

POLYMER SCIENCE AND TECHNOLOGY
Volume 12A

ADHESION AND ADSORPTION OF POLYMERS

POLYMER SCIENCE AND TECHNOLOGY

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Edited by
Lieng-Huang Lee

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PREFACE

Honolulu is a most beautiful place, suitable for all occasions. Its choice as the meeting site for the first Joint Chemical Congress between the American Chemical Society and the Chemical Society of Japan was praised by scientists from both sides. During this Congress, the International Conference on Adhesion and Adsorption of Polymers was held at the Hyatt Regency Hotel between April 2 and 5, 1979. We had speakers from ten nations presenting over forty papers related to the subject matter. It was a memorable event.

Unlike our two previous adhesion symposia held in 1971 and 1975, this was the first time in the same conference that we discussed both adhesion and adsorption of polymers simultaneously. These two important phenomena are not only inter-related, but also equally important in adhesive technology as well as biochemical processes. The papers presented to this Conference deal with these two phenomena from both fundamental and practical viewpoints. Furthermore, with the advance of new surface analytical techniques, the actual, microscopic happenings at the interfaces can be pinpointed. Thus, characterization of interface became one of the major focuses of this Conference. As a result, a broad coverage of the subject matter includes statistical thermodynamics, surface physics, surface analysis, fracture mechanics, viscoelasticity, failure analysis, surface modification, adsorption kinetics, biopolymer adsorption, etc. Thanks to the diligence of our contributors, we are now able to publish the final papers in these two volumes.



Fig. 1. From Left to Right: Dr. T. Hata, Mrs. and Dr. L.H. Lee, Dr. K. Nakao .



Fig. 2. From Left to Right: Dr. and Mrs. A. Silberberg, Dr. L.H. Lee.

In these Proceedings we present the revised papers and discussions during the Conference in eight parts:

- Part I: Polymer Surface Interactions
- Part II: Characterization of Adhesive Interfaces
- Part III: Polymeric Structural Adhesives
- Part IV: Fracture Strengths of Polymeric Systems
- Part V: Modification of Polymer Interfaces
- Part VI: Kinetics of Polymer Adsorption
- Part VII: Characterization of Adsorbed Interfaces
- Part VIII: Adsorption of Biopolymers

Several papers were published elsewhere, so, instead, we have included two "Quickies" and one contribution after the Conference.

I would like to take this opportunity to thank our co-chairmen: Dr. K. Nakao (Fig. 1) and Dr. W.H. Grant. They helped very much in soliciting papers for this Conference. We would like to thank our plenary speakers: Professors I. Prigogine and A. Bellemans, Professor T. Hata (Fig. 1), Dr. S. Tsai, and Professor A. Silberberg (Fig. 2). We are grateful to Dr. Shiro Matsuoka for his talk at our Symposium Banquet on "Energy Conservation Problems for Future Plastics Industries." We also wish to thank our sponsoring organizations, the Division of Organic Coatings and Plastics Chemistry of the American Chemical Society and the Chemical Society of Japan.

Acknowledgement is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this Symposium.

Last but not least, I would like to thank Ms. Nancy Rickey for her patience in typing the entire Proceedings in camera-ready format.

Lieng-Huang Lee

November, 1979

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PART ONE

POLYMER SURFACE INTERACTIONS

Introductory Remarks

Lieng-Huang Lee

Wilson Center for Technology

Xerox Corporation

Webster, New York 14580

This is a wonderful opportunity for us to celebrate the first Joint Chemical Congress between the American Chemical Society and the Chemical Society of Japan. The Organizing Committee of this International Conference on Adhesion and Adsorption of Polymers would like to thank you and our speakers for making this meeting possible.

There will be eight sessions of this Conference, dealing first with adhesion and then with adsorption of polymers. The subject of this session is "Polymer Surface Interactions." Some aspects of this subject matter were discussed during the two previous conferences (1,2). Today, as planned in the schedule, the first paper is a plenary lecture on "Statistical Mechanics of Surface Tension and Adsorption" by Professors I. Prigogine and A. Bellemans. Dr. Bellemans is scheduled to deliver this paper; however as a result of the United Airlines strike, he is still staying at the Los Angeles airport and waiting for an opportunity to fly out here. In the meantime, I have brought some extra sets of my own slides and shall briefly discuss the general concepts of surface tension, surface energy and surface free energy.

The second paper is another plenary lecture on "Surface and Interfacial Tension of Polymer Melts and Solutions," to be presented by Professor Toshio Hata, President of Gunma University, Japan. Dr. Hata attended our 1971 Symposium on "Recent Advances on Adhesion" and has been actively publishing papers on adhesion and rheology of polymers. It is indeed fortunate for all of us to hear Dr. Hata again during this Joint Chemical Congress.

The third paper, "Acid-Base Interactions at Interfaces." will be presented by Professor F.M. Fowkes of Lehigh University. Physicists have frequently used a similar term, donor-acceptor interaction. Now, we chemists will be hearing a stronger argument about a more familiar term, acid-base interactions. In this paper, Dr. Fowkes points out that acid-base interactions are also occurring at the polymer-polymer interfaces.

Dr. Souheng Wu will discuss the surface tension of solids in the fourth paper of this morning. Dr. Wu has made experimental measurements of surface and interfacial tensions of polymers. In this paper, he is proposing a theoretical justification for critical surface tension introduced by Dr. W.A. Zisman. Though the original title, "Surface Tension of Solids: An Equation of State Approach," has raised strong comments by reviewers, the data assembled could serve some useful purpose for practitioners.

The last paper of this session is "A Role of Molecular Forces in Adhesive Interaction of Polymers," by Professor Belyi et al. Dr. Belyi could not attend this Conference. We understand their situation in the U.S.S.R. This paper is by no means rigorous, but it sums up their view on the effect of dispersion forces on adhesion. Those who are interested in the subject matter should read a new book, Dispersion Forces (3).

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Statistical Mechanics of Surface Tension and Adsorption

I. Prigogine and A. Bellemans

Faculty of Sciences

Université Libre de Bruxelles, 1050 Bruxelles, Belgium

ABSTRACT

This introductory lecture is broadly divided into three parts. In the first one we review some fundamentals of surface phenomena; i.e., the conditions of mechanical equilibrium of an interface, Gibbs thermodynamics of surfaces and the statistical formulation of surface properties. The second part is devoted to a critical discussion of current statistical models of the surface tension of pure liquids and liquid mixtures (cell model, perfect and regular solutions, corresponding state theories, r-mer mixtures, etc...). The last part deals with the adsorption of a chain molecule at an interface, in relation with different physical parameters: interactions, length and concentration.

INTRODUCTION

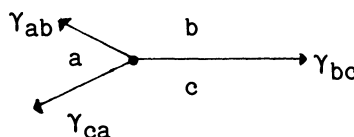
This lecture will be divided into three parts. In the first one we shall briefly survey some fundamentals of interface phenomena; i.e., the conditions of mechanical equilibrium, Gibbs thermodynamics of surfaces and the general statistical approach of interfaces. The second part will be devoted to a critical presentation of some particular models developed for describing surface properties of pure liquids and liquid mixtures. The third and last part will concern one of the central topics of this Colloquium; i.e., the adsorption of a chain molecule at an interface.

FUNDAMENTALS OF SURFACE PHENOMENA

From the macroscopic point of view the interface between two adjacent fluid phases, a, b appears as a geometrical surface where the local thermodynamic properties of the system change abruptly. As originally stated by Young (1) in 1805, this surface is mechanically equivalent to a non-rigid membrane with zero thickness, isotropically stretched by the so-called interfacial tension γ . Insofar as this membrane may be regarded as massless, its equilibrium shape is determined by the Laplace equation (2)

$$p_a - p_b = \gamma_{ab} (K_1 + K_2) \quad (1)$$

where p_a , p_b are the hydrostatic pressures in phases a, b, and K_1 , K_2 are the principal curvatures at the considered locus. Moreover, the equilibrium condition of an edge resulting from the encounter of the interfaces separating three mutually coexisting phases a, b, c, is expressed by the vectorial equation of Neumann



$$\vec{\gamma}_{ab} + \vec{\gamma}_{bc} + \vec{\gamma}_{ca} = 0 \quad (2)$$

(assuming zero edge tension).

Obviously the assumption that two adjacent phases retain their own intensive properties downright to a surface of discontinuity is only a useful way of thinking which, when necessary, must be completed by a detailed picture of what really happens at the molecular level. The interface is actually formed by a thin layer of matter operating the transition between the two bulk phases and both the mechanical and physico-chemical properties of this layer usually differ markedly from those of these phases. In particular, as originally pointed by Bakker (3), the interfacial tension is merely a macroscopic manifestation of the anisotropy of the pressure tensor within the interfacial layer.

The thermodynamics of surface phenomena was formulated by Gibbs (4) in an extremely elegant way. Indeed classical thermodynamics is devised for handling locally homogeneous systems; i.e., the change of any intensive variable is completely negligible over a few molecular diameters. This is clearly not so within the transition layer, the density of which may e.g., drop by a factor of a thousand over perhaps 10 or 20Å when passing from a liquid to a gas phase. Gibbs superseded the difficulty by introducing the concept of dividing surface. This is a geometrical surface located in the transition layer (or at least sensibly close to it) and passing through "points which are similarly situated with respect to the

condition of the adjacent matter", as worded by Gibbs himself (4). The actual system, consisting of two homogeneous bulk phases separated by a thin inhomogeneous layer, is then replaced by two homogeneous bulk phases extending on each side of the chosen dividing surface; this surface itself is treated as a homogeneous two-dimensional phase and provided therefore with appropriate mechanical and physico-chemical properties, in order to match the actual system macroscopically. E.g., its free energy F is split into three parts, respectively the two bulk phases and the surface phase s

$$F = F_a + F_b + F_s \quad (3)$$

with the following differentials (5)

$$dF_a = -S_a dT - p_a dV_a + \sum \mu_i dN_i^a \quad (4a)$$

$$dF_b = -S_b dT - p_b dV_b + \sum \mu_i dN_i^b \quad (4b)$$

$$dF_s = -S_s dT + \gamma dA + \sum \mu_i dN_i^s \quad (4c)$$

Note that we limit ourselves to systems in mechanical, thermal and chemical equilibrium, and that we are essentially interested in flat interfaces (for which $p_a = p_b$). Although eq. (4c) looks strictly similar to eqs. (4a)-(4b), one should realize that a surface phase has no real autonomy in general; its very existence is conditioned by the presence of the two "parent" bulk phases and its composition follows from the values of the set of chemical potentials $\{\mu_i\}$.

The variables $\{N_i^s\}$ specify the material content and the composition of the surface phase. In the same way as one defines bulk concentrations ($C_i^a = N_i^a / V_a$, $C_i^b = N_i^b / V_b$), it is convenient to introduce the adsorption

$$\bar{\Gamma}_i = N_i^s / A, \quad (5)$$

as the mean number of molecules of species i adsorbed on a unit area of the interface. Similar arguments which lead to the well known Gibbs-Duhem equation for the bulk, may next be used to derive the Gibbs adsorption formula

$$d\gamma = -s_s dT - \sum \bar{\Gamma}_i d\mu_i \quad (6)$$

where s_s is the surface entropy per unit area. Actually the value of $\bar{\Gamma}_i$ depends on the precise location of the dividing surface (which for a flat interface is somewhat arbitrary). The relative

adsorption of one component with respect to another is, however, a perfectly well defined quantity, independent of the choice of this surface.

Turning now to statistical mechanics, we see two main routes for developing a molecular expression of surface tension and related properties. One starts from the statistical formulation of the pressure tensor and was fully formulated by Kirkwood and Buff (6). The other route proceeds from the partition (or grand partition) function Z of the system, going to the free energy F and finally to γ by means of the two relationships

$$F = -kT \ln Z \quad (7)$$

$$\gamma = \left(\frac{\partial F}{\partial A} \right)_{T, V, \{N_i\}} \quad (8)$$

In particular, for a fluid of spherical molecules, the final expression of γ is

$$\gamma = (1/2) \int d\vec{R} \int \frac{du}{dR} \frac{x^2 - z^2}{R} n_2(z, \vec{R}) dz \quad (9)$$

where $u(R)$ is the intermolecular pair potential and $n_2(z, \vec{R})$ is the pair density within the transition layer, normally oriented to the z axis; \vec{R} is the vector joining two molecules (with components Y, Y, Z). It is only rather recently that this expression has proven really useful, when reliable information became available on $n_2(z, \vec{R})$. Generalizations of eq. (9) for polyatomic molecules have also recently been established (7).

STATISTICAL MODELS OF INTERFACES

Eq. (9) and its extensions to nonspherical molecules are of limited use because of our rather poor information concerning the pair density n_2 . Furthermore one is often interested in complex systems for which equations like (9) would not only be difficult to establish but also completely useless. Hence the deep interest in developing more or less sophisticated models specialized to different kinds of interfaces.

In this respect the Cell Model of the liquid state has been applied rather successfully to describe the liquid-gas interface far from the critical point. Let us recall here that each molecule of the liquid is supposed to be locked in a cage; given w the potential energy at the cage center and ψ the partition function of a molecule in its cage, one gets