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Workshop on Adhesion and Intermolecular Forces

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Chemistry Division

AND

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This report provides an overview of a workshop on adhesion and intermolecular forces organized by the Surface Chemistry Branch of NRL and supported by the Office of Naval Research. The workshop was held 18-19 June 1992 in Alexandria, Virginia. A summary of the panel discussion is presented, as well as extended abstracts of most of the presentations

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WORKSHOP ON ADHESION AND INTERMOLECULAR FORCES

INTRODUCTION

Recent years have seen the development of a panoply of experimental and theoretical techniques to understand better the fundamental molecular-scale forces leading to adhesion. J. W. Mintmire and R. J. Colton of the Surface Chemistry Branch of the Naval Research Laboratory, supported by and in conjunction with P. P. Schmidt and R. G. Brandt of the Office of Naval Research Divisions of Chemistry, Physics, and Materials Science, organized a two-day workshop to bring together workers from several disciplines—adhesion science, surface science, polymer science, and engineering—that have traditionally looked at these molecular-scale aspects of adhesion from differing points of view. This workshop was held in Alexandria, Virginia from June 18–19, 1992. The mix of talks and posters covered an overview of the traditional engineering concerns of adhesion and bonding, as well as an overview of new surface spectroscopy, proximal-probe microscopy, and theoretical techniques for studying the molecular-scale aspects of adhesion and bonding of dissimilar materials. A principal purpose of this workshop was to aid in the planning of Advanced Research Initiatives in the field of adhesion science that begin in FY93 both at the Office of Naval Research and the Naval Research Laboratory.

Forty-eight scientists from around the United States participated in this workshop. The meeting began with two invited talks providing a general background and introduction to the principal theme of the workshop: how are adhesion and intermolecular forces interrelated and how are these two concepts experimentally quantified and measured. Matt Tirrell of the University of Minnesota presented a broad overview of the current status of the technological and engineering aspects of adhesion science, with a view as to how developments in new experimental techniques such as surface spectroscopies, proximal probe techniques, etc. can enhance our basic understanding of adhesion. Alan Gent of the University of Akron expanded directly on the theme of the workshop with an overview on the relationships—and differences—of adhesion to intermolecular forces and bulk properties.

These two overview talks were followed by five invited talks on specific topics in adhesion—theoretical methods, surface characterization methods, surface force measurements, failure mechanisms, and adhesion in fiber-matrix composites—by Anna Balazs of the University of Pittsburgh, Guy Davis of Martin Marietta Laboratories, Roger Horn of the National Institute of Standards and Technology (now at the University of South Australia), Wolfgang Knauss of Cal Tech, and Larry Drzal of Michigan State University, respectively. Seven contributed oral talks were presented in the areas of theoretical/computational methods and surface spectroscopy methods in the study of adhesion. Twelve additional contributed presentations were made in a combination oral/poster presentation: five minute oral presentation the afternoon of

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June 18 for each speaker with a maximum of two transparencies, plus more intensive discussion of the work that evening at a standard poster session. The meeting finished with a panel discussion—which was more precisely an open discussion of all the participants present—on where should adhesion research, particularly that supported by ONR, evolve over the next few years.

In this report, we present an edited report of the panel discussion and conclusions reached from the meeting, followed by the schedule and list of participants. The remainder of the report contains a set of extended abstracts provided by the participants as summaries of their presentations and current work in adhesion science.

PANEL DISCUSSION AND CONCLUSIONS

Overview

The last event on June 19, 1992 of the Workshop was a panel discussion with those present participating in an open discussion that focused on setting priorities in adhesion research over the next few years to a decade. Matt Tirrell, Wolfgang Knauss, Paul Hansma, Anna Balazs, Guy Davis, and Roger Horn acted as the panel in leading the discussion. The following is a condensed and edited version of a transcript of that discussion. Because of time limitations, the discussion was restricted to six basic questions:

1. Will adhesion science evolve into a science-driven field rather than a technology-driven field? Is this desirable?

2. Could anything useful or practical be done with a complete knowledge of the atomic-scale mechanisms of adhesion? If so, what?

3 Are experimental measurements likely to provide any important contribution to theoretical modeling of adhesion processes over the next few years? And the reverse?

4. Can atomic-scale theoretical simulations provide the equivalent of an engineering level simulation of a "*real*" material?

5. What are the critical gaps in our ability to measure the chemical and physical properties of interface/interphase regions?

6. What systems (e.g., metal/adhesive bonds, glass/adhesive bonds, composite materials, etc.) promise the best return for basic research over the next five years?

These questions represent three basic topics focused on during the workshop. The first question asks the nature of adhesion science: How widely and rapidly is it broadening from a tightly-focused engineering field to a multidisciplinary field bringing together researchers in basic chemical and physical properties of adhesive materials and bonding? The next three questions ask to extrapolate the role of theoretical modeling and computational simulation on adhesion science. The increase of resources available to computational simulation over the last several years has made possible the serious study of materials properties at the atomic-scale traditionally considered at the macroscopic scale within a continuum model. Finally, the last two questions ask how should research be directed in adhesion science over the next few years: what are the most important gaps in adhesion science to be studied, and what topics promise the best return for a given investment of time and resources.

Evolution of Adhesion Science

This point was addressed early in the discussion by Pete Schmidt, one of the organizers from the Office of Naval Research. In making some remarks about the purpose of a new Advanced Research Initiative in adhesion science at ONR, he stressed the value of theory in figuratively acting as a thread stitching together the fabric of fields of science.

> It is my opinion that we will learn something fairly substantial by pursuing theory... In other words, in physics and in chemistry there is an underlying theory. ... we will have an underpinning of theory that will give us a way to bring diverse information together to turn it into knowledge and to turn it into something we generally call wisdom. And I think that ... the calculations and the simulations, and theory that evolves from this study should lead to some sort of underlying thread that ties all of this together.

But before a broad theory can be constructed, a systematic body of empirical evidence must be amassed from the experimental data. Schmidt argues for more emphasis on organizing the experimental data gathered according to adhesive system :

> Will there be a science of adhesion that will be born of this effort and grow? ... in this very broad area of adhesion study, not science yet, should we be focusing some attention, certainly not all, but some attention on the nature of the systems that one studies. In other words, we want to join two dissimilar things together, but we have at least three macroscopic elements, generally,...
>
> Now, as many of you have emphasized I am talking about an adhesive. It's not just one thing, it has two interfaces at least and several interphases. That aside, should we be talking about metals bonded to plastic-based adhesives, polymer-based adhesives, or other kinds of adhesives? Should in fact there be a taxonomy developed for adhesion science which will enable us to sort things out and then focus attention on those particular items, and deal with the specific physics and chemistry that is involved in those cases, and then move on to the other? And then eventually try to look for general threads that tie it all together.

Matt Tirrell continued the discussion about adhesion science:

> It seems so obvious to me that it will [evolve], ... in my own personal view. How it is going to evolve is the big question. To me the biggest reason to focus on some of the particular scientific questions that we are pursuing right now and the direction that might have the shortest term payoff, is more in the direction of non-destructive evaluation, for example, than in the complete prediction of the outcome of a mechanical test—which is a very hard job. And so, my suggestion is that we not chastise ourselves too much for not being able to achieve these goals and for the gap that exists, but

> take the benefits that do accrue from being able in well-defined situations to relate well-defined chemical or structural or mechanical information to effects that you see...
>
> I think you are right in wanting to focus the attention on specific systems. I think there is a desire, but also a risk, in striving to be too general because you tend to get too spread out. You have to focus on some specific things. I would try to focus attention on what appear to be well posed problems, irrespective of the material... There might be some categories of adhesion where we are better posed to make progress, but I think that the attention ought to be fixed on whether an approach to a particular small problem makes sense.

John Venables argued that the basic science questions tend to evolve from the engineering problems and questions. He pointed out that his group's original focus on adhesive bonding at Martin Marietta had arisen from a real problem in gluing airplanes together. The group had done little work in adhesive bonding, but were able to draw on the talents of such people as Guy Davis—with experience in surface chemistry and surface analysis—to use scanning electron microscopy as a probe of the adhesive bond.

> The focus of that problem is really what started our efforts in adhesion, and then we realized that we could really start putting some science into this thing... The driving force was a real problem that came up and that we solved... I think that was a good example of a focus first, and then the science comes and everyone was driven towards getting some answers.

Pete Schmidt completed the specific discussion on this question by outlining more specifically some of the goals of the ONR program:

> ... what I had in mind was that this effort in adhesion evolves as science first, and then perhaps we begin to focus. The question is, are there a minimum number of fundamental systems that we could look at as general classes, and evolve some notions about these?... [One of our goals is to] try to eliminate to a certain extent the trial and error aspect of designing new adhesives... I am not asking for an omnibus solution, at this stage I am asking for some simple rules of thumb based on experimental knowledge and sound theoretical efforts.

Role of Theoretical Modeling and Simulations

The discussion began on the question of what practical outcome can be expected with large-scale computing available for atomic-scale simulations. Mark Robbins and Rich Colton pointed out that a similar discussion had been held at the NATO ASI on the fundamentals of friction in Braunlage, Germany in August, 1991. Mark Robbins stated that simulations connecting the microscopic scale and the macroscopic scale had been done in a few cases:

> I think it is not necessarily trivial, but it can be done, and that's what one would like to do here by looking at the atomic-scale mechanisms, figure out what the constituent relations and boundary conditions are, and then we can use it to understand at the larger scale.

Rich Colton continued:

> What you might recall from the discussion in Braunlage, is that the definitive answer [to the second question] was no... However, one of the issues that was agreed upon was that for friction and adhesion energy, dissipation mechanisms are very important, particularly in friction, and that perhaps you need an atomic-scale measurement system or modeling system to understand that part of the phenomenon.

Steve Hues addressed the situation that atomic-scale is the appropriate scale for many properties defined by the grain-boundary dimensions of a structural material.

> I would like to comment about the application of the nanoscale type measurement, for example, to building an airplane. I think it has direct relevance, especially with advanced materials. You cannot machine the airplane out of a single crystal. Most of the materials, particularly the advanced intermetallics, are intrinsically filled with grain boundaries. The effects of these grain boundaries occur on the scale of some tens of Angstroms, and the only way you can address how to modify the interface—so that you can build an airplane wing out of a particular material—will be to examine what is the effect of the given chemical modifications on the interface and on the structure and mechanical properties on that atomic scale.

Elliot Bernstein commented both on the question of the evolution of adhesion science and the role of theoretical simulation:

> What I have noticed about science in general ... is that it has been moving in the direction of studying complexity. ... This seems to fit exactly with the work we are talking about here. The concepts of adhesion and interfaces and interphases appear to be moving in that direction, going from simple things we know about fundamental science into systems that are much more complex. This trend is happening not just in adhesion science or surface science but in studying chemical reactions, in studying physical systems,

> chaotic systems, etc. and computational simulations now. So I think that movement in this direction with both engineers and fundamental scientists in chemistry and physics is not a unique direction, but a general direction science is moving in.
>
> And as for the second question, if we can not learn more about or do something useful with the fundamental understanding of the adhesion process on a molecular level, that indeed will be very interesting and probably end up being very unique because everything else that I have ever understood on a molecular level, I have always been able to extrapolate to important more practical applications.

The discussion moved on to how experimental measurements could provide useful information for theoretical modelists, and somewhat conversely, can atomic-scale theoretical simulations be used in a predictive fashion on real materials in the near future?

Mark Robbins:

> In addition to characterizing different types and pairs of materials, theorists can also make immediate progress on identifying processes, things like cavitation, peeling, the effect of roughness, the effect of cross-stitching, how all these processes occur. I do not think that these are really known yet from the macroscopic scale, and I think theorists can play a big role in trying to understand those processes in a generic sense, and hopefully that will help in organizing data in terms of understanding how different materials behave in different ways, what type of material properties will help in optimizing those processes.

Wolfgang Knauss commented on the utility of atomic-scale simulations providing predictive results for macroscopic-scale structures:

> It is my conviction over a number of years that theory by itself is not going to do it... Consider the size scales. On one hand you are talking about an Angstrom size scale, on the other you are talking about the airplane. That is more than nine orders of magnitude. There is no way that you can easily bridge that. I think the need for the theoretical or the molecular aspects is about what happens at the submicro or micro scale, where we have difficulty even with the force microscopes [to make definitive measurements] ...
>
> At NASA, about ten years ago, higher administration said that we do not need experiments anymore, we do not need wind tunnels, we will do it all on the computer. So they discouraged the experimental side, and they now are back to running tests on the wind tunnel because they can not handle all the microscopic and macroscopic stuff. They need to verify their models, and they have to fix up things that they did not consider. So I think that is where the interface will have to be at the microscopic scales, at least from my perspective. The macroscopic properties, we can measure very well,

> but when it gets down to a micron and smaller dimensions, it's going to get very tough. That is where a lot of the adhesion problems go on.

The discussion moved into the topic of using atomic-scale simulations for larger scale macroscopic problems. Karl Sieradzki comments:

> I just wanted to address one issue with respect to the usefulness of the atomic-scale simulations for larger scale macroscopic problems: that you could use an atomic-scale simulation to elucidate one or two real mechanisms. For example, there may be a response in an overall macroscopic process. The simulations can help you understand (on the small scale) how the overall macroscopic behavior of something such as an adhesive failure may evolve. The people who do the simulations in general do not try to simulate a large macroscopic structure. Usually small problems are looked at, and they are looked at over relatively short scales.

John Mintmire:

> Let us choose a simple example for the theorists just as a survey. Let us consider something that is really at the microscale: crack formation and crack propagation. Is there a chance of atomic scale modeling to give a really comprehensive treatment of these processes, and these are something that actually should be at the atomic scale—no, you are not going to do an atomic-scale simulation of an airplane, but can we do something that will really provide fundamental insight into those processes that a continuum mechanics model could not?

Mark Robbins:

> I think the answer is yes. I do not know if you remember from Braunlage, there are simulations by Jim Belak [Lawrence Livermore National Laboratory] for a machining tool tip which has quite a few atoms inside it. I believe that he uses about a million atoms in this simulation as a whole. He actually drags the tip into a material, watches a chip fly off, watches the crack propagate, and calculates temperature fields and strain fields. And away from the cracked tip the results look very much like one gets from continuum calculations, plus one has all the richness of what happens right at the tip, The simulation is not really designed for crack propagation per se, it was designed more for machining, but you could extend that to the simple crack opening problem. It would be an easier problem.

Karl Sieradzki:

> I think that the crack problem has been looked at already... One of the difficulties in doing this simulation on the crack problem—or the major difficulty right now—revolves around not having good interatomic potentials for modeling interface cracks or even for modeling cracks in homogeneous

materials... If we had good interatomic potentials I think that we could go much further than we are now with the crack problem.

Wolfgang Knauss:

What he just said, at least to me, sounded like you have a particular model in mind where you talk about crack propagation as the separation of two layers of atoms. Very specifically, what happens in most cracks that I have seen, is that you rearrange the whole molecular and atomic structure around the tip of the crack over a domain that is on the order of microns for a system, not on the atomic scale.

Elliot Bernstein:

That may be very correct, but what he says is the main point. If you have good interatomic potentials, which is the problem in chemistry, which is the problem in physics, which is the problem in solution theory, if you have good potentials, one should be able to show that he's wrong and you're right or that you're right and I'm wrong.

Karl Sieradzki:

You can learn about the general principles without using good interatomic potentials. You could use it with a general interatomic potential, but if you want to model a specific metal/polymer interface or metal/metal interface ... and you want to check for things like dislocation behavior at an interface, then you need to have good potentials. If you want to look at general things, microscopic phenomena, then you can just use a general potential and qualitatively you will see that you will get good physics out of it. But if I want to model something like an aluminum oxide/silicon oxide interface, and I want to get behavior that I can use to predict engineering lifetime, then you will need to have good interatomic potentials.

Jonathan Harris:

I think the first stage is to use molecular models to capture the major physics, have reasonable potentials, maybe not as correct or precise enough to give quantitative results, but at least can give us an intuitive feel of the physics of the system and how it is related to the chemistry. ... If we start to get into whether this adhesive will be stronger by X amount than this adhesive quantitatively within 10%, then we will have trouble in getting those intermolecular potentials even from accurate quantum calculations. Secondly there are problems that do not even involve the intermolecular potentials, such as relaxation times of materials and impurities.

Future Directions in Adhesion Science Research

The last topic discussed involved where the adhesion science research discussed at the workshop should head. Two questions were outlined for this topic: what are the critical gaps in our ability to measure the physical and chemical properties of the important interphase regions in bonding, and what classes of adhesive bonds bear the most promise for intensive research over the next five years?

For the question on what are the critical gaps in our ability to measure properties of the interphase, several key areas stood out. John Venables began the discussion involving the discrepancy between the forces measurable by current atomic force microscopy techniques and the strong covalent forces present in adhesive bonds:

> The atomic force microscope, such as the results presented at the workshop today and yesterday, deals with van der Waals and electrostatic forces. However, those are not the types of forces that you build an airplane with. It is a completely different situation where much stronger bonds are needed, so I see a big gap here. I see a big gap from what we can learn with atomic force microscopy as it exists today, and what is needed about more information on how to build structures... The point ... is, can you handle stronger forces with an atomic force microscope, the chemical forces for example rather than van der Waals forces... ?

Paul Hansma had spoken earlier in the day on advances in atomic force microscopy incorporating zero deflection methods for force measurement which show potential for treating such covalent forces. He responded to John Venable's comment at a later point in the discussion:

> Right now, there are covalent forces in some of the [AFM] measurements. They are strong forces, but we do not really see anything about them. All we see when there are strong forces is that the tip sticks, and we have to pull like crazy to pull it off and that is all we can measure. So at the moment, those forces are there, but they are hiding from us... That is why I am saying we need this strong force feedback [technique] to keep the tip from snapping in when those strong forces are present.

Another point brought out at the workshop was the effect of the bond formation process on the adhesive bond is frequently not considered in studies, with a comment here by Larry Drzal:

> I would like to make a comment on the materials aspect. There is a common factor in all this that gets beyond the materials, and that—from my perspective—is if you look at adhesion, you are always putting a polymer in contact with a solid surface, and it is always going to the liquid state. What you ultimately want to know is how that surface—regardless of what it is—effects the ordering of that polymer near the surface and how it holds that ordering through the solidification phase until it is a solid, because the

> properties of that polymer near the surface are going to control its behavior in the solid state.
>
> Now, on the one hand, you might take any material substrate whether it is a metal, inorganic, whatever, and through various types of surface treatments, control whatever type of chemistry, or biology, or topography you want on that surface. So from that viewpoint, if you are going to concentrate your efforts, you should be looking at the ordering that occurs, and the effect of the solid surface on the structure in the liquid-modified solid state of the polymer.

Another critical gap in the infrastructure of adhesion science research was the diversity of fields involved in the area, discussed by Bill Unertl:

> From a viewpoint of someone ... outside the adhesion community, it is important to have forums like this where you have a chance to talk with someone who is studying mechanical properties so that you can have an idea of what the problems are. ... You need that external input from other people who are working on the related probems to help you decide ... which ones are going to be most interesting, or which experiments will have the most impact.

Finally, on the topic of critical needs in adhesion science, Alan Gent has offered the following unsolved problems:

(a) Accurate methods for chemical analysis at interfaces.

(b) Quantitative understanding of rheological effects.

(c) Mechanical analysis of test methods and failure processes.

(d) Methods for non-destructive evaluation of adhesive bonds.

(e) Methods for estimating durability or service life.

On the straw vote for the most promising system to study over the next five years, the results were mixed. We asked the audience what basic class of adhesive bonds they would rank as most important for research potential over the next five years.

Paul Hansma:

> Polymers on oxides would be my choice. When we talk about gluing aluminum or gluing something like that, but it is not really aluminum; it is aluminum oxide.

John Venables:

> Well, I would suggest some emphasis on printed wiring boards. There is everything in that system that you could possible imagine. There are epoxies, all types of metals, and bonding to them, one to another. [At Martin-Marietta] we have more problems with printed wiring boards than we ever had with anything else. ... [Printed wiring boards] are mostly composites, so I would vote for composites.

Guy Davis:

> The question basically states certain things that I do not think necessarily have to be identified with systems. It could, I would think, be more problem oriented by picking the system which is best suited. One example might be if you want to study the durability of an adhesive bond. In that case probably the metal- adhesive system would be your best simulant. If you wanted to look at bond formation, maybe metal-oxides or composite materials would be the appropriate sort...

Pete Schmidt wrapped up the comments on this question:

> I would like to have you walk away with the notion that, while you will pursue your own interests, at least let us start thinking about some sort of thread that runs through all of this field. Then I think we all have some appreciation of the other person's interest and research, perhaps can borrow more intelligently, and contribute more intelligently to each others research.

Conclusions

Throughout the talks and discussion at the workshop, two major critical needs in engineering applications of adhesion science were made clear:

1. the need for methods for non-destructive evaluation of adhesive bonds; and,
2. the need for practical methods for estimating the durability or service life of an adhesive bond.

These needs reflect the current trial-and-error status of much of the experimental data on adhesive systems. Further substantial progress in adhesive science depends on increasing our fundamental understanding of the adhesive bond. The concept of the interphase region in adhesive bonds has evolved over the last several years and is critical in understanding the properties of adhesives and adhesive bonds. Progress in the fundamentals of adhesion science hinges, therefore, in improving our understanding of the structure and properties of the interphase. The field of adhesion science is poised for such progress both in experimental and theoretical/computational areas.

First, efforts must be made to systematically organize what is already known about adhesive systems, for example, by classification of adhesive bonds. Advances in theoretical and computational simulations will require a coherent body of experimental information for parameterization and validation of theoretical models.

Second, the past decade has seen a remarkable advance in experimental probes of atomic-scale properties. These approaches, such as the surface-force apparatus and proximal probe techniques in conjunction with developments in atomic-scale simulations, promise a substantial return in understanding the basic properties of the interphase in adhesion, and thus on the fundamentals of the adhesive bond.

Schedule of Presentations

Workshop on Adhesion and Intermolecular Forces

June 18–19, 1992
Alexandria, VA

Thursday, June 18, 1992

8:30–9:00	P. P. Schmidt, *Office of Naval Research* *Introductory remarks*
9:00–10:00	M. Tirrell, *University of Minnesota* *Current methods and issues in adhesion science*
10:00–10:30	*Break*
10:30-11:30	A. N. Gent, *University of Akron* *Adhesion, intermolecular forces, and bulk properties*
11:30–13:30	*Lunch break*
13:30–14:15	L. T. Drzal, *Michigan State University* *Molecular, microscopic, and macroscopic aspects of fiber-matrix adhesion in polymeric matrix composites*
14:15–15:00	W. G. Knauss, *California Institute of Technology* *Failure mechanisms in adhesion*
15:00–15:30	*Break*
15:30–17:00	5 minute poster previews
17:00–19:00	*Dinner break*
19:00–20:00	Poster session

Schedule of Presentations

Workshop on Adhesion and Intermolecular Forces

June 18-19, 1992
Alexandria, VA

Thursday, June 18, 1992

19:00-20:00 Poster session

Douglas T. Smith, *NIST*
Electrostatic adhesion resulting from spontaneous charge transfer between dissimilar materials

Kenneth Liechti, *University of Texas, Austin*
Toughening mechanisms in mixed-mode interfacial fracture

Judith A. Harrison, *NRL*
Molecular dynamics simulations of atomic-scale friction and adhesion of diamond systems

Tom Furtak, *Colorado School of Mines*
Methods for optimizing Raman sensitivity allowing characterization of buried interfaces

Frank S. Bates, *University of Minnesota*
Making and measuring tailored polymer interfaces

J. Washiyama, *Cornell University*
Optimum toughening of homopolymer interfaces with block copolymers

Howard Mizes, *Xerox Webster Research Center*
Polymer-particle adhesion probed with atomic force microscopy

William N. Unertl, *University of Maine*
Interfacial adhesion studies of polyimides with the scanning force microscope

Jiong-Ping Lu, *Massachussetts Institute of Technology*
Characterization of interface chemistry and adhesion of polyimide to Cr and Al

Maria M. Santore, *Lehigh University*
An evanescent wave probe of kinetic phenomena in polymer layers adsorbed on solids

J. E. Houston, *Sandia National Labs*
Mechanical properties and adhesive behavior of monolayer organic films

S. E. Wentworth, *US Army Materials Technology Lab*
Overview of MTL adhesive bonding program: molecular dynamics simulation of adhesive/adherend interactions

Schedule of Presentations

Workshop on Adhesion and Intermolecular Forces

June 18–19, 1992
Alexandria, VA

Friday, June 19, 1992

8:30–9:15	G. D. Davis, *Martin Marietta Laboratory* *Surface spectroscopy methods in adhesion*
9:15–10:00	R. G. Horn, *National Institute of Standards & Technology* *Adhesion measurements using the surface force apparatus*
10:00–10:15	*Break*
10:15–11:00	A. C. Balazs, *University of Pittsburgh* *Theoretical models of how polymers can bind dissimilar materials*
11:00–11:20	J. G. Harris, *Massachussetts Institute of Technology* *Molecular simulations of thin alkane films between structured surfaces: effects of molecular geometry*
11:20–11:40	A. K. Chakraborty, *UC Berkeley* *Near-surface structure and dynamics at strongly interacting polymer-solid interfaces: implications for adhesion*
11:40–12:00	Mark O. Robbins, *Johns Hopkins University* *Phase transitions and dynamics in confined films*
12:00–14:00	*Lunch break*
14:00–14:20	W.-L. Wu, *National Institute of Standards & Technology* *Polymer/solid interfaces: a neutron reflectivity study*
14:20–14:40	F. J. Boerio, *University of Cincinnati* *Non-destructive characterization of polymer/metal interfaces*
14:40–15:00	Paul Hansma, *UC Santa Barbara* *Quantized adhesion observed with the atomic force microscope*
15:00–15:20	R. J. Colton, *Naval Research Laboratory* *Interpretation of force curves in atomic force microscopy*
15:20–16:00	*Break*
16:00–17:00	Panel discussion: *Whither adhesion?*
17:00	*End of meeting*

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Current Methods and Issues in Adhesion Science

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Overview

Adhesion refers to the process of joining originally separate pieces of material in a way that the joint becomes capable of transmitting mechanical stress. This can occur by direct contact between the two pieces, as is sometimes the case in welding of metals or polymers, or more frequently, by interposing an adhesive, usually a polymeric material, between the two pieces. In either case, several important processes come into play. Chronologically, during the process of joining, these process include: the establishment of contact, or wetting; chemical or physical interaction, as in reactivity or adsorptivity; establishment of structure at and near the adhesive bonding surface.

When the mechanical strength of the adhesive bond is tested to failure, another set of processes comes into play. Part of the work expended in the separation process goes into the thermodynamic energy required to create (or recreate) surface area. A substantial, often an overwhelmingly dominant, part of the work also usually goes into deformation processes of the material in or near the adhering surfaces. These surface chemical (or thermodynamic) and mechanical contributions to adhesion are difficult to separate in a quantitative experimental fashion. The best evidence [1-3] suggests that they contribute in a multiplicative manner. We shall express this idea in the following way:

$$W_p = W[1 + \phi(a_T v)] \tag{1}$$

where W_p is the practical work of adhesion measured in a mechanical experiment, W is the thermodynamic work of adhesion (the free energy change or reversible work done to separate unit areas of two pieces of material) and ϕ is a mechanical energy dissipation factor that depends, *inter alia*, on the rate of the deformation, v, and the temperature through the factor a_T. This equation implies that, even if the second term dominates the <u>magnitude</u> of W_p, the surface energetics still play a key role. If there is no basic attraction, or thermodynamic work of adhesion, the defomation processes that expend large amounts of energy in resisting separation cannot enter effectively into play.

In the technological practice of adhesion, this means that surface chemistry and rheology are both very significant in improving and manipulating adhesion. Surface chemistry is crucial but larger scale changes in the magnitude of adhesion are possible through rheological effects. From the point of view of advancing adhesion science, it must be recognized that both factors enter virtually every mechanical test of adhesion, so it is difficult to deduce clean conclusions about one factor or the other from mechanical tesing alone.

Adhesion Tests at Different Length Scales

An important direction in measuring the forces of adhesion has been in refining the measurement so that it is made over smaller contact areas [4]. Several advantages accrue in this way. Since for given materials and deformation rates the mechanical energy dissipated per unit volume due to deformation is determined, the total amount of energy dissipation (an extensive property) can be diminished by reducing the amount of material brought into play in the force measurement. This does not mean that deformation effects can be eliminated, even at the smallest scales [4, 5], however, one can approach more easily a limit where the thermodynamic surface energy can be measured at small scales. Accurate determination of the surface energies of solids is a problem of longstanding, owing to the difficulty with which surface area can be reversibly created and destroyed in solids [6]. In addition, the ideal of defect-free contact can be more nearly realized over small contact areas, along with the added advantage of being able to probe for lateral heterogeneity and structure on the scale of the contact area.

Macroscopic adhesion tests are essentially fracture tests and, like the cohesive or bulk fracture of a material, they require an understanding of the mechanics in the separation zone and of the material deformations that are caused by this mechanical situation. Adhesion tests based on fracture mechanics have recently had the most development at the macroscale [7]. Well-defined fracture mechanics tests give results for G_c, the critical value of the strain energy release rate necessary to separate the surfaces. G_c is equal to the energy required per unit of new surface area formed and as such is equal to W_p for a fracture mechanics test. G_c, in these tests, is usually orders of magnitude larger than W.

At smaller scales (meso- to nano-scopic), tests based on the theory of <u>contact mechanics</u>, rather than <u>fracture mechanics</u>, are proving increasingly useful [8,9]. These theories account for deformation but assume that it occurs elastically, incurring no energy dissipation. These analyses are useful when the forces of attraction between the two solid bodies in contact are not very strong and so do not engender plastic deformation in resisting separation. The details of the analyses are involved [10] but the basic idea of the result can be gained from a simpler argument [8]. For the sake of simplicity, consider a sphere of radius R brought into contact at zero external load with a flat surface of exactly the same constitution. Attractive forces between the surfaces produce a finite contact radius, a, established by the balance between stored elastic energy in the deformation of the bodies and diminished surface energy owing to the contact. This reduction in surface energy, E_s, is related to the surface energy per unit area of the solid, γ, by: $E_s = -\pi a^2\gamma$. The force associated with this energy change is $F_s = -dE_s/dx \sim E_s/x$, where x is the movement of the center of the sphere toward the plane, relative to their initial undeformed contact position. This movement x can be estimated from the classical elasticity theory of Hertz [10] for nonadhesive bodies, which says that $x \approx a^2/R$. Combining these equations shows that the force of adhesion will be approximately: $F_s \approx \pi R\gamma$. The detailed energy balance of Johnson, et al [8] gives the coefficient:

$$F_s = 3\pi R\gamma. \qquad (2)$$

The accuracy of this coefficient continues to be the object of some debate, owing to some simplifying assumptions made in deriving it [8], however, experimental evidence mounts that the basic theory is correct in several of its other testable predictions [8, 9,11 - 13], for example concerning the shapes of the deformed bodies, particularly when the materials in question are relatively soft.

Equation 2 can be used to determine the thermodynamic work of adhesion, W= 2γ, if there is no dissipation occurring on breaking the contact. With respect to the idea of testing adhesion at different scales, Equation 2 provides the systematic means to analyze contacts formed between curved bodies of various sizes, down to the nanoscale [4]. Recent experimental work [9, 12, 13, 14] has shown there often to be hysteresis in the compression and expansion curves associated with making and breaking contact, suggesting that there is more involved in the process than simple elastic deformation and creating or eliminating surface area. Greenwood and Johnson [15] have analyzed the effects of viscoelasticity on this theory and illustrated the connection between the theory of contact mechanics and that of fracture mechanics. Rheology and deformation thus appear to be key factors in most experimental contact mechanics tests, as well, and further analysis is needed to interpret the results.

The Role of Rheology in Adhesion

Rheology enters into observations of adhesive strength through the second term of Equation 1. Generally, the magnitude of this term increases rapidly with increasing rate of deformation during the adhesion test. For example, the surface energies ($W/2 = \gamma$) of most polymers are in the range 25 to 45 mJ/m^2. Peeling two rubbery polymer surfaces apart after establishing good contact between them can easily require W_p = 25 to 45 J/m^2 for peeling at a rate of 1 mm/s [1], that is, a factor of 1000 greater than the thermodynamic surface energy. It is very difficult to perform most common practical adhesion tests at rates sufficiently low that the second term of Equation 1 is negligible. Furthermore, these rheological effects are strongly temperature dependent. The factor a_T embodies the idea that an adhesion test at a certain deformation rate and temperature may give identical results to a test at a higher rate and a lower temperature. Abundant evidence of this exists for polymers [6] and, in fact, the "shift factors", a_T, are often quite closely related to those determined by measuring temperature dependence of the viscoelastic relaxation processes of the bulk polymer as functions of the frequency or rate of deformation.

The implication of the dominant effect of rheology under most practical circumstances of adhesion is that any search stronger adhesion should be centered on the deformation characteristics of the materials involved, while respecting the dictates of Equation 1, that surface energy plays an indispensible, if not dominant, role.

Theories of Adhesion

The aim of the various theories of, or relating to, adhesion that have been proposed [16] are to analyze the behavior of particular structures of adhesive surface regions under certain deformation conditions in order to predict quantitatively the contribution they make to one of the terms of Equation 1. Different theories have in the past been represented as though they were competitive with one another, but this is not generally true. More often, different theories have been developed to describe different effects or different situations. An comprehensive theory of adhesion does not exist.

Chemical or adsorption theories focus on the formation of bonds at the adhesion interface and on the contributions of surface energetics, namely the first term of Equation 1. The models based on acid-base interactions, advanced by Fowkes and coworkers [17], fall into this category. Interdiffusion and mechanical interlocking theories concentrate on the effects of physical/mechanical engagement between the two adhering pieces, and on the energies and forces required to pull them apart. Some of these relate to microscopically textured materials [18]; others refer to molecularly entangled polymers [19-21]. The aim of these models generally is to predict the ϕ term in Equation 1. There is a very active body of current experimental work aimed at testing predictions of these models for polymer materials [7], fueled by the fact that these models make predictions that are readily examined, such as the molecular weight dependence of W_p, provided that the idealized conditions of the models can be realized in the laboratory.

A third category of theoretical work is based on electronic structure. Early attempts in this direction were made by Deryaguin [22], and were basd on the idea that, for contacts between dissimilar materials with different electronic band structures, electron transfer can occur on contact to balance the Fermi levels, creating an electrostatic double layer and resultant electrostatic attractions at the adhesive interface. Recent experimental work has provided particularly convincing evidence of this phenomenon [23]. Modern electronic structure models of adhesion are based on quantum mechanics [24] or on simulations using realistic interatomic potentials [25].

Outlook

Advances in understanding of adhesion will come, in the foreseeable future, from more detailed studies of the relationship of structure to strength in various kinds of adhesive interfaces. Implicit in what is required for this advance is the ability to create, control, characterize and measure mechanical strength on the desired microstructures. Characterization will demand new surface analytical techniques [26,27] and computer simualtion and theory can be expected to play a continuing important role. The need for developing this understanding of the connection between structure and adhesion goes beyond that desire for intellectual satisfaction. One of the principal drawbacks to advancing the applications of adhesion is the near absence of nondestructive tests, that is how can one assess the current state of an adhesive bond, breaking it, and yet predict its adhesive performance. This is, at the same time, the most fundamental and the most practical question in adhesive science and technology.

References

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Molecular, Microscopic and Macroscopic Aspects of Fiber-Matrix Adhesion in Polymeric Matrix Composites

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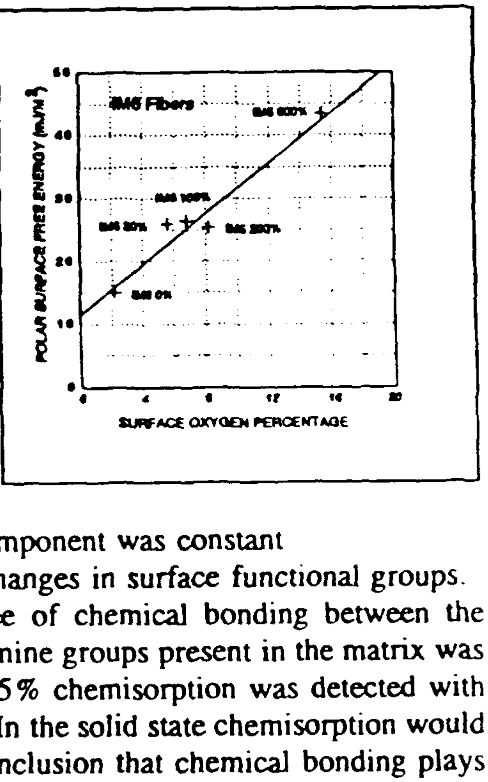
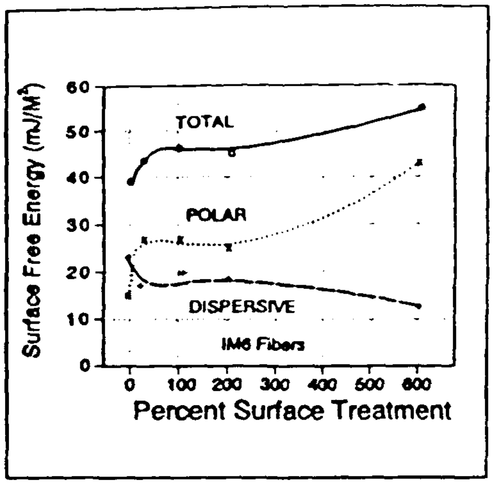
The results of an ONR supported program on developing the relationships between fiber-matrix adhesion and composite mechanical properties have established a linkage between molecular and microscopic level events with composite macroscopic mechanical behavior. For the thermoset amine-cured epoxy/IM6 carbon fiber composite system studied, it has been shown that phenomena taking place at the molecular level (fiber surface chemistry, fiber surface energetics), microscopic (polymer interphase structure, mechanical and fracture properties) and at macroscopic levels (composite shear, 90° flexure and Mode II fracture toughness) are interrelated and must be considered simultaneously in order to both understand the principles of fiber-matrix adhesion as well as to relate them to composite mechanical performance.

Molecular Level A series of IM6 fibers with 0%, 20%, 100%, 200% and 600% electrolytic anodization surface treatment levels were analyzed by Xray Photoelectron Spectroscopy (XPS) to quantify the changes in surface chemical composition with treatment. Major changes in the surface chemistry took place after the 20% surface treatment and significant but less drastic changes were noted with increasing surface treatment times. Both oxygen and nitrogen levels increased resulting in a surface with an increasing carboxylic acid and amine type functionality. Measurement of the surface energetics of these fiber surface also showed a corresponding increasing in the solid surface free energy as measured by contact angles. Extraction of the polar component of the surface free energy for these fibers showed that the dispersive component was constant while the polar component changed identically with the changes in surface functional groups.



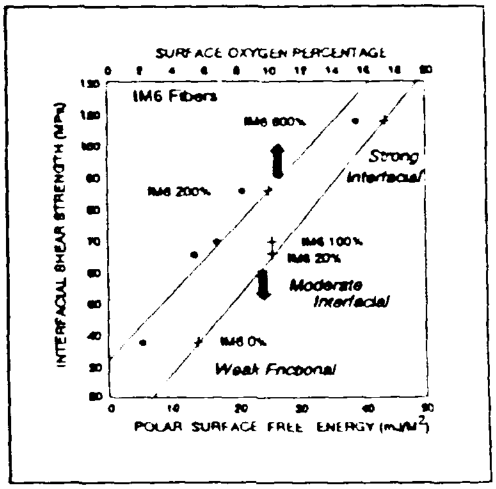
A new solution method for measuring the degree of chemical bonding between the chemical groups on the fiber surface with the epoxy and amine groups present in the matrix was developed[1]. For the 100% surface treated fiber, only 3-5% chemisorption was detected with epoxy and amine groups and none with hydroxyl groups. In the solid state chemisorption would be expected to be less than this amount leading to the conclusion that chemical bonding plays a minor role in fiber-matrix adhesion between carbon fibers and amine cured epoxies.

Based on earlier work, it was concluded that the 20% surface treatment level provided the largest increase because of the removal of the structurally weak native fiber surface and that subsequent surface treatment increases contributed primarily to the increase in surface functionality of the fiber[2].



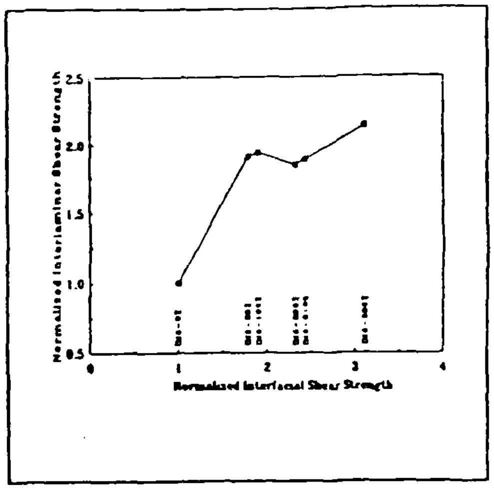
Microscopic Level The structure of the polymer near the fiber surface has been hypothesized as being the controlling factor in transferring forces from the fiber to the matrix and hence responsible for both fiber-matrix adhesion and the resulting composite properties. In order to investigate this hypothesis, epoxy-amine matrices with identical chemistry but varying in crosslink density and hence mechanical properties were prepared using a series of di- and tetra-functional epoxies with primary diamine curing agents having increasing long polyether backbones. This gave a range of epoxies with decreasing moduli and increasing strain to failure. A single fiber fragmentation specimen was used to quantify the adhesion level and document the interfacial failure mode. When these matrices were combined with the same carbon fiber, a systematic decrease in fiber-matrix interfacial shear strength was noted with decreasing matrix modulus. A linear elastic model was successfully used to model this change and documented that the fiber-matrix interfacial shear strength is linearly related of the product of the strain at failure of the matrix with the square root of the matrix shear modulus[3].

The role of the interphase matrix on fiber-matrix adhesion was further verified by measuring the temperature dependence of the fiber-matrix interfacial shear strength. It was found that superposition principles could be applied in the same manner to the interphase as to a bulk polymer. When a 100 nm thick coating of pure epoxy was applied to a carbon fiber surface and fabricated into a composite, a marked change in the temperature dependence of the fiber-matrix interfacial shear strength was noted[4]. This shift was attributable as being due to the creation of a higher modulus, lower toughness interphase around the fiber during the processing of the composite. The higher modulus increased the fiber-matrix interfacial shear strength by the lower toughness caused matrix cracking at the point of fiber failure. The results coincide with the hypothesis that the matrix interphase properties control adhesion at the single fiber level. Recent results with a glass fiber finished with a commercial sizing are another example that this model is capable of explaining fiber-matrix adhesion[5].



Macroscopic Level Single fiber measurements were made with the IM6 fibers having increasing surface treatment levels. Increases in the single fiber interfacial shear strength were measured. These increases corresponded directly with the changes in both fiber surface chemistry and fiber surface energetics.

Composites made from the same fibers and matrix and processed in a manner similar to the single fiber specimens. Composite shear, 90° flexure and toughness measurements were made according to accepted standards. Results were normalized and compared with the fiber-matrix interfacial shear strength. For the short beam shear and flexural strength, a major increase was detected after the 20% surface treatment but little additional change was measured with longer surface treatment times. The composite Mode II fracture toughness continually increased with increasing surface treatment times however. Based on examination of fracture surface and the interfacial failure from single fiber measurement methods, it was concluded that the close proximity of fibers in an actual composite prevent increases in fiber-matrix adhesion from increasing shear or 90° flexural properties. In the fracture toughness measurements however, additional work has to be done to fail the fiber-matrix interphase with increasing adhesion causing the overall composite fracture toughness to increase. This was in close agreement with a series of studies conducted with a lower modulus AS4 fiber published earlier[6,7].



Conclusions Molecular level events such as increases in surface functionality are a necessary precursor to increasing fiber-matrix adhesion through increases in fiber-matrix dispersion type interactions and increases in fiber surface energetics and wettability. However, the actual structure and properties of the matrix in the 100nm interphase region around the fiber has been shown to control fiber-matrix adhesion levels. The shear modulus of the matrix in the interphase coupled with its fracture properties can explain the composite mechanical properties and their dependence on fiber-matrix adhesion. This interphase structure can occur because of the influence of the surface on the reacting matrix or may be created through the use of fiber sizings and finishes. Results obtained with different fibers indicate that these relationships are generic and applicable to carbon fiber adhesion to thermoset matrices.

References

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Surface Spectroscopy Methods in Adhesion

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Modern surface spectroscopies, including X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES, SAM), and secondary ion (neutral) mass spectrometry (SIMS, SNMS), have made significant contributions to the understanding of adhesion and to the development of improvements in adhesive bonding. In conjunction with other material analysis techniques, they have been used to characterize adherend surfaces, metal (oxide)-polymer interphases, and failure surfaces. These investigations have allowed correlation of surface properties with bond strength and durability and determination of bond formation and degradation mechanisms. This information, in turn, has led to improvements or modifications in surface treatments, processes, and materials.

The classic approach to investigate bonding surfaces is to characterize them following various steps of the treatment/preparation procedure, prior to bonding, after environmental exposure of bare surfaces, and after bond separation (with or without aging). Investigation of buried interphases is more difficult. Conventional surface analysis techniques can be used in conjunction with means to expose the interphase, e.g., ion sputtering, angle lapping, or chemical etches. However, care must be taken to prevent artifacts caused by the material destruction, e.g., preferential sputtering or etching or ion mixing, from affecting the interpretation of the results. Nondestructive methods of interphase investigation include stepwise construction of an overlayer combined with characterization of the interphase as it is formed and the use of techniques that utilize the compositional differences or asymmetry of the interphase. These methods include surface enhanced Raman spectroscopy (SERS), second harmonic generation (SHG), sum frequency generation (SFG), Rutherford backscatter spectroscopy (RBS), nuclear reaction analysis (NRA), extended x-ray absorption fine structure (EXAFS), and x-ray absorption near-edge spectroscopy.

To elucidate mechanisms for bond formation and degradation, it is often desirable to change one parameter or characteristic of the surface or interface without changing any other property. Frequently, this is easier said than done. An illustrative example where it has been acheived is aluminum adhesive joints. By independently varying the adherend surface morphology and chemistry, it was established that 1) adherend oxide microroughness is needed for strong, durable bonds, especially those using epoxy adhesives, 2) adherend surface chemistry must be compatible with the adhesive to allow wetting and interpenetration of the "nooks and crannies," 3) coupling agents can be used to form chemical bonds between the oxide and the polymer, 4) hydration of the oxide surface is the limiting factor in the lifetime of these bonds, and 5) hydration can be slowed with the use of inhibitors. These findings help to explain the superior performance of joints using phosphoric acid anodized (PAA) adherends and has led to means to stabilize the interface and increase bond durability.

Recent and anticipated advances in technology, together with the driver of increased requirements for applications, should allow important gains in both the understanding of bonding mechanisms and adhesive joint performance and reliability. Improvements in the capability to characterize surfaces and interphases and to interpret the data will enhance our ability to achieve these gains. Particular needs in characterization include better chemical species identification, improved lateral resolution, ability to perform surface analysis in ambient environments (including liquid immersion), and ability to characterize buried interphases nondestructively. Although not all of these measurements are routine or readily available, current technology allows many of these needs to be met, at least partially. For example, improvements in the standard surface analysis techniques (XPS imaging, spatial and energy resolution, and speed; SAM spatial resolution and speed; and SIMS/SNMS higher sensitivity, mass resolution, and quantification) have resulted in improved characterization of heterogenenous and damage-senstive materials. New techniques extend the information available even further. Scanning tunneling and atomic force microscopy (STM, AFM) allow nanoscale resolution of surfaces in ambient environments and SERS, SHG, and SFG allow buried interfaces to be probed.

Improvements in data analysis are also key to enhanced characterization. One contributor to these improvements is the availability of computerized and printed databases and of material and procedural standards to characterize a given instrument and generate an internal database. Another contributor is greater data handling capabilities allowing more elaborate image and data processing. Examples include false color imaging, elemental correlation diagrams, three-dimensional representations, surface behavior diagrams, factor analysis/principal component analysis, curve fitting, and background subtraction. Each of these approaches allows additional information to derived from the data than would ordinarily be obtained.

Basic issues and needs in adhesive bonding include the connection of microcauses with macroeffects, identification of bond formation and degradation mechanisms, and the ability to predictively model from fundamental principles. An example of a microcause/macroeffect couple would be to correlate chemical and physical interfacial bonds with interfacial mechanical properties. If measured mechanical properties (e.g., peel or shear values) could then be related to the interfacial strength or fracture toughness, the foundation for predictive modelling would be laid. These improvements in characterization and understanding would ultimately result in improved processes for bonding and allow higher performance and reliability than is currently possible.

More applied issues and needs in adhesive bonding include the development of improved treatments and processes and of enhanced in-process monitoring capabilities. In addition to treatments and processes providing higher performance and reliability or bondability to new or less studied materials, there are urgent needs for environmentally benign processes that do not involve chlorofluorcarbons, chromates, and other hazardous materials; tolerant processes with wide process windows to allow cost and reliability improvements; and processes compatible with the repair of bonded components, either in the field or factory. In-process monitoring during manufacturing/repair ensures that the process is within acceptable windows and allows feedback control. The result is a more reliable product with fewer rejected parts.

Surface spectroscopy methods have made important contributions to the understanding of adhesion and adhesive bonding in the past. It is expected that they will continue to play an important role as researchers build on existing results and utilize the enhanced capabilities being developed in instrumentation and data analysis.

Adhesion Measurements using the Surface Force Apparatus

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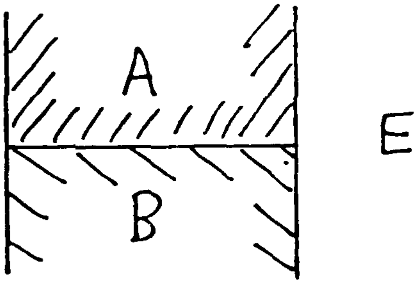
This contribution is intended to be primarily a discussion of the capabilities of the Surface Force Apparatus (SFA), particularly for measurements pertinent to problems in adhesion. Some results that have been obtained with the SFA over a number of years will be presented, not so much with the intention of providing a comprehensive review but rather to illustrate what can be and has been done with the apparatus.

The thermodynamic work of adhesion, W_{AB}, is usually defined in a thought experiment as the reversible work required to separate two materials A and B in an environment E, thereby creating two interfaces AE and BE, while removing the AB interface (the symbol E could represent a liquid L or a vapor V):

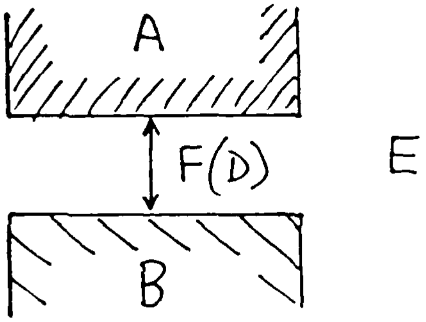
$$W_{AB} = \gamma_{AE} + \gamma_{BE} - \gamma_{AB} \quad . \qquad (1)$$



This work may be very different from the practical work of adhesion, which would include irreversible processes involving various energy-dissipating processes such as viscous effects. Nevertheless, it gives a starting point for exploring the relationship between adhesion and intermolecular forces.

The reversible work of adhesion could equally well be defined as the work done against surface forces as material A is separated from material B in environment E:

$$W = -\int_0^{\infty} F(D)dD \quad , \qquad (2)$$



where $F(D)$ is the force between A and B as a function of the separation D between their surfaces. Thus one way to measure the work of adhesion is to measure the surface force as a function of separation, and integrate it.

We can in fact take an experimental approach to performing this integration, by measuring the surface force between curved surfaces, such as two spheres, a sphere and a flat, or crossed cylinders. The total force between gently curved surfaces can be obtained by summing the force between each element of area of the surface, assuming that the element can be replaced by an element of flat surface at the same separation. This leads to the Derjaguin Approximation:

$$F_c(D) = 2\pi R E_f(D) \quad , \tag{3}$$

where F_c is the force between curved surfaces whose minimum separation is D, R is the radius of curvature of the surfaces, and E_f is the energy of interaction between two flat surfaces at the same separation.

The work of adhesion is simply equal to minus the energy of interaction of surfaces in contact:

$$W = -E_f(0) = -\frac{F_c(0)}{2\pi R} \quad . \tag{4}$$

The Surface Force Apparatus is designed to measure intermolecular forces acting between smooth solid surfaces in controlled liquid and vapor environments. The pedigree of the apparatus goes back to Tabor's group in Cambridge; the current design is due to Israelachvili, working in Australia in the mid-1970s [1], who made the key advance of building an apparatus that could be filled with liquids. Most SFA measurements have been conducted on mica, chosen for the atomic smoothness of its cleavage plane, although recently methods have been found to prepare smooth surfaces of sapphire, silica and certain polymers.

The apparatus uses thin solid sheets mounted as crossed cylinders, allowing the Derjaguin Approximation (Eq 3) to be used to relate measured forces to the energies between flats, which are easier to calculate theoretically. Forces are measured by monitoring the deflection of a cantilever spring; surface separations are measured using an optical interference technique. One feature of the spring method is that it leads to mechanical instabilities when the gradient of the surface force, dF_c /dD exceeds the spring stiffness. This can be exploited experimentally. In particular, the pull-off force, i.e. the tensile force required to separate the surfaces from adhesive contact, is easily determined by noting how far the surfaces jump apart when the spring is gradually retracted.

If this jump out occurs from contact ($D = 0$), as it often does, then the pull-off force F_p (usually give a positive sign when the surface force is negative, i.e., attractive) is immediately related to the work of adhesion through (4),

$$F_p^{DMT} = 2\pi R W = 4\pi R \gamma_{SE} \quad , \tag{5}$$

where γ_{SE} is the solid-environment interfacial energy.

This relation, associated with the names of Derjaguin, Muller and Toporov, is applicable when there is little or no elastic deformation of the surfaces under the influence of adhesive forces. In fact deformation is significant in many cases (including SFA experiments), and it has been shown by Johnson, Kendall and Roberts that the relation between pull-off force and work of adhesion then becomes

$$F_p^{JKR} = \frac{3}{2}\pi R W = 3\pi R \gamma_{SE} \quad . \tag{6}$$

A discussion of the relative merits of these two approaches to contact mechanics, along with some SFA measurements of surface profiles when mica surfaces are in adhesive contact, is given in ref [2]. It was found that the JKR prediction of surface profiles is reasonably accurate, but that a small amount of curvature occurs at the circle defining the edge of the flattened contact region, thereby avoiding the sharp bifurcation and infinite tensile stress that are inherent and obviously unphysical features of the JKR theory.

In some cases a pull-off force occurs from a finite surface separation. An example of this is found in ref [3], in which measurements were reported of forces between mica surfaces in a simple, non-polar liquid having quasi-spherical molecules. Far from being the simple monotonic van der Waals attraction that would have been predicted by continuum theory, the force shows a series of spatial oscillations with alternating repulsive maxima and attractive minima. This force is attributed to molecular packing effects: the finite-sized molecules of the liquid have a tendency to form layers in the narrow gap between the *smooth* solid surfaces, with minimum free energy when the gap is close to an integral multiple of the molecular diameter. The "oscillatory" force illustrates the important point that the measured adhesion may depend on exactly how close the surfaces approach when they are in "contact." If a molecular layer or two of liquid (or other molecules adsorbed from the environment) remains between two materials, the apparent adhesion may be reduced substantially.

There is another effect that can make a significant contribution to the measured adhesion, which is capillary condensation of a liquid from the vapor (or a second immiscible liquid) environment. A calculation of the pull-off force expected in this case, based on simple thermodynamic relations, shows that the pull-off force between a rigid sphere and a plate depends on the liquid surface tension γ_L and the contact angle θ of the liquid on the solid, but is independent of the activity, or relative vapor pressure, of the condensing liquid:

$$F = 4\pi R \gamma_L \cos\theta \quad . \tag{7}$$

This relation has been investigated in the SFA by Christenson [4], and found to be accurate at least at high relative vapor pressures. At low vapor pressures, Fogden and White [5] have shown, in the spirit of JKR theory, that the solids are likely to deform elastically under the influence of capillary pressure, with the pull-off force decreasing to

$$F = 3\pi R \gamma_L \cos\theta \quad . \tag{8}$$

The experimental results at low relative vapor pressures are consistent with this prediction. One very intriguing question which then emerges is: what happens as the vapor pressure (and Kelvin radius of the condensed liquid meniscus) approach zero? Surely bulk thermodynamics must break down at some point, when the Kelvin radius reaches molecular dimensions, and yet when the effects of surface deformation are included there is no clear experimental evidence of any departure from the thermodynamic relationship.

Another important effect that has recently been studied in the SFA is contact electrification, which occurs spontaneously between *dissimilar* materials brought into contact, and which dramatically increases the work of adhesion when those materials are subsequently separated (at least in dry environments) [6]. This work is described by Douglas Smith in a separate contribution at this workshop.

The final set of experimental data to be described concerns *dynamic* forces. By measuring the instantaneous force between surfaces when they are in relative motion, it is possible to extract information on the flow behavior and to measure viscosity or viscoelasticity of ultrathin liquid films. An example is given in Ref [7], in which a simple hydrodynamic description of viscous drag in a squeeze film was shown to hold down to near molecular dimensions, with the molecular layering effects described above becoming dominant in the very thinnest films. This theory predicts that for a simple Newtonian liquid viscous drag is proportional to $1/D$, so that it takes an infinitely long time to squeeze all the liquid out of the gap to reach $D = 0$. Conversely, it takes an extremely long time to separate two smooth surfaces in a viscous environment, if they are very close together to start with.

More recently, the groups of Israelachvili [8], Granick [9] and Klein [10] have measured dynamic lateral forces when two surfaces are slid past one another. Some fascinating behavior of lubricating molecules subjected to such shear is reported, but there is no space to describe it here.

The main weaknesses of the Surface Force Apparatus for adhesion measurements are
- the limited range of solid materials available for study;
- the fact that the interface is formed simply by bringing two materials together at atmospheric pressure and ambient temperature; and
- the measurements are time-consuming and difficult to perform.

On the other hand, the SFA technique has the following merits:
- detailed surface force vs. separation data is obtained;
- the environment is well controlled;
- surface deformations can be monitored.

These three features together mean that *mechanisms* of adhesion can usually be identified, for example whether the adhesion results from capillary condensation, contact electrification, or van der Waals forces. In addition,

- the contact mechanics of curved surfaces is straightforward, allowing the pull-off force to be related directly to work of adhesion; and
- dynamic effects can also be investigated.

The last point may prove to be an area of particular importance in adhesion studies, since it would allow viscoelastic properties of adhesive films to be studied, or work of adhesion to be measured as a function of peel rate, for example. Very few studies along these lines have been carried out so far. Other areas for future development include preparing a wider range of solid materials, preparing specimens with controlled surface roughness, chemically modifying silica surfaces to produce model surfaces of desired chemical functionality, and exploring the relationship between contact charging effects and the more familiar acid-base theories of adhesion.

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Models for Polymer Adhesion Between Dissimilar Materials

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The performance of composite materials frequently depends on the ability of polymer adhesives to bind two dissimilar substrates. We developed theoretical models to determine the polymeric properties that will provide the optimal adhesion between two different materials. In particular, we examined how copolymers can "stitch" together two phase-separated homopolymers, the behavior of primers in poor solvents, and the ability of associating polymers to form "bridges" between two parallel surfaces.

In the first study (1,2), we determined how the behavior of a linear AB copolymer at the interface between two immiscible fluids depends on: the chain's sequence distribution (arrangement of A's and B's along the backbone of a chain), solvent-polymer interaction energies and temperature (1,2). These predictions can be used in tailoring macromolecular surfactants that provide the optimal reduction in the surface tension between the two fluids. Furthermore, we predicted the range of sequence distributions for which the copolymer will form large loops as it weaves back and forth across the interface. Thus, when we consider the fluids to be two phase-separated homopolymers, the predictions can be used to design the optimal copolymer additive for improving the internal adhesion and mechanical integrity of polymer blends.

As an additional aspect of this study, we examined the behavior of an alternating AB copolymer at the fluid-fluid interface (3). Here, we investigated the effect of varying the relative affinities between the monomers and the two different fluids. Through this study, we determined conditions under which the alternating chain becomes "delocalized," i.e., drifts away from the interface and is preferentially located in one of the two fluids.

A layer of chains grafted to a surface ("primers") can be useful in promoting the subsequent adsorption and adhesion of polymers onto the surface. To optimize the role of primers, we must first thoroughly understand the characteristics of the grafted layer. To this end, we examined the effect of solvent quality on a layer of end-grafted polymers using the random phase approximation combined with a numerical mean field analysis (4). For sufficiently poor solvents, the laterally homogeneous grafted layer is linearly unstable to fluctuations tangential to the grafting plane. In the unstable regime, the grafted layer forms a "dimpled" surface in which the depth of, and the distance between the dimples depend on chain length, solvent quality and grafting density. Scaling relations are obtained for the length scale of the instability and for the phase boundary separating the linearly stable from the unstable regimes.

The general method we developed, numerical mean field analysis plus the random phase approximation, can be applied to a large class of systems to study both the equilibrium fluctuations and the structures formed when the mean field profile becomes unstable.

In the third study, we developed Monte Carlo computer simulations to model the solution behavior of associating polymers placed between two parallel plates. The simulations allowed the chains to both self-assemble and bind to parallel, dissimilar surfaces. The effects of polymer concentration and bonding energies were studied to determine the optimal characteristics for the polymers to form "bridges" between the surfaces. The results showed that strong surface-polymer bond energies did not enhance adhesion and, in fact, weaker surface bonds coupled with strong self-associating energies gave the desired properties. In particular, under these conditions, the chains form broad clusters or "trunks," which provide extensive bridging and, thus, optimal adhesion between the two substrates.

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Molecular Simulations of Thin Alkane Films Between Structured Surfaces: Effects of Molecular Geometry

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Introduction

Understanding adhesion depends strongly on understanding the factors affecting the forces between solid bodies and the wetting of solid bodies by liquids. The surface force apparatus has been used to measure solvation forces, the forces between two solid bodies immersed in various liquids. Among the interesting observations of the surface force apparatus measurements are the prediction of structural forces between linear and spherical molecules [1]. These structural forces appear as oscillations in the solvation forces at distances of .5 to 5 nm and are believed to be related to the layering of the liquid between the plates. One interesting observation of importance to lubrication and adhesion is that even slight branching (one methyl side group) can reduce or eliminate the oscillatory nature of the solvation forces. This is believed to be because the branching makes it more difficult for the molecules to layer [1].

We are using molecular simulations of thin films of octane and 2-methyl heptane (iso-octane) to examine the structure of confined films of linear and branched hydrocarbons and explain the solvation force measurements.

Model

Octane and iso-octane were modeled using the OPLS model for liquid hydrocarbons [2], but with flexible bond angles having a harmonic potential. The CH_2 and CH_3 groups are treated as united atoms with the Lennard-Jones parameters from Jorgensen's OPLS model. The torsional potential is also taken from this model and no intramolecular Lennard-Jones interactions are included for atoms separated by fewer than four bonds. Unlike the OPLS model the intramolecular Lennard-Jones interactions for atoms separated by more than three bonds are the same as the intermolecular interactions. All interactions are truncated at about 2.5 Lennard-Jones core diameters (10Å).

Although most experiments are performed upon bare mica surfaces, intermolecular potentials are not readily available for them. Some of the experiments are carried out upon mica coated with a Langmuir-Blodgett monolayer [3]. In these systems, the effects of the branching of the alkane chains is similar to those observed for the bare mica surfaces. Since reasonable alkane-alkane interaction potentials exist, we simulated the alkane fluid between Langmuir Blodgett films. The Langmuir Blodgett films were modeled assuming the prefect crystal geometry predicted by Hautman and Klein's work [4] and using the OPLS potentials with a cutoff of 1.0 nm.

System geometry

The experiments are carried out at constant chemical potential--the chemical potential of the bulk liquid, typically at ambient conditions. In order to properly compare films of different thicknesses, it is necessary to maintain a constant chemical potential. We do this by simulating the confined fluid in equilibrium with the liquid at its vapor pressure. This was accomplished by simulating a film of finite extent in one direction (the y-direction) confined between two crystalline solid surfaces (a slit pore geometry). Periodic boundary conditions are applied in the x- direction. The simulations reported here included 48 liquid molecules in slabs separated by either 1 or 2 nm. In the thinner films, a significant portion of the molecules formed a liquid bubble at the edge of the slab. The width of the films in the y direction was 2.5 nm. Density profiles and other data were taken for liquid molecules within the middle 2 nm of the slab. Equilibration times were about 1 nanosecond and sampling times approximately five nanoseconds for the simulations reported here.

Results

For both the 2 nm and the 1 nm samples the total carbon density profiles are oscillatory as shown in Figs. 1 and 2. The iso-octane density profiles are less oscillatory than the octane ones. The difference for the narrower pores is much more significant than for the wider pores.

The effects of confinement on the chain orientation can be seen by examining an orientational order parameter defined by the angle between the interface normal and some vector describing the local orientation of the molecule. A convenient vector for this is the vector connecting two carbon atoms that are two units apart in a molecule (e.g. atoms 1 and 3). If an n-carbon molecule is in the all trans state all n-2 of these vectors will be parallel to each other. If Θ is the angle between one such vector and the interface normal, a convenient order parameter is

$$P = 1/2 < 3\,\mathrm{COS}^{2}(\Theta) - 1 >$$

where the average is taken over all vectors and time steps within a given region. The position of the vector is given by the midpoint of the line connecting the atoms. If the molecules in a region are completely randomly oriented, P=0. When the vectors all are parallel to the surface then P= -1/2. When the vectors all are normal to the surface P=1.

Figures 3 and 4 indicate that the chains are oriented parallel to the interface. The chains in the layers closest to the solid surfaces are almost entirely parallel to the surface. This orientational order persists to some degree throughout the slab. In the 1 nm thick sample the branching significantly reduces the degree of orientational order in the center of the slab.

Acknowledgements:

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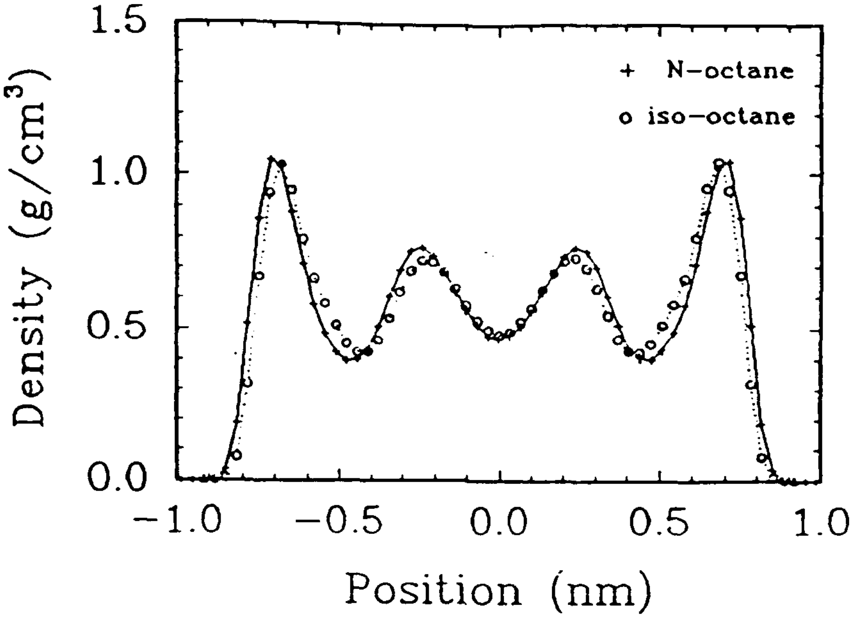
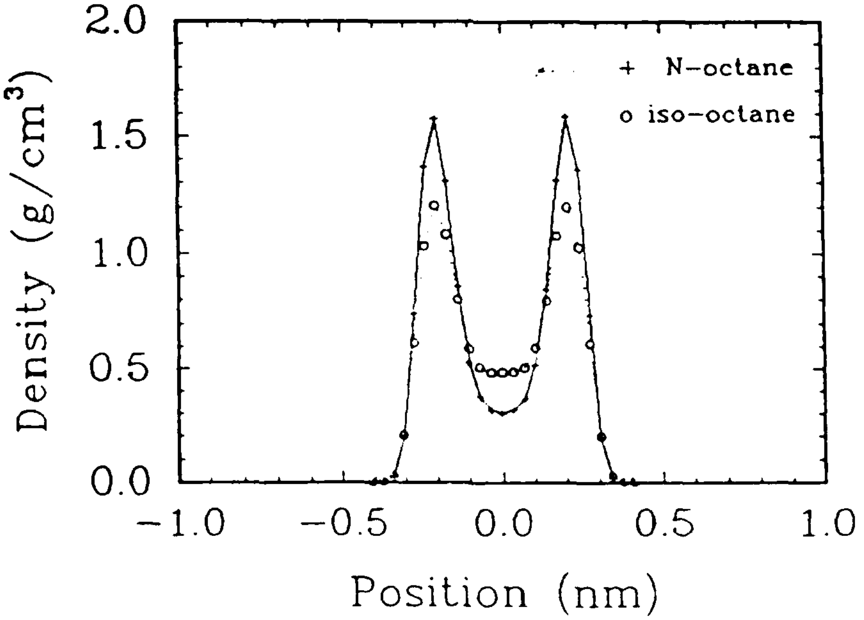
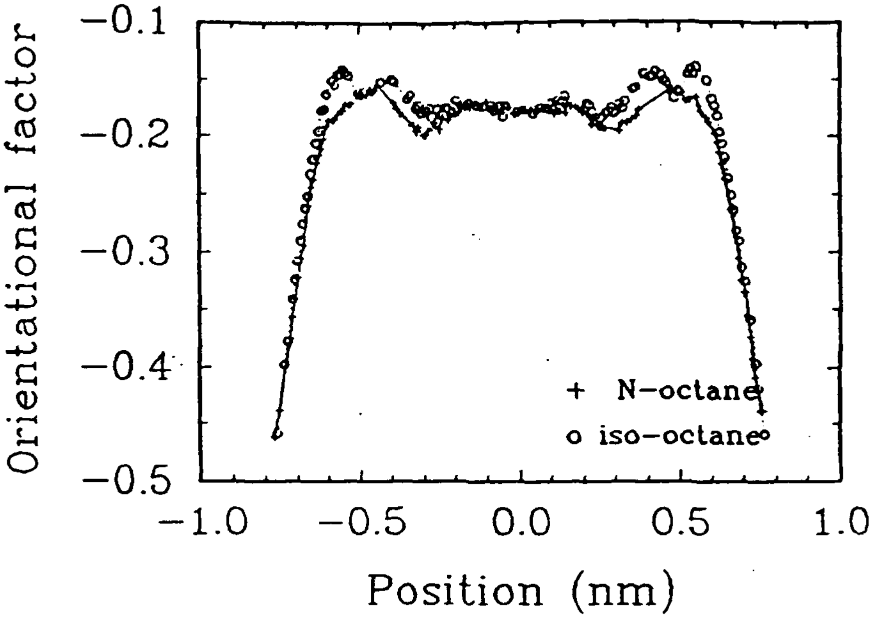


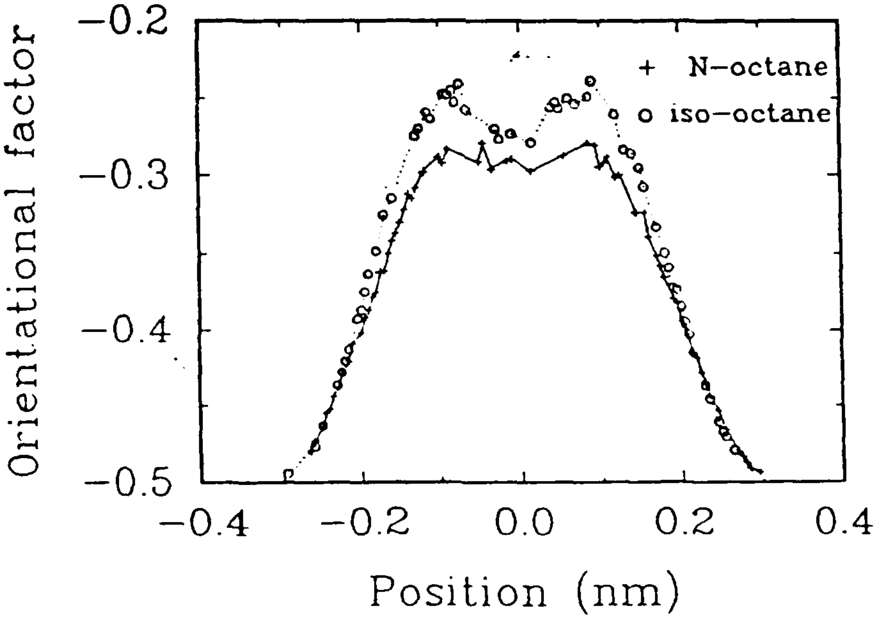
1. Total carbon density profiles for n-octane (+) and 2-methyl heptane (o) between two solid surfaces separated by 2 nm.



2. Total carbon density profiles for octane (+) and 2-methyl heptane (o) between two solid surfaces separated by 1 nm.



3. Orientational order parameter (P) as a function of position for n-octane (+) and 2 methyl-heptane (o) between two solid surfaces separated by 2 nm.



4. Orientational order parameter (P) as a function of position for n-octane (+) and 2 methyl-heptane (o) between two solid surfaces separated by 1 nm.

Near - Surface Structure and Dynamics at Strongly Interacting Polymer/ Solid Interfaces: Implications for Adhesion

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The synthesis of adhesive joints between organic polymers and solid substrates is of increasing importance in a variety of technological applications. As such, these interfacial systems have been the subject of considerable recent attention [e.g., 1-5]. Polymer/solid interfaces may broadly be classified into two categories. One class is comprised of systems wherein the segment/surface interactions are characterized by weak and dispersive interactions. A second class encompasses systems wherein the segment/surface interactions are strong and specific. This category is best exemplified by the interfaces between organic polymers and metallic substrates. In these cases specific functional groups of the organic polymer may chemisorb on the solid substrate. In addition to being stronger than dispersive interactions, chemisorption is also very specific. In other words, only particular functional groups of the organic polymer interact strongly with the surface. The interplay between the resulting strong and specific enthalpic driving forces that favor preferential adsorption of specific functional groups, and the entropic constraints associated with confining chain molecules to a region near a solid surface determines the structure and dynamics of the interfacial chains. In turn, the structure and the dynamical behavior of the interfacial chains play a crucial role in determining the adhesive properties of the interface.

In order to study strongly interacting polymer/solid interfaces from a theoretical/ computational point of view, the approach that must be adopted is a hierarchical one. This is so because for the systems under consideration, the segment/surface potentials are not known apriori. Quantum mechanical calculations provide us with the energy hypersurfaces that characterize these interactions. Using these proper potentials, statistical mechanical approaches must then be used to elucidate interfacial chain conformations and dynamics.

We use density functional theory [6] to map out the energy hypersurfaces for the interactions of poly-methyl methacrylate with aluminum surfaces. Hohenberg and Kohn [7] have shown that the energy is a unique functional of the electron density distribution ($n(r)$),and that the energy is variational with respect to the electron density distribution.

Using this variational principle, the local density approximation for the exchange-correlation energy [8], two different models for an aluminum surface, and an atomistic representation for the segments of PMMA we have calculated the energy hypersurface for the interactions of PMMA oligomers with aluminum surfaces as a function of several external and internal degrees of freedom [12].

The extensive calculations that we have performed to map out the interaction energy hypersurface (over 1000 calculated points) may be summarized as follows. The energy hypersurface is characterized by several configuration and orientation dependent local minima. Many of these minima are much deeper than the thermal energy at room temperature, and are often separated by barriers that are also larger than the thermal energy (kT). The energy hypersurfaces that we have calculated have been fit to an empirical force field, which is neccessarily beyond a two-body potential because it represents chemisorptive interactions. This force field, which is derived from quantum mechanical calculations, can be used in simulations to obtain the structure and dynamics of long chain molecules adsorbed to the surface.

The fact that the energy hypersurface for the segment/surface interactions is characterized by several local minima that are often separated from each other by energy barriers that are greater than kT leads to the conclusion that, for the systems under consideration, the chain molecules adsorb in non-equilibrium conformations. The interfacial chains thus constitute a collection of non-equilibrium conformations, and may be viewed to be analogous to a bulk glassy polymer. Note that no connection is to be made with the bulk glass transition temperature of the polymer. Kremer [9] has noted that due to the enhanced density near the surface, a polymer whose bulk glass transition temperature is below the temperature of the experiment may vitrify near the surface. The physical phenomena that we are considering here is totally different. In our case, the nature of the segment/surface interactions leads to the interfacial chains being trapped in non-equilibrium conformations.

The existence of non-equilibrium interfacial chain conformations implies that the structure of the interface will be determined by the dynamics associated with adsorption. Furthermore, the dynamical behavior of the interfacial chains as a function of temperature (or segment/surface interaction energy scale) should prove revealing regarding the behavior of these unique confined fluids. Brute force molecular dynamics simulations are too compute intensive to probe the relevant time scales that characterize the relaxation kinetics of the interfacial chains under consideration. As such, we have developed a stochastic model of the interfacial dynamics. Prior to studying the dynamical behavior of a specific system, we considered a model system that captures the essential physics. Specifically, we have considered the adsorption of linear polymer chains with each segment containing two functionalities that may bind strongly to the surface; one of these stickers binds more strongly than the other, and hence, our model polymer is a simple representation of the PMMA/aluminum system.

The development of our model commences from the observation that the first step of adsorption from solution is fast. This has been demonstrated both experimentally [10], and by MD simulations [11]. It is the subsequent relaxation of the adsorbed chain that occurs over long time scales. Furthermore, once the chain is adsorbed, each sticker may be considered to be in either of two states, stuck or unstuck. Thus, there is an isomorphism between the adsorbed chain structure and a spin 1/2 Ising model, with each sticker being an Ising spin. The collection of spin states constitutes our model of the adsorbed chain structure. The dynamics of the adsorbed chain is given by the temporal evolution of the spin states, which can be described by a Master equation. The rate of an individual spin flip is not independnt, but rather, it depends strongly on the state of the neighboring spins. This is so because the spins are connected along a chain, and the neighboring segments place impediments on the escape routes for desorption or channels for adsorption that are available to independent stickers. Thus, the rate of desorption (or rate of a spin flipping up) may be written as:

$$r_{des.} = \alpha\, f(\text{local spin state}) \exp(-E/kT) \quad (2)$$

where α is an intrinsic time scale or attempt frequency, E is the depth of the binding well, and f is a function that reflects the cooperativity associated with spin flips. The corresponding rate of adsorption is determined by the condition of detailed balance. We have invented a set of rules that prescribe f for the problem at hand [13]. We do not detail the rules that we have invented herein. We simply state that since these rules were obtained by physical induction rather that rigorous deduction, we tested our model against full MD for short chains, and found the agreement to be excellent. Our kinetic Ising model for adsorbed chain dynamics was then used to probe the dynamics of long chains over time scales that are inaccessible to MD. We now summarize these results.

At low temperatures, the chain molecules are frozen in non-equilibrium states that do not relax to equilibrium in experimental time scales. At higher temperatures, relaxation to equilibrium does occur. However, the kinetics of relaxation cannot be described by a single exponential. The data at higher temperatures is best fit by stretched exponential functions. This non-Debye relaxation is very characteristic of fragile glass forming liquids [14]. Note, however, that in our case the cooperative motions that lead to glassy behavior are due to the nature of the interactions of the chain molecules with the surface. In fact, some arguments suggest [13] that our dynamical model may be in the same universality class as the general hierarchically constrained dynamical models proposed by Palmer, Stein and Anderson [15]. Our prediction of constrained relaxation for strongly adsorbed polymer chains has been observed experimentally by Granick and co-workers [10, 16].

The surface - induced vitrification of strongly adsorbed polymer chains is further demonstrated by the temperature dependence of a nonlinear average relaxation time associated with adsorbed chain relaxation. Our results show that these data are highly non-Arrhenius in form. In fact, the results are best fit by the Vogel - Fulcher law. For temperatures that are such that $E/kT > 1.54$, the adsorbed chains dynamically fall out of equilibrium and ergodicity is effectively broken. We note that our prediction of the temperature dependence of the relaxation times has been observed experimentally by Johnson and Granick [16].

The existence of glass - like structures at the interface has many practical implications for polymer - metal adhesion. Herein we mention just two important ones. First, since at room temperature the chains adsorb in non - equilibrium conformations, the structure of the interface will depend on the history of preparation of the joint. In other words, the way in which the interface is prepared will influence the adhesive properties. Second, the frozen polymer chains in the near - surface region may not entangle as well with the flexible chains in layers further away from the surface. As such, there is the possibility of creating a second interface between the near - surface chains and the bulk polymer which may actually be weaker than the polymer - solid interface. This may lead to the primary mechanism for failure in these systems being cohesive rather than adhesive.

We have also studied the dynamical behavior of the PMMA - aluminum interface using transition state theory and stochastic simulations. In this case, the transition probability matrix is not obtained by inventing rules that capture the essential physics. Rather, we carry out a detailed transition state theory analysis of the quantum mechanically calculated energy hypersurface to obtain the rates of state to state transitions. The stochastic dynamics are then performed by partitioning the configurational space into a set of macrostates. The results of these calculations show the same qualitative trends as those exhibited by the model system described above. However, many interesting system specific features emerge. From the viewpoint of relevance to adhesion, perhaps the most important feature is the dramatic dependence of the relaxation dynamics on chain tacticity. In other words, we find that the interfacial chain conformations and dynamics are very sensitive to the tacticity. This implies that the adhesive properties of polymer - metal joints will depend on the tacticity of the polymer.

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Polymer Density Profile Near A Flat Substrate

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The density at the interface of an amorphous polymer near a flat solid surface was investigated using neutron reflectometry. Bulk poly- (methyl methacrylate) with a monodisperse molecular weight in contact with a silicon single crystal wafer was the first system studied, and the emphasis was placed on the temperature dependence of the polymer density profile near the interface. The glass transition temperature of the polymer was embraced in this study, and a reversible change in the density profile was discovered.

The density of a bulk polymer in contact with a solid is an important subject in the area of polymer adhesion; in the practical world the interface bonding strength is one of the most elusive factors controlling the performances of adhesive joints and polymeric composites. The integrity of protective coatings is another example directly related to the subject to be addressed in this talk. Considerable progress in predicting the polymer density near a surface using computer modelling has been made in recent years. However, experimental data in this area is still absent. In this presentation some results of the first part of a series of experiments probing the polymer/solid interfaces will be given.

For polymers with monodisperse molecular weight the molecules near a flat surface will deviate from a Gaussian coil if the space filling requirement is to be fulfilled. Qualitatively one can easily envision that these molecules must be distorted such that the dimension perpendicular to the surface, hereafter referred to as the z axis, must be decreased; the dimensions along the interface (the x-y plane) must be increased. Recent results from theoretical calculation indeed support the above notion of chain distortion. The segment density of the bulk, not of individual chains, must be determined by the balance of the loss in entropy due to the chain distortion and the cohesive enthalpy as well as the adhesive enthalpy between the polymer and the substrate. We postulated that above certain elevated temperatures the entropy contribution reaches the same order of magnitude of the enthalpy, beyond which the space filling constrain is expected to relax and the density of the polymer near the interface is expected to be lower than its bulk value.

It is the objective of this work to test the above hypothesis using the neutron reflectivity measurements.

Deuterated PMMA with a polydispersity of 1.10 and Mn of 135000 synthesized via group transfer polymerization method. The polymer is approximately 57% syndiotactic, 37% atactic and 6% isotactic. The glass transition temperature was found to be 115°C as determined by DSC.

Silicon single crystal wafer with (100) surface was used as the substrate. The neutron reflectivity result from the silicon/air surface indicated a roughness of 4Å RMS (root mean square). A PMMA film of 0.5mm thick was prepared in vacuum at 150°C in direct contact with the polished surface of a wafer. This polymer/silicon sample was then placed between two aluminum plates in contact with a heating block. All the neutron measurements were performed in vacuum of 10^{-4} torr. The sample temperature was measured via a thermocouple placed within the aluminum block contacting the polymer, and the distance between the probe and the polymer was less than 1mm. The BT-7 reflectometer at the reactor of the National Institute of Standards and Technology was used for all the measurements.

The reflectivity results at six different temperatures were fitted with the theoretical ones based on a matrix method calculation. Two variables were allowed, one is Q_c^2, the square of the critical Q in $Å^{-1}$, which is linearly proportional to the polymer density remote from the interface, the other is the width of the interface. An error function profile was assumed. Q is the momentum transfer between the reflected (or scattered) beam and the incident beam. The fitted results are listed in the following table.

The curve fitting results of PMMA/ Silicon Interface

Temperature (°C)	Width (Å)	Q_c^2 ($Å^{-2}$)	Density(g/cm^3)
92.6	3.06	3.688 E-4	1.242 (1.170)
101.1	1.5	3.626 E-4	1.221 (1.168)
117.8	14.61	3.503 E-4	1.180 (1.164)
125.0	17.6	3.437 E-4	1.157 (1.158)
144.0	21.0	3.283 E-4	1.105 (1.147)
80.6	1.0	3.669 E-4	1.235 (1.174)

The most striking feature revealed by these results was the temperature dependence of the interface width; it became broader at elevated temperatures and was thermally reversible.

The polymer density calculated based on Q_c^2 was listed in the fourth column of the above table. The density calculated based on a literature value of 1.188 at 25°C was also listed inside the parenthesis of column 4., thermal expansion coefficient of 2.6 E-4, and 5.8 E-4 for temperatures below and above T_g respectively was used for the density calculations. The measured density at lower temperature is far greater than the bulk values, whereas the value at 144°C is less than the calculated bulk value. The high density or Q_c^2 at low temperatures can be accounted for by the absorption of PMMA chains at interface. Absorption could result in a high population of "train", hence could enhance the local segment density within the first few hundred angstroms from the interface.

The unexpected low value of density calculated from Q_c^2 at 144°C is rather puzzling, this could imply that the density profile reduced from the reflectivity is not the asymptotical bulk density value far remote from the interface. Rather, this value could represent a local average density near the interface, since at large distances away from the interface the density has to follow the bulk one. However, the reflectivity result by itself does not carry enough information enabling us to determine a unique and true density profile. The uniqueness of the solution is a common one as one tries to deconvolute the scattered or reflected intensity.

The above experiment was repeated with a spin coated PMMA film of 2700 Å thick. The substrate was also silicon single crystal wafer. The results, although similar to what observed in the thick samples, were different quantitatively. The transition from a steep to a gradual density profile took place at somewhat higher temperature; the width of the transition region at high temperature near the interface was narrower. This observation points to the complexity of interface problems; the structure is rather sensitive to the sample preparation technique.

Non-Destructive Characterization of Polymer/Metal Interfaces

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The long term goal of our research is to determine the effects that substrates have on the molecular structure of polymer interphases and to relate the molecular structure of interphases to the performance of adhesive joints and composite materials. Our approach is to use a variety of analytical techniques, including reflection-absorption infrared spectroscopy (RAIR), X-ray photoelectron spectroscopy (XPS), and ellipsometry to determine the molecular structure of polymer interphases.

We are especially interested in the relatively new technique known as surface-enhanced Raman scattering (SERS). SERS is a process in which the Raman scattering cross section of molecules adsorbed onto the roughened surfaces of certain metals is greatly enhanced compared to the cross section for normal Raman scattering. Two mechanisms appear to be responsible for most of the enhancement. One is associated with large electric fields that can exist at the surfaces of metal particles with small radii of curvature. The other mechanism is related to distortions of the polarizablity of the adsorbed molecules by formation of charge-transfer complexes with the metal surface. Enhancement due to the charge-transfer mechanism is restricted to molecules immediately adjacent to the substrate but enhancement due to the electromagetic mechanism may extend several molecular layers away from the metal surface. The total enhancement decreases quickly as a function of distance and little enhancement is obtained for molecules that are more than a few monolayers away from the surface. As a result, SERS is *surface selective* and can be used for *in-situ, non-destructive* characterization of interfaces between polymers and metals.

When SERS spectra were obtained from films of the polyamic acid of pyromellitic dianhydride (PMDA) and oxydianiline (ODA) which were spin-coated onto silver substrates, several important results were obtained (1). The SERS spectra were independent of the polymer film thickness, indicating that the spectra were characteristic of the polymer/substrate interface, not the bulk polymer films. SERS spectra of the polyamic acid were characterized by a band near 1412 cm^{-1} which was not observed in normal Raman spectra of the polyamic acid. This band was assigned to the symmetric stretching mode of carboxylate species formed by interaction of acid groups in the polyamic acid with silver ions. In addition, the SERS spectra of the polyamic acid films after curing were similar to SERS spectra of the polyamic acid before curing, indicating that curing was inhibited by carboxylate formation.

SERS spectra obtained from thin films of the polyamic acid of PMDA/ODA spin-coated onto gold substrates were considerably different (2). No bands characteristic of carboxylate species were observed, indicating that there was little interaction between the polyamic acids and gold substrates. Moreover, SERS spectra obtained after the polyamic acid films on gold were cured were similar to normal Raman spectra of the polyimide, indicating that curing was not inhibited by the gold substrate.

RAIR spectra obtained from films of polyamic acid spin-coated onto silver substrates were a strong function of thickness (3). Thus, a band near 1722 cm^{-1} which was related to carbonyl stretching in acid groups, decreased in intensity as the film thickness decreased and a band near 1400 cm^{-1}, which was assigned to carboxylate species, increased in intensity. Spectra obtained from the films after curing were also a strong function of thickness. A band near 1379 cm^{-1}, which was assigned to imide groups, decreased in intensity as the film thickness decreased. These changes in relative band intensity as a function of film thickness were mostly attributed to interaction of the polyamic acid with the silver substrate within the interphase region.

RAIR spectra of polyamic acid films on gold did not change much as a function of thickness (2). These spectra were always characterized by a band near 1720 cm^{-1} that was related to acid groups. After curing, the films were always characterized by bands near 1720 and 1380 cm^{-1} that were related to imide groups, indicating that curing occurred normally, even near the gold surface.

When thick films of polyimide were delaminated from silver substrates, it was observed that failure always occurred near the polymer/metal interface. However, examination of the fracture surfaces by XPS revealed that failure was actually cohesive within the polyimide, near the interface between a layer of partially cured polyimide adjacent to the metal surface and the fully cured bulk polymer (1). It was thus concluded that silver substrates had a strong effect on the structure and properties of adhesive bonds between polyimides and silver substrates.

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Quantized Adhesion Detected with the Atomic Force Microscope

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Much of what we know about forces between surfaces, including adhesion forces, stems from work using the surface force apparatus (SFA)[1]. This work has resulted in a variety of "force laws" describing interactions of different geometries with different types of forces. These force laws often use very rough approximations of atomic and molecular parameters. Indeed it is rare that properties of atoms and molecules can be scaled to describe the behaviour of macroscopic objects. One of the few examples is that atomic polarizability correlates closely to the dielectric properties of a substance. Now, molecular dynamics is a promising approach to bridging this gap between atoms and molecules and the behaviour of large molecular ensembles. A significant hurdle that has slowed this approach is the lack of direct measurements of atomic scale interaction parameters. The atomic force microscope offers a possible solution to this problem by making direct measurements of atomic scale interactions between macroscopic objects[2, 3]. Recent measurements have shown that quantitative information about interactions can be obtained[4, 5].

In our efforts to explore fundamental interaction forces with the AFM we have recently detected the quantization of adhesion forces between silicon nitride and glass surfaces[6]. With careful control of solution pH, the adhesion force could be reduced until quantization became apparent. The size of the "force quantum" between immediately sequential adhesion measurements (within 2 seconds), over a contact area estimated to be several 10's of nm^2 based on Hertzian deformation at contact, is near 1×10^{-11} N (Figure 1). These experiments were performed with a specially constructed analog system in order to avoid digital signal noise which otherwise interfered with the measurements. While the exact mechanism for this quantization remains to be proven, one current hypothesis is that it results from the breaking of individual hydrogen bonds. Interaction measurements on this scale will hopefully soon provide data appropriate for testing molecular dynamics simulations. Indeed such modeling of AFM results has already begun[7].

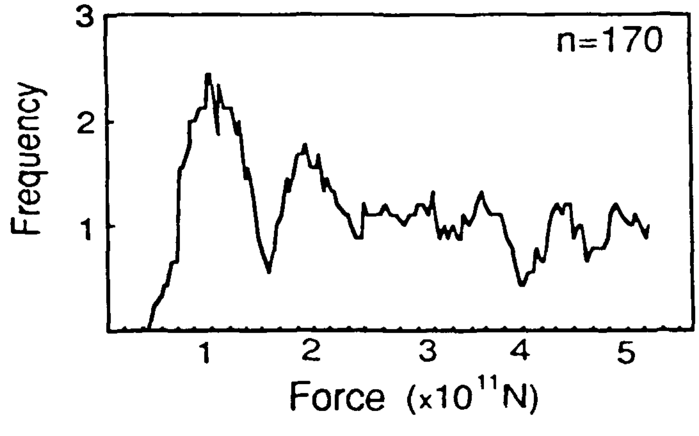

Figure 1. Quantization of the adhesive interaction between silicon nitride and glass. The difference between sequential adhesion measurements differs by roughly 10^{-11}N.

A fundamental goal for our future work in this area is the development of an attractive-mode force microscope that can resolve surface forces spatially in all three dimensions. Specifically it would use active force feedback to measure the force versus distance curves quantitatively all the way into contact. It would allow the aquisition of a full range of quantitative information with high resolution on the forces present between well characterized probes and surfaces. Imaging in the other two dimensions will allow us to characterize the surface and detect local variations in interaction forces, for example at step and kink sites. These interaction forces will also, of course, depend on the chemical composition of the surface[8] and may, in the future, help the atomic force microscope move beyond topography to chemical identification.

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Interpretation of Force Curves in Atomic Force Microscopy[†]

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Atomic Force Microscopy (AFM) was invented in 1986 by Binnig, Quate and Gerber [1] as "a new type of microscope capable of investigating surfaces of insulators on an atomic scale." Stemming from developments in scanning tunneling microscopy, it now became possible to image insulators--organic and biological molecules, salts, glasses, and metal oxides--some with atomic resolution. Being able to obtain high-resolution, topographical images of insulators under a variety of conditions--at ambient pressure, in aqueous or cryogenic liquids, etc.--has created many applications and sold many commercial instruments. In 1987, Mate and coworkers [2] introduced a new direction for AFM where atomic-scale frictional forces could be measured. Likewise, in 1989, Burnham and Colton [3] used AFM to measure the surface forces and nanomechanical properties of materials. Today, there are many examples of using AFM as a high-resolution profilometer, surface force probe and nanoindentor. Several new imaging techniques have been introduced depending on the types of forces measured, e.g., magnetic, electrostatic, capacitative, etc. Because of the diverse nature of the field and instrumentation, the names scanned probe microscopy [4] and XFM (where X stands for the force being measured, e.g., MFM is magnetic force microscopy) have been adopted.

A force microscope consists of a sensor that responds to a force and a detector that measures the sensor's response. The sensor--a cantilever beam with an effective spring constant, k--moves in response to the forces acting on its tip. The detector measures the cantilever's position, which can be converted to force using Hooke's Law, $F = -kz$, where z is the cantilever displacement. (The displacement can be measured by tunneling, capacitive or optical instruments.) If the cantilever beam is either microfabricated or a thin wire, then small spring constants (0.1-100 N/m) are possible. For 0.01 nm displacement sensitivity, 10^{-8}-10^{-12} N forces are measurable. These forces are comparable to the forces associated with chemical bonding, e.g., $\sim 10^{-7}$ N for an ionic bond and $\sim 10^{-11}$ N for a hydrogen bond.

Both attractive and repulsive forces can be measured, as well as the adhesive force needed to separate the cantilever tip and sample surface once in contact. Figure 1 illustrates the force measurement between several different materials. The curves depict the net forces acting between the tip and sample as a function of distance from point of contact. The cycle starts (at the left) with the sample far away and the cantilever in its rest position. As the separation decreases, the cantilever bends towards the sample (below the baseline) responding to an attractive force. In Figure 1, the attractive force between the diamond tip and graphite is much higher than the attractive force in the other two systems due predominately to the higher surface energy of the graphite [5]. Continuing to push the sample in the direction of the cantilever after contact until a predetermined load is reached causes the cantilever to deflect through its original rest position. The slope of the curve in this repulsive force region (above the baseline) is a function of the nanomechanical properties and local geometry of the tip and sample. The steeper the slope, the higher the modulus of the material as seen in comparison of the nickel, graphite, and diamond data. When the load is removed, the curve shows hysteresis due in part to adhesion between the tip and sample.

During tip-sample approach, the force curve can be divided into three separate parts: a purely attractive part where the cantilever bends towards the sample, a predominately repulsive part where the sample is under an applied load, and the transition region between the attractive and repulsive parts where the tip and sample make contact and may undergo deformation. Upon tip-sample retraction, hysteresis in the curve may also appear due to the mechanical response of the materials to an applied load and to adhesion between the tip and sample such that the pull-off force is typically greater than the pull-on force.

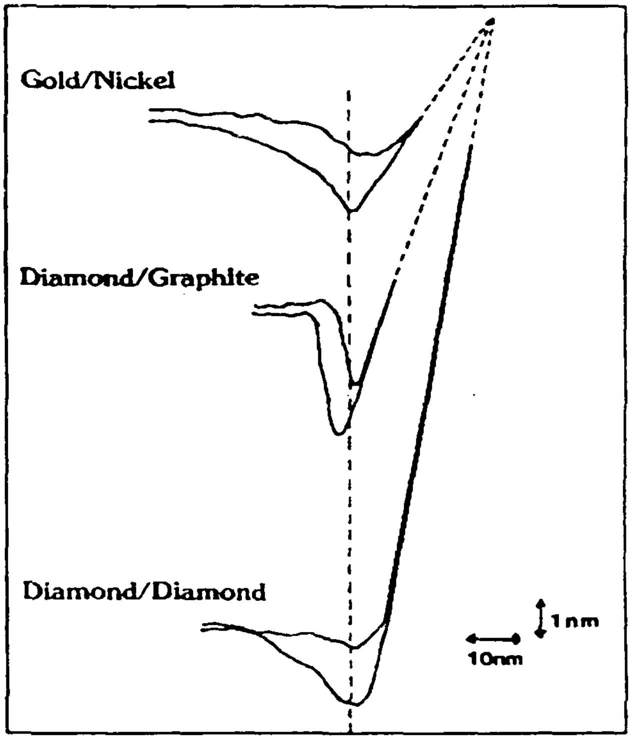

Figure 1 Surface force versus distance curves for different tip/sample materials. Vertical axis is cantilever deflection (1 nm ≈ 260 nN). Horizontal axis is sample displacement (nm).

At NRL, we having been working to fully interpret these force curves. The types of information that one can obtain from force curves includes 1) the magnitude and functional dependence of attractive and adhesive forces, 2) the point of tip-sample contact, 3) the tip-sample contact area, and 4) the elastic modulus and plasticity of thin and thick films. This type of information not only provides information about the mechanical properties of materials, but it also provides significant insight to the imaging mechanism in AFM.

The repulsive part of the curve is easiest to explain qualitatively. Accordingly to the classical relationships derived by Hertz [6], the slope of a curve plotting the force versus the contact area or penetration depth is dependent on the geometry of the indentor and on the modulus of the material. Figure 1 clearly shows this trend where the slope increases with the modulus of the material. The radius of the contact area predicted by the Hertzian relation is an estimate of the minimum radius as it ignores any tip-sample deformation caused by local surface forces.

The attractive part of the curve should likewise be easy to explain given the extent of our understanding of intermolecular and surface forces based on van der Waals theories. However, unlike experiments done with the surface force apparatus [7] with clean mica surfaces in which a $1/D^2$ dependence for the nonretarding dispersive force is measured over a distance of 10 nm, the attractive force measured by AFM is typically much longer ranged. While van der Waals forces certainly exist and should be readily measurable by AFM, their relative magnitude and distance dependence are masked by other forces due to capillary and patch charge effects (see below) caused by adsorbed films and contaminants. By controlling the cleanliness of these surfaces (as can be done in an UHV environment), the van der Waals forces should become the dominant attractive force between uncharged, nonmagnetic surfaces. In solution, other forces associated with double-layer and hydration need also to be considered.

As an example of our current work dealing with attractive forces, we have developed a model based on work function anisotropies (and their associated patch charges) as an origin of long-range surface forces [8]. The work function is very sensitive to perturbations at the surface of a material. Surface preparation, uneven distribution of adsorbates, crystallographic orientation, the presence of surface steps, hillocks, pits or defects can all influence the work function leading to regions on the surface with slightly different electrostatic potentials or patch charges. We have recently modelled the interaction between patch charges on the tip and sample and obtain the result shown in Figure 2. Clearly the shapes of the theoretical and experimental curves for a diamond tip and graphite surface are similar, and the distance dependence of the model appears to be correct. A van der Waals force curve is also shown for comparison.

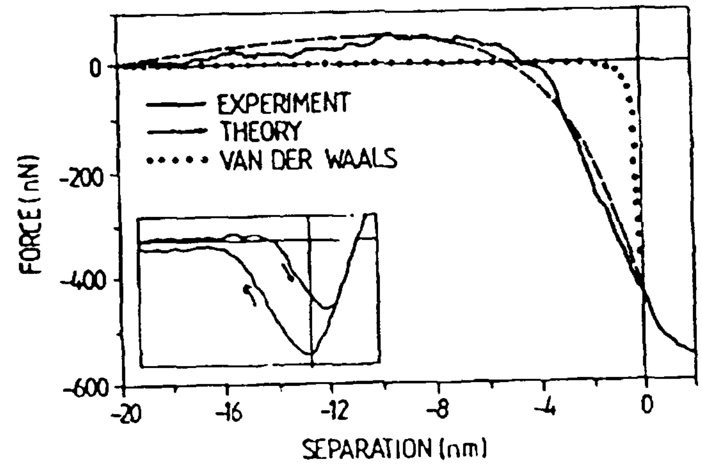

Figure 2 AFM experimental data (solid line), the theoretical fit (dashed line), and a van der Waals interaction (dotted line), where force is shown as a function of tip-sample separation. Inset shows full force curve.

The deformation part of the curve where tip and sample make contact, while perhaps the most interesting part, is the most difficult to interpret. In the Hertzian model, when two elastic sphere make contact, they meet at a point. When the spheres are loaded, they deform causing the contact area to increase. Removing the load causes the contact area to decrease, until at zero applied load, the surface are once again in point contact. At this point, the surface can be separated with zero pull-off force. The shortcoming of the Hertzian model is that it neglects the attractive forces between the two surfaces in and around the contact region. The local attractive forces are typically strong enough to cause the materials to deform thereby increasing the area of contact. There are two classical models which describe the contact deformation of elastic materials: the Johnson-Kendall-Roberts-Sperling (JKRS) theory and the Derjaguin-Muller-Toporov (DMT) theory [6]. The JKRS theory modifies the Hertzian model by adding a short-range, attractive force in the contact area only, forming a connective neck between the materials. This model works well for materials with low moduli, high work of adhesion and large radii (e.g., Ni/Au). The DMT theory adds a long-range attractive force outside the contact area. The theory works well for materials with high moduli, low work of adhesion and small radii (e.g., diamond/diamond). Each theory predicts a finite pull-off (or adhesive) force to break contact at zero applied load and reduces to the Hertzian model at high loads.

As an example, we have used these contact deformation theories to estimated (from the pull-off forces measured by AFM) the contact area radii and pressures at zero applied load. We find that even at zero applied load the contact area is quite large and never atomic even for diamond tips/samples whose high moduli resists deformation. The contact pressures under the tip are also appreciably high causing soft samples, like gold, to be deformed plastically.

An intermediate goal of our research is to describe the shape of the force curve analytically [9]. We have recently derived an expression using the relationships described above. With this expression we can fit the shape of the force curve, particularly in the deformation region, using moduli and contact area as fitting parameters. From these curve fitting routines it then becomes possible to determine the mechanical properties of materials irregardless of their thickness (i.e., the mechanical properties of monolayer films and adsorbates can be studied). The remaining goals of the research involve a comparison of the classical models with atomistic models as described by Harrison at this workshop, and the development of a full atomistic mechanism of the nanomechanical properties of materials including adhesion.

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[†] *Work done in collaboration with Nancy A. Burnham (KFA-Jülich,FRG) and Hubert M. Pollock (U. Lancaster, UK).*

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Electrostatic Adhesion Resulting from Spontaneous Charge Transfer between Dissimilar Materials

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The Surface Force Apparatus (SFA) has for some time been used to study adhesion at interfaces. Capillary forces, van der Waals forces and hydrodynamic forces in molecularly thin liquid films have all been investigated using the SFA. Since the measured molecular forces are often very short range, the surfaces used must be smooth on that length scale; cleaved mica has traditionally been the preferred material. Recently, the development at NIST of a technique for preparing smooth silica surfaces[1] has made possible the study of the adhesion at the interface between dissimilar insulators, either by using the silica-mica interface directly, or by chemically modifying silica surfaces.

When the adhesion between silica and mica was first measured in the SFA, a striking effect was observed[2]. Charge spontaneously transferred from one surface to the other during contact; subsequent separation of the surfaces required the separation of a charge double layer. The force required was 10 times greater than that necessary to separate a comparable mica-mica or silica-silica interface, and the work required was 100 times greater. This work of adhesion was typically in the range 6-8 J/m^2, comparable to the cohesive energies of the individual solids. A technique was developed[3] to measure both force and the amount of charge transferred in contact, and a model was developed which explains the observed distance dependence of the force in terms of a simple electrostatic attraction.

The mica and silica to be studied are prepared as thin (few μm), smooth samples and are mounted on cylindrical lenses of 10 mm radius. The lenses are mounted with their axes at right angles so the surfaces meet at a point. Figure 1 shows the sample mounting in detail. Force is measured by the deflection of a double cantilever spring. Surface separation is controlled with two mechanical stages and a piezo-electric tube, and is measured using an interferometry technique. Separation can be controlled and measured with 0.1 nm accuracy. The apparatus is sealed to permit control of the environment.

Charge which transfers from one surface to the other when the surfaces are in contact is measured by using the Ag layers as electrometer proof planes. Contact electrification at the interface creates a charge double layer. If the Ag layers are held at fixed potential, image charge current will flow in or out of each layer when the interface is separated. In the experiment, the Ag layers are held at ground through an electrometer circuit based on a very high impedance, low bias current FET op-amp which is built into the SFA.

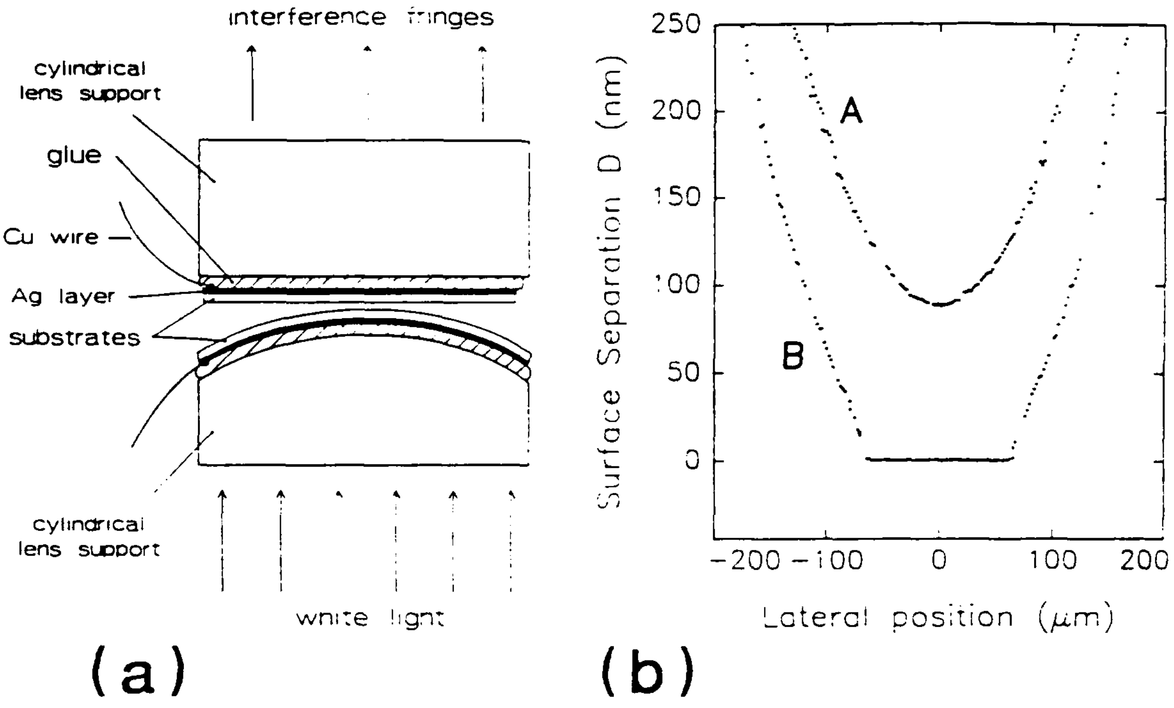

Figure 1. Schematic of the crossed cylinders and interference fringes. (a) Each substrate receives a 50 nm coating of silver and is then glued to the cylindrical lens support. A fine Cu wire is attached to each Ag layer, for use in the surface charge measurement. (b) Interference fringes are viewed by eye or by video (shown); 0.1 nm resolution in separation is possible. "A" shows a separation profile for surfaces out of contact. In contact, the glue deforms elastically to create a circular contact area whose diameter (typically 50 - 150 μm) can be measured accurately ("B"). Note the difference in scale between the axes - the curvature is greatly exaggerated.

The force is measured between a silica surface and a mica surface in dry nitrogen gas as a function of separation *D*. On approach (i.e., before contact) there is no force between the surfaces until they are less than 50 nm apart, where a small van der Waals attraction is observed. Something dramatically different is observed when the surfaces are separated: a strong, long-ranged attraction with a series of discontinuities (discussed below), as shown in Figure 2. The work of adhesion *W* represented by the area under the separation curve is $W = 6.6\ \mathrm{J/m^2}$, comparable to the fracture energies of ionic-covalent materials. Electrometer measurements reveal that the observed force is the result of a transfer of charge from one surface to the other. The silica acquires a net negative charge, the mica an equal amount of positive charge. Because of the extreme smoothness of the surfaces, the macroscopic contact area observed with the interference fringes is a good measure of the actual microscopic contact area (unlike the case of rough surfaces touching only at asperities). Using the observed contact areas and total surface charge, we determine that the surface charge density after contact of silica with mica is in the range $5 - 20\ \mathrm{mC/m^2}$, higher than typically seen in contact

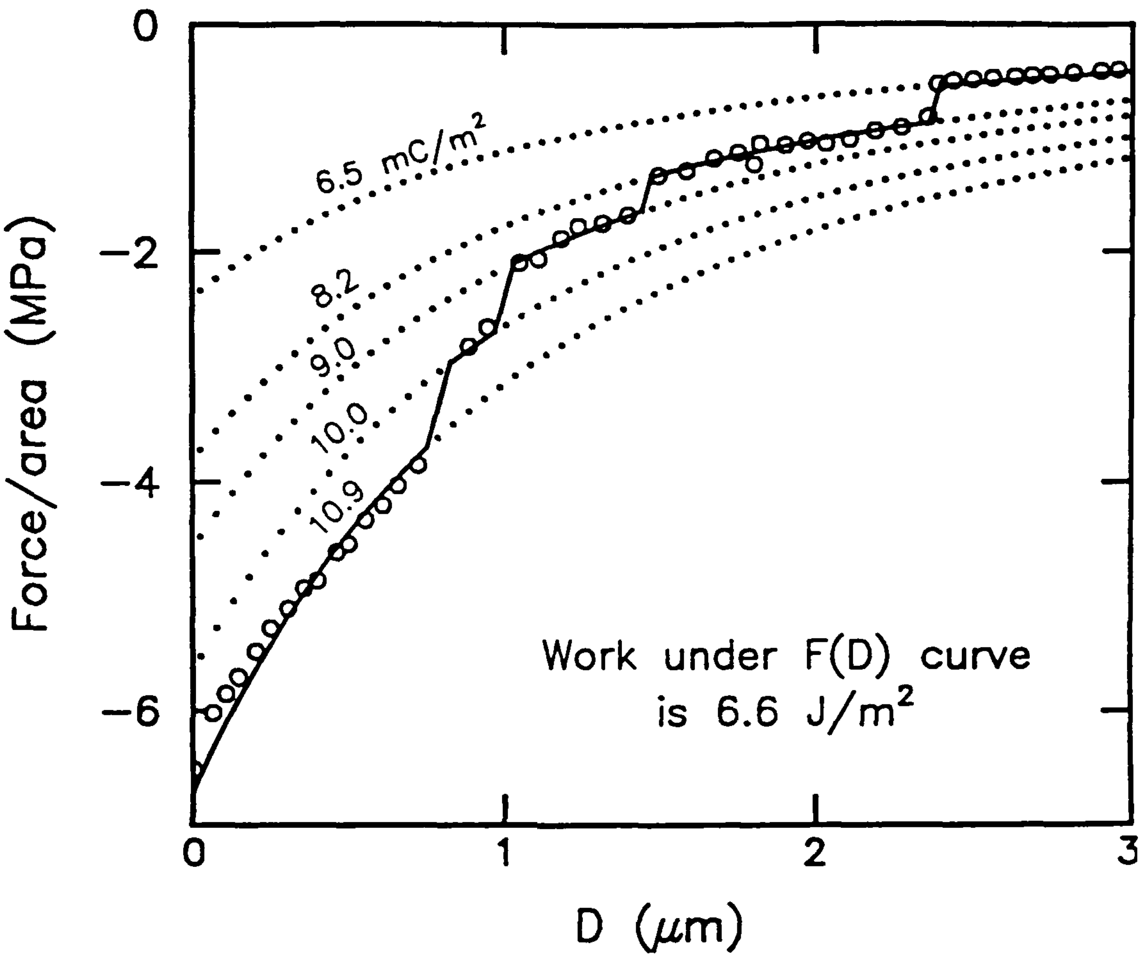

Figure 2. The force between silica and mica in dry N_2 gas measured while separating the surfaces from contact to 3 µm (negative force denotes attraction). Breaks in the force curve are the result of discharges across the nitrogen gap. The dotted curves are the calculation of the force using a four-layer parallel-plate capacitor model; each curve shows the expected result for a different surface charge density. The integral of the solid force curve gives a work of adhesion of 6.6 J/m^2.

electrification experiments.

The high charge densities create a field of magnitude 10^9 V/m across the gap when the surfaces are first separated, comparable to the dielectric strength of the intervening N_2 gas. This field drops with increasing *D* as image charge accumulates in the silver layers. Electrometer measurements confirm that the discontinuities in the separation force curve are the result of charge recombining across the gap in discrete discharges of approximately 10^8 charges each. The discharges are believed to depend on the mean free path in the gas; the separation at which the first discharge occurs increases linearly with $(N_2 \text{ pressure})^{-1}$. When the N_2 pressure is 1 atmosphere, the first discharge is observed for *D* in the range 0.5 - 1.0 µm.

In spite of the slight curvature of the surfaces, the electrostatic attraction between the surfaces can be modeled with an infinite parallel-plate system, because the charged area is typically 100 μm across, while the separation is only a few micrometers. For a simple system with two charge layers, such a model would predict a force that is independent of *D*. The experimental system, however, includes two image charge layers; charge density in these layers increases with *D*, reducing the force across the gap.

Some preliminary work has been done to explore the effects of water vapor on both the amount of charge transferred and the rate at which the surface charge decays. The work above was performed at "0%" relative humidity (RH), achieved by flushing the apparatus with N_2 gas that was passed through a liquid-N_2 cold trap. Charge was observed to decay with a time constant of $2\text{-}4\times10^4$ seconds. Raising RH to 11% had no effect on the amount of charge transferred, but the decay constant dropped to 600-800 seconds, a change of almost two orders of magnitude. At higher relative humidities the decay constant continued to drop, reaching less than 10 seconds at 60% RH. The amount of charge transferred appeared to drop as well, but that measurement may have been affected by the fast decay.

The technique described in this report offers the capability of measuring directly both charge transfer and adhesion force in the same experiment, with accurate monitoring of microscopic contact area and surface deformation. The number of materials available for study can be expanded to include polymers, metals and metal oxides. Various monolayer treatments are being developed to systematically vary the electronic states (or acid-base character) of silica surfaces to explore the effects of surface chemical modification on the charge transfer process. In addition, the apparatus is being modified to permit the sliding of one surface over another for the study tribocharging in various environments.

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TOUGHENING MECHANISMS IN MIXED-MODE INTERFACIAL FRACTURE

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EXTENDED ABSTRACT

There are many levels of describing the degree of adhesion between different materials. These essentially differ in the scale on which the descriptions are based; generally from microscopic levels to macroscopic levels without much integration or interaction from one level to another. As materials scientists have begun to probe interfacial regions, it has become clear that there are inadequacies in the classical continuous mechanical description of interfaces, which are modeled as being planes across which there is a jump in properties but zero jump in displacements. As the nature of these interface regions becomes better understood, the force deflection response of interphase regions must be included as an independent entity in the stress analyses of adhesively bonded components. Another benefit of this approach is that interfaces may be designed or tailored for specific requirements in a rational manner.

On the macroscopic scale, fracture mechanics has been used as one representation of the resistance that adhesively joined components, from fibers bonded to matrix materials to structural lap joints, have to failure or separation. The fracture toughness of an adhesive or an interface has been used to represent the resistance to catastrophic crack growth. Other fracture mechanical parameters are used to characterize an interface's resistance to fatigue, creep, or environmentally assisted crack growth by relating fracture parameters such as stress intensity factors or energy release rates to crack growth rates.

It has been appreciated for some time [1] that, since the path of interfacial cracks is constrained, the toughness of interfaces may depend on the ratio of normal to shear stresses, or fracture mode-mix, that act on the interface. The toughnesses of a number of interfaces have been shown to increase with increasing shear [2-5]. The widest range of fracture mode-mixes considered to date was obtained by subjecting a single specimen to a variety of biaxial loads [6]. The data obtained from glass/epoxy specimens is shown in the plot (Fig. 1) of toughness vs. mode-mix parameter, Ψ. Opening or tensile mode fracture is represented by $\Psi \approx 0°$, whereas as in-plane shear corresponds to $\Psi \approx \pm 90°$. It can be seen that the toughness rises for positive and negative shear by about a factor of 10 over the mode I value. The distribution of the toughness is not symmetric about the mode I value but rises more steeply for negative shear, possibly due to crack face contact effects.

Since interfacial crack growth ultimately involves the breaking of adhesive bonds, we expect that the intrinsic adhesion of any particular interface should be independent of the fracture mode-mix. The toughening effect noted in Figure 1 must therefore reflect other dissipative effects such as the (visco)plasticity of the bulk constituents, interfacial toughness [7] and frictional crack face contact. Because the glass substrate was highly polished, interfacial roughness or asperity locking did not contribute to the toughening noted in Figure 1. However, optical interference measurements of normal crack opening displacements revealed that crack initiation and stable growth was accompanied by

increasing amounts of inelastic deformation as the shear component was increased. Plastic zone sizes, though small scale in extent, followed the same bell-shaped distribution with mode-mix as the toughness [5]. Preliminary estimates of plastic and viscoelastic dissipation did not fully account for the toughening effect and more detailed analyses are now being conducted that account for inelastic behavior of the epoxy and the transition from initiation to steady crack growth.

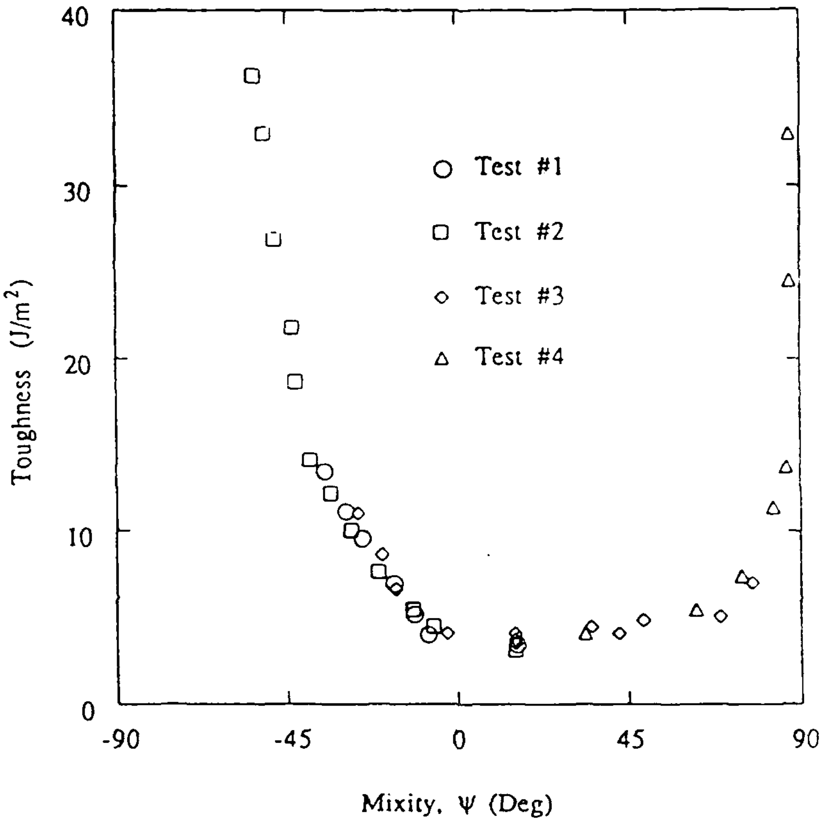

Fig. 1 Toughness of a Glass/Epoxy Interface

Further funding would enable fracture experiments to be conducted where the glass/epoxy adhesion would be controlled by mixtures of silane coupling agents that promote or diminish the bonding between glass and epoxy. The result of such experiments would be toughness vs. mode-mix curves for a range of intrinsic adhesions. For low intrinsic adhesion, there would probably be relatively little toughening with increasing shear, making a constant toughness criterion valid. On the other hand, for high intrinsic adhesion, we expect that the toughness would be highly dependent on Ψ, even in the region $|\Psi| \approx 0°$. Once models of the various sources of dissipation have been developed, the toughness curves could be predicted, if measurements of toughness at $\Psi \approx 0°$ were to be associated with the intrinsic adhesion provided by the various mixtures of silane coupling agents.

The approach described in the previous paragraph still relies on classical continuum mechanical descriptions of the interface and a measurement of the intrinsic adhesion. The next step in the modelling process would be to obtain the force deflection response of the interphase regions. This could be achieved experimentally from in-situ loading experiments in the SEM and digital image correlation techniques [8] to extract force deflection responses. Such data could then be included in line-spring finite element models [9,10] which could then be used to predict crack initiation and the accompanying dissipation.

An even deeper level of analysis could be developed on the basis of spectroscopic analyses that would identify the nature of the dominant bonds and species in the interphase region [11]. This information would allow molecular dynamics models of the interphase force deflection response to be constructed and compared with the results from the in-situ SEM experiments. The subsequent synthesis of molecular dynamics and finite element modelling would then allow toughness as a function of fracture mode-mix to be predicted in the manner described above.

SUMMARY

An incremental approach has been described whereby it should be possible to predict the strength and toughness of any interface, once the primary components of the interphase have been identified. The approach is initially based on fracture mechanics concepts and experiments but, in the final stages, is really independent of fracture mechanics in the sense that force deflection responses of interphase regions are used explicitly.

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Molecular Dynamics Simulations of Atomic Scale Friction and Adhesion of Diamond Surfaces

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The friction which occurs when two diamond (111) hydrogen-terminated surfaces are placed in sliding contact is investigated for sliding in different crystallographic directions (the $[11\bar{2}]$ and the $[1\bar{1}0]$), as a function of applied load, temperature, and sliding velocity, ν; via molecular dynamics and an empirical hydrocarbon potential.[1] This potential is potential II of reference 1 with additional terms that better describe torsional forces[2] and short-range, repulsive terms[3] which may prove important under high compression. Recently, this potential has been used to model the scattering of C_{60} from diamond surfaces[4] and the compression and indentation mechanisms in diamond (111) crystals.[5]

These simulations are carried out in the follow way. A hydrogen-terminated diamond lattice is placed over a second hydrogen terminated diamond lattice so that the (111) face of the upper lattice will be in close proximity to the (111) face of the lower lattice. Each lattice is composed of 12 layers. The outer three layers of each lattice are held rigid in the direction perpendicular to the (111) surfaces. The rigid layers of the upper surface are then moved at a constant velocity in the desired sliding direction. The forces normal, F_z, and parallel (or frictional force), F_y or F_x, to the sliding direction are monitored thoughout the course of the simulation. The friction coefficient is defined as the average frictional force divided by the average normal force. For example, for sliding in the $[11\bar{2}]$ direction, $\mu = < F_y > / < F_z >$; similarly for sliding in the $[1\bar{1}0]$ direction, $\mu = < F_x > / < F_z >$.

The friction coefficient is shown as a function of $< F_z >$ in Fig. 1 for sliding in the $[11\bar{2}]$ direction. As the normal load is increased μ increases. In contrast, the friction coefficient is approximately zero[6] when sliding in the $[1\bar{1}0]$ direction and is independent of normal load. For both crystallographic directions examined here, the sliding process did not result in adhesion between the two surfaces, even at large loads.

This directional dependence of μ is a direct result of the different atomistic sliding mechanisms when sliding in the two directions. For the starting configurations examined here, when sliding in the $[11\bar{2}]$ direction the hydrogen atoms of the upper surface are aligned with the hydrogen atoms of the lower surface in the sliding direction. As a result of hydrogen-hydrogen repulsion during sliding, the hydrogen atoms of the upper sliding surface must *revolve* around the hydrogen atoms of the lower surface to continue moving in the sliding direction. This effect becomes more pronounced at larger loads, increasing μ and eventually leading to an "atomic-scale stick-slip" type of behavior (This is also known as ratcheting) Thermal activation aids the *revolution* of the hydrogen atoms, thus μ decreases as the temperature increases as shown in Fig. 2. No such alignment of the hydrogen atoms occurs

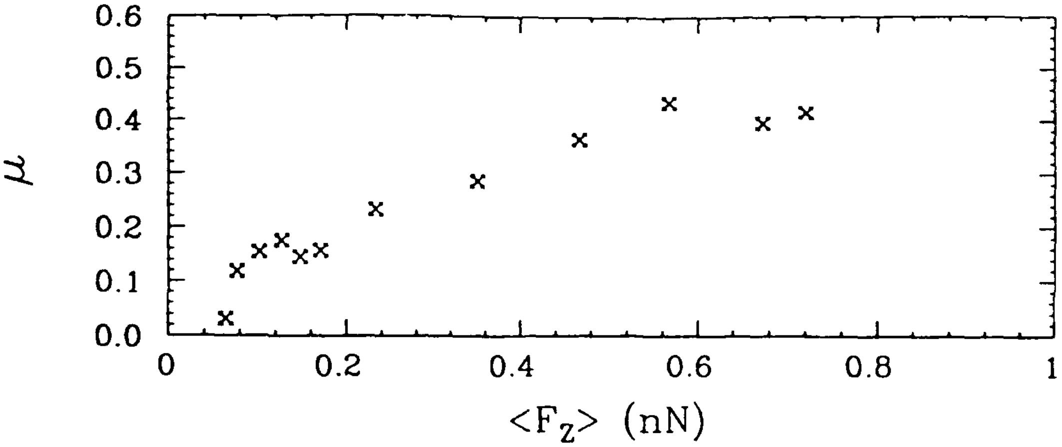

Figure 1. Friction coefficient as a function of load for sliding in the [11$\bar{2}$] direction at 1.0 Å/ps and 300 K.

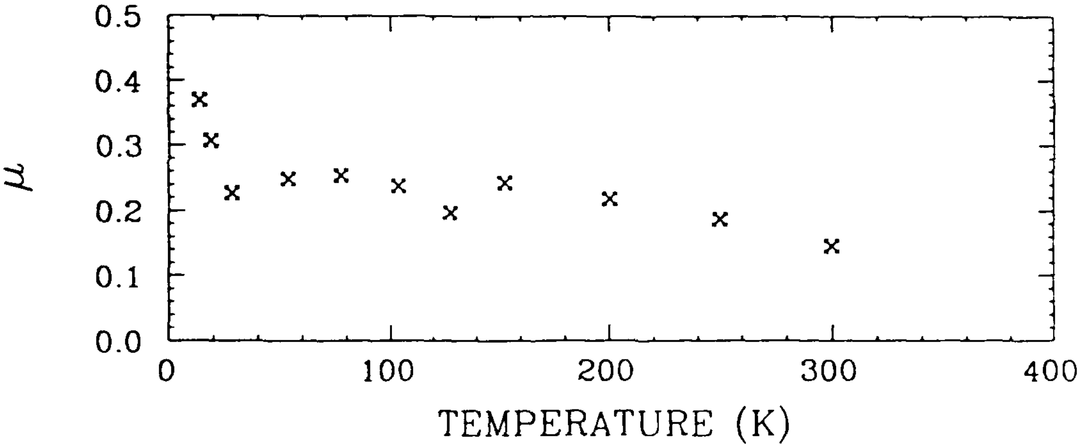

Figure 2. Friction coefficient as a function of temperature for sliding in the [11$\bar{2}$] direction at 1.0 Å/ps and 300 K. $< F_z >$ is in the range 0.109 to 0.148 nN for all runs.

when sliding in the [1$\bar{1}$0] direction. The hydrogen atoms of the sliding surface appear to *zig-zag* over the lower surface, going from a position over the second layer carbon atoms to a position over the fourth layer carbon atoms (i.e., holes in the surface) then back over second layer carbon atoms (see reference 6).

Lastly, we find for the sliding speeds investigated here, 0.5 and 1.0 Å/ps, μ is independent of sliding velocity.

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Making and Measuring Tailored Polymer Interfaces

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Practical uses of condensed matter are frequently dictated by physical and chemical interactions that occur within the first few nanometers of a surface. Adhesion, lubrication wetting, catalysis, and corrosion are just several amongst many processes that depend directly on surface composition and structure. Surface activity in polymer mixtures can generally be anticipated based on the difference in surface tension between the pure components and the substrate. However, when chemically different polymers are connected into block copolymers the conformational constraints associated with microphase separation and ordering can lead to qualitatively different surface properties that may significantly alter the adhesive behavior. In this abstract we describe our initial findings regarding the interfacial characteristics of symmetric and asymmetric polyolefin block copolymers.

Diblock copolymers containing poly(ethylene) (PE), poly(ethylethylene) (PEE), and poly(ethylene-propylene) (PEE) were synthesized by anionic polymerization and catalytic hydrogenation as described elsewhere (1). Neutron contrast was obtained through the use of deuterated monomer, or by substituting deuterium for hydrogen in the saturation reaction. Thin films were prepared by spin casting the material from solution onto a variety of flat surfaces. In all cases the results reported here were found to be independent of the substrate (e.g., Si, Ag, quartz, polystyrene and SiO_2 surfaces have been used). Specimens were annealed under vacuum at elevated temperatures (100 – 150°C) for several hours prior to making the measurements reported below. In each case the annealing temperature was less than 30°C below the order-disorder transition temperature (2) thereby facilitating equilibration.

Two types of measurements were conducted. Phase interference microscopy (Zygo microscope) was used to evaluate the uniformity of the thin films (3). Neutron reflection experiments were employed to evaluate the internal structure of the films and to determine the surface active blocks, both at the substrate and air interface (4, 5); the latter was corroborated with SIMS measurements.

We have separated our results into two categories: i) symmetric PE-PEP, PEP-PEE, and PE-PEE diblock copolymers, $f_A \cong 1/2$ where f represents the volume fraction of block A, and ii) an asymmetric, $f_{PEP} = 0.75$ PEP-PEE specimen. The compositionally symmetric materials ($f \cong 1/2$) all formed lamellar thin-film microstructures that possessed two common features. Non-integral amounts of polymer produced islands or holes of lamellar thickness d as illustrated in Figure 1 (3). However, unlike previous reports that deal with poly(styrene)-poly(methylmethacrylate) (PS-PMMA) diblock copolymers (3, 6) we discovered that in every instance, and on every substrate, the same block segregates to both the air and solid interfaces (5). We have attributed this finding to conformational asymmetry. In the three diblock copolymers examined, the surface active block is characterized by the smaller statistical segment length a where $Rg = a(N/6)^{1/2}$ in which Rg is the unperturbed radius-of-gyration and N is the degree of polymerization. Thus, while $N_A \cong N_B$, $Rg_{,A} > Rg_{,B}$ which entropically favors placing the B block at the film interfaces. This is intuitively obvious since the A block will penetrate further across a lamellae making the creation of an A surface of thickness $d/4$ more difficult. In the absence of a significant enthalpic driving force, as occurs with the polyolefins, this entropic effect will dominate. A crude model of this concept is given in Figure 1.

Asymmetric films behave quite differently. Because the favored microstructure for $f = 0.75$ is cylinders, there are additional mechanisms for avoiding the topological defects that characterize lamellae. We find that the internal structure of such thin films depends on the film thickness. However, in all cases, the asymmetric films are relatively smooth, regardless of the overall amount of polymer deposited. Figure 2 illustrated three representative results. In the ultrathin limit preferential segregation is observed, as in the symmetric case. At intermediate thickness a pseudo-hexagonally packed arrangement of cylinders is found where the lattice constant closely matches the bulk value (7). Increasing the film thickness to $\gtrsim 10$ lattice spacings leads to the formation of two distinct packing symmetries: hexagonal and tetragonal. We interpret these results based on the documented tendency for uniform (i.e., defect-free) film formation. At ultrathin and intermediate thicknesses lattice distortion provides a mechanism for accommodating nonintegral amounts of polymer. This can be accomplished without distorting the microdomain interfacial area, unlike with lamellae. By splitting into two ordered packing geometries, with different lattice parameters (and cylinder diameters) the thick films can minimize the overall free-energy with a minimal amount of distortion.

In summary, we have identified three aspects of polyolefin block copolymer thin films that may be tailored by controlling molecular structure. Firstly, surface segregation is strongly influenced by conformational asymmetry with a tendency for the block containing the smaller statistical segment length to locate of film surfaces. Secondly, surface topology is controlled by the film microstructure. And thirdly, the internal structure in asymmetric block copolymers is affected by the overall film thickness. Each of these factors will influence the adhesive properties of this important class of materials. We believe that independent control of these factors may be possible using mixtures of block copolymers.

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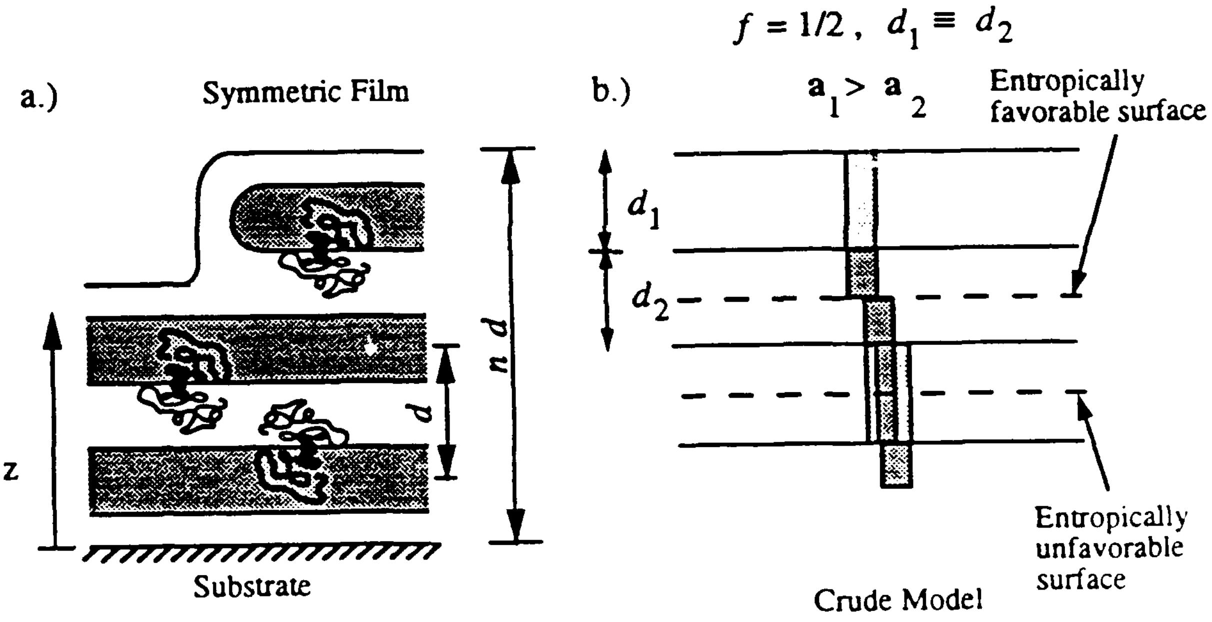

Figure 1. a) Symmetric lamellar thin film containing a non-integral amount of polymer. The layered microstructure leads to the formation of islands and holes. b) Crude model illustrating the concept of entropically driven surface segregation of the block containing a smaller statistical segment length (i.e., Rg).

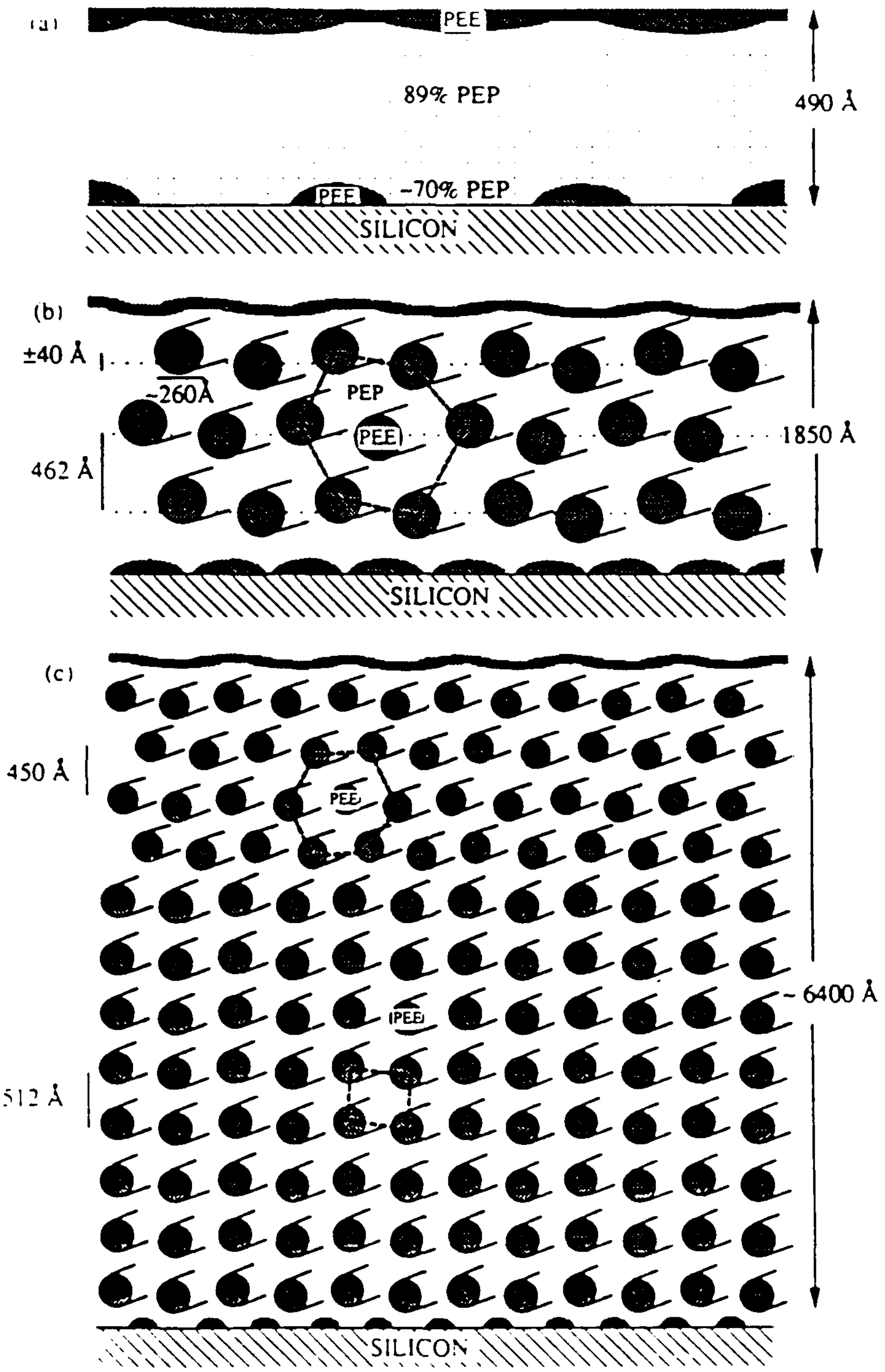

Figure 2. Thin film microstructure for an asymmetric PEP-PEE diblock copolymer determined by neutron reflectivity measurements. Ultrathin (a) and intermediate (b) thick films contain a distorted lattice while thick films (c) are characterized by two ordered structures (hexagonal and tetragonal. These results are attributed to the uniform (defect-free) films formed by this materials.

Optimum Toughening of Homopolymer Interfaces with Block Copolymers

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Introduction: Block copolymers have been widely used to reinforce interfaces between immiscible polymers. The reinforcement mechanism is believed to be a "stitching" effect; i.e. block copolymer chains form inter-phase junctions through which stress can be transferred, which results in a substantial reinforcement of the interfaces themselves [1]. Recent studies have examined the reinforcement effects of various combinations of block copolymers added to the interfaces between immiscible homopolymers [2,3]. Concurrently, theoretical models [4,5] and a fracture mechanism map [6] have been developed to explain the reinforcement effect of block copolymers at the interfaces between immiscible homopolymers.

When the concentration of block copolymer chains exceeds its critical micelle concentration, block copolymer chains can no longer organize as a brush at the interface and then generate other phases, such as micelles and lamellae, at or near the interface, and these phases can, in principle, affect G_c. A detailed investigation of toughening effect of block copolymer, especially in higher chain density regime is the object of this study. We have chosen polystyrene (PS) and poly(2-vinylpyridine) (PVP) homopolymers as the immiscible polymer pair and dPS/PVP block copolymers, whose PS block is deuterium labelled, as the compatibilizer to reinforce the interface between PS and PVP.

Experimental: PS and PVP homopolymers purchased from Aldrich Chemical Company Inc. were of commercial grade with weight average molecular weight of 250,000 and 200,000, respectively. The dPS/PVP block copolymers (580/220, 510/540 and 800/870) were synthesized by anionic polymerization: the polydispersity indices of these block copolymers were 1.1 or less. The block copolymer with PS block polymerization index of 580 and PVP block polymerization index of 220 will be designated by 580/220. The PS block is deuterium labelled so that the quantity of the PS block at the interface can be analyzed with forward recoil spectrometry (FRES).

A sandwich sample of PS and PVP whose interface was reinforced with a block copolymer was fabricated by compression molding at 160°C for 2 hours, which was then cut with a diamond saw to obtain strips for the following fracture toughness measurement. The dimensions of the strips were 50.8 mm long × 8.7 mm wide × 4.0 mm thick (2.3 mm and 1.7 mm for PS and PVP, respectively). One of these strips was then cut into smaller pieces for the microtomy.

Fracture toughness of the interface, G_c, which is characterized by the critical energy release rate of an interfacial crack, was measured using an asymmetric double cantilever beam (ASDCLB) geometry. The measurement was performed by inserting a single edge razor blade at the interface and pushing it at a constant rate of 3×10^{-6} m/sec using a servo-controlled motor drive. The steady state value of the crack length preceding the razor blade was measured at a regular interval. After the G_c measurements, both fracture surfaces were examined by FRES to determine the areal chain density, Σ, of block copolymer. More details about the ASDCLB can be found elsewhere [3].

We have used the cross-sectional TEM method to investigate the interface structure and deformation mechanisms of the interface. Details of this technique can be found elsewhere [7].

Results and Discussions: Figure 1 shows G_c as a function of Σ for the asymmetric (580/220) system. After exhibiting a discontinuous jump at $\Sigma^*=0.04$ chains/nm^2, G_c remained approximately constant at higher Σ. TEM observation of the interface revealed that at large Σ (>0.12 chains/nm^2) the asymmetric block copolymer formed spherical micelles near the interface, and that a craze was formed on the PS side and broke at the PVP/PS craze interface. This observation indicates that the spherical micelles have no effect on G_c.

In contrast to these results for the asymmetric block copolymer, we observed that block copolymer formed lamellae at the interface at large Σ's of symmetric block copolymers (510/540 and 800/870), and that this lamellar structure affected G_c. As shown in figure 2, in both cases, after exhibiting a maximum at the Σ corresponding to the saturation coverage of the interface with block copolymer chains, G_c began to decrease and finally reached a constant value when the interface was fully covered with one additional block copolymer lamella. Similar results have been reported by Brown [2]. TEM observation showed that in both cases fracture mechanism is crazing followed by craze breakdown. FRES analysis revealed that the fracture took place in the lamellar structure for 800/870, where the interfacial crack propagated both within the dPS sub-lamella and at the interface between outer block copolymer chains of lamella and PS homopolymer, while fracture took place between the dPS block at the saturated interface and the dPS block of the lamella for 510/540.

These results show that there are limits to the interface toughening that can be produced by adding diblock copolymers especially for symmetric block copolymers. Adding more block copolymer than needed to saturate the interface actually produces secondary (lamellar) interfaces which are weaker than the original saturated homopolymer one.

Conclusions: We have investigated fracture toughness and fracture mechanisms of PS/PVP interfaces reinforced with either asymmetric (580/220) or symmetric (510/540 and 800/870) dPS/PVP block copolymers.

Asymmetric block copolymer chains form spherical micelles on the PS side of the interface at large Σ's, however, G_c remained approximately constant, indicating that these block copolymer micelles does not affect G_c. FRES and TEM observations showed that fracture took place by crazing on the PS side followed by craze breakdown at the PVP/PS craze interface.

In contrast to these results for the asymmetric block copolymer, symmetric block copolymers (510/540 and 800/870) form lamellar phase at the interface at large Σ's, and this lamellar phase affected G_c. In both cases, after exhibiting a maximum at the Σ corresponding to the saturation coverage of the interface with block copolymer chains, G_c began to decrease and finally reached a constant value when the interface was fully covered with one additional block copolymer'lamella. TEM observation showed that fracture mechanism is crazing on the PS side followed by craze breakdown in both cases. FRES analysis revealed that the locus of fracture was within the block copolymer lamella for the 800/870 system, where an interfacial crack trajectory had an oscillating characteristic, while fracture took place between the dPS block at the saturated interface and the dPS block of the lamella for the 510/540 system.

These results show that there are limits to the interface toughening that can be produced by adding diblock copolymers especially for symmetric bcp's. Adding more bcp than needed to saturate the interface actually produces secondary (lamellar) interfaces which are weaker than the original saturated homopolymer one.

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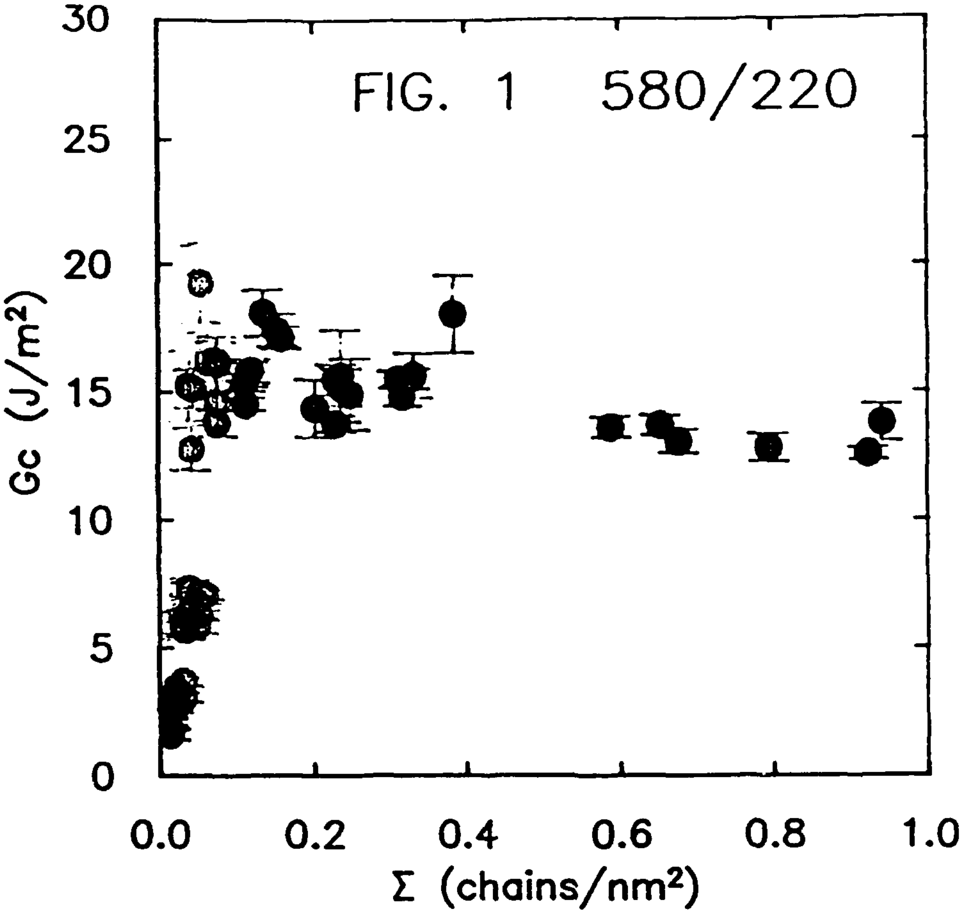
FIG. 1 580/220

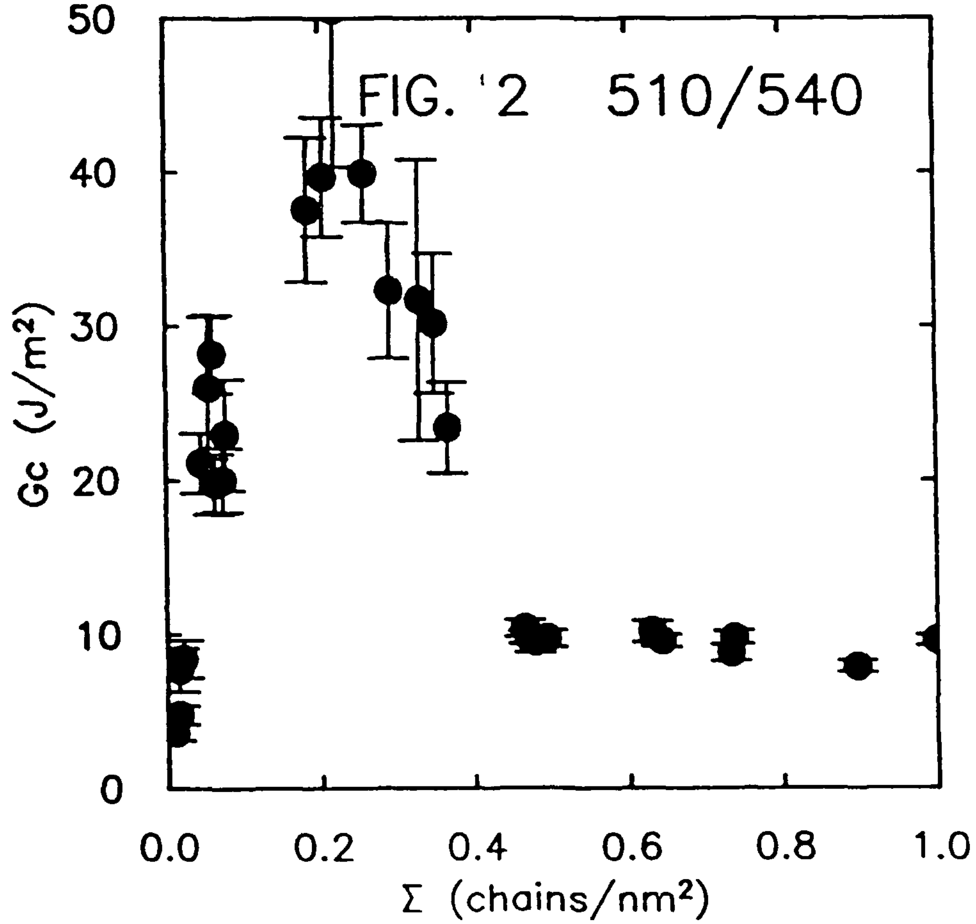
FIG. 2 510/540

Polymer-Particle Adhesion Probed with Atomic Force Microscopy

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The technique of atomic force microscopy (AFM) can directly measure the adhesion of small particles to a surface from the force required to remove them using a soft cantilever.

The adhesion of a particle to a surface is extracted from a loading curve.[1] The sample, which is mounted on a piezoelectric transducer, is driven towards the particle under computer control. The motion of the tip of the cantilever to which the particle is intimately attached is monitored as a function of sample displacement. The sample is pushed against the particle until the cantilever is bent backwards. When the sample is retracted, the particle continues to adhere to the surface, until the cantilever is bent forward enough to generate enough force to break the adhesion. The cantilever then springs back to its resting position. The adhesion force is proportional to the distance the cantilever springs backwards.

A loading curve measurement is shown in Fig. 1. From the loading curve, one can extract both the particle adhesion, indicated by the extent of the vertical arrow, and the relative height of the sample, indicated by the extent of the horizontal arrow. Multiple contacts show that successive adhesion determinations are repeatable, with fluctuations about the mean adhesion of only 2%. The adhesion force is independent of the duration of contact and the loading force.

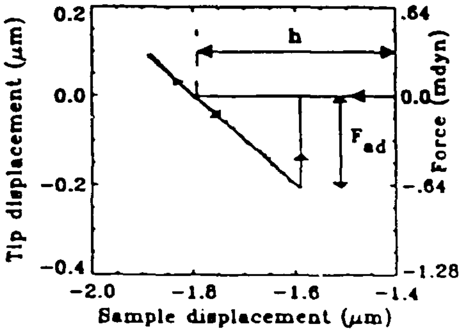
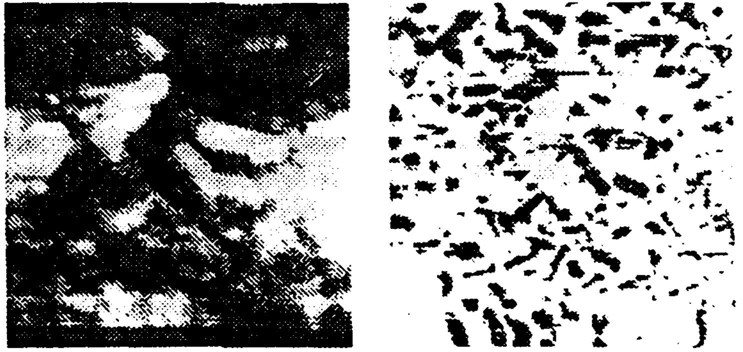


Fig. 1

One can simultaneously generate a high resolution map of surface topography and adhesion by performing the loading curve measurements in a grid pattern over a region of the sample.[2] In Fig. 2 we plot the topography and spatial dependence of adhesion between a Si_3N_4 particle and a rough Tedlar/polycarbonate blend. 128 × 128 loading curves



topography map Fig. 2 adhesion map

were taken over a 2×2 micron area. Comparison of adhesion and topography over the same areas shows that adhesion is small on the top of the polymer bumps and larger in between the bumps. The decrease of adhesion on top of the bumps may either be due to a smaller area of contact, a decreased Van derWaal attraction, or a combination of both effects.

By generating spatial maps of adhesion variations, one can use AFM to distinguish materials. In Fig. 3 we show the adhesion map of an interface between a thin gold film on silicon and the silicon substrate. In the topographic image (not shown), the gold film is difficult to pick out because of its smooth transition to full thickness, but in the adhesion map the contrast is extremely high. By comparing the adhesion across interfaces, we have determined the relative particle-substrate adhesion for a number of materials.

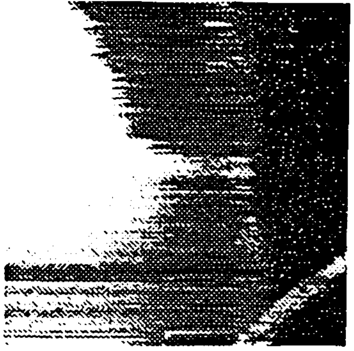


Fig. 3

Adhesion maps can resolve features that are not apparent in surface topography. In Fig. 4 we show a 2×2 µm adhesion map of molecularly doped polycarbonate film. While the topography (not shown) was featureless, the adhesion image shows that this sample has local regions of high adhesion that appear as dendrites emanating from a central location.

Fig. 4

We have begun some studies of adhesion for probe particles other than the Si_3N_4 pyramids. We have attached toner particles used in the electrophotographic process to the cantilever with epoxy. In Fig. 5 we plot the adhesion of the toner particle to a gold substrate vs. contact number for 3 different series of contacts over 3 different areas. The blunter toner-gold contacts are seen to asymptotically approach a stable value over a large number of contacts. The apparent height of the sample is not changing for these contacts, evidence that no plastic behavior is occurring. This adhesion change is never seen for the sharp Si_3N_4 contacts to any surface.

We attribute the increase in adhesion to contact charging. A similar asymptotic increase in charge on a surface is seen for metal-polymer contacts.[3] Contact charging is not expected to occur for the sharp Si_3N_4 pyramid because the contact area is much smaller.

In conclusion, we have shown that spatial maps of adhesion can probe the stickiness of polymer surfaces in new ways. Adhesion maps made with more well defined particles and surfaces can be used to directly test the geometric theories of van der Waal adhesion. Adhesion maps can also identify regions of different materials on the surface. The spatial resolution has been demonstrated to be 6 nm, but for sharp, soft contacts, we believe it could be improved to molecular dimensions and used to identify adsorbed molecules.

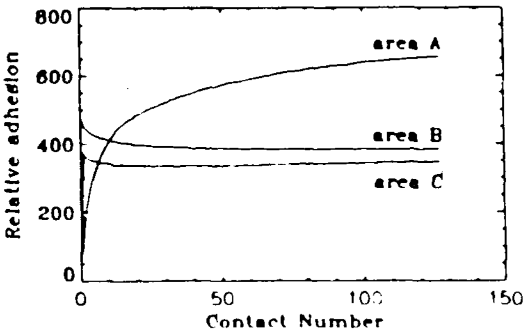


Fig. 5

molecules. For blunter particles, we see changes in adhesion which may be due to contact charging. With more controlled experiments, it should be possible to study this fundamental process on a single electron scale.

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Interfacial Adhesion Studies of Polyimides with the Atomic Force Microscope

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Polyimides are a class of high temperature polymers. Their important applications include microelectronics packaging, wire insulation, and fillers in composite materials. Good interfacial adhesive and mechanical properties are important in each of these applications.

We use the atomic force microscope (AFM) for both destructive and non-destructive studies of the near surface properties of polyimides and related materials. Materials studied so far are Kapton-H, PMDA-ODA, BPDA-pPDA, ODPA-ODA, 6FDA-ODA, and the polyetherimide, Ultem. Measurements are made out in both air and fluid environments and correlated with results of other techniques including x-ray photoelectron spectroscopy and photoelectron microscopy.

The most straightforward application of AFM is direct imaging of clean and metallized polyimides. The clean polyimide surfaces are extremely flat. RMS surface roughnesses are typically only a few Å -- comparable to an oxidized Si wafer. The ultimate resolution is an important quantity for imaging applications. The best resolution we have demonstrated so far with 100 - 400 Å radius tips is 150 - 200 Å. This value agrees well with the contact area calculated using JKR elasticity theory. In general, molecular resolution on polymer samples seems unlikely.

We have also used the sharp tip of the AFM to fabricate and then image a variety of sub-micrometer structures. These include grooves with widths as small as 20 nm, hillocks with heights up to 1 nm above the original surface, and pits with depths of 0.1 µm. The groove profiles indicate that the primary mechanism for groove formation is microplowing; i.e., mass transport by plastic deformation rather than removal of material from the surface. Plastic deformation occurs when the load applied to the AFM tip exceeds the yield stress of the polymer. Since tip-surface contact areas are typically 20-40 nm in diameter, forces of about 100 nN are sufficient to plastically deform the surface of most polymers. Surface deformation occurs only above a threshold load that is near the yield stress. This makes possible nondistructive AFM imaging of the modified surfaces. The dimensions of the grooves depend only weakly on the speed of the tip across the surface.

We have also fabricated hillocks and pits. For example, pits up to 900 Å deep have been formed on Kapton-H surfaces. The structure at the bottom of these pits appears to be closely related to the degree of crystallinity near the surface. At present, the mechanisms of pit formation are poorly understood. In addition to plastic deformation, we believe that cutting, viscoelastic flow, and frictional heating are involved. Reliable data about the nanometer scale mechanical properties are needed.

One monolayer of Au evaporated onto the surface is sufficient to prevent groove formation. The gold agglomerates to form particles about 40 Å high.

Metallization of polyimides with Cu has also been studied with the AFM. Cu interacts very weakly with all the polyimides. Cu films up to 50 Å mean thickness have been studied. AFM images reveal non-uniform coverage. Instead, grains with 20-120 nm lateral sizes and heights up to about 250 Å cover the surface. Cu films on the fluorinated polyimide 6FDA-ODA have the largest grain size and surface roughness.

Characterization of Interface Chemistry and Adhesion of Polyimide to Cr and Al

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Multilayer structures involving polymers and metals are used increasingly in electronic packaging applications. In particular, polyimides are finding widespread use because of their unique chemical and physical properties. Two very different interfaces are typically formed in the manufacture of metal-polymer multilayer structures, (1) the *metal-on-polymer* interface formed by vacuum deposition of a metal onto an already cured polyimide film and (2) the *polymer-on-metal* interface formed by curing of polyamic acid precursors on a thin metal film. Understanding of the chemical and mechanical properties of both interfaces is critical to the performance and reliability of devices. However, the majority surface science investigations have focused on the metal-polymer interface, which can be explored under ultrahigh vacuum (UHV) conditions with standard electron spectroscopies.

We have utilized combined surface spectroscopy and adhesion studies to explore the chemical reactions taking place at the polymer-metal interface and their relation to mechanical properties (*e.g.* adhesion) of the final polymer-metal composite. Fourier transform infrared spectroscopy (FTIR) and x-ray photoelectron spectroscopy (XPS) techniques have been used to explore interface reactions occurring when thin polyimide films are spin cast and cured on metal films. Being an optical technique, FTIR has the advantages of not needing UHV conditions and of being applicable at actual processing conditions. The technique is further useful by directly probing polymer functional groups. This information complements composition and electronic binding information obtained by XPS. XPS is a surface sensitive technique, while IRRAS samples the entire film depth. In the case of very thin films (< 100 Å), the two techniques probe similar sample depths and yield valuable new insight into interfacial reactions.

Polyimide thin films on Cr, Al and Au surfaces were prepared by curing a spin-casted polyamic acid precursor [biphenyl-tetracarboxylic dianhydride (BPDA) - p-phenylene diamine (PDA) (Dupont PI2611)]. The curing processes were performed in a nitrogen purged sample cell that enabled *in-situ* monitoring of curing kinetics by FTIR. Based on *in-situ* curing studies, a curing procedure for preparing very thin films (~100 Å thick) was established that was different from the curing schedule conventionally employed for thick (~1 μm) films. The imidization process proceeded at temperatures higher than 90°C and was competed at 250°C. Anhydride was formed as an intermediate and it was observed to convert to polyimide at 250°C. For very thin polymer films on Cr surfaces, the polyamic acid precursor reacted with the native chromium oxide to form a carboxylate salt. This carboxylate salt formation was not detected on Al and Au surfaces.

Thin polyimide films on Cr, Al and Au were characterized by both FTIR and XPS, as a function of film thicknesses in the range 100-1000Å. The film thickness was controlled by varying the dilution of the polyimide precursors. More contributions to the infrared signal from interfacial region were observed as the film was thinned. The vibrational bands observed include imide C=O stretching at 1775 and 1735 cm^{-1}, aromatic ring absorption at 1620, 1515 and 1420 cm^{-1}, and C-N stretching of the imide ring at 1360 cm^{-1}. No significant changes in absorption band shapes and relative intensities were observed as a function of precursor dilution for polyimide on Au, while thin polyimide films on Cr behaved quite different. As the film thickness decreases, a systematic change in IR spectra was detected. Specifically, the imide C-N (1359 cm^{-1}) intensity *vs.* semicircle aromatic ring stretching band (1516 cm^{-1}) decreased with reduced film thickness, while the absorption band around 1620 cm^{-1} became broader. The IR spectral changes were attributed to strong chemical interactions at the polyimide-Cr interface, with both aromatic rings and imide rings perturbed by the interfacial interactions. In contrast, no significant change was observed as film thickness was varied on Al substrates, which implies a weaker interaction of the polyimide with Al than Cr. The conclusions drawn from the IR spectroscopy observations were confirmed by XPS analysis.

The interface chemistry information has been correlated with adhesion data for PI2611 polyimide films (~15 µm) on Cr and Al. The adhesion measurements were obtained by the island blister test and they revealed stronger adhesion for polyimide to Cr than to Al, consistent with the levels of chemical interfacial interactions establish spectroscopically.

Systematic studies of polymer-metal interfaces continue to be carried out using this combined approach of interface-chemistry spectroscopy and adhesion measurements. Several important issues in adhesion and interface bonding are being addressed, including (i) the different chemical and mechanical properties of polymer-on-metal and metal-on-polymer interfaces, (ii) the relationship between microscopic chemical interactions at the polyimide-metal interface and adhesion properties of the multilayer structure, and (ii) optimum conditions for fabrication of specific polymer-metal structures that are stable in subsequent processing steps and end-use applications.

An Evanescent Wave Probe of Kinetic Phenomena in Polymer Layers Adsorbed on Solids

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Polymers adsorbed from solution onto solids have become the subject of scientific study because of their historic role in colloidal stabilization and because of their potential for applications such as lubrication, adhesion, and corrosion inhibition. Over the past 50 years, the collection of experimental observations concerning colloidal stability and hydrodynamic properties of adsorbed layers has led to much speculation about their structure. Within the past 10-15 years detailed and generally-accepted models have been developed to describe the structure within equilibrated layers.[1] According to mean field theory, interactions between substrate, polymer, and solvent determine the relative amounts of trains, loops, and tails within an equilibrated layer, where the former lie flat on the substrate and the latter extend far into solution to dominate the layer's hydrodynamic properties.[2] Scaling theory predicts that when the surface is saturated, homopolymer layers have a self-similar structure.[3]

In practice, the situation is complicated by observations that adsorbed polymer layers are often not fully equilibrated and that their <u>history</u> plays a major role in determining interfacial structures and the ability of a system to respond to changes in bulk solution.[4] First, it is generally observed that homopolymers accumulate rapidly at an interface, so that the time is soon approached where *there is no further net flux to the surface.* After this time, however, radiotracer studies reveal that there is a continual exchange of chains between the interface and the bulk.[5] Adsorbed layers are generally resistant to desorption into pure solvent, which could lead to non-equilibrium scenarios. It has also been observed that bulk concentration and incubation time (the time the adsorbed layer contacts the solution, prior to any desorption or exchange steps) greatly influence the kinetic behavior of a layer, and therefore must impact the structure at the interface. For instance, chains can be desorbed into pure solvent if desorption is commences immediately after mass accumulates at the interface. The desorption is hindered if, after the surface excess reaches a constant level, the layer is incubated in the polymer solution prior to desorption. The longer the incubation period, the more difficult the desorption.[5] This suggests that although no changes appear in the adsorbed layer during the incubation, the chains relax slowly on the surface. Further, these experiments suggest that the original adsorption protocol did not lead to a fully equilibrated layer. How then, can one assess whether a system is equilibrated and how can one probe the route by which adsorbed polymer layers approach equilibrium states?

Our work at Lehigh focuses on issues of equilibration timescales and the kinetic behavior of adsorbed polymer layers. The program (which is less than two years old) aims to develop novel experimental techniques that can probe interfacial phenomena more directly than commonly-employed methods. We have recently constructed a Total Internal Reflectance Fluorescence (TIRF) instrument[6] that monitors adsorption, desorption, and exchange kinetics in situ. Its advantage over conventional techniques is its ability to monitor populations of chains ~50 nm. from a substrate. Interfacial accumulation and diffusion are measured, and there is the potential to track slow interfacial relaxations[7] (whose presence can only be deduced from the results of previous studies.)

In TIRF, a laser is totally internally reflected inside a clear substrate (a glass or sapphire prism) that contacts a polymer solution. The total internal reflection generates an evanescent wave or electric field whose strength decays exponentially into the polymer solution (λ ~50nm). As fluorescently-labeled polymer chains diffuse into the evanescent zone and adsorb on the substrate, an interfacially-generated fluorescence signal can be monitored and the kinetics of these processes analyzed. Experiments can be run so that fluorescent chains are introduced into the bulk solution after an unlabeled layer is partially established, to probe the interplay between bulk solution and adsorbed layers. Interfacial relaxations can be monitored directly by careful choice of the fluorescent probe. If the fluorophore is chosen to interact with the substrate or is pH-sensitive, the signal will be influenced by the polymer configuration, for instance, the relative amounts of segment-substrate contacts, and proximity of the labels to the substrate or to other labels.

The advantage of TIRF lies in its ability to monitor kinetic processes in situ, and to attribute phenomena within the layer to specific populations of chains, unlike neutron reflectivity. The latter provides less ambiguous data but requires up to 11 hours for each measurement. The TIRF signal must be carefully interpretted and series of tests run to confirm a particular interpretation. TIRF has the further disadvantage that fluorescent labels must be added to the chains of interest, however, labeling is required in small amounts (1 label / 200K of backbone) and parallel measurements with varied degrees of labeling will easily demonstrate when the labels perturb the interface. TIRF requires optically clear substrates, but is not limited to glass. Indeed, a polymeric substrate can be spincast onto optical flat which is then coupled to a prism waveguide.

The work presented in the poster comprises our early results with a number of fluorescein-labeled polymers, demonstrating the extreme sensitivity of the technique. These experiments employ a flow cell with a laminar slit geometry such that the composition of the bulk solution is nearly constant, and wall shear rates are sufficiently low (3 s^{-1}) so that shear is not expected to deform the adsorbed layers. While instrumental improvements are ongoing to increase the signal/noise ratio, a number of qualitative features are apparent in these water-soluble systems where chains adsorb only a glass substrate though hydrogen bonding:

- Initial accumulation of interfacial mass is rapid, consistent with previously documented studies.

- Adsorbed homopolymer layers are resistant to wash-off (desorption) in the solvent from which they were adsorbed. Here hydroxyethyl cellulose adsorbs in less than half an hour but there is significant retention after 7 hours of exposure to flowing solvent.

- The fluorescein label is sensitive to the pH of the local environment. While a pH 7.2 phosphate buffer has minimal impact on the fluorescence of the labeled polymer solution in bulk, the presence of the buffer (not itself fluorescent) is necessary for the interfacial signal. Flushing water into the cell causes complete signal loss. We know that the polymer is retained at the interface, since replenishing the buffer causes the signal to be recovered. Hence slow changes in signal from the fluorescein label may be an "average sense" indicator of the proximity of these labels to the silica substrate, which is acidic. (Much future work will go towards quantifying this effect.)

- Polyethylene oxide, labeled on one end only, exhibits a rapid overshoot during adsorption. This may be a result of polydispersity in this sample, micellization in bulk solution, or rearrangements during the adsorption process that become more visible because of the end-labeling.

Ongoing groundwork will facilitate quantifiable signals in terms of adsorbed amounts. Tests are also being designed so that interpretations concerning interfacial relaxations and overshoots can be substantiated. Future work involves instrumental calibrations, and independent measures of the adsorbed amount with reflectivity and less pH-sensitive dyes such as rhodamine. With this groundwork is laid, efforts will then focus on fundamental issues of adsorption kinetics.

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