Relationships Between Surface Wettability and Glass Temperatures of High Polymers*

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Synopsis

The adhesion between a polymer and a solid substrate may be considered to be one type of complex liquid–solid interaction. Relationships between surface wettability and bulk properties of liquidlike polymers are discussed. A new and direct empirical relationship between the glass temperature (T_g) and critical surface tension of a polymer (γ_c) is established:

$$\gamma_c^{0.86} = (0.03RT_g - 1.5)(n\Phi^2/V_m^{0.71})$$

where n = degree of freedom, defined by Hayes, V_m = molar volume, and Φ = interaction parameter, or the ratio between reversible work of adhesion and geometrical mean of the work of cohesion. The effect of polarity and hydrogen bonding on this relationship is also discussed. The calculated γ_c's are much closer to the observed values than those calculated on the basis of parachor. With this new wettability relationship the wettability of polymers, especially of those forming no hydrogen bonds, can be related to thermal, rheological, mechanical, and relaxational properties.

INTRODUCTION

Physical interaction between a liquid and a solid is chiefly governed by physical adsorption.[1] Recently Huntsberger[2] reviewed the current status of the understanding of the wettability–adhesion relationship on the basis of physical adsorption. Unfavorable views of this concept of wetting have been expressed by others, including Voyuskii, the proponent of the diffusion theory.[3] However, although some of Voyuskii's statements regarding the misconception about wetting might well be correct, his recent paper[4] contained no data to support his arguments. According to Huntsberger, wetting is both a process and a state. The wetting process is simply one of achieving interfacial contact, and the state of wetting is a measure of the number or density of the interfacial contacts and the uniformity of each at the interface. The main source of misunderstanding is the common practice of equating the spreadability of a droplet with its ability to wet the same substrate. Most observers still consider wetting to be the key to adhesion.

Relationships between surface wettability and bulk properties of high polymers were discussed in our previous publication.[5]   In the present paper we focus on our finding regarding the important relationship between surface wettability and glass temperatures of liquidlike polymers.   Glass temperature is one of the key thermodynamic, relaxational, and rheological properties and is affected by both intermolecular and intramolecular forces.[6]   By treating these two types of force independently Gibbs and Di Marzio[7] further established the existence of the equilibrium second-order transition temperature (T_2).   Recently Eisenberg and Saito[8] showed that these two types of force were not independent but were actually interrelated.

The purpose of this study is to show how our finding on the wettability– glass temperature relationship bridges the gap between surface and bulk properties to liquidlike polymers and does not merely serve to develop a new method of calculating the surface tension of a polymer.   Four parameters discussed in this paper—cohesive energy density, parachor, critical surface tension, and glass temperature–are not exact values.   In the literature the solubility parameter of a polymer[9,10] often has more than one value; the parachor is affected by density and hydrogen bonding.   The critical surface tension[11] is an empirical surface tension of a low-energy solid, obtained by assuming the spreading pressure and the interfacial tension to be negligible.   Recently some doubts were expressed by Johnson and Dettre[12] regarding these two assumptions.   The effect of density on critical surface tension has also been reported.[13]   The glass temperature of a polymer is also indefinite and depends on the method and the rate of determination.[6]   Since all these parameters are inexact, the model relationship discussed in this paper is only semiquantitative.

THEORETICAL CONSIDERATIONS

Cohesive-Energy Density and Polarity

Cohesive-energy density (CED)[14] is the energy, in calories per cubic centimeter, necessary for an infinite separation of the molecule in 1 cm.[3] of liquid versus the action of intermolecular attraction:

$$CED = \delta^2 = (\Delta H_v - RT)/V_m \tag{1}$$

where δ is the solubility parameter (cal./cm.^{3}),$^{1/2}$ ΔH_v is the molar heat of vaporization (cal./mole), R is the gas constant (cal./mole-deg.), T is the temperature (°K.), and V_m is the molar volume (cm.^{3}/mole).   In the subsequent discussion we frequently use the term *solubility parameter* instead of CED.

The effects of polarity and hydrogen bonding on solubility parameters recently have been reported.[15–17]   From eq. (1) we note the close relation between the heat of vaporization and the solubility parameter.   It was noted [18] that polarity and hydrogen bonding could affect the heat of vaporization.   Bondi and Simkin[18] then proposed to divide ΔH_v into two terms:

$$\Delta H_v = \Delta H_v{}^d + \Delta H_v{}^h \tag{2}$$

where the superscripts d and h refer to dispersion energy and hydrogen bonding, respectively. Actually the second term contains the contribution of dipole interaction. On the basis of the above approach Hansen[17] suggested separation of the solubility parameter into two terms:

$$\delta^2 = \delta_d{}^2 + \delta_a{}^2 \tag{3}$$

$$\delta_a{}^2 = \delta_p{}^2 + \delta_h{}^2 \tag{4}$$

where the subscripts, d, p, h, and a represent dispersion energy, dipole interaction, hydrogen bonding, and the association energy. Originally Small[19] pointed out that the dipole interaction, or δ_p in the above equation, was negligible; therefore, the combination of δ_p and δ_h is justifiable.

According to the foregoing, the total solubility parameter of a liquid, regardless of its nonpolarity or polarity, can be calculated from the total heat of vaporization. Problems arise in the case of polymers for which we cannot determine the heat of vaporization. Most indirect methods measure only the partial solubility parameter; therefore, the values obtained by various methods differ,[8,9] and the effect of polarity on the polymer solubility parameter remains a problem of major concern.

Cohesive-Energy Density and Liquid Surface Tension

An empirical relationship between the solubility parameter and the liquid surface tension of a nonpolar liquid was obtained by Hildebrand and Scott:[14]

$$\delta_l = 4.1(\gamma_l/V_m{}^{1/3})^{0.43} \tag{5}$$

where δ_l is the solubility parameter of a liquid, γ_l is the liquid surface tension (dynes/cm.), and the unit for 4.1 is $(cal./cm.^3)^{1/2}$ $(dynes/cm.)^{-0.43}$ $(cm.^3/mole)^{0.143}$. We have not seen an equivalent relationship for a polar or hydrogen-bonded liquid, but as we suspect that the general relationship should hold for these liquids, too. Our reasonings will follow.

We note that not only does the total solubility parameter contain two terms, as discussed in the preceding section, but the total surface tension also contains two terms on the basis of Fowkes' work:[20]

$$\gamma = \gamma^d + \gamma^h \tag{6}$$

where the superscripts d and h represent dispersion energy and hydrogen bonding, respectively. Furthermore, the total surface tension has been directly related to the total heat of vaporization.[21] We therefore theorize that, if the solubility parameter and surface tension of a nonpolar liquid are related by eq. (5), a similar relation should hold for polar and hydrogen-bonded liquids. Let us propose the following equation to represent the general case of both polar and nonpolar liquids:

$$\delta_l = K(\gamma_l/V_m{}^{1/3})^a \tag{7}$$

where K and a are constants.

Cohesive-Energy Density and Solid-Surface Tension

For solids both the cohesive-energy density and the surface tension must be determined indirectly. In both cases only approximate values can be obtained. A semiquantitative relation can be derived by considering the following steps. First, we can eliminate the interfacial tension, if it is substantial, by introducing the interaction parameter Φ, defined by Girifalco and Good:[22]

$$\gamma_s = \gamma_l[(1 + \cos\theta)/2\Phi]^2 \tag{8}$$

where Φ is the ratio between the reversible work of adhesion ($\gamma_A + \gamma_B - \gamma_A\gamma_B$) and the geometrical mean of the work of cohesion of the two components. For low-energy solids Gardon[23] assumed that Φ is greater than 0.8 but less than 1. This parameter, Φ, is similar to, but not identical with, the interaction parameter introduced by Walker.[24] Therefore, it automatically contains a correction factor for polarities of a liquid and a solid at the interface.

On the basis of this equation Good and Girifalco[25] substituted eq. (5), to obtain a relation between the solid-solubility parameter and liquid surface tension without questioning whether the equation may be applied to polar liquids or solids:

$$\delta_s = 2.05(\gamma_l/V^{1/3})^{0.43} \times [(1 + \cos\theta)/\Phi] \tag{9}$$

Actually, the correct substitution should yield the following equation instead of eq. (9):

$$\delta_s = 4.1(\gamma_l/V^{1/3})^{0.43} \times [(1 + \cos\theta)/2\Phi]^{0.86} \tag{10}$$

In our subsequent derivation we used eq. (9) as the approximate form. In the case in which a liquid spreads over a solid, γ_l approaches γ_s and θ becomes zero. Consequently, the value of $\cos\theta$ becomes unity. By substituting $\Phi = 1$ we obtain the original equation of Hildebrand and Scott, eq. (5).

Despite the approximation, Zisman's critical surface tension[11] still provides the most convenient means of expressing the surface tension of a solid. Gardon[23] later suggested a possible linear relationship between the critical surface tension γ_c and the solubility parameter for liquidlike polymers. He proposed the following relation between solid surface tension and critical surface tension:

$$\gamma_s = \gamma_c/\Phi^2 \tag{11}$$

when $\Phi = 1$ and $\gamma_s = \gamma_c$. By substituting γ_c for γ_l in eq. (9) we can obtain the following equation, basically derived for nonpolar, liquidlike polymers:

$$\delta_s = 4.1(\gamma_c/V_s^{1/3})^{0.43} \times (1/\Phi) \tag{12}$$

Actually, the exact form of eq. (12) should be:

$$\delta_s = 4.1(\gamma_c/V_s^{1/3})^{0.43} \times (1/\Phi)^{0.86} \tag{13}$$

Cohesive Energy and Glass Temperature

Both intermolecular and intramolecular forces influence the glass temperature T_g. However, no equation has been formulated that can precisely describe the complicated relationships. Some time ago Hayes[26] published the empirical relationship between molar cohesion and glass temperature:

$$H_c = 0.5nRT_g - 25n \tag{14}$$

where H_c is the molar cohesive energy (cal./mole), n is a dimensionless number analogous to the degree of freedom, R is the gas constant (cal./mole-deg.), and T_g is the glass temperature (°K.). The unit for the constant, 25, in the second term is cal./mole. According to Hayes, this equation does have limitations; for example, it cannot differentiate between a stereoregular and an amorphous polymer.

On the basis of Hayes' equation we shall discuss one model relationship between surface tensions and glass temperatures of liquid-like polymers. We shall then compare the experimental results on critical surface tensions and those calculated from the derived relationship. We shall then compare the effectiveness of this relationship in predicting critical surface tension with the effectiveness of those discussed previously.[5] The scope and limitations of our finding are mentioned at the end of this paper.
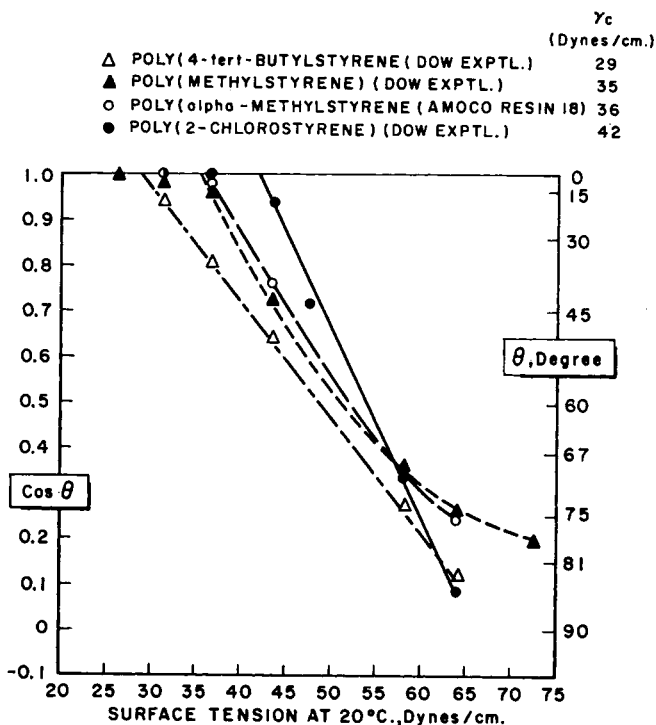

Fig. 1. Wettability of vinyl aromatic polymers.

EXPERIMENTAL

Determination of Critical Surface Tension

The detailed method of preparing samples was reported previously.[27] The first apparatus used for measuring the contact angle was built after the model described by Fort and Patterson.[28] For contact angles above 90° we used a goniometer manufactured by Rame-Hart, Inc., according to the model designed by the Naval Research Laboratory. The liquids used were water, glycerol, formamide, alcohols, and long-chain polyglycols (Dow Polyglycols P-1200, E-200, and 15-200). Since these glycols have high R/OH ratios, they are less affected by hydrogen bonding than short-chain alcohols. The advancing contact angles of various liquids on polymers were determined between 20 and 25°C. and 20 and 30% R.H. A typical plot of $\cos \theta$ versus γ_{LV} is shown in Figure 1. The data on critical surface tensions are used for comparison with those calculated from the proposed equation. The data obtained from the literature are cited in the related table.

RESULTS AND DISCUSSION

Glass Temperature and Critical Surface Tension

Experimental results on critical surface tensions have been published previously.[5,27,29] In a previous publication we also compared the observed critical surface tensions with those calculated form the solubility parameter–surface tension and the parachor–surface tension relationships. In this section we first demonstrate how to derive the glass temperature–surface tension relationship and then compare the calculated surface tensions with those obtained by us and others.

On the basis of eq. (12) we can obtain the following expression for CED, or δ^2:

$$\delta^2 = 16.8(\gamma_c/V_m^{1/3})^{0.86} \times (1/\Phi^2) \qquad (15)$$

By equating this to eq. (1) we obtain:

$$\gamma_c^{0.86} = 0.06(\Delta H_v)\Phi^2/V_m^{0.71} \qquad (16)$$

Here the unit for the constant, 0.06, is $(cal./cm.^3)^{-1}(dynes/cm.)^{0.86}(cm.^3/mole)^{0.71}$. Incidentally, ΔH_v here and H_c in Hayes' equation are synonymous.

Using ΔH_v as a connecting link between eq. (16) and Hayes' equation, we then derive a new empirical equation relating glass temperature and critical surface tension, predominantly for nonpolar polymers:

$$\gamma_c^{0.86} = (0.03RT_g - 1.5)(n\Phi^2)/V_m^{0.71} \qquad (17)$$

If higher accuracy is needed for the data, we should use $\Phi^{1.72}$. However, the difference is negligible.

The γ_c's for thirty-three polar and nonpolar polymers were calculated from glass temperatures by assuming $\Phi = 1$ (Table I). Surprisingly, the calculated results agreed well with the observed critical surface tensions.

Excellent agreement was found even for the fluorine-containing polymers. On the other hand, poor agreements were found for polyamides, for which an improved relationship is needed that will take hydrogen bonding into account.

Comparison of the Effectiveness of the Three Methods

With the wettability–glass temperature relationship discussed above we have three ways of calculating the critical surface tension of a polymer. As shown previously,[5] the exact calculation cannot be obtained until the parameter Φ is determined for each polymer. For this comparison we assume $\Phi = 1$ and evaluate the calculated critical surface tensions as listed in Table II.

The mean deviations, variance, standard deviations, and correlation coefficients are:

Methods	Mean deviation	Variance	Standard deviation	Correlation coefficient
Parachor	+10.0	189.58	13.77	0.240
Solubility parameter	−5.5	170.98	13.08	0.743
Glass temperature	−1.3	166.54	12.90	0.614

The analysis of variance (tested at the $F.99$ level) of the deviation data indicates a significant difference between methods. Bartlett's test for the equality of variance indicates that there is a significant difference between the means of the parachor method from the other two methods. However, there is not a significant difference between the solubility parameter method and the glass temperature method. These two methods are more effective for predicting purposes indicated by the higher coefficients when correlated with the observed values.

We separately evaluated the effectiveness of the methods, considering the chances of predicting γ_c to be within 3 dynes/cm., 5 dynes/cm. and greater than 10 dynes/cm. The results are as follows:

Chances of success of prediction, dynes/cm.	Solubility parameter	Parachor	Glass temperature
Within ±3	0.15	0.13	0.29
Within ±5	0.20	0.25	0.40
Beyond ±10	0.50	0.45	0.37

Here, the glass temperature method offered the highest chances of predicting the critical surface tension within 3 dynes/cm. However, this does not mean that we have now derived an ideal way of predicting the critical surface tension. Further improvements in both parameters, Φ and n, are no doubt desirable. Ideally, the chance of predicting beyond 10 dynes/cm. should be nil before the method can be considered useful.

TABLE I.   Relationship Between Glass Temperatures and Critical Surface Tensions of Polymers[a]

Polymers	Hayes' deg. freedom[b] n	Glass temp.[c] T_g, °K.	Molar vol. V_m, cm.³/mole	Crit. surf. tens.[d] γ_c, dynes/cm.		
				Calcd.	Obsd.	Δ
Poly(tetrafluoroethylene)	16	160	45.5	12		−6
		223		17	18*	−1
Poly(chlorotrifluoroethylene)	16	318	56.2	26	31	−5
Poly(vinylidene fluoride)	16	228	36.4	23	25*	−2
Poly(1,2-butadiene)	19	269	56.4	25	25	0
Poly(2-methylpropene) Poly(isobutylene)	22	200	63.0	17	27	−10
Poly(vinyl fluoride)	16	323	32.0	41	28*	+13
Poly(vinyl methyl ether)	25	260	55.6	23	29	−6
Poly(propylene)	19	253	46.2	28	29	−1
Poly(tert-butylstyrene)	32	403	169.0	33	29	+4
Poly(2-methyl-1,3-butadiene), trans	27	213	72.4	22	30	−8
		220		23	30	−7
Poly(2-methyl-1,3-butadiene), cis	27	200	75.0	20	31	−11
Polyethylene						
high density (0.95)	27	237	29.6	30	31	−1
" " "	27	148	29.6	16	31	−15
low density (0.91)	27	237	31.0	23	31	−8
" " "	27	148	31.0	14	31	−17
Poly(1,3-butadiene), trans	24	255	58.2	30	31	−1
Poly(1,3-butadiene), cis	24	165	60.1	16	32	−16
Poly(propylene oxide)	25	198	58.0	23	32	−9
Poly(ethyl methacrylate)	42	338	103.0	50	33	+23
Poly(ethyl acrylate)	39	249	91.0	33	35*	−2

Surface Wettability and Glass-Temperature Relationship; Scope and Limitations

The scope and limitations of wettability–glass temperature relationship are summarized as follows:

(1) Thermodynamically, both surface tension and glass temperature should be related. However, the glass temperature generally encountered is not a thermodynamic-equilibrium temperature. The ultimate relationship should stem from the equilibrium second-order transition temperature T_2, defined by Gibbs and Di Marzio.[7]

(2) Kinetically, both glass temperature and wetting involve relaxation phenomena. The glass temperature–wettability relationship further supports the view that wetting is a process. It is known that the temperature dependence of polymer relaxation generally follows the Williams-Landel-Ferry (WLF) relation:[30]

$$\log a_T = -[17.44(T - T_g)]/[51.6 + (T - T_g)] \qquad (18)$$

TABLE I (continued)

Polymers	Hayes' deg. freedom[b] n	Glass temp.[c] T_g, °K.	Molar vol. V_m, cm.^{3}/mole	Crit. surf. tens.[d] γ_c, dynes/cm.		
				Calcd.	Obsd.	Δ
Polystyrene, atactic	23	373	100.0	29	36	−7
Poly(formaldehyde)	14	188	21.0	25	36	−11
Poly(vinyl acetate)	31	301	72.4	40	37*	+3
Poly(vinyl alcohol)	22	358	34.2	49	37*	+12
Poly(methyl methacrylate)	34	378	84.8	53	38	+15
Poly(2-chloro-1,3-butadiene)	24	225	72.0	21	38	−17
Poly(vinyl chloride)	16	354	44.6	36	39	−3
Poly(vinylidene chloride)	16	254	58.0	19	40	−21
Poly(methyl acrylate)	31	279	70.5	39	41	−2
Poly(2-chlorostyrene)	31	392	111.0	36	42	−6
Polycarbonate	42	422	212.0	38	42	−4
Poly(6-aminocaproic acid) Nylon 6	53	323	100.0	65	42*	+23
Poly(ethylene oxide)	22	206	39.2	30	43	−13
Poly(ethylene terphthalate)	45	342	143.0	44	43*	+1
Poly(acrylonitrile)	16	378	45.4	39	44	−5
Poly(hexamethylene adipamide) Nylon 6.6	106	330	182.0	96	46*	+50

[a] Equation: $\gamma_c^{0.86} = (0.03RT_g - 1.5)(n\Phi^2/V_m^{0.71})$, assuming $\Phi = 1$ and $\gamma_c = \gamma_s$.

[b] The degree of freedom values were calculated on the basis of the data in Table II of the Hayes' paper (J. Appl. Polymer Sci., 5, 318 (1961)).

[c] The glass temperatures were obtained from Table (III-61) compiled by W. A. Lee and G. J. Knight in Polymer Handbook edited by J. Brandrup and E. H. Immergut (Interscience, 1966).

[d] The critical surface tensions marked with star (*) were obtained from Table (III-113) compiled by E. G. Shafrin in the Polymer Handbook. Other values were determined by us. The differences between the calculated and the observed are listed under Δ.

where a_T is the shift factor. On the basis of the relationship between glass temperature and surface tension we should anticipate that the apparent surface tension would follow the same WLF relation. A recent work by Schonhorn et al.[31] could afford strong evidence of this prediction. They proposed the equation $a_T = \gamma L_w \eta$, where L_w is the length characteristic of the polymer–substrate system, and η is the viscosity.

(3) Conventionally, the rheology of a polymeric adhesive is treated separately from the wettability concept. On the basis of the glass temperature–surface tension relationship we can relate surface tension to viscosity through the following modified WLF equation:

$$\log (\eta_g/\eta) = [40(T - T_g)]/[52 + (T - T_g)] \qquad (19)$$

where η is the viscosity of the polymer, and the subscript g indicates the viscosity at the glass temperature.

(4) Self-diffusion of a polymer was related by us[1] to the physical state with the aid of the Buche-Cashine-Debye equation. On the basis of the glass temperature–surface tension relationship we can now use the glass

TABLE II
Comparison of Critical Surface Tensions Calculated by the Three Methods

| | Critical surface tension γ_c, dynes/cm. | | | |
Polymers	Parachor P	Solubility parameter δ	Glass temperature T_g	Obsd.
Poly(tetrafluoroethylene)	53	9	12, 17	18
Poly(chlorotrifluoroethylene)	53	14	26	31
Poly(vinylidene fluoride)	63	14	23	25
Poly(1,2-butadiene)	44	14	25	25
Poly(2-methylpropene	33	18	17	27
Poly(vinyl fluoride)	63	20	41	28
Poly(vinyl methyl ether)	33	17	23	29
Poly(propylene)	36	23	28	29
Poly(4-tert-butylstyrene)	16	29	33	29
Poly(2-methyl-1,3-butadiene), *trans*	40	20	22, 23	30
Poly(2-methyl-1,3-butadiene), *cis*	33	20	20	31
Poly(ethylene), high density (0.95)	53	14	30	31
low density (0.91)	44	14	23	31
Poly(1,3-butadiene), *trans*	36	20	30	31
Poly(1,3-butadiene), *cis*	33	20	16	32
Poly(propylene oxide)	23	18	23	32
Poly(ethyl methacrylate)	40	27	50	33
Poly(ethyl acrylate)	36	30	33	35
Polystyrene, atactic	40	28	29	36
Poly(formaldehyde)	69	22	25	36
Poly(vinyl acetate)	40	28	40	37
Poly(vinyl alcohol)	58 (30)[a]	45	49	37
Poly(methyl methacrylate)	44	27	53	38
Poly(2-chloro-1,3-butadiene)	44	25	21	38
Poly(vinyl chloride)	53	25	36	39
Poly(vinylidene chloride)	58	47	19	40
Poly(methyl acrylate)	44	32	39	41
Polycarbonate	36	46	38	42
Poly(2-chlorostyrene)	36	43	36	42
Poly(6-aminocaproic acid)	58 (36)[a]	73	65	42
Poly(ethylene oxide)	44	17	30	43
Poly(ethylene terephthalate)	40	51	44	43
Poly(acrylonitrile)	69	46	39	44
Poly(hexamethylene adipamide)	83 (53)[a]	87	96	46

[a] The values in parentheses were calculated with the correction of maximum numbers of hydrogen bonds.

temperature as a criterion for predicting whether the wetting process involves diffusion.

(5) The effect of molecular weight on glass temperature was shown by Fox and Flory[32] to follow their equation

$$T_g = T_g(\infty) - k/M \tag{20}$$

where $T_g'(\infty)$ is the glass temperature at relatively high molecular weight. Since the glass temperature used in Hayes' equation is always $T_g(\infty)$, the molecular weight M does not affect the surface tension in our equation.

(6) Plasticization generally lowers the glass temperature, but it also changes n and V_m in Hayes' equation, if a diluent other than the monomer is used, or it changes n if the monomer is used.   As a result, we cannot predict the effect of plasticization on surface tension on the basis of glass temperature alone.

(7) A serious limitation of Hayes' equation is that the n value does not take into account the chain stiffness as a result of stereoregularity, cross-linking, or steric hindrance.   For instance, the n values for both poly(vinyl chloride) and poly(vinylidene chloride) are identical, while the chain stiffness in terms of flex energy ($\Delta\epsilon$) is 1.16 for the former and 0.97 for the latter.

(8) Crosslinking generally raises the glass temperature.   Since neither Hayes' original equation nor our equation takes into consideration the effect of crosslinking, we cannot predict the effect of crosslinking on surface tension.
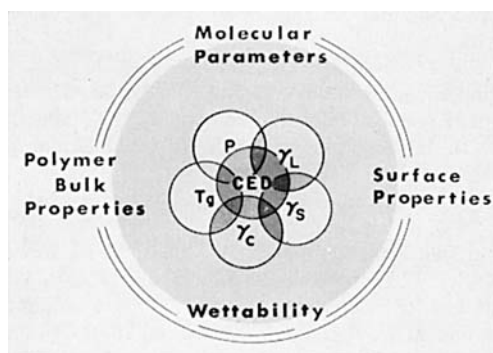

Fig. 2. Surface wettability and bulk properties of high polymers.

(9) Polarity and hydrogen bonding are other complicating factors.   An improved relationship is needed, to account for the effect of hydrogen bonding.

(10) Unless both n and V_m are identical for a series of polymers, our equation does not give a linear relationship between critical surface tensions and glass temperatures for these polymers.

(11) The deviation of the calculated critical surface tension could be partially contributed to by the diffuseness of glass temperature and by the inexactness of the observed critical surface tension.

CONCLUSIONS

It appears that the model glass temperature–wettability relationship we have developed is more effective for predicting critical surface tensions of polymers than the parachor method discussed in the foregoing.   Further refinement of the model equation is needed, especially with respect to hydrogen bonding, before it may be used to predict wettability with great accuracy.   The importance of our finding is in the revelation of a strong tie between the surface and the bulk properties of liquidlike polymers through cohesive-energy density (Fig. 2).   On the basis of our equation surface

wettability can be related to thermodynamic, relaxational, rheological, and mechanical properties of polymers through the glass temperature.

References

1. L.-H. Lee, *Polymer Preprints*, **7**, 910 (1966); *idem.*, *J. Polymer Sci. A-2*, **5**, 75 (1967).

2. J. R. Huntsberger, *P. Paint Technol.*, **39**, 199 (1967); *idem.*, in *Treatise of Adhesion and Adhesives*, R. L. Patrick, Ed., Dekker, New York, 1966, p. 119.

3. S. S. Voyutskii, *Autohesion and Adhesion of High Polymers*, Interscience, New York, 1963.

4. S. S. Voyutskii, *Kolloid-Z. Z. Polymere*, **214**, 97 (1966).

5. L.-H. Lee, *Proc. Soc. Plastics Ind. Reinf. Plastics Div.*, 22nd Ann. Tech. Conf., Sect. 13-C, 1967, p. 1.

6. R. F. Boyer, *Rubber Chem. Technol.*, **36**, 1303 (1963).

7. J. H. Gibbs and E. A. Di Marzio, *J. Chem. Phys.*, **28**, 373 (1958).

8. A. Eisenberg and S. Saito, *Polymer Preprints*, **7**, 473 (1966).

9. H. Burrell and B. Immergut, in *Polymer Handbook*, J. Brandrup and E. Immergut, Eds., IV-341, Interscience, New York, 1966.

10. J. L. Gardon, *Encyclopedia of Polymer Science and Technology*, Vol. III, Interscience, New York, 1965, p. 856.

11. W. A. Zisman, *Ind. Eng. Chem.*, **55**, 19 (1963); *idem.*, *Encyclopedia of Polymer Science and Technology*, Vol. I, Interscience, New York, 1964, p. 445.

12. R. E. Johnson and R. H. Dettre, *J. Colloid Interface Sci.*, **21**, 610 (1966).

13. H. Schonhorn and F. W. Ryan, *J. Phys. Chem.*, **70**, 3811 (1966).

14. J. H. Hildebrand and R. Scott, *The Solubility of Non-Electrolytes*, Rheinhold, New York, 1950.

15. J. L. Gardon, *J. Paint Technol.*, **38**, 43 (1966).

16. J. D. Crowley, G. S. Teague, Jr., and J. W. Lowe, Jr., *J. Paint Technol.*, **38**, 269 (1966); *ibid.*, **39**, 19 (1967).

17. C. M. Hansen, *J. Paint Technol.*, **39**, 104 (1967).

18. A. Bondi and D. J. Simkin, *A. I. Ch. E. J.*, **3**, 473 (1957).

19. P. A. Small, *J. Appl. Chem.*, **3**, 71 (1953).

20. F. M. Fowkes, *Chemistry and Physics of Interfaces*, Vol. 1, American Chemical Society, Washington, D.C., 1965.

21. D. S. Viswanath and N. R. Kuloor, *J. Chem. Eng. Data*, **11**, 69 (1966).

22. L. A. Girifalco and R. J. Good, *J. Phys. Chem.*, **64**, 561 (1960).

23. J. L. Gardon, *J. Phys. Chem.*, **67**, 1935 (1963).

24. E. E. Walker, *J. Appl. Chem.*, **2**, 470 (1952).

25. R. J. Good and J. A. Girifalco, *J. Phys. Chem.*, **61**, 904 (1957).

26. R. A. Hayes, *J. Appl. Polymer Sci.*, **5**, 318 (1961).

27. L.-H. Lee, *Polymer Preprints*, **7**, 916 (1966); *idem.*, *J. Polymer Sci. A-2*, **5**, 1103 (1967).

28. T. Fort, Jr., and H. T. Patterson, *J. Colloid Sci.*, **18**, 217 (1963).

29. L.-H. Lee, *Advances in Chemistry Series*, American Chemical Society, Washington, D.C., in press.

30. M. L. Williams, R. F. Landel, and J. D. Ferry, *J. Am. Chem. Soc.*, **77**, 3701 (1955).

31. H. Schonhorn, H. L. Frisch, and T. K. Kwei, *J. Appl. Phys.*, **37**, 4967 (1966).

32. T. G Fox and P. J. Flory, *J. Chem. Phys.*, **21**, 581 (1950).