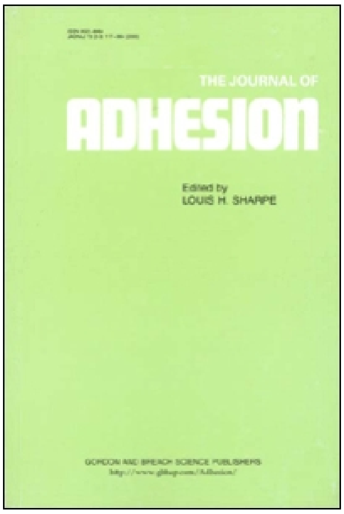

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Interfacial Interactions in Polymers: The Dependence of the Measured Surface Tension of Solid Polymer on the Surface Tension of Wetting Liquid

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Interfacial Interactions in Polymers: The Dependence of the Measured Surface Tension of Solid Polymer on the Surface Tension of Wetting Liquid

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Careful measurements of the surface tension of solid polymers, γ_S, based on the data on contact angles for wetting liquids with various surface tension, γ_L, allows one to establish the functional dependence of $\gamma_S = f(\gamma_L)$. This dependence is divided into three zones: one zone, where there is no dependence of γ_S on γ_L and two zones where γ_S changes linearly with γ_L.

Keywords: Surface tension; thermodynamic work of adhesion; wetting; contact angle; zone of surface polarization and depolarization

INTRODUCTION

In studying thermodynamics of interfacial interactions in polymeric systems a great deal of attention is paid to the estimation of the contribution to the interaction of various forces, especially of donor-acceptor forces[1–3]. Of course, the contribution of specific interactions may be essential for adhesion phenomena at the interface between polymers and surfaces with high surface energy. However, to find the general regularities of interfacial interactions in polymer systems one has to use the full work of adhesion, as was done recently by Nardin, Schultz and others[4–7]. To find such regularities, we have for many years used the hypothesis of minimization of free energy for two-phase systems[8, 20]. Presently this hypothesis is proved theoretically[10] and we can estimate the mutual influence of the surface tension of coexisting phases and, hence, the thermodynamic work of adhesion (TWA) at the interface.

From contact angle measurements we can determine both thermodynamic work of adhesion and surface tension of a solid polymer, using various wetting liquids. For this purpose we apply the equivalent forms of the equation[8, 10, 20]

$$W_a = W_{ci}^{(S)} \tag{1}$$

and

$$\gamma_S = 0.5 \cdot \gamma_L(1 + \cos\vartheta) \tag{2}$$

where γ_L is the surface tension of the wetting liquid, γ_S is the surface tension of a polymer in a zone of interfacial nonuniformity (in the interphase, *i.e* in the zone of ternary contact)[20], ϑ_a is the advancing contact angle[9], W_a is the work of adhesion and $W_{ci}^{(S)}$ is the work of cohesion of an interphase of the solid polymer.

Earlier[9] it was shown that in Eq. (2) one has to use the advancing contact angle. Simultaneously, due to the statistical character of the regularity we are in search of, the data for liquids with high specificity of interaction should be eliminated[10].

RESULTS AND DISCUSSION

Surface tensions of liquids and advancing contact angles have been depermined according to procedures in Ref. 11. The results of the measurements were averaged from 4–5 values for each liquid. The wetting of poly (tetrafluoroethylene) was determined using the liquids given in Table I. This polymer is convenient, being insoluble and not capable of swelling in the majority of organic liquids. In the series shown, the results of measurements are given for liquids with surface tension above 30 mN/m. The selection will be clear later. Table II gives the estimations of experimental errors and presents non-averaged data. The results are arranged according to measured (after

TABLE I Measured and calculated value on wetting PTFE by various liquids (20°C)

liquid	γ_L	$\cos\vartheta_a$	γ_S
tetrachloroethylene	31.38	0.6428	25.78
vaseline oil	31.53	0.6389	25.94
oleic acid	32.72	0.5219	24.90
dioxane	32.69	0.6042	26.22
cyclohexanone	34.47	0.4931	25.73
tetrachloroethane	35.63	0.4620	26.04
dibromoethane	38.77	0.3690	26.54
acetophenone	39.28	0.3459	26.43
o-nitrotoluene	41.56	0.2378	25.72
aniline	42.77	0.1938	25.53
diethylene glycol	46.63	0.0931	25.48
ethylene glycol	48.36	0.0804	26.13
formamide	57.63	−0.1133	25.55
glycerol	63.16	−0.1714	26.17
water	72.52	−0.3412	23.89

TABLE II Non-averaged data from Table I for ethylene glycol and water

liquid	γ_L	σ_{γ_L}	$\cos\vartheta_a$	$\vartheta_a(deg)$	σ_ϑ	γ_S	σ_{γ_S}
ethylene glycol	47.69		0.0781	85.5		25.71	
	48.36		0.1060	83.9		26.74	
	48.37		0.0630	86.4		25.71	
	48.67		0.1094	83.7		27.00	
	48.72		0.0457	87.3		25.47	
means	48.36	0.37	0.0804	85.4	1.6	26.13	0.62
water	72.36		−0.3149	108.4		24.79	
	72.51		−0.3615	111.2		23.15	
	72.59		−0.3597	111.1		23.24	
	72.60		−0.3287	109.2		24.37	
means	72.52	0.10	−0.3412	110.0	1.4	23.89	0.71

measurement of contact angle) values of surface tension of the liquids, the value γ_S including all artifacts connected with measurement of contact angle.

The mean-square error has been calculated as $\sigma_x = \sqrt{(\Sigma_i(\bar{x} - x_i)/n)}$, where x_i is the measured or calculated value in the i-th experiment, $\bar{x} = (1/n)\Sigma_i x_i$, the error of the mean value being $\sigma_{\bar{x}} = \sqrt{(\sigma_x^2/(n-1))}$ and the accuracy, $ac = \sigma_{\bar{x}}/\bar{x}$.

The errors in measurements of the contact angles given in Table II ($\sim 2^0$) are satisfactory and the calculation of the surface tension of poly (tetrafluoroethylene) is correct to within 2.4%. The contribution of the first factor in Eq. (2) is 0.8% and of the second factor 1.6%. The accuracy of calculation by water is 3.0%, contribution of the first factor being only 0.14%. The accuracy of the data allows one to conclude that Table I contains reliable results.

The closeness of the values in the last column of Table I show that they do not depend on the surface tension of the wetting liquid. To be sure, let us calculate the value of γ_S and the deviation from the mean value, using for calculation some experimental values for each liquid without averaging. The value found is $\bar{\gamma}_S = 25.68$ mN/m, with dispersion $\sigma_x = 0.85$ mN/m, and dispersion of mean value $\sigma_{\bar{x}} = 0.12$ mN/m.

The verification of the distribution law for deviations using the Pirson criterion[12] has shown that with probability 0.5 (this value is a high probability for the distribution law[12] the hypothesis about the normal distribution is valid. Therefore, we have $\gamma_S = 25.7 \pm 0.3$ mN/m with a confidence of 0.95.

Poly(tetrafluoroethylene) is a widely investigated material and we can check the regularity found by us, using data published in the literature[13–16]. Of course, one should bear in mind, that the measurements have been done by various authors and in most cases (except one[14]) by the sessile drop method without control of the surface tension of the wetting liquid. It should be expected that these data give larger scatter. Table III presents the results of calculation for the liquids with the surface tensions of the same order as in Table I. The results of wetting by some esters[13] are considered as not belonging to the "normal totality"[9] (see Tab. X).

The statistical analysis of the data in Table III gives $\bar{\gamma}_S = 26.13$ mN/m, $\sigma_y = 1.94$ and $\sigma_{\bar{y}} = 0.34$ mN/m. As one could expect, the scattering of the data is higher as compared with the data in Table I. However, the mean value is in good accordance with our experimental data; therefore, all the mean values belong to one and the same general universe.

To establish the correlation between the values of γ_L (variable x) and γ_S (variable y) we performed a correlation analysis for the data in Table III (our data have too small dispersion to discover correlation). For this purpose, the range of measurements of γ_L (31–73 mN/m) may be divided into intervals, each 7 mN/m, and inside these intervals the

TABLE III Values of surface tension for PTFE, calculated from Eq. (2) and from the data Refs. 13–16

liquid 1	γ_L 2	*cos*ϑ_a 3	γ_S 4	*Ref* 5
carbon disulfide	31.4	0.470	23.08	13
tetrachloroethylene	31.7	0.656	26.25	"
dicyclohexyl	33.0	0.530	25.26	16
t-butyl naphthalene	33.7	0.423	23.98	13
hexachloro butadiene	35.3	0.522	26.87	14
"	36.0	0.500	27.00	13
tetrachloroethane (symm.)	36.3	0.559	28.30	"
perchlorocyclopentadiene	37.5	0.391	26.08	"
benzylphenyl undecanoate	37.7	0.391	26.22	"
hexachloro propylnene	38.1	0.423	27.11	"
"	38.1	0.514	28.85	16
benzaldehyde	40.6	0.307	26.53	15
tricresyl phosphate	40.9	0.259	25.75	13
formic acid	42.9	0.249	26.79	15
polyethylene glycol-400	43.1	0.225	26.40	14
tetrachlorodiphenyl	44.2	0.208	26.70	13
-bromonaphthalene	44.6	0.292	28.81	"
"	47.0	0.139	26.77	15
nitrobenzene	44.7	0.218	27.22	15
trichlorodiphenyl	45.3	0.156	26.18	13
ethylene glycol	47.7	0	23.85	"
"	49.0	−0.052	23.23	15
tetrabromoethane (symm.)	49.7	0.191	29.60	13
diiodomethane	49.1	0.019	25.02	15
"	50.8	0.035	26.29	13
"	50.8	0.140	28.95	16
hexantriol-1,2,6	51.8	−0.070	24.09	14
formamide	58.2	−0.052	27.60	16
"	58.2	−0.044	27.82	14
"	58.2	−0.035	28.08	13
glycerol	63.4	−0.174	26.18	"
"	64.9	−0.334	21.61	15
water	71.9	−0.391	21.90	16
"	72.8	−0.309	25.15	13
"	72.3	−0.317	24.68	14

group mean values $\bar{y}_i$ may be estimated, which are necessary to calculate the empirical correlation ratio, r_e:

$$r_e^2 = 1 - (\sigma_{y/x}/\sigma_y)^2 \tag{3}$$

$$\sigma_{y/x}^2 = \sum_k^i (y_k - \bar{y}_i)^2/(n-1))$$

Because the results of the calculations are important for substantiating our concept, the data are given in Table IV.

The last three intervals, due to an insufficient amount of experimental data, are united according to the rules of correlation analysis. From the data in Table IV it is seen that $\sigma^2_{y/x} = 3.36$. Using the calculated value of $\sigma^2_y = 1.94$ in accordance with Eq. (3) we have $r_e = 0.39$ with accuracy 49%. It may be shown that the interval estimation of r_e leads to the appearance of a zero value of the correlation ratio inside this interval. That means we have, with high probability, the lack of correlation between the values of γ_L and γ_S in the investigated, range of values of γ_L for PTFE. We have to add that the empirical correlation ratio overestimates the closeness of connection of the variables[12].

In the same way, we have analyzed the data published in the literature for some fluorine containing polymers and copolymers, which have low solubility in liquids used for measurement of contact angles. Table V shows the results of measurements made by Fox and Zisman[17] and results of our calculations for copolymers of tetrafluoroethylene and chlorotrifluoroethylene. At the end of the upper part of the Table the values of γ_S and their accuracies are given which were calculated for liquids separated by the dotted line. The same analysis was done for the data on wetting of copolymers of tetrafluroethylene and hexafluoropropylene[16, 18] (see Tab. VI).

Rather low values of deviations from the mean value in all the cases allow the following conclusion to be drawn: in a definite interval of surface tensions of wetting liquids (contacting phase) and in the absense of specific interactions at the interface[9], the thermodynamic work of adhesion and the surface tension of a polymer do not depend

TABLE IV Calculation of the sum of squares of the deviations from the group mean values according to the data[13–16] given in Table III

Interval x	*Number of exp . points, k*	$\bar{y}_i$	$\Sigma_K(y_K - \bar{y}_i)^2$
31–38	9	25.89	20.23
38–45	9	27.10	8.89
45–52	9	26.00	39.28
52–59	3		
59–64	1	25.38	45.68
64–73	4		

TABLE V Surface characteristics of tetrafluoroethylenechlorotriftoro-ethylene copolymers according to the data of Fox and Zisman[17] (20°C)

liquid	γ_L	*amount of chlorotrifluoroethylene, %*								
			20	γ_s		*40*	γ_s		*90*	γ_s
		$\cos\vartheta_a$	W_A	γ_s	$\cos\vartheta_a$	W_A	γ_s	$\cos\vartheta_a$	W_A	γ_s
1	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*	*10*	*11*
Water	72.8	−0.174	60.1	30.1	0.070	67.7	33.9	0.000	72.8	36.4
Glycerol	63.4	−0.105	56.7	28.4	0.052	66.6	33.3	0.139	72.2	36.1
Formamide	58.2	−0.017	57.2	28.6	0.259	73.3	36.7	0.139	66.3	33.1
Diiodomethyl	50.8	0.105	56.1	28.1	0.242	63.1	31.5	0.438	73.1	36.5
-bromnaphthalene	44.6	0.391	62.0	31.0	0.454	64.9	32.5	0.669	74.4	37.2
Tricresyl phosphate	40.9	0.391	56.9	28.4	0.559	63.8	31.9	0.719	70.3	35.2
			γ_s	29.1			33.3			35.8
			ac,%	1.6			2.3			1.7
Benzene	28.8	0.707	49.2	24.6	0.906	54.9	27.5		spreads	
Dioctyl-ether	27.7	0.731	48.0	24.0	0.875	51.9	26.0		"	
Hexadecane	27.6	0.799	49.6	24.8	0.914	52.8	26.4		"	
Diheptyl-ether	27.0	0.755	47.4	23.7	0.927	52.0	26.0		"	
Tetradecane	26.7	0.819	48.6	24.3	0.921	51.3	25.6		spreads	
Dodecane	25.4	0.819	46.2	23.1	0.946	49.4	24.7		"	
Diamyl-ether	24.9	0.838	45.8	22.9	0.988	49.5	24.8			"
Decane	23.9	0.891	45.2	22.6		spreads			"	
Nonane	22.9	0.899	43.5	21.7		"			"	
Dibutyl-ether	22.8	0.906	43.5	21.7		"			"	
Dipropyl-ether	20.5	0.990	40.8	20.4		"			"	
Heptane	20.3	0.990	40.4	20.2		"			"	
Hexane	18.4		spreads			"			"	

on the surface tension of the contacting phase. This zone may be called the unperturbed zone. Within the limits of this zone one can estimate the surface tension of a solid polymer (see the data in Tabs. I, III, V, VI), using liquids belonging to the normal totality[9].

Consider the interrelation between γ_S and γ_L for the same polymers in the zone of low values of surface tension of wetting liquid. We can use the data[13] where all the liquids used belong to the normal totality[9], including ethers and *n*-heptyl acid[19]. Figure 1 compares values of γ_S and γ_L for PTFE. Results of our own measurements are included.

TABLE VI Surface tensions of tetrafluoroethylene-hexafluoro-propylene copolymers according to the data of Bernett and Zisman[16, 18] (25°C)

liquid	γ_L	*amount of hexafluoropropylene, %*							
		0	*6*	*8*	*12*	*14*	*16*	*23*	*100*
water	71.9	21.9	23.7	22.5	21.9	21.3	21.9	21.3	21.3
Formamide	58.2	27.6	27.1	26.1	25.6	25.1	25.1	23.5	20.6
Diiodomethane	50.8	28.9	28.9	28.1	27.6	27.2	26.7	25.8	23.6
Ethylene glycol	47.7	23.9	24.7	24.3	23.9	23.9	23.4	22.6	19.3
Hexachloropropylene	38.1	28.9	28.6	28.6	28.3	28.0	28.0	27.4	25.6
Dicyclohexyl	33.0	25.2	25.7	25.2	25.0	25.0	24.8	24.5	22.7
	γ_S, mN/m	26.1	26.5	25.8	25.4	25.1	25.0	24.2	22.2
	accuracy%	4.5	3.2	3.5	3.7	3.8	3.2	3.4	3.8
Hexadecane	27.6	23.4	23.4	23.0	22.8	22.5	22.5	22.1	20.5
Tetradecane	26.7	23.0	23.1	22.6	22.3	22.3	22.1	21.9	20.6
Dodecane	25.4	22.3	22.4	22.1	–	21.8	–	21.7	20.5
Decane	23.9	21.6	21.9	21.5	–	21.2	–	21.1	20.4

In this case, the calculation of regression according to the equation

$$\gamma_S = a\gamma_L + b \tag{4}$$

(a and b are coefficients) leads to values $a = 0.58$ with accuracy 0.74% and $b = 7.55$ with accuracy 1.5%. The errors in determination of coefficients of Eq. (4) have been found using the well-known relation, $\sigma_\gamma = m\sigma_a + n\sigma_b$, where coefficients n and m are found from the coefficients of the system of normal equations, used at the same time to find coefficients a and b. The correlation coefficient for linear approximation is $r_a = 0.98$ with accuracy 3.7%. The high value of r_a shows we really observe some regularity.

The linear dependence is restricted from both sides: from above by the unperturbed zone and from below by the value of surface tension of liquid for which the contact angle becomes equal to zero (γ_c). Using the coefficients of Eq. (4) we have $\gamma_c = \gamma_L = 0.58\ \gamma_L + 7.55$, or $\gamma_c = 18.0$ with an accuracy of 2.2%. Although this value was obtained by

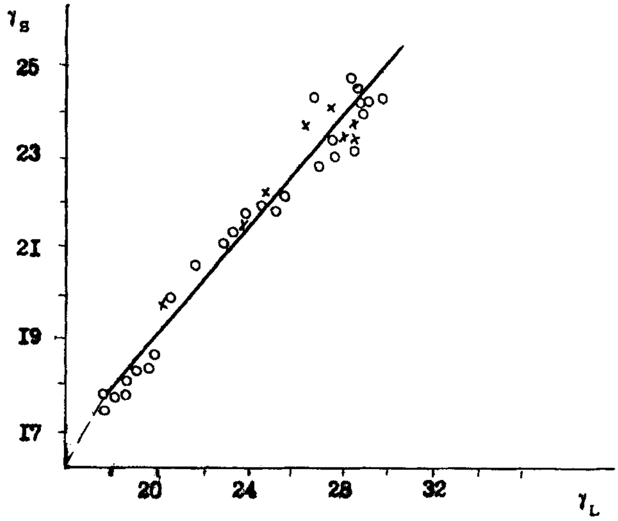

FIGURE 1 Dependence $\gamma_S = f(\gamma_L)$ for PTFE (x-our own data).

another way, its meaning is the same as Zisman's critical surface tension. An analagous result was observed for copolymers of tetrafluoroethylene and chlorotrifluoroethylene[17] (Fig. 2). The equation of approximation is

$$\gamma_S = 0.64\gamma_L + 8.7 \tag{5}$$

for the 60:40 composition and

$$\gamma_S = 0.56\gamma_L + 8.8 \tag{6}$$

for the 80:20 composition. The corresponding values of γ_c are 24.2 mN/m with accuracy 0.9% and 20.1 mN/m with accuracy 0.7%. We have not plotted the data for other copolymers because of the small amount of experimental data in this region (see Tab. VI), in spite of this the same tendency is preserved.

Figure 3 shows the results of calculations from the data[17] on wetting for the 1:1 copolymer of tetrafluoroethylene and ethylene. Both zones are clearly seen. For the unperturbed zone $\gamma_S = 34.3$ mN/m with

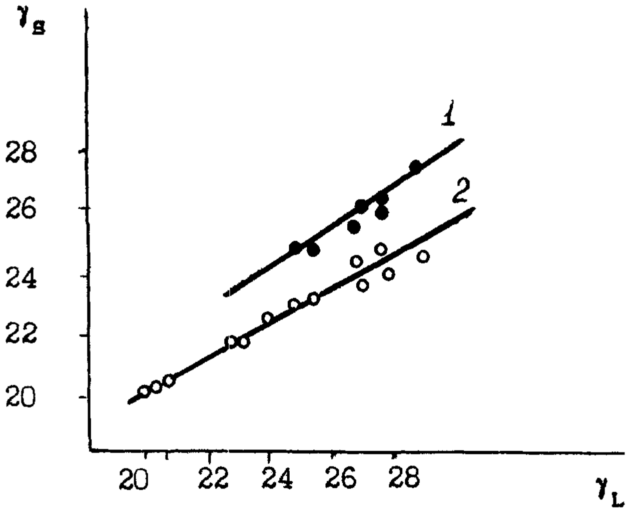

FIGURE 2 Dependence $\gamma_S = f(\gamma_L)$ for copolymer. Tetrafluoroethylene-trichloroethylene (ratio of components: 1–60:40, 2–80:20).

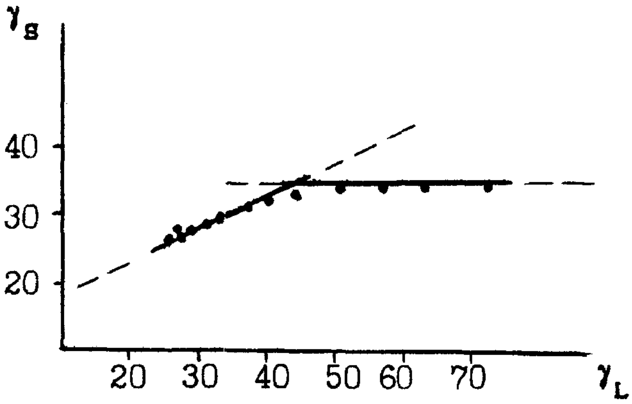

FIGURE 3 Dependence $\gamma_S = f(\gamma_L)$ for tetrafluoroethylene-ethylene copolymer (1:1).

accuracy $= 1.2\%$ and for the depolarization zone $a = 0.50$, $b = 13.0$ and $\gamma_c = b/(1-a) = 26.0$ mN/m, in excellent accordance with experiment.

To prove the discovered dependence it is necessary to know whether other polymers, including polar ones, follow the same dependence. For this purpose we cannot use the literature data, because they were obtained by using droplets of wetting liquid, which does not allow one to estimate possible dissolution or swelling of a polymer. The last factor prevents the gathering of reliable data, for example, for polyethylene. Using the method mentioned in Ref. 11 we have tried to estimate the wetting of polyethylene and have found a change in weight of the meniscus of wetting liquids with time. This effect was discovered for liquids with surface tension below 35 mN/m. Because of this, we did not use such liquids for measurements. Of course, by this we restrict ourselves in statistical estimation and obtain less reliable mean values.

In Table VII the results of measurements and calculations for 6 different polymers are given for the unperturbed zone. It is seen that for the polymers presented in the Table, the deviations are even less as compared with fluoropolymers. Therefore, the regularity found is valid in the unperturbed zone for polymers of various chemical structure. For the zone where the dependence between γ_S and γ_L may be observed, we have performed especially careful measurements of wetting for poly (oxymethylene), as nonpolar liquids are not capable of dissolving or swelling it (as distinct from polyethylene, where it is impossible to perform measurements with nonpolar liquids). The results are given in Table VIII. It is seen that the accuracy of measurements is rather high : for calculated values or γ_S, accuracy = 0.12 mN/m.

TABLE VII Surface tension of some polymers in unperturbation zone

N polymer	*numb. of liq*	*number of measurem.*	$\bar{\gamma}$	σ_γ	*ac*,%*
1 poly (ethylene)	12	31	30.8	1.3	0.78
2 poly (propylene)	4	10	31.1	0.5	0.54
3 polystyrene	5	10	34.0	1.7	1.60
4 epoxy polymer**	6	19	39.6	0.8	0.46
5 poly (methyl-methacrylate)	4	11	40.0	2.9	2.16
6 poly (oxymethylene)	4	17	41.0	2.3	1.38

*ac = accuracy.

**Commercial epoxy resin based on bisphenol A and epichlorohydrin, with 20% initial epoxy groups, hardened with polyethylene polyamine.

TABLE VIII Calculated values of surface tension of poly (oxymethylene) (POM) where $\gamma_S = a\gamma_L + b$

liquid	*numb of m*	γ_L	*ac** *%*	$cos\vartheta_a$	*ac** *%*	γ_S	*ac** *%*
heptane	5	20.36	0.09	20.26	0.15	20.31	0.12
isopropyl alcohol	5	21.13	0.21	21.01	0.06	21.07	0.14
ethyl acetate	5	24.06	0.15	23.92	0.13	23.99	0.14
amyl alcohol	5	25.25	0.05	24.69	0.08	24.97	0.07
butyl acetate	7	25.28	0.05	24.92	0.70	25.10	0.50
tetrachloromethane	6	26.80	0.09	26.80	0.19	26.80	0.14
toluene	5	28.76	0.08	28.53	0.07	28.60	0.08
benzene	5	28.95	0.08	28.43	0.10	28.69	0.09
tetrachloroethylene	9	31.82	0.09	31.54	0.09	31.68	0.09
dichloroethane-(symm.)	7	32.11	0.04	31.21	0.09	31.66	0.07
dioxane	5	32.82	0.04	31.11	0.10	31.96	0.07
cyclohexanone	6	34.62	0.03	33.98	0.20	34.30	0.14

*ac = accuracy.

Figure 4 shows the dependence between the two values, the straight line being plotted on the basis of the least squares method:

$$\gamma_S = 0.968\gamma_L + 0.66 \qquad (7)$$

where for the slope the accuracy = 0.4% and for the free term the accuracy = 14%. The value $\sigma_{y/x}$ is equal to 0.18 mN/m and $\tau_a = 0.999$ with accuracy 0.9%. If we take into account that in Table VIII liquids of various nature* are presented, the results obtained seem to confirm the existence of the regularity. We should also emphasize that the deviation of the value *a* from unity is meaningful, *i.e* in this region there is no spreading (for $\gamma_L = 36$, $\gamma_L - \gamma_S = 0.49$).

The calculation of the value γ_c seems to be unreasonable because the difference $(1 - a)$ due to the small magnitude has an accuracy no better than 12%. The accuracy of the free term is 14%.

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*The different nature of the liquids was estimated from the fraction, f_d of dispersion intermolecular forces, using data given in Ref. 21, from the ratio $f_d = \mathrm{CED}_d/\mathrm{CED}$, where CED is the cohesive energy density of the wetting liquid and CED_d is the dispersion part of the CED. Our calculations show that for the twelve liquids in Table VIII, eight have the following order of $f_d < 1$ in the series of γ_L: 0.45 for isopropanol; 0.67 for ethyl acetate; 0.54 for amyl acetate; 0.82 for butyl acetate; 0.98 for toluene, benzene and tetrachloroethylene; 0.86 for dioxane and 0.76 for cyclohexanone. These data prove that low values of γ_L are not necessarily connected with dispersion molecular forces.

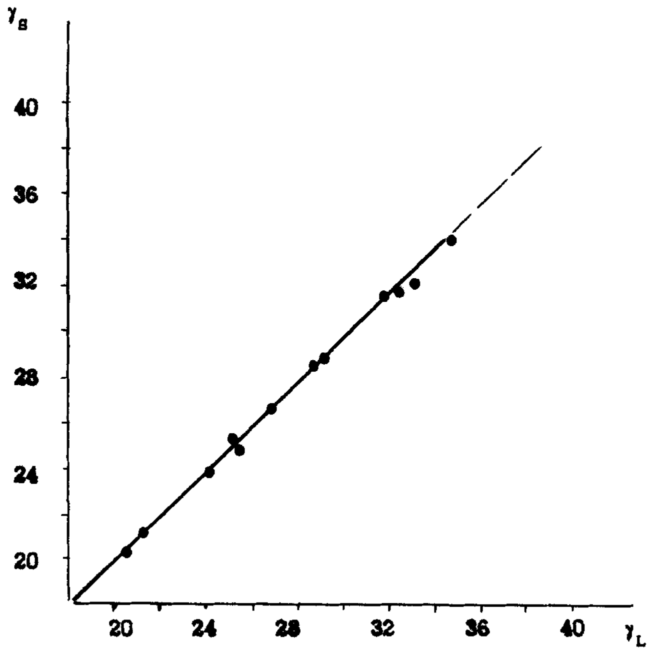

FIGURE 4 Dependence $\gamma_S = f(\gamma_L)$ for polyoxymethylene.

For other four polymers given in Table VII the results of calculations are presented in Figure 5:

$$\gamma_S = 0.984\gamma_L + 0.109 \tag{8}$$

The accuracy of the slope is 0.26% (the number of experimental points is 45) and for the free term is 55%. The coefficient of linear approximation is high, $\tau_a = 0.995$ with accuracy 1.5%.

Thus, the detailed analysis of experimental data on the wetting of polymers, using Eq. (1) and (2) allows the following conclusions to be drawn (see Fig. 6).

The dependence of surface tension of solid polymer on wetting liquids with not too high values of surface tension may be divided into two zones. In one of them the surface tension of solid polymer does not depend on the surface tension of wetting liquid. This zone was called the unperturbed zone because, for this case of wetting, the

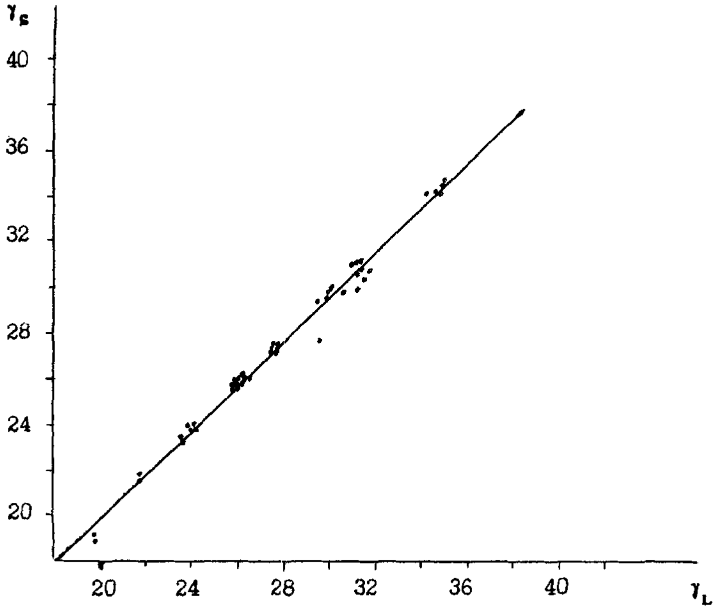

FIGURE 5 Dependence $\gamma_S = f(\gamma_L)$ for polar polymers.

cohesive energy of the interphase layer of polymer does not change as compared with the coexisting phase and is equal to th cohesive energy in the bulk of the polymer. In this zone, the TWA does not depend on the surface tension of wetting liquid.

Upon decreasing surface tension (to some limit), there appears a zone where the surface tension of polymers increases linearly with surface tension of wetting liquid, being lower than the value in the unperturbed zone. This zone should be considered as a zone of depolarization because decreasing surface tension of wetting liquid leads to diminishing surface tension of solid polymer. Correspondingly, the TWA in this zone increases linearly with surface tension of wetting liquid.

The measurements in the region of high surface tension of wetting liquid are difficult because of the lack of a set of such liquids. For this reason we have used only one liquid, namely mercury. The experimental method used allowed one to measure simultaneously both surface

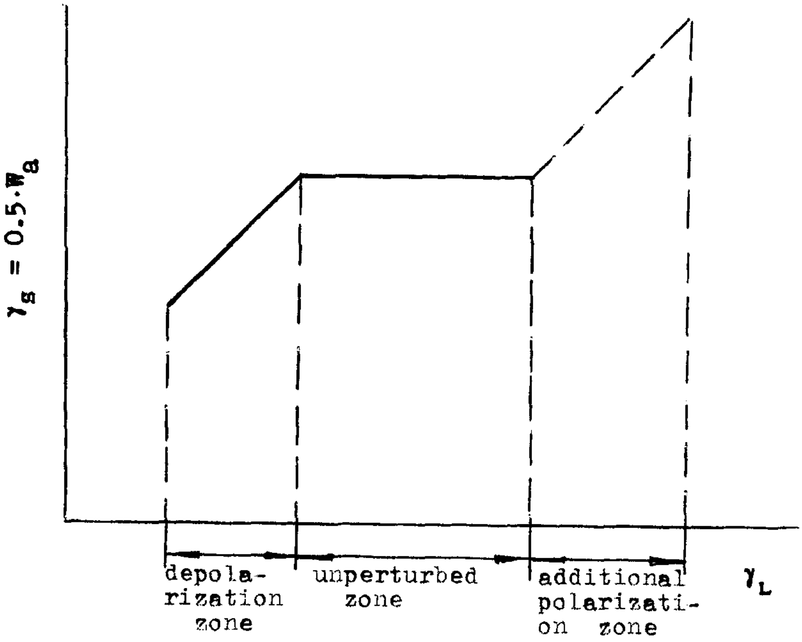

FIGURE 6 Generalized dependence $\gamma_S = f(\gamma_L)$ for two zones.

TABLE IX Surface tension of some polymers at the interface with mercury[20]

polymer	$\cos\vartheta_a$	γ_S	σ_γ
PTFE	−0.63	84	1.7
PE	−0.61	87	0.6
epoxy polymer	−0.77	52	0.8
PS	−0.64	82	1.0
PMMA	−0.62	87	0.9

tension of Hg and advancing contact angle on the polymer surface[20]. The data are presented in Table IX. It is seen that the surface tension of polymer at the interface with a liquid of high surface energy really increases. That means in this case a zone with additional polarization appears. It may be seen that the effects of polarization-depolarization are connected with the fact that at the point of ternary contact the surface force field solid-air is substituted by the field solid-liquid (γ_{SL}).

Therefore, if $\gamma_S \gg \gamma_{SL}$, the depolarization zone appears and when $\gamma_S \ll \gamma_{SL}$ a zone of additional polarization appears. In the zone where $\gamma_S \approx \gamma_{SL}$ the polarization of the molecules of the solid stays the same as it was at the solid-air interface. One has not to forget that the field of the surface forces is an anisotropic one. In this sense, the physical meaning seems rather clear. But we have to emphasize that in this work we only describe the shape of the functional dependence of γ_S on γ_L and we do not try to explain this shape.

Finally, there are liquids with specific interactions at the interface. These liquids may be distinguished according to the interrelation between their surface tension and dielectric permeability, being liquids of specific totality[9]. To make such a selection, we have created a plane in coordinates $\gamma_L - \Pi = (\varepsilon - 1)/(\varepsilon + 2)$ (Π is polarization and ε is dielectric constant) and put on it the corresponding values for 72 liquids. Then the linear approximation was constructed as $\gamma_L = c + d \cdot \Pi$ with $c = 16.4$ and $=23.6$ (see Ref. 9). Liquids, whose characteristics lie below the approximation line, relate to specific totality. Therefore, if for a given value of γ_L the dielectric permeability ε is higher than ε^*

$$\varepsilon^* = (2\gamma_L - 2c + d)/(c + d - \gamma_L) \tag{9}$$

(with $c = 16.4$ and $d = 23.6$, Ref. 9) then the liquid belongs to the specific totality. The molecules of such liquids are capable of orientation by flow, which is reflected in a deep minimum of free energy in interfacial interaction by advancing contact angle (as compared with liquids of normal totality). As a consequence the surface tension of a solid polymer has a lower magnitude in every zone.

Table X confirms the decreasing value of surface tension, and therefore of TWA, estimated from the data on liquids of specific totality[9]. The values of ε were taken from Ref. 19.

For such liquids, the higher hysteresis of wetting is characteristic, and, hence, the lower $\cos\vartheta_a$ and higher $\cos\vartheta_r$. That means that in the advancing regime these liquids have lower TWA (and calculated γ_S) and in the receding regime they have higher TWA as compared with liquids of normal totality.

TABLE X Surface tension of PTFE calculated from wetting data [13] for some liquids with large value of ε

liquid	ε	ε^*	γ_L	$\cos\theta_a$	γ_S
methyl cellosolve	17.5	4.8	31.5	0.375	21.7
pentaerithritol tetracaproate	10.3	4.1	30.4	0.438	21.9
1,6-hexamethyleneglycol-2-ethylhexanoate	9.7	4.0	30.2	0.454	22.0
di-2-ethylhexyladipate	7.3	4.0	30.2	0.485	22.4

CONCLUSIONS

The experimental data evidence in favour of the existence of a complicated dependence of the surface tension of solid polymer on the surface tension of wetting liquid. For the liquids of normal totality, there exist three various zones. In one zone the surface tension of polymer does not depend on the surface tension of wetting liquid (unperturbed zone). In two other zones there exists linear dependence of $\gamma_S = f(\gamma_L)$. These zones are: a zone of depolarization (surface tension of polymer is lower as compared with unperturbed values) and a zone of additional polarization (where surface tension of polymer is higher than in the unperturbed zone).

For liquids of specific totality in all the zones diminished values of surface tension of polymer and TWA are observed when measured from advancing contact angles and correspondingly higher values for the receding regime.

In such a way, the full description of the functional dependence $\gamma_S = f(\gamma_L)$ is given. This description, based on the voluminous experimental data and application of the rule of interfacial equilibrium[10], seems to be trustworthy.

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