 min. Only advancing contact angles on previously unwetted portions of the samples were taken. No receding contact angles were measured, and no comments on contact angle hysteresis are possible. Purity of the test liquids was checked using a Rosano Wilhelmy plate surface tensiometer based on a manual Roller–Smith precision balance. The surface tension was 71.6 mN/m (23°C) for water and 49.4 mN/m (23°C) for methylene iodide.

The combined Owens-Wendt/Young equation used is:

$$\frac{\sigma_1(1 + \cos\theta)}{2\left(\sigma_1^d\right)^{1/2}} = \left(\sigma_2^d\right)^{1/2} + \left(\sigma_2^p\right)^{1/2}\left(\frac{\sigma_1^p}{\sigma_1^d}\right)^{1/2}$$

where θ is the contact angle, and σ is surface tension.

Subscript 1 refers to the contact angle test liquids, subscript 2 to the solid. Superscript d refers to the dispersion force component of surface tension, superscript p to the polar component. The values used for these components come from Kaelble et al.[5] The solid surface tension can be readily obtained from the intercept and slope of this equation.

XPS data were collected on a cryopumped Perkin Elmer Physical Electronics Model 550 ESCA/AES instrument with double-pass cylindrical mirror analyzer. A pass energy of 100 eV was used for both the survey and atomic composition multiplex spectra in conjunction with the Mg anode x-ray source. Raw spectral data were manipulated using Physical Electronics version V MACS software.

The basic elastomer formulation used was 100 parts gum, 10 parts filler treatment, 35 parts MS75 silica filler and 0.5 parts Lupersol 101 catalyst. This constant level of catalyst should give similar crosslinking densities. No attempt was made to relate crosslink density differences to surface tension. Previous work with PDMS[6] showed no systematic variation of surface tension with crosslink density

RESULTS AND DISCUSSION

Sample descriptions are given in Table I, XPS data in Table II, and contact angle data and derived solid surface tensions in Table III. The key piece of data is given first. This is freshly cleaved, crosslinked PTFPMS without the complications of added filler and filler treatments. Significant accumulations of minor impurities driven by surface tension differences or incompatibility

TABLE I
Description of Elastomer Samples

Sample no.	Polymer (all cross linked)	Filler	Type of surface
1	PTFPMS	None	Cleaved
2	PTFPMS	None	Molded against PTFE
3	PTFPMS	PTFPMS–treated silica	Molded against PTFE
4	PTFPMS	PDMS-treated silica	Molded against PTFE
5	PTFPMS	PTFPMS-treated silica	Molded against Al
6	PTFPMS	PTFPMS-treated silica	Cleaved
7	PTFPMS	PDMS-treated silica	Cleaved
8	PDMS	PDMS-treated silica	Molded against Al

TABLE II
XPS Data

Sample no.	Atomic composition (%)			
	F	O	C	Si
1	38.1	11.1	40.7	10.1
2	38.3	11.3	39.8	10.5
3	37.3	11.9	39.8	11.1
4	37.9	12.0	39.0	11.1
5	36.4	12.8	39.7	11.2
6	35.7	13.7	39.0	11.6
7	29.6	18.5	37.8	14.2
PTFPMS theory	33.3	11.1	44.4	11.1
PTFE theory	66.7	0	33.3	0
PDMS theory	0	25	50	25

TABLE III
Contact Angle Data

| | Contact angle (°) | | Solid surface tension (mN/m) | | |
Sample no.	Water	Methylene iodide	Polar component	Dispersion force component	Total
1	104	90	2.8	10.8	13.6
2	110	92	1.4	10.6	12.0
3	104	89	2.6	11.2	13.8
4	104	89	2.6	11.2	13.8
5, region A	96	71	1.6	20.7	22.3
5, region B	96	86	3.9	12.0	15.9
6	102	87	3.0	12.0	15.0
7	102	87	3.0	12.0	15.0
8	96	68	2.0	22.1	24.1
Unfilled PDMS[7]	102	69	0.8	22.7	23.5
PTFE[4,8]	108	88	1.5	12.5	14.0
PTFE (This work)	106	88	2.2	11.9	14.1

take time to develop and the use of freshly cleaved surfaces avoids this problem.

Sample preparation evolved during the study as we became aware of possible contamination problems. Initial samples were molded against PTFE, but this was later changed to solvent cleaned aluminum (toluene and acetone), as shown in Table I. These latter surfaces were not disturbed until the measurements were taken. Earlier samples were lightly rinsed with absolute ethanol before measurement. Under sideways tension, PTFPMS elastomers can be smoothly cleaved with little more pressure than the weight of a sharp, clean knife. Using this technique, we obtained fresh, smooth surfaces which gave consistent contact angles.

If we accept the XPS composition of sample no. 1 as defining the surface composition of pure PTFPMS, then it is noticeable that other PTFPMS surfaces studied of similar composition, notably samples 2, 3, and 4 which were molded against PTFE liners, have similar surface tension. The simplest interpretation is that these four surfaces are all pure PTFPMS and the unexpectedly low solid surface tension is characteristic of PTFPMS. An alternative hypothesis that was held early on in this study, but no longer believed, is that these surfaces are contaminated with PTFE. This was because of the closeness of the derived surface tension to that of PTFE (see Table III) and the somewhat higher XPS fluorine content than theoretical (see Table II). However, the freshly cleaved surface does not fit this hypothesis. Moreover, XPS agreement with theory is not bad; it is within 10–15% of expectation, only a little worse than the 5–10% usually experienced with PDMS.

Sample 5 molded against aluminum, with a lower fluorine content nearer theoretical expectation, was initially felt to be cleaner but is now believed to be contaminated with PDMS. This view is consistent with the contact angle data. This sample, and other similar unreported samples, showed a marked variability. The water contact angle is quite uniform across the samples

(±5°). Methylene iodide, however, gives two sets of values from different positions on the sample; one set clustered near 70° (called region A in the table) and the other set around 90° (called region B). Region A gives solid surface tension values similar to those of PDMS. Region B is lower with values close to that of PTFE.

Two hypotheses are possible: Region A is PTFPMS with region B being contaminating PTFE, or region B is PTFPMS with region A being contaminating PDMS. This latter hypothesis best fits our results. Elastomers were prepared without PTFE liners in an effort to eliminate supposed PTFE contamination. Because this introduced variability in the contact angle data, it implies that, contrary to causing PTFE contamination, such liners actually prevent PDMS contamination.

The contact angle data for the cleaved, filled PTFPMS elastomers also support the idea that PTFPMS has a very similar solid surface tension to PTFE if we suppose that the cleavage is through the PTFPMS and not the filler or its treatment. This is a reasonable supposition. The XPS data show lower fluorine and higher oxygen than pure PTFPMS with the PDMS fluid-treated material (sample 7), expectedly deviating more than the PTFPMS fluid-treated material (sample 6).

This study establishes that the solid surface tension of PTFPMS elastomers is very similar to that of PTFE, i.e., significantly lower than that of PDMS. On the other hand, the liquid surface tension of PTFPMS seems definitely established as higher than that of PDMS. Such statements seem contradictory only to those conditioned to the liquid, solid, and critical wetting surface tensions being very close to each other as is the case with PDMS. In fact, similar situations exist in other polymer systems. Table IV compares PDMS and PTFPMS with two other fluorine-containing polymers, one of which, polychlorotrifluoroethylene (PCTFE), is rather like PDMS in that all three surface tensions are quite similar (although significantly higher than PDMS), and the other, PTFE, is very like PTFPMS.

How then should we explain the data summarized in Table IV? Perhaps, there is nothing to explain. The liquid surface tension values for PTFE and PCTFE are based on extrapolation, the first, an MW extrapolation,[9,10] and the second, a temperature extrapolation (from higher temperature liquid studies).[13] Such extrapolations are open to the objection that a step change may occur at the phase transition between liquid and solid. Moreover, the

TABLE IV
Comparison with Other Polymers[a]

	Equilibrium liquid surface tension	Ref.	Critical surface tension of wetting				Solid surface tension[b]	Ref.
			n-alkanes	Ref.	Other test liquids	Ref.		
PTFPMS	24 (300 cs)	1	21	14	21	14	14–15	This work
PTFE	26 (MW → ∞)	9, 10	19	8	16–22	15	14	4
PDMS	21 (MW → ∞)	11, 12	22	14	24	2	19–25	6, 7
PCTFE	31	13	—		31	8	27	5

[a]All values in mN/m, quoted to nearest whole number.
[b]Owens–Wendt technique, water and methylene iodide test liquids.

solid surface tension derived by equations such as the Owens–Wendt equation used here is an empirical quantity dependent on assumptions, some of which are known to be wrong. Therefore, the difference between liquid and solid surface tensions may be an artifact of the derivation. However, the major false assumption in the Owens–Wendt approach is not with the dispersion force component which dominates the surface energy of both PDMS and PTFE so that this cannot account for the closeness of the liquid and solid values for PDMS and their considerable separation for PTFE. Perhaps some property of fluorine accounts for the parallelism between PTFE and PTFPMS and their divergence from the PDMS pattern, although this is unlikely as there are fluorine-containing polymers such as PCTFE that behave more like PDMS than like PTFE and PTFPMS.

In this study we have ignored the effect of equilibrium spreading pressure. The discrepancy between the solid and liquid surface tensions of PTFPMS may be explained in terms of the equilibrium spreading pressure. However, one might expect similar differences for PDMS which is not the case.

Possibly these differences are real and reflect orientational and packing density differences in different states. For instance, with PTFE in the liquid state, molecular motion will disrupt the close packing of adjacent molecules induced by the considerable crystallinity of PTFE in the solid state. Such crystallinity will also minimize the effect of any polar end groups resulting from the initiator and maximize the effect of any CF_3 groups that are present by freezing the former out of, and the latter into, the surface. This type of effect is known with paraffin wax which has a significantly lower critical surface tension of wetting than the liquid surface tension of longer n-alkanes such as hexadecane. This is because of close-packing of methyl groups in the surface caused by alignment of the paraffin chains in the solid state.

In the case of PDMS, which at room temperature is far above its glass transition temperature (T_g) and has end groups composed of the same entities as the pendent side chains (CH_3) and also has no crystallization tendencies as might occur between aligned chains of CH_2 and CF_2 entities, the closeness of liquid and solid surface tensions is to be expected.

With PTFPMS it cannot be orientation of the end groups as these are Me_2ViSi which should be of higher solid surface energy. PTFPMS is well above its T_g at room temperature. However, there must be different degrees of freedom in the liquid and solid state. The interaction of fluorines with adjacent silicons (both in the next monomer unit and in neighboring macro-molecules), which Lavigin[16] has suggested causes higher surface energies, may be easier in the liquid state than in the solid. There is also the complication that $CF_3(CH_2)_2$— contains two entities, one that is more surface active than CH_3— and one that is less. In the liquid state, the —CH_2— may play a more significant role than in the solid where motion of the $CF_3(CH_2)_2$— group in space is reduced and an orientation stressing external CF_3 may be induced. In this view, solid PTFPMS has most of the CF_3— in the surface. The effect of this is diminished by the CF_3—CH_2— dipole immediately below. There will also be some —CH_2— and CH_3— in the surface. In PTFE the surface consists of —CF_2— groups, but there is no CF—CH dipole to detract from their effect. The combination of these various factors produces two surfaces of very similar solid surface energy.

One defect of comparing surface tensions from different sources is that the well-known effect of surface roughness on contact angle cannot usually be quantitatively accounted for. The relative similarity of cleaved and molded samples in our study and the agreement in the case of PTFE with other reported studies suggests that this is not a significant factor in explaining the surface tension differences that are considered here.

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