

AN ABSTRACT OF THE THESIS OF

Sidney A. Kirtley for the degree of Master of Science in Food Science and Technology presented on August 26, 1991.

Title: Use of Contact Angle Analysis for the Measurement of the Relative Hydrophilicity of Food Contact Surfaces.

Abstract approved: _____

 Dr. Joseph McGuire

A simple method for evaluation of food contact material surface properties related to their hydrophilic-hydrophobic balance is presented. Contact angle analysis was used to determine properties related to the polar and dispersive contributions to surface energy for thirty different test materials. For each material, the surface property $W_{a^p, \text{water}}$ (mJ/m^2), defined as the polar component of energy required to separate water from its surface, was then calculated. In general, it was found that $W_{a^p, \text{water}}$ increased with increasing test material hydrophilicity. A relationship between this contact surface property and adhesion of Bacillus subtilis ATCC 6633 spores to food contact materials was plotted. The number of spores adhering to the different test materials was quantified by a ^{14}C -labelled spore adhesion assay; adhesion was observed to increase with increasing contact surface hydrophobicity, as quantified by $W_{a^p, \text{water}}$.

**Use of Contact Angle Analysis for the Measurement of the
Relative Hydrophilicity of Food Contact Surfaces**

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A THESIS

submitted to

Oregon State University

in partial fulfillment of the
requirements for the Degree of

Master of Science

Completed August 26, 1991

Commencement June 1992

APPROVED:

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Date thesis is presented August 26, 1991

Typed by the author Sidney A. Kirtley

ACKNOWLEDGEMENT

This work was supported by the Western Dairy Foods Research Center, Logan, Utah; Oregon State, Utah State, and Brigham Young Universities cooperating. I am appreciative to the Department of Food Science and Technology at Oregon State University for awarding me an assistantship which helped financially for the pursuit of this degree.

I would like to thank Dr. Joseph McGuire for encouraging me to attend graduate school, accepting me as one of his students, and for his help throughout my Master's degree work at Oregon State University.

I am grateful to K. Mark Wiencek at the Department of Microbiology, North Carolina State University, for his work on the bacterial spore adhesion assay.

Of course, I cannot forget those closest to my heart. A tremendous thank you to Craig for his support, patience, and encouragement. Special thanks to my mom, cat (Tasselhoff), and friends for their support and ever listening ear. Without each of these special people, I would never have accomplished this goal.

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NOMENCLATURE

W_a	Work of adhesion between a solid and liquid phase (J/m^2)
W_a^d, W_a^p	Dispersive (d) and polar (p) components of W_a (J/m^2)
W_a^p, water	Polar component of energy required to separate water from the surface of each material (J/m^2)
$\gamma_s, \gamma_L, \gamma_{s,L}$	Surface or interfacial energy at a: solid-vapor (S), liquid-vapor (L), and solid-liquid (S,L) interface (J/m^2 ; also referred to as surface or interfacial tension, N/m)
γ^d, γ^p	Dispersive (d) and polar (p) components of surface or interfacial energy (J/m^2)
π_s	Equilibrium spreading pressure (J/m^2)
θ	Contact angle ($^\circ$)

USE OF CONTACT ANGLE ANALYSIS FOR THE MEASUREMENT OF THE RELATIVE HYDROPHILICITY OF FOOD CONTACT SURFACES

INTRODUCTION

There is much interest in relating the surface properties of materials to the responses they evoke upon contact with fluid foods. Such relationships would be useful as they may be incorporated into methods for prediction of contact surface-fluid food constituent interactions, such as biofilm formation on a membrane, heat exchange, or food packaging surfaces. An understanding of this relationship is within reach, and past research suggests that it will provide a means for both prediction and control of unwanted particle-surface interactions (biofilm development: spore adhesion, bacterial colonization with resulting production of proteolytic enzymes, etc.). This would be particularly useful for shelf-life prediction. By simple manipulation of the packaging polymer chemistry or type of package, an optimal packaging material could be selected for a product to provide the longest shelf-life.

Contact angle measurements are the basis for one of the most sensitive, yet simple techniques for describing surface energetics and thermodynamics. Contact angle data have been used extensively to evaluate solid surface properties related to surface energy. The derivation of these techniques and their development are discussed in most surface chemistry texts (Aveyard and Haydon, 1973; Hiemenz, 1986).

The major purpose of this work was to provide direction for the use of contact angle methodology for characterization of surfaces in contact with foods, based on surface chemistry principles, and to defend its usefulness in aiding

the prediction of food protein behavior at interfaces.

Bacterial colonization on solid surfaces has been associated with the contamination and fouling of several diverse materials, including food contact surfaces (Speers et al., 1984), drinking water pipelines (LeChevallier et al., 1987), and contact lenses (Miller and Ahearn, 1987). Adhesion of bacteria or fungi to inanimate material can lead to complex biofilm development, physical destruction of the surface material, or product spoilage (Lappin-Scott and Costerton, 1989).

Detailed studies have been conducted on the adhesion of bacterial vegetative cells to various materials (Marshall, 1985; Rosenberg and Kjelleberg, 1986). The adhesion of bacteria to inanimate surfaces has been correlated with the surface properties of the microorganism and the contacting material. The contact angles exhibited by drops of various liquids applied to the surface are often reported as indicators of the surface hydrophobicity; these angles can be used to calculate surface free energy (Absolom et al., 1983; van Pelt et al., 1985), or critical surface tension (Dexter, 1979).

The results from several adhesion studies suggest that bacteria tend to adhere to materials with low surface free energies, and that hydrophobic bacteria are generally more adherent to surfaces than are non-hydrophobic bacteria (Hogt et al., 1983, Rosenberg and Kjelleberg, 1986; van Loosdrecht et al., 1987a).

Despite several reports of the increased hydrophobicity of bacterial spores relative to vegetative cells (Doyle et al., 1984; Craven and Blankenship, 1987; Koshikawa et al., 1989; Wiencek et al., 1990), comprehensive, quantitative studies of the effects of surface properties on the adhesion of bacterial spores to solid surfaces are lacking. Due to their extreme resistance to

chemical and physical sterilization agents, bacterial spores are the target of sterilization processes for foods, pharmaceuticals, and medical supplies (Edwards et al., 1965; Smith and Brown, 1980; Stannard et al., 1983). Several species of the genera Bacillus are capable of causing illness or product spoilage if the spores survive a sterilization process. An understanding of the interactions which influence the adhesion and removal of spores from inanimate surfaces could aid the selection of materials which minimize spore adherence. Thus, it was the further goal of this work to relate the adhesion of Bacillus spores to contact surface properties for a number of packaging materials.

LITERATURE REVIEW

The Contact Angle

The contact angle, θ , formed when a drop of liquid is in contact with a solid surface is shown in Figure 1. The subscripts L, S, and S,L refer to the liquid-vapor, solid-vapor, and solid-liquid interfaces, respectively.

Young's equation (a force balance) for the drop of liquid at equilibrium on the plane surface is

$$\gamma_S = \gamma_{S,L} + \gamma_L \cos \theta \quad (1)$$

where γ is the surface (interfacial) tension.

The Dupre equation (an energy balance) defines the work of adhesion, W_a , as the energy required to part the liquid from the solid,

$$W_a = \gamma_S + \gamma_L - \gamma_{S,L} \quad (2)$$

The quantity $\gamma_{S,L}$ can be measured experimentally (Neumann and Good, 1974), but the method is associated with important limitations. Therefore, the Young and Dupre equations are usually combined to yield the following relationship for the work of adhesion between the solid and the liquid:

$$W_a = \gamma_L (1 + \cos \theta) \quad (3)$$

Rigorously, equation (3) is applicable only to a system at equilibrium. Consequently, the liquid must be saturated with the solid, and the vapor and solid surface must be at adsorption equilibrium. This is not often the case, and values of θ for a given system may vary widely. Additionally, it should be noted that direct application of equation (3) to common engineering materials may

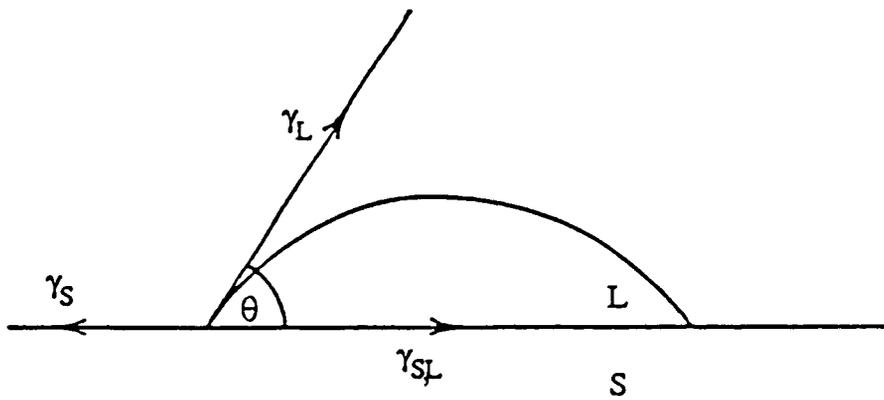


FIGURE 1:

The contact angle, θ , formed when a drop of liquid is brought into contact with a solid surface.

yield misleading results, as these surfaces exhibit energetic heterogeneities and other surface irregularities.

Use of θ in Evaluation of Properties Related to Surface Energy

The most common methods used to identify differences in surface constitution for materials used in contact with biological fluids are sessile drop techniques. These are classified as advancing angle techniques, as during drop formation and contact, the liquid advances along a part of the surface with which it has not previously been equilibrated. Alternatively, the line of solid-liquid contact may occur at a position on the solid which has previously been immersed in the test liquid, i.e. the liquid recedes or is pulled back across the part of the surface with which it has reached equilibrium. Obtained in this way, θ is referred to as the receding contact angle.

Zisman Plot Method

Adopting the most common sessile drop procedure, θ is determined for a series of homologous liquids (usually hydrocarbons) in contact with a solid test surface. The cosines of the angles are then plotted against the liquid-vapor surface tension of the corresponding liquids. Zisman (1964) developed this method extensively and found empirically that, for a given surface, a rectilinear fit to the data is most often obtained. The intercept at the $\cos \theta = 1$ axis is termed the critical surface tension for the particular solid. The critical surface tension is suggested to be both a function of surface properties of the solid alone, and related to the true surface energy of the solid. However, as the data

points fall within a rectilinear band, different values of the critical surface tension may be determined for a given material. Additionally, as suggested by Andrade (1985), the method can be highly misleading when examining the properties of solids for use in aqueous environments. This is in part a result of surface restructuring which may occur under water as a more energetically favorable state is attained. Water is often used as a test liquid in the Zisman plot method, and this serves to cloud data interpretation as well. Particularly in the case of hydrophilic surfaces, water rarely falls within the band of data determined with the other test liquids commonly used. This is in part owing to water penetration into the surface (facilitated by its small molecular volume) and in part to the surface restructuring which may take place upon water-solid contact.

In less commonly used receding contact angle experiments, reasonable correlations have been achieved between surface energetics of polymers and both protein adsorption and cell adhesion (Young, 1982). This is probably a result of surface characterization having been performed on water-equilibrated surfaces, i.e. the surfaces were characterized in a state they would experience if they were in contact with an aqueous (food liquid) system. Receding angle data recorded with liquids other than water, however, are representative of the solid equilibrated with that liquid only and do not represent surface properties at the solid-water interface.

Kaelble's Method

For a more quantitative treatment of contact angle data, Fowkes (1964) introduced the London dispersion force contribution to the surface free energy, γ_L^d . Liquid surface tension may be expressed as

$$\gamma_L = \gamma_L^p + \gamma_L^d \quad (4)$$

where superscripts p and d refer to polar and dispersive force components. The polar contribution to surface tension represents the sum of all forces which may be referred to as nondispersive (e.g. hydrogen bonding, electrostatic, and dipole - dipole interactions). At the interface between any liquid and another in which the intermolecular attraction is entirely due to London dispersion forces, the only appreciable interfacial interactions to which these liquids are subject are London dispersion forces.

Moreover, Fowkes (1964) showed that the geometric mean of the dispersion force attractions should predict the magnitude of the interaction between dissimilar materials. Therefore, if only dispersive interactions are present at a liquid-liquid interface, the effect of interfacial attraction on the tension in the interface can be predicted by the geometric mean of the dispersion force components of the surface tension of two liquids 1 and 2 as $(\gamma_1^d \gamma_2^d)^{0.5}$. The tension in the interfacial region of liquid 1 is then $\gamma_1 - (\gamma_1^d \gamma_2^d)^{0.5}$, and that in the interfacial region of liquid 2 is $\gamma_2 - (\gamma_1^d \gamma_2^d)^{0.5}$. The interfacial tension is the sum of the tensions in both regions and is given by

$$\gamma_{1,2} = \gamma_1 + \gamma_2 - 2(\gamma_1^d \gamma_2^d)^{0.5} \quad (5)$$

By analogy with the Dupre equation, the energy required per unit area to separate the liquid-liquid interface is expressed as

$$W_a = \gamma_1 + \gamma_2 - \gamma_{1,2} \quad (6)$$

and, since W_a may also be divided into dispersive and polar components, i.e.

$W_a = W_a^d + W_a^p$ (Fowkes, 1972), then

$$W_a^d = 2(\gamma_1^d \gamma_2^d)^{0.5} \quad (7)$$

Kaelble (1970) applied these concepts to liquid contact with low-energy solids and developed a method for determining both the dispersive and polar components of γ_S from contact angle data ($\gamma_S = \gamma_S^p + \gamma_S^d$). Given a pure liquid, L, whose γ_L , γ_L^p , and γ_L^d are known, if θ is the contact angle between the liquid and some solid, S, the interaction was described in terms of the reversible work of adhesion (per unit area), W_a , as

$$\gamma_L(1 + \cos \theta) = W_a = (W_a^d + W_a^p) = 2(\gamma_L^d \gamma_S^d)^{0.5} + 2(\gamma_L^p \gamma_S^p)^{0.5} \quad (8)$$

Contact angle data from two liquids, therefore, provides two equations containing the unknowns, γ_S^d and γ_S^p . For each set of n pure liquids on a given surface, n equations can be written where any and all pairs of equations can be solved simultaneously for γ_S^d and γ_S^p . Finally, the mean values of γ_S^d and γ_S^p are determined by averaging the results. Kaelble's method is mathematically convenient, and it has been adopted as more quantitative than the Zisman plot method (Nyilas et al., 1972; McGuire and Swartzel, 1987). Problems associated with interpretation of the data arise from the fact that there is no theoretical basis for equating W_a^p to the geometric mean of the polar components of solid and liquid surface tension as was done in evaluation of W_a^d in equation (7) (Fowkes, 1972). Thus, equation (8) is consequently incorrect and must be rewritten

$$\gamma_L(1 + \cos \theta) = W_a = 2(\gamma_L^d \gamma_S^d)^{0.5} + W_a^p \quad (9)$$

The value of the polar contribution to the work of adhesion, W_a^p , depends upon the polar character of both the solid and the liquid which are in

contact, i. e.

$$W_a^P = f(\gamma_S^P, \gamma_L^P) \quad (10)$$

However, there is no way of calculating γ_S^P directly, and the functional representation of equation (10) is not known. It seems clear that development of an expression for W_a^P would contribute to a sound theoretical basis for calculation of γ_S .

Equation-of-State Method

Of the four quantities in Young's equation (eq.1), only the liquid surface tension (γ_L) and θ are readily determined experimentally; determination of a further relation between these quantities is necessary to determine γ_S . It has been shown from thermodynamic considerations that an equation of state relation of the form:

$$\gamma_{S,L} = f(\gamma_S, \gamma_L) \quad (11)$$

must exist (Ward and Neumann, 1974). Using experimental contact angle data and liquid-vapor interfacial tensions, Neumann, et al. (1974) formulated equation 11, the equation of state, explicitly as follows:

$$\gamma_{S,L} = [(\gamma_S)^{0.5} - (\gamma_L)^{0.5}]^2 / [1 - 0.015(\gamma_S \gamma_L)^{0.5}] \quad (12)$$

In conjunction with Young's equation, this relationship yields:

$$\cos \theta = [(0.015 \gamma_S - 2.00)(\gamma_S \gamma_L)^{0.5} + \gamma_L] / [\gamma_L(0.015(\gamma_S \gamma_L)^{0.5} - 1)] \quad (13)$$

Thus, with equation 13 the unknown surface tension of the substratum, γ_S , may be determined from the easily measurable quantities γ_L and θ . This approach is still widely used today (Ward and Neumann, 1974), but does have

some serious limitations. These limitations include the fact that the equation can only be used for very low energy surfaces and that the equation is not functionable as the quantity $[0.015 (\gamma_s \gamma_L)^{0.5}]$ approaches unity.

Bacterial Adhesion

The adhesion of bacteria to the surface of inanimate materials is a complex event which can be influenced by characteristics of the microorganism, the material, and the environment. Interactions between a microorganism and contact surface can be categorized as specific or non-specific. Specific interactions refer to the bacterial cell surface structures that have specific affinity for receptors on the material surface. This type of interaction is generally thought to be responsible for the adhesion of microorganisms to biological materials such as tissue and can occur after direct contact is initially established through non-specific interactions. Non-specific interactions between the microorganism and the inanimate material are processes that generally attract the microorganism to the material surface, once it enters the interface.

The consequence of bacterial adhesion can be beneficial or detrimental to man. The adhesion of bacteria or yeast within fixed-film fermentation reactors can be critical in the extraction of product from the reaction vessel (Atkinson and Fowler, 1974; Characklis and Cooksey, 1983). Mammalian cell adhesion processes are important in research associated with biologically compatible materials to be used as artificial implants and grafts (Horbett et al., 1985).

The harmful effects of bacterial adhesion are widespread. Bacterial adhesion to inanimate, manufactured materials can result in the physical

deterioration of the material surface, primarily metals, through metabolic end-products which corrode the material (Lappin-Scott and Costerton, 1989). Heat exchanger efficiency can be compromised by bacterial attachment and subsequent biofilm development (Characklis and Cooksey, 1983; Lappin-Scott and Costerton, 1989). Contamination of medical supplies such as catheters (Hogt et al., 1983; Sheth et al., 1983), sutures (Chu and Williams, 1984), and other fabrics (Ghione et al., 1989; Hsieh and Merry, 1986), and biomaterials such as denture resins (Minagi et al., 1985) can result from microbial adhesion to a surface. The dental industry has been involved extensively with the adhesion of hydrophobic bacteria to teeth and the oral cavity, which results in biofilm development in the form of plaque (Lappin-Scott and Costerton, 1989; Rosenberg and Kjelleberg, 1986; Van Dijk et al., 1988). Manufacturers of contact lenses and pharmaceuticals are extremely concerned with the control of bacterial adhesion and sterility in their products. Miller et al (1988) cited increases in the incidence of microbial keratitis caused by the adhesion of Pseudomonas aeruginosa to soft contact lenses.

In most of these examples of biofouling or product contamination, hydrophobic interactions between the microorganism and the material surface have been implicated as primary forces involved in adhesion. Thus, more study on the hydrophobic nature of microorganisms and the materials they contact might assist in formulating a solution to reduce microbial adhesion to such surfaces.

MATERIALS AND METHODS

Evaluation of Surface Properties

All liquids used had their surface tension measured by the ring method with a DuNouy tensiometer (CSC Scientific Co., Inc., Fairfax, VA). Measurements were performed at approximately 25° C. and were reproducible to within 0.1 mN/m. Test liquids (hydrocarbons and aqueous solutions of ethanol and methanol) (E.M. Science, Cherry Hill, NJ and Aldrich Chemical Co., Inc., Milwaukee, WI) used are listed in Tables 1 and 2. Test contact materials and their origins are listed in Table 3. Each test material was cleaned with acetone and then with deionized water prior to contact angle analysis.

The contact angle formed by a sessile drop on a given surface is measured routinely with a contact angle goniometer. This instrument consists of a light source which illuminates a stage on which the liquid drop/solid system rests, and a telescope, with cross-hairs and a 360° scale around the eyepiece to enable rapid, accurate measurement of the contact angle. All contact angle data were obtained with a sessile drop contact angle goniometer (Rame-Hart, Inc., Mountain Lakes, NJ), and were reproducible to within 2°. An environmental sample chamber was attached to the goniometer to maintain an approximate 25° C temperature and water-saturated conditions. The water-saturated conditions were assured by the presence of cotton saturated with warm water being placed inside the closed sample chamber.

Evaluation of both the dispersive and polar components of the test liquid surface tension was essential. In a given solid-liquid contact, if the surface tension of either the solid or the liquid has only a dispersive component

TABLE 1

Surface Tension of Nonpolar Liquids

Test liquid	$\gamma_L (= \gamma_L^d)$ mN/m
Nonane	22.78
Decane	23.86
Dodecane	25.20
Dicyclohexyl	25.62
Hexadecane	27.36
1-Bromonaphthalene	44.41
Diiodomethane	52.24

TABLE 2

Surface Tension Components of Aqueous Ethanol and Methanol Solutions

Ethanol-water and Methanol-water concentrations % (v/v)	γ_L	γ_L^d mN/m	γ_L^p
0 (water)	71.17	34.03	37.14
10 (ethanol)	49.86	22.63	27.23
20	40.72	24.08	16.64
30	35.40	26.70	8.70
40	34.22	28.17	6.05
50	29.64	24.80	4.84
60	28.00	22.20	5.80
70	26.96	22.49	4.47
80	25.79	23.26	2.53
90	24.40	21.53	2.87
100 (ethanol)	22.40	19.45	2.95
0 (water)	71.17	34.03	37.14
10 (methanol)	58.80	40.40	18.40
20	50.74	33.39	17.35
30	45.32	28.79	16.53
40	40.13	27.51	12.62
50	36.53	28.50	8.03
60	33.81	29.51	4.30
70	31.37	25.43	5.94
80	28.77	23.64	5.13
90	26.10	20.17	5.93
100 (methanol)	23.35	17.69	5.86

TABLE 3
Test Materials and Suppliers

Material	Supplier
1. Acetal	Universal Plastics Co.
2. Ethylene vinyl alcohol (EVOH)	International Paper Co.
3. Fluorinated ethylene propylene (FEP)	DuPont Co.
4. Germanium (Ge)	Analect Instruments, Utica, NY
5. Glass ₁	Erie Scientific Co., Portsmouth, NH
6. Glass ₂	Becton, Dickinson & Co., Parsippany, NJ
7. Glass ₃ (GOLD SEAL)	Fisher Scientific, Dallas, TX
8. Glycol-modified Polyethylene Terephthalate (PETG) ₁	Eastman Chemical Products, Inc., Kingsport, TN
9. (PETG) ₂	Lustro Co., Evanston, IL
10. High Density Polyethylene (HD)	Universal Plastics Co.
11. Linear Low Density Polyethylene (LLD)	Molded Container Corp., Portland, OR
12. Nylon ₁	Kraft, Inc., Glenview, IL
13. Nylon ₂	Universal Plastics Co.
14. Nylon ₃	DuPont Co., Wilmington, DE
15. Paraffin	N. Engineering & Plastics Corp., Portland, O
16. Polyethylene (PE) ₁	International Paper Co. (not water-equil.)
17. Polyethylene (PE) ₂	N. Engineering & Plastics (not water-equil.)
18. Polyethylene (PE) ₃	Northern Engineering & Plastics
19. Polyethylene (TETRABRIK) (PE-1)	AB Tetra Pak, Lund, Sweden
20. Polyethylene (IP) (PE-2)	International Paper
21. Polyhexamethylenedipamide (NY-1)	Penn Fiber
22. Polyhexamethylenedipamide (NY -2)	DuPont Co.
23. Polytetrafluoroethylene (PTFE) ₁	Universal Plastics Co., Portland, OR
24. Polytetrafluoroethylene (PTFE) ₂	DuPont Co.; dist. by Fluorocarbon, Anaheim, CA
25. Polypropylene (PP) ₁	Universal Plastics Co.
26. Polypropylene (PP) ₂	Penn Fiber, Philadelphia, PA
27. #304 Stainless Steel (SS) ₁	Alaskan Copper & Brass Co., Portland, OR
28. Ultra-High Molecular Weight PE (UHMW)	Universal Plastics Co.
29. Viton ₁	International Paper Co., Raleigh, NC
30. Viton ₂	DuPont Co.

(i.e. γ_S^P or $\gamma_L^P = 0$), then the interaction between the two is entirely due to dispersive forces (Fowkes, 1964,1972). For this case, equation (9) may be written

$$W_a = \gamma_L(1 + \cos \theta) = 2(\gamma_L^d \gamma_S^d)^{0.5} = W_a^d \quad (14)$$

i.e. the work of adhesion is totally a result of dispersive (nonpolar) interactions.

Rearranging,

$$\gamma_L^d = \gamma_L^2 (1 + \cos \theta)^2 / 4 \gamma_S^d \quad (15)$$

γ_L and θ are readily measurable. Consequently, given a solid surface of known γ_S^d with which no polar interactions may take place, the dispersive component of liquid surface tension, γ_L^d , may be found with a single contact angle measurement. Paraffin wax is such a solid, for which $\gamma_S = \gamma_S^d$. Obviously, evaluation of γ_S^d requires knowledge of γ_L^d . Fortunately, many liquids exist (particularly hydrocarbons) whose surface tension is totally due to dispersive forces. For these liquids, $\gamma_L = \gamma_L^d$, where γ_L was measured by the conventional ring method.

A different rearrangement of equation (9) yields

$$\cos \theta = [2(\gamma_S^d)^{0.5}(\gamma_L^d)^{0.5}/\gamma_L] - 1 \quad (16)$$

Choosing a series of nonpolar liquids, for any solid a plot of $\cos \theta$ vs. $(\gamma_L^d)^{0.5}/\gamma_L$ should be a straight line with slope $2(\gamma_S^d)^{0.5}$ intercepting the vertical axis at -1.

Bacterial Spore Adhesion Assay

All bacterial adhesion work was done at North Carolina State University

by K. Mark Wiencek while all surface characterization work, as well as analysis of adhesion - surface property relationships, was performed at Oregon State University by myself. Bacillus subtilis ATCC 6633 was obtained from the American Type Culture Collection (Rockville, MD). Spores were prepared as detailed by Wiencek et al. (1990) and stored in distilled water at 4° C.

Spores of B. subtilis ATCC 6633 were labeled with ¹⁴C-glucose and ¹⁴C-L-amino acids during sporulation in a liquid glucose-salts medium (Hodges et al., 1980) modified by the addition of 50 mCi each of three ¹⁴C-labeled L-amino acids, alanine (170.0 mCi/mmol), aspartic acid (220.4 mCi/mmol), and glycine (111.2 mCi/mmol), and 50 mCi of ¹⁴C-glucose (13.5 mCi/mmol) (New England Nuclear, Dupont Co., Wilmington, DL). This sporulation method produced a high percentage of phase-bright spores with 2380 colony forming units (CFU) per count per minute (CPM).

The materials used in this assay are listed in Table 3 (surfaces 20-31). Despite the attempt to obtain unused materials, the purity of only a few materials could be guaranteed. Glass cover slips (12 mm diameter, Fisher Scientific Co., Dallas, TX) served as glass coupons. Stainless steel coupons were prepared as 9.5 mm diameter discs cut from type 304 stainless steel with a standard #4 industrial finish. Glass and stainless steel coupons were cleaned prior to the adhesion assay by sonification in methanol for five minutes followed by flame drying. Coupons (6.4 mm diameter) of all other materials were produced using an office-grade paper hole puncher.

¹⁴C-labeled Spore Adhesion Assay

Coupons of each material were mounted onto 12 mm diameter glass

cover slips using a cryogenic glue to provide a firm base for handling the coupons with forceps. Glass cover slips were used as the test coupons for glass. Mounted coupons were placed in petri dishes containing moist paper towels to minimize evaporation of the applied spore suspension. A suspension of ^{14}C -labeled B. subtilis ATCC 6633 spores, tempered to 25° C, was pipetted (40 ml) onto each coupon. After 1 hour, the surface of each coupon was rinsed four times with 25 ml of distilled water (total of 100 ml) to remove loosely bound and residual suspended spores. The rinse water drained by gravity from a 25 ml plastic pipette which was held directly above the coupon. Immediately after rinsing, each coupon was shaken gently to remove excess water and placed in a 20 ml scintillation vial containing 5 ml of "ScintiVerse II" scintillation cocktail (Fisher Scientific Co., Dallas, TX). Each vial was shaken vigorously for 20 seconds. Attached spores were measured (CPM) with a Beckman LS 3801 liquid scintillation counter (Beckman Instruments, Inc., Irvine CA). New coupons were prepared for each of ten replicate trials. The number of spores per CPM was calculated from colony counts on plate count agar (Difco Laboratories, Detroit, MI) and used to convert CPM to spore concentration.

RESULTS AND DISCUSSION

Surface Characterization

To determine accurate values of the contact angle, θ , the system defined by the drop and solid surface must be in equilibrium with water. These conditions are met if aqueous solutions are chosen as test liquids, and if contact angles are measured on water-equilibrated surfaces. Receding angle experiments performed with aqueous solutions meet these requirements. However, receding angle experiments require larger volumes of each test liquid and generally require more expensive equipment. Additionally, more simple sessile drop techniques and associated equipment are currently used for quality control by food packaging manufacturers where polymeric coatings are applied to paper. It is suggested that sessile drop techniques should not be abandoned but simply modified to incorporate the above mentioned changes. This may be accomplished if contact angles are recorded in a controlled environment of water-saturated air.

When using a series of nonpolar liquids, the plot of $\cos \theta$ vs. $(\gamma_L^d)^{0.5}/\gamma_L$ for any solid should be a straight line with slope $2(\gamma_S^d)^{0.5}$, intercepting the vertical axis at -1. Such a plot was made for paraffin wax using the liquids listed in Table 1 and is presented in Figure 2. The γ_S^d for paraffin wax was found to be 23.85 mN/m. This is within the range found in the literature: 23.19 mN/m (Kaelble, 1970) to 25.5 mN/m (Fowkes, 1964). Similarly, the values of surface tension shown in Table 1 agree well with corresponding values cited in the literature (Kaelble, 1970; Nyilas

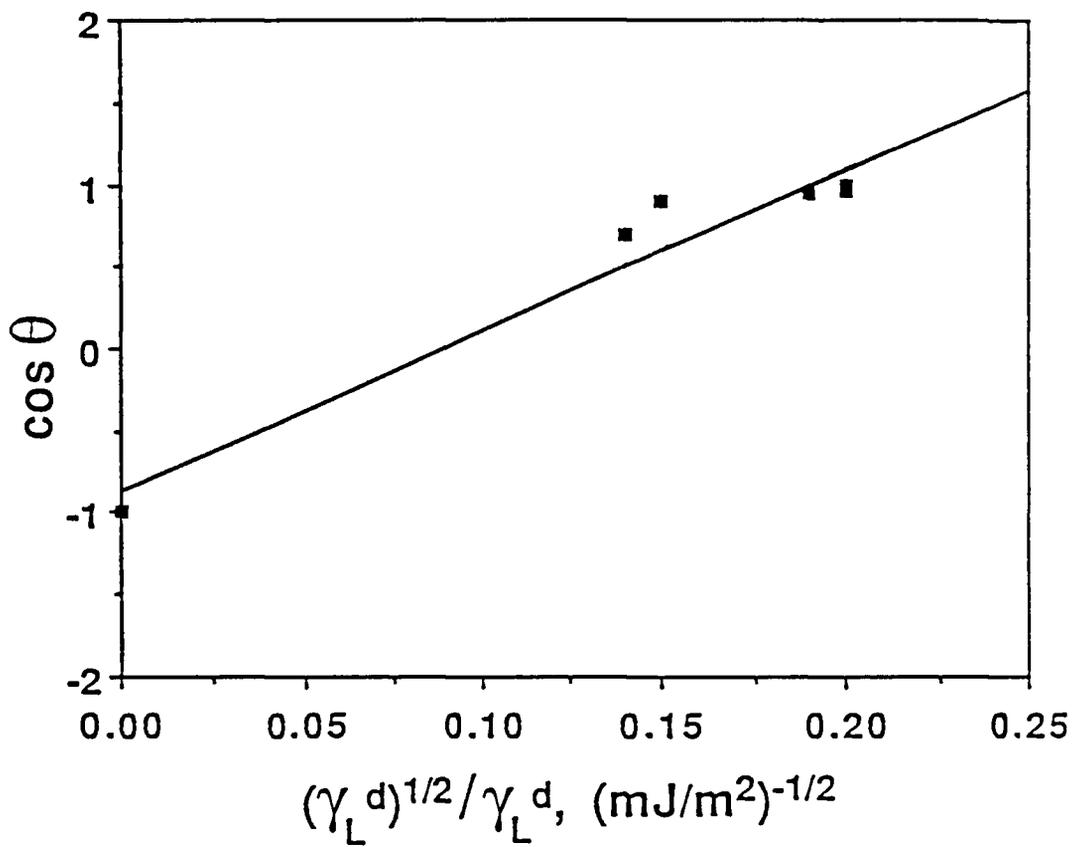


FIGURE 2:

Estimation of the dispersive component of the solid surface tension of paraffin wax.

et al., 1977; Weast, 1981). It should be noted that both 1-bromonaphthalene and di-iodomethane have been observed to possess some polar character; however, their surface energies are for the most part (> 95%) a result of dispersive forces (Kaelble, 1970; Nyilas et al., 1977).

With test liquids of known γ_L , γ_L^d , and γ_L^p , and with methodology for evaluation of γ_S^d , elucidation of the relationship between W_a^p and γ_L^p for a given surface is possible. Rearranging equation (9),

$$W_a^p = \gamma_L(1 + \cos \theta) - 2(\gamma_L^d \gamma_S^d)^{0.5} \quad (17)$$

Equation (17) can be used to evaluate W_a^p for each test liquid brought into contact with a given material. As γ_L^p for each test liquid is known, plots of W_a^p vs. γ_L^p can be constructed for any food contact material. Consequently, the relationship between W_a^p and γ_L^p , suggested to be unique for each material as a result of differences in γ_S^p , may be determined.

This procedure was carried out with all of the materials listed in Table 3. By methods identical to those used to evaluate γ_S^d for paraffin wax, Figure 3 was constructed for polypropylene. The results for both paraffin wax and polypropylene (PP)₁ are representative results for all test materials. The presence of fewer data points than are associated with paraffin simply reflects the fact that polypropylene (PP)₁ exhibits a higher-energy surface; fewer hydrocarbons are able to form a nonzero contact angle on polypropylene (PP)₁. Equation (17) was solved for each liquid from the ethanol-water series dropped

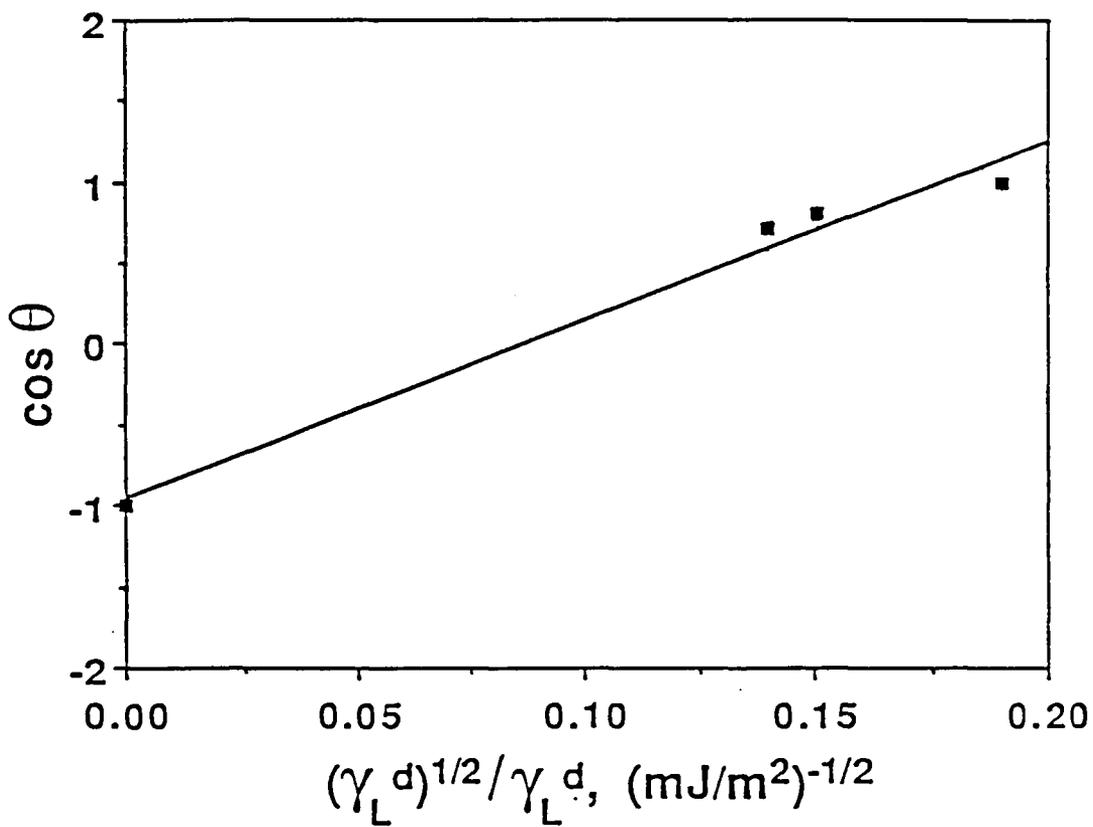


FIGURE 3:

Estimation of the dispersive component of the solid surface tension of polypropylene₁.

on the solid surface. The resulting relationship between W_a^p and γ_L^p for polypropylene (PP)₁ is presented in Figure 4. Clearly, a linear relationship with γ_L^p is supported, rather than the dependence on $(\gamma_L^p)^{0.5}$ as suggested by equation (8). A linear relationship between W_a^p and γ_L^p was observed for all test materials listed in Table 3; all with differing values of slope, k and intercept b . Table 4 shows selected surface properties for the test materials. Such a relationship between W_a^p and γ_L^p was predicted earlier by Dann (1970 a, b), resulting from a study of the influence of γ_L^p on a variable representing “stabilization by nondispersion forces”. Dann (1970 a) suggested also that negative values of W_a^p are physically realistic and reflect the reduction in surface energy associated with adsorption of vapor from the test liquid, i.e. they may be a measure of the spreading pressure, π_S . Plots of W_a^p vs. γ_L^p were observed to be linear for all test materials, as can be representatively seen in Figures 4, 5, 6, 7, and 8, using data from both ethanol-water and methanol-water diagnostic liquids, indicating that the relationship is independent of diagnostic liquid used.

These results imply that equation (9) may be further resolved to

$$\gamma_L(1 + \cos \theta) = W_a = 2(\gamma_L^d \gamma_S^d)^{0.5} + k\gamma_L^p + b \quad (18)$$

Since two different series of diagnostic liquids (ethanol-water and methanol-water) yield similar results (see Figures 5 and 6), support is generated for the identity of k as a true surface property related only to γ_S^p , and independent of the diagnostic liquid used. Some values of W_a^p determined with the diagnostic liquids from the ethanol-water and methanol-water series were

TABLE 4**Composite Surface Properties of Selected Test Materials**

Material	γ_s^d (mJ/m ²)	$W_{a^p,water}$	k (dimensionless)	b
FEP	19.82	0.00	0.00	-3.34
(PTFE) ₁	22.58	0.00	0.00	0.00
Viton	26.68	0.00	.165	-7.84
PE-1	30.48	0.00	0.00	-1.77
Paraffin	31.55	0.00	0.00	0.00
(PP) ₂	29.96	3.08	.076	.26
(PTFE) ₂	22.58	4.54	.502	-14.10
PE-2	30.90	5.65	.243	-3.38
Polyethylene	32.11	19.69	.625	-3.52
HD PE	31.83	25.64	.864	-6.45
LLD PE	32.39	27.04	.868	-5.20
UHMW PE	32.40	28.10	.956	-7.41
(PP) ₁	30.69	29.45	1.01	-8.06
NY-1	46.49	32.65	1.31	-16.00
Acetal	46.36	35.12	1.39	-16.50
(PETG) ₂	32.79	36.03	.969	.04
NY-2	32.02	37.03	1.10	-3.82
Nylon	33.25	38.82	1.23	-6.86
Ge	32.40	42.99	1.28	-4.55
EVOH	32.10	56.90	1.76	-8.47
Glass ₁	27.54	66.43	1.91	-4.51
Glass ₃	31.56	69.28	2.04	-6.49

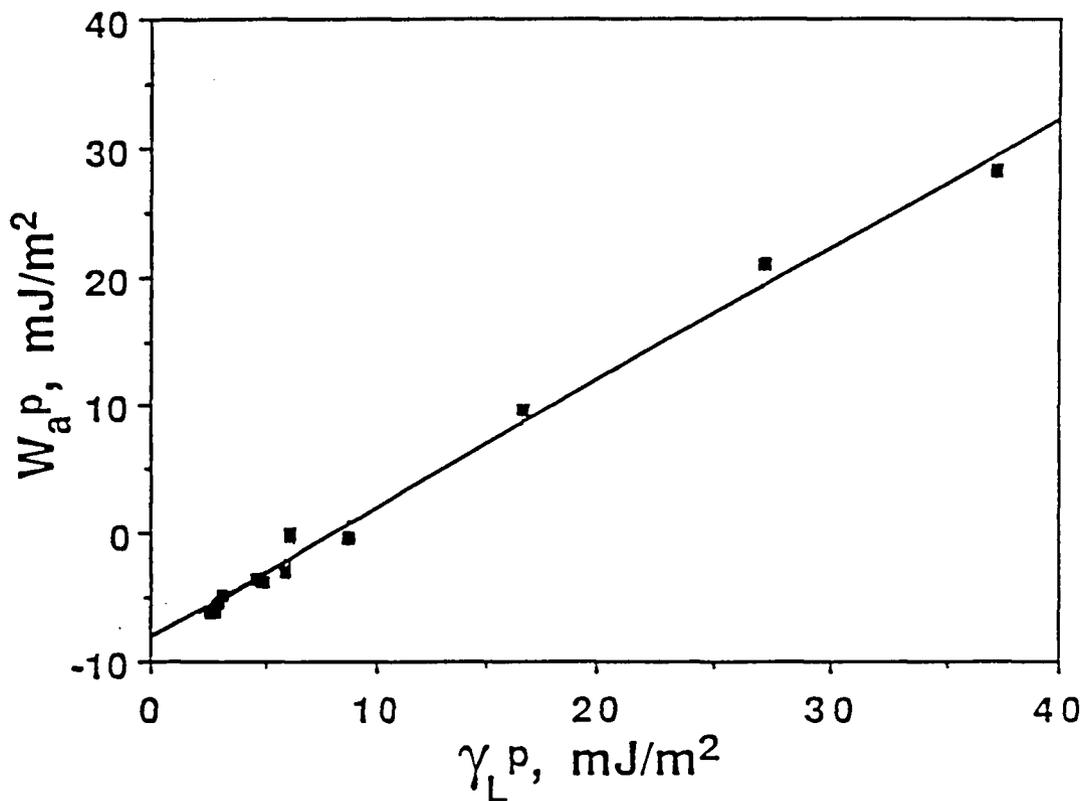


FIGURE 4:

Relationship between the polar component of the work of adhesion and the polar component of liquid surface tension for polypropylene₁.

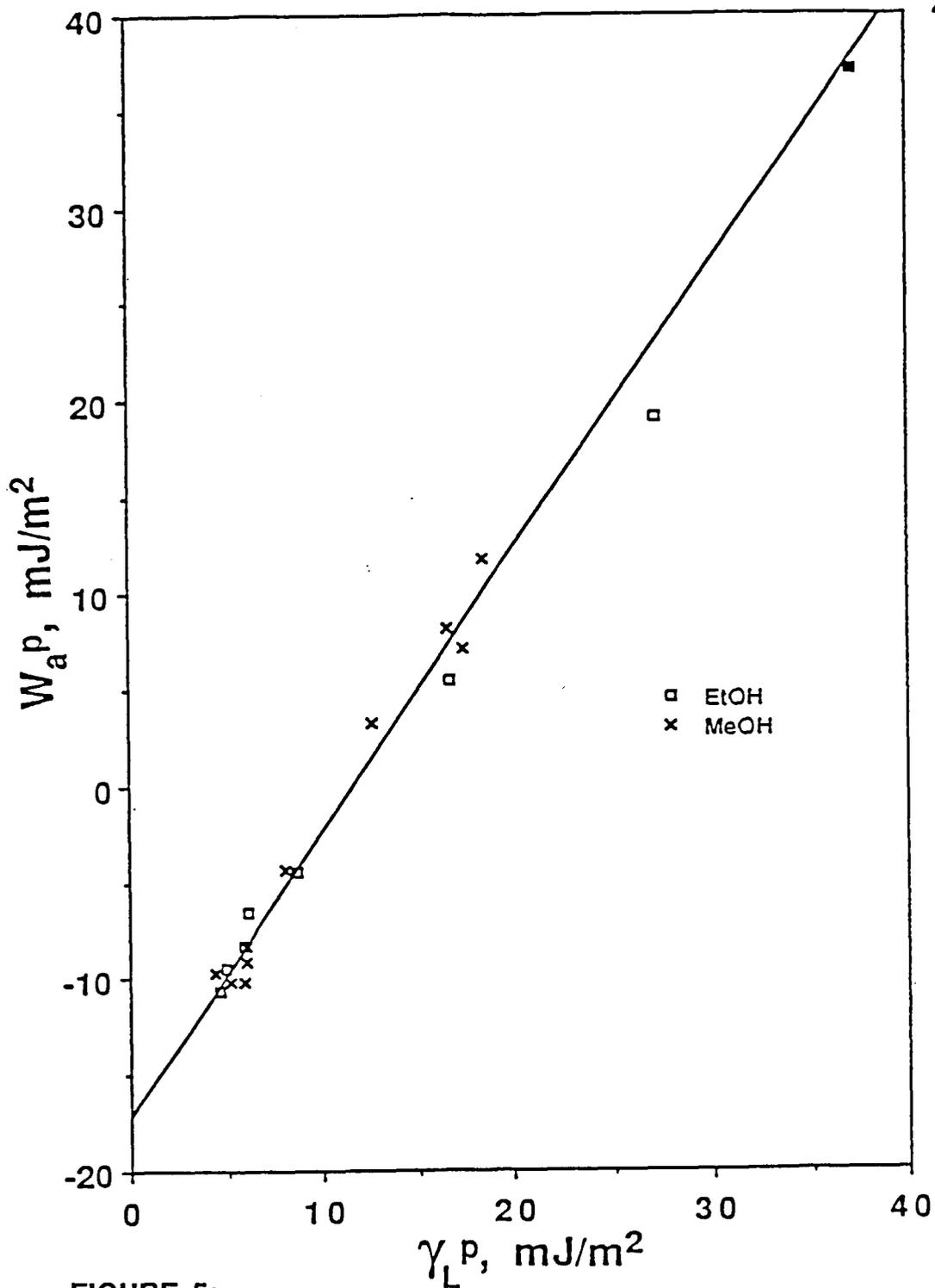


FIGURE 5:

Linear relationship achieved between the polar component of the work of adhesion and the polar component of liquid surface tension for acetal using both ethanol-water (EtOH) and methanol-water (MeOH) solutions as diagnostic liquids.

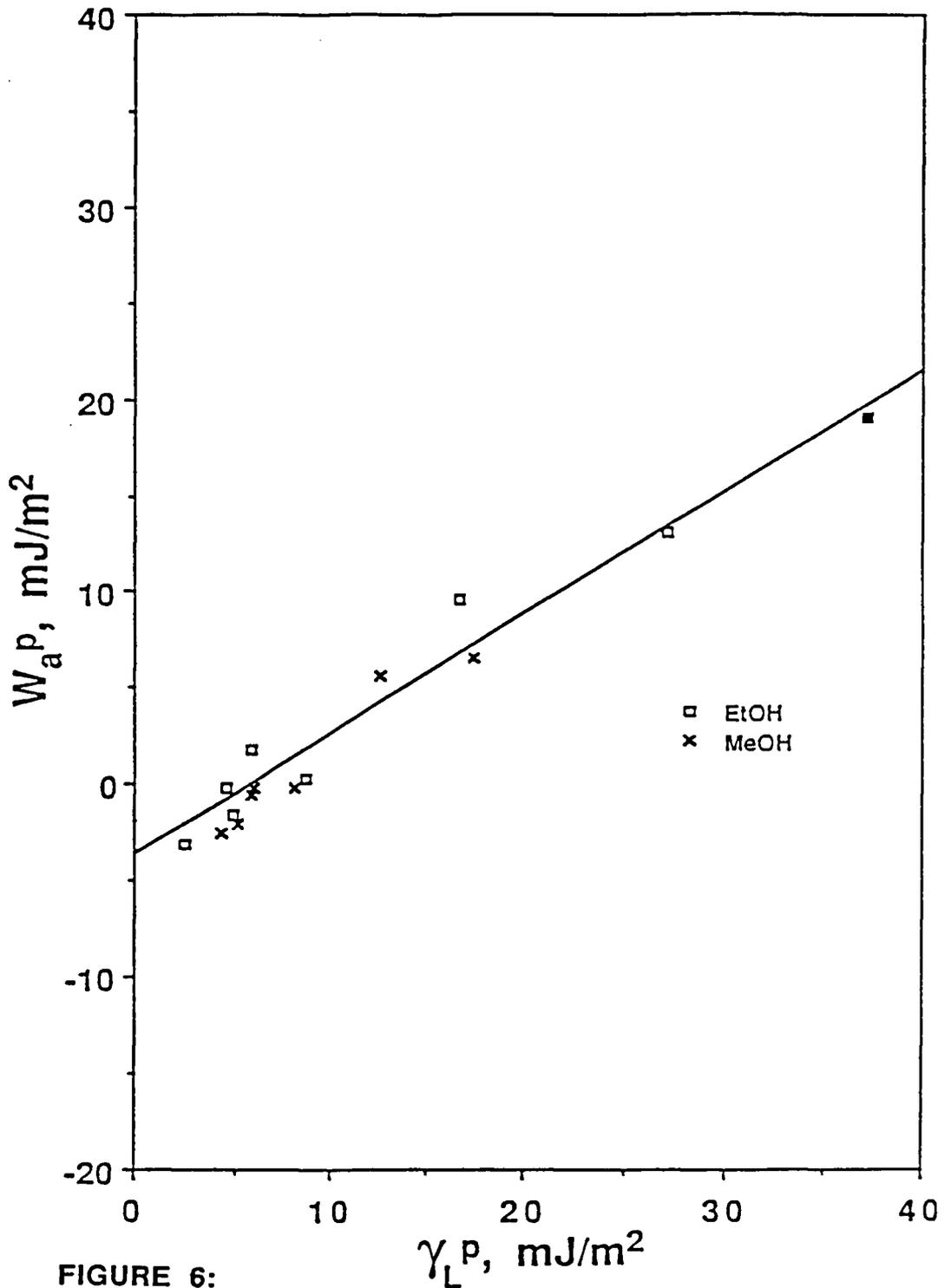


FIGURE 6:

Linear relationship achieved between the polar component of the work of adhesion and the polar component of liquid surface tension for a commercially prepared polyethylene₃ using both ethanol-water and methanol-water solutions as diagnostic liquids.

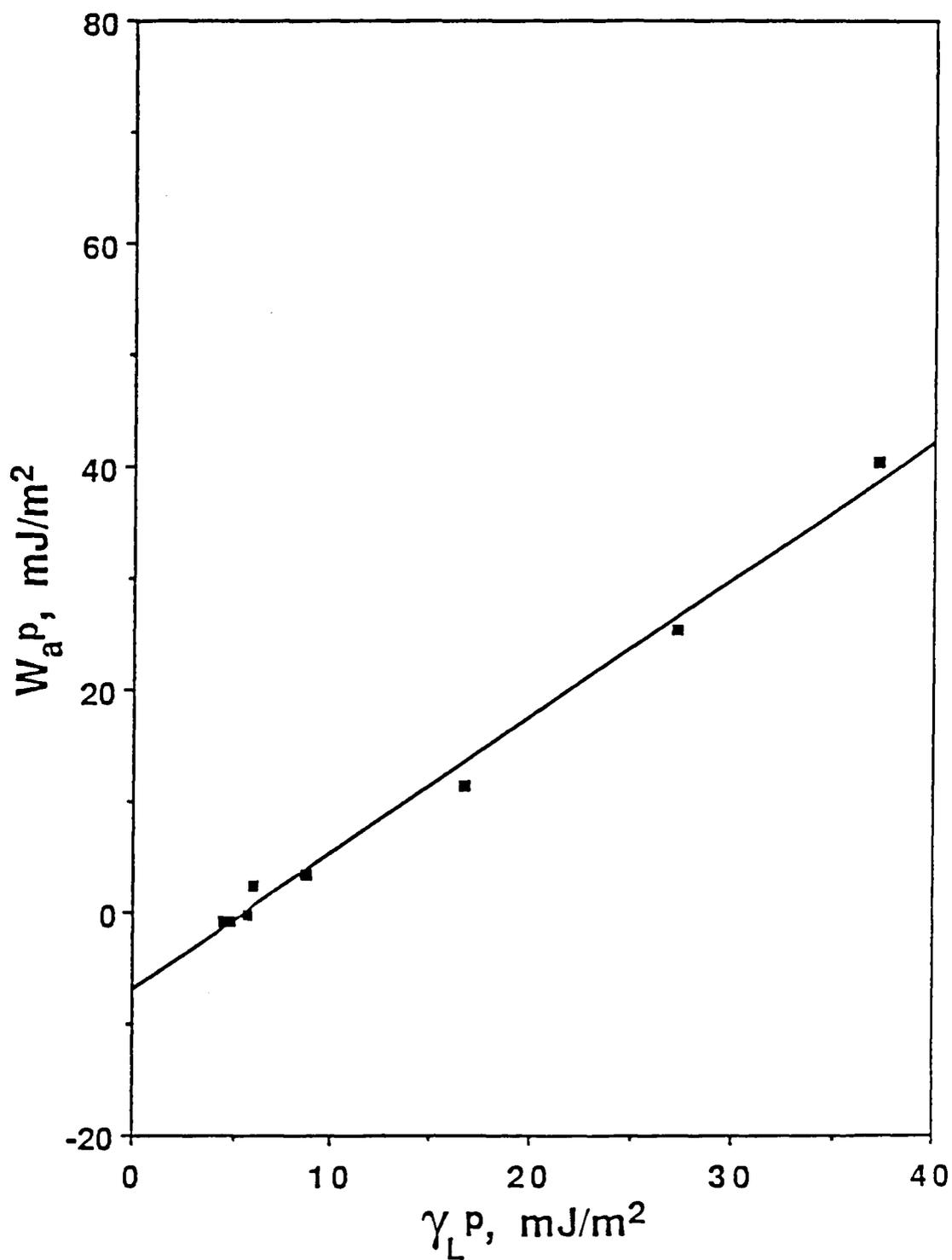


FIGURE 7:

Linear relationship achieved between the polar component of the work of adhesion and the polar component of liquid surface tension for nylon₂.

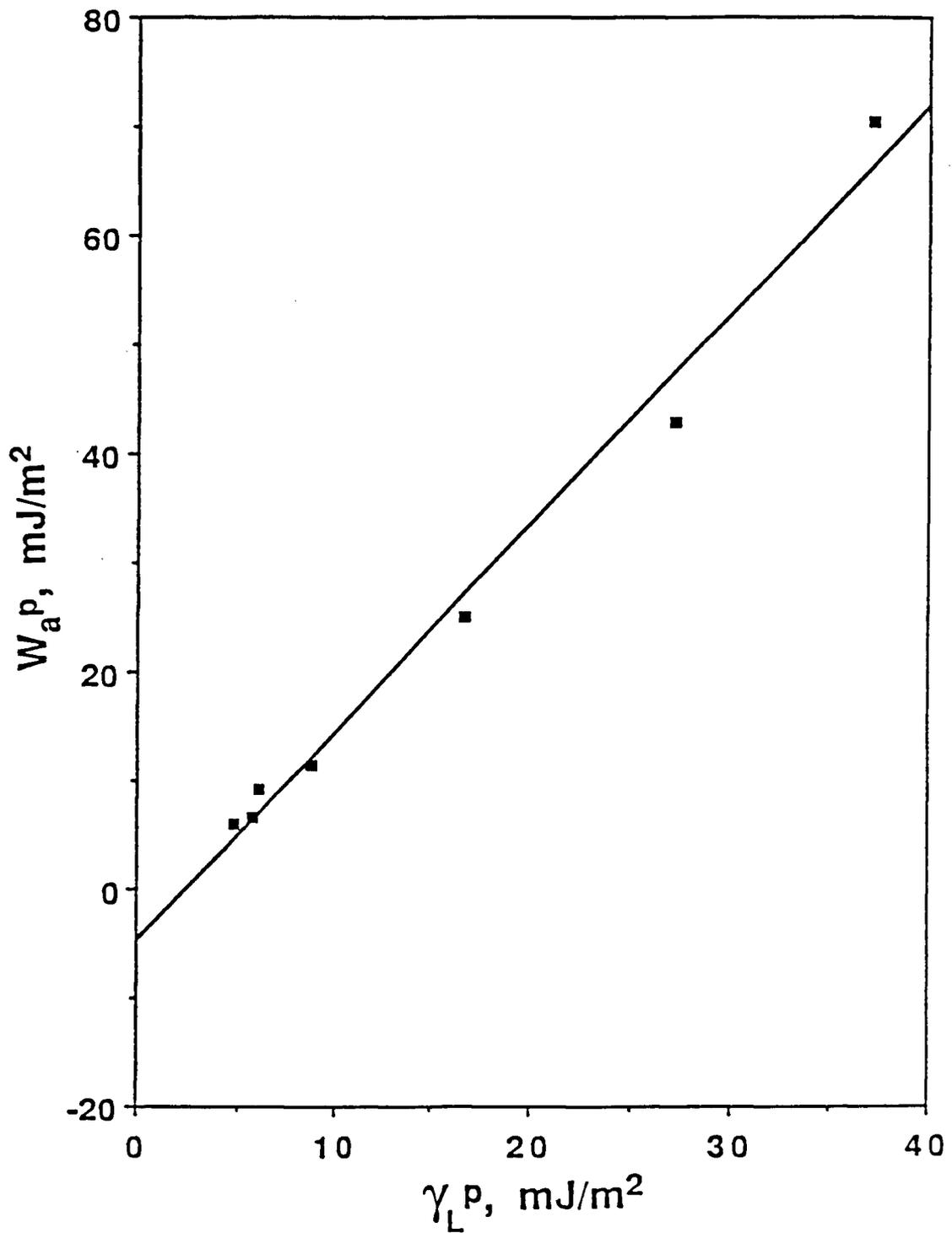


FIGURE 8:

Linear relationship achieved between the polar component of the work of adhesion and the polar component of liquid surface tension for glass₁.

invariably less than zero. The slope of such a line is suggested to have no physical significance. Two such surfaces with no polar character, i.e. $W_a^P < 0$ for all γ_L^P , are paraffin and PTFE. It should be noted that the values of k reported for the surfaces of PTFE and paraffin are defined as zero. Additionally, for solids that interact by dispersion forces only, all theoretical and experimental evidence predicts that adsorption of high energy material cannot reduce the surface energy of a low energy material. For example, the surface energy of PTFE or paraffin cannot be reduced by adsorption of the aqueous solutions selected here as diagnostic liquids. The fact that a given liquid has a contact angle greater than zero degrees on a given low energy solid surface is evidence that the liquid surface energy is greater than that of the solid and π_S should be zero. Consequently, b has been defined as zero for PTFE and paraffin. The graphical method of W_a^P vs. γ_L^P presented here yields a generally better fit to the data than the graphical method (Zisman plot method) used to evaluate the critical surface tension, γ_C . This point is clearly illustrated with comparison of Figures 7 and 8 to Figure 9. Figure 9 is a Zisman plot constructed with the same data used in the previous figures constructed for nylon (NYLON)₂ and glass (GLASS)₁. With respect to nylon (NYLON)₂ and glass (GLASS)₂, greater confidence should be associated with estimations of k and b relative to estimations of γ_C . It should be noted that while γ_S^d , k , and b may be determined unambiguously, the use of aqueous liquid mixtures rather than pure liquids in evaluation of k and b may yield misleading results. It has been recommended that at least two different series of liquids be used if results are to be considered of theoretical value (Good, 1979). The results shown here for (NYLON)₂ and (GLASS)₁ are

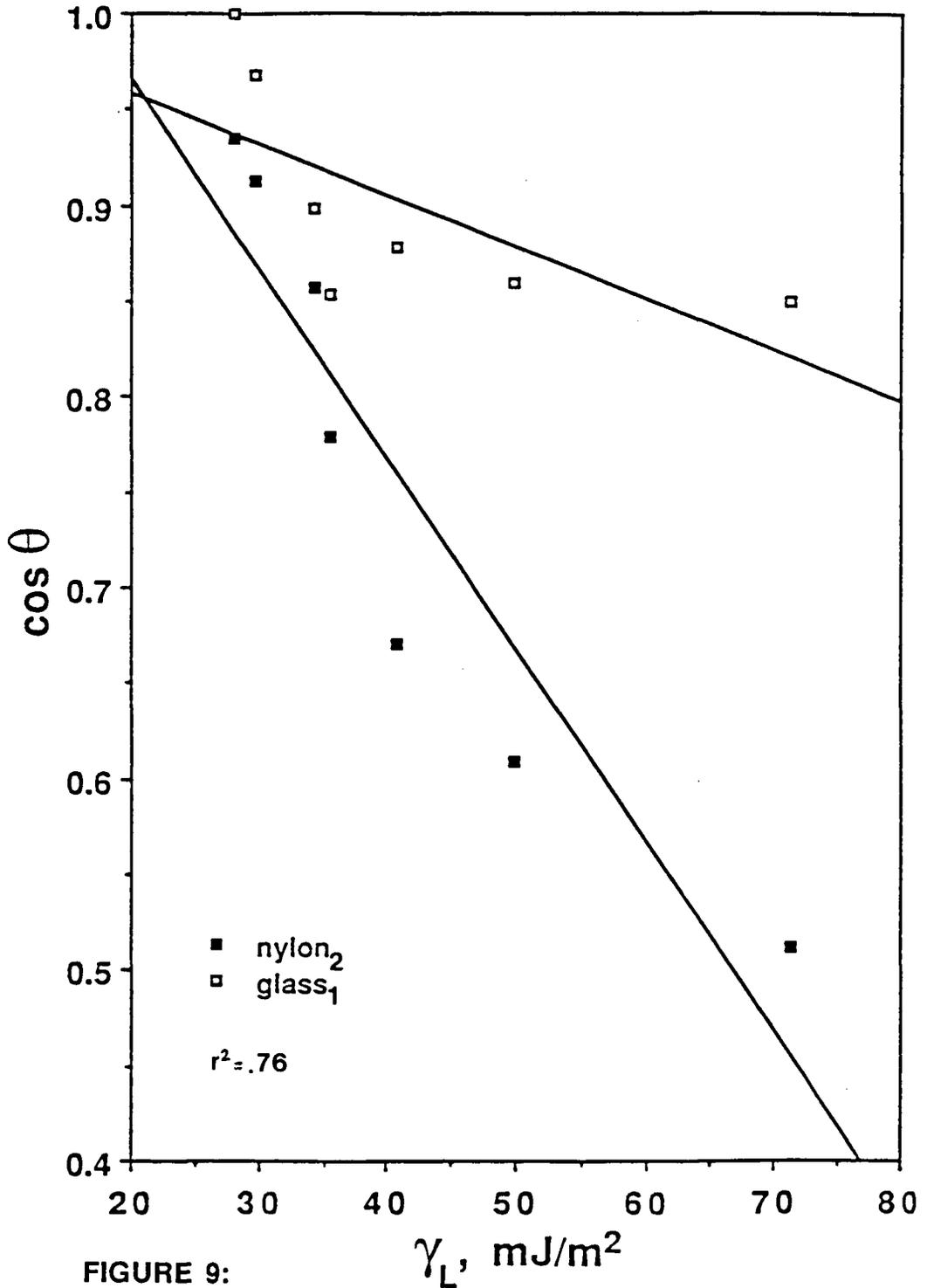


FIGURE 9:

Relatively poor fit achieved by plotting the cosine of contact angles measured on nylon and glass against the surface tension of the corresponding diagnostic liquid (the Zisman plot method).

representative for all test materials.

The polar component of the energy required to separate water from the surface of each material, ($W_{a^P,water}$), as determined with the following equation

$$W_{a^P,water} = k(\gamma_L^P,water) + b \quad (19)$$

was recorded as it provides an index of relative hydrophobicity or hydrophilicity of the surface. Qualitatively, one might expect the relative magnitude of k among surfaces to be similar to corresponding relative magnitudes of $W_{a^P,water}$, neglecting the influence of spreading pressure. The results, as shown on Table 4, seem to indicate that surfaces with a low $W_{a^P,water}$ have a high hydrophobic character. This can be seen in the test materials glass and polyethylene for example. Glass (GLASS)₁ has a very hydrophilic surface structure and its $W_{a^P,water}$ value is 66.43 mJ/m². Conversely, polyethylene (PE)₃ has a much more hydrophobic surface structure and its $W_{a^P,water}$ value is much lower, 19.69 mJ/m².

It is probable that the functional relationship of $\gamma_S^P = f(k,b)$ is not simple. At the very least, however, γ_S^d , k , b , and $W_{a^P,water}$ are unambiguously calculable and may be related to the biological response evoked upon material surface contact with fluid food. Such relationships would prove useful in attempts to characterize, predict, and ultimately control food particle behavior at interfaces.

Certainly, fluid foods exhibit strong polar character, and the potential for contact surface interactions with constituents of a fluid food will be dependent to some extent on the polar character of the solid surface. Use of the parameter k alone would be unsatisfactory as it provides no insight with respect to differences in nonpolar materials. Rather, construction of a composite surface

energy related to γ_s^d , k , and b appears to be one logical application to these methods. Kirtley and McGuire (1989) evaluated a composite surface energy for a variety of materials and related it to the extent of β -lactoglobulin adhesion. The published manuscript is in Appendix I.

Bacterial Spore Adhesion Study

The influence of contact surface properties on the adhesion of bacterial cells has been reported in several studies. Increased bacterial adhesion has been correlated with increasing contact surface water contact angle (Fletcher and Loeb, 1979; Hogt et al., 1985) and decreasing surface free energy (Absolom et al., 1983; van Pelt et al., 1985). However, similar detailed studies on the adhesion of bacterial spores is lacking.

According to Table 5 and Figure 10, the ^{14}C -labelled **B. subtilis** (ATCC 6633) spores adhered much more to the hydrophobic surfaces than to the hydrophilic surfaces. The most hydrophilic surface, glass (GLASS)₃, registered only 167 CPM/coupon whereas PE-1, a very hydrophobic surface, registered 1694 CPM/coupon. The **B. subtilis** spores have a relatively hydrophobic character. This characteristic did not seem to influence the adhesion to relatively non-hydrophilic surfaces like glass (GLASS)₃ and nylon (NY-2).

Possibly a reduction in spore adhesion could be achieved by altering either the spore or contact surface properties. It is suggested that a reduction in surface hydrophobicity might significantly reduce the number of adhered spores. A reduction in surface hydrophobicity resulting from the action of chemical or physical agents such as cleaning or sanitizing chemicals, might aid in the removal of attached spores. Hubbell, et al. (1991) found that using

TABLE 5

Surface Properties of Materials used in Bacterial Spore Adhesion Assay

Material	$W_{a^p,water}$ (mJ/m ²)	Counts/min/coupon
FEP	0.00	1197
PE-1	0.00	1694
Viton	0.00	318
(PP) ₂	3.08	1646
PTFE	4.54	1508
PE-2	5.65	1480
NY-1	32.65	682
EVOH	35.95	660
(PETG) ₂	36.03	700
NY-2	37.03	622
(SS) ₂	56.90	723
Glass ₃	69.28	167

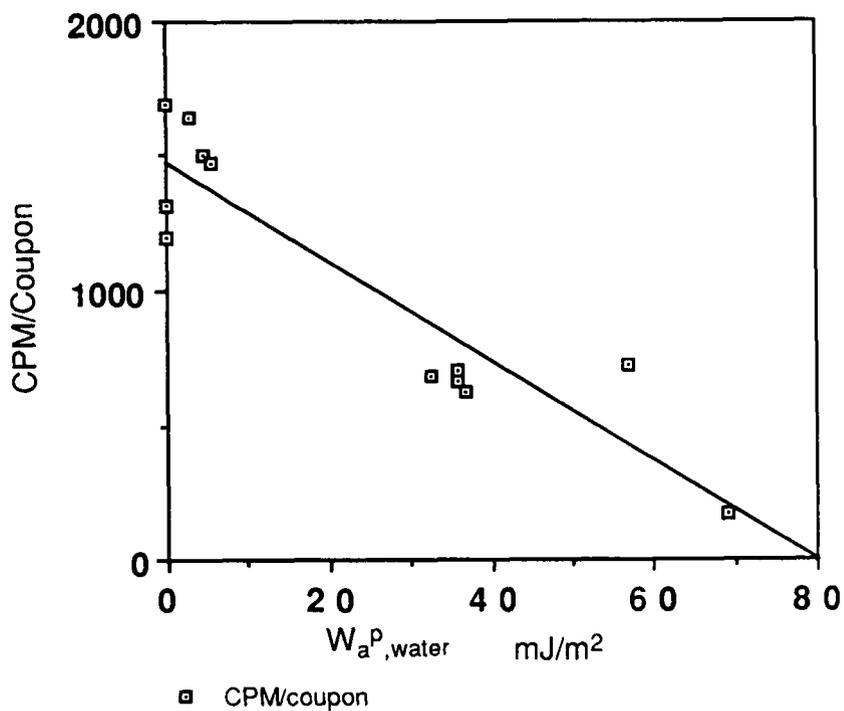


FIGURE 10:
Relationship achieved between the polar component of the work of adhesion and the number of bacterial spores adhered to test materials.

polyethylene/glycol (PEO/PEG) as a coating for polyethylene terephthalate (PET) substrates reduced protein adsorption and bacterial adhesion to the surfaces. However, further research is needed to determine the effects of hydrophobic interactions on the strength of adhesion.

CONCLUSIONS

1. The surface energetic parameters k and $W_{a^p, \text{water}}$ evaluated by contact angle methods can provide a measure of surface hydrophobicity.
2. Overall, $W_{a^p, \text{water}}$ for a given material qualitatively agrees with its surface chemical structure; surfaces characterized by a high value of $W_{a^p, \text{water}}$ are more hydrophilic whereas, surfaces characterized by a low value of $W_{a^p, \text{water}}$ are more hydrophobic in nature.
3. Test material hydrophobicity was observed to influence adhesion of Bacillus subtilis ATCC 6633 spores. Adhesion increases with increasing substrata hydrophobicity.

RECOMMENDATIONS

To improve and further the experiments presented in this paper, there are a number of suggestions I would propose. Two widely used methods for the evaluation of solid surface energies, one empirical and the other semi-quantitative, have been suggested to be inadequate. The modified sessile drop technique described here makes valid the assumptions of the Young and Dupre equations, and is simpler than receding angle methods. Quantitative analysis of results suggests that the identity of the proportionality constant k be explored, particularly with regard to its uniqueness for a given surface and its relationship to γ_{SP} . Possibly a study to determine the effect of ionic strength, pH, and/or temperature effects on the parameter k would be helpful. This should lead to a means for rapid, unambiguous surface characterization with a sound theoretical basis, and aid the development and use of models which predict contact surface influences on both food particle adhesion to surfaces and their removal.

The adhesion of bacterial spores to packaging materials and processing equipment may lead to product contamination and spoilage. A reduction in the amount of bacterial contamination might be achieved by the selection of relatively nonhydrophobic materials or by modification of the material surface resulting in a decrease in hydrophobicity. Future research is needed to determine if a reduction of bacterial spore hydrophobicity through modification of the spore surface by chemical or physical agents, such as may occur with sanitation treatments, could aid in the removal of attached spores.

Specifically, in the bacterial adhesion study, I would suggest the use of another Bacillus strain which has a much lower hydrophobic nature so that a

comparison could be made between the amount of spores adhering to certain test materials. Thus, a more accurate conclusion could be made about the cause of increased spore adhesion: i.e., is increased spore adhesion caused by hydrophobic spores, hydrophobic test materials, or some combination of the two. Along the same lines, one could try to reduce the hydrophobicity of bacterial spores in an attempt to determine any possible reduction in adhesion.

When performing contact angle measurements on test materials it is important to use materials that are of similar specifications to those used in the food industry. If the material characteristics are dissimilar to those used in the industry, the conclusions reached will be less applicable to specific food industry problems and solutions.

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APPENDICES

APPENDIX I**On Differences in Surface Constitution of Dairy Product Contact Materials****SIDNEY A. KIRTLEY**

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key words: surface energy, surface characterization, adsorption, adhesion,
packaging, contact material

ABSTRACT

Dairy products are processed and packaged in contact with materials which exhibit markedly dissimilar surface properties. Pertinent surface properties of several dairy contact materials were quantified, and the relative tendency of each material to adsorb β -lactoglobulin was observed. The presence of a minimum in a plot of mass of β -lactoglobulin adsorbed vs. a property related to contact surface energy is discussed. Knowledge of the selection of contact materials best suited for particular processing or packaging applications, and may provide direction for control of deleterious adhesive events common to dairy manufacturing.

INTRODUCTION

Film accumulation and microbial colonization in milk storage tanks, fouling of heat exchangers, and spore adhesion on packaging surfaces are several examples of surface phenomena of critical importance to the dairy industry. Apparently, these sanitation problems are initiated by fundamentally similar events. Control of these problems may more readily develop if more attention was focused at the dairy product/contact surface interface.

Bacterial attachment to contact surfaces is associated with rather well-defined problems (9). For example, adhesion of microorganisms is a major feature of biofouling, and serves as a potential source of contamination. Moreover, bacterial attachment to food contact surfaces may lead to transmission of disease or economic losses due to food spoilage. Bacterial and fungal spores are the targets of treatments used to sanitize or commercially sterilize packaging materials and other contact surfaces critical for aseptically or otherwise thermally processed dairy products. The significance of bacterial spores relative to fungi will increase as aseptic processes for dairy-based products are developed and become more common in the marketplace. However, bacterial spores may be more difficult to kill than fungal spores; the consequences of error include spoilage as well as food-borne illnesses (15).

The simple apparent answer to increasing the effectiveness and rate of commercial sterilization is to increase the concentration of chemical sanitizing agents. However, this is probably unacceptable since increased concentrations of sanitizers may pose health risks to employees, possibly result in unacceptable chemical residuals in the product, and increase production costs. Additionally, higher chemical concentrations do not necessarily result in greater

sanitation efficiency. It has been suggested that chemical sanitizing agents act by modifying the exterior spore coat, consequently modifying its adhesive characteristics (6). Consequently, an alternative approach to optimal sanitation strategies is to focus attention on contact surface properties and the interactions between spores (and other dairy fluid constituents) and the surfaces with which they make contact.

Limited information is available in the literature concerning the adhesion of bacterial spores to polymers and packaging films used for fluid milk and cream products. However, much evidence has been generated and accumulated in fields outside of dairy research which suggest that spore and microbial adhesion do not occur unless a macromolecular conditioning film is pre-adsorbed onto the contact surface. Additionally, all subsequent adsorptive events have been observed to be highly dependent upon the conformational state of this pre-adsorbed film, which in turn is highly dependent upon properties of the bare contact surface.

It should be noted that although some microbes adhere via polymeric exudates, it is likely that these exudates still must adhere to the pre-adsorbed film (2-5, 17). In fact, adhesion of some microbes is enhanced by three orders of magnitude when allowed to adsorb on surfaces treated with pre-adsorbed serum protein relative to surfaces treated with pre-adsorbed exudate material derived from the microbe itself (5, 17). Baier (3) has suggested that the predominantly glycoproteinaceous chains of the exudate bind to similar chains of non-microbial origin which stem from the conditioning film present on the contact surface. Once adsorption of spores and microbes occurs, even though their initial concentration in the product may be extremely low, it has been argued that they thrive and multiply due to the exceptionally nutritious nature of

the surface environment, where the concentrations of molecules (nutrients) needed for growth are much greater than in the bulk fluid (4, 5).

The conformation of adsorbed protein may continuously change, the extent of which depends upon properties of the contact surface. Adsorbed protein may establish an equilibrium with the bulk fluid, resulting in a passive surface unable to harbor whole cells and spores, or adsorbed protein may, depending on properties of the bare surface, continue to denature to such an extent that great numbers of sites are made available for further denaturation, accumulation, biofilm development and colonization.

An understanding of the initial behavior of milk constituents at their contact surfaces may lead to a means for prediction and control of unwanted particle-surface interactions. Additionally, knowledge of the interfacial chemistry would be useful for selecting appropriate surface sanitizing systems, and would increase options available to dairy processors by providing the information on which to base decisions for alternative packaging materials and sanitation strategies. As not only new products, but also new packaging materials are introduced, so is the associated problem related to choosing which material is best suited for a particular product.

To effectively characterize the influence of contact surface properties on the adhesion of milk components, a reliable means of calculating such surface properties is required. For decades, clinical researchers have attempted to relate surface properties of biomaterials to the response they evoke upon contact with blood. Surface characterization methodology from such efforts has recently been modified and adapted to fluid food processing and packaging applications (11, 13).

It is the purpose of this paper to demonstrate how measurable contact

surface properties can be used to quantify subtle differences in materials targeted for milk product contact, and to suggest how knowledge of these differences might provide direction for control of deleterious adhesive events common to dairy processing.

MATERIALS AND METHODS

Aqueous solutions of methanol and ethanol (E.M. Science, Cherry Hill, N.J.) of concentrations ranging from 0 - 100% were prepared as diagnostic liquids (i.e., test liquids used to form drops on each test material for contact angle analysis) and had their surface tensions measured by the ring method (18). Polymeric materials used included high density (HD) polyethylene, nylon, polypropylene, and polytetrafluorethylene (PTFE) (Universal Plastics Co., Portland, OR). Also, a commercial polyethylene (Northern Engineering and Plastics Corp., Portland, OR), targeted for dairy product contact, along with hard Pyrex[®] glass and clean, unpolished #304 stainless steel (SS) (Alaskan Copper and Brass Co., Portland, OR) were used.

The dispersive and polar components of liquid surface tension, the dispersive component of solid surface tension, and contact angle data were evaluated by methods published earlier (13).

β -lactoglobulin (3X crystallized and lyophilized; Sigma Chemical Co., St. Louis, MO) was dissolved into a 0.01 M phosphate (NaH_2PO_4) buffer solution and used at a concentration of 100 mg/l. Buffered solutions were brought to a pH of 7.0 with sodium hydroxide (E.M. Science, Cherry Hill, N.J.) prior to introduction of protein. All materials were contacted with β -lactoglobulin solutions. PTFE, polypropylene, polyethylene, and nylon were used in the form of uniform disks. Glass was used in the form of nonporous beads, and HD polyethylene was used in the form of pellets, as this material was originally targeted for injection molding. The #304 stainless steel was used in the form of cylindrical pellets.

Approximately 50 cm² of each material was cleaned and placed into individual 250 ml flasks. Aliquots (100 ml) of the buffered β -lactoglobulin solutions were subsequently introduced into each flask; the flasks were then placed into a constant temperature shaker bath (Yamato Scientific Co., LTD, Tokyo, Japan) which operated at 120 rpm. Contact was maintained between the solid surfaces and β -lactoglobulin for six hours at 30° C. During each test run, a control flask containing 100 ml of β -lactoglobulin solution in the absence of a test surface was also placed into the shaker bath. Final solution concentrations were determined with a uv spectrophotometer (Beckman Co., Fullerton, CA, Model DU[®]-62). The amount of protein adsorbed on each of the test surfaces was subsequently calculated by simple mass balance.

RESULTS AND DISCUSSION

Evaluation of Surface Properties

Measurement of food contact surface energetics by analysis of contact angle data has been recently reviewed (11, 13), and the need for evaluation of the dispersive and polar components of the work of adhesion between a diagnostic liquid and the solid surface was emphasized. The work of adhesion, W_a (mJ/m²), is the free energy change per unit area associated with separation of an interface.

Liquid surface tension may be expressed as

$$\gamma_L = \gamma_L^p + \gamma_L^d \quad (1)$$

and solid surface energy as

$$\gamma_S = \gamma_S^p + \gamma_S^d \quad (2)$$

where superscripts p and d refer to polar and dispersive (nonpolar) force components. Evaluation of the polar and dispersive components of liquid surface tension is straightforward, and such values have been evaluated for a variety of liquids (7, 8, 10). Similarly, the dispersive component of solid surface tension is measurable with some certainty (7, 8, 10). Clearly, ability to calculate γ_S^p would enable evaluation of the solid contact surface energy with use of equation 2.

Fowkes (8) emphasized that W_a may also be divided into dispersive and polar components, i.e.,

$$W_a = W_a^p + W_a^d \quad (3)$$

where measurement of the dispersive component of W_a was shown to be straightforward. The polar component of W_a is calculable as developed

previously (13):

$$\gamma_L(1 + \cos \theta) = W_a = W_a^p + W_a^d = 2(\gamma_L^d \gamma_S^d)^{0.5} + W_a^p \quad (4)$$

or, rearranging

$$W_a^p = \gamma_L(1 + \cos \theta) - 2(\gamma_L^d \gamma_S^d)^{0.5} \quad (5)$$

where γ_L , θ , γ_L^d , γ_S^d are easily measured; θ is the value of the contact angle.

Certainly, the influence of polar interactions would be present in many dairy fluid-contact surface interactions. The polar contribution to the work of adhesion depends upon the polar character of both the solid and the liquid which are in contact, i.e.,

$$W_a^p = f(\gamma_L^p, \gamma_S^p) \quad (6)$$

Elucidation of the relationship between W_a^p and γ_L^p has received much interest since according to equation 6, it is a result of the influence of γ_S^p alone.

Figure 1 illustrates the approach used here to evaluate the polar surface properties of four of the materials used in this study: Glass, nylon, polypropylene, and polyethylene. Similar plots have been constructed previously for all materials used in this study in addition to several other food contact materials. The magnitude of the slope of each line agrees with the expected polar contribution of the solid surface it represents. Each line, of course, is characterized by its slope, k , and intercept, b ; the physical significance of these parameters was detailed earlier (13).

It should be noted that direct application of the preceding development to common engineering materials may yield misleading results, as these surfaces exhibit energetic heterogeneities and other surface irregularities. Nevertheless, for the purpose of identifying differences in performance among

contact materials which exhibit smooth, clean surfaces, this development is useful. Its support, based on shortcomings of several other methods used to evaluate properties related to surface energy, was provided previously (13).

Additional comment is also warranted with respect to relating surface properties evaluated at or near normal ambient temperatures to phenomena which are certainly experienced at the high temperatures associated with processing. Although solid surface energy is expected to decrease with increasing temperature, due to the immobility associated with a solid surface relative to a liquid surface, this temperature dependence is not expected to be great. Moreover, with respect to fouling of heat exchange surfaces by milk, it has been shown that relative responses evoked by different materials are not only conserved, but also become more clearly defined at elevated temperatures (12). A study dealing with the influence of temperature on solid surface energetic parameters has recently been completed in our laboratory and will contribute to the subject of future reports.

W_a^p is a function of both γ_L^p and γ_S^p , and the following equation is therefore valid:

$$\gamma_S^p = f(k, b) \quad (7)$$

Although it is probable that the functional relationship of equation 7 is not simple, construction of a composite surface energy related to k , b , and γ_S^d has recently been developed with justification (13):

$$\gamma_S^* = (kW_{a^p, \text{water}} + \gamma_S^d - b) \quad (8)$$

where γ_S^* is the composite surface energy (mJ/m^2) of a contact material.

$W_{a^p, \text{water}}$ refers to the polar component of the work required per unit area to

separate water from the interface; it provides an index of the hydrophobicity or hydrophilicity of the surface. In equation 8, γ_S^p is represented by the expression

$$\gamma_S^p = k W_{a^p, \text{water}} - b \quad (9)$$

Values of $W_{a^p, \text{water}}$, γ_S^p , γ_S^d , and the composite surface energy were calculated for each material and are enumerated in Table 1.

Influence of Surface Properties on Adhesion of β -lactoglobulin

We are currently studying the relationship between γ_S^* and both the post-adsorptive and equilibrium behavior of β -lactoglobulin. Figure 2, constructed from a set of studies involving β -lactoglobulin contact with seven different materials, is an example of the typical nonlinear relationship observed when biological adhesion is plotted as a function of surface energy. That is, an intermediate range of surface energies seems to correlate best with minimal biological adhesion. Materials characterized by values of surface energy higher or lower than the minimum evoke a greater interaction with fluid food, with the interaction increasing at a reduced rate as the value of surface energy is further increased.

The part of the curve immediately prior to and following the minimum has received much attention. A second order polynomial seems to fit the data in this portion of the curve rather well, yielding an unambiguous minimum (in this case, equal to 45.7 mJ/m²). At least quantitatively, the observations presented in Figure 2 are strikingly similar to those observed by Baier (4) with respect to the relationship between cell adhesion and γ_C (the critical surface tension: a parameter related to

γ_S), McGuire and Swartzel (11, 12) with respect to the relationship between dairy protein adhesion and γ_S evaluated by Kaelble's method (10), and Absolom et al. (1) with respect to the relationship between endothelial cell adhesion and γ_S evaluated by an equation of state approach (16).

The presence of a value or range of values of surface energy which characterize a passive surface for milk contact contributed to a recently developed predictive model for food particle interactions with contact surfaces (14). The model is particularly useful for comparing relative adhesive properties of different materials targeted for dairy fluid contact. As might be expected, the model suggests that if the value of γ_S for a given material is sufficiently close to the value of γ_S characterizing the minimum ($\gamma_{S,min}$), it should subsequently evoke little interaction with the fluid. Figure 2 provides further evidence for a potential role of $|\gamma_S - \gamma_{S,min}|$ as an indicator of the available driving force for permanent adhesion.

CONCLUSIONS

Depending upon solid surface energetics, past research suggests that protein adsorption may occur and establish a dynamic equilibrium, in which bulk and surface protein exchange is maintained and further adsorption does not occur. Alternatively, effected by simple change in contact material, protein adsorption may be followed by denaturation to an irreversibly adsorbed species leading to further desorption and biofilm development. Moreover, microbial and spore adhesion are suggested to occur only when a macromolecular conditioning film is pre-adsorbed onto the contact surface. All subsequent adsorptive events have been observed to be dependent upon the conformational state of this pre-adsorbed film, which in turn is dependent upon properties of the original contact surface. Apparently, a quantitative understanding of contact material surface properties and their relationship to the initial macromolecular adsorptive events associated with dairy fluid contact should provide direction for better control of biofilm formation.

Dairy products are processed and packaged in contact with materials which exhibit markedly dissimilar surface properties. Pertinent contact surface properties are quantifiable, as is the specific adsorptive behavior of the dairy product itself. The presence of a property which characterizes non-interacting contact surfaces may provide some important direction in selecting contact materials which are best suited for particular processing or packaging applications. Methods discussed here may lead to more efficient dairy processing practice, particularly with respect to areas in which surface chemical aspects have not been appropriately addressed.

ACKNOWLEDGEMENT

This work is supported by the Western Dairy Foods Research Center, Logan, UT: Oregon State, Utah State, and Brigham Young Universities cooperating.

Composite Surface Energies of Contact Materials

Material	γ_s^d	$W_{a^D, \text{water}}$ (mJ/m ²)	γ_s^D	γ_s^*
PTFE	22.58	0	0	22.6
Polyethylene	32.11	19.69	12.3	47.9
HD Polyeth.	31.83	25.64	22.2	60.4
Polypropylene	30.69	29.45	29.7	68.5
#304 ss	32.44	34.08	38.3	78.4
Nylon	33.25	38.82	47.5	87.6
Glass	27.54	66.43	127	159

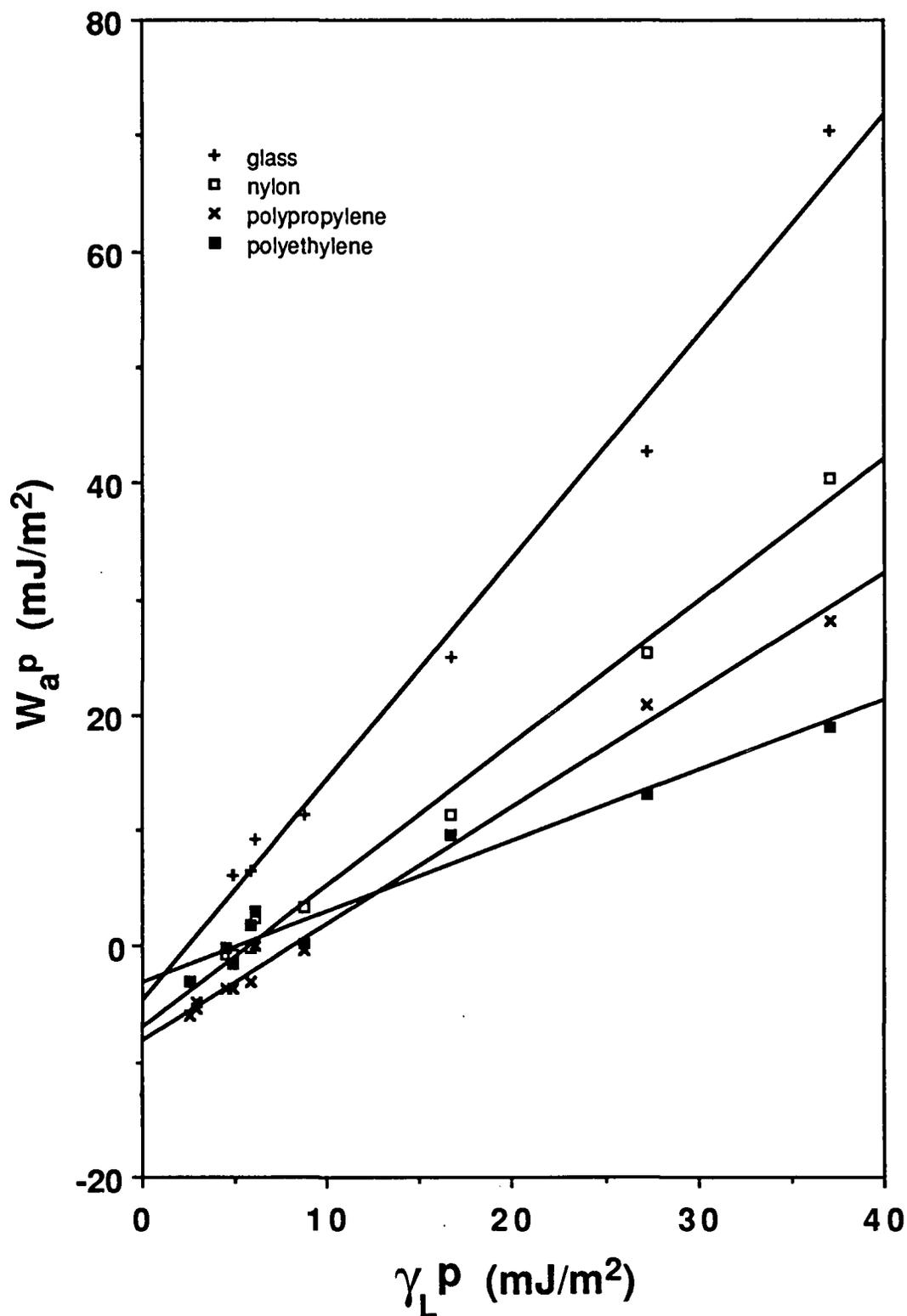


FIGURE 1.1: Evaluation of contact material properties related to the polar character of their surfaces.

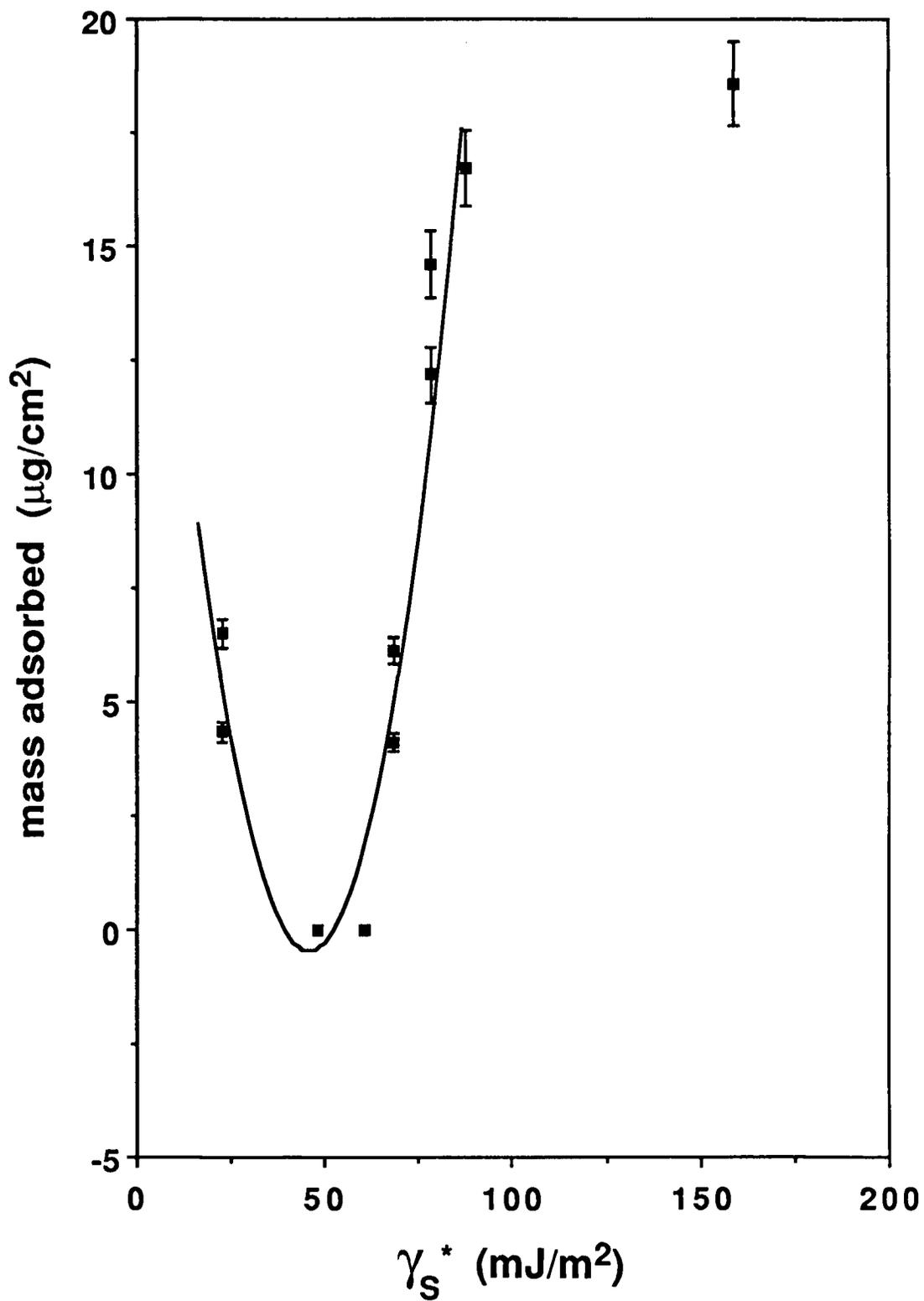


FIGURE 21 :Minimum absorption related to composite surface energy.

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APPENDIX II

Raw Data Information

All raw data and written material is available from Dr. Joseph McGuire, Department of Bioresource Engineering, Gilmore Hall 116, Oregon State University, Corvallis, Oregon, 97331-3906 (phone: 503/737-6306).