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SUBTLE AND SURPRISING ANOMALIES REGARDING SURFACE ENERGY AND ADHESION:

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It is pretty much an article of faith that the surface energies of solids largely dictate how well coatings and adhesives will wet and adhere to them. What is less understood is the fact that under certain circumstances the conventional wisdom on how surface energy affects adhesion fails to understand some of the more subtle aspects of how surface energy relates to wetting and adhesion.

By way of investigating these phenomena, this issue of the Newsletter elaborates on a most interesting paper by Charles Paul¹ wherein he points out that the wetting behavior of an adhesive between two substrates is much less dependent on surface energetics than is the case for coatings. In particular one does not expect a relatively high surface tension liquid like water to spread very well on a low surface energy material like poly(dimethyl-siloxane) and this is indeed universally what is observed. However, what is not expected is that when the same liquid is sandwiched between two low surface energy surfaces one readily gets complete wetting between the layers. This is demonstrated for two liquids between silicone release layer surfaces. The editorial essay in this issue develops a simple thermodynamic model which explains this seemingly counter intuitive behavior.

This issue would also like to bring attention to the upcoming:

SHORT COURSE ON THE CHEMISTRY, PHYSICS AND MECHANICS OF SURFACE SCIENCE AND ADHESION to be held November 12-14, 2018 at the Marriott Inn in Newburgh, NY

We cordially invite all readers of the newsletter to join us at this event wherein we delve into the nature of the surface interactions which hold the world together and also cause it to fall apart and further elucidate the science and technologies which explain which outcome will prevail.

ELEMENTARY MODEL FOR WETTING OF SESSILE DROPS

Turning to the problem of the wetting behavior of coatings vs the behavior of adhesive layers we adopt a simple thermodynamic model for the free energy of a liquid drop on a solid surface. This problem has been worked out in detail by Bormashenko² who derives the following formula for a general drop described by the shape function $h(x,y)$:

$$F[h(x,y)] = \iint_S [\gamma_{LV} (1+(\nabla h)^2)^{1/2} + (\gamma_{SL} - \gamma_{SA})] dx dy \quad (1)$$

Where:

- γ_{LV} = Liquid surface tension
- γ_{SA} = Solid surface tension
- γ_{SL} = Solid-liquid interface tension

For present purposes Eq.(1) is rather more detailed than what we require. In what follows we assume that the drop shape is closely approximated by a spherical shape and the surface integral can be replaced by the surface area of a spherical section times the relevant surface tension. Fig.(1) depicts the simplified geometry for a drop of volume V_s .

¹ "How Thermodynamics Drives Wet-out in Adhesive Bonding: Correcting Common Misconceptions", Charles W. Paul, JAST, 22, 31 (2008).

² "Wetting of Real Surfaces", Edward Yu. Bormashenko (Walter de Gruyter GmbH, 2013) p. 14 Eq. (.3)

From elementary geometry the volume and surface areas of the sessile drop in Fig. (1) are given by:

$$\begin{aligned} \text{Drop volume} &= V_s = \pi h (3r^2 + h^2)/6 \\ \text{Area of drop cap} &= A_c = \pi (r^2 + h^2) \\ \text{Area of drop base} &= A_b = \pi r^2 \end{aligned}$$

The volume of the drop is taken to be constant so which implies the following relation between r and h :

$$r = (2V_s/(\pi h) - h^2/3)^{1/2}$$

With these relations in hand we can immediately write down the following simple expression for the surface free energy of the sessile drop in Fig.(1):

$$F_h = \gamma_{LV} A_c + A_b (\gamma_{SL} - \gamma_{SA})$$

Inserting the geometric relations listed above and further performing some relative light algebra we arrive at :

$$\begin{aligned} F_h &= \frac{2V_s}{h} [\gamma_{LV} + \gamma_{SL} - \gamma_{SA}] \\ &+ \frac{\pi h^2}{3} [2\gamma_{LV} + \gamma_{SA} - \gamma_{SL}] \end{aligned} \quad (2)$$

Since the volume of the original drop is constant we can scale the drop height by the original drop radius d to get:

$$h = h/d$$

Furthermore $V_s = (4/3)\pi d^3$ and the original drop surface area = $A_s = 4 \pi d^2$.

Using these relations Eq. (2) can be rescaled into dimension less form as:

$$\begin{aligned} F_h &= \frac{F_h}{A_s} = \frac{2}{3h} [\gamma_{LV} + \gamma_{SL} - \gamma_{SA}] + \\ &\frac{h^2}{12} [2\gamma_{LV} + \gamma_{SA} - \gamma_{SL}] \end{aligned} \quad (3)$$

GEOMETRY OF SPHERICAL SEGMENT

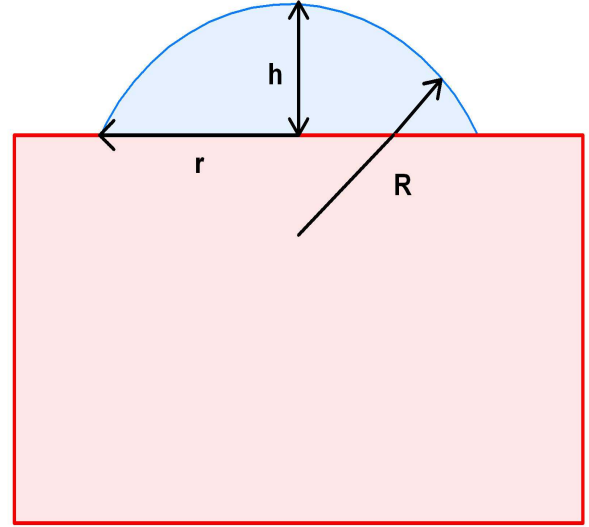


Figure 1 Cross section of a sessile drop on a surface assumed to take the shape of a segment of a sphere of radius R .

In Eq. (3) the scaled drop height h can be considered as an order parameter and the equilibrium value is that which minimizes the free energy F_h . Thus the equilibrium value of h satisfies the equation:

$$\frac{\partial F_h}{\partial h} = 0 \quad (4)$$

Performing the derivative indicated in Eq. (4) we find the following expression for the scaled equilibrium drop height:

$$h = 4^{1/3} \left[\frac{\gamma_{LV} + \gamma_{SL} - \gamma_{SA}}{2\gamma_{LV} + \gamma_{SA} - \gamma_{SL}} \right]^{1/3} \quad (5)$$

Table I displays the predicted values of h using data from ref.(1) on mineral oil and methylene iodide on a silicone release layer:

TABLE I: SCALED DROP HEIGHT OF MINERAL OIL AND METHYLENE IODIDE ON A SILICONE RELEASE LAYER ($\gamma_{SA} = 20 \text{ mJ/m}^2$)				
LIQUID	γ_{LV} (mJ/m ²)	γ_{SL} (mJ/m ²)	Contact angle on silicon release layer (deg.)	Scaled drop height h
MINERAL OIL	29	6.4	62	0.95
METHYLENE IODIDE	51	13.8	83	1.18

Table I basically confirms what we already suspect that the two relatively high surface energy liquids mineral oil and methylene iodide will bead up on the low surface energy silicone release layer. The drop height of the mineral oil is calculated to be 0.95 times the original drop radius and methylene iodide is 1.18 times the drop radius.

Moving on, we now investigate the situation when the two liquids are sandwiched between two silicon release layers. Figure (2) shows the revised geometry for this case.

We treat the sandwich as a spherical layer of radius r and height h as shown in Fig. (2). The revised geometrical formulae are as follows:

σ

LAYER VOLUME:

$$V_s = \pi h (3\rho^2 + 3r^2 + h^2)/6 \quad (6)$$

WITH

$$\rho^2 = r^2 - h^2$$

GEOMETRY OF SPHERICAL LAYER

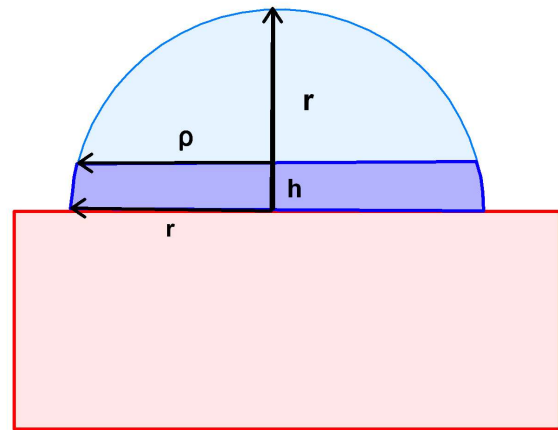


Figure 2: Layer segment of a sphere of radius r

The free energy of the layer is now given by the sum of the surface tensions times the relevant surface areas as follows:

$$F = \gamma_{LV} A_{rim} + (\gamma_{SL} - \gamma_{SA}) (A_t + A_b) \quad (7)$$

WHERE:

$$A_{rim} = 2\pi r h ; A_b = \pi r^2 ; A_t = \pi \rho^2$$

Inserting the given formulae for the relevant surfaces areas into the free energy expression and further using Eqs.(6) to eliminate r and ρ in favor of V_s and h plus some more relatively light algebra gives the following formula for F in terms of V_s and h :

$$F = 2\pi h \gamma_{LV} \left[\left(\frac{V_s}{\pi h} \right) + \frac{h^2}{3} \right]^{1/2} + (\gamma_{SL} - \gamma_{SA}) \left(\frac{2V_s}{h} - \frac{\pi h^2}{3} \right) \quad (8)$$

We now assume that the original drop had a radius d and therefore $V_s = (4/3)\pi d^3$ and the drop surface area = $4\pi d^2$. As before it is now convenient to rescale the free energy F by the drop surface area $F = F/(4\pi d^2)$ and the drop height by d ($h = h/d$) giving a rescaled version of Eq.(8) where the units on both sides of the equation are mJ/m^2 :

$$F = \frac{\gamma_{LV} h}{2} \left[\frac{4}{3h} + \frac{h^2}{3} \right]^{1/2} + (\gamma_{SL} - \gamma_{SA}) \left(\frac{2}{3h} - \frac{h^2}{12} \right) \quad (9)$$

Figure (3) shows a plot of Eq.(9) for the case of methylene iodide sandwiched between two silicon release layers as per the data in Table I. The minimum of the free energy is clearly achieved for a layer thickness approaching zero and thus Eq.(9) unequivocally predicts complete wetting between the release layers in an apparent contradiction of the drop beading behavior predicted by Eq.(5) for the sessile drop.

We can easily reconcile this result with Eq.(5) by simply noticing that the free surface area of the sandwiched drop is at least an order of magnitude smaller than for the sessile drop. Thus if we reduce the γ_{LV} term in Eq.(5) by a factor of 10 we would get essentially the same prediction as Eq.(9). From this point of view we conclude that wet-out between sandwiched layers is essentially a geometric effect.

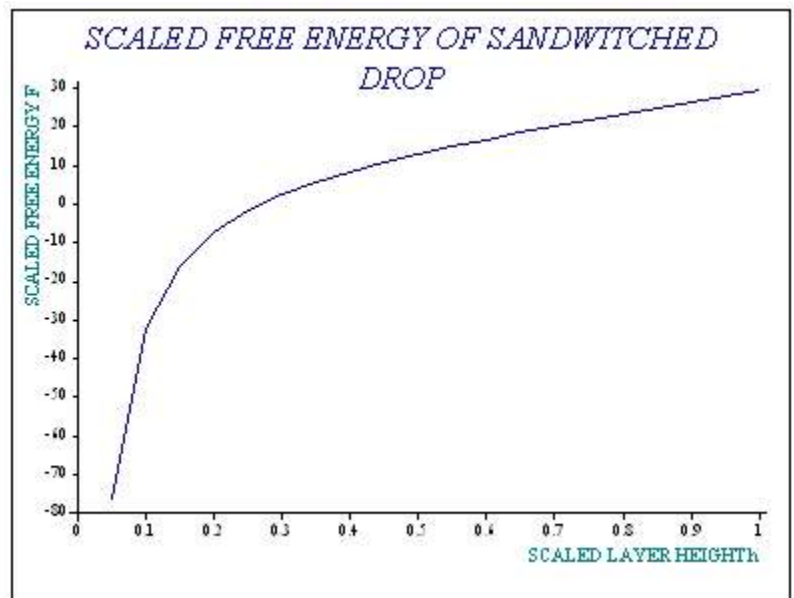


Figure 3: Plot of Eq.(9) for the case of methylene iodide on silicone release layer (surface energy data data from Table I).

More unexpected results surface as we look more closely at the effect of surface energy on peel strength.

SURFACE ENERGY AND PEEL STRENGTH ADHESION

The effect of surface energy on adhesion as measured for instance by the peel test can be rather perplexing indeed. As an example Abbott³ has pointed out that in the case of pressure sensitive adhesives (PSA) the surface energies are known to be close to $50\text{mJ}/\text{m}^2$, yet the measured peel strengths are close to $100\text{J}/\text{m}^2$ which is some 2000 times larger. Further experiments on the auto adhesion of poly(ethylene) (PE) sheets add another layer to the dilemma. PE sheets of both low and high density were laminated under pressure. Without any pre treatment the adhesion was quite poor as expected. After plasma treatment the adhesion improved quite substantially again as expected. However, what was not expected is that subsequent experiments

³ : "Adhesion Science: Principles and Practice", Steven Abbott (DEStech Publications, Inc., Lancaster, PA (2015)) Chapter 1 pp. 10-20.

clearly demonstrated that the improved adhesion could not be attributed to either surface functionalization or to the removal of weak boundary layers as would be expected. Rather the data unambiguously support the notion that the plasma field effectively broke up the surface crystallinity of the PE sheets thus allowing inter-chain penetration and entanglement of the PE chains between the two sheets. These are known to be highly dissipative mechanisms which can clearly account for the improved adhesion. Abbott goes on to argue that, though surface interactions are necessary to establish anchor points, it is really inter-chain penetration and entanglements that give rise to strong adhesion especially in materials such as the PSAs.

Interestingly the story does not end here. Up to this point surface energetics appear to play a secondary role in peel adhesion. However, things look significantly different when we are peeling metals off rigid surfaces. The soft metals such as copper, aluminum and lead also give rise to highly dissipative flow mechanisms. This was quite convincingly demonstrated by Farris and Goldfarb⁴ who did peel tests of aluminum on polyimide in a microcalorimeter which allowed them to track the flow of heat within the system as the peel test proceeded. Figure (4) exhibits their remarkable results. When peeling aluminum off polyimide over 90% of the work done by the test machine goes into heat dissipation arising from the plastic flow of the aluminum at the peel bend. In the case of peeling polyimide off aluminum, however, the work done by the test machine is divided roughly evenly between viscous dissipation and stored elastic energy in the polyimide. It should

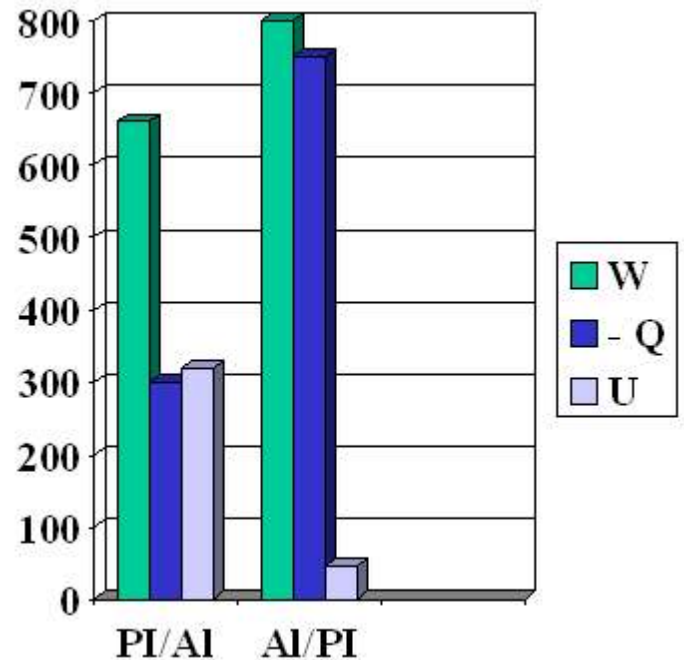


Figure 4 Partitioning of energy flow when peeling aluminum off polyimide as compared to peeling polyimide off aluminum. Note that the interfacial surface energies have to be the same for both these cases.

be further emphasized that in both cases the surfaces energies are identical so the remarkable difference between the two cases must be attributed to entirely different dissipative mechanisms within the polyimide and the aluminum.

We now ask what is the consequence of these two different dissipative mechanisms on the effect of surface energy when peeling a metal off a rigid surface. Fortunately we can rely on the work of Kim and Kim⁵ who have done an exhaustive study on the mechanics of peel testing for metals on rigid substrates. Following their analysis we can compute the effect of increasing the surface fracture energy on the peel adhesion for the case of a copper thin film on a silica glass surface. The results are displayed in Fig.(5). From the

⁴ "An Experimental Partitioning of the Mechanical Energy Expended During Peel Testing", R. J. Farris and J Goldfarb, in Adhesion Measurement of Films and Coatings, K. L. Mittal, Ed. (VSP, Utrecht, The Netherlands, 1995).

⁵ "Elasto-Plastic Analysis of the Peel Test for Thin Film Adhesion", K. -S. Kim and J. Kim, Journal of Engineering Materials and Technology, 110, 266 (1988).

numerical data we see that increasing the surface fracture energy from 0.05 Nt/m to 0.47 Nt/m increases the peel strength from a very modest 2 Nt/m to a quite significant 40 Nt/m. Thus we see from this simple example that we can expect the surface energy to play a much more significant role in increasing the peel strength of elastic-plastic metals as opposed to the case of viscoelastic polymers.

All of this brings us to the major purpose of this issue which is the announcement of the next session of the short course on the Chemistry, Physics and Mechanics of Surface Science and Adhesion which is designed to guide the student through the labyrinth of subtle adhesion phenomena by explaining the fundamental principles which ultimately control this behavior.

3- Day Impact Course The Chemistry, Physics & Mechanics of Surface Science and Adhesion

November 12-14, 2018
Courtyard by Marriott, Stewart-
Newburgh, New York
SCENIC HUDSON VALLEY

Topics to be Covered

- I. Surface Contamination and Cleaning
- II. Theories or Mechanisms of Adhesion
- III. Contact Angle, Wettability and Adhesion
- IV. Investigation of Interfacial Interactions
- V. Surface Modification Techniques including Plasma
- VI. Ways to improve Adhesion of Organic Coatings

PEEL FORCE OF COPPER ON SILICA GLASS

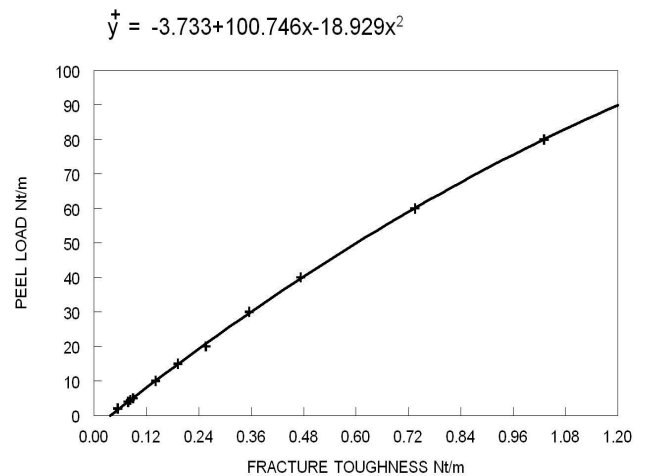


Figure 5 Computed effect of increasing the surface fracture energy on the peel load for the case of copper on silica glass. Analysis was carried out using the elasto-plastic analysis of the peel test as derived by Kim and Kim (Ref. 5).

- VII. Silanes and Other Adhesion Promoters
- VIII. Adhesion Aspects of Thin Films
- IX. Adhesion Measurement of Films and Coatings
- X. Basics of Adhesion Measurement
- XI. Residual Stress and Material Mechanical Properties
- XII. Setting Adhesion Requirements for Coating Applications
- XIII. Adhesion Measurement at Atomic and Molecular Level
- XIV. Fundamental Adhesion Applications

Audience: Scientists and professional staff in R&D, manufacturing, processing, quality control/reliability involved with adhesion aspects of coatings and adhesion sensitive applications.

Level: Beginner- Intermediate; introduction/overview

Prerequisites: Elementary background in chemistry, physics or materials science.

Duration: 3 days

Course fee and materials: \$1,295, includes break refreshments, complete set of lecture notes and copy of handbook and reference guide ADHESION MEASUREMENT METHODS: THEORY AND PRACTICE, (CRC PRESS, 2006)

How You Will Benefit From This Course

You will understand advantages and disadvantages of a range of adhesion measurement techniques. You will be able to select the right surface cleaning technique including the use of atmospheric plasmas. You will utilize the concept of acid-base interactions in improving adhesion and acquire basic skills for addressing adhesion failure problems, analyze the alternatives and select the optimum technique for improving adhesion and structure durability. Know where help is available in emergency situations and learn how to select the best measurement technique for a given application.

Adhesion's Important Role Today

Adhesion plays an important role in many technologies and industries, viz., aerospace, microelectronics, automotive, thin films, optics, coatings, paint and so on. Broadly speaking, the topic can be divided into two categories: film or coating/ substrate combination and adhesive joints. Films and coating are used for a variety of purposes and irrespective of their intended function, these must adhere adequately to the underlying substrate. So the need for understanding and controlling the factors affecting adhesion is quite patent.

Furthermore, the durability of the bond (on exposure to process chemicals, moisture, corrosives, etc.) is of paramount concern and importance. This course presents an overview of the chemistry, physics and mechanics of adhesion in regard to understanding fundamental adhesion

mechanisms. You will learn how to improve and control them and the latest adhesion measurement techniques which are being used to evaluate the PRACTICAL ADHESION of coatings and laminate structures.

Emphasis is given to methods which can be carried out in a manufacturing environment as well as in the lab environment which give results that are directly relevant to the durability and performance of the structures under investigation. The effects of coating elastic properties and residual stress are considered as well as other external influences which affect durability under use conditions.

Learn From Internationally Recognized Professionals

This course is being taught by Drs. Kash Mittal and Robert Lacombe. Dr. Mittal is an internationally recognized authority on adhesion and surface science topics. He was Editor-in-Chief of the Journal of Adhesion Science and Technology one of the premier international journals in adhesion science for 25 years since 1987 and is currently editor of Reviews of Adhesion and Adhesives a prestigious journal that accepts papers by invitation only. He has also edited over 100 books dealing with all aspects of adhesion and surface and interface technology. His accomplishments in this field have recently been recognized at a special symposium in his honor at the 240th meeting of the American Chemical Society held in Boston, MA, August 2010. He has received many awards and honors and has given this course worldwide.

Dr. Lacombe has been involved in adhesion and surface science technology as a scientist and engineer in the microelectronics industry dealing with problems arising in the development and manufacture of multilevel thin film

structures at the heart of modern computer and hand held device technology. He has taught a short course on adhesion measurement methods for the past 15 years and has published an authoritative handbook and reference volume on this topic which will be made available to all students who attend the course.

Drs. Mittal and Lacombe have jointly organized over 60 international symposia dealing with all aspects of adhesion phenomena and surface science and have attracted the participation of the world's leading researchers on these topics. Much of the content of the course has been derived from this long and productive interaction with the world's leading investigators in adhesion and surface science. It is expected that the student

will benefit not only from the extensive experience of the instructors but also from face to face discussions on topics of particular interest.

INSTRUCTORS AND CONTACT INFORMATION

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For detailed information and registration:
www.mstconf.com/AdhesionCourse.htm