latter systems by the infrared spectroscopic study depicted in Figure 6. There is a complete absence of hydrogen bonding of PAM ester carbonyl to pyruvic acid, as evidenced by the lack of any shift of the normal carbonyl vibration frequency at 1729 cm^{-1}. Note especially (D) where use of PAM solution in the reference beam reproduces only the spectrum due to pyruvic acid. The ester segments of PAM·VP also show no evidence of hydrogen bonding. However, the small absorption peak at 1694 cm^{-1} (E) due to vinylpyrrolidone carbonyl is observed to shift virtually completely to 1628 cm^{-1} (F) in the presence of pyruvic acid. The value here of $\Delta\nu/\nu = 0.039$ is very similar to the value of 0.040 found[15] for N,N-diethyldodecanamide adsorbed on silica. In the latter studies, dodecyl esters adsorbed on silica gave smaller values of $\Delta\nu/\nu$ of around 0.02 in accord with the relative polarity of esters and amides. It is surprising that in the present studies the ester segments show such complete inactivity; the reason for this is not apparent. Unfortunately, it is not feasible to compare the behavior of PAM and PAM·VP with solubilized pyruvic acid in a study such as that of Figure 6 because the acid C=O absorptions are then large enough to jam the spectral region of interest.

A spectrophotometric examination of mixtures of the polymers with the surfactant PB·TETA showed no evidence of interactions. This is to be expected since no donor–acceptor relationship exists in this case.

Nature of the Synergism. The evidence presented here suggest that the more highly polar vinylpyrrolidone segments of the detergent copolymer interact with the acid solute in the interior of the surfactant micelle. This interaction must be *via* hydrogen bonding of pyrrolidone carbonyl oxygen to the carboxylic hydrogen. It is interesting to note that even in aqueous systems[1,2] Saito found[16] that the synergizing polymer causes a shift in the spectrum of the solubilized dye.

The amine surfactant PB·TETA must obviously interact with the acid solute to form a salt. Thus, the active micellar species is actually the ionic salt, PB·TETA pyruvate. Certain mixtures of ionic with nonionic surface-active agents demonstrate an increased efficiency of formation of microemulsions.[17] Goodrich[18] suggests that the binding forces between the ionic and nonionic surfactants reside in the van der Waals attraction between the paraffin chains and that, in addition, the repulsive forces between the charged ionic head groups are reduced by the screening effect of the intervening polar, nonionic groups. It is possible then that the synergistic effect of the detergent copolymer PAM·VP on the solubilization of pyruvic acid by the surfactant PB·TETA is the result of analogous interplay between the ionic amine–salt head of the surfactant and the nonionic pyrrolidone groups of the copolymer.

Acknowledgment. The author wishes to thank Mr. G. L. Matthias for carrying out the experimental measurements in this work.

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(15) B. J. Fontana, *J. Phys. Chem.*, 70, 1801 (1966).

(16) S. Saito, *Kolloid Z.*, **168**, 128 (1960).

(17) C. E. Cooke, Jr., and J. H. Schulman, Proceedings of the Second Scandinavian Symposium on Surface Activity, Stockholm, 1964, pp 231–251.

(18) F. C. Goodrich, *Proc. Intern. Congr. Surface Activity, 2nd, London*, **1957**, **1**, 85 (1957).

Heterogeneous Nucleation of Polymer Melts on High-Energy Surfaces. II. Effect of Substrate on Morphology and Wettability[1]

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ABSTRACT: Heterogeneous nucleation and crystallization of polymer melts against high-energy surfaces (*e.g.*, metals, metal oxides, and alkali halide crystals) have been found to result in marked changes in both the surface region morphology and wettability of these polymers even though the chemical constitution of the polymer is unchanged. The critical surface tensions (γ_C) of a variety of polymers nucleated against gold are considerably in excess of the commonly accepted values. Employing a modified Fowkes-Young equation can account for these sizable differences if the surface layer of these crystallizable polymers generated against high-energy surfaces is essentially crystalline.

Although considerable effort has been expended in determining the relationship between the contact angle of a liquid on a polymer surface and the chemical constitution of that surface, little attention has been paid to the detailed physical properties (*e.g.*, molecular weight distribution, density, crystallization behavior, etc.) of the polymer and, more important, the detailed procedure for preparing the polymer surface for wettability studies.[2a] In general, there is rather widespread agreement in the acceptable values for the critical surface tensions of wetting for a variety of polymeric

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(1) Presented at the American Chemical Society Symposium on Polymeric Detergents, Chicago, 1967.

(2) (a) W. A. Zisman, Advances in Chemistry Series, No. 43, American Chemical Society, Washington, D. C., 1964, p 1; J. J. Scholz, B. R. Ray, and J. Anderson, *J. Phys. Chem.*, **62**, 1227 (1958); (b) E. Shafrin, "Polymer Handbook," J. Branderup and E. H. Immergut, Ed., Interscience Publishers, Inc., New York, N. Y., 1966.

Table I

Comparison of Extrapolated Melt Surface Tensions of Nonpolar Polymers and Their Critical Surface Tension of Wetting

Polymer	γ_{LV}^{20}, dyn/cm	γ_C^{20}, dyn/cm[a]
Polyethylene	36.2[b]	31
Polypropylene	28.0[c]	29
Polychlorotrifluoroethylene	30.8[d]	31
Polydimethylsiloxane	20.6[e] 21.6[f]	22
Polystyrene	32.4[g]	33

[a] W. A. Zisman, Advances in Chemistry Series, No. 43, American Chemical Society, Washington, D. C., 1964, p 1. [b] H. Schonhorn and L. H. Sharpe, *J. Polym. Sci., Part A*, **3**, 569 (1965); R. H. Dettre and R. E. Johnson, Jr., *J. Colloid Sci.*, **21**, 367 (1966); see also ref 5. [c] H. Schonhorn and L. H. Sharpe, *J. Polym. Sci., Part B*, **3**, 235 (1965). [d] H. Schonhorn, F. W. Ryan, and L. H. Sharpe, *ibid., Part A-2*, **4**, 538 (1966). [e] See ref 5. [f] H. Tarkow, *J. Polym. Sci.*, **27**, 35 (1958); $T = 30°$. [g] J. E. Marian, *ASTM Spec. Tech. Publ.*, **340**, 122 (1963).

species.[2b] In most tabulations, the wettability of a species is related to the presence of a particular functional group that resides in the outermost surface layer.

In this paper we shall attempt to delve deeper into the concept of wettability. We shall confine our critical remarks to polyethylene but shall extend the analysis to a variety of polymers.

Surface Density and Wettability. All polyethylenes for which data are reported have been observed to have essentially the same value of γ_C, the critical surface tension of wetting (*i.e.*, 31–36 dyn/cm). Although polyethylenes may have a density range of 0.855 g cm^{-3} for the amorphous polymer to 1.00 g cm^{-3} for the crystalline species, until recently no significant differences have been reported in their γ_C values.[3] The density range noted above is comparable to the difference between hexane and hexadecane, two hydrocarbons which differ considerably in their surface chemical properties. Apparently, there is some feature common to all polyethylenes which tends to equate their wettabilities.

We compare the extrapolated values of the melt surface tension of several nonpolar polymers and their commonly accepted γ_C values in Table I. The comparisons are striking. These data led the author to postulate that $\gamma_{LV} = \gamma_C$, where γ_{LV} is the surface tension, for melt-crystallized nonpolar polymers.[4] Obviously, when $\gamma_{LV}^d \neq \gamma_{LV}$, where the superscript d refers to the dispersion component of the surface free energy, the above relationship is no longer valid. We concluded from this comparison that the surface layer of these melt-crystallized polymers is essentially amorphous. Roe[5] and Lee, Muir, and Lyman[6] have shown that to obtain reasonable agreement between γ_C and the parachor, the amorphous density of the polymer has to be used. Apparently, all polyethylenes when prepared in the conventional manner behave in respect to wettability as if they have a surface layer which is essentially that of the supercooled liquid. Although their bulk densities may vary over a considerable range, if their surface densities are similar this would account for their similar wettability behavior. Recently, Schonhorn and Ryan[3] have shown that a well-characterized preparation of polyethylene single crystal aggregates has a γ_C ($\sim$54 dyn/cm), considerably in excess of the commonly accepted value.

In this instance, the surface density of the polymer is no longer 0.855 g cm^{-3} but is computed to be approximately 0.94 g cm^{-3}. The low value of 0.94 cm^{-3} for the surface density of single crystal aggregate may result from the defects presumed to be present in the fold structure.[7]

We shall demonstrate in later sections, employing a wettability approach, that the formation of the surface region of melt-crystallized polymers, particularly polyethylene, and the morphological structure of this region are strongly dependent upon the manner in which the surface region of the polymer is generated.

Interfacial Contact between Polymer Melt and Substrate. Generally, to facilitate ease of removal from molds, polymers have been prepared for wettability studies by pressing or solidifying in contact with low-energy solids, *e.g.*, polytetrafluoroethylene (PTFE), or with high-energy surfaces for short times at low temperatures, *i.e.*, just above the melting point of the polymer. Experience has shown that if longer periods of time are used at relatively high temperatures on high-energy surfaces, it is difficult to remove the polymer from the metal surface without damaging the surface layer of the polymer. Longer dwell times of the polymer melt on the surface of the metal results in the formation of a strong adhesive joint, provided that the metal does not have a weakly adherent oxide layer. If a weak oxide layer were present, it is conceivable that this could be transferred to the polymer affecting the wettability results.

We have shown in a recent study of the kinetics of wetting of polymer melts on surfaces[8] that the ability of a polymer melt to attain a stable contact angle with a solid substrate is proportional to the surface tension of the polymer melt (γ_{LV}) and inversely proportional to the melt viscosity (η). Since the viscosity varies strongly with temperature, to preclude interfacial voids in the polymer melt–high energy surface (*i.e.*, metal, metal oxide) system, it is important to allow sufficient time at low temperatures to ensure complete mating of the surfaces. Figure 1a indicates a poorly wetted situation. Although the thermodynamic requirements for spreading are fulfilled (*i.e.*, $\gamma_{SV} > \gamma_{LV} + \gamma_{SL}$), spreading of the polymer may not take place because of the kinetic requirements. Enhancement of wetting is rather easy to accomplish by employing higher temperatures and longer times. Since η decreases markedly with increasing temperature, relatively short times are required at elevated temperatures to achieve extensive mating of the liquid and high-energy solid (Figure 1b).

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

(4) H. Schonhorn, *ibid.*, **69**, 1084 (1965).

(5) R. J. Roe, *ibid.*, **69**, 2809 (1965).

(6) I. J. Lee, W. M. Muir, and D. J. Lyman, *ibid.*, **69**, 3220 (1965).

(7) P. H. Geil, "Polymer Single Crystals," Interscience Publishers, Inc., New York, N. Y., 1963.

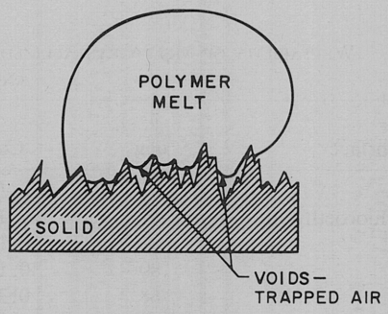
(8) H. Schonhorn, H. L. Frisch, and T. K. Kwei, *J. Appl. Phys.*, **37**, 4967 (1966).

Effect of Substrates on Surface Region Morphology. Surface studies on crystallizable polymers (*e.g.*, polyethylene) have ignored, in general, the nature of the nucleating phase (*i.e.*, vapor, solid, or liquid) and the details of formation of the polymer *melt*–nucleating phase interface which, on solidification by cooling, results in a polymer *solid*–nucleating phase interface.

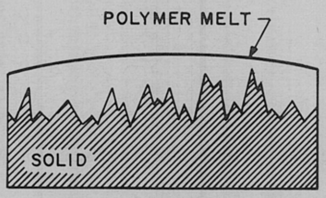
Extensive heterogeneous nucleation of polyethylene melts on high-energy surfaces results in generation of transcrystallinity in the interfacial region [(S–L) → (S–S)][9] (Figure 2). Koutsky, Walton, and Baer[10] have observed that there is a variation in the extent of supercooling which may depend upon surface energy and interatomic spacing in the substrate. Effective nucleating agents allowed for only small supercoolings. Sharples[11] has concluded that stresses at the interface set up during cooling from the melt are important in determining the subsequent morphology. Since a large number of nuclei are generated at the solid–liquid interface, provided that extensive contact has been established between the substrate and the molten polymer, the spherulites are inhibited in their lateral growth and only propagate in a direction transverse to the plane of the substrate.

Low-energy surfaces (*e.g.*, PTFE) are apparently ineffective nucleating agents. When polymers are cooled in contact with these surfaces, nucleating is precluded at the solid–liquid interface and is apparently initiated in the bulk. Sufficient supercooling has not occurred at the solid–liquid interface to nucleate the interfacial region before nucleation occurs in the bulk. Apparently, this is the reason for the lack of a well-defined transcrystalline region when polyethylene is nucleated against a low-energy solid. As crystallization proceeds in the bulk, polymer molecules which cannot be accommodated into the crystal lattice during crystallization are rejected to the interface.[12]

Employing high-energy surfaces for the nucleation of a polymer melt is effective only if sufficient time is allowed for the polymer melt to achieve extensive and intimate contact with the substrate. This is a kinetic requirement and is strongly dependent on the viscosity of the melt.[8] If sufficient time has not been allowed, considerable interfacial voids will result and nucleation will generally occur in the bulk. If sufficient time is allowed for spreading to occur, a situation similar to that of Figure 1b will result, where interfacial voids are precluded and nucleation occurs predominantly at the S–L interface. The mere presence of a high-energy surface in itself does not ensure that extensive and intimate contact will occur, and a highly nucleated surface region will result, upon solidification of the polymer melt.



(a) NOTE LOW REAL AREA OF INTERFACIAL CONTACT



(b) NOTE LACK OF VOIDS FROM TRAPPED AIR IN PORES AND CREVICES

Figure 1. (a) Poorly wetted surface; (b) extensive intermolecular contact.

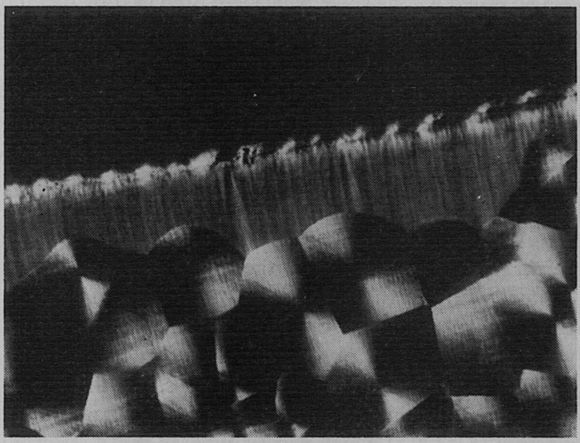


Figure 2. Transcrystalline region in polyethylene formed in contact with etched aluminum foil. Foil dissolved from polymer prior to sectioning.

Wettability and Surface Morphology. Knowing that the morphology of polyethylene is strongly dependent upon the polymer melt–substrate system, we became concerned about possible substrate effects on the wettability of polymers. Since we have ensured that extensive interfacial contact has been achieved between the polymer melt and substrate, we have in effect prepared a strong adhesive joint. To avoid damaging the surface region of the polyethylene (after solidification) by mechanical means, we resorted to dissolution techniques for separating the polyethylene from the substrate. For all the substrates listed in Table II, except polytetrafluoroethylene, gold and the salt crystals, we dissolved the substrates in either concentrated hydrochloric acid or sodium hydroxide at temperatures below 30°. The gold was dissolved by either amalgamation with mercury or exposure to a concentrated aqueous sodium cyanide solution. There

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(9) E. Jenckel, E. Teege, and W. Hinrichs, *Kolloid Z.*, **129**, 19 (1952); R. J. Barriault and L. F. Gronholz, *J. Polym. Sci.*, **18**, 393 (1955); R. K. Eby, *J. Appl. Phys.*, **35**, 2720 (1964); H. Schonhorn, *J. Polym. Sci., Part B*, **2**, 465 (1964).

(10) J. A. Koutsky, A. G. Walton, and E. Baer, *ibid., Part B*, **5**, 185 (1967).

(11) A. Sharples, "Introduction To Polymer Crystallization," St. Martin's Press, New York, N. Y., 1966, p 25.

(12) H. D. Keith and F. J. Padden, Jr., *J. Appl. Phys.*, **35**, 1270, 1286 (1964).

TABLE II

WETTABILITY OF MELT-CRYSTALLIZED POLYETHYLENE FILM FORMED BY NUCLEATION AT SOLID–LIQUID AND LIQUID–VAPOR INTERFACES[a]

Surface	θ, deg	Cos θ	$\rho_s^{a,ac,c}$, g/cm^3	$V_{sp}^{a,ac,c}$, cm^3/g	$\gamma_{LV}^*(\gamma_C)$, dyn/cm	% crystallinity
Nitrogen	81	0.1564	0.855	1.1695	36.2	0
Polytetrafluoroethylene	81	0.1564	0.855	1.1695	36.2	0
Mylar	81	0.1564	0.855	1.1695	36.2	0
Copper	80	0.1737	0.862	1.1601	37.4	5.1
Nickel	68	0.3746	0.933	1.0718	51.3	53.3
Tin	66	0.4067	0.944	1.0593	53.8	60.1
Aluminum	65	0.4226	0.949	1.0537	54.9	63.2
Glass (microscope slide)	65	0.4226	0.949	1.0537	54.9	63.2
Chromium	64	0.4384	0.954	1.0482	56.1	66.2
Mercury	57	0.5446	0.989	1.0111	64.8	86.4
Gold	53	0.6018	1.007	0.9930	69.6	93.6
Tantalum	60	0.5000	0.975	1.0256	61.4	78.5
NaCl	57	0.5446	0.989	1.0111	64.8	86.4
KBr	57	0.5446	0.989	1.0111	64.8	86.4
KCl	57	0.5446	0.989	1.0111	64.8	86.4
CaF$_2$	55	0.5736	0.998	1.0020	67.3	91.4

[a] Polyethylene was in contact with surfaces for 30 min at 200°. All measurements were performed at 20° using glycerol as the wetting liquid.

is enough dissolved oxygen in the aqueous phase to oxidize the gold and enable it to be complexed. The salt crystals were dissolved by exposing the solid polyethylene–crystal system to water. The polyethylene–polytetrafluoroethylene composite separated by itself on cooling from the melt.

The polyethylene specimens were prepared by placing a piece of polymer (~10 mil thick) onto an evaporated metal film (deposited on glass microscope slide, 3 in. × 1 in. × $^1/_{16}$ in.), a freshly cleaved salt crystal, or a piece of polytetrafluoroethylene (3 in. × 1 in. × $^1/_{16}$ in.), and placing the composite in an oven at 200° in a nitrogen atmosphere. The composites remained in the oven for a period of 30 min, an interval sufficient to allow for extensive contact between the polymer melt and the substrate. One surface of the polymer melt was in contact with the vapor (nitrogen) to provide a control. If extensive oxidation or degradation were to result, we might expect to observe its effect on the polymer melt–vapor generated surface. In all cases, the vapor-nucleated polyethylene surface gave contact angles with glycerol ($\theta = 81°$) which were similar to those reported by Zisman.[13] The variation in the contact angle measurement is ±1°. Dissolution of the substrates from the solidified polymer did not alter the contact angle of glycerol on the vapor-nucleated surface. After dissolution, no residue of the substrates was detected by conventional analytical techniques (atomic absorption spectroscopy, electron microprobe, etc.). The contact angle goniometer and the details of the contact angle measurements are described elsewhere.[3]

The wettability results in Table II are striking. For polyethylene nucleated and solidified in contact with nitrogen of polytetrafluoroethylene, the glycerol contact angle is similar to that reported by Zisman.[13] For polyethylene nucleated and solidified on a variety of high-energy surfaces, except copper, a marked decrease in θ is noted. Films generated against these high-energy surfaces were examined using ATR infrared techniques to determine if oxidation were taking place. No evidence for oxidation was found. Gold and the salt crystals produced polyethylene surfaces with the lowest glycerol contact angle. If oxidation were taking place it is reasonable to assume it would occur more readily when the polymer melt is in contact with a metal oxide. A more conclusive argument will be presented later, when we shall describe the wettability behavior of a variety of thermoplastic polymers nucleated and solidified against gold.

Apparently, as a result of extensive nucleation of molten polyethylene on high-energy surfaces (Table II), there is generated a plane of spherulitic cores[11] which exhibit quite low contact angles with glycerol. When polyethylene is nucleated against a low surface energy phase (polytetrafluoroethylene or nitrogen) or a high surface energy phase that is poorly wetted with the polymer melt, all polyethylenes examined regardless of their bulk densities exhibit the same contact angle with glycerol.

Recently, Schonhorn and Ryan[3] have modified the Fowkes–Young equation[14] to account for possible differences in the surface density of polymers. Using a similar analysis for polyethylene nucleated on a variety of substrates, the values of the surface density were computed. Schonhorn and Ryan have shown that

$$(\cos\theta)_{a,ac,c} = \frac{2\left(\frac{\rho_s^{a,ac,c}}{\rho_s^{a}}\right)^2 [(\gamma_{LV}^{d})_p \gamma_{LV}^{d}]^{1/2}}{\gamma_{LV}} - 1 - \frac{\pi_e}{\gamma_{LV}} \tag{1}$$

where θ is the contact angle of the sessile drop of liquid on the polymer surface, ρ_s is the surface density, γ_{LV} is the surface tension, the subscript p refers to the polymer, the superscript d refers to the dispersion component of the surface free energy, the superscripts a, ac, and c refer to amorphous, partially crystalline, and crystalline, respectively, and π_e is the spreading pressure (γ_S −

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[13] See Table I, footnote *a*.

[14] F. M. Fowkes, *Ind. Eng. Chem.*, **56**, 40 (1964); *J. Phys. Chem.*, **67**, 2538 (1963).

TABLE III
WETTABILITY OF POLYETHYLENE AT 20°

Liquid	γ_{LV}, dyn/cm	$\gamma_{LV}{}^d$, dyn/cm	$\sqrt{\gamma_{LV}{}^d}/\gamma_{LV}$, l./(dyn/cm)$^{1/2}$	Single crystal θ, deg	Single crystal Cos θ	Nucleated against PTFE θ, deg	Nucleated against PTFE Cos θ	Nucleated against Gold θ, deg	Nucleated against Gold Cos θ
Water	72.8	21.8	0.0641	93	−0.052	94	−0.070	84	0.105
Glycerol	63.4	37.0	0.0959	67	0.391	79	0.191	53	0.602
Formamide	58.2	39.5	0.1080	55	0.574	77	0.225	41	0.755
α-Bromonaphthalene	44.6	44.6	0.1497	Spreads	1.000	35	0.818	Spreads	1.000

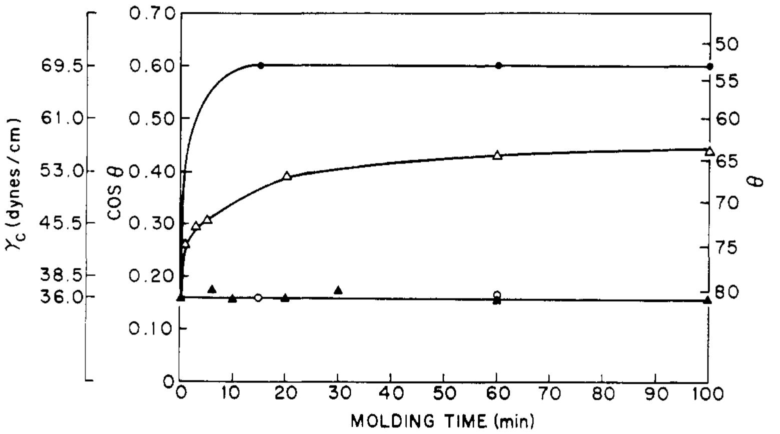

Figure 3. Variation of θ, cos θ, and γ_C obtained from the wetting of glycerol on polyethylene which was molded for varying lengths of time at 200° on a variety of surfaces in a nitrogen atmosphere. Metal substrates removed by dissolution. PTFE composite separates on cooling: ●, gold; △, aluminum (etched); ○, nitrogen; ▲, PTFE.

γ_{SV})—the difference between the surface free energy of the surface of the polymer under vacuum and in equilibrium with the vapor of the wetting liquid. We have ignored π_e/γ_{LV} in our computation since $\theta > 0$.[14] In eq 1 we have assumed a fourth power dependence of the density ($\gamma_{LV} \alpha \rho^4$). Roe[5] has shown that a third power relation is sometimes found.

When the surface density of the solid is essentially that of the amorphous solid or supercooled liquid, eq 1 becomes the familiar Fowkes–Young expression.[14] Based on the generally accepted value of $\rho_s{}^a$ for polyethylene, $\rho_s{}^{ac}$ values are computed. From these values, the specific volumes are obtained. The per cent crystallinity in the surface region is computed from the specific volume where

$$\%\ \text{crystallinity} = 100\left(\frac{V_{sp}{}^{ac} - V_{sp}{}^{a}}{V_{sp}{}^{c} - V_{sp}{}^{a}}\right) \qquad (2)$$

The values of $\gamma_{LV}{}^*$ (of γ_C) were computed from eq 1 by assuming a fourth power dependence of γ_{LV} on the density and the known amorphous density. Here

$$\gamma_{LV}{}^* = \left(\frac{\rho_s{}^{a,ac,c}}{\rho_s{}^a}\right)^4 \gamma_{LV} \qquad (3)$$

The rationale for $\gamma_{LV}{}^*$ is that if we had a hydrocarbon liquid whose surface density was equivalent to $\rho_s{}^{ac,c}$, then the surface would have a critical surface tension of wetting equal to $\gamma_{LV}{}^*$. When the surface layer is amorphous, $\gamma_{LV}{}^* = \gamma_{LV}$. When the surface layer of the polymer is partially crystalline or crystalline, $\gamma_{LV}{}^* > \gamma_{LV}$. Apparently, gold is the most effective nucleating agent for producing a surface layer of the highest density.

The variation of cos θ, θ, and γ_C, or $\gamma_s{}^d$ (a,ac,c) as a function of polymer melt–substrate (aluminum, gold, polytetrafluoroethylene, and nitrogen) contact time is shown in Figure 3. It is of interest to note that the γ_C of the polymer generated against both polytetrafluoroethylene and nitrogen is esentially constant. The values of cos θ for both aluminum and gold approach the limiting values recorded in Table II. For shorter times, a spectrum of γ_C values can be computed. This probably reflects the poor extent of wetting for shorter times, resulting in a situation such as Figure 1a, where nucleation occurs both at the metal and in the bulk phase. A surface layer is formed which is less dense than one where extensive contact has been achieved.

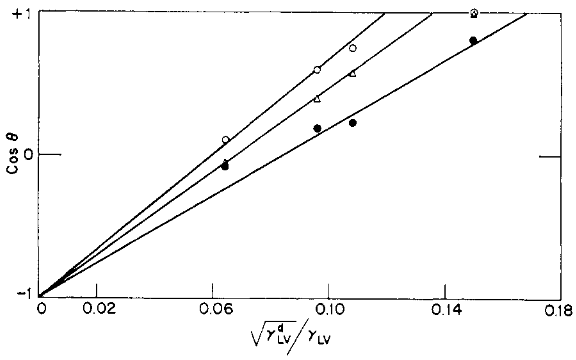

Figure 4. Typical Fowkes plot of wettability data for several polyethylenes: ●, nucleated in N_2 or molded against low-energy surface; △, single crystal aggregate; ○, gold nucleated.

A comparison between the contact angles for a variety of liquids on polyethylene surfaces generated against polytetrafluoroethylene and gold are presented in Table III. Included with these data are the wettability

TABLE IV
WETTABILITY DATA FOR POLYMER–GLYCEROL SYSTEMS AT 20°

Polymer	Bulk density, g/cm^3	Temp of prep, °C	θ_{MV},[d] deg	θ_{lit},[a] deg	θ_{AU},[c] deg	γ_{LV}, dyn/cm	γ_C dyn/cm	ρ_s^a, g/cm^3	V_{sp}^a, cm^3/g	ρ_s^c, g/cm^3	V_{sp}^c, cm^3/g	ρ_s^{ac},[b] g/cm^3	V_{sp}^{ac}, cm^3/g	$(\gamma_C)_{AU}$,[e] dyn/cm	% crystallinity in surface region[f]
1. Polyethylene	0.95	190	81	81	53	36.2	35	0.855	1.1695	1.014	0.9862	1.007	0.993	69.6	96.3
2. Nylon 6-6	1.14	280	60	60	35	46	46	1.09	0.9174	1.24	0.8065	1.23	0.813	74.4	94.1
3. Polychlorotrifluoroethylene	2.12	230	86	86	62	30.8	31	1.925	0.5195	2.19	0.4566	2.264	0.4417	58.9	100
4. Polypropylene (isotactic)	0.90	220	92	92	78	28.0	29	0.855	1.1695	0.930	1.0753	0.932	1.0729	39.5	100
5. Polypropylene (atactic)	0.86	220	92	92	92	28.0	29	0.855	1.1695	0.930	1.0753	0.855	1.0729	28.0	0.0
6. Poly(4-methylpentene-1)	0.83	230	95	. . .	96	22.6	. . .	0.838	1.1933	0.827	1.2092	0.827	1.2092	22.0	100

[a] See Table I, footnote *a*. [b] Computed from eq 1. [c] θ_{AU}, contact angle of glycerol on a surface generated at the polymer melt–gold interface. [d] θ_{MV}, contact angle of glycerol on a surface generated at the polymer melt–vapor interface. [e] $(\rho_s^c)/\rho_s^a)^4\gamma_{LV} = (\gamma_C)_{AU}$. [f] % crystallinity in surface region $= 100[(V_{sp}^{ac} - V_{sp}^a)/(V_{sp}^c - V_{sp}^a)]$.

results obtained for the polyethylene single crystal aggregates. The gold-nucleated polyethylene is considerably more wettable than the polyethylene single crystal aggregates. In Figure 4 a Fowkes-type plot of the data in Table III is constructed. The value of γ_s^d for the gold-nucleated surface is 69.6 dyn/cm, considerably in excess of the values 53.6 and 36.2 dyn/cm for the polyethylene single crystal aggregate and the PTFE-nucleated polymer, respectively. It appears that γ_C varies with the substrate used in preparing the polyethylene surface. Apparently for polyethylene we may have 36.2 dyn/cm $\leq \gamma_C \leq$ 69.6 dyn/cm.

For a typical wetting liquid such as glycerol it is possible to construct a cos θ *vs.* ρ plot (Figure 5) to demonstrate the variation in θ as a function of the variation of ρ_s^{ac}. Similarly, a γ_C *vs.* ρ plot, for the glycerol–polyethylene system (Figure 6), indicates the relationship between the surface density and the critical surface tension of wetting.

Surface Density of Other Polymers Nucleated on Gold. One argument against possible contamination of the polymer surface when in contact with gold is that atactic polypropylene (amorphous) exhibits the same contact angle with glycerol whether it has been formed at the polymer melt–gold interface or at the polymer melt–vapor interface (Table IV). In addition, poly(4-methylpentene-1), whose crystal density is reported to be less than the amorphous density, shows a slight increase in the contact angle for the surface generated at the polymer melt–gold interface. If surface contamination were substantial, increases in wettability would also be observed with these polymers.

Based on the extrapolation of the melt surface tension data for polyethylene, polypropylene, polychlorotrifluoroethylene (Table I) and the suggestion that $\gamma_{LV} = \gamma_C$,[4] values of (γ_{LV_p}) for polymers in Table IV were estimated. For all the polymers in Table IV but nylon 6-6, $\gamma_{LV}^d = (\gamma_{LV_p}) = \gamma_C$. For nylon 6-6, the value of (γ_{LV_p}) was computed for a 60° glycerol contact angle which is representative of the amorphous surface. Employing eq 1 and the values of (γ_{LV_p}), θ, ρ_s^a,[7] γ_{LV}^d of glycerol,[14] and neglecting the contribution of π_e/γ as suggested by Fowkes,[14] ρ_s^{ac} values were computed.

The somewhat high value of ρ_s^{ac} for polychlorotrifluoroethylene may be either as a result of employing a fourth power dependence of the density in deriving eq 1, or a low estimate for the literature value of ρ^c.

In measuring γ_C, investigators have agreed generally to certain values which are representative of the constitution of a polymeric species (Table IV).[2b] This has been related to the presence of a particular functional group. The data in Table IV indicate that the wettability of a crystallizable polymer can be made to vary within limits by controlling the nature of the heterogeneous nucleation and subsequent formation of the surface region of the polymer. Heterogeneous nucleation of certain polymers on high-energy surfaces can lead to surface densities, as computed from wettabilities, which are similar to the single crystal densities.

Stability of Surface Region with Respect to Temperature. Stability of the surface with respect to the temperature was examined to determine if the surface was

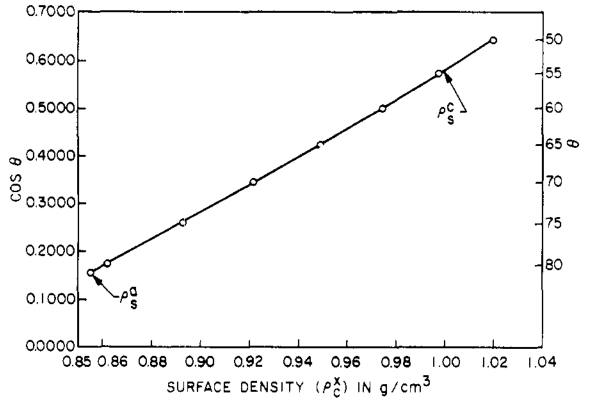

Figure 5. Computed surface densities of polyethylene based on various cos θ values for glycerol.

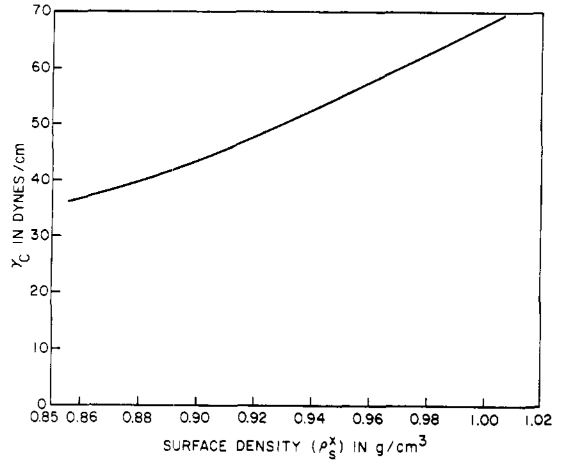

Figure 6. The variation of γ_C as a function of the surface density of polyethylene.

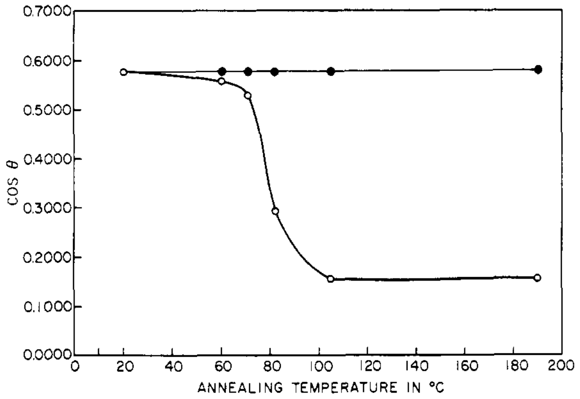

Figure 7. Contact angle of glycerol on annealed polyethylene. Specimens were annealed a minimum of 5 hr at the cited temperatures in a nitrogen atmosphere: ○, films nucleated against gold, cooled to 20°, then gold was dissolved; films annealed at specified temperatures; ●, films nucleated against gold, cooled to 20°; films in contact with gold were annealed, lowered to 20° then gold was removed by dissolution.

subject to reorganization. Composites consisting of gold–polyethylene–gold were formed at 200° for 0.5 hr in a nitrogen environment. The effect of annealing at elevated temperatures on the gold-clad and gold-stripped films was followed by measuring the contact angle of glycerol on these surfaces. Figure 7 shows these data. If the film is annealed in contact with the gold, the observed contact angle is unchanged. If the composite is stripped of gold (by dissolution, as before) and then the films are annealed, there is a marked change in θ. The contact angle approaches that of the PTFE-nucleated film. Apparently, there is sufficient surface melting of the small crystallites formed at the solidified polymer melt–gold interface even at these low temperatures. If the polymer is in contact with the gold during the annealing, the absorbed species apparently have insufficient mobility to reorganize.