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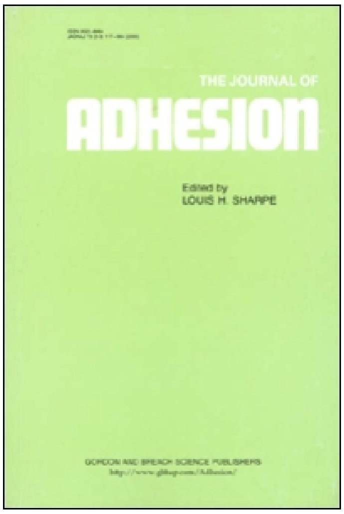

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A Reinterpretation of Organic Liquid-Polytetrafluoroethylene Surface Interactions

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ABSTRACT

The wettability of polytetrafluoroethylene (PTFE) by organic liquids is reanalyzed in terms of dispersion-polar interactions across the liquid-solid interface. The analysis provides values of $\gamma_s^d = 19.6$ dyne/cm, and $\gamma_s^p = 2.0$ dyne/cm for the respective dispersion and polar parts of the surface tension $\gamma_s = 21.6$ for PTFE. The definition of a polar contribution to the surface tension of PTFE clarifies detailed aspects of the wettability of this polymer by different homologous liquid series. A modified analytical definition for work of adhesion is developed and applied to this discussion.

INTRODUCTION

THE SURFACE free energy or surface tension of solids cannot be directly measured due to the elastic and viscous restraints of the bulk phase. This necessitates the use of indirect methods of estimating solid surface tension. Zisman and coworkers [1,2] use extrapolated contact angle θ measurements to define a critical surface tension of wetting, γ_C, for low energy surfaces. This technique represents the best documented approach to characterizing low energy solid surfaces. Shafrin [3] has collected the γ_C values for polymers. Crocker [4] has recently extended this compilation of γ_C for polymers and also oriented monolayers. A method of calculating γ_C based upon structural group properties has been successfully developed by Wu.[5]

This discussion reexamines the extensive contact angle data of over sixty liquids to polytetrafluoroethylene (PTFE) due to Fox and Zisman.[1] From this study the standard value $\gamma_C = 18.5$ dyne/cm for PTFE is defined. A recent statement for work of adhesion developed by Good[6] is modified and applied to identify separable dispersion (d) and polar (p) contributions to interfacial work of adhesion $W_a = W_a^d + W_a^p$. The new relation for work of adhesion provides a means of intercomparing the methods of Zisman and coworkers, [1,2] Fowkes, [7,8] and Good and coworkers. [6,9,10] Table 1 summarizes the symbols and nomenclature employed in this discussion.

The objective of the present discussion is to reexamine and provide some additional interpretation of the surface properties of PTFE in the light of a revised definition of work of adhesion. The discussion is intended to set forth propositions and comparisons between differing estimates for the surface properties of this polymer rather than provide a new conclusive result. The present theories defining W_a are still too inexplicit to present a detailed definition of either liquid or solid surface properties. This discussion must assume, for example, idealized surface smoothness and homogeneity for the substrate, an ideal adsorption without interdiffusion at the liquid-solid interface, and zero adsorption of the vapor of the wetting liquid at the gas-solid interface.

TABLE 1:
NOMENCLATURE

Symbol	Meaning
γ_C	critical surface tension for wetting
γ_S, γ_L	solid and liquid surface tension
γ_S^d, γ_L^d	dispersion part of γ_S and γ_L
γ_S^p, γ_L^p	polar part of γ_S and γ_L
W_a	work of adhesion
W_a^d, W_a^p	dispersion and polar parts of W_a
γ_{LS}	interfacial tension
ϕ	bonding efficiency factor
d, p	dispersion and polar fractions of surface tension
Δ	excess quantity

THEORY

A detailed redevelopment of Good's[6] model for interfacial interactions provides the following equation for work of adhesion:[11]

$$W_a = 2(\gamma_1\gamma_2)^{1/2}\Big[(d_1d_2)^{1/2} + p_1p_2)^{1/2} + \Delta_{12}\Big] \qquad (1)$$

where the subscripts represent the surface properties of components 1 and 2 at the 12 interface. By assuming $\Delta_{12} = 0$ we obtain the working relation for this discussion:

$$\begin{aligned} W_a &= 2(\gamma_L\gamma_S)^{1/2}\Big[(d_Ld_S)^{1/2} + (p_Lp_S)^{1/2}\Big] \\ &= 2\Big[(\gamma_1^d\gamma_S^d)^{1/2} + (\gamma_L^p\gamma_S^p)^{1/2}\Big] \\ &= W_a^d + W_a^p \qquad (2) \end{aligned}$$

When equation (2) is substituted into the Young equation $W_a = \gamma_L(1 + \cos\theta)$ we obtain:

$$1 + \cos\theta = 2\left(\frac{\gamma_S}{\gamma_L}\right)^{1/2}\left[(d_L d_S)^{1/2} + (p_L p_S)^{1/2}\right] \tag{3}$$

By solving equation (3) for the critical wetting condition $\cos\theta = 1.0$ which defines the critical surface tension of wetting $\gamma_L = \gamma_C$ we obtain:

$$\gamma_L = \gamma_C = \gamma_S\left[(d_L d_S)^{1/2} + (p_L p_S)^{1/2}\right]^2 \tag{4}$$

Equation (4) indicates that $\gamma_C = \gamma_S$ only when $d_L = d_S$ and $p_L = p_S$ such that the fractional dispersion and polar components of surface tension in liquid and solid exactly match. Equation (4) points out that the critical surface tension γ_C is a property of the liquid-solid bonding efficiency:

$$\phi_{LS} = (d_L d_S)^{1/2} + (p_L p_S)^{1/2} \tag{5}$$

as well as the solid surface tension γ_S. The bonding efficiency parameter ϕ_{LS} is seen to be a dimensionless quantity with a maximum value of unity. We shall see that γ_C is very sensitive to ϕ_{LS}.

Figure 1 presents curves of equation (5) for selected values of d_S for solids. The right side of Figure 1 represents nonpolar liquids such as hydrocarbons with $d_L = 1.0$. As the value of d_L diminishes, the liquid surface interacts with more polar character. Water with a surface and bulk value of $d_L \cong 0.3 \pm 0.1$ is the most common liquid with predominantly polar character.[7,12] The hydrated surfaces of glass, silica, and common metals such as characterized by Zisman and coworkers[13,14] may display values of $d_s \cong 0.2$ to 0.3 characteristic of bulk water. Solids with $d_S \cong 0.3$ to 1.0 which interfacially contact liquids with organic liquids or water with $d_L \cong 0.3$ to 1.0 should, according to equation (5), display a range of $\phi_{LS} \cong 0.55$ to 1.0. Introducing ϕ_{LS}

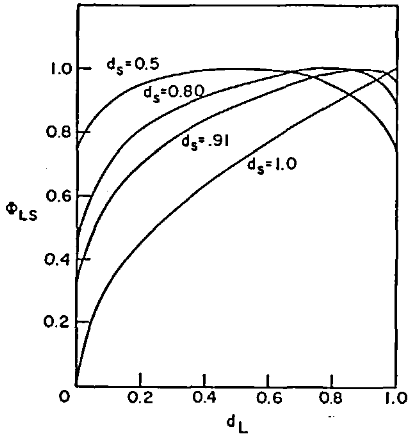

Figure 1 Interfacial bonding efficiency $\phi_{LS} = W_a/2(\gamma_L\gamma_S)^{1/2}$ defined as functions of liquid d_L and solid d_S *dispersion fractions.*

$= 0.55$ to 1.0 into equation (4) predicts that values of $\gamma_C = 0.3\gamma_S$ to $1.0\gamma_S$ can result when equation (3) is utilized to define the intercept of the cos θ versus γ_L function.

The close relation between equations (2) through (5) of this section to the earlier definitions of Good and Fowkes is readily noted. These relations differ from those of Good[6] in the statement for ϕ_{LS} provided by equation (5) which is expressed here purely by the dispersion-polar balance across the adsorption interface. Equations (2) through (5) represent a more narrow and explicit form of the statements of Good.[6]

Conversely, equations (2) through (5) provide expressions more general than equations due to Fowkes.[7,8] Equation (2), for example, becomes identical with the Fowkes' equation when $W_a^p = 0$. In this same sense equation (3), which will be applied in the next section, is more versatile and reduces to the familiar Fowkes' equation as a special case when either $p_L = 0$ or $p_S = 0$. In other words equations (2) through (5) define interactions between either nonpolar-nonpolar, polar-nonpolar, and polar-polar surfaces.

Perhaps the most revealing form of these new definitions is obtained by combining equation (2) with the Young-Dupre relation so as to obtain:

$$\gamma_L + \gamma_S - \gamma_{LS} = 2\left[(\gamma_l^d\gamma_S^d)^{1/2} + (\gamma_l^p\gamma_S^p)\right]^{1/2}$$

The above expression, upon substitution of the relations $\gamma_L = \gamma_L^d + \gamma_L^p$ and $\gamma_S = \gamma_S^d + \gamma_S^p$ and rearrangement, provides the following new and informative relation for interfacial tension:

$$\gamma_{LS} = \left[(\gamma_L^d)^{1/2} - (\gamma_S^d)^{1/2}\right]^2 + \left[(\gamma_L^p)^{1/2} - (\gamma_S^p)^{1/2}\right]^2 \qquad (6)$$

Equation (6) states that interfacial tension achieves a minimum value by the individual minimizations of the dispersion and polar components of γ_L and γ_S. Equation (6) further points out that $\gamma_{LS} = 0$ only when $\gamma_L^d = \gamma_S^d$ and $\gamma_L^p = \gamma_S^p$ which may be presumed to be a unique situation except for autohesion or self-bonding of two parts of the same material.

ANALYSIS OF PTFE WETTABILITY

The first three columns of Table 2 summarize the data to be analyzed in terms of equations (2) through (5). The standard method of plotting such data is illustrated in the graph of cos θ versus γ_L shown in Figure 2. It may be noted that these data are shown for over fifty liquids on PTFE. The value of $\gamma_C = 18.5$ obtained by Fox and Zisman for PTFE places special emphasis on the contact angle data for the nonpolar n-alkanes.[1] This special correlation obtained for n-alkanes is indicated by the open circles and short dashed curve in Figure 2. In order to incorporate all of the contact angle data into a narrowest rectilinear band of $\Delta\gamma_L$, as shown by the solid curves of Figure 2, we obtain values of $\gamma_C = 6.6$ dyne/cm and $\gamma_C = 19.2$ dyne/cm.

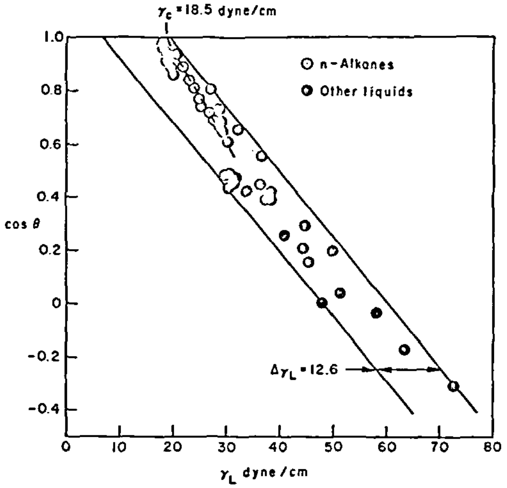

Figure 2 Wettability of polytetrafluoroethylene.

Table 2

Dispersion and Polar Contributions to Liquid-Polytetrafluoroethylene Interactions at 20°C

Liquid	γ_L (*dyne/cm*)	$\cos\theta$	ϕ_{LS}	d_L
n-Alkanes				
Hexadecane	27.6	.695	.96	1.00
Tetradecane	26.7	.719	.95	1.00
Dodecane	25.4	.743	.94	1.00
Undecane	24.7	.777	.96	1.00
Decane	23.9	.819	.96	1.00
Nonane	22.9	.848	.95	1.00
Octane	21.8	.899	.95	1.00
Di (n-alkyl) ethers				
Dioctyl ether	27.7	.656	.94	1.00 (.65)
Diheptyl ether	27.0	.682	.94	1.00 (.65)
Diamyl ether	24.9	.766	.95	1.00 (.67)
Dibutyl ether	22.8	.857	.95	1.00 (.67)
Dipropyl ether	20.5	.946	.95	1.00 (.67)
n-Polymethyl Siloxanes				
Heptadecamer	19.9	.866	.90	.55
Dodecamer	19.6	.875	.87	.47
Nonamer	19.2	.899	.89	.52
Heptamer	18.6	.914	.89	.52
Hexamer	18.5	.946	.90	.55
Pentamer	18.1	.966	.90	.55
Tetramer	17.6	.990	.90	.55

Table 2 (continued)

Liquid	γ_L *(dyne/cm)*	*cos* Θ	ϕ_{LS}	d_L
n-Alkyl benzenes				
Hexylbenzene	20.0	.616	.95	1.00 (.67)
Butylbenzene	29.2	.656	.96	1.00 (.70)
Propylbenzene	29.0	.656	.96	1.00 (.70)
Ethylbenzene	29.0	.669	.96	1.00 (.70)
Methylbenzene	28.5	.731	1.00	.91
Benzene	28.9	.695	.98	.98 (.76)
Halocarbons				
Methylene iodide	50.8	.035	.80	.34
Sym-tetrabromoethane	49.7	.191	.90	.54
Trichlorodiphenyl	45.3	.156	.84	.41
α-Bromonaphthalene	44.6	.292	.93	.62
Tetrachlorodiphenyl	44.2	.208	.86	.46
Hexachloropropylene	38.1	.423	.94	.64
Perchlorocyclopentadiene	37.5	.391	.91	.57
Sym-tetrachloroethane	36.3	.559	1.01	.91
Hexachlorobutadiene	36.0	.500	.97	.99 (.72)
Tetrachloroethylene	31.7	.656	1.00	.91
Carbon tetrachloride	26.8	.809	1.01	.91
Esters				
Tricresylphosphate	40.9	.259	.86	.45
Benzylphenylundecanoate	37.7	.391	.92	.59
Di-(2-ethylhexyl)-phthalate	31.2	.454	.87	.48
Di-(2-ethylhexyl)-sebacate	31.1	.470	.88	.50
Pentaerythritol-tetracaproate	30.4	.438	.85	.43
1, 6-Hexamethylene-glycol di-2-ethyl hexanoate	30.2	.454	.86	.45
Di-(2-ethylhexyl)-adipate	30.2	.485	.88	.50
Tri-(2-ethylhexyl)-tricarballate	29.6	.485	.87	.47
Miscellaneous				
Water	72.8	-.309	.64	.15
Glycerol	63.4	-.174	.71	.22
Formamide	58.2	-.035	.79	.33
Ethylene glycol	47.7	0	.74	.25
ter-Butylnaphthalene	33.7	.423	.89	.52
Carbon disulphide	31.4	.470	.89	.52
n-Heptylic acid	28.3	.656	.95	.67 (1.00)

A practical test for a theoretical argument is seen here to be: (*1*) to explain the values of γ_C obtained by Fox and Zisman for specific homologous series of liquids, (*2*) to define the scatter of typical cos θ versus γ_L data, (*3*) explain the tendency for cos θ versus γ_L data to form linear curves or bands. We will now apply equations (2) through (5) to this problem.

When a large variety of liquids such as listed in Table 2 are involved in a wettability study we are permitted an assumption that some will display an ideal interaction so that $\phi_{LS} = 1.0$ in equation (5). For this special case equation (3) becomes:

$$1 + \cos\theta = 2\left(\gamma_S/\gamma_L\right)^{1/2} \tag{7}$$

Making the standard assumption that n-alkanes are completely nonpolar such that $d_L = 1.00$ and $p_L = 0$, then equation (3) takes on a second special form which is:

$$1 + \cos\theta = 2\left(\gamma_S^d/\gamma_L\right)^{1/2} \tag{8}$$

Equation (7) predicts the upper limit of cos θ for a given value of γ_L. The upper portion of Table 3 identifies four liquids from the group of fifty which

Table 3

Calculated Surface Tension Properties of PTFE

Liquid	γ_S ***(calc.)*** *(dyne/cm)*
Sym-tetrachloroethane	21.9
Tetrachloroethane	21.6
Methylbenzene	21.6
Carbon tetrachloride	21.4
	ave. = 21.6
Liquid	γ_S^d ***(calc.)*** *(dyne/cm)*
Hexadecane	19.8
Tetradecane	19.8
Dodecane	19.3
Undecane	19.5
Decane	19.8
Nonane	19.5
Octane	19.7
	ave. = 19.6

most closely coincide with $\phi_{LS} = 1.0$. A value of $\gamma_S = 21.6$ dyne/cm is obtained for PTFE based on the solution of equation (7) for these four liquids. The lower portion of Table 3 tabulates the calculated value of γ_S^d for PTFE calculated from equation (8) for γ_L and cos θ data using seven n-alkanes. A nearly constant value of $\gamma_S^d = 19.6$ dyne/cm is obtained which does not depend upon the molecular weight of the alkane or other variable properties of these liquids.

Having defined both γ_S and γ_S^d in terms of equation (3) we obtain $\gamma_S^p = \gamma_S - \gamma_S^d = 2.0$ dyne/cm and $d_s = 1 - p_s = 0.91$ as a complete definition of Teflon surface properties in terms of the restricted definition of equations (2) through (5). We may now exploit this definition of the surface properties of PTFE to calculate the bonding efficiency ϕ_{LS} from the data of Table 2 by restating equation (3) as follows:

$$\phi_{LS} = (1 + \cos\theta)\ /2(\gamma_S/\gamma_L)^{1/2} \qquad (9)$$

where for PTFE the value of $\gamma_S = 21.6$ dyne/cm. The fourth column of Table 2 tabulates the calculated values of ϕ_{LS} obtained from equation (9). These values for ϕ_{LS} and $d_S = 0.91$ and $p_S = 0.09$ may be reinserted into equation (5) to identify the characteristic value of the dispersion fraction d_L for the wetting liquid. The curves of ϕ_{LS} presented in Figure 1 illustrate that only the limiting case where $d_S = 1.0$ does a single value of d_L uniquely define ϕ_{LS}. In the case of PTFE with $d_S = 0.91$ the curve of Figure 1 shows that when $.954 < \phi_{LS} < 1.0$ equation (5) identifies two possibilities for d_L. It is left to the context of the liquid in the series it represents and the judgment of the user of equation (5) to select the most appropriate value of d_L where these dual values appear.

The right hand column of Table 2 presents the calculated values of d_L and where dual values are obtained the less favored of the two results is enclosed in parentheses. These double values of d_L that appear in the curves of Figure 1 and also in Table 2 point out an important fact. That is, when d_S is less than unity two liquids of different d_L values but equivalent γ_L may display equivalent values of cos θ and W_a.

The curves of Figure 3 display the general application of equation (3) to the extensive data of Table 2. Each curve represents a different value of d_L for a constant value of $\gamma_S = 21.6$ dyne/cm and $d_S = 0.91$. The upper curves of Figure 3 displaying $d_L = 0.91$ and $d_L = 1.00$ present the respective graphical forms of equation (7) for ideal interaction $\phi_{LS} = 1.0$ and equation (8) for pure dispersion interactions with $\phi_{LS} = 0.954$. The curves of Figure 3 dramatize the specific character of interaction by homologous liquid series. The liquid-PTFE interactions are easily distinguished in Figure 3 based upon the average d_L values for a homologous series. Table 4 summarizes average d_L values for five groups of liquids included in the study of Fox and Zisman. It may be noted in Table 2 that the halocarbons and miscellaneous liquids

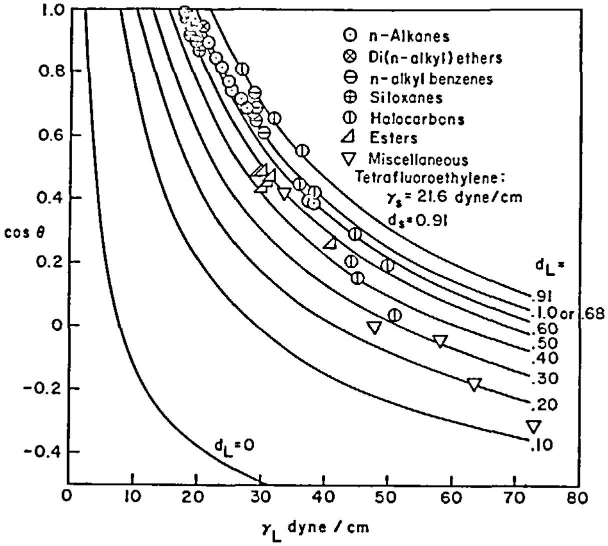

Figure 3 Classification of the dispersion fraction d_L for liquids on PTFE.

provide a broad spectrum of d_L values and therefore do not follow a specific $\cos\theta$ versus γ_L curve in Figure 3.

The three points raised in a previous paragraph concerning the clarification of the meaning of the linear $\cos\theta$ versus γ_L functions described in Figure 2 may now be easily resolved. Intercomparing Figure 1 and Figure 3 we can correlate the following γ_C and W_a definitions:

$$\cos\theta = 1 + b(\gamma_C - \gamma_L) \tag{10}$$

$$W_a = 2\gamma_L + b\,\gamma_L(\gamma_C - \gamma_L) \tag{11}$$

due to Zisman and coworkers[2] with the relations of this discussion. The short dashed curve applied in Figure 2, which defines $\gamma_C = 18.5$ dyne/cm for PTFE, is a linearized segment of the curve of Figure 3 for $d_L = 1.0$. It is evident that linear extrapolation of data where $0.8 < \cos\theta < 1.0$ can provide reasonable estimates of specific values of γ_C for specific liquid-solid interactions where ϕ_{LS} is constant. Linear extrapolation to define γ_C is, however, a questionable procedure since the curves of Figure 3 show that the slope factor of equation (10) is a variable of both d_L and $\cos\theta$. This analysis provides a ready explanation, through equation (4), for the specific dependence of γ_C upon specific liquid-solid interactions.

Equation (3) provides a detailed explanation of both the magnitude and variability of the slope factor of equation (10). By differentiating equation (3) we obtain the following expression for the tangent slope:

$$b = -\frac{d\cos\theta}{d\gamma_L} = \frac{\phi_{LS}}{\gamma_L}\left(\frac{\gamma_S}{\gamma_L}\right)^{1/2} = \left(\frac{\gamma_C}{\gamma_L^3}\right)^{1/2} \tag{12}$$

which follows the definition of equation (10). At the condition of critical weting, where $\cos\theta = 1.0$ and $\gamma_L = \gamma_C$, equation (12) predicts a maximum slope $b_C = 1\ \gamma/_C$. Equation (12) indicates the analytically defined slope is a variable of liquid surface tension γ_L. The constant slope shown by the rectilinear band of $\cos\theta$ versus γ_L in Figure 2 is an artifact produced by the tendency for organic liquids to display increasing polar p_L characteristics with increasing surface tension. The scatter of $\cos\theta$ versus γ_L data in Figure 2 results from liquids of equivalent surface tension displaying differing values of p_L. The lower portion of Figure 4 illustrates these p_L versus γ_L trends which form the basis for the use of equation (10).

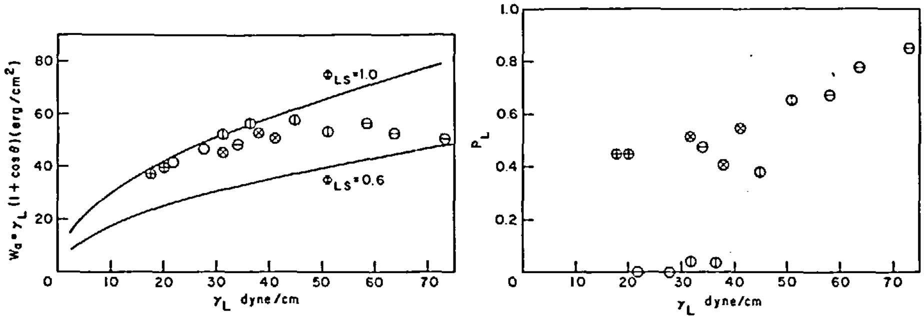

Figure 4 (left) Characteristic variations in work of adhesion W_a with variation in liquid surface tension γ_L.
(right) Variation of liquid polar fraction p_L of surface tension and surface tension γ_L.

The left portion of Figure 4 displays the variation of experimental values of W_a versus γ_L. The experimental data are enclosed in two curves representing equation (2) for $\gamma_S = 21.6$ dyne/cm and $\phi_{LS} = 1.0$ and $\phi_{LS} = 0.6$ characterizing interaction with nonpolar and polar liquids respectively. As γ_L and p_L increase, the W_a versus γ_L values displayed in upper Figure 4 shift in a systematic manner toward the theoretical curve of low ϕ_{LS}. This characteristic reduction in ϕ_{LS}, due to increased p_L, versus γ_L accounts for the characteristic maximum in W_a values with varied γ_L which forms the basis of equation (11).

The right portion of Figure 4 reemphasizes the important point that a simple dependence of p_L upon γ_L values is not obtained from PTFE wettability data. Gardon[11] has shown a similar broad scatter of fractional polarity versus cohesive energy density when evaluating bulk properties of liquids. Table 4 indicates that silicones and esters display much higher fractional polarity in interfacial interactions to PTFE than one would assume from bulk properties. The small variations of $p_L = 1\text{-}d_L$ shown by different members of the silicone and ester groups of liquids may indicate a significant structural group interaction for both types of liquids to PTFE.

Table 4

Average Values of the Interfacial Dispersion Character d_L of Liquids to PTFE

Liquid Series	*d_L (Average)*
n-Alkanes	1.0 (by definition)
di(n-Alkyl) ethers	1.0
n-Alkyl benzenes	0.99
n-Polydimethylsiloxanes	0.53
Esters	0.48

CONCLUSIONS

This analysis of organic liquid-PTFE surface interactions provides values of $\gamma_S = 21.6$ dyne/cm, $\gamma_S^d = 19.6$ dyne/cm and $\gamma_S^p = 2.0$ dyne/cm. The result of this analysis for γ_S^d is equivalent to a value $\gamma_S^d = 19.5$ dyne/cm calculated by Fowkes.[8] The value of γ_S deduced here is lower than $\gamma_S = 24$ dyne/cm calculated for PTFE by Good.[6] The definition of $d_S = 0.91$ and $p_S = 0.09$ as dimensionless dispersion and polar fractions of the surface tension of PTFE resolves a number of detailed aspects concerning the wettability properties of this polymer.

The analysis points out that the critical surface tension of wetting for PTFE is controlled by the dispersion-polar balance of surface interactions which determine the bonding efficiency factor ϕ_{LS}. The apparent dispersion fractions d_L of over fifty liquids are cataloged with respect to surface interaction with PTFE. The empirical development and applicability of the relation $\cos\theta = 1 + b(\gamma_C - \gamma_L)$ is analyzed with regard to both the slope factor b and the intercept γ_C by means of the new relations for work of adhesion.

REFERENCES

1. H. W. Fox and W. A. Zisman, *J. Coll. Sci.*, **5**, 514 (1950).
2. W. A. Zisman, in "Adhesion and Cohesion" (Ed.: P. Weiss), Elsevier, Amsterdam (1962). p. 172.
3. E. G. Shafrin, in "Polymer Handbook," (Eds.: J. Brandrup and E. H. Immergut), Wiley-Interscience, New York (1966).
4. G. J. Crocker, *Rubber Chem. & Tech.*, **42**, 30 (1968).
5. S. Wu, *J. Phys. Chem.*, **72**, 3332 (1968).
6. R. J. Good, in "Adv. in Chem. Series No. 43," (Ed. R. F. Gould). Amer. Chem. Soc., Washington, D.C. (1964). p. 75.
7. F. M. Fowkes, Ibid., p. 99.
8. F. M. Fowkes, *J. Phys. Chem.*, **66**, 382 (1962); **66**, 1863 (1962); **67**, 2538 (1963).
9. L. A. Girifalco and R. J. Good, *J. Phys. Chem.* **61**, 904 (1957).
10. R. J. Good and L. A. Girifalco, Ibid., **64**, 561 (1960).
11. D. H. Kaelble, "Physical Chemistry of Adhesion", Wiley-Interscience, New York (in press).
12. J. L. Gardon, in "Enc. of Polymer Sci. & Tech." (Eds.: H. F. Mark, N. G. Gaylord, N. M. Bikales) Vol. 3, Wiley-Interscience, New York (1966). p. 833.
13. E. G. Shafrin and W. A. Zisman, *J. Amer. Ceramic Soc.*, **50**, 478 (1967).
14. M. K. Bernett and W. A. Zisman, *J. Coll. and Interface Sci.*, **28**, 243 (1968).