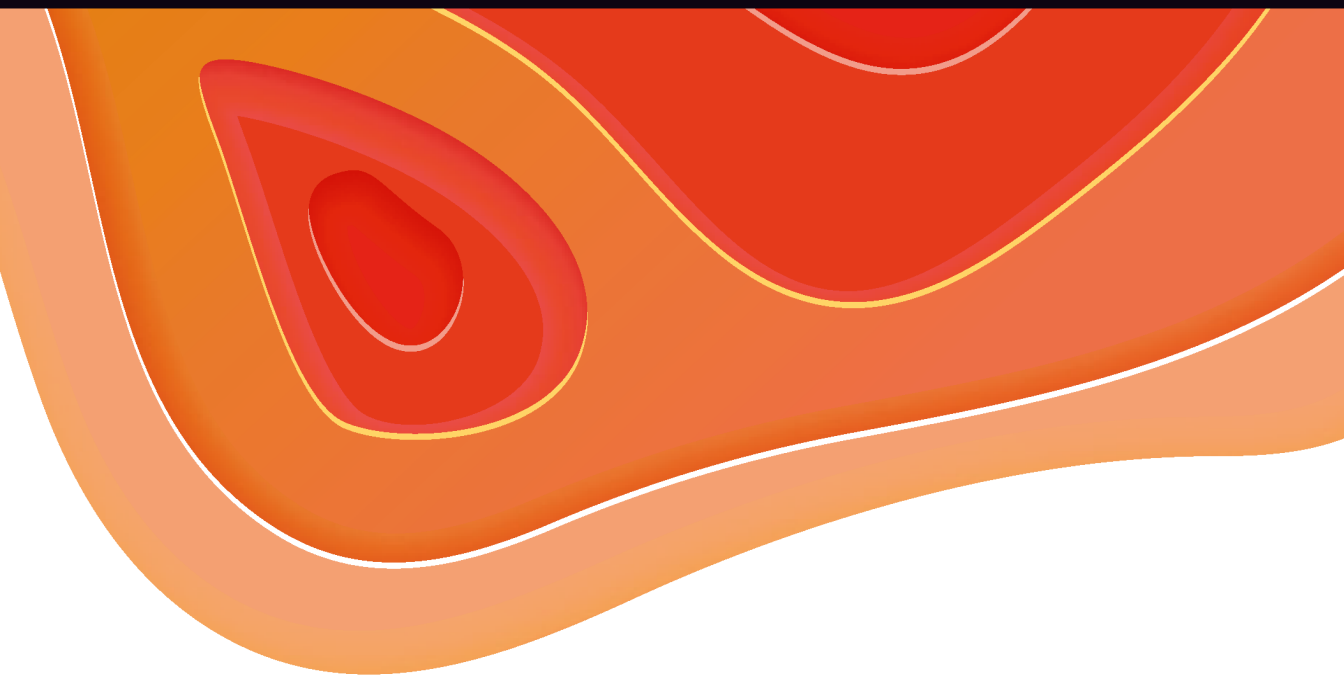
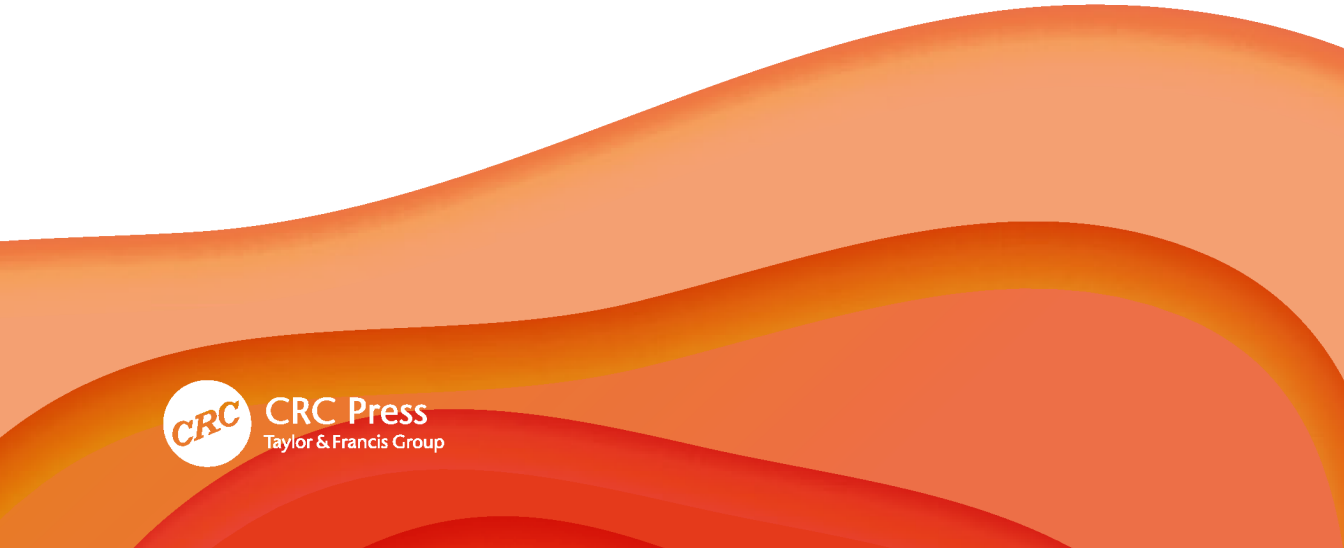
Wetting: Theory and Experiments, Two-Volume Set



WETTING EXPERIMENTS

ELI RUCKENSTEIN
GERSH BERIM



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Wetting Experiments

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Eli Ruckenstein
Gersh Berim

Volumes in the Set:

Wetting Theory (ISBN: 9781138393301)

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Wetting Experiments

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Contents

Preface

This book contains papers published by Professor Ruckenstein and his coworkers on the theoretical and experimental investigation of wetting of solid surfaces. It is one of two standalone books that comprise *Wetting: Theory and Experiments, Two-Volume Set*, which contains six chapters, each of which is preceded by a short introduction. Each volume making up the set is available to be read and understood on its own. Reading both volumes together provides the reader with a comprehensive view of the subject. The papers of the chapters are selected according to the specific features being considered and they are arranged in logical rather than chronological order. The main attention is given to the wetting on the nanoscale (nanodrops on solid surfaces, liquid in the nanoslit) considered on the basis of microscopic density functional theory, and to dynamics of fluid on the solid surface considered on the basis of hydrodynamic equations. Along with this, experimental studies of wetting related to various applications are presented. A description of the contents of each volume within the Set follows.

Wetting Theory **(ISBN: 9781138393301):**

In Chapter 1, various microscopic processes (static and dynamic) in a liquid in contact with a solid are considered. They are the flow of liquid along horizontal and inclined surfaces, slipping of the contact line of a liquid on a solid, etc.

Chapter 2 is about the symmetry breaking of fluid density distribution in nanoslit between parallel solid walls. One component classical and quantum fluids and binary mixtures are considered and conditions for symmetry breaking to occur are examined.

In Chapter 3, the microscopic approach is applied to the treatment of macroscopic drops on smooth or rough, planar or curved, solid surfaces. It is based on fluid–fluid and fluid–solid interaction potentials and considers the drop equilibrium state as that having the minimum of total potential energy. The concept of microscopic contact angle is introduced and both macroscopic (classical) contact and microscopic angles are calculated.

In the next chapter, Chapter 4, a liquid drop on a smooth or rough planar solid surface is examined on the basis of a microscopic nonlocal density functional theory in canonical ensemble. The variety of characteristic features are examined including nonuniform fluid density distribution inside the drop, drop profile, microscopic contact angle, sticking force, etc. The results are compared with predictions of classical theories for macroscopic drops and similarities and differences between them are analyzed.

In the last chapter, Chapter 5, the theory of the rupture of liquid and solid films is developed, first in the linear approximation, and then extended to the case of perturbations of finite amplitude. The theory provides, in particular, the conditions for the instability, the dominant wavelength of the disturbances, and the time of rupture of the films. Along with this, the rupture of liquid films supported on a solid surface is examined on the basis of a thermodynamic approach which considers the change of the free energy of the film after the formation of a hole in it. The theory is applied to the practically important problem of tear film stability and rupture.

Wetting Experiments **(ISBN: 9781138393332):**

This volume focuses on experimental studies of wetting that are related to biological problems, polymers, and catalysts. The biology-related studies are devoted to the problem of selecting synthetic materials for use in biological media. The polymers are examined to estimate experimentally various surface characteristics such as the ability of polymeric solids to alter their surface structures between different environments in order to minimize their interfacial free energy. The investigation of catalysts concentrates on their physical and chemical changes, formed of small crystallites of Pt, Pd, Ni, Co, Fe, or Ag supported on alumina.

Authors

Eli Ruckenstein, National Academy of Engineering and National Academy of Art and Science member, National Medal of Science winner, SUNY Distinguished Professor of CBE Eli Ruckenstein's copious and pioneering contributions to chemical engineering have been rewarded with numerous distinctions, including the 2004 National Academy of Engineering Founders Award, the 2002 American Institute of Chemical Engineers (AIChE) Founder's Award, AIChE's 1988 Walker Award, the 1977 AIChE's Alpha Chi Sigma Award, the 1986 American Chemical Society's (ACS) Kendall Award, the 1994 ACS Langmuir Lecture Award, the 1996 ACS E.V. Murphree Award, the 1985 the Alexander von Humboldt Foundation's Senior Humboldt Award, and the 1985 NSF Creativity Award. Ruckenstein joined the School's faculty in 1973, and was the first full-time SUNY system professor elected to the NAE. A leading influential chemical engineer, he has made numerous contributions to modernizing research and development in key areas of chemical engineering. He is a fellow of AIChE which with the occasion of its 100th anniversary designated him as one of 50 eminent chemical engineers of the Foundation age. Dr. Ruckenstein published about 900 papers in various areas of Chemical and Biological Engineering.

Gersh Berim earned a Ph.D. degree in Physics in 1978 from Kazan State University, Russia. Till 2001, his research was focused on nonequilibrium properties of low dimensional spin system. In 2001 he joined the group of Professor Eli Ruckenstein at SUNY at Buffalo where have been studying various topics of Chemical Physics especially related to nanosystem. He has authored or co-authored more than 70 papers.

1 Biology Related Experiments

Eli Ruckenstein and Gersh Berim

INTRODUCTION TO CHAPTER 1

Chapter 1 consists of four sections and contains biology-related experimental studies of wetting. These studies are devoted to the problem of selecting synthetic materials for use in biological media. In Sec. 1.1, the suitable methods to deposit thin films on substrates of interest (such as the apatitic tooth surface or stainless-steel heat exchange surfaces) are developed. In Sec. 1.2, a surface energetic criterion of biocompatibility of foreign surfaces is suggested, which is based on an analysis of the surface interactions between a typical biological fluid (i.e. blood) and synthetic surfaces. In the second part of this investigation (Sec. 1.3), it is shown that the experimental approach involving the radio frequency sputter deposition of thin solid films of tightly adhering polymeric compounds on materials with the desired bulk characteristics is a promising method of tailoring the surface properties of many types of synthetic materials for use in biological environments. In the final part of this investigation (Sec. 1.4), the possibility of affecting a drastic reduction in the solid-water interfacial free energy of the sputtered polymer surfaces by physical and/or chemical modification of their surfaces and thereby improving their biocompatibility is illustrated.

1.1 A Nondestructive Approach to Characterize Deposits on Various Surfaces*

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1. INTRODUCTION

Surface interactions play an important role in several situations such as remineralization of teeth (1), thrombus formation (2–4), metastasis (5), fouling of heat transfer surfaces by food fluids (6), and the deposition of Brownian particles or cells on collector surfaces (7–9). In all these cases, deposit formation on various types of substrates is involved.

Multiple internal reflection spectroscopy (10) is a very sensitive approach to nondestructively characterize either *in vivo* or *in vitro* films deposited on artificial substrates. In the application of this technique, the choice of a suitable internal reflection element is of great importance. The internal reflection element must not only simulate the surface of interest, but must also be transparent to the appropriate radiation (infrared, ultraviolet, or visible) over a wide range of frequencies. Frequently, however, it is found that many surfaces of interest (such as the apatitic tooth surface or stainless steel heat exchange surfaces) are unsuitable as internal reflection elements. To overcome this problem, germanium internal reflection elements have been widely used to characterize the films formed in various environments. Recently, oral *in vivo* films were also characterized on germanium internal reflection elements of varying surface energies (11). Though germanium is an ideal substrate for studies of this kind, it still does not accurately mirror the properties of the real surfaces of interest, such as the tooth surface in the oral environment.

* *Journal of Colloid and Interface Science.* Vol. 96. No. I, p. 245, November 1983. Republished with permission.

In this paper, we suggest an approach by which it is possible to study nondestructively, the deposits formed on real surfaces of interest, by using multiple internal reflection spectroscopy. This involves the deposition of thin solid films of the substrata of interest on suitable internal reflection elements. For illustrative purposes, we provide details concerning the preparation and characterization of a hydroxyapatite film on a germanium internal reflection element and the use of multiple internal reflection infrared spectroscopy to detect the molecular structure of salivary components adsorbed on the apatite surface.

2. DEPOSITION OF HYDROXYAPATITE ON GERMANIUM SURFACES

Hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$) forms the major constituent (~95%) of the outermost part of the human tooth enamel (surface enamel). The actual tooth contains 1% of organic material which also play an important role in the salivary adsorption processes. However, here we illustrate our procedure with pure hydroxyapatite. To identify the adsorbed species on hydroxyapatite coated germanium internal reflection elements by multiple internal reflection infrared spectroscopy, the apatite coating must be considerably thinner than the depth of penetration of the infrared beam. The depth of penetration (d_p) of the beam can be calculated from (10)

$$d_p = \frac{\lambda_1}{2\pi\left(\sin^2\theta - n_{21}^2\right)^{1/2}},$$

where λ_1 is the wavelength of the radiation in the denser medium, θ is the angle of incidence, and n_{21} ($=n_2/n_1$) is the ratio of the refractive indices of the rarer and denser media. Germanium is transparent to infrared radiation in the wavelength range of 2 to 12 μm. At the lowest wavelength (2 μm) the value of d_p for germanium surfaces coated with hydroxyapatite is of the order of 10^3 Å, for $\theta = 45°$. Therefore, to detect the adsorption of salivary components on hydroxyapatite, the apatite coating must be at least less than 1000 Å thick.

The deposition of multicomponent compounds such as hydroxyapatite, poses one major problem, namely, that of preserving the chemical composition of the bulk material when it is coated as a thin solid film on a substrate. During vacuum evaporation, these materials tend to fractionate, giving rise to chemically dissimilar films. To overcome these limitations, we tried sputtering, a technique which is widely recommended for the deposition of multicomponent materials. Sputtering also often gives rise to films which are more tightly adherent than those obtained by evaporation. In this technique, energetic particles bombard the surface of any material and eject surface atoms from it. Under sufficiently high vacuum, the sputtered atoms travel until they strike another surface and deposit there. For conducting materials, dc sputtering can be used, while for insulators, such as hydroxyapatite, radiofrequency sputtering is necessary.

To sputter the powder form of hydroxyapatite, we used a sputter-up configuration, in which, the target (hydroxyapatite, Bio-Gel HTP, Bio-Rad Labs, Richmond, Calif.) was pressed well on an aluminum plate and the plate was placed below the substrate (germanium internal reflection element) in the sputtering chamber, as shown in Fig. 1. Argon was used as the sputtering gas. Typical conditions adopted for sputtering were (a) rf power of 500 W, (b) pressure of 10 to 15 μm in the chamber, (c) target to substrate spacing of 2.5 cm, and (d) sputtering time of 2 hr.

The above conditions led to the reproducible deposition of tightly adherent films of this compound.

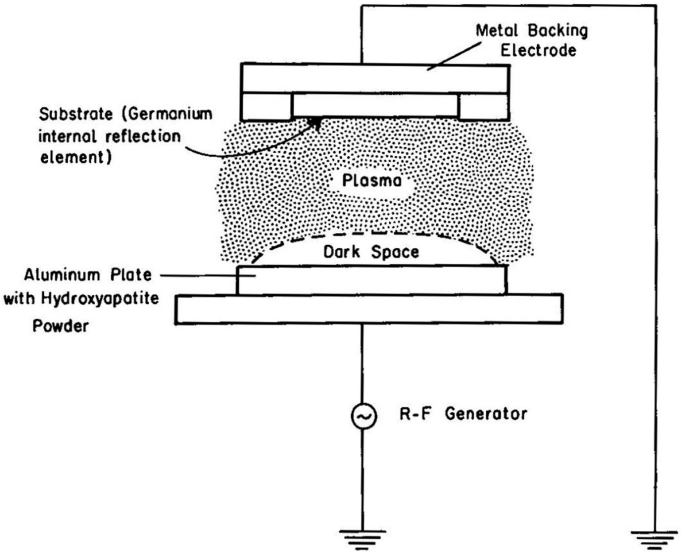

FIG. 1. Essential features of the radiofrequency sputtering setup.

3. CHARACTERIZATION OF HYDROXYAPATITE FILMS ON GERMANIUM SURFACES

The sputtered films of hydroxyapatite were characterized for their molecular structure, calcium to phosphorus ratio, surface texture and thickness, by multiple internal reflection infrared spectroscopy, energy dispersive X-ray analysis, scanning electron microscopy and ellipsometry, respectively. The infrared spectrum in Fig. 2 reveals the presence of the phosphate group (characteristic absorption band at 1070 cm^{-1}) in the sputtered film. A comparison of this

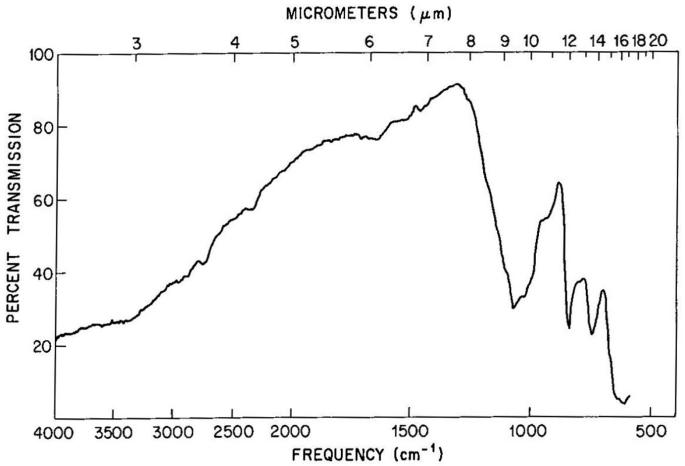

FIG. 2. Multiple internal reflection infrared spectrum of a film of hydroxyapatite, deposited on a Ge internal reflection element, under the following conditions: (a) rf power of 500 W, (b) pressure of 10 to 15 μm in the chamber, (c) target to substrate spacing of 2.5 cm, and (d) sputtering time of 2 hr.

TABLE I
Results of Energy Dispersive X-Ray Analysis

Material	(Ca/P) Ratio 1	2	3	4	$(Ca/P)_{avg}$	Remarks
Hydroxyapatite film on germanium	1.977	1.981	1.99	1.999	1.987	Count time was 192 sec for all readings
Hydroxyapatite powder (Bio-Gel HTP, Bio-Rad)	2.006	1.982	2.021	1.979	1.997	Count time was 20 sec for all readings

spectrum with that of pure hydroxyapatite powder placed on a germanium internal reflection element showed that the molecular structure of the solid film was very close to that of the bulk material. The calcium to phosphorus ratios of a thick film formed in a 3.5 hr sputtering run, are listed in Table I, along with the ratios of the bulk powder. It can be seen that the average (Ca/P) ratios of the film formed by sputtering, differed only by 0.5% from that of the bulk powder. This provides satisfactory evidence that the chemical composition of the solid film is very close to that of hydroxyapatite. By scanning electron microscopy, it was found that the films were deposited uniformly over the exposed region of the substrate, as shown in Fig. 3.

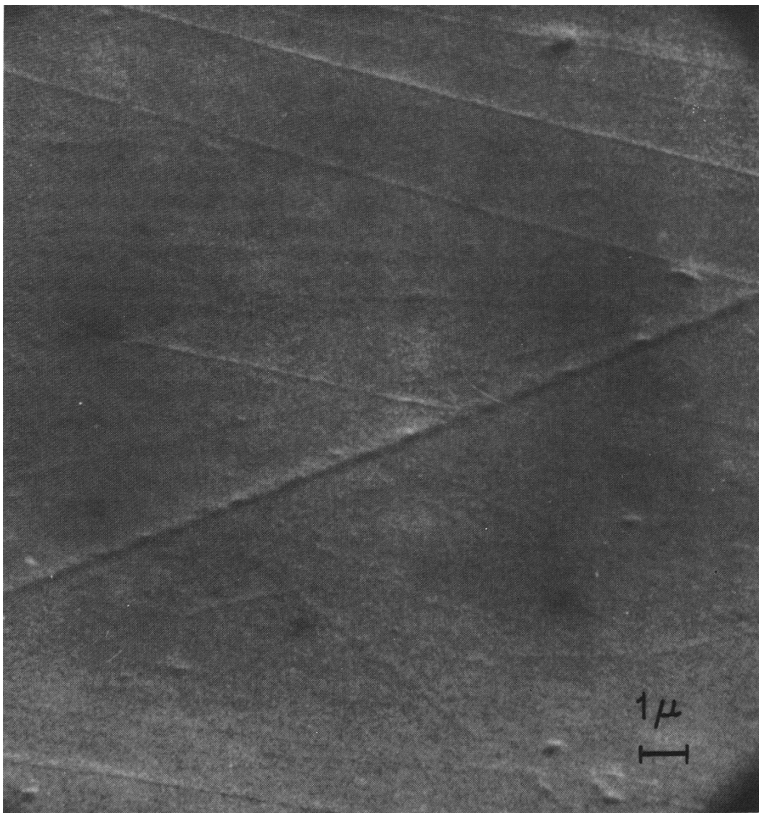

FIG. 3. SEM picture of the hydroxyapatite film of Fig. 2.

Film thicknesses measured by ellipsometry showed them to be considerably less than 1000 Å thick (about 200 Å for films formed in 2 hr sputtering experiments).

4. DISCUSSION

To test the usefulness of the sputter coated germanium internal reflection elements, an experiment was performed, in which, saliva flowed for 15 min between two parallel surfaces of apatite coated germanium internal reflection elements. The flow conditions of saliva resembled those encountered in the oral cavity. The test plates were then rinsed with distilled water for 7.5 min (to remove loosely adhering deposits) and air dried. An infrared spectrum of one of these dried surfaces is shown in Fig. 4, where protein adsorption is indicated (characteristic absorption bands at 3300, 1650, and 1550 cm^{-1}) on the hydroxyapatite surface. This shows the applicability of multiple internal reflection spectroscopy to characterize deposits formed on surfaces which closely resemble the real ones.

This approach, namely, to use appropriate procedures to deposit thin films of the substrata of interest on internal reflection elements and then to characterize the deposits formed on these surfaces by nondestructive techniques, promises to be a very useful method of studying the surface interactions in many environments. Studies on the mechanisms involved in the biofouling of heat exchangers in the dairy industry and marine environment and the adsorption of surfactants on minerals in surfactant enhanced oil recovery, seem particularly well suited to this approach.

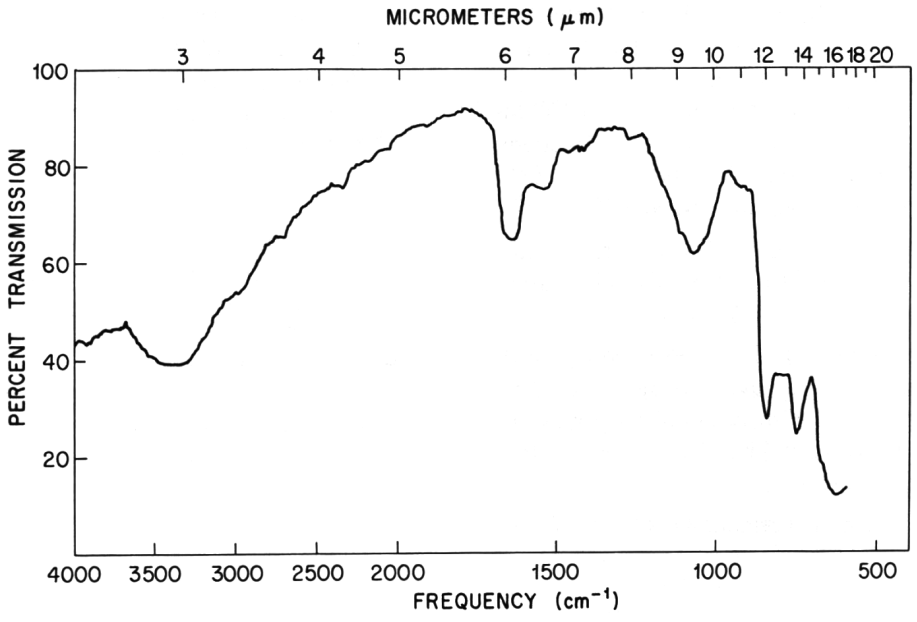

FIG. 4. Multiple internal reflection infrared spectrum of an apatite coated germanium internal reflection element, after it was exposed to saliva flowing at 1.2 ml/min for 15 min, rinsed with distilled water for 7.5 min, and air dried.

ACKNOWLEDGMENT

The authors are indebted to Dr. Cecilia Bengtsson for her help in conducting the saliva experiments, to Mr. Mark Fornalik for his help in the SEM analyses, and to Mr. E. Rastefano for his help with the sputtering equipment.

REFERENCES

1. Tencate, J. M., *in* "Dental Plaque and Surface Interactions in the Oral Cavity" (S. A. Leach, Ed.), p. 273. Proceedings of a workshop on Dental Plaque and Surface Interactions in the Oral Cavity, ICI Ltd, Macclesfield, Cheshire, England, November 7–9, 1979.
2. Marmur, A., and Ruckenstein, E., *in* "Advances in Biomedical Engineering" (D. O. Cooney, Ed.), part p. 341. Dekker, New York, 1980.
3. Gordon, J. L., and Mitner, A. J., *in* "Platelets in Biology and Pathology" (J. L. Gordon, Ed.), p. 1. North-Holland, Amsterdam, 1976.
4. Berger, S., Saltzman, E. W., Merrill, E. W., and Wong, P. S. L., *in* "Platelets: Production, Function, Transfusion and Storage" (M. Baldini and S. Ebbe, Eds.), p. 299. Grune & Stratton, New York, 1974.
5. Weiss, L., *in* "Chemotherapy of Cancer Dissemination and Metastasis" (S. Garattani and G. Franchi, Eds.). Raven Press, New York, 1973.
6. Sandu, C., and Lund, D. B., *in* "Proceedings of the Food, Pharmaceutical, and Bioengineering Division Symposium," 89th National meeting of the American Institute of Chemical Engineers, Portland, Oreg., in press.
7. Ruckenstein, E., and Kalthod, D. G., *in* "Fundamentals and Applications of Surface Phenomena Associated with Fouling and Cleaning in Food Processing," (B. Hallström, D. B. Lund, and Ch. Trägärdh, Eds.), p. 115. Proceedings of an international workshop arranged by the division of Food Engineering, Lund University, Sweden, April 69, 1981.
8. Ruckenstein, E., and Prieve, D. C., *in* "Testing and Characterization of Powders and Fine Particles," (J. K. Beddow and T. Meloy, Eds.), Heydon, London, 1980.
9. Ruckenstein, E., and Prieve, D. C., *J. Chem. Soc. Faraday Trans. 2* **69**, 1522 (1973).
10. Harrick, N. J., "Internal Reflection Spectroscopy." Interscience, New York, 1967.
11. Baier, R. E., and Glantz, P-O., *Acta Odontol. Scand.* **36**, 289 (1978).

1.2 A Surface Energetic Criterion of Blood Compatibility of Foreign Surfaces*

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1. INTRODUCTION

In the selection of biomaterials for use in long-term biomedical applications, two important criteria are involved, namely (i) the blood compatibility of the foreign surface and (ii) suitable mechanical properties for the specific blood contact application. By blood compatibility, it is meant that, when a foreign surface is placed in contact with blood, it should not provoke adverse responses, such as thrombosis, destruction of the cellular components of blood, alteration of plasma proteins, damage to adjacent tissue, and toxic and allergic reactions.

Several materials have been tried to date in the continuing search for a suitable biomaterial and although many of them exhibited some desirable virtues (like a satisfactory degree of antithrombogenicity or good mechanical properties or short-term blood compatibility), none of them has emerged as truly outstanding in terms of fulfilling the rather rigorous twin requirements of long-term blood compatibility as well as good mechanical strength. Some examples of biomaterials which have shown promise for use as blood-contacting devices, but are still far from being biocompatible on a long-term basis, include the following: (a) hydrogels or grafted hydrogels, such as those based on poly (hydroxyethyl methacrylate) and polyacrylamide, (b) LTI (low-temperature isotropic) carbons, (c) silicone–urethane copolymers (such as "Avcothane"), and (d) segmented polyurethanes (such as "Biomer").

A central feature of the search for new and better biomaterials has been the tendency to empirically correlate the performance of materials which have already been tested as blood-contacting devices (in either *in vivo, ex vivo,* or *in vitro* tests), with some characteristic properties of these materials. Many such correlations have been based on the surface properties of biomaterials, which is not surprising, in view of the fact that adsorptive events at the blood–biomaterial interfaces undoubtedly play a major part in determining the blood compatibilities of foreign surfaces. One of the earliest of such correlations was proposed by Baier (1), who suggested that, materials which possess a critical surface tension (γ_c) in the range of 20–30 dyn/cm would be more blood compatible than those with either lower or higher critical surface tensions. Nyilas *et al.* (2) have suggested that the polar component fraction of a solid's surface free energy $\left(\gamma_S^p/\gamma_S\right)$ is primarily responsible for its performance as a biomaterial. Kaelble and Moacanin (3) conclude that materials with high dispersion and low polar surface free energies will be more blood compatible than those with low dispersion and high polar surface free energies. Akers *et al.* (4) have defined a zone of biocompatibility, comprising a range of values of polar and dispersion components of solid surface free energies. Ratner *et al.* (5)

* *Journal of Colloid and Interface Science.* Vol. 101, No. 2. p. 436, October 1984. Republished with permission.

have suggested that a balance of polar and apolar sites on a surface may be important for its blood compatibility. Though each of the above empirical correlations may explain the observed behavior of some biomaterials, none of them can satisfactorily account for the performance of a wide variety of biomaterials tested to date. This fact led Bruck (6) to conclude that the surface energetic properties of materials cannot be correlated with their blood compatibilities. However, the above mentioned correlations [with the exception of ref. (3)] emphasize only the surface properties of the biomaterials, namely, either their total surface free energies, or the fractional contributions of their component surface free energies, as parameters with which their blood compatibilities could be related. But, in fact, all biomaterials interact with blood, which is a complex fluid and whose stability under normal conditions is governed by a delicately maintained equilibrium between its various components. Therefore, when a foreign surface is placed in contact with this fluid, the responses of its components to the presence of the "stranger" in their midst will be determined not only by the surface properties of the biomaterial but also by those of blood. Thus, it becomes necessary to consider the surface properties of both the biomaterial and blood as important determinants of the performance of the former as a blood contacting device.

It is the objective of this paper to suggest a surface energetic criterion of blood compatibility of foreign surfaces, which is based on an analysis of the surface interactions between the two media (blood and biomaterial). More specifically, it will be shown that, in order to achieve satisfactory blood compatibility, the magnitudes of the individual surface free energy components of a biomaterial, namely, the polar and dispersion components of the solid surface free energy, must separately be sufficiently near to their respective surface free energy counterparts of blood, so as to cause a low (but not very low) blood–biomaterial interfacial tension. Based on an analogy with the highly biocompatible cellular elements of blood, it will be shown that a spectrum of combinations of polar and dispersion components of solid surface free energies can result in both satisfactory blood compatibility of biomaterials as well as mechanical stability of the blood-biomaterial interface.

Second, the possibility of improving the surface properties of polymeric materials, in order to enhance their blood compatibilities, will be discussed.

2. SURFACE INTERACTIONS BETWEEN BLOOD AND BIOMATERIAL

In order to analyze the surface interactions between blood and a biomaterial, it will be necessary to briefly review the adsorptive events which take place when a foreign surface is exposed to blood. Almost instantaneously upon encountering a foreign surface, specific blood proteins, mainly fibrinogen, adsorb onto the solid surface (7). Continued adsorption of proteinaceous components takes place until a film of proteins has covered the surface of the biomaterial. Adhesion of the cellular components of blood begins only after this protein film has built up to a critical thickness, which varies for different substrates, depending on the surface properties of the materials. Platelets are known to be the first cellular components to adsorb onto the proteinated solid surface. These adherent platelets can flatten and become activated, which then leads to their irreversible aggregation (with other platelets from blood) and a chain of highly unpredictable events involving several components of blood, and culminating in the formation of either a red thrombus (interwoven mesh of red blood cells in fibrin) or a white thrombus (interwoven mesh of white blood cells in fibrin).

From this highly simplified picture of the encounter between a thrombogenic foreign surface and blood, it is evident that the cellular components of blood, which are chiefly responsible for thrombus formation, do not interact directly with the surface of the biomaterial. Therefore, the influence of the substrate is conveyed to the cells only through the preadsorbed protein film. This then poses the following questions, in connection with the pursuit of relating the surface properties of biomaterials with their blood compatibilities: (i) How do proteins interact with solid surfaces? (ii) What are the consequences of the surface-induced conformational changes of initially adsorbing blood proteins on the events of cellular adhesion and thrombosis? In an attempt to answer the above questions, let us consider more specifically, the surface interactions of a biomaterial with the initially adsorbing plasma proteins.

When a foreign surface is placed in contact with blood, a new interface is created in the environment of the latter. Therefore, there is a thermodynamic driving force for minimizing the blood-biomaterial interfacial tension. As a result of this, the most surface active components of blood, namely, proteins (mainly fibrinogen), adsorb at the solid–liquid interface almost instantaneously following the contact of the foreign surface with blood. Upon adsorption, the first layer of proteins may denature on the solid surface, depending on the magnitude of the blood-biomaterial interfacial tension. If this interfacial tension is high, the adsorbed proteins will anchor at multiple sites on the solid surface, in order to interact strongly with the solid surface and thereby decrease the solid-liquid interfacial tension. Therefore the adsorbed proteins will be considerably denatured in this case. On the contrary, if the blood-biomaterial interfacial tension is low, the adsorbed proteins will undergo minimum distortion of their native configuration.

Let us first consider the case in which the initially adsorbed proteins are considerably denatured on the solid surface, as a result of a high solid-blood interfacial tension. These denatured proteins will be rigidly attached to the solid (at multiple adsorption sites on the solid surface) and the proteinated solid surface will now form a new interface with blood plasma. The interfacial tension at this new interface will also be quite high, though it will be smaller than the initial blood-biomaterial interfacial tension, for the following reason: The solution state configuration of proteins in blood plasma must be optimal in terms of increasing their interaction with the solvent and thereby minimizing the free energy of the system. This means that, in their solution state configuration, the hydrophylic portions of the blood proteins will be oriented toward the aqueous phase (subject to steric constraints). However, when these proteins adsorb at multiple sites on solid surfaces, their configuration is altered and, therefore, a large part of their hydrophylic portions may not be exposed to the aqueous phase. As a result of this, the adsorbed (denatured) proteins will no longer interact as strongly with blood plasma and therefore the interfacial tension between the denatured protein covered solid surface and the surrounding medium will not be small. Due to this interfacial tension, there will be a further driving force for the adsorption (followed by denaturation) of a second layer of proteins, resulting in the creation of another interface with the medium and likewise, a succession of new interfaces will thus be presented to the components of blood within the first few minutes of their encounter with a foreign surface. Consequently, a sequence of hierarchical adsorption of blood components takes place, with the most surface active components preferentially adsorbing at each stage, until, finally, platelets begin to adsorb. Since the proteinated surface-blood interfacial tension is still high, it is likely that the adsorbed platelets will flatten and thereby become activated, thus releasing agents such as ADP. Due to this release, the platelets will interact more strongly with the proteinated solid surface, which causes their further activation. Platelet adsorption and activation generally herald the beginning of a chain of highly unpredictable and poorly understood events, involving several components of blood and culminating in thrombosis.

Contrary to the above example, let us consider the case in which the blood–biomaterial interfacial tension is relatively low. In this situation, the driving force for adsorption will be smaller because the interactions in the adsorbed state (protein-plasma and proteinsolid) are not too different from the interactions which exist between proteins and plasma in the bulk. Moreover, the conformation of the initially adsorbed proteins will not be very different from that of their solution state, because the latter configuration offers a greater entropic freedom. Therefore, the adsorbed proteins will retain much of their interactions with blood plasma in this case (because only a small part of their surface will be attached to the solid). As a result of this, the interfacial tension between the protein covered solid surface and blood plasma will be relatively small and so there will not be a significant driving force for the further adsorption of blood components. This provides a much higher blood compatibility to a foreign surface than in the previous case. However, if the blood-biomaterial interfacial tension is very low, the plasma proteins may not even adsorb to any significant extent on the surface of the biomaterial. As a result of this, one will not witness the formation of a cascade of interfaces or ultimate thrombosis on such surfaces.

From the above discussion, it is clear that the surface properties of a biomaterial must be selected with the view of minimizing the blood–biomaterial interfacial tension and thereby minimizing the denaturation of the initially adsorbing plasma proteins as well. Though an interfacial tension of zero will be ideal for blood compatibility of a foreign surface, it will be undesirable from the point of view of the mechanical stability of the blood-biomaterial interface. This is because, at very low interfacial tensions, any interface will be highly susceptible to perturbations (see Appendix 1). In other words, mechanically or thermally induced corrugations of such an interface will tend to grow in time. Due to this, some of the surface components of the solid can dissolve into blood and/or blood can be absorbed into the solid, events which can trigger the thrombotic sequence and thereby render the foreign surface incompatible with blood. Therefore, for satisfactory biocompatibility of a foreign surface, the blood biomaterial interfacial tension must be sufficiently low (but not very low) in order to comply with the dual requirements of a low driving force for the adsorption of blood components and a mechanically stable blood-biomaterial interface. In order to estimate a suitable non-thrombogenic value of the blood-biomaterial interfacial tension, one can note the high compatibility as well as the interfacial stability of the cellular elements, with blood plasma. The cell–medium interfacial tension is generally considered to be of the order of 1-3 dyn/cm, though for certain cells, it can be as low as 0.1 dyn/cm (8,9). How well these measured interfacial tensions portray the actual values is a matter that needs confirmation. Therefore, it seems reasonable to suggest that the blood-biomaterial interfacial tension should also be maintained close to this range ($\gamma_{SL} \approx 1-3$ dyn/cm) in order to ensure the compatibility of a foreign surface as well as the mechanical stability of its interface, with blood plasma.

3. BLOOD-BIOMATERIAL INTERFACIAL TENSION

Now, an expression which relates the surface energetic properties of a biomaterial to its blood compatibility, will be derived. Assuming that the principle of additivity of different interactions is valid, the total surface free energy of the biomaterial, denoted by γ_S, and that of blood, denoted by γ_L, can each be represented as the sum of several independent contributions, such as those arising from dispersion forces, dipole interactions, hydrogen bonding, etc. (10). Therefore,

$$\gamma_S = \gamma_S^p + \gamma_S^d + \gamma_S^h + \cdots \quad [1]$$

and

$$\gamma_L = \gamma_L^p + \gamma_L^d + \gamma_L^h + \cdots, \quad [2]$$

where the superscripts p, d, and h denote the polar, dispersion, and hydrogen bonding contributions, respectively, to the surface free energies. Similarly, the expression for the work of adhesion between the solid and liquid phases, W_{SL}, can also be expressed as the sum of several contributions, as follows:

$$\begin{aligned} W_{SL} &= \gamma_S + \gamma_L - \gamma_{SL} \\ &= W_{SL}^p + W_{SL}^d + W_{SL}^h + \cdots, \end{aligned} \quad [3]$$

where γ_{SL} is the solid–liquid interfacial tension. The dispersion component of the work of adhesion could be related by a geometric mean expression of the form, $W_{SL}^d = 2\left(\gamma_L^d \gamma_S^d\right)^{1/2}$ (10). Kloubek (11) has shown that a geometric mean expression could be used for the polar component of the work of adhesion as well, i.e., $W_{SL}^p = 2\left(\gamma_L^p \gamma_S^p\right)^{1/2}$. Fowkes (12) has emphasized that hydrogen bonding interactions are only a subset of acid-base interactions and that the latter cannot be predicted by a geometric mean expression. Instead, the acid-base interactions could be predicted from the equation of Drago (13, 14). In the systems considered by Fowkes, the contribution of polar interactions was negligible in comparison to those of acid-base interactions and, therefore, he regarded the total

work of adhesion as arising only from that due to dispersion and acid-base interactions. However, he noted that polar interactions can be considerable in solvents of high dipole moment. Since blood is a good example of such a system, one can expect a significant contribution from polar interactions between blood and a biomaterial, if the latter has sufficient polarity. Though acid-base interactions may also contribute to the work of adhesion between blood and a biomaterial, it is currently not possible to estimate the magnitude of such interactions when they are present alongside with dispersion and polar interactions. In addition, the following contributions to the work of adhesion between blood and a biomaterial are neglected: (1) the contribution of the double layer, which is always present in the vicinity of a solid surface in contact with blood (15, 16) and (2) that of the polarization layer generated in the liquid, by the dipoles present on the solid surface (17). Therefore, this analysis will be restricted to only those types of biomaterials which interact with blood largely by means of nonspecific interactions, such as dispersion and polar forces. For these cases, the work of adhesion between blood and a biomaterial can be approximated by

$$\begin{aligned} W_{SL} &= W_{SL}^{p} + W_{SL}^{d} \\ &= 2\left\{\left(\gamma_L^p \gamma_S^p\right)^{1/2} + \left(\gamma_L^d \gamma_S^d\right)^{1/2}\right\}. \end{aligned} \quad [4]$$

From Eqs. [3] and [4], an expression for the blood-biomaterial interfacial tension follows as

$$\begin{aligned} \gamma_{SL} &= \gamma_S + \gamma_L \\ &\quad -2\left\{\left(\gamma_L^p \gamma_S^p\right)^{1/2} + \left(\gamma_L^d \gamma_S^d\right)^{1/2}\right\}. \end{aligned} \quad [5]$$

This equation can be further transformed by observing that $\gamma_S = \gamma_S^p + \gamma_S^d$ and $\gamma_L = \gamma_L^p + \gamma_L^d$ (see Appendix 2), to obtain (18)

$$\begin{aligned} \gamma_{SL} &= \left\{\left(\gamma_L^p\right)^{1/2} - \left(\gamma_S^p\right)^{1/2}\right\}^2 \\ &\quad + \left\{\left(\gamma_L^d\right)^{1/2} - \left(\gamma_S^d\right)^{1/2}\right\}^2. \end{aligned} \quad [6]$$

This equation is quite revealing from the point of view of blood-biomaterial interfacial tension considerations. It shows that, γ_{SL} can have its minimum, which is zero, when $\gamma_S^p = \gamma_L^p$ and $\gamma_S^d = \gamma_L^d$. When $\gamma_{SL} = 0$, a biomaterial can be theoretically expected to remain in perfect compatibility with the components of blood, without promoting any adhesive events. However, as mentioned before, one must attempt to maintain a blood-biomaterial interfacial tension of the order of 1-3 dyn/cm, in order to ensure the mechanical stability of the blood–biomaterial interface as well as the compatibility of the foreign surface in the environment of blood.

Equation [6] shows that several combinations of polar and dispersion components of solid surface free energies can lead to a blood-biomaterial interfacial tension $\left(\gamma_{SL}\right)$ of about 1–3 dyn/cm. To graphically illustrate this spectrum of combinations of blood compatible surface free energy components, it can be seen from Eq. [6] that a plot of $\left(\gamma_L^p\right)^{1/2} - \left(\gamma_S^p\right)^{1/2}$ vs $\left(\gamma_L^d\right)^{1/2} - \left(\gamma_S^d\right)^{1/2}$ describes the locus of all points on a circle of radius $\left(\gamma_{SL}\right)^{1/2}$. Figure 1 shows such a plot. The shaded area in this figure represents the zone of suggested biocompatibility (i.e., blood compatibility of the biomaterial as well as mechanical stability of the blood-biomaterial interface). Table I shows a few typical combinations of surface free energy components, taken from that zone of Fig. 1. From this table it can be seen that, even solids whose total surface free energies differ considerably (for example, a surface such as C with a γ_S of 46.7 dyn/cm and a surface such as C' with a γ_S of 104.49 dyn/cm) can bear the same interfacial tension with blood and thereby remain equally compatible with blood. This happens because the individual surface free energy components (γ_S^p and γ_S^d) of the solids are

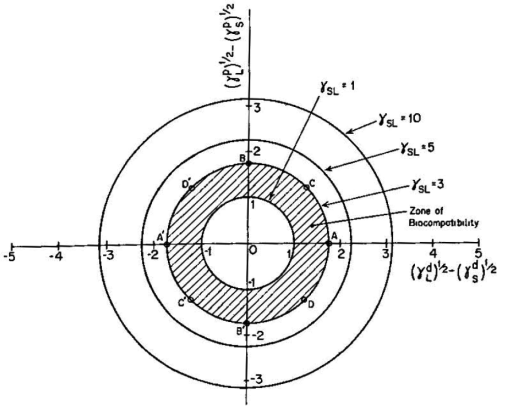

FIG. 1. Plot of Eq. [6]. The circles of this figure represent the locus of all points (different combinations of γ_S^p and γ_S^d values), which give rise to the same value of blood- biomaterial interfacial tension (i.e., $\gamma_{SL} = 1$, 3, 5, or 10).

in suitable conformity with those of their respective counterparts of blood (γ_L^p and γ_L^d). From this, it is clear that, neither the total surface free energy of the solid (γ_S), nor the fractional contributions of the solid's component surface free energies $\left(\gamma_S^p/\gamma_S, \gamma_S^d/\gamma_S\right)$ can be considered as indicators of its blood compatibility. Rather, one must separately consider the polar and dispersion components of a solid's surface free energy, in relation to their respective surface free energy counterparts of blood, in attempting to correlate the surface energetic properties of biomaterials with their blood compatibilities.

As early as 1973, Andrade (19) postulated that a minimum blood–biomaterial interfacial tension (preferably zero) can provide ideal blood compatibility to a biomaterial. He considered that this situation can be brought about by using materials such as hydrogels, whose high water contents can lead to low values of blood–biomaterial interfacial tensions. Andrade regarded the total surface free energy of the solid as the parameter to be related with the blood–material interfacial tension. However, Eq. [6] shows that, even if the total surface free energies of different solids are

TABLE I
Typical Combinations of Surface Free Energy Components and the Corresponding Solid–Water Interfacial Tensions from the Biocompatible Zone of Fig. 1

Surface (from Fig. 1)	γ_S^p (dyn/cm)	γ_S^d (dyn/cm)	γ_S (dyn/cm)	γ_{SW} (dyn/cm)
A	50.8	8.63	59.43	3
A′	50.8	40.97	91.77	3
B	29.11	21.8	50.91	3
B′	78.49	21.8	100.29	3
C	34.84	11.86	46.7	3
C′	69.76	34.74	104.49	3
D	69.76	11.86	81.62	3
D′	34.84	34.74	69.58	3

equal to that of water (72.6 dyn/cm), they can give rise to different interfacial tensions with water, depending on the magnitudes of their individual surface free energy components. For example, let us consider two hypothetical surfaces, A and B, whose total surface free energies are both equal to 72.6 dyn/cm, but whose polar and dispersion components differ considerably, as follows: $\gamma_A^p = 15$ dyn/cm, $\gamma_A^d = 57.6$ dyn/cm, $\gamma_B^p = 45$ dyn/cm, and $\gamma_B^d = 27.6$ dyn/cm. From Eq. [6], it can be seen that the interfacial tensions of these two surfaces with water are: 19 dyn/cm for surface A and 0.5 dyn/cm for surface B. This illustrates the fact that any attempt to relate the surface energetic properties of materials with their blood compatibilities on the basis of interfacial tension considerations must be based on an appropriate matching of the respective individual surface free energy components of both the biomaterial and blood.

The above considerations are valid for solid surfaces which interact with blood via dispersion as well as polar forces. We will consider below the case of a special class of materials, namely, nonpolar solids, which contain little or no polarity and, therefore, can interact with blood only via dispersion forces.

4. BLOOD COMPATIBILITY OF NONPOLAR SOLIDS

Many solids which are considered nonpolar are also usually low surface free energy materials. Since a number of these low surface energy, nonpolar materials (especially polymers) possess some desirable qualities for blood contact applications (like good mechanical strength, chemical inertness to blood components, nontoxicity, etc.), they have been widely tried as biomaterials, with the expectation that their low surface free energies would induce minimal adhesion of blood components on their surfaces. The results, however, have been contrary to such expectations. For example, Teflon is a low surface energy material, which is relatively nonpolar. Though this material has a high degree of inertness to many chemicals, its blood compatibility has been found to be poor (6). The reason for this can be explained by examining Eq. [6]. For nonpolar solids, $\gamma_S^p = 0$, $\gamma_S^d = \gamma_S$ and Eq. [6] reduces to

$$\gamma_{SL} = \left\{\left(\gamma_L^d\right)^{1/2} - \left(\gamma_S\right)^{1/2}\right\}^2 + \gamma_L^p. \qquad [7]$$

This equation shows that, for the case of nonpolar surfaces, the blood–biomaterial interfacial tension attains a minimum value when $\gamma_S = \gamma_L^d$. However, the magnitude of this minimum is equal to γ_L^p[= 50.8 dyn/cm, considering the surface tension properties of water and blood plasma to be equal (3)]. This represents a considerable blood–biomaterial interfacial tension, well outside the range of 1–3 dyn/cm that is considered suitable for providing satisfactory blood compatibility to a foreign surface. From this, it is clear that, nonpolar surfaces (like Teflon) can never remain in long term compatibility with blood.

Schrader (20) has also used Eq. [7] to note that γ_{SL} has a minimum when $\gamma_S = \gamma_L^d$ and he has used this fact to explain the experimental observations of Baier (21) concerning the existence of minimal bioadhesion on solids whose critical surface tensions $\left(\gamma_c\right)$ range from 20 to 30 dyn/cm. Even though Eq. [7] was used by both of us, our conclusion concerning the blood compatibility of nonpolar solids is distinctly different from that of Schrader.

5. CHARACTERIZATION OF BIOMATERIAL SURFACES

One important consideration remains to be emphasized in order to ensure an unambiguous interpretation of any surface energetic criterion of blood compatibility of foreign surfaces. It has been noted that many solids possess the tendency to rearrange their surface structures in response to their local environments (22,23). This observation is particularly applicable to polymeric surfaces, many of which possess sufficient mobility to adopt different surface configurations in different environments. As a result of this, such materials may be hydrophobic when exposed to air (unhydrated state), but in

the aqueous environment (hydrated state), they will display a reasonable hydrophilicity. This behavior is much more pronounced in the case of many hydratable and mobile polymers, like hydrogels (24) and polydimethyl siloxane (25), respectively. Even some relatively rigid polymers like polymethyl methacrylate seem to display this type of behavior (23). An important implication of this is the fact that the polar and dispersion components of the surface free energies of such solid surfaces can be grossly different in the aqueous environment (hydrated state) in comparison to the air environment (unhydrated state). A recent study by Ko *et al.* (26) provides a good illustration of the above consideration. These authors determined the individual surface free energy components of several grafted copolymers of hydroxy ethyl methacrylate (HEMA) and ethyl methacrylate (EMA) of varying compositions and water contents, in both the hydrated and unhydrated states. The values obtained for some solid surfaces in the two environments are listed in Table II. Unprimed quantities refer to the surface free energies in the hydrated state, while the primed symbols represent the surface free energies in the unhydrated state. It can be seen that, for all the solid surfaces, the polar component of the solid's surface free energy is increased and its dispersion component is decreased in the hydrated state, in comparison to the unhydrated state. However, in general, the change in the polar component is much more pronounced than that of the dispersion component. The solid–water interfacial tensions, γ_{SW}, of these surfaces, calculated from Eq. [6], for both the cases (hydrated as well as unhydrated solids), are also included in Table II and plotted in Fig. 2. From Fig. 2, it can be seen that the values of the individual surface free energy components in the unhydrated state can cause a misleading estimate of their blood compatibilities. For example, the experimental results of Ratner *et al.* (5) revealed that a grafted copolymer of poly(hydroxy ethyl methacrylate) and poly(ethyl methacrylate) which contained about 15% water had the highest blood compatibility in comparison to surfaces which contained either higher or lower water contents. These authors did not determine the individual surface free energy components of their materials. However, from the measurements of Ko *et al.* (26) for similar surfaces, the values obtained for a solid surface which contained about 17% water (which is near to Ratner *et al*'s. 15% water content surface) are included in Table II. One can see from Table II and Fig. 2 that the interfacial tension of this surface with water is 0.92 dyn/cm, if it is based on the hydrated solid's surface free energy components (γ_S^p and γ_S^d), while it is as high as 21.57 dyn/cm, if it is based on the unhydrated solid's surface free energy components ($\gamma_S^{p'}$ and $\gamma_S^{d'}$). The former value, which is closer to the actual value, is certainly more indicative of the high blood compatibility of this material. From this example, it appears that the surface characterization of biomaterials in their hydrated state only can provide an accurate indication of their blood compatibilities.

TABLE II

Water Content, Surface Free Energies, and Solid–Water Interfacial Tensions of Mixtures of HEMA–EMA Grafted Polyethylene Films, Characterized in Air and under Water[a]

HEMA (%)	Water content (%)	$\gamma_s^{d'}$ (dyn/cm)	γ_s^d (dyn/cm)	$\gamma_s^{p'}$ (dyn/cm)	γ_s^p (dyn/cm)	$\gamma_s^{d'}/\gamma_s^d$	$\gamma_s^p/\gamma_s^{p'}$	γ'_{sw} (dyn/cm)	γ_{sw} (dyn/cm)
0	1.7 ± 1.1	39.1	_	3.7	24.3	_	6.57	29.59	_
20	2.0 ± 0.5	42.6	7.5	3.8	44.6	5.68	11.74	30.26	3.93
40	3.5 ± 0.3	41	4.4	4.4	47	9.32	10.68	28.31	6.68
50	8.0 ± 1.6	53.1	8.3	1.8	48.4	6.40	26.89	40.33	3.23
60	8.6 ± 0.6	50.7	10.6	2.0	49.2	4.78	24.60	38.65	2.01
80	17.3 ± 0.3	42.4	13.8	8.2	49.8	3.07	6.07	21.57	0.92
100	25.6 ± 0.8	35.9	14.6	20.0	50.0	2.45	2.50	8.80	0.72

[a] From Ref. (26).

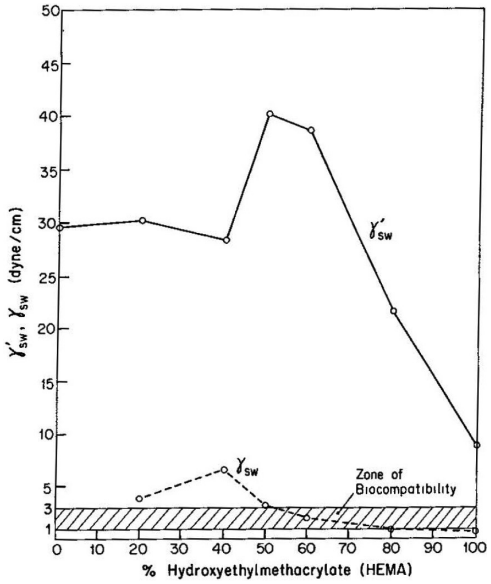

FIG. 2. Solid-water interfacial tension, calculated on the basis of the surface free energy components of the hydrated as well as unhydrated surfaces of HEMA-EMA grafted polyethylene films, which were measured by Ko *et al.* (26).

In this connection, it is necessary to mention some of the limitations of the techniques [like Hamilton's technique (27)] which are currently used to evaluate the polar and dispersion surface free energy components of biomaterials in the hydrated state. In all such techniques, the solid-fluid-water contact angles of only two fluids (i.e., either two water immiscible liquids or one water immiscible liquid and one vapor) are used for the evaluation of the polar and dispersion surface free energy components of the hydrated surface. It is well known that the magnitudes of the individual surface free energy components (polar and dispersion) of unhydrated solids are sensitive to the test liquids used for measuring the solid-liquid-air contact angles. For this reason, the contact angles of several pairs of test liquids are used to calculate the average polar and dispersion surface free energy components of solids in the unhydrated state (18, 28). In the light of this fact, it may perhaps be important to rely on the solid-fluid-water contact angles of several pairs of test fluids, in order to arrive at a more accurate estimate of the polar and dispersion surface free energy components of solids in the hydrated state also. In addition, it must be noted that, due to the lack of general validity of the expressions which are used to evaluate the individual surface free energy components, there may be some uncertainty in the calculated values of γ_S^p and γ_S^d.

6. DISCUSSION OF THE SURFACE ENERGETIC CRITERION OF BIOCOMPATIBILITY OF FOREIGN SURFACES

We will now discuss the performance of some prominent biomaterials, in relation to their surface energetic properties. For this discussion, we will consider the following materials, whose blood compatibilities range from excellent to poor: (i) hydrophilic, cross-linked polymeric gels (hydrogels), (ii) LTI (low temperature isotropic) carbons, (iii) ethyl cellulose perfluorobutyrate, (iv) "Avcothane," (v) "Biomer" polyurethane, (vi) polyalkylsulfone, (vii) Teflon, and (viii) glass. Hydrogels have shown good promise for blood contact applications since the early sixties (29). Their poor mechanical properties are also being overcome by covalently grafting them onto the surfaces of materials (like polymers) which possess suitable mechanical properties. Ratner *et al.* (5) recently evaluated the

performance of several grafted hydrogels, by conducting different blood compatibility tests on them. Relevant to this discussion is their results on a series of p (HEMA-EMA) copolymers of varying water contents. In this series of copolymers, they observed that the 1:1 p (HEMA–EMA) graft, which contained about 15% water, showed superior blood compatibility in comparison to surfaces which contained either higher or lower water contents. This result was observed in both the tests conducted on such materials, namely, the low shear rate vena cava ring test and the high shear rate A–V shunt test. This fact led to Ratner *et al*'s. hypothesis that a balance of hydrophylic and hydrophobic sites on a surface may be important for the blood compatibility of a biomaterial. As noted before, this superior blood compatible surface is likely to bear an interfacial tension of about 0.92 dyn/cm with water.

The experimental results of Ratner *et al*. (5) thus lend support to our point of view that, just as a high blood–biomaterial interfacial tension (such as that caused by the low water content (p (HEMA-EMA)) surfaces) is undesirable for the blood compatibility of the foreign surface, a very low blood-biomaterial tension (such as that caused by the high water content [p (HEMA–EMA) surfaces] is also equally detrimental to the performance of the biomaterial. A high thermodynamic driving force for the adsorption of blood components is responsible for the low blood compatibility of the p (HEMA–EMA) surface in the former case, while in the latter case, the poor mechanical stability of the blood-biomaterial interface may be the cause of adverse effects such as the dissolution or leaching of some of the surface components of the solid into blood and/or the absorption of blood into the solid, events which are capable of triggering the thrombotic sequence and thereby resulting in the poor blood compatibility of the foreign surface. From this, it appears that an optimum blood-biomaterial interfacial tension [which is sufficiently low (but not very low)] can provide a satisfactory blood compatibility to a foreign surface. Of course, the exact range of optimum interfacial tension values must be determined by suitable experiments (it may vary slightly from the range of 1–3 dyn/cm suggested here).

Let us next consider the case of LTI (low-temperature isotropic) carbons, whose blood compatibility is excellent (6). The surface of this material has been characterized only in the unhydrated state, for its polar and dispersion surface free energy components (3), which are as follows: $\gamma_S^{p'} = 4.16$ dyn/cm and $\gamma_S^{d'} = 54.46$ dyn/cm. As noted earlier, the polar surface free energy component of a number of solids is grossly underestimated and the dispersion component is usually overestimated in the unhydrated state (in comparison to the hydrated state). This fact is evident from the study of Ko *et al*. also (26). This is because many solids possess the ability to reorient their surface structures and maintain a minimum interfacial energy with the surrounding medium, so as to comply with the thermodynamic requirement of minimizing the free energy of the system. This behavior has been demonstrated for the case of hydrogels by Holly and Refujo (24). Subsequently, Yasuda *et al*. (22) have demonstrated (by means of contact angle hysteresis experiments) that the concept of orientation of surface molecules at an interface is also applicable to some other polymer surfaces (like oxygen-plasma treated polypropylene). More recently, Andrade *et al*. (23) have shown (by means of contact angle hysteresis experiments) that, even a rigid, hydrophobic polymer surface, such as polymethyl methacrylate, could display modest hydrophilicity under water due to interfacial restructuring in the aqueous environment. In the light of these observations, it appears plausible to suggest that the surface structure of LTI carbons may also be significantly altered in the blood environment (in comparison to the air environment) so as to maintain a sufficiently low interfacial tension with blood, which can provide this material with a high blood compatibility. Note that some specific interactions such as the acid-base interactions may also play a role. Based on the same reasoning, one may be able to account for the excellent blood compatibility of ethyl cellulose perfluorobutyrate (6), the good blood compatibilities of "Avcothane" and "Biomer" polyurethane (6) and the moderate–good blood compatibility of polyalkylsulfone (6).

The characterization of these biomaterial surfaces (for their polar and dispersion surface free energy components) in the aqueous environment can confirm the validity of the above explanation.

Let us now discuss the blood compatibilities of two materials which differ considerably, among other things, in their polar surface free energies. Teflon is a classic example of a low surface energy, nonpolar surface, whose blood compatibility is poor (6). The surface of this material remains nonpolar even in the aqueous environment (27). Therefore, as mentioned earlier, any nonpolar surface will bear a very high interfacial tension with blood plasma ($\gamma_{SL} \geqslant 50.8$ dyn/cm), as a result of which, its blood compatibility will be poor, as is indeed the case with Teflon. Another example of a thrombogenic material is glass, which has been characterized only in the unhydrated state, in which its surface free energy components are as follows (19): $\gamma_S^{p'} = 90$ dyn/cm and $\gamma_S^{d'} = 80$ dyn/cm. Since this material presents such a highly polar surface character even to an apolar phase like air, one can conclude that it has a very rigid surface structure and so it cannot undergo significant surface restructuring in the aqueous environment. Therefore, if it is assumed that the unhydrated surface free energy components of this material will be valid for its hydrated state also, then one can note that this material will bear a very high interfacial tension with blood ($\gamma_{SL} = 23.8$ dyn/cm), and consequently, it will be thrombogenic, as is the observed case.

7. THERMODYNAMIC AND KINETIC CONSIDERATIONS IN THE BLOOD COMPATIBILITY OF FOREIGN SURFACES

It is necessary to mention that the surface energetic criterion suggested in this paper is based on thermodynamic considerations and, therefore, it is valid for the long-term blood compatibility of foreign surfaces. In some instances, however, it is possible for a biomaterial to remain in compatibility with blood for a fairly long time, even when this thermodynamic criterion of biocompatibility is not satisfied. This may take place due to many factors like steric repulsion, double layer forces, hydration forces, etc., which can give rise to the "kinetic compatibility" of a biomaterial for a reasonable length of time, much like the well-known kinetic stability of thermodynamically unstable colloidal suspensions (30-32). The following observations illustrate this point: Bruck (6) has hypothesized that the electrical and semiconduction properties of some natural and synthetic polymers may bear a relationship to their blood compatibilities. This may be due to double layer repulsion. Ikada *et al.* (33) suggest that, if a material presents a diffuse interfacial structure (as opposed to a rigid one) when it is placed in the aqueous environment, then it may exhibit excellent antithrombogenicity. This may arise as a result of steric repulsion between the solid surface and the adsorbing components. Barenberg *et al.* (34) conclude that, if a surface appears as an ordered ionic array, it will invite a thrombogenic response, while if it appears as a disordered array, only limited thrombogenesis will take place on it. All these and many other surface properties of materials can result in their compatibility with blood for varying periods of time (sometimes sufficiently long for practical purposes), thereby providing a "kinetic compatibility" to a biomaterial. While a low blood-biomaterial interfacial tension can ensure the long-term blood compatibility of a foreign surface, "kinetic biocompatibility" may often be adequate for practical purposes.

8. SURFACE MODIFICATION OF POLYMERS BY ULTRAVIOLET IRRADIATION AND ITS IMPLICATIONS FOR BIOMATERIAL BLOOD COMPATIBILITY

In order to satisfy the criterion of blood compatibility suggested in this paper, it is necessary to either find materials whose individual surface free energy components belong to the biocompatible range ($\gamma_{SL} \simeq 1-3$ dyn/cm) or else, it is necessary to modify the surface properties of existing materials, in order to improve their blood compatibilities. The former alternative places a high premium on a trial and error search for suitable biomaterials. On the other hand, it is a more attractive proposition to attempt an improvement of the blood compatibilities of existing biomaterials which possess good mechanical properties.

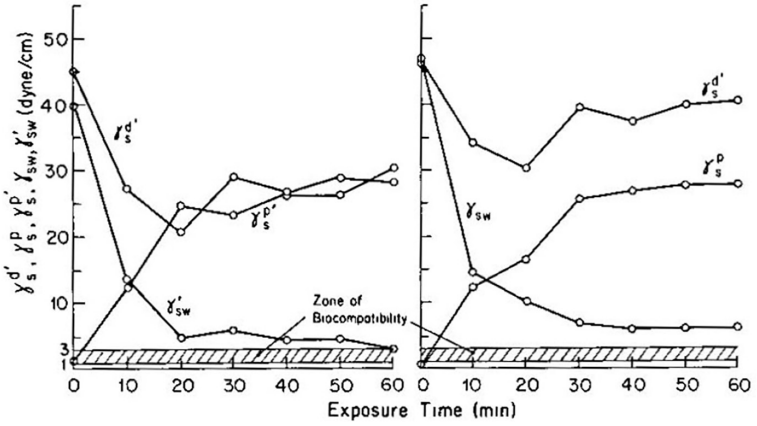

FIG. 3. Effect of ultraviolet irradiation (for various exposure times) on the surface free energy components of poly(diphenyl siloxane) (35). The solid–water interfacial tension is also plotted for different exposure times. The left-hand side shows the values of $\gamma_S^{p'}$ and $\gamma_S^{d'}$ (evaluated by Kaelble's method), while the right-hand side shows the values of γ_S^{p} and $\gamma_S^{d'}$ (evaluated by Fowkes–Hamilton method).

A number of polymers, like Teflon for example, possess some desirable properties for blood contact applications (such as nontoxicity, good mechanical properties, etc.), but they are incompatible with blood largely because of their poor surface properties. Moreover, most polymeric biomaterials have a very small value of γ_S^p, which results in their high interfacial tension with blood plasma, since the latter has a relatively high polar component of surface tension ($\gamma_L^p \simeq 50.8$ dyn/cm). Therefore, in order to improve the blood compatibilities of such polymeric biomaterials, it will be necessary to considerably increase their polar surface free energy components.

The recent study of Esumi *et al.* (35) shows that ultraviolet irradiation of polymer surfaces can result in considerable changes in their polar surface free energy components. Therefore, this technique seems particularly promising for altering the surface properties of several types of polymeric biomaterials, in order to enhance their blood compatibilities.

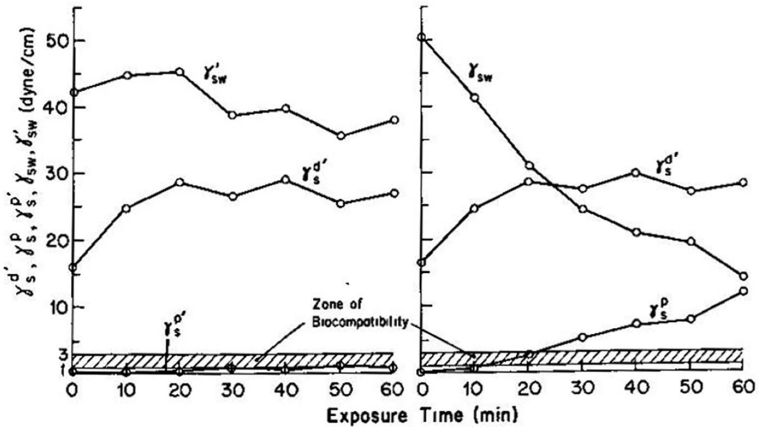

FIG. 4. Effect of ultraviolet irradiation (for various exposure times) on the surface free energy components of copolymer dimethyl siloxane PS255 (35). The solid–water interfacial tension is also plotted for different exposure times. The left-hand side shows the values of $\gamma_S^{p'}$ and $\gamma_S^{d'}$ (evaluated by Kaelble's method), while the right-side shows the values of γ_S^{p} and $\gamma_S^{d'}$ (evaluated by the Fowkes-Hamilton method).

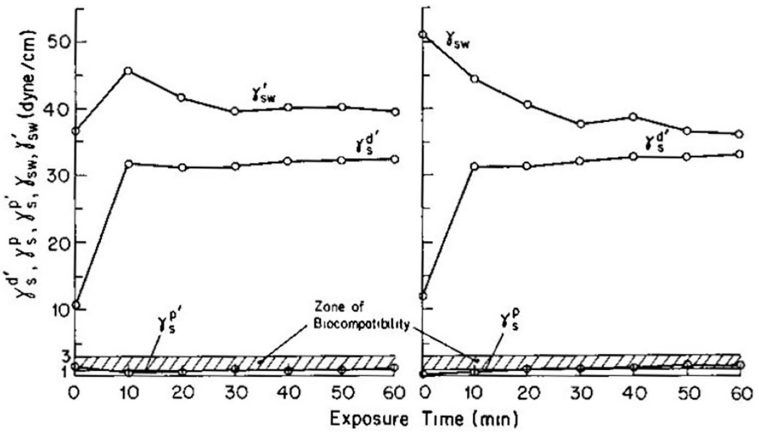

FIG. 5. Effect of ultraviolet irradiation (for various exposure times) on the surface free energy components of copolymer dimethyl siloxane PS054 (35). The solid-water interfacial tension is also plotted for the different exposure times. The left-hand side shows the values of $\gamma_S^{p'}$ and $\gamma_S^{d'}$ (evaluated by Kaelble's method), while the right-side shows the values of γ_S^{p} and $\gamma_S^{d'}$ (evaluated by Fowkes–Hamilton method).

Figures 3 to 6 and Table III show some of the results obtained by Esumi *et al.* (35) regarding the effects of ultraviolet irradiation on polymer surfaces. The surface free energy components, evaluated by two different techniques, namely, Kaelble's method (18, 28) and Fowkes-Hamilton method (27), are shown in these figures. While the former technique was used to calculate the solids' surface free energy components in the unhydrated state ($\gamma_S^{p'}$ and $\gamma_S^{d'}$), the latter method provided the value of the polar surface free energy component in component in the unhydrated state $\left(\gamma_S^{d'}\right)$. For the hydrated state $\left(\gamma_S^{p}\right)$ and the dispersion each combination of component surface free energies, the value of the solid-water interfacial tension (calculated from Eq. [6]), is also shown in Figs. 3 to 6 and Table III.

Figure 3 and Table III show that, exposure to UV radiation for 1 hr increases the polar surface free energy component of poly- (diphenyl siloxane) in the hydrated state, from an initial value of 0.37 dyn/cm to a value of 28 dyn/cm. The dispersion component changed far less dramatically

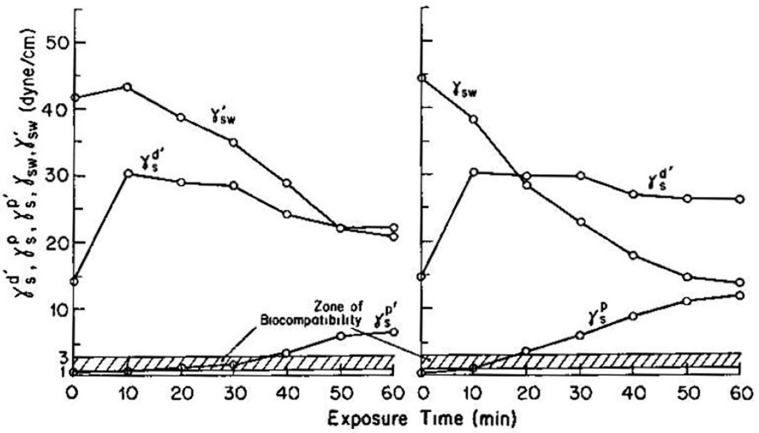

FIG. 6. Effect of ultraviolet irradiation (for various exposure times) on the surface free energy components of copolymer dimethyl siloxane PS264 (35). The solid-water interfacial tension is also plotted for different exposure times. The left-hand side shows the values of $\gamma_S^{p'}$ and $\gamma_S^{d'}$ (evaluated by Kaelble's method), while the right-side shows the values of γ_S^{p} and $\gamma_S^{d'}$ (evaluated by Fowkes-Hamilton method).

TABLE III
Changes in Surface Free Energy Components and Solid-Water Interfacial Tensions of Polymers as a Result of Exposure to UV Radiation[a]

			Kaelble surface energies (dyn/cm)			Fowkes–Hamilton surface energies (dyn/cm)		
No.	Polymer	Exposure time (min)	$\gamma_S^{d'}$	$\gamma_S^{p'}$	γ'_{sw}	$\gamma_S^{d'}$	γ_S^{p}	γ_{sw}
1	Poly(diphenyl siloxane)	0	45.32	1.27	40.26	46.5	0.37	47.12
		10	27.36	12.19	13.54	34.27	12.26	14.55
		20	20.74	24.58	4.72	30.3	16.48	10.11
		30	29.03	23.40	5.76	39.61	25.70	6.87
		40	26.58	26.25	4.25	37.54	26.85	5.91
		50	28.81	26.16	4.54	40.11	28.00	6.14
		60	28.32	30.34	3.05	40.60	28.00	6.27
2	Copolymer dimethyl siloxane (PS255)	0	16.09	0.41	42.52	16.48	0.0012	50.68
		10	24.84	0.18	45.03	24.56	0.51	41.21
		20	28.92	0.18	45.43	28.58	2.63	30.77
		30	26.62	0.84	38.82	27.42	4.97	24.31
		40	29.13	0.72	39.95	29.73	6.98	20.73
		50	25.47	1.36	35.68	26.85	7.63	19.32
		60	27.09	0.95	38.14	28.00	11.83	13.99
3	Copolymer dimethyl siloxane (PS054)	0	10.58	1.49	36.90	11.83	0.046	49.3
		10	31.85	0.18	45.88	31.45	0.29	44.30
		20	31.15	0.53	41.78	31.45	0.70	40.46
		30	31.32	0.80	39.71	32.02	1.18	37.47
		40	32.01	0.73	40.33	32.59	1.00	38.63
		50	32.01	0.73	40.33	32.59	1.39	36.46
		60	32.37	0.85	39.55	33.15	1.50	36.03
4	Copolymer dimethyl siloxane (PS264)	0	14.00	0.54	41.72	14.53	0.26	44.53
		10	30.28	0.37	43.19	30.30	1.00	38.24
		20	28.85	0.91	38.60	29.73	3.37	28.62
		30	28.17	1.59	34.82	29.73	5.78	22.92
		40	24.13	3.19	28.59	26.85	8.67	17.76
		50	22.21	6.00	21.88	26.28	10.99	14.74
		60	21.99	6.52	20.92	26.28	11.83	13.81

(from an initial value of 46.5 dyn/cm to a final value of 40.6 dyn/cm after 1 hr of exposure), though this component was estimated only for the unhydrated solid. As a result of these changes in the individual component surface free energies, the solid-water interfacial tension changed considerably, from an initial value of 47.12 dyn/cm to a value of 6.27 dyn/cm after only 1 hr of exposure to UV radiation. Though these values of γ_{sw} may not represent the actual values attained by such surfaces when they are placed in contact with blood (as a result of using the unhydrated solid's dispersion surface free energy component), they are expected to reasonably approximate the actual values of γ_{sw} (which are based on the hydrated solids' surface free energy components, γ_S^p and γ_S^d).

Figures 4 to 6 show the effect of ultraviolet irradiation on other types of polymers. Even though these materials (in Figs. 4 to 6) were relatively nonpolar initially, exposure to ultraviolet radiation caused an increase in their component surface free energies (both γ_S^p and $\gamma_S^{d'}$), so as to cause a marked decrease in their interfacial tensions with water. It must be noted that Esumi *et al.* have

characterized the surfaces of the UV-irradiated polymers, after 2 days of dark aging (to enable the escape of volatile irradiation products). However, the long-term stability of these irradiated surfaces in an aqueous environment (such as that of blood) is not yet known.

It can be seen from Figs. 3 to 6 that the component surface free energies of various polymers are affected to different extents, by this surface modification technique. But this example is discussed only to illustrate the possibility that such a technique may be useful in improving the blood compatibilities of those polymers that can undergo significant surface modification, as a result of this treatment.

From Figs. 3 to 6 and Table III, it can be seen that such a surface treatment usually leads to a considerable decrease of the solid–water interfacial tension. This presents the promising possibility that the above technique may be useful in enhancing the blood compatibilities of a wide variety of polymeric biomaterials, whose mechanical properties are already suitable for blood contact applications.

9. CONCLUSIONS

A surface energetic criterion of biocompatibility of foreign surfaces which is based on two considerations, namely (i) a low blood–biomaterial interfacial tension and (ii) a mechanically stable blood-biomaterial interface, is suggested. To fulfill both these conditions, a sufficiently low (but not very low) blood- biomaterial interfacial tension is necessary. Since the cellular elements are compatible with blood and their interface with the medium (blood plasma) is also mechanically stable, it is considered that a blood-biomaterial interfacial tension of about the same magnitude as the cell-medium interfacial tension ($\gamma_{SL} \simeq 1$–3 dyn/cm) will provide a foreign surface with both long-term compatibility as well as a mechanically stable interface, with blood. In order to satisfy these conditions, a suitable correspondence between the respective individual surface free energy components of the biomaterial and blood is necessary. As a result of this condition, it is possible that even solids which differ appreciably in their total surface free energies can exhibit equal compatibility with blood. It is also noted that nonpolar surfaces $\left(\gamma_S^p = 0\right)$ cannot remain in long-term compatibility with blood.

On the basis of some examples, it is shown that the characterization of biomaterial surfaces (for their surface free energies) in their hydrated state (as opposed to their unhydrated state) is an important requirement for the successful interpretation of any surface energetic criterion of biocompatibility of foreign surfaces.

Finally, a surface modification technique, involving the irradiation of surfaces with ultraviolet radiation, is suggested as a promising method of improving the surface energetic properties of polymeric biomaterials, in order to enhance their blood compatibilities.

APPENDIX 1: INTERFACIAL INSTABILITY AT LOW INTERFACIAL TENSIONS

There are no theoretical treatments concerning the stability to large perturbations of solid-liquid interfaces, when their interfacial tensions are low. However, the information which is available, in particular, for the stability to small perturbations, provides support to our considerations on the stability of the blood-biomaterial interface. Investigations concerning the stability to small perturbations of fluid-liquid and fluid-solid interfaces of sufficiently thin films (<1000 Å) supported on a solid have shown that the time of rupture of the films becomes smaller as the interfacial tensions of these interfaces decrease. In fact, for liquid films, the available analytical expressions show that the time of rupture of sufficiently thin films becomes zero for a zero liquid-fluid interfacial tension (36–38). In the case of sufficiently thin solid films, analytical expressions which relate the time of rupture to the solid-fluid interfacial tension, are not available. Numerical calculations, however, appear to suggest that the time of rupture of thin solid films will also become very small when the solid-fluid interfacial tension attains very low values (39).

In the case of brittle solids, fracture mechanics demonstrates (40) that the critical stress σ_c needed to initiate crack propagation is given by the expression

$$\sigma_c = \left(\frac{2E\gamma_{SL}}{\pi r} \right)^{1/2},$$

where E is the Young elastic modulus, γ_{SL} is the interfacial tension, and r is a length characterizing the crack. This expression also shows (although it is limited to brittle solids only) that at very low values of γ_{SL}, any crack of the interface can grow easily (since σ_c is small).

In addition, let us note that a thermal perturbation of the interface can also generate large amplitudes of the interfacial fluctuations (41). The mean of the square of the amplitude of the interfacial fluctuations is proportional to kT/γ_{SL}. Therefore, the effect of the thermal perturbations is expected to become more pronounced when γ_{SL} is small.

APPENDIX 2: JUSTIFICATION OF THE EXPRESSION $\gamma_L = \gamma_L^p + \gamma_L^d$

The evaluations of Coulson (42) indicate that in water the covalent interactions (≈ -8.0 kcal/mol) and overlap repulsions ($\approx +8.4$ kcal/mol) nearly cancel each other. As a result of this, the orientation plus induction interactions (≈ -6 kcal/mol) and the dispersion interactions (≈ -3 kcal/mol) are mainly responsible for the overall interaction energy. For this reason, one can approximate γ_L by the sum $\gamma_L^p + \gamma_L^d$.

APPENDIX 3: NOMENCLATURE

γ_L	Surface tension of the liquid, dyn/cm
γ_S	Surface free energy of the solid, dyn/ cm
γ_{SL}	Solid–liquid interfacial tension, dyn/ cm
γ_{SW}	Solid–water interfacial tension, dyn/ cm
W_{SL}	Work of adhesion between the solid and liquid phases, dyn/cm

Superscripts

′	Denotes solid–air interface
d	Denotes the dispersion contribution
h	Denotes the hydrogen bonding contribution
P	Denotes the polar contribution

REFERENCES

1 Baier, R. E., *in* "Adhesion in Biological Systems" (R. S. Manly, Ed.). Academic Press, New York, 1970.
2 Nyilas, E., Morton, W. A., Cumming, R. D., Lederman, D. M., Chiu, T. H., and Baier, R. E., *J. Biomed. Mater. Res. Symp.* **8**, 51 (1977).
3 Kaelble, D. H., and Moacanin, J., *Polymer* **18**, 475 (1977).
4 Akers, C. K., Dardik, I., Dardik, H., and Wodka, M., *J. Colloid Interface Sci* **59**, 461 (1977).
5 Ratner, B. D., Hoffman, A. S., Hanson, S. R., Harkar, L. A., and Whiffen, J. D., *J. Polym. Sci. Polym. Symp. No.* **66**, 363 (1979).
6 Bruck, S. D., *J. Polym. Sci., Polym. Symp. No.* **66**, 283 (1979).
7 Baier, R. E., and Dutton, R. C., *J Biomed. Mater. Res.* **3**, 191 (1969).
8 Troshin, A. S., "Problems of Cell Permeability." Pergamon Press, New York, 1966.
9 Weiss, L., "The Cell Periphery, Metastasis and Other Contact Phenomena." North Holland, Amsterdam, 1967.
10 Fowkes, F. M., *Ind. Eng. Chem.* **56**, 40 (1964).

11 Kloubek, J., *J. Adhesion* **6**, 293 (1974).
12 Fowkes, F. M., *in* Physicochemical Aspects of Polymer Surfaces (K. L. Mittal, Ed.), Vol. 2. Plenum Press, New York, 1983.
13 Drago, R. S., Vogel, G. C., and Needham, T. E., *J. Amer. Chem. Soc.* **93**, 6014 (1970).
14 Drago, R. S., Parr, L. B., and Chamberlain, C. S., *J Amer. Chem. Soc.* **99**, 3203 (1977).
15 Verwey, E. J. W., and Overbeek, J. M. G. "Theory of the Stability of Lyophobic Colloids." Elsevier, Amsterdam, 1948.
16 Ruckenstein, E., and Krishnan, R., *J. Colloid InterfaceSci.* **76**, 201 (1980).
17 Schiby, D., and Ruckenstein, E., *Chem. Phys. Lett.* **95**,' 435 (1983); **95**, 439 (1983); **100**, 277 (1983).
18 Kaelble, D. H., and Uy, K. C., *J. Adhesion* **2**, 50 (1970).
19 Andrade, J. D., *Med. Instrumentation* **7**, 110 (1973).
20 Schrader, M. E., *J. Colloid Interface Sci.* **88**, 296 (1982).
21 Baier, R. E,, *in* "Proceedings of Third International Congress on Marine Corrosion and Biofouling" (R. F. Acker, B. F. Brown, J. R. Depalma, and W. P. Iverson, Eds.). Northwestern University Press, Evanston, 111., 1973.
22 Yasuda, H., Sharma, A. K., and Yasuda, T., *J. Polym.Sci*., *Polym. Phys. Ed*. **19***,* 1285 (1981).
23 Andrade, J. D., Gregonis, D. E., and Smith, L. M., *in* "Physicochemical Aspects of Polymer Surfaces" (K. L. Mittal, Ed.), Vol. 2. Plenum Press, New York, 1983.
24 Holly, F. J., and Refujo, M. F., *J. Biomed. Mat. Res.* **9** 315 (1975).
25 Owen, M. J., *I EC Prod. Res. Dev.* **19**, 97 (1980).
26 Ko, Y. C., Ratner, B. D., and Hoffman, A. S., *J.Colloid Interface Sci*. **82**, 25 (1981).
27 Hamilton, W. C., *J. Colloid Interface Sci.* **47**, 672 (1974).
28 Kaelble, D. H., *J. Adhesion* **2**, 66 (1970).
29 Wichterle, O., and Lim, D., *Nature (London)* **185**, 117 (1960).
30 Overbeek, J. Th. G., *J. Colloid Interface Sci.* **58**, 408 (1977).
31 Ottewill, R. H., *J. Colloid Interface Sci*. **58**, 57 (1977).
32 Marmur, A., and Ruckenstein, E., *in* "Advances in Biomedical Engineering (D. O. Cooney, Ed.), Vol. II. Marcel Dekker, New York, 1980.
33 Ikada, Y., Iwata, H., Horii, F., Matsunaga, T., Taniguchi, M., Suzuki, M., Taki, W., Yamagata, S., Yonekawa, Y., and Handa, H., *J. Biomed. Mater. Res.* **15**, 697 (1981).
34 Barenberg, S. A., and Mauritz, K. A., *in* "Biomaterials: Interfacial Phenomena and Applications," ACS, Adv. Chem. Series, no. 199, p. 195. Amer. Chem. Soc., Washington, D. C., 1982.
35 Esumi, K., Schwartz, A. M., and Zettlemoyer, A. C., *J. Colloid Interface Sci.* **95**, 102 (1983).
36 Ruckenstein, E., and Jain, R. K., *J. Chem. Soc. Far aday Trans.II* **70**, 132 (1974). (Section 5.1 of Volume I).
37 Maldarelli, C., Jain, R. K., Ivanov, I. B., and Ruckenstein, E., *J. Colloid Interface Sci*. **78**,118 (1980).
38 Williams, M. B., and Davis, S. H., *J. Colloid Interface Sci*. **90**, 220 (1982).
39 Ruckenstein, E., and Dunn, C. S., *Thin Solid Films* **51**, 43 (1978) (Section 5.2 of Volume I).
40 Griffith, A. A., *Phil. Trans. R. Soc., Ser. A* **221**, 163 (1920).
41 Mandelstam, L., *Ann. Phys.* **41**, 609 (1913).
42 Coulson, C. A., *in* "Hydrogen-Bonding" (Hazdi, D., and Thomson, H. W., Eds.), p. 339. Pergamon Press, London, 1959.

1.3 Surface Characterization of Solids in the Aqueous Environment*

Sathyamurthy V. Gourisankar and Eli Ruckenstein

A surface energetic criterion was recently suggested for the selection of blood compatible surfaces (1). It was based on the thermodynamic consideration that the solid–blood plasma (i.e., water) interfacial free energy must be sufficiently low (but not too low) in order to ensure the long-term compatibility of a foreign surface in the environment of blood. In that treatment, it was also shown that widely differing combinations of polar and dispersion surface free energy components of solids in the aqueous environment can give rise to the same value for the solid–water interfacial free energy that is considered suitable for endowing a foreign surface with blood compatibility (see Table I of Ref. (1)).

The polar and dispersion surface free energy components of solids in an aqueous environment are usually estimated by underwater surface characterization techniques such as Hamilton's method (2) and the two liquid methods (35). While the former technique relies on the measurement of the contact angle of octane on the solid specimen underwater to obtain an estimate of the polar surface free energy component of the solid, the latter techniques rely on the measurement of the contact angles of two water-immiscible fluids (such as octane and air, for example), to estimate both the dispersion and polar surface free energy components of the solid in the aqueous environment. As rightly pointed out by Jho (6), these underwater contact angle techniques suffer from the limitation that they do not permit the estimation of the polar surface free energy component of a solid that is greater than that of water, i.e., 50.8 erg/cm^2. In the case of Hamilton's technique for example, the polar surface free energy component of the solid under water is given by the expression

$$\gamma_s^p = \left(\gamma_w + \gamma_{ow}\cos\phi_o - \gamma_o\right)^2/4\gamma_W^P, \qquad [1]$$

where γ_w is the surface tension of water (=72.6 erg/cm^2), γ_o is the surface tension of octane (= 21.8 erg/cm^2), γ_{ow} is the octane-water interfacial tension $\left(= 50.8\ \text{erg/cm}^2\right)$, γ_w^p is the polar component of the surface tension of water (=50.8 erg/cm^2), and ϕ_0 is the solid–octane–water contact angle (measured through the water phase). From this equation, it is clear that γ_s^p, will be a maximum (i.e., 50.8 erg/cm^2) when $\phi_0 = 0°$. This expression for γ_s^p, which is independent of the dispersion surface free energy component of the solid under water $\left(\gamma_s^d\right)$, arises as a result of the coincidence that the surface tension of octane is equal to the dispersion component of the surface tension of water. If alkanes other than octane are employed, then it is necessary to measure the solid–fluid–water contact angles of a pair of fluids and solve two simultaneous equations to estimate the polar and dispersion surface free energy components of the solid in the aqueous environment. It is to be noted, however, that even in the case of the other alkane probe fluids, the maximum value of γ_s^p that can be detected by underwater contact angle goniometry will not be significantly different from the value of 50.8 erg/cm^2. This is because all the alkane fluids are nonpolar and the values of their surface tensions and interfacial

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tensions with water do not differ much. This limitation does not, however, mean that the underwater surface characterization technique is incapable of detecting γ_s^p values greater than 50.8 erg/cm^2. In order to extend the range of values of γ_s^p that can be experimentally detected, the problem is to select a pair of appropriate probe fluids which will be water immiscible and possess considerably different interfacial tensions with water than the conventional probe fluids in current use (such as the alkanes and air). To illustrate this point, let us first inspect Eq. [1], Although this equation is applicable to the case of octane only, it is still suggestive of the main limiting factor involved in the underwater surface characterization of solids. This expression shows that the maximum detectable value of γ_s^p is limited by the octane–water interfacial tension. Therefore, if we select a probe fluid such as mercury, which bears a very high interfacial tension with water (γ_{Hg-w} = dyn/cm (7)), then it appears possible to estimate solid polar surface free energy components that are greater than 50.8 erg/cm^2. The same observation was recently made by Andrade (8). The dispersion component of the surface tension of mercury has been estimated as 200 erg/cm^2 and its total surface tension is 484 erg/cm^2 (7). It has also been suggested that mercury and water interact mainly by means of dispersion forces and that the dipole-metal image forces are relatively insignificant (7). Therefore it appears reasonable as a first approximation to consider that the interaction of mercury with most solids will also take place predominantly by dispersion forces. Based on these considerations, mercury seems to be a potentially useful probe fluid for the underwater surface characterization of solids. However, one more probe fluid is still necessary to permit the determination of both the dispersion and polar surface free energy components of the solid in the aqueous environment. In our search for a second probe fluid which will also be water-immiscible and maintain a high interfacial tension with water, we find that gallium (which is a liquid metal at room temperature) appears to be suitable for underwater contact angle characterization of solids. The surface tension of this liquid is 718 erg/cm^2 (9). Its individual component surface tensions and interfacial tension with water are unknown at present but it appears to be a potentially useful probe fluid (along with mercury) for detecting solid polar surface free energy components that are larger than 50.8 erg/cm^2 in the aqueous environment. Thus, in principle, it seems feasible to detect γ_s^p values greater than 50.8 erg/ cm^2, by using some novel probe fluids such as mercury and gallium. It must be noted though that the probe fluids must be well characterized for their surface tension components and interfacial tension with water, prior to their use in underwater surface characterization. In the light of these considerations, the comment of Jho (6) that the limitation of underwater contact angle goniometry is due to the presence of water and has nothing to do with the choice of the probe fluid, seems applicable only to the conventional probe fluids (such as alkanes and air) which are in current use.

Regarding Jho's comments on the underwater surface characterization of glass, the following point is to be noted: the values obtained by both Jho (5) and Coleman *et al.* (10) for the polar and dispersion surface free energy components of glass under water were close to the maximum values of these components, i.e., 50.8 and 21.8 erg/cm^2, respectively, that could be detected by using air and octane as probe fluids in the two liquid underwater contact angle technique. Coleman et al. (10) found that the contact angles of both air and octane on the glass surface under water were less than 10° (see Table 1 of Ref. (10)), indicating that the contact angles of these two probe fluids were very close to their limiting values, i.e., 0°, on the glass surface. Based on the upper value of 10° for the contact angle of both these fluids, the estimated values of the dispersion and polar surface free energy components of glass were (10): γ_s^d = 21.3 erg/cm^2 and γ_s^p = 49.7 erg/cm^2. The results of Jho (5) showed slightly higher values of octane and air contact angles on the glass surface under water but the estimated surface free energy components were close to those of Coleman et al. It must be remembered, however, that the surface free energy component of glass was estimated from Eq, [1], by Jho. As discussed earlier, this equations does not permit the detection of γ_s^p values that are larger than 50.8 erg/cm^2. It can be seen from Eq. [1] that the value of the solid–octane–water contact angle (ϕ_0) is dependent only on the value of γ_s^p and independent of the value of γ_s^d. Therefore, even if the actual values of γ_s^p were higher than 50.8 erg/cm^2, then also the limiting value of $\phi_0 = 0°$ would have been observed. Consequently, the estimated value of γ_s^p will still be equal to 50.8 erg/cm^2 and thus

provide a misleading indication of the real value. Moreover, when air is used as a second probe fluid, the expression for the dispersion component of the surface free energy of glass under water, i.e., γ_s^d, can be written as

$$\gamma_S^d = \left(\gamma_o + \gamma_w \cos\phi_A - \gamma_{ow} \cos\phi_o\right)^2 / 4\gamma_{w.}^d \quad [2]$$

In this equation, γ_s^d is the dispersion surface free energy component of the solid under water, ϕ_A is the solid–air–water contact angle (measured through the water phase) and γ_w^d is the dispersion component of the surface tension of water. This equation shows that, for a solid on which $\phi_o = 0$ $\left(\text{i.e., } \gamma_s^p = 50.8 \text{ erg/cm}^2\right)$, the maximum value of γ_s^d that could be detected is 21.8 erg/cm^2, when $\phi_A = 0$. The values of γ_s^d for glass that were obtained by both Coleman *et al.* and Jho were very close to this upper limit. Here also it may be observed that higher values of γ_s^d could have given rise to the same limiting value of $\phi_A = 0°$ and thereby provided a misleading γ_s^d estimate of 21.8 erg/cm^2.

From the above discussion, it appears that the values reported by Coleman *et al.* and Jho for the surface free energy components of glass underwater, may be somewhat lower than the actual values. This is due to the limitation on the maximum values of both the polar and dispersion surface free energy components of a solid that can be detected by using octane and air as probe fluids in the underwater contact angle technique. In this context, it may be noted that the polar and dispersion surface free energy components of glass in air are (11): $\gamma_s^d = 80$ erg/cm and $\gamma_s^p = 90$ erg/cm^2. Realizing that the surface of glass is very rigid and therefore it is not expected to undergo any significant restructuring under water, it seems unlikely that its surface free energy components underwater will be drastically different from the above values. The underwater surface characterization of glass with higher surface tension probe fluids such as mercury and gallium may reveal if it does indeed possess larger values of polar and dispersion surface free energy components than those reported by Coleman *et al.* and Jho.

In conclusion, it can be stated that the main limitation of the techniques used to characterize the surfaces of solids in the aqueous environment, namely, the upper limit (of about 51 erg/cm^2) on the detectable value of the solid's polar surface free energy component, can be overcome by resorting to the use of probe fluids like mercury and gallium, which are both very high surface tension liquids and therefore will bear high interfacial tensions with water, unlike the conventional probe fluids such as the alkanes and air, which are in current use. An important element in the use of this newer class of probe fluids is the fact that they must be well characterized for their individual surface tension components and their interfacial tension with water, prior to their use in underwater contact angle surface characterization.

REFERENCES

1. Ruckenstein, E., and Gourisankar, S. V., *J. Colloid Interface Sci.* **101**, 436 (1984) (Section 1.2 of this volume).
2. Hamilton, W. C., *J. Colloid Interface Sci.* **47**, 672 (1974).
3. Andrade, J. D., Ma, S. M., King, R. N., and Gregonis, D. E., *J. Colloid Interface Sci*. **72**, 488 (1979).
4. Ko, Y. C., Ratner, B. D., and Hoffman, A. S., *J. Colloid Interface* **82**, 25 (1981).
5. Jho, C., *J. Colloid Interface Sci.* **94**, 589 (1983).
6. Jho, C., *J. Colloid Interface Sci.* **109**, 000 (1986).
7. Fowkes, F. M., *Ind. Eng. Chem.* **56**, 40 (1964).
8. King, R. N., Andrade, J. D., Ma, S. M., Gregonis, D. E., and Brostrom, L. R., *J. Colloid Interface Sci.* **103**, 62 (1985).
9. Allen, B. C., *in* "Liquid Metals—Chemistry and Physics" (S. Z. Beer, Ed.), p. 186. Dekker, New York, 1972.
10. Coleman, D. L., Gregonis, D. E., and Andrade, J. D., *J. Biomed. Mater. Res.* **16**, 381 (1982).
11. Andrade, J. D., *Med. Instrum.* **7**, 110 (1973).

1.4 Preparation and Characterization of Thin Film Surface Coatings for Biological Environments*

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In the selection of synthetic materials for use in biological media, two important considerations are involved, namely, (i) the compatibility of the solid in the environment of the fluid and (ii) the suitability of its mechanical properties for a given application. For the first requirement it is necessary that when a foreign surface is placed in contact with a biological fluid, it must not provoke adverse responses such as excessive deposition of the fluid's components, or toxic and allergic reactions, or thrombosis in the case of blood contacting devices. For the suitability of their mechanical properties, the selected materials need to possess satisfactory levels of resistance to compression, tension or shear depending on the specific application. In some applications such as synthetic vascular prostheses or catheters for use in biomedical applications for instance, a high degree of flexibility is called for, while in some other applications such as artificial heart valves or heat exchange equipment used to process biological fluids (as in the milk pasteurization industry), one requires materials with some rigidity.

A closer examination of these two requirements reveals that they call for adequacy of two totally different aspects of material properties. The biocompatibility condition is really a reflection of the surface characteristics of solids. Contrary to this, the mechanical properties of solids are largely a manifestation of their bulk characteristics. Therefore, an 'ideal' synthetic material for use in biological fluid contact applications must be satisfactory in both its surface and bulk characteristics. This is a rather formidable demand on the currently available synthetic materials for it seems to be almost a paradox of nature that materials which possess suitable surface properties for biological fluid environments fail on account of their poor mechanical properties and *vice versa*. To illustrate this, it may be noted that some types of hydrogel biomaterials (which are crosslinked, hydrophilic, polymeric gels) are known to be highly compatible in the environment of blood though their poor mechanical properties precludes them from being successful as long-term artificial implant devices. On the other hand, materials such as metals and ceramics possess suitable mechanical characteristics for many applications but their surface properties are inadequate for use in a number of biological fluid environments. It is pertinent to note in this context that with the considerable advances in the areas of material processing and fabrication, it is now possible to prepare synthetic materials with suitable mechanical properties for almost any specific biological fluid contact application but what has really proven to be elusive is the identification of materials with suitable surface properties for use in biological media.

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