

Notes

Theoretical Analysis of the Soiling of "Nonstick" Organic Materials

Calum J. Drummond* and Derek Y. C. Chan†

CSIRO Division of Chemicals and Polymers, Rosebank MDC, Private Bag 10, Clayton, Victoria 3169, Australia, and Department of Mathematics, The University of Melbourne, Parkville, Victoria 3052, Australia

Received November 28, 1995. In Final Form: March 1, 1996

"Nonstick" solid materials are desired for many applications, including stain resistant surfaces, contact lenses, prosthetic implants, and ships' hulls where biofouling needs to be minimized.

Surface free energies are frequently employed to rank the relative adhesive properties of solids. The surface free energy per unit area is equal to half the reversible work required to create a new surface by cleaving a homogeneous material. Therefore, the surface free energy reflects the interaction between identical materials across vacuum (or air). The adhesion associated with the soiling of surfaces usually involves the interaction of dissimilar materials across an intervening medium, which is not necessarily air. Adhesion between "soils" and solid substrates can be associated with a complex interplay of van der Waals (dispersion), electrostatic, chemical, steric, solvation, and hydrophobic interactions. van der Waals interaction always operates between a "soil" and a solid substrate. The nonretarded van der Waals free energy of interaction per unit area ($E_{123}(H_0)$) for two planar surfaces at a separation H may be expressed as^{1–4}

$$E_{123}(H_0) = \frac{-A_{123}(H_0)}{12\pi H^2} \quad (1)$$

where $A_{123}(H_0)$ is the nonretarded Hamaker constant that is governed by the dielectric properties of the two interacting materials (1 and 3) and the intervening medium (2). The expressions relating to nonplanar surface geometries are different from eq 1 but the strength of the interaction is characterized by the Hamaker constant.^{3,4}

Here we report the calculation of the nonretarded van der Waals interaction of representative organic "soils" with low-density (LD) and high-density (HD) poly(tetrafluoroethylene) (PTFE), two amorphous copolymers of perfluoro-2,2-dimethyl-1,3-dioxole with tetrafluoroethylene (Teflon AF 1600 and 2400; the TFE:dioxole ratio is 34:66 and 16:84, respectively)⁵ that have the lowest reported⁶ surface free energies for solid homogeneous organic

* Author to whom correspondence should be addressed at CSIRO Division of Chemicals and Polymers. Fax: 61-3-95422515. Phone: 61-3-95422617. E-mail: c.drummond@chem.csiro.au.

† The University of Melbourne.

(1) Lifshitz, E. M. *J. Exp. Theor. Phys. USSR* 1995, 29, 94–110 (*Sov. Phys. JETP* 1956, 2, 73–83).

(2) Parsegian, V. A. In *Physical Chemistry: Enriching Topics from Colloid and Surface Science*; van Olphen, H., Mysels, K. J., Eds.; IUPAC Communication 1.6; Theorex: La Jolla, CA, 1975; Chapter 4.

(3) Israelachvili, J. N. *Intermolecular and Surface Forces*, 2nd ed.; Academic Press: London, 1992; Chapter 11.

(4) Hough, D. B.; White, L. R. *Adv. Colloid Interface Sci.* 1980, 14, 3–41.

(5) Lowry, J. H.; Mendlowitz, J. S.; Subramanian, N. S. *Opt. Eng.* 1992, 31, 1982–1985.

materials, a hypothetical perfluoropolymer (TPFP) considered to have the optimum "nonstick" properties for a solid homogeneous organic material (see below), liquid and solid poly(dimethylsiloxane) (PDMS(l) and PDMS(s)), a low-density poly(ethylene) (PE.LD), and natural rubber. Liquid PDMS was included in the comparison because its refractive index suggests that it would represent the lower limit of surface free energy for a solid homogeneous silicone or hydrocarbon material (see below). In the case of the organic "soils", mineral oils are represented by hexadecane, octane, and *p*-xylene; essential oils by *d*- α -pinene (turpentine); triglyceride-based vegetable oils and animal fats by olive oil and sunflower oil (lard and butter fat have very similar dielectric properties to olive oil); fatty acids by 22-tricosenoic acid; soaps by cadmium arachidate; carbohydrates and other polyhydroxy compounds by cellulose and poly(vinyl alcohol) (PVA); and proteins by bovine serum albumin (BSA) and nylon 6 (a very simple polypeptide analogue).

Lifshitz theory was employed to determine the nonretarded Hamaker constants.¹ The nonretarded Hamaker constant for the interaction between dissimilar half spaces with dielectric permeability $\epsilon_1(\omega)$ and $\epsilon_3(\omega)$ across an intervening medium of dielectric permeability $\epsilon_2(\omega)$ is given by

$$A_{123}(H_0) = \frac{3k_B T}{2} \sum_{n=0}^{\infty} \sum_{s=1}^{\infty} \frac{(\Delta_{12}\Delta_{32})^s}{s^3} \quad (2)$$

where

$$\Delta_{kj} = \frac{\epsilon_k(i\xi_n) - \epsilon_j(i\xi_n)}{\epsilon_k(i\xi_n) + \epsilon_j(i\xi_n)} \quad (3)$$

and

$$\xi_n = (4\pi^2 k_B T/h)n \quad (4)$$

The prime on the summation in eq 2 denotes that the term at zero frequency ($n = 0$) is given half weight. k_B , T , and h denote the Boltzmann constant, absolute temperature, and Planck's constant, respectively. $\epsilon(\omega)$ is dealt with as a function of the complex variable ω only on the imaginary axis $\omega = (i\xi)$. The Ninham–Parsegian representation⁷ of the dielectric permeability as a function of imaginary frequency $i\xi$ was used with

$$\epsilon(i\xi) = \epsilon_0, \quad \text{when } \xi = 0$$

$$\epsilon(i\xi) = 1 + \frac{C_{IR}}{1 + (\xi/\omega_{IR})^2} + \frac{C_{UV}}{1 + (\xi/\omega_{UV})^2}, \quad \text{when } \xi > 0 \quad (5)$$

where ϵ_0 is the static dielectric constant, C_{IR} and C_{UV} are related to the oscillator strengths of the absorption bands in the infrared (IR) and ultraviolet (UV) regions, and ω_{IR} and ω_{UV} are the frequencies of the absorption band maxima. In order to obtain the representations of the dielectric permeability functions, we generally followed

(6) Drummond, C. J.; Georgakis, G.; Chan, D. Y. C. *Langmuir* 1996, 12, 2617–2621.

(7) Ninham, B. W.; Parsegian, V. A. *Biophys. J.* 1970, 10, 646–663.

the Hough and White methodology.⁴ The C_{UV} and ω_{UV} values for the materials were determined from Cauchy plots of refractive index (n) data from the low-frequency side of the ultraviolet absorption, where the extinction coefficient is negligible (i.e., in plots of $n^2 - 1$ versus $(n^2 - 1)\omega^2$, where the axis of ordinates intercepts gives C_{UV} and the gradient gives $1/\omega_{UV}^2$). It was assumed that⁴

$$C_{IR} = \epsilon_0 - C_{UV} - 1 \quad (6)$$

The dielectric constants, optical dispersion, and location of the principal IR absorption bands for the organic materials were obtained from a wide range of literature sources.^{4-6,8-25} For water we have used the Gingell-Parsegian $\epsilon(i\xi)$ representation.² Table 1 contains the dielectric properties of the organic materials studied and literature values for the surface free energies of the "nonstick" substrates.^{6,26-29}

For simple dispersive perfluorocarbon, silicone, and hydrocarbon materials the UV part of the dielectric permeability function has a large influence on the van der Waals interaction. The hydrocarbon and silicone solids have similar ω_{UV} values, which are markedly lower than the ω_{UV} values for the perfluorocarbons (Table 1). On this basis, the hydrocarbons and silicones can be characterized as belonging to the same family of dispersive "nonstick" materials, and the perfluorocarbons as belonging to a different family. Within the same family, there is a correlation between C_{UV} ($\approx n_D^2 - 1$, where n_D is the refractive index measured with 589 nm light) and surface free energy; lower n_D corresponds to lower surface free energy (Table 1).

The theoretical lower limit for the n_D of a solid perfluorocarbon polymer is 1.26.³⁰ Perfluoroheptane has

- (8) Sowers, B. L.; Williams, M. W.; Hamm, R. N.; Arakawa, E. T. *J. Appl. Phys.* **1971**, *42*, 4252-4257.
- (9) Cooper, P. R. *Appl. Opt.* **1982**, *21*, 3414-3415.
- (10) Ashok, J.; Varaprasad, P. L. H.; Birch, J. R. In *Handbook of Optical Constants of Solids II*; Palik, E., Ed.; Academic Press, Inc.: New York, 1991; pp 957-987.
- (11) Newman, S. B. In *Analytical Chemistry of Polymers Part III. Identification Procedures and Chemical Analysis*; Kline, G. M., Ed.; Interscience: New York, 1962; p 283.
- (12) Partington, J. R. *An Advanced Treatise on Physical Chemistry. Vol. 4. Physico-Chemical Optics*; Longmans: London, 1953; pp 52-53.
- (13) Kanthack, R. *Tables of Refractive Indices. Vol. II: Oils, Fats and Waxes*; Adam Hilger Ltd.: London, 1921.
- (14) Barnes, W. L.; Sambles, J. R. *Thin Solid Films* **1986**, *143*, 237-247.
- (15) Pockrand, I.; Swalen, J. D.; Gordon, J. G., II; Philpott, M. R. *Surf. Sci.* **1977**, *74*, 237-244.
- (16) Frey-Wyssling, A. *Helv. Chim. Acta* **1936**, *19*, 900-914.
- (17) de Vries, H. *Ann. Sci. Text. Belg.* **1955**, *4*, 286-301.
- (18) Swalen, J. D.; Santo, R.; Tacke, M.; Fischer, J. *IBM J. Res. Dev.* **1977**, *21*, 168-175.
- (19) Angad Gaur, H.; De Vries, H. *J. Polym. Sci., Polym. Phys. Ed.* **1975**, *13*, 835-850.
- (20) Imagaki, T.; Hamm, R. N.; Arakawa, E. T.; Birkhoff, R. D. *Biopolymers* **1975**, *14*, 839-847.
- (21) Sober, H. A., Ed. *CRC Handbook of Biochemistry*, 2nd ed.; CRC Press: Cleveland, OH, 1970.
- (22) Weast, R. C., Ed. *CRC Handbook of Chemistry and Physics*, 60th ed.; CRC Press: Boca Raton, FL, 1981.
- (23) Roff, W. J.; Scott, J. R. *Fibres, Films, Plastics and Rubbers: A Handbook of Common Polymers*; Butterworths: London, 1971.
- (24) Oliver, G. D.; Blumkin, S.; Cunningham, C. W. *J. Am. Chem. Soc.* **1951**, *73*, 5722-5725.
- (25) Pouchert, C. J. *The Aldrich Library of Infrared Spectra*, 3rd ed.; Aldrich Chemical Co.: Milwaukee, WI, 1981.
- (26) *Information about Silicone Fluids*; Dow Corning Corporation: 1980.
- (27) Chaudhury, M. K.; Whitesides, G. M. *Langmuir* **1991**, *7*, 1013-1025.
- (28) Mangipudi, V.; Tirrell, M.; Pocius, A. V. *J. Adhes. Sci. Technol.* **1994**, *8*, 1251-1262.
- (29) Johnson, K. L.; Kendall, K.; Roberts, A. D. *Proc. R. Soc. London, A* **1971**, *324*, 301-313.
- (30) Groh, W.; Zimmermann, A. *Macromolecules* **1991**, *24*, 6660-6663.

Table 1. Dielectric Properties of the "Nonstick" Organic Substrates and Representative Organic "Soils" at $20 \pm 5^\circ\text{C}^a$

| materials | ϵ_0 | C_{IR} | ω_{IR} ($\times 10^{-14}$ rad \cdot s $^{-1}$) | C_{UV} | ω_{UV} ($\times 10^{-16}$ rad \cdot s $^{-1}$) | γ_d (mN \cdot m $^{-1}$) |
|---------------------|--------------|----------|---|----------|---|---------------------------------------|
| Substrates | | | | | | |
| TPFP | 1.765 | 0.186 | 2.356 | 0.579 | 2.620 | 13.0 ± 0.6 |
| Teflon AF 2400 | 1.904 | 0.239 | 2.356 | 0.665 | 2.522 | 15.2 ± 1.3 |
| Teflon AF 1600 | 1.934 | 0.225 | 2.356 | 0.709 | 2.457 | 16.4 ± 1.4 |
| PTFE.LD | 2.0 | 0.21 | 2.356 | 0.792 | 2.654 | 24.7 ± 1.8 |
| PTFE.HD | 2.1 | 0.21 | 2.356 | 0.890 | 2.640 | >27.3 |
| PDMS(l) | 2.64 | 0.738 | 2.026 | 0.902 | 1.648 | 20.1 |
| PDMS(s) | 2.75 | 0.789 | 2.026 | 0.961 | 1.698 | 21.8 ± 0.8 |
| PE.LD | 2.26 | 0.114 | 5.540 | 1.141 | 1.576 | 33.3 ± 1.6 |
| natural rubber | 2.35 | 0.10 | 5.540 | 1.250 | 1.519 | 35 ± 2 |
| "Soils" | | | | | | |
| hexadecane | 2.051 | 0.025 | 5.540 | 1.026 | 1.848 | |
| octane | 1.948 | 0.025 | 5.540 | 0.925 | 1.863 | |
| p-xylene | 2.27 | 0.095 | 5.540 | 1.175 | 1.344 | |
| d- α -pinene | 2.7 | 0.592 | 5.540 | 1.108 | 1.674 | |
| olive oil | 2.54 | 0.417 | 5.540 | 1.122 | 1.797 | |
| sunflower | 2.54 | 0.394 | 5.540 | 1.147 | 1.711 | |
| 22-tricosenoic acid | 2.6 | 0.356 | 5.540 | 1.244 | 1.733 | |
| cadmium arachidate | 2.8 | 0.514 | 5.540 | 1.286 | 1.378 | |
| cellulose | 3.2 | 0.896 | 6.282 | 1.303 | 1.891 | |
| poly(vinyl alcohol) | 3.5 | 1.243 | 6.282 | 1.257 | 1.842 | |
| BSA | 4.0 | 1.60 | 6.282 | 1.4 | 1.79 | |
| nylon 6 | 3.7 | 1.417 | 6.282 | 1.283 | 1.686 | |

^a Surface free energies (γ_d) for the "nonstick" organic materials are also included. We could not find ϵ_0 for some of the materials. In these cases we substituted the value for a close structural analogue. The calculated nonretarded Hamaker constants are not sensitive to small variations in ϵ_0 , C_{IR} , and ω_{IR} . For birefringent materials, unless otherwise stated, C_{UV} and ω_{UV} are the average values for the transverse magnetic (TM; n_L) and transverse electric (TE; n_L) modes. To our knowledge, there is no report of high-quality experimental refractive indices as a function of wavelength in the visible region for PTFE. Therefore, we calculated the low-density ($2.1 \text{ g}\cdot\text{cm}^{-3}$) and high-density ($2.3 \text{ g}\cdot\text{cm}^{-3}$) PTFE C_{UV} and ω_{UV} values from the optical data for perfluorohexane and perfluoroheptane by using the Lorenz-Lorentz equation.⁶ PDMS(l) refers to a silicone liquid manufactured by Dow Corning under the trade name DC-200. The average molecular formula for this material was $(\text{CH}_3)_3\text{-Si}-\text{O}-[(\text{CH}_3)_2\text{-Si}-\text{O}]_{14}\text{Si}-(\text{CH}_3)_3$.⁸ PDMS(s) refers to a silicone elastomer manufactured by Dow Corning under the trade name Sylgard182.⁹ We could only find refractive indices (n) for triglyceride liquids at 40 °C. To obtain n values at 20 °C we assumed a temperature coefficient dn/dT of -3.66×10^{-4} .¹³ The triglyceride dispersion data was quoted¹³ only as n_D and $(n_D - 1)/(n_F - n_C)$, where n_D , n_F , and n_C are the refractive index at 589, 486, and 656 nm, respectively. Therefore, for the triglycerides we assumed that the Cauchy plot was linear and used a least squares method to obtain C_{UV} and ω_{UV} . For 22-tricosenoic acid C_{UV} and ω_{UV} refer to the TE mode.¹⁴

a similar n_D value and, based on the assumption that all perfluorocarbon materials are likely to have similar ω_{UV} and ω_{IR} values, we can use this perfluorocarbon liquid to model the van der Waals interaction of the theoretical perfluoro polymer (TPFP) with n_D equal to 1.26.

The van der Waals interaction between materials, either solid or liquid, across air (vacuum) will always be attractive. Therefore, it is impossible to obtain a truly "nonstick" material in air and it is only possible to minimize adhesion to given an ultra-low-adhesive material. For two different materials with an intervening liquid, and when the dielectric properties of the liquid are intermediate between the materials, there may be a repulsive van der Waals interaction that prevents adhesion. As shown in Figure 1, all the Hamaker constants for interaction across air and water are positive. The Hamaker constants for the interaction across water are approximately a factor of ten lower than those for the interaction across air. The

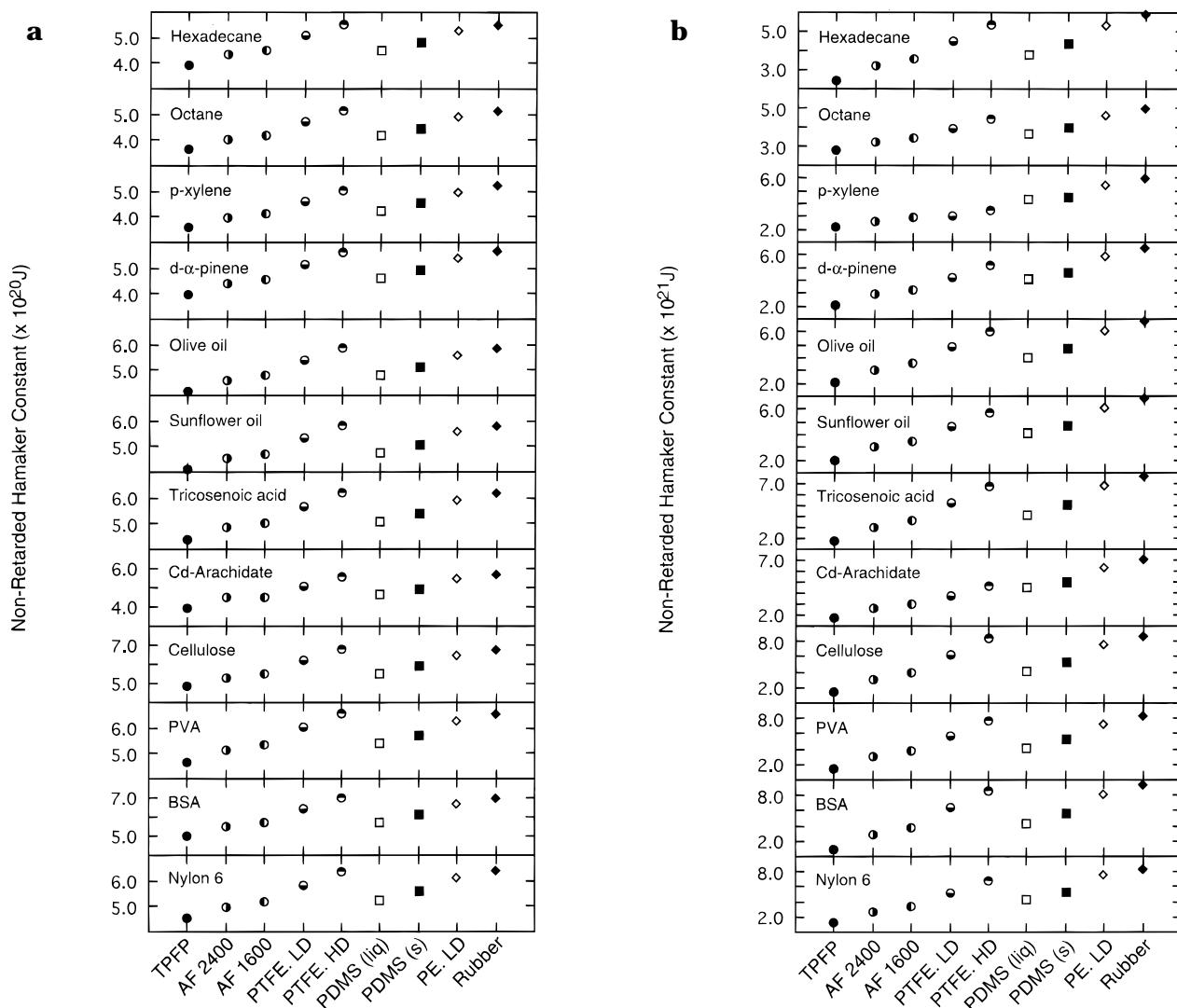


Figure 1. Nonretarded Hamaker constants for the van der Waals interaction of low surface free energy ("nonstick") organic materials with representative organic "soils" across (a) air and (b) water.

surface interaction in aqueous solution is low-adhesive rather than truly "nonstick". High surface free energy surfaces, such as metals and metal oxides, have significantly greater Hamaker constants than the low surface free energy materials that are discussed in this work (Figure 1). For example, the Hamaker constants describing the interaction of gold with the organic "soils" octane and BSA are 1.2×10^{-19} and 1.6×10^{-19} J across air and 7.3×10^{-21} and 4.1×10^{-20} J across water, respectively, while for the interaction of aluminum oxide with octane and BSA the Hamaker constants are 8.3×10^{-20} and 1.1×10^{-19} J across air and 7.6×10^{-21} and 2.6×10^{-20} J across water, respectively (Drummond, C. J.; Chan, D. Y. C. Unpublished).

Within the same family of dispersive "nonstick" materials, the surface free energies are a reasonable guide to the relative nonretarded Hamaker constants that describe the interaction of dissimilar materials across either air or an intervening liquid (e.g., review the nonretarded Hamaker constant trends in Figure 1 with the surface free energy sequences for the two families of dispersive "nonstick" materials which are given in Table 1). A comparison of the surface free energies of dispersive organic materials from different families may not provide a good relative guide to the adhesive properties (e.g., compare the data for LD.PTFE with that of PDMS(s), Figure 1b and Table 1).

The ω_{UV} values of most of the organic "soils" are very similar; p-xylene and cadmium arachidate are the exceptions. Consequently, the organic "soils" that possess the larger C_{UV} values generally exhibit the greater van der Waals attractions for a particular low surface free energy surface (cf. Table 1 with Figure 1).

The results for TPFP (Figure 1b) suggest that it is extremely unlikely that any solid homogeneous bulk organic polymer will be truly "nonstick" toward organic "soils" in an aqueous environment. We have gone through the exercise of determining what perfluorocarbon dielectric properties would be necessary in order to obtain repulsive van der Waals interaction between a fluorocarbon and an organic "soil" across water. The requisite C_{UV} and C_{IR} values are significantly less than those possessed by any known perfluoro liquid.⁶ Therefore, on the basis of the theoretical consideration of the van der Waals interaction, the introduction of a significant repulsive steric/entropic component to the overall energy of interaction would seem necessary to achieve a truly "nonstick" solid organic surface in aqueous solution.

One of the common applications for perfluorocarbon materials is in "nonstick" cookware (e.g., PTFE coated frying pans). The solid content of most foodstuffs is either proteinaceous (meat, fish, and eggs) or carbohydrate (vegetables and grains) in origin. The Hamaker constants

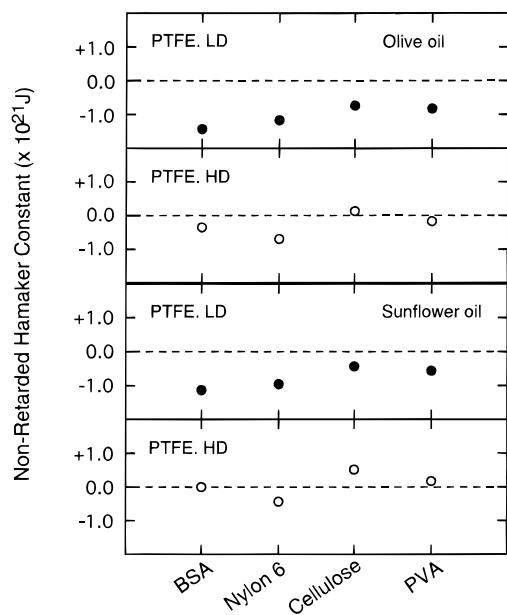


Figure 2. Nonretarded Hamaker constants for the van der Waals interaction of low-density and high-density poly(tetrafluoroethylene) with model proteinaceous (bovine serum albumin and nylon 6) and carbohydrate (cellulose and poly(vinyl alcohol)) materials across representative cooking oils (olive oil and sunflower oil).

for the interaction between PTFE (low and high density) and model proteinaceous and carbohydrate materials with representative cooking oils as the intervening media are

displayed in Figure 2. The Hamaker constants are either very small or negative (repulsive van der Waals interaction) and suggest that low-density PTFE is truly "nonstick" in these systems, while high-density PTFE varies between truly "nonstick" and ultra-low-adhesive depending on the exact system.

In summary, in this note we have presented theoretical evidence that surface free energies are a good guide to the relative adhesive behavior of low surface free energy ("nonstick") fluorocarbon, silicone, and hydrocarbon solids toward organic "soils" when the interactions are governed by van der Waals (dispersion) forces and comparisons are restricted to similar families of materials. Our theoretical considerations also suggest that fluorocarbons are the best candidates for ultra-low-adhesive materials, and no smooth homogeneous organic solid can be strictly "nonstick" toward organic "soils" in water but poly(tetrafluoroethylene) surfaces can be truly "nonstick" toward foodstuffs placed in common cooking oils.

Acknowledgment. We thank Nicole Moriarty for assistance in collating some of the dielectric permeability data and George Georgakis for help with manuscript preparation. This work was begun while C.J.D. was a recipient of a Queen Elizabeth II Fellowship from the Australian Research Council.

LA951081T