MODIFIED SCANNING PROBES FOR THE ANALYSIS OF POLYMER SURFACES

A Dissertation

Presented to

The Graduate Faculty of The University of Akron

In Partial Fulfillment

of the Requirements for the Degree

Doctor of Philosophy

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August, 2009
ABSTRACT

Scanning probe microscopies (SPMs) allow the observation and measurement of surface properties on a highly local level based on the interaction between a very sharp probe and the surface. Interaction stability and probe integrity, at least during the scanning time, are necessary, but still a challenge. Conventional scanning probes have been used for revealing morphological features connected with macroscopic properties of complex latex films. These films, when dry, are sufficiently hard to be studied with minimal distortion of the surface by the probe. By comparing formulations with various fluorosurfactant concentrations, it was demonstrated how the fluorosurfactant, which is known heuristically to improve leveling, gives the system more mobility before drying. Specifically, in styrene-butadiene copolymer formulations, sub-micrometer differences in surface morphology, observed as a function of fluorosurfactant concentration, correlated with differences in gloss.

In some cases, surfaces are too soft or too adhesive to be studied by conventional probes. Modification of scanning probes with hydrophobic layers having methyl or fluorinated end groups has been used to weaken the probe-surface interaction to study model adhesive surfaces. Acrylic block copolymers with well-defined molecular weight and composition were synthesized by controlled radical polymerization to create models of pressure sensitive adhesives to evaluate performance after aging or humidity exposure.
Macroscopically, tack measurements demonstrated that blending a triblock copolymer with a homopolymer of the midblock polymer can be used to tailor the tack value. Microscopically, force-penetration curves of the acrylic blends showed a superficial phase separation into two mixed phases as homopolymer content was increased. Hydrophobic modification made it possible to measure these surfaces that would otherwise be too adhesive to study with conventional probes.

Modification of scanning probes has also been used to bring robustness to high resolution chemical imaging. Addition of a 2-3 nm Al₂O₃ protective layer on silver-coated scanning probes dramatically reduced degradation of the probes with time, without sacrificing initial probe efficiency. In addition, the protective layer improved markedly the wear resistance of the probes. The surface morphology of the silver structure was not altered and the signal enhancement decay was completely stopped. These results agree with the conjecture that an ideal dielectric coating shifts the epicenter of the electromagnetic field enhancement in plasmonic structures, a behavior previously simulated, but not demonstrated. New types of plasmonic structure fabrication were also explored as means to surpass currently available signal enhancements by controlled size and shape, increased roughness or higher crystallinity. A single metal nano-pillar deposited by electron beam induced deposition (EBID), crystalline dendritic structures deposited by metal replacement reactions, and layers with sharper asperities deposited by ion sputtering were all fabricated on conventional scanning probes. The last produced a significant enhancement. In addition, strong signal fluctuations in Raman band intensity (“blinking”), similar to those seen in single molecule surface enhanced Raman spectroscopy, were also observed. This approach opens exciting new possibilities.
ACKNOWLEDGEMENTS

I thank God for giving me the strength to become a researcher, Neissa for her love and for sharing this life with me, and Santiago and Marcela for always believing. I thank Prof. Mark D. Foster for his support, guidance, patience and commitment to shape independent researchers. I also thank Prof. Alexei P. Sokolov for his guidance and encouragement and Mr. Andrey Malkovskiy, Dr. Nam-Heui Lee, Dr. Ryan Hartschuh, Dr. Alex Kisliuk, Mr. James Robbins, and Dr. Rick Thomas for their collaboration in this work. I thank my colleagues in the Polymer Surfaces & Interfaces Group for many useful conversations about science, engineering and life. Dr. Bojie Wang’s valuable help with the electron microscopes and Prof. Edward Evans assistance with the physical vapor depositions is greatly appreciated. I also thank Prof. Darrell Reneker, Prof. Ali Dhinojwala and Prof. Bi-min Newby for their helpful suggestions and comments. I am very grateful with all my friends for their support during all these years, in particular the Cano and the Hartschuh families. Finally, I sincerely thank The Department of Polymer Science and all my professors and teachers for devoting their lives to the noble occupation of forming individuals. I acknowledge the help of Dr. Jason Fowlkes from Oak Ridge National Laboratory (ORNL) for the preparation of electron beam induced deposited structures for TERS. Financial support from the Army Research Office (W911NF-07-1-0470 and DAAD19-03-1-029344249-MS) and the Omnova Solutions Foundation is greatly appreciated.
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CHAPTER I

INTRODUCTION

A very sharp probe scanning a surface in a raster pattern is the enabling element of all scanning probe microscopies (SPMs). Current development in SPM instrumentation allows not only imaging surfaces with nanometer lateral resolution, but also obtaining physical and chemical information. Techniques developed from SPM allow the observation and measurement of surface properties on a highly local level and in a way such that bulk dissipative mechanisms play a much less prominent role than they do in macroscopic measurements. Atomic force microscopy (AFM), the most popular form of SPM for the study of polymer surfaces, relies on the mechanical interaction between the probe and the surface to obtain topography images and measure mechanical properties; scanning tunneling microscopy (STM) provides information on surface topography on the basis of electric interaction between a conductive probe and a conductive surface; and near-field scanning optical microscopy (NSOM) uses a combination of mechanical and optical interactions to obtain simultaneous chemical and topography information. Independent of the type of interaction, stability and probe integrity, at least during the scanning time, must be satisfied. While most of the progress in SPM instrumentation has been made by improving control on probe position and increasing sensitivity for detection, not much change has been made in the enabling element: the probe.
Ideally, the probe must be precisely defined and should maintain its integrity during scanning. This is rarely the case due to strong compression forces during the first approach and to frictional forces during scanning.

This work focuses on three interrelated problems. The first section presents how conventional SPM techniques can be used for revealing morphological features that can be connected with macroscopic properties. Conventional scanning probes are used here for analysis of hard, complex latex films. Unfortunately, the use of these probes is limited when the interaction between the probe and the surface is strong and unstable, as is the case for soft or sticky surfaces, evidencing the need for means to weaken this interaction.

The second section presents hydrophobic modification of probes as a way to reduce the strength of the interaction with the surface by reducing complications from capillary and adhesive forces when making Force-distance measurements on adhesive surfaces. Changes in non-tackified adhesive surfaces with aging, especially under various levels of humidity, are studied with hydrophobically modified scanning probes. The modification reduces the magnitude of pull-off forces measured on model pressure sensitive adhesives (PSA), making it easier to measure adhesive surfaces. Acrylic block copolymers of well-defined molecular weight and composition are synthesized by controlled radical polymerization to create models of acrylic PSAs. These materials may not have to be tackified, and therefore will have superior aging properties and are more suitable for food and drug applications.

In the third section, means to protect metallized scanning probes and to create active probes used in high resolution chemical imaging by apertureless near-field optics
are presented. Tip enhanced Raman spectroscopy (TERS) is an emerging technique that combines SPM with optical spectroscopy to obtain chemical images with nanometer lateral resolution. Unfortunately, metallic or metallized scanning probes available for optical applications when this work was started were neither stable nor extremely highly enhancing, with enhancement factors in the order of $10^4$. Ultrathin dielectric layers, with thicknesses lower than 5 nm, are fabricated and tested as means to protect metallized probes against wearing and chemical degradation. New types of probe design and plasmonic structure fabrication are explored as means to surpass currently available signal enhancements using three different fabrication techniques that provide, respectively, controlled size and shape, higher crystallinity, and increased roughness.
CHAPTER II
BACKGROUND

2.1 Surface characterization of hard polymer surfaces using conventional scanning probes for atomic force microscopy (AFM)

The Atomic Force Microscope (AFM) is the instrument used for the most popular form of scanning probe microscopy (SPM) in the polymer community. Its functioning principle is based on the mechanical interaction between a very sharp probe and a surface\(^1\). Conventional SPM probes for AFM are commonly made of hard materials such as silicon or silicon nitride and are manufactured in such a way that they are positioned at the end of force sensing cantilevers. Scanning in a raster pattern the probe over the surface or scanning the surface under the probe, depending on the instrument, allows one to obtain topographic images with nanometer scale resolution. Since the technique of atomic force microscopy is sensitive to a variety of forces, including van der Waals forces, electrostatic forces, adhesion forces and frictional forces, different AFM modes can be sensitive to different material properties.

A piezoelectric scanner moves the sample under the probe or the probe over the sample in a raster pattern while forces or height are measured by the deflection of the cantilever. A feedback loop monitors the probe-sample force and adjusts the sample Z-position to hold the force constant to operate in constant-force mode, or adjust the force on the sample to hold the Z-position constant to operate in constant-height mode.
Commercially available cantilevers have micrometer-size dimensions, spring constants ranging from 0.01 to 100 N/m, and resonant frequencies ranging from 5 kHz to over 300 kHz\textsuperscript{5}. Conventional SPM probes for AFM are micro fabricated by lithographic and anisotropic etching techniques\textsuperscript{6}. In early SPM, probes were created by gluing diamond fragments to the foil cantilevers or by electrochemically etching the wires to a sharp point\textsuperscript{1}. Current methods involve etching an array of small square openings in a SiO\textsubscript{2} mask layer over a silicon surface and coating low stress Si\textsubscript{3}N\textsubscript{4} layers to define cantilever shapes and to create pyramidal probes\textsuperscript{7}. The lateral resolution of imaging depends on the probe radius of curvature and the heights of features on a sample surface, as illustrated in Figure 1.

![Figure 1. Schematic of the scanning probe. A probe with a radius of curvature R scans two very sharp objects separated by a distance d with a height difference Δh. Adapted from Ref. 8.](image)

The minimum separation, $d$, that results in a depression of depth, $\Delta z$, that must be higher than the instrument noise level to be resolved, for spikes with height difference, $\Delta h$, imaged by a parabolic probe with a radius of curvature, $R$, is given by the equation:

$$d = \sqrt{2R \left( \Delta z + \sqrt{\Delta z + \Delta h^2} \right)}$$  

(2.1)

Then, for a conventional silicon probe with a $R = 10$ nm, a minimum detectable $\Delta z$ of 0.5 nm, and two sharp elements with a high difference of 1 nm, the highest lateral resolution achievable with AFM is 11 nm, roughly the radius of curvature of the probe.

High resolution and high-aspect-ratio probes are produced by oxide sharpening by focused ion beam (FIB) or milling by electron beam deposition (EBD). Recently, carbon nanotubes are receiving some attentions for their use as SMP probes$^9$. Their nanometer-scale diameter, long length, high stiffness, high conductivity, and elastic buckling properties lead some to tout them as the ultimate material for probes$^{10}$. Unfortunately, attachment or growth of nanotubes to or from conventional scanning probes is difficult and requires detailed positioning devices or very sophisticated deposition techniques.

Even with probe materials as hard as silicon or silicon nitride, wearing is one of the most frequent operational problems in any scanning probe microscope$^{11,12}$. Chung et al.$^{12}$ have demonstrated that fracture of a silicon probe readily occurred due to impact during the approaching process even at extremely low normal loads. Strategies for minimizing wear including the addition of lubrication layers$^{13}$, protective layers$^{14}$, or even new geometric designs$^{15}$ have been suggested, but, unfortunately, wearing still persists as a major limitation.
2.1.1 Imaging

Conventional scanning probes, i.e. those without any modification, can be successfully used for the morphological study of a wide variety of polymer surfaces, so long as these are of sufficiently high modulus and sufficiently low adhesiveness. In this work we take the case of imaging latex-based floor polishes as an example of an application, which shows both the power of atomic force imaging and related techniques as well as the limitations of topographical imaging with polymers when the sample material parameters vary widely.

2.1.2 Adhesion measurements

By far the most widely used means of gathering information on adhesion forces has been inference from macroscopic measurements of quantities such as surface tension, elastic moduli, and tack. Although these determinations provide important information, it is difficult to infer from them the role played by the surface. Techniques developed from scanning probe microscopy (SPM) can be used, among other things, to differentiate surface adhesion between phase-separated microdomains in films of block copolymers or immiscible blends.

Methods using conventional SPM probes for local force measurements provide important information about surface mechanical properties. In particular, force-based techniques using an oscillating probe are feasible to study soft samples such as polymers and biological systems. Phase images, which are based on differences between the excitation and the response phase of an oscillating probe, can reflect very small variations of the local properties of the sample surface\textsuperscript{16,17}, as shown in Figure 2. Each of the
individual contact-release cycles contains specific information about the probe-surface interaction, useful for characterizing samples showing small-scale compositional heterogeneity, for instance materials having hard and soft regions or areas with different adhesiveness. Unfortunately, the interaction between a conventional probe and a soft/adhesive surface is very complex and strong, and may not allow obtaining an image of the surface.

Figure 2. Schematic of a probe operating in tapping mode. The phase difference varies in response to the mechanical properties of the sample surface and to the strength of the probe-surface interaction.

2.1.2.1 Force-distance measurements

Force-distance (F-d) measurements using scanning probe microscopy (SPM) are used to determine surface forces acting between the probe and the surface\textsuperscript{18-20}. In the F-d curve of an ideal hard sample, as that shown in Figure 3, zero force is initially registered as the probe approaches the surface before the contact\textsuperscript{21,22}. When the probe is close enough to the surface for attractive intermolecular forces to be sufficiently strong, the
probe is pulled into the surface at what is commonly known as the “snap-in” point. Once in contact, the cantilever is loaded to a pre-defined force by increasing the probe pressure on the surface. In cases in which the sample is significantly stiffer than the cantilever, only bending occurs during loading. As a result, the slope of the loading curve can be used as a measure of the cantilever stiffness. However, when the surface is softer than the cantilever, bending is accompanied by probe indentation into the surface and information about the sample stiffness can be obtained from the slope. Unfortunately, when the material is too soft, indentation is accompanied by an important change in contact area, making its quantification difficult. After reaching the appropriate loading force on the surface, the sample is retracted until the probe is very close to separating from the surface. Then there is an abrupt jump back to the zero-level force. Most often, the unloading curve manifests a characteristic, attractive force that acts on the cantilever beyond the zero force point. This pull-off, or adhesion, force is measured as the difference between the point of minimal force on the unloading curve and the zero force level.

Figure 3. Schematic of a Force-distance (F-d) curve measured by SPM for an ideal hard sample.
F-d results are extremely sensitive to environmental and experimental conditions, including humidity level and measurement rate, which are of particular interest when studying adhesive and mechanical properties of polymer surfaces, due to the presence of viscoelasticity\textsuperscript{30}. When a hydrophilic silicon or silicon nitride scanning probe is in contact with a wet surface, or in contact with a surface in a humid atmosphere, water from the surroundings condenses at the probe-sample contact and forms a capillary meniscus\textsuperscript{31}. In addition to that, soft materials have more complicated molecular and mechanical interactions with the probe than do hard surfaces. The registered force is actually a combination of interfacial and capillary forces when the measurement is conducted under ambient conditions, making the quantification of the adhesive force difficult. Furthermore, the contact area with soft materials is continuously changing during the loading/unloading process, making its quantification a difficult task.

The amount of moisture in the air, i.e. the relative humidity (RH), controls the thickness of the layer of absorbed water that will be present on all surfaces\textsuperscript{31}. In order to investigate the behavior of adhesive samples under different levels of relative humidity (RH) using F-d measurements, it is necessary to eliminate the effects of these capillary forces\textsuperscript{32}. Sheiko\textsuperscript{32} presented the problems in SPM measurements arising from atmospheric contamination under ambient conditions. Salmeron et al.\textsuperscript{33} determined two different regimes of water coverage on mica at room temperature under increasing temperature, one below and one above RH = 20\%, using Force-distance curves and different pull-off forces were found. At low levels of RH, Xiao and Qian\textsuperscript{34} believed that the water layer was too thin for capillary condensation to have a significant impact compared with van der Waals forces, which are dominant under those conditions. Direct
imaging of the meniscus formed under different RH has been also reported\textsuperscript{35}. Then, the effect of capillary forces can only be neglected when the surface of the probe is hydrophobic or when the relative humidity around the probe/surface interface is below 20\%\textsuperscript{33,34,36,37}. Self-assembly of organic molecules on conventional Si or Si\textsubscript{3}N\textsubscript{4} to form an ultrathin film with a hydrophobic surface has been used to measure the adhesive and frictional forces between the probe and the sample with the purpose of mapping the spatial arrangement of chemical functional groups\textsuperscript{38,39}. Both reduction of humidity around the tip and modification of the tip have been previously used in our group to study the properties of polymer surfaces\textsuperscript{40}.

2.1.3 Analysis of hard surfaces: Latex films used in floor polish applications

AFM can be used to investigate the fate of fluorosurfactants in complex latex films. The dependence of the final floor polish topography on the action of surfactant in floor polish formulations has not been understood. A floor polish is a complex emulsion, commonly based on styrene-acrylic copolymers, used to protect and improve the appearance of floors. It is formulated as a liquid, but performs as a thin, solid film. It is designed to be durable to intense shear with only a few thin coats and it is commonly applied using a string mop. Some materials used in floor polishes formulation are surface-active. Surfactants emulsify and stabilize the polymers in water. Coalescents and plasticizers help the formation of a strong, durable film. Polyethylene and polypropylene waxes impart scuff resistance to the film due to a reinforcing effect given by crystalline regions. Defoamers reduce and prevent defects during drying by minimizing foam formation. Surfactants lower the surface tension of the latex to improve
wetting, flow and leveling of the polish. Unfortunately, the individual effect of each of these components in the emulsion is very difficult to determine, but their final effect on the microscopic morphology of the dry film can be observed by SPM.

Surfactants are used to disperse, stabilize, and improve leveling and flow before drying. During drying the surfactant can either dissolve in the polymer and plasticize it, or form a continuous membrane at the internal polymer/polymer interfaces, or phase separate from the latex polymer and enrich the film interfaces\textsuperscript{41,42}. The latter phenomenon has been observed in several model latex systems in which surfactant bloomed to the film/air and the film/substrate interfaces\textsuperscript{43-45}.

2.1.3.1 Surface-active materials in a floor polish formulation

Due to the relative complexity of latex based floor polish formulations compared with the model latex systems commonly found in the literature, very little research on the surface characteristics of these durable yet removable finishes has been conducted. An excess of leveling agent in a floor polish is expected to have a negative impact on film properties. If it accumulates at the film/air interface, it could negatively affect gloss and scratch resistance of the film, while accumulation at the film/substrate interface could weakens adhesion and peel strength by softening of the polymer. Excess surfactant between particles during the film formation process may hinder coalescence and results in weak films.

Rates of surfactant desorption and migration vary with composition and drying conditions\textsuperscript{46}. Migration of surfactant to either the film/air interface or the film/substrate interface is an effect of the system trying to minimize the surface tension\textsuperscript{47}. A high
enrichment at the air side is due to transport of surfactant by a water flux during drying\textsuperscript{45,47,48}. In the dry state, surfactant/polymer incompatibility provides the driving force for surfactant migration, but this process is very slow.

There are several problems associated with the leveling agent performance, commonly a fluorinated surfactant, in a floor polish. Without fluorosurfactant, a floor polish will usually not completely level before drying. If too much fluorosurfactant is present, defects during the application of the coating can appear as a result of excess foaming, in addition to the normal foaming observed due to the presence of stabilizers and surfactants. If a film has inferior wetting behavior, commonly promoted by a mismatch between the formulation surface tension and the substrate surface energy, the formulation will flow to form ridges while wet and mobile. When a leveling problem exists, the wet film will appear to be smooth and uniform during drying until the later stages of drying, when an uneven gloss will appear. The leveling ridges appear to follow the high shear trail of the string mop, even when the coat has been evenly applied.

The fluorinated surfactant is not the only surface active material in a floor polish formulation. Other materials such as coalescents and plasticizers contribute significantly to surface tension reduction, adding up to 6\% wt. of the entire formulation. Tributoxy ethyl phosphate or phthalates as well as ethylene and propylene based glycol ether are commonly used plasticizers and coalescents, respectively. Additionally, excess of surfactants used to emulsify polymers and waxes before formulation of the floor polish can decrease the surface tension. In order to more readily identify the phenomena of central interest Cartwright et al.\textsuperscript{49} considered a simple, model polish formulation consisting of only water, coalescent, plasticizer, and latex polymer. This formulation had
a surface tension of 30 mN/m that was very close to the surface tension of 28 mN/m for formulations containing fluorosurfactant. Even with all the components except fluorosurfactant, the surface tension was low enough for good performance. Unfortunately, leveling was compromised by the absence of fluorosurfactant.

2.1.3.2 Surfactant migration to the surface

As the latex emulsion dries into a film, the excess surfactants can either dissolve into the polymer and plasticize it, form a continuous membrane at the internal polymer/polymer interfaces, or phase separate from the latex polymer and enrich the film interfaces.\textsuperscript{41,43-45} Due to transportation of free surfactant by a water flux during the drying process, surfactant enrichment at the surface is often more pronounced than at the film/substrate interface\textsuperscript{45,48}. This is inherently related to the system trying to minimize its surface tension and can drastically affect the macroscopic properties of the film. If excess surfactant migrates to the surface, the formation of a haze on the surface of the latex film can occur. The accumulation of surfactant at the film/substrate interface can weaken the adhesion of the latex film to its substrate and negatively impact the peel strength required to remove the latex film. If excess surfactant stays between the latex particles during the film formation process, the coalescence of the latex particles can be hindered resulting in latex films with weak cohesive properties.

Wheeler et al\textsuperscript{50} and later Voyutskii\textsuperscript{51} reported that surfactants segregate from the polymer particles in model latex formulations. Tzitzinou et al.\textsuperscript{45} detected an increased concentration of anionic surfactant at the surface by using Rutherford Backscattering (RBS) in acrylic latexes, regardless of temperature and time of film formation. AFM was
used to reveal the manner in which the film features developed with time and/or as a function of surfactant concentration. At low concentrations, the latex forms a thin uniform layer. At high surfactant concentrations, the films contain finger like, flat droplets or larger hemispherical blobs, depending on the concentration. They conjectured that in their system, the surfactant was not expelled from the bulk latex, but it was deposited at the sample surface during the drying process. Sein has also shown that similar latex films display a wide range of aggregate morphologies, depending on the anionic surfactant's concentration. It has been conjectured that as film formation proceeds and particles come into contact, the surface area of each particle available for surfactant adsorption is reduced, facilitating desorption of surfactant to the air-water interface while water is still present during the drying of the film-forming latex. Lee et al. modeled the behavior of different surfactants in model latex films and predicted their segregation to form 30-50 nm thick films at the surface depending on the type of surfactant.

2.1.3.3 Surface morphology and gloss

Gloss relates to the ability of a surface to direct reflected light and is a key macroscopic property desired by customers. High gloss is a key objective of commercial formulation and latex film development. Gloss is not affected by individual material properties, but by a combination of properties and environment factors such as refractive index, angle of incidence of light and surface topography. Gloss may be improved by the selection and concentration of some formulation ingredients, but commonly at the expense of sacrificing durability. In a protective coating, gloss can be affected by the
chemistry of the base polymer and by surface active additives, such as surfactant, plasticizer, coalescent and leveling agent that end up affecting flow and distribution of components in the film before drying\textsuperscript{55}. The surface morphology of a dry latex film, especially at length scales affecting the scattering of visible light, is expected to have a dominant influence on gloss. Unfortunately, it is still not clear whether surface roughness or structure heterogeneity at the surface is the key element affecting gloss.

Due to the relative complexity of latex based floor polish formulations compared with the model latex systems previously discussed, very little research on the surface characteristics of these durable, yet removable, finishes has been conducted. Conventional scanning probes for AFM can be used to probe, on the scale of the wavelength of light, the surface morphology, after drying, of latex films formulated for use as floor polish. Elucidating how fluorosurfactant affects surface topography and its effect on a film’s gloss is still of industrial interest and is one of the objectives of this work. A hypothesis is that surfactant impacts surface morphology on a length scale commensurate with the wavelength of light and therefore impacts gloss. This hypothesis will be tested and an attempt made to correlate microscopic morphology changes with gloss observed on a macroscopic scale.

2.1.4 Soft and adhesive surfaces

Measurement of F-d profiles allows the quantification of snap-in forces, which reflect attractive forces between the probe and the surface, and pull-off force, which is dictated not only by surface properties, but also by bulk properties as well\textsuperscript{21}. They present problems when conventional scanning probes are used with very sticky materials.
Another complication in the interpretation of nanoscale adhesion and mechanical properties measurements is the fact that the contact sizes are below the optical limit (1 μm) and not easily measured. Also, when using AFM for nanoindentation studies, undesirable surface interactions from charging or contamination may arise. For micro- and nanoscale studies, the dimensions of both the contact and residual deformation (if any) are below the optical limit. The main problem involves a non-perpendicular penetration resulting in significant lateral force contributions during indentation, which could easily occur. Additionally, the compliant material has significant time-dependent material properties (creep relaxation and viscoelastic behavior) that complicate (and even prevent) analyses of simple force-displacement curves to extract mechanical properties. Despite these challenges, useful qualitative information can be extracted from carefully done experiments.

In a force-penetration curve, it is important to note that if the sample stiffness is low enough (as might be the case for low modulus polymers), the sample surface may be distorted to come into contact with the probe when the contact is formed, rather than the probe jumping to the sample surface. In the Johnson-Kendall-Roberts (JKR) theory (applicable in the limit of low elastic modulus, large radius and small surface energy) and the Derjaguin-Muller-Toporov (DMT) theory (applicable for high modulus, small radius and large surface energy) the adhesive force is predicted to be a linear function of probe radius, R, and the work of adhesion, W. One of the important features of a force-penetration curve is the shape of the loading region and the value of the slope of that region, if well-defined. Some recent work has focused on the behavior of these curves for very elastic materials, where the plastic deformation is negligible\textsuperscript{56}. The probe is used
as an indenter. Unfortunately, contact mechanics models cannot explain plastic deformation of viscoelastic materials. Therefore, AFM nanoindentations still constitute semi-quantitative investigations.

2.2 Highly localized adhesion measurements of soft or adhesive materials with functionalized scanning probes

Many questions remain about the role of humidity in the performance of adhesives and how modified scanning probes could contribute to understanding surface properties of soft materials. SPM has been extensively used for adhesion studies with nanometer-scale contacts involving rigid surfaces, but its use with soft and adhesive surfaces\(^57\) still presents big challenges. These surfaces present contradictory requirements for SPM analysis. On one hand is the requirement of light tapping to avoid surface damage, and on the other, the need for energetic tapping to enable the probe to lift off the surface. Information from the sub-surface is best obtained with a stiff cantilever (\(k > 15\) Nm) with a large free oscillation frequency (\(f > 150\) kHz)\(^58\). Unfortunately, the use of SPM to study the adhesive behavior of viscoelastic materials has been restricted mainly by the complexity and geometry of the interaction. It is difficult to scan a very sticky surface with a very compliant probe if the interaction between surfaces is strong. Previous work in our group has focused on studying tackified pressure sensitive adhesives and the effect of component migration on surface properties\(^24-27,59\). In that work, SPM was only used effectively on samples after they had been aged for long times due to the impossibility of using conventional scanning probes to study freshly cast, sticky samples. Hydrophobic coatings, especially very thin layers such as self-assembled monolayers (SAMs), have
been applied on silicon and silicone nitride probes with the purpose of improving image resolution by reducing probe-sample interfacial adhesion\textsuperscript{60,61}.

2.2.1 Functionalization with hydrophobic silane layers

Alkylsilanes can directly react with the oxide layer present on some types of probes\textsuperscript{62,63} to form a self-assembled monolayer, the surface of which has a chemical character completely different from that originally at the surface. Figure 4 schematically describes this reaction. Alkylsilane SAMs are both physically robust and chemically stable\textsuperscript{62}, making functionalized probes suitable to measure adhesion forces and to image surfaces otherwise unseen by decreasing other forces acting on the probe during the F-d measurements\textsuperscript{40,64}.

![Figure 4. Silane reaction on silicon oxide surface.](image)

\[\begin{array}{c}
\text{Physisorption} \\
\text{Hydrolysis} \\
\text{Grafting and crosslinking}
\end{array}\]
Knapp and Stemmer\textsuperscript{61} studied the effect of three different hydrophobic layers on probe properties and performance with the particular interest of improving image resolution. It was shown that image resolution improved for hydrophilic biological surfaces imaged in a buffer solution with probes hydrophobically modified by a self-assembled monolayer due a reduced contact area and reduced probe-sample adhesion, even though the probe radius was slightly increased. Gold, hexafluoropropene (HFP), and octadecyltrichlorosilane (OTS) coated probes were chosen. The authors reported that the OTS layer was the most hydrophobic, the pull-off from a standard sample with probes coated with OTS was insensitive to RH, and produced the smallest change in radius in the probe. Overney et al.\textsuperscript{65} have investigated the F-d behavior of a probe coated with a hydrophobic OTS SAM layer. When the probe was coated with OTS, and in agreement with Knapp’s results, there was no apparent dependence of pull-off force on RH. The authors interpreted this insensitivity to RH as a proof that the hydrophobic layer on the probe prevented a capillary meniscus from forming.

The deposition of n-hexadecyltrichlorosilane (HTS) as a hydrophobic self-assembled monolayer on an scanning probe has been used before to decrease the forces acting on the probe during the F-d measurements\textsuperscript{40}. The advantage brought by the probe modification was first demonstrated when pull-off forces measured by the modified probe on a simple, hard silicon surface remained nearly constant under increasing levels of RH. For soft adhesive samples, the values of pull-off force and work of adhesion using the modified probe are lower than those measured using an unmodified probe. This is also advantageous because the pull-off force for an unmodified probe on a good adhesive can become so large that the surface cannot be effectively studied with SPM.
2.2.2 Model adhesive system: acrylic triblock copolymer films

Polyacrylates of appropriate monomer composition are inherently pressure sensitive adhesives without compounding with additives due to their low glass transition temperature \( T_g \) and high cohesive strength, and offer some properties that are superior to those of pressure sensitive adhesives based on other types of polymers. Acrylic triblock copolymers have received attention for their potential in the formulation of thin adhesive films and the possibility of serving as substitutes for styrene-based block copolymers. They have the characteristics inherent to thermoplastic elastomers (TPEs) and possess some properties superior to those of other polymers. Acrylic polymers are colorless, more resistant to oxidation than conventional diene TPEs, a wide variety of monomers are available to tailor the final adhesive properties, and the upper service temperature (UST) can be much higher given the appropriate selection of monomers. Unfortunately, the application of these materials is restricted by low cohesive strength at low molecular weights and the need of low molecular weight additives to improve their properties for specific applications.

Substantial benefits could be realized by developing pressure sensitive adhesives (PSAs) from acrylic block copolymers. Shull and collaborators discussed creating PSAs from acrylic block gels. Yamamoto and coworkers synthesized poly(acrylic acid)-b-polybutylacrylate-b-poly(acrylic acid) (PAA-b-PnBA-b-PAA) triblock copolymers and reported bulk viscoelastic characteristics and “holding power” of films. Chen and Shull reported that triblock copolymers with polyethyleneglycol acrylate midblocks could be used to eliminate adhesion to a surface in an aqueous environment. Drzal and Shull studied the adhesive failure criteria in PSAs of anionically polymerized
polymethylmethacrylate - b- poly(n-butylacrylate) – polymethylmethacrylate (PMMA-b-PnBA-b-PMMA). Shull and coworkers\textsuperscript{71} have also studied the thin films created by the deposition of micelles of PMMA-b-PnBA.

Ordered diblock and triblock copolymers exhibit microstructures that vary with the block composition and this microstructure is the reason for important properties. To perform incisive experiments on the relationship between adhesive performance and aging, well-defined homopolymers, diblock, and triblock copolymers of poly(methyl methacrylate) (PMMA) and poly(n-butyl acrylate) (PnBA) can be synthesized by controlled radical polymerization. For the formulation, block copolymers blended with other block copolymers with different concentrations or even with pure homopolymers can be considered with the aim of reducing the amount of low molecular weight additives used to improve mechanical properties.

2.2.2.1 Synthesis by atom transfer radical polymerization (ATRP)

Controlled radical polymerization can be used to synthesize well defined diblock and triblocks copolymers of poly (methyl methacrylate) (PMMA) and poly (n-butyl acrylate) (PnBA) for the formulation of acrylic adhesives. The chain molecular weight and single chain composition of the rubbery PnBA block and glassy PMMA can be adjusted to obtain the best model adhesive. A blend of PMMA-b-PnBA-b-PMMA triblock and PMMA-b-PnBA diblock copolymers without tackifier is expected to give the best adhesive and mechanical properties\textsuperscript{72,73}.

Living polymerizations, in which neither transfer nor termination takes place, allow one to gain control not only over the molecular weights and polydispersities of
polymer chains, but also their architecture and end-groups. Living polymerizations may be carried out using anionic, cationic, or group transfer polymerizations schemes, but each of these requires specific experimental conditions that often make their industrial application difficult. Recently, atom transfer radical polymerization (ATRP), a controlled radical polymerizations method, has been developed and successfully used for the synthesis of acrylic block copolymers\textsuperscript{74}.

The general mechanism of ATRP, shown schematically in Figure 5, involves the abstraction of a halogen from the dormant chain by a metal center (such as complexes of Cu) in a redox process\textsuperscript{74}. Upon halogen abstraction, the free-radical (active species) formed can undergo propagation as in conventional free radical polymerization. However, the free radical is also able to abstract the halogen back from the metal, reproducing the dormant species. These processes are rapid, and the equilibrium that is established favors the dormant species. Because of this, two requirements for a controlled system are fulfilled. First, all chains can begin growing at the same time, and second, the actual concentration of free radicals is quite low, resulting in a markedly reduced amount of irreversible radical-radical termination, especially when low molecular weights are desired.

\[
\begin{align*}
P_n - X + M_t^n - Y / L & \quad \xrightarrow{k_a} \quad P_n^* + X - M_{t}^{n+1} - Y / L \\ & \quad \xrightarrow{k_{da}} \quad P_n^* + X - M_{t}^{n+1} - Y / L
\end{align*}
\]

Figure 5. General mechanism of ATRP.
2.2.2.2 Macroscopic debonding experiments

"Tack" is a complex property of pressure sensitive adhesives (PSAs) that allows them to adhere instantaneously when brought into contact with a surface under very light pressure. Superior tack involves both an adhesive having a sufficiently low modulus at frequencies characteristic of bonding, while having sufficiently high modulus at frequencies characteristic of the stresses placed on adhesive in applications. Conventionally, the tack is quantified using the energy required to break a bond measured by the "probe tack" tests\(^75\). In the "probe tack" test the tip of a macroscopic probe, commonly a flat cylinder with a ¼” diameter, is brought in contact under low pressure for a short time with the adhesive and the tensile strength of the bond formed between them is measured\(^76\). The big size of the probe, compared with a scanning probe, makes this measurement less sensitive to environmental conditions, such as humidity, but excludes the possibility of obtaining information about bond formation. Although tack determinations provide important information, it is difficult to infer from them the role played by the surface of the adhesive in determining tack.

For a polymer or polymer blend to be used as a pressure sensitive adhesive, the material must be able to dissipate a large amount of deformation energy during debonding. This energy dissipation seems to be connected with the formation and growth of fibrils during debonding. Zosel\(^77\) demonstrated that fibril formation and deformation lead to high fracture energy and high tack. A macroscopic debonding plot with a force maximum and a pronounced shoulder leading to a large area under the curve and a high distance at break is observed for polymers with high tack and has been associated with the presence of fibrillation. Fibrillation can be separated in three consecutive steps of
formation of fibrils, deformation of fibrils and debonding from the probe surface by adhesive fracture\textsuperscript{77}. Figure 6 shows a typical debonding profile for a pressure sensitive adhesive measured in a macroscopic probe tack test.

![Debonding profile](image)

Figure 6. Typical debonding profile for a pressure sensitive adhesive. Adapted from reference \textsuperscript{77}.

A debonding profile, commonly shown as a stress versus strain curve when the force and the distance are divided by an assumed contact area and the initial thickness of the film, respectively, offers a way to characterize the formation and growth of fibrils more quantitatively than by simple visual inspection. Three quantities can be deduced from such a curve: the apparent maximum force (corresponding to the maximum contact area), which can be regarded as the critical force for cavitation and fibril formation; the height of the shoulder, which is the force required to deform the fibrils; and the distance at fracture, which is the maximum elongation of the fibrils. The nucleation of cavities under the influence of the stress and their growth is believed to be the origin of fibrils. The real contact area is generally unknown and it is smaller than or equal to the
geometric contact area\textsuperscript{57}, although in the case of research instrumentation with visualization of the contact area it can be estimated. Fibril formation is assumed to start at the probe/polymer interface. That seems reasonable, but has not been verified experimentally. In highly deformable materials, intrinsic flaws exist and their growth under applied stress does not lead to a catastrophic failure of the material\textsuperscript{78}. Rather, failure involves the formation of cavities and the orientation and extension of polymer chains in order to resist the fracture. The nucleation and growth of cavities is enhanced by the degree of confinement of the layer since this increases the hydrostatic component of the load\textsuperscript{79}.

While conventional SPM provides nanoscale information on the behavior and morphology of hard or soft surfaces, there is still a need for a robust, non-invasive imaging technology capable of simultaneously obtaining morphological and chemical composition with molecular scale resolution. This capability would allow, for example, identifying the chemistry of the structures at the surface of latex coatings or determining the composition of the materials segregating to the surface of adhesive films. The next section introduces fundamentals, development, applications and challenges of tip enhanced Raman spectroscopy (TERS), a surface characterization tool suitable for the nanoscale chemical analysis of surfaces. TERS combines scanning probe microscopy with optical spectroscopy taking advantage of apertureless near-field optics. It shows promise but its application has been limited by the fragility and low activity of the probes currently used to study surfaces.
2.3 High resolution chemical imaging with metallized scanning probes

Optical techniques such as fluorescence, infrared (IR), and Raman spectroscopies are very effective and popular imaging tools, but have spatial resolutions limited to typically 200 nm (~\(\lambda/2\)) by the diffraction law\(^{80}\). For spectroscopic imaging, the traditional approach to overcome this limit has been aperture-limited near-field optics, or near-field scanning optical microscopy (NSOM)\(^{81}\). NSOM uses a sub-wavelength diameter optical fiber placed at 5-10 nm over the surface with a lateral resolution of 50-100 nm. However, apertured probes decrease the optical signal by a factor of \(10^3\)-\(10^6\), decreasing the intrinsically low Raman signals to undetectable levels. Raman NSOM is thus limited to long collection times, even with fiber diameters and resolution of 100 nm.

An alternative approach, apertureless near-field optics, takes advantage of high local amplification of optical signals by the surface plasmons of a metallized probe\(^4\). The concept of using an apertureless mechanical/optical probe to obtain chemical information on surfaces was first proposed by John Wessel in 1985\(^{82}\) as surface enhanced optical microscopy. He proposed that one could obtain a 1 nm spatial resolution unlimited by diffraction using optical-field confinement by surface plasmons of a submicrometer-sized metal particle, as shown schematically in Figure 7. In this technique, features would be mapped by scanning a metallic or metallized probe across the surface, using piezoelectric translators, while the enhanced electromagnetic field in the vicinity of the probe apex was used to obtain the chemical image.
Figure 7. Schematic of the optical probe. The optical probe particle (a) intercepts an incident laser beam, of frequency $\omega_{\text{in}}$, and concentrates the field in a region adjacent to the sample surface (b). The Raman signal from the sample surface is reradiated into the scattered field at frequency $\omega_{\text{out}}$. The surface is scanned by moving the optically transparent probe-tip holder (c) by piezoelectric translators (d). Adapted from reference $^{82}$.

The particle-plasmon electromagnetic field is responsible for the enhancement extending beyond the first atomic layer. The external electromagnetic field couples directly to these surface plasmons and a strong field associated with the plasmon resonance builds up at the particle surface. The enhancement factor, that is the ratio between the highly localized field or near field and the entire illuminated field or far field, is strongly dependant on probe material, geometry of the probe, and the source of excitation.

Raman spectroscopy provides an ideal spectroscopic probe for surfaces, responding to surfaces vibrations that reveal bonding and structure. Unfortunately, the cross-section of Raman scattering is very low (typically $\sim 10^{-30}$ cm$^2$), much lower that that of infrared absorption of molecular vibration (typically $\sim 10^{-20}$ cm$^2$) and the Raman peaks could be too small to distinguish from the broadband peak of fluorescence interference (for which the cross-section is typically $\sim 10^{-16}$ cm$^2$). Furthermore, peaks obtained in areas of hundreds of squared nanometers would have even lower intensities.
Raman gain is linearly dependant on beam intensity and therefore high signal levels would require intensity near the damage threshold, that for the case of silver occurs for intensities of about $10^6 \text{W/cm}^2$. This agrees with predictions based on thermal damage by direct plasmon absorption.$^82$

A solution to the problem of weak Raman intensity has been found for some situations using what is known as surface enhanced Raman spectroscopy (SERS). The SERS technique exploits a property of nanometer sized metal particles or rough metal structures. Incident laser photons are absorbed into the metal particles through oscillations of surface electron charge density (plasmons). These plasmons can couple with molecules in close proximity and provide an efficient pathway to transfer energy to the molecular vibrational modes, and generate Raman photons. Enhancement is maximized when the metal grains are smaller than the incident laser wavelength and the metal plasmon resonance matches the incident laser wavelength. Enhancement factors ($\text{EF} = \frac{E_{\text{loc}}}{E_{\text{ex}}}$, where $E_{\text{loc}}$ is the localized field and $E_{\text{ex}}$ is the external field) as large as 1000 can be obtained, and higher enhancements are achieved in regions of high surface curvature (due to what is known as the "lightning-rod" effect). The field associated with the Raman scattered light is also enhanced by the particle plasmons before reaching the detector.

The enhancement of the excitation field by a metallic probe in the vicinity of the probe has been successfully used for infrared absorption imaging$^{83,84}$ and for two-photon-excited fluorescent imaging$^{85}$. Even modest enhancement factors lead to huge increases in nonlinear processes, such as Raman scattering. In 1991, Pohl at al.$^{86}$ simulated the electromagenitic field enhancement between a silver probe and a silver
surface and proved theoretically the concept of enhanced Raman spectroscopy produced by a probe. However, experimental verification of TERS was not achieved until 2000, when Zenobi et al.\textsuperscript{87}, Anderson et al.\textsuperscript{4} and Kawata et al.\textsuperscript{88} independently used metallized commercial scanning probes for AFM to show experimental evidence of surface enhanced optical microscopy with Raman spectroscopy. It was demonstrated that a conventional scanning probe for AFM, coated with gold or silver, provides spatially selective enhancement of a Raman signal using the SERS effect. Use of this effect to achieve imaging with SPM has become known as tip enhanced Raman spectroscopy (TERS).

In TERS, resonant plasmon excitations, the collective electronic excitations in noble metal films or nanoparticles, allow the localization and amplification of light in very small volumes\textsuperscript{89}. The field enhancement mechanisms are usually distinguished as the surface plasmon\textsuperscript{90}, the lightning rod effect\textsuperscript{91} and chemical enhancement\textsuperscript{92,93}. Most of the work in the field of TERS has focused on understanding TERS with the aim of increasing sensitivity\textsuperscript{94}, improving signal enhancement either by designing structures or by tuning the resonant frequency of the plasmonic structure\textsuperscript{95}. Only a few studies have paid attention to preserving the plasmonic structure once an enhancement has been obtained. Probes are needed that not only highly enhance the weak Raman signals of materials with low scattering cross section, but also remain sharp and stable in order to obtain nanometer spatial resolution reproducibly and at commercially relevant cost. Means to protect metallized scanning probes and to create very active probes used in high resolution chemical imaging by apertureless near-field optics is still a challenge.
2.3.1 Tip enhanced Raman spectroscopy (TERS) Instrument

Despite experimental demonstration of a remarkable lateral resolution ~ 14 nm\textsuperscript{96}, the fabrication of probes is still a challenge. In order to use apertureless optics and tip enhancement for surface Raman imaging, the metallized probe must be incorporated into an apparatus that provides several capabilities: focusing of a light beam of appropriate wavelength on the sample, high resolution scanning of the sample, and simultaneous collection of the topographic and chemical images. A schematic of the instrumentation required to provide these capabilities is shown in Figure 8.

![Diagram of TERS Instrument](image)

Figure 8. Generalized schematic of the instrument used for tip enhanced Raman spectroscopy (TERS).

A key variation among the research instruments for TERS, which have already been described in the literature, has been the geometry of the topics. Published approaches have included bottom or top\textsuperscript{4,97}, and side illumination of the probe\textsuperscript{98,99}, as
shown in Figure 9. In bottom illumination, the probe is illuminated from below the sample using a beam shining vertically through a transparent substrate. It has the advantages of allowing the use of high numerical aperture (NA) optics for illumination and detection because of the versatility in distance control between objective lens and sample and the high NA makes it possible to minimize the focus size. Novotny and coworkers\textsuperscript{96} demonstrated a 14 nm lateral resolution in TERS imaging of single walled carbon nanotubes by bottom illumination. Unfortunately, nontransparent samples and samples on nontransparent substrates cannot be studied with bottom illumination.

![a) Bottom Illumination](image1)

![b) Side Illumination](image2)

Figure 9. Schematic of illumination geometries for TERS. a) bottom illumination and b) side illumination.

The side illumination method is the most flexible approach to analyze opaque and non-transparent samples\textsuperscript{100}. Side illumination optics overcomes this limitation despite the limits it places on numerical aperture that can be used and difficulties in alignment. However, side illumination has the advantage of offering the possibility of optimization of the incident polarization for better resonance\textsuperscript{101-103}. Excitation of the enhancement has been only seen for p-polarization illumination, but not for s-polarization\textsuperscript{103}. P-
polarization corresponds to alignment of the electric field vector with the axis of the probe. Recently, a variation of side illumination using a parabolic mirror\textsuperscript{94} to focus the incident light was also reported.

2.3.2 Metallized scanning probes for TERS

The key element of TERS, a plasmonic structure on a very sharp probe, provides a high amplification ($\sim 10^3$-$10^4$) of the Raman signal by surface plasmon resonance. Etched metal probes are used in STM TERS and tuning fork based shear-force mode TERS. These are made by electrochemical etching and sometimes with additional focused ion beam milling to further sharpen the apex\textsuperscript{104,105}. Electrochemical etching of probes from solid wires makes the probe smooth and sharp, but a shear-force AFM instrument or scanning tunneling microscopy instrument for TERS is required\textsuperscript{106}. Probes prepared by a surface etching technique using a square-wave electrical pulse to etch gold probes having radius of curvature of 25 nm have been recently reported\textsuperscript{106}. Unfortunately, fabrication of etched probes with a radius of curvature lower than this value is still a challenge. In the case of AFM based TERS, physical vapor deposition is the preferred way to metallize conventional probes\textsuperscript{4,88,99}.

Contrast, which relates the total signal measured when the probe is in contact to the signal measured when the probe is withdrawn, is the key parameter controlling one's ability to image with the probe\textsuperscript{100,107}. Contrast and enhancement factor are based on comparison of "withdraw" and "contact" signals. The "withdraw" signal is measured with the probe pulled far from the sample so that there is no enhancement from the probe. The signal observed is the far-field signal ("far") collected from the entire area illuminated by
the incident beam with diameter of about 1 micron. The signal measured in this case is unenhanced and not localized. The "contact" signal is measured with the probe in contact with sample. In this case, there is strong enhancement in a nanoscale region about the contact with the probe. The near-field signal ("near") from this very small region is strongly enhanced. The collected signal, however, contains both the far-field and near-field signals ($I_{far}+I_{near}$), so the overall increase in signal seems modest. In order to calculate the actual enhancement of signal one must account for the large difference in the volume of the region from which the far-field signal comes and the volume of the region from which the near-field signal comes. Therefore, to characterize the probes, the "enhancement factor" (EF) has been introduced:

$$EF = \frac{I_{near}}{I_{far}} \frac{V_{far}}{V_{near}} = \left( \frac{I_{total}}{I_{far}} - 1 \right) \frac{V_{far}}{V_{near}}$$  \hspace{1cm} (2.2)

where $V_{near}$ and $V_{far}$ are the sampling volumes from which the near-field and far-field signals come. Experimentally, one measures $I_{total}$ and $I_{far}$ relative to each spectrum base line. Contrast, the ratio of the total signal measured when the probe in contact to the signal measured when the probe is withdrawn, is given as:

$$Contrast = \frac{I_{near}}{I_{far}} = \left( \frac{I_{total}}{I_{far}} - 1 \right)$$  \hspace{1cm} (2.3)
Probe characteristics such as roughness\textsuperscript{108}, shape\textsuperscript{109}, radius, and material under the plasmonic structure\textsuperscript{110}, determine both the spatial resolution and the contrast. However, the metal plasmonic structures suffer from limited lifetimes due to changes resulting from heating\textsuperscript{111}, wear during imaging\textsuperscript{112}, and chemical degradation\textsuperscript{113,114}. Maintaining the morphological, mechanical, and chemical integrity of these structures during scanning, i.e. keeping their optical properties unaltered, is crucial for reproducibly obtaining undistorted optical images with nanometer scale resolution. This is especially problematic for silver-based structures that usually provide the best enhancements, but mechanically and chemically degrade very quickly. Gold-based structures are chemically more stable, but suffer mechanical degradation to an extent similar to that seen for silver-based structures.

A metallized apertureless probe usually consists of a silicon or silicon nitride probe covered with a thin, rough layer of a metal such as gold (Au) or silver (Ag). In this work we adopt the convention of designating the "thickness" of the metal film with the thickness calculated from measurements of mass deposited made with an oscillator crystal during the deposition using an assumed area of deposition. TEM images of metallized films show that this nominal thickness generally substantially overestimates the actual thickness. Metallized scanning probes with a plasmonic layer of the typical 50 nm nominal thickness actually have a metallized apex with a radius between 20 and 25 nm with the thickness of the metal layer decreasing towards the base of the probe. In any case, giving a thickness for the structure is problematic, since the films are intentionally made thin enough so that they are thermodynamically unstable and dewet from the probe surface, forming droplets that have the size necessary for optimized plasmonic activity.
In metallized probes, the low yield of highly enhancing probes is due mainly to the lack of precise control of those parameters. In one report\textsuperscript{115}, Yeo et al. reported that the yield of highly enhancing metallized probes can be significantly improved by changing the material of the probe. Commercial probes are commonly made of silicon, silicon nitride, or glass. Those authors argued that the localized plasmon resonant frequency is a function of the refractive index of the material under the metal layer. This contention was supported by simulations\textsuperscript{110} by the same group.

Anderson et al.\textsuperscript{4} used gold metallized probes with a mean diameter of 45 nm, and bottom illuminated a thin sulfur film (10 micrometers). An enhancement factor of about $10^4$ was reported. Also, a sample surface was scanned at high probe force, in contact mode, to remove some of the material being measured, a C\textsubscript{60} hard solid, and the Raman spectrum obtained, so the spectrum was intentionally a spectrum of what was collected on the probe. From all the probes used during the course of that study, 50% produced some enhancement and only 5% produced large enhancements $\sim 10^4$. Kawata et al. reported the use of an AFM probe with 40 nm thick silver coating for imaging using enhancement of the Raman signal from Rhodamine 6G(Rh-6G) molecules on silver islands films with 50 nm lateral resolution. Silver tarnishing was only mentioned, and its effect reduced by preparing samples and probes just before the experiment. Zenobi\textsuperscript{87} used a silver-coated probe and reported an enhancement factor of more than 2000 with the dye brilliant cresyl blue. Unfortunately, in none of these publications were stability problems originating from scanning with tips covered only with pure metal films commented upon. Abrasive frictional forces between the metal layer and the surface under analysis could be an important source for degradation of the metal structure during
"contact" or "tapping" mode scanning. While non-contact mode imaging is also possible, it is more challenging to implement robustly.

2.3.3 Degradation of scanning probes used in high chemical imaging

Pure metals can deteriorate irreversibly under exposure to light and common environmental conditions, as in the case of silver. Changes in the probe’s metal structure caused by wearing\textsuperscript{14,16}, heating\textsuperscript{111}, and/or chemical degradation\textsuperscript{114} make plasmon-based enhancement unstable during imaging. Developing noble metal probes with stable plasmonic activity is essential to achieve robust chemical imaging with nanometer scale lateral resolution.

2.3.3.1 Physical

Even hard silicon or silicon nitride conventional scanning probes for AFM have been reported to show physical degradation during use\textsuperscript{13,15}. In these, wearing is the main source for physical degradation. In an attempt to reduce the highly destructive forces between a probe and the surface when they are in contact, lubrication films\textsuperscript{13,15}, and even new geometrical designs\textsuperscript{15} have been proposed. More challenging problems are expected when the probe is a metallized probe because the Vickers hardness of, for example, Ag and Au, which are 251 MPa and 216 MPa, respectively, are substantially lower that that of silicon (1415 MPa), or silicon nitride (Si$_3$N$_4$) (2040 MPa). In scanning probes for high resolution chemical imaging containing rough metal structures, annealing caused by heating is also a source of physical degradation. Due to the nature of the pure metal thin film, metallized probes have low wearing resistance and sometimes cannot even
withstand approaching and scanning pressures without deformation\textsuperscript{112,117} in addition to a low yield of highly enhancing probes. Pure metal layers are ductile and fragile\textsuperscript{118}, and in the specific case of silver coated probes, their surface is not chemically inactive. Enhancement can fade even after half a day under common environmental conditions\textsuperscript{107,119}. This is likely caused by the deformation and/or the fracture of the metal film during the contact with the surface as well as the chemical degradation of the metal.

Only a few reports have commented on the challenges from the materials viewpoint of using pure metal films as probes for high resolution chemical imaging. For example, bending of sharp, etched silver probes, principally due to the high ductility of silver\textsuperscript{116}, has been demonstrated during AFM imaging. Martinez et al.\textsuperscript{120} showed SEM images of a gold metallized probe before and after use for aNSOM tip enhanced florescence applications, demonstrating wear of the probe after only 10 hours of use. From their figure, it is clear that the gold wears away from the probe end with use, effecting the surface enhancement over time.

In a recent attempt to understand and develop improved wear resistance metallized probes for ferroelectric data storage, another application that uses metallized probes and that requires extreme wearing resistance, Bhushan et al.\textsuperscript{14,121} have reported on nanoindentation and nanoscratch experiments to quantify effective hardness and elastic modulus of metal coated probes. In ferroelectric data storage, a conductive atomic force microscope probe with a noble metal coating is placed in contact with a hard substrate, commonly a lead zirconate titanate (PZT) film, which serves as the ferroelectric material. Probe wearing is an important consequence of this harsh contact made multiple times in a very short time. Metal alloys, such as Pt-Ir, were found to exhibit the highest hardness,
highest elastic modulus and lowest creep resistance among the materials tested. This is in contrast with a pure Pt metal coating that shows the lowest scratch resistance. The hardness of Pt is about twice than that of silver or gold and, unfortunately, metal alloys have surface plasmonic activity inferior to that of pure metals.

Changes in surface morphology caused by the heating generated by the localized enhancement of the electromagnetic field are another sort of physical degradation affecting metallic or metallized probes for optical applications. Heating of SERS substrates caused by the enhanced field anneals structured metal films, reducing the plasmon resonance activity due to a decrease in roughness\textsuperscript{111}. Similar effects are expected for rough probes used in TERS. This increase in temperature has been demonstrated theoretically\textsuperscript{111} to be as high as 25°C.

2.3.3.2 Chemical

Another type of degradation that occurs for silver-coated probes is atmospheric corrosion at low temperatures, known as tarnishing. This typically takes the form of sulfdation rather than formation of silver oxide. Silver sulfidizes upon exposure to several gaseous sulfur-containing compounds in the atmosphere\textsuperscript{122-124}, hydrogen sulfide (H\textsubscript{2}S) and carbonyl sulfide (OCS) being the most important\textsuperscript{124}. This sulfidation can strongly affect the optical properties of silver plasmonic structures\textsuperscript{125}. These reactions are even more important when the silver layer or silver particle has a nominal size of tens of nanometers because the corrosion layer can completely destroy the silver structure. Environmental conditions\textsuperscript{114} or intense light\textsuperscript{111} become very important at this length scale. SPM probes with Ag structures having a radius of 25-30 nm at the apex no longer
provide plasmon enhancement after 24 hours of continuous exposure in ambient to a 1μm diameter confocal beam of power 1 mW in an apparatus designed for measuring tip-enhanced Raman spectroscopy\textsuperscript{126}. At increased temperatures, the plasmon collective oscillation of the electrons at the surface of features of the rough metal coating can be completely destroyed as Ag structures are oxidized to form silver oxide and changes will also occur upon sulfidation\textsuperscript{125}. Resistance to deformation when the probe is in contact with the surface and to heating produced by the laser must be a priority in the design of robust probes for TERS. The effect of protective coatings on the mechanical and optical properties of probes for TERS has not yet been systematically studied and this is the focus of the next section.

2.3.4 Protection of scanning probes by ultrathin coatings

An adequate protective coating must conformally follow the surface topography and completely cover the metal structure without altering the optical properties of probes. Silica and alumina dielectric coatings were tested as means to protect metallized probes used in TERS against physical and chemical degradation.

2.3.4.1 Ultrathin silica (SiO\textsubscript{x}) coatings

The coating of metallic substrates with silica thin films for surface enhanced Raman spectroscopy has already received some attention. Walls and Bohn\textsuperscript{127} showed that sputtering SiO\textsubscript{x} films thicker than 3 nm on top of 5 nm silver islands imparted resistance to chemical attack of the metal structures. Lacy et al.\textsuperscript{128} have shown that
evaporative deposition of SiO at $9 \times 10^{-6}$ Torr results in complete and uniform SiO$_x$ 5 nm thick films able to completely cover 4.5 nm thick Ag islands.

Efforts to predict the effect of a silica thin coating on the optical properties and enhancement of a metallized tips were reported$^{119}$ in the course of this research, after the author had undertaken experimental work on SiO$_2$ coatings. That simulation revealed that a thin additional coating layer results in only a minor wavelength shift in the optical response of the tip, while still maintaining high field enhancement, provided appropriate choices of layer material and thickness have been made. The scattering of a plane wave excitation source in the blue-green region of the visible spectrum from the simulated nanostructures was numerically solved by the finite element method (COMSOL multiphysics) in conjunction with a realistic metallic materials model. In the 3D simulations, the tip was modeled as an inverted dielectric cone with a full-angle of 60° and with a tip apex terminated in a hemisphere with a diameter of 10 nm. Coating layers were assumed to uniformly cover the surfaces and be concentric to the tip's end. The resulting tip geometry was truncated at the height of 520 nm and a TM mode incident light beam (E parallel to the tip axis) was employed for the full 3D simulation. As shown in Figure 10, after a 5 nm thick SiO$_2$ coating is added, the resonance frequency shifts to higher wavelength - a "red shift" - by 3 nm (from 538 nm to 541 nm), and the maximal field enhancement is increased by 30% while a 6 nm red-shift is associated with a layer thickness of 10 nm.
Figure 10. Predicted optical emission spectra for a bare metallized tip and metallized tips with 5 nm or 10 nm thick ideal SiO$_2$ dielectric coating. Field enhancement from three dimensional simulations is plotted as a function of the incident wavelength for a two-layer nanoshell model. Reprinted with permission from Elsevier. Copyright 2008.

It was proposed that the field enhancement caused by the addition of the thin SiO$_2$ coating could be attributed to an increased coupling between the plasmons on the inner and outer sides of the silver layer and the localized surface plasmon on the outer side of this layer. The field distribution for the SiO$_2$ coating with respect to its resonance is shown in Figure 11. Physical and chemical properties of ultrathin dielectric coatings are not completely understood. On the scale of a few nanometers, most materials reveal new and unexpected features. This is particularly valid for ultrathin oxide films, as demonstrated by Scheffler$^{129}$ et al. This makes prediction of ultrathin film structure and properties not an easy task. Alexandrova$^{130,131}$ et al. reported on the stoichiometry and morphology of thin (200 nm to 2 micrometers) silica (SiO$_x$) films prepared by thermal evaporation of silicon monoxide. The atomic ratio of oxygen to silicon atoms $x$, varies between 1.1 and 1.7. These films have also been reported to be photoluminescent$^{132,133}$, and this characteristic may have an impact on the optical properties of these films.
2.3.4.1.1 Ultrathin alumina (Al₂O₃) coatings

Alumina thin films show high wear resistance and high dielectric constant and are commonly used in applications ranging from friction and corrosion protection to microelectronics and optical devices. In combination with acrylic polymer films, alumina thin films have also showed a four orders of magnitude decrease in gas permeation rates over the polymer sheet alone\textsuperscript{134} with water permeation rates as low as 0.0155 g/m\textsuperscript{2} day\textsuperscript{135,136}. Sapphire, α-Al₂O₃, is known for being exceptionally hard and optically transparent from the near infrared through the visible region into the ultraviolet. Preparation methods include magnetron sputtering, atomic layer deposition, chemic al vapor deposition dual ion-beam sputtering, spray pyrolysis, and evaporation\textsuperscript{137}, but not too much work has been done on the effect of alumina ultrathin layers on surface enhancing structures. Some work on the structure of Al₂O₃ films has been done that
could be helpful to understanding how they might influence field enhancement at the surface of a plasmonic structure. Murray and Allara\textsuperscript{138,139} studied the effect on SERS of separating an analyte molecule from a silver substrate by layers of aluminum and alumina (Al\textsubscript{2}O\textsubscript{3}) and a polymer thin film, as shown in Figure 12. They suggested some synergistic effect of the aluminum with the silver increased the enhancement.

![Figure 12. Schematic of the multilayer film. The multilayer film containing a rough silver layer (top), a polymer thin film of PPNS poly (p-nitro styrene) (medium) and an Al/Al\textsubscript{2}O\textsubscript{3} film (bottom) used by Murray and Allara\textsuperscript{138}. Adapted from reference\textsuperscript{139}.](image)

Van Duyne et al.\textsuperscript{140} found that placing even a 0.2 nm layer of aluminum oxide by atomic layer deposition (ALD) on triangular silver nanoparticles with a perpendicular bisector \~ 100 nm created for catalysis applications provided heat resistance and improved the preservation of sharp plasmonic structures. Furthermore, it has recently become known that alumina ultrathin layers have excellent gas barrier properties. Park et al.\textsuperscript{141} showed in 2005 that the volume expansion that occurs upon oxidation of aluminum generates a coating so dense that it is impermeable even to hydrogen. Hakim and coworkers\textsuperscript{142,143} then showed that highly conformal Al\textsubscript{2}O\textsubscript{3} layers could be deposited on titania and that iron nanoparticles coated by alumina using atomic layer deposition (ALD)
are resistant to oxidation, even at high temperatures. Very recently, publications for alumina gas barrier coatings on plastics have appeared because thin alumina layers are optically transparent and very hard (Vickers Hardness 2600 MPa).

Recent model calculations and experimental results have shown that an amorphous state for the initial oxide growth on a bare Al substrate is thermodynamically favored up to a certain critical oxide film thickness of about 1-3 nm. This is attributed to the lower sum of surface and interface energies of the amorphous state compared with the corresponding crystalline state. The preference for an amorphous initial layer growth could be advantageous for giving good adhesion to plasmonic structures upon which an oxide film might be placed for protection.

Olbrich et al. has studied by conductive atomic force microscopy (C-AFM) the uniformity of Al2O3 films fabricated by first evaporating an Al film and subsequently oxidizing in oxygen plasma. C-AFM allows the local electrical characterization of thin dielectrics at nanometer length scale with an uncertainty in film thickness below 0.2 nm. It was found that 1.2 nm thick alumina films are amorphous and conformally follow the characteristics of the substrate. A variation of 0.3 nm in thickness was reported for a Al2O3 layer of average thickness 1.2 nm over a line scan from a 500 nm by 500 nm image.

One of the advantages of depositing aluminum to obtain the alumina ultrathin film is the possibility of creating a gas-tight thin film by the volume expansion of the oxidized metal layer. By exposure to atmosphere, oxygen starts to diffuse into the metal layer. The surface reaction is generally instantaneous in transition metals and the structure at the surface changes by forming an oxide layer even at room temperature. Aluminum is
known to make a protective superficial oxide layer that strongly resists further oxygen diffusion.

2.3.5 Methods for controlled fabrication of plasmonic structures

Since resolution and sensitivity of apertureless near field optics strongly depend on size and plasmonic activity of the metal structure, development of probes exhibiting not only stable but also strong enhancements is still required. If the proposed performance goals of probes with enhancement factors of $> 10^5$ can be met, a next generation of microscopes capable of simultaneously imaging physical and chemical structures with real nanoscale lateral resolution will be a reality. New probe designs and means of plasmonic structure fabrication must be explored as approaches to achieve higher signal enhancements.

2.3.5.1 Electron beam induced deposition (EBID)

It has been proposed theoretically that cascade amplification and self-similar antenna geometries of apertureless tips can result in enhancements factors of the optical signal of the order of $10^5$ or higher\textsuperscript{148,149}. Li, Stockman and Bergman\textsuperscript{149} proposed a cascade setup that purportedly could provide enhancement of the electric field of light up to ~400–600, with the commensurate remarkable enhancement of the Raman signal by $\sim 10^{12}–10^{13}$. The cascade effect is achieved by placing smaller particles, under plasmon resonance conditions, in the field of bigger ones. While the idea is theoretically solid, no experimental verification has been reported. In fact, no one has demonstrated systematic and controlled creation or observation of such regions of most remarkable enhancement,
known as “hot spots”. These plasmonic structures require fabrication with a very high precision as well as high purity of the deposited material.

One fabrication technique that might be useful for creating new designs, but has not yet been used, is Electron beam–induced deposition (EBID). EBID is based on the local decomposition of precursor molecules adsorbed on a surface by a focused electron beam\textsuperscript{150,151} and it allows creating single structures with high precision. Generally, the precursors used for gold deposition are organic. Deposits made with organometallic precursors usually result in nanocomposite materials with metal scattered within an amorphous organic matrix. Carbon and oxygen are commonly found impurities limiting optical applications of EBID deposited structures. Current development in EBID focuses on obtaining “cleaner” metal nanostructures\textsuperscript{151}. Good reviews on this technique have been published by Randolph, Fowlkes, Rack\textsuperscript{150} and van Dorp and Hagen\textsuperscript{152}.

2.3.5.2 Dendritic metal structures by metal replacement

Recently, dendritic metal nanostructures have become the focus of several studies due to their potential application in superhydrophobic surfaces and SERS substrates. By using deposition methods from solution, controlled synthesis of nanocrystals can be achieved\textsuperscript{153}. Fang and co-workers\textsuperscript{154} have used a zinc plate to grow gold dendrites in a very controlled fashion. It has been proposed that gold nuclei nanocrystals first form on the zinc substrate through a direct surface reaction and that the subsequent crystal growth takes place on the preformed gold crystals. This reactions have been shown to give different structures depending if the reaction take place in organic solvent\textsuperscript{155}, water\textsuperscript{153} or ionic liquids\textsuperscript{156}.
Metal replacement reactions are an effective means for preparing sharp and crystalline metallic nanostructures by deposition of the most reactive metal (oxidizing agent)\textsuperscript{153,157}. In the replacement reaction, a metal substrate A is used as a sacrificial metal to generate dendritic structures of Metal B with a higher redox potential than Metal B. A dendrite is a tree-like structure of crystals (or mesocrystals) produced by faster growth along energetically favorable crystallographic directions. The electrochemical series predicts the course of a reaction when two redox systems with different standard redox potential values (E) are brought into contact. The electrons for the reaction are provided by the dissolution of the metallic structure. The mechanism is chemical displacement where the substrate metal functions as the reducing agent to displace the metal ions from the solution to coat the surface with metal. This plating process only occurs when the substrate metal has a lower oxidation state potential than the metal in solution and continues only as long as the substrate metal is exposed. When the base metal is completely covered by the metal deposited from this solution, the reaction stops.

2.3.5.3 Rough metal films by ion sputtering

Surface roughness is a defining property for plasmonic activity. It has been demonstrated by others how sharp edges and increased surface roughness can improve the enhanced signals from metallized TERS probes\textsuperscript{108}. Ion sputtering deposition, a physical vapor deposition process, occurs when ions incite on a target to physically remove surface atoms, which ballistically flow and are deposited to a substrate. This is a “cold” deposition process, compared to thermal evaporation, and films are commonly rougher than the thermally evaporated counterparts deposited at the same deposition rates.
Ion sputtering is a process that provides independent control over the flux and energy of ions incident on a target. Additionally, ion sputtering provides the possibility of controlling angle of incidence.

2.4 Statement of the problem and approach

So far, literature reveals that scanning probe microscopy (SPM) techniques already provide several means for studying polymer surfaces. The approach of opening new opportunities by modifying probes has been established. Areas remain where the power of SPM techniques for revealing morphological features that can be connected with macroscopic properties has not yet been exploited. We will consider complex latex films as one example. Many questions remain about the role of humidity in the performance of adhesives and how modified tips could contribute to understanding how soft surfaces change when exposed to intense aging conditions. In particular these questions remain open for acrylic block copolymer adhesives, which have newly become available as a result of new synthetic techniques, and which may offer superior performance in difficult conditions. Finally we pursue the exploitation of probe modification to bring robustness to a non-invasive imaging technology capable of simultaneously obtaining morphological and chemical information of polymer surfaces, with molecular scale resolution based on the exquisite chemical specificity provided by Raman spectroscopy. While the attainment of substantial enhancement and remarkable resolution have already been demonstrated, key questions remain, including i) how tip lifetime can be improved without giving up enhancement performance and ii) how even higher enhancements might be achieved using new types of tip design or new plasmonic
structure fabrication in order to open up more polymer systems to study. These are the questions that will be addressed with the experimental methods described in the next chapter and with the results presented in Chapter IV.
3.1 Conventional probes for surface topography and adhesion measurements of hard surfaces

Floor polishes are sufficiently hard to be studied with minimal distortion of the surface by the probe. Conventional scanning probes were successfully used for the morphological study of floor polishes.

3.1.1 Probes

Conventional silicon non-contact probes (MikroMash, NSC15/AIBS, manufacturer spring constant of shortest probe = 14 N/m) with rectangular cantilevers were used to obtain surface topography images and contact probes (MikroMash, CSC21/AIBS, MikroMash, manufacturer spring constant of 0.12 N/m) were used to obtain surface topography images and F-d measurements of the latex films. An Atomic Force Microscopes Autoprobe™ CP (Park Scientific) was used for all measurements.

3.1.2 Latex samples

Emulsions based on poly (styrene-acrylate) or poly (styrene-butadiene) copolymers containing various elements of a commercial floor polish formulation with
the generic compositions summarized in Tables 1 and 2 were obtained from Omnova Solutions Inc. Four sets of acrylic formulations included one “complete” emulsion having the typical concentration of fluorosurfactant, one control without any fluorosurfactant, one emulsion without fluorosurfactant and without wax, and one emulsion with the typical concentration of fluorosurfactant, but without wax.

All concentrations of the remaining components were kept constant. Six sets of films based on styrene-butadiene copolymers formulations with different concentrations of fluorosurfactant included a control set (without fluorosurfactant), and sets containing 100 ppm, 200 ppm, 300 ppm, 400 ppm, or 600 ppm of fluorosurfactant. In all cases, the coalescent (glycol ether) to plasticizer (tributoxyethyl phosphate) ratio was 50/50 by weight and the weight percent content of remaining components was constant.

Three consecutive coatings were applied at 15 minute intervals on the 100 face of a 1 mm thick silicon wafer having a 3” diameter (Umicore, Boston, Massachusetts) using cotton gauze to imitate the real application of the polish using a mop. In order to test the leveling of the coating, in some cases wrinkles were intentionally made on the surface. Similar experiments were done on vinyl tiles to test the effect of substrate on morphology at the air/film interface and no differences were found. Gloss was measured by a glossmeter (Gardner multiangle glossmeter) at 20°, 60° and 85° specular angles.
Table 1. Compositions of generic styrene-acrylic (SA) copolymer based floor polish formulations evaluated by AFM.

<table>
<thead>
<tr>
<th>Formulation Components</th>
<th>Composition (wt. %)</th>
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<tbody>
<tr>
<td></td>
<td>SA 1</td>
</tr>
<tr>
<td>Deionized Water</td>
<td>44.8</td>
</tr>
<tr>
<td>Styrene Acrylic Latex Polymer</td>
<td>34.9</td>
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<tr>
<td>Ethylene and Propylene Based Glycol Ether Coalescents</td>
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<td>PE and PP Based Waxes</td>
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<tr>
<td>Acrylic Terpolymer Resin</td>
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</tr>
<tr>
<td>Overall Fluorosurfactant (30% active)</td>
<td>0.0</td>
</tr>
</tbody>
</table>

Table 2. Composition of generic styrene-butadiene (SB) copolymer based floor polish formulations evaluated by AFM.

<table>
<thead>
<tr>
<th>Formulation Components</th>
<th>Composition (wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SB 1</td>
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<tr>
<td>Styrene Butadiene Latex Polymer</td>
<td>39.5</td>
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<tr>
<td>Ethylene and Propylene Based Glycol Ethers</td>
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<tr>
<td>Phosphate and/or Phthalate Based Plasticizers</td>
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<tr>
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<tr>
<td>Acrylic Terpolymer Resin</td>
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<tr>
<td>Overall Fluorosurfactant (30% active)</td>
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A qualitative, and in some cases quantitative, understanding of mechanical properties at the nanoscale was inferred from the measurement of Force-distance (F-d) curves using the Autoprobe™ CP microscope. In order to define the effect of fluorosurfactant on surface morphology, experiments were performed to survey and classify morphological differences at different scales among the samples prepared from different formulations.

3.2 Functionalized probes for adhesion measurements

In some cases, the interaction between a conventional probe and a sticky surface is so strong that the probe cannot be easily removed from the surface to allow imaging. For those cases, a hydrophobic layer was successfully used to weaken the strength of the interaction, allowing imaging and adhesion measurements.

3.2.1 Probes

Silicon non-contact probes (Contact Ultralevers™, Veeco, manufacturer spring constant 16 N/m) were cleaned in hot piranha solution for 30 s and then rinsed with deionized water. The chips were dried in a 140°C oven for 4 hours before modification.

3.2.1.1 Functionalization

A hydrophobic layer was deposited on a probe by immersing it in a 1mM solution of octadecyltrichlorosilane (OTS), heptadecafluoro - 1,1,2,2 - tetra hydrodecyl trichlorosilane (FTS), heptadecafluoro - 1,1,2,2 - tetra hydrodecyl methyl dichlorosilane (FDS) or a mixture of FTS and FDS in anhydrous toluene at 30°C for 12 hours. After the
reaction, the chips were rinsed with toluene and tetrahydrofuran (THF) to remove residual deposition solution. Depositions from the mixture of trichloro- and dichlorosilanes were done to look for possibilities of obtaining increased packing density. The hydrophobic layers formed on the surface of the probes were characterized using transmission electron microscopy (TEM), ellipsometry, and water contact angle measurements.

3.2.1.2 Imaging

Imaging modified scanning probes is not an easy task. Both modified and unmodified probes were imaged using a FEI Technai 12 Scanning Transmission Electron Microscope operating at 120 kV and a sample holder especially constructed for SPM probes, as described elsewhere. The sample stage was tilted at an angle of 55° with respect to the surface plane to image the probes and several images were taken at various magnifications.

3.2.1.3 Contact angle measurements

The static water contact angles for each of the modified chips were measured using a Rame Hart NRL-110 goniometer. Two to four 10 µL drops of distilled, deionized water were placed on each chip and the equilibrium contact angles were measured. The environment inside of the chamber was saturated by maintaining a large drop of DI water in the chamber during measurements. The angle was read by eye (+/- 2°).
3.2.1.4 Ellipsometric thickness measurements

The hydrophobic layers thicknesses were measured using a Gaertner L116C ellipsometer. The instrument was equipped with a He-Ne laser (\(\lambda=632.8\) nm) fixed at an incident angle of 70° with respect to surface normal. All thicknesses reported were obtained by subtracting the thickness of the silicon oxide (SiO\(_x\)) from the that of the hydrophobic layer with the oxide using a single layer model with refractive index values of 1.456 for SiO\(_x\), 1.450 for OTS, and 1.349 for FDS, FTS, and the FDS-FTS mixture. A minimum of five measurements of at least five different locations at the surface were acquired.

3.2.1.5 Force-distance curves

The main purpose of this work was to study bonding and debonding processes of a model adhesive at a very small scale using a modified probe. F-d curves were obtained using unmodified and modified probes under ambient conditions or under humidity controlled conditions (<10% or 60% RH) with the AutoProbe\textsuperscript{TM} CP microscope. A 100 micron scanner was used and several curves were obtained in various locations within 10 \(\mu\)m x 10 \(\mu\)m images. Measurements were performed with a 1Hz sweep frequency. For each set of measurements on a given sample, the ratio of piezo extension to retraction was adjusted to achieve as consistent loading force as possible, close to 20 nN.

3.2.2 Model adhesive based on acrylic triblock copolymers

Controlled radical polymerization was used to synthesize well defined triblocks and diblock copolymers of poly (methyl methacrylate) (PMMA) and poly (n-butyl

52
acrylate) (PnBA) for the formulation of model adhesive films. Blends of PMMA-\textit{b}-PnBA-\textit{b}-PMMA triblock and PMMA-\textit{b}-PnBA diblock copolymers or PBA homopolymer without tackifier were used.

3.2.2.1 Synthesis

The general mechanism of ATRP involves the abstraction of a halogen from the dormant chain by a metal center (such as complexes of Cu) in a redox process\textsuperscript{74}. Upon halogen abstraction, the free-radical (active species) formed can undergo propagation as in conventional free radical polymerization. However, the free radical is also able to abstract the halogen back from the metal, reproducing the dormant species. These processes are rapid, and the equilibrium that is established favors the dormant species. Because of this, two requirements for a controlled system are fulfilled. First, all chains can begin growing at the same time, and second, the actual concentration of free radicals is quite low, resulting in a markedly reduced irreversible radical-radical termination, especially when low molecular weights are desired.

The PMMA macroinitiator for the diblock copolymer was synthesized following a procedure similar to that presented elsewhere\textsuperscript{74}. Methyl methacrylate (MMA) was polymerized with methyl 2-bromopropionate (MeBrP) in conjunction with copper (I) bromide (CuBr) and 1,1,4,7,7-pentamethyldiethylenetriamine (PMDETA) in anisole at 90°C in a Schlenk reactor. After purification, the PMMA sample was used as a macroinitiator for the polymerization of the n-butyl acrylate block, again using CuBr and PMDETA as the catalyst. In all the cases, 0.5 equivalent of catalyst to initiator was used.
in order to reduce the concentration of radicals in the medium. Complexation of copper by PMDETA allowed the reaction mixture to be homogeneous.

3.2.3 Tack experiments

Macroscopic tack measurements were done on films prepared on 1” x 1” glass slides that were oven dried under roughing vacuum at 130°C for 24 hours. Film thicknesses ranged between 30 µm and 40 µm. Tack measurements were performed at room temperature using a TA-XT2i Texture Analyzer (by Stable Microsystems) with the collaboration of Goodyear Chemical (now part of Sartomer Company Inc.). A 0.25 in. (0.64 cm) diameter flat probe was used with contact forces of 49 mN (5g), 196 mN (20g), 402 mN (41g), and 980 mN (100g). Contact times of 0.5s, 1s, 5s and 10 s and a constant separation rate of 1cm/s were used. Force-distance curves were obtained at three different locations on each of the films. The formulation is not the optimum, but has reasonable tack performance and reflects key characteristics of acrylic block copolymer PSAs.

3.2.3.1 Microscopic study of aged samples

The behavior of an acrylic block copolymer film with aging and exposure to humidity was studied, beginning with a tacky film obtained by blending a triblock copolymer with PnBA homopolymer. In these formulations, reasonable tack performance reflects key characteristics of a model pressure sensitive adhesive (PSA). A total of sixteen F-d curves were measured for each of the conditions tested. The four aging conditions were as follows. The sample aged “dry” was kept in a dark desiccator at
very low RH during the three weeks of aging. The sample aged under the “humid” protocol was placed in an environment with a relative humidity (RH) of 90% at ambient temperature for three weeks. The “high T” protocol was to age the sample at a temperature of 70°C and RH of 30% in the dark for three weeks. The “UV” aged sample was exposed to a UV lamp (λ=250 nm) at ambient temperature and temperature for three weeks. This name does not reflect in any way the conditions under which the samples were measured when they were fresh. All were measured under dry conditions at ambient temperature.

3.3 Robust probes for high resolution chemical imaging

Tip enhanced Raman spectroscopy is capable of simultaneously obtaining morphological and chemical information, with molecular scale resolution. Unfortunately, its progress has been limited by the fragility of the metallic or metallized probes. Coating of the metal structure with an ultrathin layer was explored as a way to impart robustness to probes for TERS.

3.3.1 Surface enhanced Raman spectroscopy (SERS) substrates

In some cases, coatings studied for potential use on tip enhanced Raman spectroscopy (TERS) probes were investigated first on plasmonic structures on flat (zero curvature) surfaces. Such "flat" plasmonic structures are used for surface enhanced Raman scattering measurements, and therefore in some portions of the dissertation are referred to as "SERS substrates."
3.3.1.1 Metallization and protection of flat substrates

Metallized substrates were prepared by physical vapor deposition of silver at low pressures ($10^{-7}$ Torr). Depositions were performed using a conventional vacuum chamber designed for evaporation of metal and deposition onto a flat substrate. The thickness of the deposited layer was controlled by manipulating deposition rate and was monitored with a Sycon (STM-100) quartz-crystal microbalance. Silver and silicon monoxide (SiO) were evaporated from separate tungsten boats. A deposition rate of 0.2 Å/s was used for deposition of the silver. Silicon monoxide was deposited at a typical rate of 0.6 Å/s, higher than that of silver, to minimize exposure of the substrate and the silver structure to the high temperatures required for this evaporation. However, this rate was low enough to ensure a complete and uniform deposition. Protected and unprotected substrates were removed from the deposition chamber and placed inside a desiccator to minimize contact with humidity. Others were stored under ambient conditions to evaluate the effect of commonly used storage conditions on the optical properties and protective layers.

For some studies of the plasmonic behavior, "multilayer" samples were needed in which the silver plasmonic layer was placed atop a polystyrene layer. In this case the PS film had to be created first. This was done by spin coating a 2.5% wt. toluene solution at 2000 RPM for 2 minutes on a silicon wafer from which the native oxide had been etched using a 50% hydrofluoric acid (HF) solution. Etching improves the spreading of the polymer film on the substrate. After annealing the polystyrene film in a high vacuum oven, at approximately $10^{-7}$ Torr at 180°C for 2 days, to remove residual solvent and any stress from the coating step, two different types of SERS substrates were fabricated. In one case, the plasmonic structure was deposited directly on the polystyrene film. In the
other, an ultrathin silica layer was deposited on the polymer film first, and then the plasmonic structure was deposited to produce a SiO$_x$/Ag/SiO$_x$/polymer multilayer structure. In both cases, the surface of the metal structure in contact with air was protected by a 5 nm thick SiO$_x$ layer. All of these layers were deposited by thermal evaporation PVD as described above and in all cases the plasmon-active structure was deposited as a silver layer of nominal 4.5 nm thickness. All silicon oxide coatings (SiO$_x$) were deposited by evaporation of a silicon monoxide (SiO) precursor.

3.3.1.2 Signal enhancement

The nano-Raman system consists of a Horiba Jobin Yvon Labram HR-800 Raman spectrometer coupled with a Quesant (QScope 250) atomic force microscope (AFM) and side illumination optics. A confocal microscope using a long-working distance Mitutoyo (APO SL50) objective (50X, 0.42 NA$^{99,158}$) was used for measuring optical properties and signal enhancement. The objective is fixed on a XY-stage controlled by step motors with an accuracy of ~ 40 nm to position the objective with respect to the probe. The 514.5 nm line of an argon ion laser (green) and the 647 nm line of a krypton laser (red) were used to obtain the Raman signals with an incident power < 2 mW on the sample. The objective was placed at a 65° angle with respect to the surface normal. Figure 13 shows an illustration of the nano-Raman instrument with side illumination. The same instrumentation, but without the Quesant AFM, was used to measure the enhancements from flat SERS substrates. The signal was measured at three different locations on the surface.
3.3.1.3 Morphology characterization

A Park Scientific Autoprobe® CP atomic force microscope operated in tapping mode with rectangular silicon cantilevers (Veeco, manufacturer's specifications: $k=16$ N/nm and $r_{\text{curvature}} < 10$ nm) was used to characterize the surface morphology and thickness of unprotected and protected plasmonic structures on flat substrates.

![Schematic of the elements of the Nano-Raman instrument with side illumination. The insert shows details of the objective, the beam path, and the AFM head.](image)

3.3.2 Metallized probes for tip enhanced Raman spectroscopy (TERS)

The nano-Raman instrument described above was used to characterize signal enhancement and optical spectra of unprotected and protected probes. TERS contrasts provided by the probes were estimated using measurements on a 50 nm thick poly(3,4-thylenedioxythiophene)/poly(styrenesulfonate) (PEDOT/PSS) film spin coated on an aluminum mirror. The error in the determination of the contrast was estimated to be ±10%. At least three different probes were scanned at three different positions on a sample.
3.3.2.1 Signal enhancement and optical spectra

Generally the highest force that will be applied between the probe and sample occurs upon first contacting the probe and the sample, an operation known as the "approach" and which is done by a stepping motor. The highest possibility of probe damage occurs during the approach and therefore a critical aspect of the wear of the probes has been tested in these experiments, even when no imaging was done. This is particularly important to note when collection of experimental data, such as those for the change in enhancement with time, involve many approaches. The original approach program for the Quesant AFM was modified to provide a “softer landing” of the probe on the surface. Unprotected and protected probes approached the sample using a piezo scanner extension speed of 0.7μm/s until the 10nN set point was reached. Protected probes were approached 2-3 times on PEDOT/PSS and silicon flat samples before the aging experiments. TEM images collected before and after preliminary approaches suggested that the morphologies of the metal structures were not affected by these approaches alone.

To measure the optical properties of the probes, the set-up of the nano-Raman instrument was modified. A trapezoidal quartz prism under the AFM head and a white light beam from a Xenon short-arc lamp was used to illuminate the side surfaces of the prism and create an evanescent field above the prism that could excite emission from a probe brought in contact with that surface. The white light was focused on the top surface of the prisms. Optical resonance spectra were measured for both metalized probes and protected metallized probes. Laboratory temperature and humidity were monitored at the time of each measurement using a digital VWR hydrometer.
3.3.2.2 Thickness and morphology of protective coatings

A FEI Technai12 Transmission Electron Microscope operating at 120 kV was used to measure thickness and to observe the morphology of the protective coatings using a sample holder specially constructed for SPM probes. The sample stage was tilted at an angle of 55° with respect to the surface plane to image the probes and several images were taken at various magnifications. A low beam during focusing and a short acquisition time of 1 s were used to reduce cantilever bending caused by heating of the different layers covering the probe.

Qualitative elemental analyses of the probes were obtained using the energy dispersive X-ray spectrometer (EDX) coupled to the JEOL JSM 7501 Scanning Electron Microscope (SEM), to check for degradation and contamination of the probes. An accelerating voltage of 10kV was used with an acquisition time of 10 s.

3.3.2.3 Metallization and protection of probes

The protected probes were prepared by sequential physical vapor deposition of silver and silicon monoxide (SiOₓ) or silver and aluminum (Al) at low pressures (10⁻⁷ Torr) using the same vacuum chamber used for flat substrates. A deposition rate of 0.2 Å/s was used for deposition of the silver to minimize distortion of the cantilever. Silicon monoxide was deposited at a typical rate of 0.6 Å/s, higher than that of silver, to minimize exposure of the cantilever and the silver structure to the high temperatures required for this evaporation. Annealing of unprotected or protected probes was avoided in order to reduce any chemical degradation and any bending of the cantilever caused by the difference in thermal expansion coefficients of the different layers.
In the case of aluminum, a deposition rate slower than 0.2 Ångstroms/s was used. Silver and aluminum were evaporated from separate tungsten boats. The adhered Al layer easily generates a passivating Al$_2$O$_3$ coating due to the high reactivity of Al with environmental O$_2$ under normal conditions$^{159,160}$. One duplicate of each protected and unprotected metallized probe was removed from the deposition chamber, placed inside a plastic desiccator containing fresh desiccant, and kept under vacuum to minimize contact with humidity or other possible contaminants. This storage condition is very close to a completely dry atmosphere (relative humidity ~0). Others were stored under ambient conditions to evaluate the effect of commonly used storage conditions on signal enhancement and optical properties.

3.3.3 Measurement of changes in signal enhancement over time

Probes protected by a 1 nm or a 2 nm thick alumina coating and their corresponding unprotected controls were analyzed during winter when a relative humidity between 5% and 15%, and a temperature of 77°F ± 3°F generally prevailed in the laboratory. Probes protected by 3 nm of alumina and their corresponding controls were analyzed during fall, when relative humidities ranged between 10% and 35%, and similar temperatures prevailed. When monitoring changes in probe characteristics with time, all probes were exposed to prevailing conditions one hour per day for the entire length of the experiment. For each set of fabrication conditions, the behaviors of at least three probes were analyzed, each time using three positions on a control TERS sample, in order to determine data reproducibility. No experimentally significant difference was found between the initial contrast for a protected probe of a certain sort, e.g. 2 nm
alumina protected probe, and the contrast of its corresponding control, which was an unprotected probe prepared right before the set of protected probes was prepared. Estimates of the variability in contrast due to variability in deposition were obtained using measurements of probes' contrasts all made on the same day. For such batches of measurements, the standard deviation in contrast for a particular type of probe, averaged over the various sorts of probes studied, was 7%. Comparisons between the contrasts for two different types of fresh probes, e.g. protected and unprotected, were therefore done with batches of measurements all made on the same day.

3.3.4 Measurement of changes in chemical stability over time

A PHI VersaProbe X-ray photoelectron spectrometry (XPS) Microprobe was used to obtain depth profiling of protected and unprotected samples. Two flat plasmonic surfaces prepared at the same time, but in different ways, one protected with a 3 nm thick Al₂O₃ layer and the other unprotected, were used to determine how chemical degradation, principally generated by sulfur containing gases in the atmosphere and promoted by atmospheric humidity, is affected by the presence of the ultrathin Al₂O₃ layer. X-ray photoelectron spectra were measured after 2 months of storage under ambient conditions.

Spectra were obtained for different depths within the sample by sequentially sputtering away 1 nm of the sample and measuring again. By sputtering and measuring successively information on compositions still deeper in the sample could be reached. The spectra were obtained with a 300 μm focused monochromatic x-ray beam, with a power of 75W, pass energy of 94 eV, and emission angle of 45°.
3.4 Novel designs for highly enhancing probes used in high resolution chemical imaging

New probe designs and variations of plasmonic structure fabrication were explored as approaches to achieve higher signal enhancements. Structures creating enhancement factors of the order of $10^5$ or higher, are still required for high resolution chemical imaging for a broader palette of materials and for pushing the spatial resolution to still smaller features.

3.4.1 Probes with an optical antenna at the apex prepared by electron beam induced deposition

The gold nanopillar was grown via electron-beam-induced deposition using an FEI Nova 600 dual electron/ion beam system and dimethyl acetylacetonate gold $(\text{CH}_3)_2(\text{C}_5\text{H}_7\text{O}_2)\text{Au}$ as the precursor gas. The precursor was introduced in close proximity to the substrate using a positioned gas injection needle. The apex of a Cr-coated Si$_3$N$_4$ contact probe was used as support. The purpose of the 20 nm thick Cr layer was to improve the adhesion between the gold and the Si$_3$N$_4$. The apex was reshaped using both ion sputtering and gas–assisted, electron beam–induced etching$^{161}$.

3.4.2 Probes with dendritic metal structures prepared by metal replacement

All depositions were performed by immersing a previously metallized conventional SPM probe in the metal solution. A 10 nm zinc thin film was first deposited on the surface of the tip by thermal evaporation. Zinc shots 99.99% provided by Williams Acquisition LLC were used. A dendritic structure was deposited on a probe by immersing it in a 1 mM solution of HAuCl$_4$ in deionized water at 30°C for 10 seconds.
After the reaction, the chips were rinsed with deionized water to remove residual deposition solution. The structures formed on the surface of the probes were characterized using TEM and enhancement activity measured on PEDOT/PSS films.

### 3.4.3 Probes metallized with ion sputtered films

We have used controlled deposition using ion sputtering from a silver target on conventional Si contact SPM probes. Films were prepared by ion beam sputtering of silver on conventional silicon SPM contact probes for AFM from a silver target (99.99%), 2” diameter, 0.125” thick acquired from Kurt J. Lesker. The chamber was evacuated to 9 x 10^{-6} Torr before introducing Ar gas into the chamber, then maintained at 7 mTorr during deposition. The radio frequency (RF) power was maintained at 5 Watts, and a deposition rate of 0.5 Å/s maintained until 50 nm of silver were deposited. The thickness of the deposited layer was monitored with a Sycon (STM-100) quartz-crystal microbalance. The distance between the sample and the target was 4 cm and the tip was always facing the center of the target.
CHAPTER IV
RESULTS AND DISCUSSION

4.1 Conventional probes for surface topography imaging

Conventional scanning probes, i.e. without any modification, can be successfully used for the morphological study of hard surfaces, such as floor polishes. The polishes are latex emulsion formulations, and when dry the films are sufficiently hard that they can be studied with AFM with minimal distortion of the surface by the probe. In this section, the dependence of floor polish topography on the action of fluorinated surfactant in emulsions based on poly (styrene-butyl acrylate) or poly (styrene-butadiene) polymers containing all the elements of a commercial formulation are presented. Unfortunately there were a few cases in which one of the components was intentionally removed from the formulation, and the surfaces were too soft to be studied by conventional probes or in which any sort of surface chemical information was strongly desired. This evidences the need for modified probes for the study of soft and/or sticky surfaces and provides an example of one of the most important limitations of conventional SPM. SPM probes are not capable of providing any surface chemical information beyond the indirect information available by using chemically modified probes. The need of a robust, non-invasive imaging technology capable of simultaneously obtaining morphological and chemical information, with molecular scale resolution, will become evident after the first section of this work.
4.1.1 Surface morphology of acrylic latexes with or without fluorosurfactant

The images presented in Figure 14 were obtained from dry samples made using two acrylic formulations differing only in the presence or the absence of fluorosurfactant. Each complete set of images contained square images at various scales, ranging from 80x80 \( \mu \text{m}^2 \) to 200x200 \( \text{nm}^2 \), in order to capture different surface morphologies at different length scales.

Surface topography images of size 10x10 \( \mu \text{m}^2 \) of samples without fluorosurfactant (Figure 14a) show 5 \( \mu \text{m} \) wide depressions that are at least 50 nm deep, while in images of samples with fluorosurfactant (such as Figure 14b) such depressions are rare. Remarkable differences in size, organization and compactness of structure are seen in the 2x2 \( \mu \text{m}^2 \) images of films with fluorosurfactant and without fluorosurfactant. A raspberry-like structure, probably corresponding to the presence of micellar aggregates with a mean size close to 500 nm formed from small spheres in the 30 to 50 nm diameter range, can be recognized at the highlighted location in Figure 14c. These small particles look bigger, look more compact, have a narrower distribution of sizes and are more highly organized in the sample without fluorosurfactant than in the sample with fluorosurfactant. Additionally, the outlines of the micellar aggregates are more sharply defined in the samples without fluorosurfactant. In samples containing fluorosurfactant the particle outlines are indistinct. The particles seemed to have coalesced some before the film dried. This observation is consistent with the speculation, made before the experimental study, that the fluorosurfactant improves leveling and coalescence of micellar particles before the film completely dries.
Figure 14. Surface morphology of films based on styrene-acrylic copolymer. 2D (left) and 3D (right) surface morphology images. Scanned areas of a) $10 \times 10 \mu m^2$ from a formulation without short chain fluorosurfactant, b) $10 \times 10 \mu m^2$ from a formulation with short chain fluorosurfactant, c) $2 \times 2 \mu m^2$ from a formulation without short chain fluorosurfactant, and d) $2 \times 2 \mu m^2$ from a formulation with short chain fluorosurfactant. Full scale height = 50 nm. $R_{\text{rms-c}} = 6.3$ nm. $R_{\text{rms-d}} = 4.6$ nm. The contours in image c highlight locations in which the "raspberry-like" structure, described in the text, may be seen.
Analysis of a large set of images from the two samples was used to quantify the perceived differences. In order to obtain a higher resolution, a scanned area of 1 μm x 1 μm was used for this new set of images. Figure 15 shows the particle size distributions and the aspect ratios, that is the ratio of the longest to the shortest dimensions, of the samples without and with fluorosurfactant.

The main differences are not in the average sizes but in the widths of size distributions of small particles near the surface. The mean sizes of latex particles near the surface are 41 ± 7 nm and 34 ± 20 nm for the control samples and samples containing fluorinated surfactant, respectively. Differences in the particle size distributions are evident from the shapes of the fitted distributions. In the case of the control samples a narrow Lorentzian distribution reasonably captured the character of the distributions, while the particle size distributions of samples containing fluorinated surfactant were best represented by broad normal distributions. The differences in distribution breadths are quantified by differences in the magnitudes of the median variances for the two cases. There was no significant difference in aspect ratios. At the macroscopic level, gloss, the reflection of visible light from the coating, was not different among the samples tested and their values were 54 ± 2 and 59 ± 2, for samples without and with fluorosurfactant, respectively. A difference of at least 5 gloss units is necessary to be perceptible to a trained human eye\textsuperscript{162}.
Figure 15. Distributions of particle mean diameter and aspect ratio of small particles in topographic images. a) Particle mean diameters of samples without fluorosurfactant, b) particle mean diameters of samples with fluorosurfactant, c) aspect ratios of samples without fluorosurfactant, and d) aspect ratios of samples with fluorosurfactant. Noise in the distributions was filtered for diameters lower than 7 nm and higher than 120 nm and for aspect ratios lower than 0 and higher than 5. Measurements from three different samples at three different locations at the surface.

Imaging was also performed on films free of both wax and fluorosurfactant to evaluate if inclusion of the wax had a similar effect on surface morphology to that of the fluorosurfactant. Polyethylene and polypropylene waxes of low molecular weight are commonly used in floor polish formulations to improve scuff and slip resistance. An image from one of these surfaces is shown in Figure 16. The surface morphology of a dried film prepared from a formulation without wax and fluorosurfactant seems even
more organized than the surface morphology of the samples shown in Figure 14 and the small particles show a remarkable good packing. Samples containing fluorosurfactant but not wax were too soft to be imaged with conventional tips. It is known that waxes have a positive effect on film formation, leveling, and wetting. By comparing the surface morphology of formulations without wax and fluorosurfactant it has been seen how these two components, that are known heuristically to improve leveling, seem to break the order and give the system more mobility before drying on length scales below 500 nm. This behavior has also been reported in similar formulations used in adhesive systems.

![Image of topographic images](image.png)

**Figure 16.** Topographic images of a sample that did not contain wax or fluorosurfactant in the original formulation. a) 2D image. b) 3D image. RMS Roughness: 6.4 nm.

4.1.2 Effect of fluorosurfactant on surface morphology of styrene-butadiene (SB) latexes and F-d measurements

The morphology and mechanical properties of dried latex films based on poly (styrene butadiene) at length scales in the 1 – 20 μm range change markedly with the
concentration and type of fluorosurfactant. At this scale, changes in surface morphology are expected to affect the reflection of visible light from the coating, quantified as gloss, more directly than in the case of acrylic films, for which morphology changes are observed on length scales below 1 μm. When a short chain fluorosurfactant is used in the poly (styrene butadiene) formulation, circular-like features are evident at the surface. They become more numerous, smaller, and taller as the concentration increases. It is also more difficult to remove a conventional silicon probe from the surface as the concentration of fluorosurfactant increases, and this effect increases nonlinearly with concentration. This suggests that the adhesiveness of the surface involves a complicated interaction of surfactant with the other film constituents. It appears that the surface structure and properties are dictated by the interplay between mass transfer of various components to the surface and changes in mobility that occur during drying.

Surface topography images, examples of which are shown in Figure 17, were obtained at different square image sizes, ranging from 40x40 μm² to 2x2 μm², with the purpose of finding a convenient scale to highlight morphological differences among the samples. Only examples of 40x40 μm² images are shown here. Samples without fluorosurfactant do not show particles at the surface with size (i.e. largest dimension) smaller than 5 μm (Figure 17a). Samples containing any fluorosurfactant show smaller particles having diameter < 1 μm (Figure 17b-f). Examples of the F-d curves from which various observations about the effect of surfactant level on mechanical properties were derived are shown in Figure 18 for samples with 100 ppm and 300 pmm of short chain fluorosurfactant. Table 3 shows the pull-off forces and the stiffness of the system for all samples.
F-d curves for films in the set sampled in Figure 17 indicated the presence of a tackier material at the surface as the concentration of short chain fluorosurfactant increased. These soft areas become tacky when the concentration of short chain surfactant reaches 300 ppm. One possible explanation would be that "bloom" of the surfactant to the surface creates a layer very rich in surfactant that has markedly different properties. However, a layer of pure, or nearly pure, surfactant is not expected to cause this sort of behavior.

Figure 17. Topography images measured in contact mode for SB samples. Samples contained a) 0 ppm, b) 100 ppm, c) 200 ppm, d) 300 ppm, e) 400 ppm, and f) 600 ppm short chain fluorosurfactant and a constant coalescent to plasticizer ratio (C/P) of 50/50 wt/wt. Full scale height values in all figures have been set to 80 nm to facilitate comparison. The tones in the height scale have been inverted to highlight differences (dark = top, clear = bottom). Imaged using conical silicon tip in contact mode (k=0.12N/m); force during scanning = 6nN; scan area = 40μm x 40μm. Note that the control sample, i. e. the sample with 0 ppm of fluorosurfactant, has been magnified to show the smooth areas not seen in the rest of the images.
Figure 18. F-d curves of selected SB samples. F-d curves of a) the highest region of samples containing 100 ppm of short chain fluorosurfactant, b) the lowest region of samples containing 100 ppm of short chain fluorosurfactant, c) the highest region of samples containing 300 ppm of short chain fluorosurfactant, and d) the lowest region of samples containing 300 ppm of short chain fluorosurfactant. Soft contact tips (k = 0.12 N/m) were used for all measurements. The black and grey curves in the graph represent the tip approaching and tip withdrawing processes, respectively.

Table 3. Stiffness and pull-off forces of highest and lowest points of samples containing different concentrations of short chain fluorinated surfactant.

<table>
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<th>Lowest points</th>
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<tr>
<td></td>
<td>Stiffness (N/m)</td>
<td>Pull-off force (nN)</td>
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<tr>
<td>0</td>
<td>2.0 ± 0.2</td>
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<td>100</td>
<td>2.5 ± 0.1</td>
<td>52 ± 2</td>
</tr>
<tr>
<td>200</td>
<td>2.3 ± 0.2</td>
<td>190 ± 72</td>
</tr>
<tr>
<td>300</td>
<td>2.1 ± 0.1</td>
<td>388 ± 45</td>
</tr>
<tr>
<td>400</td>
<td>1.9 ± 0.2</td>
<td>143 ± 30</td>
</tr>
</tbody>
</table>
Rather the surfactant must be interacting with the other materials in the formulation so that the probe adheres well to the coating and, at the same time, mechanisms for viscous dissipation of energy in the coating are invoked when the probe is pulled from the surface. The composition at the surface is most probably not dictated by a thermodynamic equilibrium, but by a complicated interplay of the drying speed and the rates of mass transfer of various components to the surface and, in some cases, into the atmosphere. As the concentration of short chain fluorosurfactant reaches 300 ppm, the tackiness of the surface seems to be at a maximum. Again, rather than suggesting blooming of pure or nearly pure surfactant to the surface, this suggests a more complex interaction between surfactant and the coating constituents that leads to enhanced tack. For comparison, samples containing different concentrations of a long chain fluorosurfactant were also imaged. Those samples contained particles at the surface with size (i.e. largest dimension) bigger than 100 nm, as shown in Figure 19, and also showed a drastic transition in character when the concentration of long chain surfactant was increased from 25 ppm to 50 ppm.

Transitions in the morphology at the surface of SB latex films are evident from the topography images and seem to be dependent on the type and concentration of fluorosurfactant. So far, the most drastic changes in morphology have been observed when the concentration of short chain fluorosurfactant is increased from 200 ppm to 300 ppm and when the concentration of long chain surfactant is increased from 25 ppm to 50 ppm. These changes occur on the 10-40 μm length scale for SB samples and occur at the same concentration at which a sharp change in the macroscopic appearance, as quantified by gloss measurements, is observed. Details are presented in Appendix A.
Figure 19. Contact mode topography images of SB samples containing a long chain fluorosurfactant. Samples contained a) 0 ppm, b) 25 ppm, and c) 50 ppm, of fluorosurfactant. Full scale height values in all figures have been set to 40 nm to facilitate comparison. The tones in the height scale have been inverted to highlight differences (dark = top, white = bottom). Imaged using conical silicon tip in contact mode (k=0.12N/m); force during scanning = 6nN; scan area = 40μm x 40μm.

4.2 Functionalized tips for adhesion measurements

Conventional silicon or silicon nitride SPM tips were used in the previous section to study the surface morphology of hard surfaces, and have been extensively used by others for adhesion studies with nanometer-scale contacts involving other rigid surfaces\textsuperscript{164-167}. Unfortunately, the use of such tips for soft and adhesive surfaces still presents big challenges\textsuperscript{17,57}. These surfaces present contradictory requirements for AFM analysis. On one hand is the requirement of light tapping to avoid surface damage\textsuperscript{168}, and on the other, the need for energetic tapping to enable the tip to lift off the surface. Information on the structure lying below the surface is best obtained with a stiff cantilever (k > 15 Nm) and a large free amplitude of oscillation (f>150kHz)\textsuperscript{58}. The use of
SPM to study the adhesive behavior of viscoelastic materials has been restricted mainly by the complexity and geometry of the interaction. It is difficult to scan a very sticky surface with a very compliant probe if the interaction between surfaces is strong. In these cases, the interaction between the probe and the surface is so strong and unstable that it is difficult for a conventional tip to stabilize and scan the surface. Previous work in our group has focused on studying tackified pressure sensitive adhesives and the effect of component migration on surface properties. In those works, conventional SPM tips were only used effectively on samples after they had been aged for long times. It was not possible to use them to study freshly cast, sticky samples.

The deposition, on a conventional SPM tip, of octadecyltrichlorosilane (OTS), heptadecafluoro - 1,1,2,2 - tetra hydrodecyl trichlorosilane (FTS), heptadecafluoro - 1,1,2,2 - tetra hydrodecyl methyl dichlorosilane (FDS) or a mixture of FTS and FDS to form an ultrathin hydrophobic layer, ideally a self-assembled monolayer (SAM), has been used to decrease the forces acting on the tip during F-d measurements. The advantage brought by the tip modification was first demonstrated when pull-off forces measured by the modified tip on a simple, hard silicon surface remained nearly constant under increasing levels of relative humidity. For soft samples, the values of pull-off force and work of adhesion using the modified tip are lower than those measured using an unmodified tip. This is advantageous for the study of a good adhesive, because the pull-off force for an unmodified tip on a good adhesive can become so large that the tip cannot be removed from the surface.

An ideal self-assembled monolayer changes the functionality of a surface by completely covering it. Figure 20 shows a transmission electron microscopy (TEM)
image of one functionalized tip. Because the surface available for measuring contact angle on the chips themselves was very small, a separate silicon chip was modified along with the tip and contact angle measurements made on that separate chip. Table 4 shows the properties of the films on the flat surfaces of the chips. Thicknesses and contact angles of the films on the tips themselves could not be measured. All thicknesses reported were obtained by subtracting the thickness of the silicon oxide (SiO$_x$) measured by ellipsometry from the thickness of the SAM with the oxide (SAM + SiO$_x$) also measured by ellipsometry using a single layer model with the refractive index for SiO$_x$.

![Modified Silicon tip](image)

**Figure 20.** Hydrophobically modified scanning probe. a) Schematic and b) TEM image after use of a scanning probe that has been functionalized with a layer of octadecyltriethoxysilane (OTS). Scale bar is 10 nm.

<table>
<thead>
<tr>
<th>Hydrophobic Silane Layer</th>
<th>Ellipsometric Thickness (Å)</th>
<th>Static Water Contact Angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>---</td>
<td>4 ± 1</td>
</tr>
<tr>
<td>OTS</td>
<td>21 ± 2</td>
<td>106 ± 3</td>
</tr>
<tr>
<td>FTS</td>
<td>45 ± 1</td>
<td>106 ± 2</td>
</tr>
<tr>
<td>FDS</td>
<td>15 ± 3</td>
<td>103 ± 2</td>
</tr>
<tr>
<td>FTS/FDS</td>
<td>113 ± 8</td>
<td>103 ± 2</td>
</tr>
</tbody>
</table>

Table 4. Thickness and static contact angles of hydrophobic layers.
The contact angles of the four layers are comparable, indicating comparable levels of hydrophobicity. However, the thicknesses of the layers vary widely. The OTS and FDS depositions appeared to form true monolayers on flat surfaces under the conditions used. The thicknesses seen for the FTS and FTS/FDS mixtures suggested multilayer deposition on flat surfaces in those cases. These multilayers probably have a low density of fluorinated groups at the surface, and that can explain the similarity between the contact angles for surfaces that are supposed to be fluorinated and those that should be covered with methyl groups. It has been demonstrated by others that the backbone of the fluorinated molecule plays a key role in imparting hydrophobicity to the surface\textsuperscript{169}. Tips modified with OTS or FDS were used to image and study model adhesive surfaces with SPM-based techniques.

4.2.1 Synthesis of a model adhesive film based on acrylic triblock copolymers

Ordered diblock and triblock copolymers exhibit microstructures that vary with the block composition and this microstructure is the reason for important properties. All-acrylic block copolymers have recently received attention for their use in the formulation of pressure sensitive adhesives\textsuperscript{170,171}. To perform incisive experiments on the relationship between pressure sensitive adhesive performance and aging, well-defined homopolymers, diblock, and triblock copolymers of poly(methyl methacrylate) (PMMA) and poly(n-butyl acrylate) (PnBA) were synthesized by controlled radical polymerization. For the measurements, triblock copolymers were blended with shorter di- and tri-block copolymers or with homopolymers to tune-up the adhesive properties of the film without using low molecular weight additives such as tackifiers and plasticizers. Avoiding the
use of low molecular weight additives is crucial in skin contact applications of pressure sensitive adhesives.\textsuperscript{172}

Based on the behavior observed in studies of block copolymer adhesives based on styrene and diene monomers,\textsuperscript{173} it is expected that the molecular weight of the middle block will play the most important role in determining the bulk mechanical properties. Most of the commercial applications of thermoplastic elastomers use polymers with a rubbery block in the middle and glassy end blocks comprising no more than 15\% or 20\% of the total volume of the chain. The poly ($n$-butyl acrylate) molecular weight for entanglement ($M_c$) is 28k and samples having molecular weights similar to, higher than, or lower than this entanglement value are expected to perform differently from one another. All samples having PMMA end blocks with molecular weights of about 10k or higher are expected to form microdomains, differing in the symmetry of the domains depending on the fractions of each of the blocks. Also, the properties of a film of a blend will depend on the diblock/triblock ratio. It is known that this ratio controls the entanglement to crosslink ratio and has a determining role for the large strain properties in block copolymer adhesives made with styrene-diene materials. In particular, the addition of a significant fraction of diblock causes a very pronounced strain softening, which in nominal stress terms can cause a decrease in stress with increasing extension.\textsuperscript{121} The relations among microdomain formation, chain size, macroscopic properties and surface properties are some of the most important factors when formulating an adhesive film.
4.2.2 Macroscopic debonding experiments

One of the most important goals when designing pressure sensitive adhesives based on acrylic block copolymers is to reduce the amount of low molecular components. Different blends were formulated to study how the mechanical properties change relative to those of the pristine block copolymer. First, an acrylic triblock copolymer (PMMA-\textit{b}-PBA-\textit{b}-PMMA / 13k-61k-13k) was blended with an acrylic triblock copolymer of lower molecular weight (PMMA-\textit{b}-PBA-\textit{b}-PMMA / 3k-28k-3k). Second, the triblock copolymer was blended with polybutylacrylate homopolymer. Finally, two different diblock copolymers were blended with a low molecular weight triblock and the homopolymer. Below, microscopic characterization of the triblock copolymer/homopolymer blend is presented. Details of the synthesis and macroscopic behavior of this and other blends are presented in Appendix B and Appendix C, respectively.

4.2.3 Microscopic characterization of adhesive surfaces using a functionalized probe

Adhesive films were studied freshly coated and after aging for short times. In Figure 21 the surface of a film formed from high molecular weight triblock copolymer is shown. When an attempt was made to scan this surface with an unmodified tip, the interaction between the tip and sample surface was so strong that once the tip made contact it could not escape the surface, so “tapping” was not possible. Two microphases are evidenced in the phase image of the surface. They differ somewhat in stiffness. The two microphases do not appear to be associated with marked topographical features. However, whether both microphases actually are found at the outermost surface or
whether the microphase-separated structure lies somewhat beneath the surface cannot be decided by looking at tapping mode images alone. When “tapping” one actually probes the properties not only of the surface, but also of the material just beneath the surface.  

Figure 21. Surface morphology of adhesive film. a) AFM height image and b) phase image of a film formed from pure 87k triblock copolymer obtained with an FDS-modified hydrophobic tip. X and Y scales in micrometers.

F-d curves of pure triblock copolymer collected using a modified and unmodified tip evidence the difficulty of characterizing samples having more than 50 wt % homopolymer. The pull-off force obtained using the modified tip is lower than that obtained using an unmodified tip. This is due both to the reduction of the influence of the water bridge between the sample and the tip in the case of the modified tip, and the smaller interaction of the adhesive with the lower energy surface. Further studies are necessary to differentiate the roles of these two contributions. Force-penetration curves were obtained using SPM modified tips. Samples were evaluated at time zero and after 3 weeks of aging under four different aging conditions to analyze the effect of the environment on the surface properties.
4.2.3.1 Effect of homopolymer concentration

Figure 22 presents two force-distance curves, measured at 20% humidity, that exemplify important features seen in many of the curves. The curve on the left is typical of freshly cast blend films having 0%, 10% or 20% homopolymer. As the tip approaches the surface there is a point where the tip snaps into contact and the force of this interaction seems to be related with tack. After passing this point, the probe is loaded and two regions with two different slopes are obtained. After the maximum force has been applied, the unloading curve starts, showing a decreasing force until a minimum is reached, followed by a smooth increase to the initial level of force. Samples without viscoelastic effects show abrupt jump out of contact, so the manner of breaking the contact reflected in the F-d curve must be related to the viscoelastic character of the adhesive. One possibility is that contact area decreases gradually and continuously upon withdrawing the probe. Another possible explanation of the curve shape is that the contact area remains constant over some fraction of the debonding phase, but there is cavitation or necking of the material that remains attached to the probe, leading to a reduction in tensile force with retraction. With the F-d curve alone it is impossible to separate these two interesting cases. For samples containing 30% homopolymer, a completely different force-penetration curve is obtained. As soon as the probe reaches the surface, the tip is pulled in (probably progressively engulfed) by the film until a minimum (corresponding to strong tensile force) is reached and then finally the force starts becoming less tensile until the force becomes positive (compressive) and then a maximum is obtained.
Figure 22. F-d curves of selected adhesive films. a) Typical force-distance curve of blends containing 0%, 10% or 20% of homopolymer and b) samples containing 30wt.% homopolymer. The minimum on the ordinate is much lower in the case of the right hand plot.

After this, the unloading curve follows almost the same path of the loading curve to finally reach the initial point. It is possible that this behavior results from a vertical phase separation of the blend into a phase rich in homopolymer and a phase containing less homopolymer, with the homopolymer rich phase going preferentially to the surface. In that case the elasticity provided by the crosslinking created by microphase separation would not be evident at the surface, even though it could contribute to macroscopically measured behavior. For samples containing lower contents of homopolymer a more elastic behavior at the surface must be found.

4.2.3.2 Effect of humidity

To verify that the effect of humidity was negligible in the range of humidities studied, the distribution of pull-off forces was measured for one modified tip under different humidity conditions. A variation of less than 10% in the mean of the distributions showed that the effect of capillary forces is much smaller for the case of the
modified tip than for the case of unmodified tips\textsuperscript{34}. Unfortunately, unmodified tips broke before debonding from the surface and comparison with unmodified tips is unavailable. The distributions are shown in Figure 23.

![Figure 23](image)

Figure 23. Distribution of pull-off forces for a hydrophobic modified tip.

4.2.3.3 Effect of aging conditions

Finally, the effect of aging on the surface adhesiveness was studied by considering four specific instances of aging. Here, samples freshly cast and samples after 3 weeks of aging are compared. Figure 24 presents two rather complicated plots. The plot in Figure 24a summarizes pull-off forces for all of the samples measured immediately after casting. A total of sixteen samples were measured. Four of the samples were made of pure 87k triblock copolymer. The results for these samples are shown in the far left panel of Figure 24a. The four samples are denoted with shorthand names that indicate how the sample will be aged. For example, the “humid” sample was
to be aged in a humid environment. This name does not reflect in any way the conditions under which the samples were measured when they were fresh. All were measured under dry conditions at ambient temperature. The four aging conditions were as follows. The sample aged “dry” was kept in a dark desiccator at very low RH during the three weeks of aging. The sample aged under the “humid” protocol was placed in an environment with a relative humidity (RH) of 90% at ambient temperature for three weeks. The “high T” protocol was to age the sample at a temperature of 70°C and RH of 30% in the dark for three weeks. The “UV” aged sample was exposed to a UV lamp (\( \lambda = 250 \) nm) at ambient temperature and temperature for three weeks. Results for the fresh samples with 10 % homopolymer are in the second panel of four data points. The results for the 20% samples are in the third panel, and the results for the 30% samples in the last panel.

![Figure 24](image)

Figure 24. Microscopic pull-off forces of homopolymer/triblock copolymer blends. a) Before aging and b) after 3 weeks of aging. The detailed structure of the plots is explained in the text. In Figure 24b five results are shown for the samples with 30% homopolymer because two different sorts of behavior were observed for the sample aged under humid conditions, as explained in the text. The pertinent averages are labeled “humid 1” and “humid 2”.

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In comparing the behaviors of the fresh samples, the following observations can be made. The value shown for each sample is a mean with an error bar determined from the statistics of trials at 50 points on the surface. Since all four samples represented in the first panel are made of the same material in the same way, the variations in the means measured reflect the sampling uncertainty and in fact the error bars reported are consistent with the differences in means from sample to sample. These remarks on statistics apply equally well for the three types of samples with 0, 10, or 20% homopolymer. However, the sampling of the fourth type of sample, with 30% homopolymer, shows something interesting. Even for the “as cast” samples the mean value for one of the four samples is much different than the others and this difference lies outside the uncertainties estimated for the four samples of 30% homopolymer. This suggests that for the 30% samples even in the as-cast or fresh condition the surface may not be laterally uniform or there may be some inconsistency in the composition of surface formed that can be affected by very small differences in the way individual samples of the same composition are made. The pull-off force varies only modestly as homopolymer composition is increased from 0 to 10 to 20%. For the 30% samples the pull-off force averaged over all four samples is markedly higher, and the shape of the force-distance curve is qualitatively different.

Pull-off forces for samples after 3 weeks aging are shown in Figure 24b. Since acrylates are supposed to be resistant to aging, but had not been much studied when this work was undertaken, the small changes seen represent significant, positive findings. Interestingly, the pull off force actually increased with aging for all four of the samples made with pure triblock copolymer. The pull-off force from the pure triblock copolymer
films roughly doubled for all four aging protocols, suggesting that the time of aging, and therefore some rearrangement of the sample, was key rather than any sort of chemical change in the sample. Increases are seen with aging as well for the samples with 10 or 20% homopolymer, with the improvement being weaker as the fraction of triblock copolymer in the sample decreases. For both the 10 and 20% homopolymer samples the pull-off force is also not significantly affected by changes in the aging protocol. For the 30% samples, however, large differences among the samples aged in different ways are observed. Pull-off force is enhanced very strongly by aging in a humid environment, but the humidity also leads to the presence of two distinct behaviors. That is, the distribution of pull-off values over locations on the sample surface is strongly bimodal. The values from the two modes are labeled in the last panel of Figure 24b with the designations “humid 1” and “humid 2”. The uncertainties shown for the two values of the modes give some impression of how well defined they are. The shapes of the force-penetration curves for these two different types of surface are also different, suggesting that one sort of region on the surface is stiffer than the other. The development of this laterally inhomogeneous structure can be somehow facilitated by the humidity, most likely by plasticization of the film.

The samples subjected to the “high T” and “UV” aging protocols also display surface behaviors that are more broadly distributed than the behavior before aging, as indicated by the error bars shown. However, for these two cases, clearly separated modes were not identified. The “high T” sample had a mean pull-off force after aging that seems to fit approximately with an average of the two values seen for the sample aged under humidity.
In other words, when the molecular mobility of the sample is enhanced by rising the temperature, the overall mean pull-off force is enhanced to a degree comparable to that seen when molecular mobility is enhanced with plasticization, but lateral differentiations in surface structure do not arise so readily. Finally, the UV aging was detrimental to pull-off force. The mean value seen in that case was the same as that seen for triblock alone, but the distribution of pull-off force values was higher than before aging.

From a survey of the shapes of all the force-distance curves (not shown here), it appears that both the snap-in force and the slope of the region just after snap-in change with composition of homopolymer. Samples of pure triblock copolymer showed a snap-in force lower than those of samples containing 10, 20, or 30% homopolymer. Unfortunately, further analysis of these results remains limited by the difficulty to quantify the contact area at every of these stages.

In the previous section and this section, SPM has been used to provide nanoscale information on the behavior and morphology of hard latex films or soft adhesive materials. It was also shown that by functionalizing a conventional SPM probe broader opportunities for studying material surfaces are opened up. Unfortunately, most SPM techniques used currently are not capable of providing any chemical information on surfaces beyond the indirect information available by using chemically modified tips. Additionally, there are not robust commercially available techniques that can provide surface chemical information resolved laterally on a nanoscale level. Also techniques available that do provide chemical specificity, but not very fine resolution, require
complicated sample preparation procedures or extreme (e.g. high vacuum) measurement conditions.

A non-invasive imaging technology capable of simultaneously obtaining morphological and chemical information, with molecular scale resolution, would be a break-through for materials science in general and for surface science in particular. TERS is still under development and its progress has been limited by the fragility of the probes. In the next section, a very effective approach to fabricate robust metallized probes is presented, taking the development of this technique a step closer to the goal of robust high resolution chemical imaging.

4.3 Robust metal probes for chemical imaging

In order to characterize changes in the plasmonic structures that typically occur without protection of that structure, an energy dispersive X-ray spectroscopy (EDX) spectrum was obtained from a tip coated with a 50 nm thick silver film left unattended under ambient conditions for 1 week during the summer (higher humidity). Figure 25 shows the EDX spectrum obtained. The EDX spectrum indicates the presence of sulfur, consistent with the contention that the silver coating on the tip chemically degrades under ambient conditions.
Figure 25. EDX spectrum of an unprotected, unused silver-coated tip after one week of storage under ambient conditions showing traces of sulfur that evidence tarnishing. The inset is an SEM image showing the area of the tip from which the spectrum was obtained using an accelerating voltage of 15 keV and a tilt of 0°.

Surface protection is crucial for designing stable plasmonic devices but there are a few reasons why the selection of a protection scheme is not trivial. The coating must not shift the original resonance frequency of the tip, the enhancement must be preserved, and the increase in radius of the tip that comes with depositing additional material on it must not affect the spatial resolution. An optically invisible protective coating brings wear resistance to the metal, while minimizing chemical reactions responsible for degradation and mitigating structural changes due to heating.

A first step in the development of effective coatings was to identify the characteristics needed in such a coating. In tip enhanced Raman spectroscopy (TERS), two types of probes are commonly used: etched metal wires tips or metal-coated scanning probes. Localized surface plasmon resonance is a surface process and the enhanced field does not extend more than 20 nm in the direction perpendicular to the surface of the
plasmonic structure. Because of the very specific characteristics of a material for optical applications at the interface between the plasmonic material and the surface under analysis, the appropriate protective coating must have the following properties.

- Ultrathin (actual thickness < 5 nm) to avoid attenuation of the enhancement so that the sample may still come within the region of space in which the local field is highly enhanced

- Physically and chemically homogeneous

- Can be deposited conformally on the structure of the metal

- Optically inactive, in order to reduce overlapping with the spectroscopic signal of interest

- Harder than the metal of the plasmonic structure, in order to protect the plasmonic structure from deformation

- Dense (or low porosity) to reduce gas permeation of corroding gases from the atmosphere to the metal

- A strong adhesive interaction with the metal

Ultrathin layers that can deposited in a controlled manner include self-assembled monolayers (SAMs), silica thin films prepared by the sol-gel method or thin oxide layers prepared by thermal evaporation methods. The first two types of films were tested and found to be inferior to the third type. Hexadecanethiol has been proven to form SAMs on flat silver substrates and even to give some corrosion protection\textsuperscript{174}. They must assemble into a highly packed film in order to be effective. Unfortunately, the strength of the S-Ag bond (~1500 eV) makes it unstable under illumination and this protective layer is not suitable for optical applications. Thin films based on sol-gel are a potential candidates,
but substantial shrinkage during drying and low density from inherently high organic content cause local defects resulting in heterogeneous films, poor metal coverage, and gas permeation through the film. The best protection was obtained by the use of an ultrathin oxide layer prepared by the physical vapor deposition (PVD) thermal evaporation of either SiO or Al. We demonstrated experimentally and Zenobi et al.\textsuperscript{119} have demonstrated theoretically that a SiO\textsubscript{x} layer can protect metallized tips for TERS. Also, we have demonstrated that controlled thermal evaporation, physical vapor deposition (PVD) of silicon monoxide (SiO) and aluminum can be used to create an ultrathin oxide coating (<5 nm) that improves significantly the stability and wear resistance of plasmonic Ag-nanostructures on tips for apertureless near-field optics without substantial degradation of their advanced optical properties.

4.3.1 Demonstration of protection with silicon oxide using plasmonic structures on flat surfaces

The first PVD coating investigated was a coating of silicon oxide (SiO\textsubscript{x}). SiO\textsubscript{x} was chosen because it is chemically inert, harder than the metal layer, and can be easily deposited by evaporation techniques. It is known that the evaporation of silicon monoxide (SiO) results in a film of amorphous silicon oxide (SiO\textsubscript{x}) at residual pressures higher than 10\textsuperscript{-6} Torr\textsuperscript{175}. Study of such a protective layer on the highly curved surface of an SPM probe is challenging, so study of the optical properties and Raman signal enhancement of plasmonic structures protected with SiO\textsubscript{x} was first done using plasmonic structures deposited on flat substrates. The lifetimes of silver plasmonic structures on flat
surfaces (as model systems) have been extended by depositing over the silver an ultrathin silicon oxide (SiO$_x$) coating and details are presented in Appendix D.

4.3.2 Morphology and optical properties of silica protected silver coated probes

An adequate, thin protective coating must conformally follow the surface topography of the silver structure and completely cover the entire metal structure to reduce attack from environmental agents. A TEM image of one SiO$_x$-coated metallized tip, shown in Figure 26, reveals the morphology of a 3 nm SiO$_x$ layer fabricated by PVD on the Ag plasmonic structure (50 nm nominal deposition thickness) already present on the tip. From TEM images of several representative tips, the radii of the protected, metallized tips were determined to be 20-25 nm. That is, the thickness of Ag layer deposited on the apex of the tip is substantially less than the nominal layer thickness expected from the deposition monitor.

![Figure 26. TEM image of a metallized silicon nitride tip with a 50 nm Ag film protected by 3 nm of SiO$_x$.](image)

After seeing that the protective coating did not significantly affect the morphology of the plasmonic structure, it was important to compare the optical properties
of unprotected and protected tips. Optical spectra for an unprotected silver tip and a SiO$_x$ protected silver tip are shown in Figure 27. Silicon nitrite uncoated tips showed an optically flat spectrum with a very low signal intensity. The spectra from the unprotected and protected metallized tips both showed wavelength dependence with a maximum at a wavelength between 650 nm and 700 nm. However, details of the shapes of the resonance spectra and maxima positions for the tips with protected and unprotected films differed. The spectrum from the SiO$_x$ protected tip showed two local maxima. One peak was located between 550 nm and 600 nm and the other peak between 680 and 730 nm. Two peaks were seen for multiple tips from two different batches of tips. It may be that multiple resonances result from the coating interacting with the one particle or cluster of particles at the tip apex and the photoluminescent response of the SiO$_x$ layer containing regions rich in crystalline Si$^{130}$. 

![Figure 27](image)

Figure 27. Optical spectra for (a) unprotected silver-coated Si$_3$N$_4$ tip and (b) silver-coated Si$_3$N$_4$ tip protected by a 3 nm thick SiO$_x$ layer. Light intensity was calculated as $(I_{\text{near}} - I_{\text{far}})/I_{\text{far}}$. 

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4.3.3 Raman signal enhancement from silica protected silver coated probes

The appropriate coating for optical applications must not diminish the plasmon activity of the metal structure. The objectives of protecting plasmonic structures for optical applications are achieving corrosion protection and improving wear resistance without compromising enhancement. Whether these objectives were met was determined by measurements on thin, spun-cast films of a conductive polymer blend (PEDOT/PSS) and an inorganic material (CdS). The results were similar for the two films, though the intensity of the signal was higher for the inorganic layer. Most of the results presented in this section are related to the CdS film.

Comparison of signals from protected and unprotected tips and quantification of the phenomena central to defining the behavior of such structures is based on “contrast”, the key parameter controlling one’s ability to image with the probe that relates the total signal measured when the probe is in contact to the signal measured when the probe is withdrawn.

Contrasts of tips coated with 50 nm silver layers were similar whether measured on the PEDOT/PSS sample or on the CdS sample, though the intensity of the signal was higher from the inorganic layer. When a tip coated with a 50 nm silver film was used in TERS, a contrast factor of 2.0 was achieved on a CdS film. The contrast was reduced by only 10% when the 3 nm thick protective coating was added to the tip. The thickness of the protective coating and the material characteristics make it a suitable protective coating for optical applications.
Figure 28. Contact (solid lines) and withdraw (dotted lines) signals from a 20 nm thick CdS film on an aluminum mirror. Contact signals were collected using a metallized silicon nitride tip with 50 nm of silver. a) unprotected and b) protected by 3 nm of SiOx. The measured contrast factors are 2.0 and 1.8, respectively.

One of the main problems of unprotected silver plasmonic structures upon exposure to environmental conditions is a decay of the enhanced signal over time due to silver degradation. For this particular set of data, the initial contrast for the unprotected tip was about 10% higher than the contrast for the protected tip, possible due to the unprotected tip having a better plasmonic structure or to the coating on the protected tip causing a slight loss of intensity. After being used at summer humidity for multiple measurements over a period of three weeks and stored in between under dry conditions, the contrast for an unprotected metallized silicon nitride tip has dropped to 0.4, while the contrast for the silica-protected analog tip has dropped to 0.7, as shown in Figure 29.
Figure 29. Contact (solid lines) and withdraw (dotted lines) signals from a 20 nm CdS film on an aluminum mirror. Contact signals were collected using a metallized silicon nitride tips with 50 nm of silver a) unprotected and b) protected by 3 nm of SiO₂ after multiple measurements made over a period of 3 weeks, with the tips having been stored under dry conditions between uses. Contrast factors are 0.4 and 0.7, respectively.

The rate at which the signal decayed was reduced by addition of the protective coating, as shown in Figure 30. The rate of decay was documented over 30 days. Addition of the protective coating clearly slows the degradation of the signal over a 30 day period. This was also true for protected flat plasmonic substrates and details are shown in Appendix D.
Enhancements for unprotected tips have been measured for many tips and this initial contrast of 2.0 for the unprotected tip is consistent with that larger body of measurements. These results show a higher decrease in contrast for the unprotected tip, over a time of 30 days, than for the protected tip. After 30 days of use, with storage under dry conditions, the protected metallized tip still produces a signal enhancement 75% higher than that of the unprotected tip.

4.3.4 Wearing resistance of silica protected silver-coated probes

During scanning the tip is in direct contact with the sample and they wear. Wear increases the tip radius, decreasing the resolution of the topography image and the image changes with time as the wear occurs. It would be desirable for a protective coating to prevent wear of the plasmonic structure on the tip as well as alleviating degradation of the signal enhancement due to chemical changes. Plasmonic structures protected with
SiO$_x$ coatings are expected to show higher wear resistance than their unprotected counterparts as well as prolonged life of effective enhancement. TEM images of three tips, shown in Figure 31, illustrate the kinds of changes that occur with wear for an unprotected and protected tip. The image of an unprotected tip fabricated by PVD of 50 nm Ag plasmonic structure on a Si$_3$N$_4$ SPM tip before it has been used for any scanning shows complete coverage of the tip by the silver coating. After a silver-coated tip without protection has been used to scan a thin polymer film three times, the metallic structure has been removed from the apex and silver has been pushed away from the apex and it has accumulated on the base of the blunted tip (middle image). Traces of what look like silver particles left on the tip are evident in the image. In the case of the SiO$_x$ protected Si$_3$N$_4$ tip, after scanning the same polymer film three times the apex is not as sharp as it was originally, but the silver layer remains intact.

Figure 31. TEM images showing morphologies of tips. a) Unprotected, silver-coated Si$_3$N$_4$ tip before use, b) unprotected tip after scanning a PEDOT/PSS thin film three times, and c) tip with a SiO$_x$ coating after similar use. Note that the magnifications differ somewhat from image to image.
4.3.5 Morphology, optical properties and signal enhancement of alumina protected silver-coated probes

Since SiO$_x$ is not capable of completely stopping the degradation of signal enhancement over 30 days of use, a coating even more capable of protecting the plasmonic structure was sought. The very high density of Al$_2$O$_3$ and its successful use as a protective layer in other applications recommended it as an excellent candidate layer material. TEM images of one tip protected with a Al$_2$O$_3$ coating reveal a morphology in which the 3 nm thick coating effectively covers the Ag plasmonic structure on the tip (Figure 32a,b). From TEM images of several representative tips the radii of the protected, metallized tips were determined to be 25-30 nm, very close to the radii of unprotected tips. TEM images (Figure 32c) also reveal a striking example of wear of an unprotected tip. After scanning a relatively soft polymer film only three times with the same tip, the metallic structure has been completely removed from the apex and silver has accumulated on the base of the now blunted, unprotected tip at a distance of about 200 nm from the apex. For an Al$_2$O$_3$ protected tip, after three scans of a hard, patterned silicon substrate (Figure 32d), the interface between the protected silver plasmonic structure and the silicone nitride tip is evidently damaged, but the integrity of the plasmonic structure seems unaffected. The force applied in all cases during scanning was kept at 10nN.
Figure 32. TEM images of a metallized silicon nitride tip with a Ag film of 50 nm nominal thickness protected by 3 nm of Al$_2$O$_3$. (a) freshly prepared tip, (b) tip after 40 days of measuring enhancement of a polymer film, (c) morphology of an unprotected, silver-coated Si$_3$N$_4$ tip after scanning a PEDOT/PSS thin film three times, and (d) tip with a 3 nm Al$_2$O$_3$ protective coating, after scanning a hard silicon substrate three times. Note that the magnification and orientation of the tip axis differ somewhat from image to image. Scale bar represents 50 nm.

The PEDOT/PSS polymer blend film has a Young’s modulus of at least 1 GPa, and the polymer surface is not expected to be affected during approaching due to the very low cantilever spring constant (0.1N/m), minimal set point force (10nN), and weak laser power intensity (<2mW) during illumination. For the polymer and silicon samples the types of contact that occur also differ somewhat. In a patterned silicon sample there are periodically spaced structures of significant height. When scanning is done, there is contact between the tip and the sample asperities at locations on the tip ~400 nm away from the apex.
An excellent protective coating should not alter the optical properties of the TERS tip and no large difference has been observed between the optical spectra of the unprotected and protected tips for the case of the Al₂O₃ coating: Both spectra shown in Figure 33 show a broad peak at ~650-700 nm, but the protected tip shows a bit sharper resonance. These characteristics were seen for multiple tips from two batches. The measurements clearly demonstrate that the contrast (~ 1.15 ± 0.1) remains unaffected when the protective alumina coating of thickness up to ~3 nm is added (Figure 34).

![Graphical representation of Figure 33](image.jpg)

Figure 33. Optical (plasmon resonance) spectra for a freshly prepared (a) unprotected silver-coated Si₃N₄ tip, and (b) silver-coated Si₃N₄ tip protected by a 2 nm thick Al₂O₃ ultrathin coating. Light intensity was calculated as \((I_{\text{near}}-I_{\text{far}})/I_{\text{far}}\).

The contrast was monitored over 40 days (Figure 35), during which a tip was stored either in air or in a desiccator. The tips were exposed to 1mW laser light for less than 1h during measurement of each point. The contrast of an unprotected tip completely decayed over 5 to 40 days, even when the tip was not used for imaging (Figure 35a).
Figure 34. Contact (upper thick lines) and withdraw (lower thin lines) Raman signals from a 50 nm thick PEDOT/PSS film using (a) an unprotected tip and (b) a tip protected with a 2 nm thick Al$_2$O$_3$ layer at the beginning of the aging experiment (t=0). The measured contrast factors were 1.15 ± 0.10.

Figure 35. TERS contrasts (measured at wave number 1450 cm$^{-1}$) as a function of time for a 50 nm thick PEDOT/PSS film for unprotected silver-coated (25 nm radius at apex) Si$_3$N$_4$ tips (left) and silver-coated Si$_3$N$_4$ tips protected by an Al$_2$O$_3$ thin layer (right). (a) Comparison between different unprotected tips and (b) similar comparison for tips coated with 1 nm (triangles), 2 nm (diamonds), or 3 nm (circles) of Al$_2$O$_3$. Some tips were stored under ambient conditions (open symbols) and some inside a plastic desiccator (filled symbols).
The rate of decay for an unprotected tip, shown in Figure 35, did not seem to depend as strongly on the storage conditions as on the degradation mechanism. Tips that exhibited catastrophic mechanical wear after complete loss of enhancement, such as the tip shown in Figure 32c, were also observed to have reached the point of complete loss much more rapidly than in the case of tips for which the mechanical degradation was much less remarkable. In the case of catastrophic failure illustrated here, enhancement was totally lost in five days. In these cases the protective coating was evidently badly damaged during one of the earliest measurements of enhancement, providing avenues for degradation different than for tips in which the protective coating wore more gradually. For those tips, for which the contrast decayed gradually over 30 to 40 days, chemical degradation may have been more important than mechanical degradation. An unprotected tip completely loses its signal enhancement in about the same amount of time whether it is used for imaging or not, as long as catastrophic wear does not foreshorten the tip lifetime. At the same time, the contrast decreased only ~20% for tips protected by 1 nm of Al₂O₃ and remained unaffected for those protected by 2 nm or 3 nm of Al₂O₃, after 30 and 40 days, respectively, as shown in Figure 35b. Addition of the protective coating stops degradation of tip efficiency over a period longer than a month, even in open air.

4.3.6 Chemical protection by the alumina ultrathin coating

The protection against chemical degradation was studied by x-ray photoelectron spectroscopy (XPS). The spectra of an unprotected 50 nm thick Ag film and a similar film protected by 3 nm of alumina, measured after being stored for two months under
normal environmental conditions, are presented in Figure 36. The spectrum of a pristine Ag film is presented as a reference. In a pristine silver film, only the 4s, 4p and 4d silver peaks are seen at 97.5, 59.3 and 5.6 eV, respectively. The spectrum taken from the unprotected sample after two months of storage shows sulfur peaks at ca. 230 keV and 160 keV, respectively, as well as other peaks associated with contamination of the surface. The spectrum from the protected surface, aged for the same period of time, shows none of the peaks corresponding to sulfur compounds.

Figure 36. X-ray photoelectron spectroscopy (XPS) spectra of an unprotected 50 nm thick Ag film and a similar film protected by 3 nm of an alumina after being stored for two months under normal environmental conditions. The spectrum of a pristine Ag film is presented for comparison.
Figure 37 presents spectra of the protected sample measured at various depths in the sample. Spectra were obtained for different depths by sequentially in-situ sputtering away 1 nm of the sample and measuring again. After removing 1 nm, the Al signal decreased, the Ag signal increased, and there was still no presence of sulfur compounds. By sputtering and measuring successively, information on compositions still deeper in the sample could be reached. Spectra are also shown after sputtering away 2 nm or 3 nm of the film. The last spectrum corresponds to the silver/alumina interface. The intensity of the sulfur peaks is at the level of the noise, evidencing how the alumina ultrathin film has protected the silver surface from chemical degradation even after two months.

Figure 37. X-ray photoelectron spectroscopy (XPS) spectra of (a) an alumina protected 50 nm thick Ag film after two months of storage under normal environmental conditions and the same film after (b) 1 nm, (c) 2 nm, (d) 3 nm or (d) 4 nm of alumina have been sputtered away by an argon beam. The spectrum of a similarly aged unprotected Ag film is presented for comparison (f).
The ultrathin Al$_2$O$_3$ coatings are the most effective means to protect silver films from degradation among the types of coatings studied in this work. The much lower rate of signal decay with an Al$_2$O$_3$ coating is due to at least three factors. First, Al$_2$O$_3$ is harder than SiO$_x$ and that makes the bilayer structure more resistant to wearing. Secondly, what is actually deposited is an aluminum metal layer that oxidizes to Al$_2$O$_3$. The volume expansion that occurs upon oxidation of this aluminum layer creates a layer of Al$_2$O$_3$ that strongly resists further diffusion of oxygen and is impermeable even to hydrogen$^{141}$. This volume expansion makes the film denser and reduces defects in the ultrathin film. Thus, the permeability of the coating to damaging gases in the atmosphere is very low for Al$_2$O$_3$. Thirdly, volume expansion during the oxidation of the aluminum metal creates a stronger Al$_2$O$_3$/silver interface compared to that of SiO$_x$/silver. Metal to metal adhesion affinity is typically better than metal to oxide adhesion$^{177}$. Thus, first creating the interface with the silver using a metal deposition is advantageous. The detailed structure of the interface or interphase next to silver after the aluminum has oxidized remains to be elucidated.

4.4 Novel designs for highly enhancing probes used in high resolution chemical imaging

New probe designs and means of plasmonic structure fabrication were explored as approaches to achieve higher signal enhancements. These structures are our group’s first attempt to achieve enhancement factors of the order of $10^5$ or higher, a requirement for high resolution chemical imaging for a broader palette of materials or for pushing the spatial resolution to still smaller features (or single molecules). Reproducible and robust
fabrication techniques of probes with stable enhancement of optical signals in the level of $10^7$ would revolutionize near-field optics\textsuperscript{178}.

4.4.1.1 Optical antennas by electron-beam induced deposition

One approach to achieve higher signal enhancements is to more tightly control parameters of the plasmonic structure, because size and shape are definitive in defining plasmonic activity of metal particles\textsuperscript{90,109}. Greater control over geometry was achieved using electron beam induced deposition (EBID). In collaboration with the Center for Nanophase and Material Sciences (CNMS) at Oak Ridge National Laboratory (ORNL), electron beam induced deposition was used for the fabrication of a gold nanopillar at the apex of a conventional SPM probe, as is shown if Figure 38. Au was the initial metal of choice due to its good plasmon resonance, higher stability in air than Ag, and because structures as small at 20 nm have been successfully achieved\textsuperscript{151,179}.

Figure 38. Gold nanopillar fabricated by electron beam stimulated deposition (EBSD) for high resolution chemical in collaboration with CNMS – ORNL. a) Schematic and b) scanning electron microscopy image. The pillar is 400 nm high and has a diameter of 70 nm.
Signal enhancement from this probe was tested on a PEDOT/PSS thin film, but, unfortunately, the contrast of this probe is of the order of 0.13, compared with 1-2 obtained by thermal evaporations. For the tip design for which this fabrication technique was tried, a single metal nanopillar, no useful enhancement was found. Historically, beam dissociation of this precursor has led to contaminated deposits\textsuperscript{180,181}. Further study is needed to overcome the contamination issue in order to really test the promise of this elegant means of tip structure manufacture. Growing parameters such as beam accelerating voltage, current, beam dwell and refresh time, and precursor flux, need to be explored to improve deposit purity. The CNMS staff is currently developing the fundamental processes to determine the ultimate nanopillar resolution and morphology\textsuperscript{182-184}.

4.4.1.2 Dendritic metallized scanning probes by metal transfer deposition

The third approach involved obtaining highly crystalline dendritic structures by replacement reactions. We report, for the first time, the growth of a very sharp, highly crystalline structure on the surface of a silicon or silicone nitride SPM tip. This is made by the sacrifice of a previously deposited metal film. We deposited a zinc thin film by thermal vapor deposition on the surface of a Si$_3$N$_4$ probe, to grow from a solution of Au, high crystalline structures. Highly crystalline structures covering the surface of the probe were obtained, as shown in Figure 39, that provided enhancement in specific peaks, but greater control of the dendrite growth is needed. Figure 39 shows a metallized silicon scanning probe covered by gold dendrites prepared by metal replacement and Figure 40 the Raman spectra from a PEDOT/PSS in contact with the probe.
Despite negligible enhancement of the main PEDOT band at 1425 cm$^{-1}$, the band at 1530 cm$^{-1}$ shows a contrast of 0.4. Despite negligible blinking of other peaks, the 1530 cm$^{-1}$ band was enhanced by the metal dendritic structure. This could be the effect of a segment of the polymer molecule strategically located between two consecutive dendrites.

By changing the deposition conditions, a single crystalline aggregate was deposited very close to the tips apex. Figure 41 shows a SEM image of that probe.

Figure 39. Ultra-rough gold structure at the apex of a SPM tip prepared by galvanic replacement reactions. Only one of the many points will be in contact with the surface.

Figure 40. Signal enhancement of one of the resonant peaks from a PEDOT/PSS film using the tip shown in Figure 39: withdraw signal (lower curve) and contact signal (upper).
4.4.1.3 Rough metallized scanning probes by ion sputtering

All metallized probes presented in the previous sections have been prepared using thermal evaporation PVD of thin metal layers\textsuperscript{99,107,158}. This technique allows good control of the deposition rate and has produced probes with consistent signal enhancement\textsuperscript{99,107,112,158,185}. The second new approach to tip modification considered was ion sputtering, which provided access to metallized scanning probes with greater microroughness. It has been demonstrated by others how sharp edges and increased surface roughness can improve the enhanced signals from metallized TERS probes\textsuperscript{108}. The deposition resulted in metal layers with thickness the same as those of layers previously prepared by thermal evaporation, but rougher and showing independent metal entities\textsuperscript{186}. 

Figure 41. Gold crystalline aggregate created by metal replacement reactions. A) Side view and b) top view.
The signal enhancement from a PEDOT/PSS film was measured, and intensity and position fluctuations of some Raman bands over time, also known as “blinking”, were observed. The Raman spectrum of the PEDOT/PSS film without any surface enhancing mechanism shows characteristic bands at 990, 1270, 1375, 1425, 1500, and 1570 cm\(^{-1}\) with the band at 1424 cm\(^{-1}\) being the highest in intensity and commonly associated to PEDOT\(^{187-189}\). This band is usually assigned to the ring CC stretching vibration arising from neutral parts existing between localized elementary excitations such as positive polarons or bipolarons generated upon doping. Spectra obtained from a PEDOT/PSS film in contact with a thin metal film show bands at 620, 960, 1325, and 1450 cm\(^{-1}\), probably shifted from the positions of the conventional bands due to the enhancement mechanism. When a probe coated with 50 nm of ion sputtered silver is placed in contact with the surface, a new set of peaks appear for very short periods of time, as shown in Figure 43.
Figure 43. Sequential Raman spectra from a PEDOT/PSS film obtained with a scanning probe coated with 50 nm of ion sputtered silver every second after the first contact. a) Withdraw signal and contact signals after b) 1 s, c) 2 s, d) 3 s, e) 4 s, and f) 5 s. The excitation source had a wavelength of 514.5 nm.

Once the tip is placed in contact with the polymer film for the first time, the common PEDOT/PSS spectrum is obtained. Interestingly, as spectra were captured every 1 s, different peaks with very high intensities, compared with bands previously obtained for the same sample, appeared and disappeared until the signal finally stabilized after approximately 5 seconds. These very intense bands are located at 1145, 1275, 1325, and 1400 cm\(^{-1}\), as well as at the position typically followed in our experiments, 1425 cm\(^{-1}\). An extraordinary peak is also observed at 1525 cm\(^{-1}\). The peak at 1525 cm\(^{-1}\) could
correspond to the tangential benzene ring stretching mode, as an effect of a highly enhanced field. These new peaks (1145 cm\(^{-1}\), 1275 cm\(^{-1}\), 1325 cm\(^{-1}\), 1400 cm\(^{-1}\), 1525 cm\(^{-1}\)) appear and disappear as time progresses. It is worth mentioning that the laser power on the sample for this set of spectra was < 0.2 mW. Blinking was always observed upon initial contacts with a PEDOT/PSS sample, and persisted for up to 3 seconds for most fresh silver metallized SPM probes prepared by ion sputtering.

It has been demonstrated that for SERS substrates, sharp edges and small protrusions created by high roughness are ways to produce high enhancements that some times even create a “signal blinking effect”\(^{190}\). In some structures such as aggregates with a size < 1 \(\mu\)m or touching particles, intensity and peak frequency fluctuations have been previously reported for highly enhanced fields \(^{191}\), single molecule detection\(^{192,193}\), and photodynamic effects\(^{194}\). These fluctuations in the Raman signal for TERS can be associated with i) molecules diffusing or reorienting under the probe, ii) physical and/or chemical changes promoted by heating of the probe due to a very intense electromagnetic field, or iii) analyte degradation under the intense enhanced field. A good review on this topic has been recently published by Zenobi and coworkers\(^{195}\). Independently of the source for the signal fluctuation, probes generating “blinking” seem to create a very intense but short-living signal enhancement that if extended, represents an exciting opening to real highly selective and highly sensitive chemical imaging.
CHAPTER V
SUMMARY

Hard latex films used in floor polishes have been studied to show how conventional scanning probes, i.e. without any modification, can be used for revealing morphological features that can be connected with macroscopic properties. These films, when dry, are sufficiently hard to be studied with minimal distortion of the surface by the probe. By comparing styrene-acrylate formulations with and without fluorosurfactant, it was demonstrated how this component, that is known heuristically to improve leveling, seems to give the system more mobility before drying on length scales below 500 nm. In styrene-butadiene copolymer formulations, sub-micrometer differences in surface morphology observed as a function of fluorosurfactant concentration correlated with differences in gloss, a key optical property desired by customers and an important objective of commercial formulation and latex film development.

In a few cases, surfaces are too soft to be studied by conventional probes. Modification of scanning probes with hydrophobic layers having methyl and fluorinated end groups were used to weaken the interaction between a probe and a surface to study model soft and adhesive surfaces. Such modification successfully reduced the strength of the interaction when in contact with soft and sticky surfaces and made it possible to measure adhesive surfaces that would otherwise be too adhesive to study.
Acrylic block copolymer adhesives, which have newly become available as a result of new synthetic techniques, and which may offer superior performance in difficult conditions, are a good example of these materials. To perform incisive experiments on these systems, well-defined homopolymers, diblock, and triblock copolymers of poly(methyl methacrylate) (PMMA) and poly(n-butyl acrylate) (PnBA) were synthesized by atom transfer radical polymerization, a controlled radical polymerization, to evaluate performance as a function of storage time and conditions. Macroscopically, tack measurements demonstrated that blending a block copolymer with a homopolymer of the midblock polymer can be used to tailor the tack value. Microscopically, Force-distance curves of acrylic block copolymer-homopolymer blends showed a transition point in which the slope of the loading region changes to almost twice its original value, followed by a constant force region just before debonding. Such behavior is commonly related to phase separation between the two components of the blend and fibrillation processes, respectively. The surface enrichment on one of the components was facilitated by the water surrounding the surface in a high humidity environment. This information was impossible to obtain without understanding how a nanometer scale probe interacts with the surface and without reducing the strength of the probe/surface interaction.

Modification of scanning probes has also been used to bring robustness to a non-invasive imaging technology capable of simultaneously obtaining morphological and chemical information of polymer surfaces, with molecular scale resolution based on the exquisite chemical specificity provided by Raman spectroscopy. Protection of metallized scanning probes used in tip enhanced Raman spectroscopy (TERS) improved physical and chemical stability. By adding a 2-3 nm thick alumina protective layer on silver-
coated scanning probes dramatically reduced degradation of the tips with time, without sacrificing initial tip enhanced Raman scattering (TERS) efficiency, as quantified by contrast. These results show for the first time how an ideal dielectric coating shifts the epicenter of the electromagnetic field enhancement in plasmonic structures, a behavior previously simulated, but not demonstrated experimentally. In addition, the Al₂O₃ protective layer improved the wear resistance of the probes. The surface morphology of the silver structure was not altered by the deposition of the protective layer, a crucial property when protecting plasmonic structures for which activity is strongly dependant on surface roughness. Coatings as thin as 1 nm provided substantial improvement in lifetime and 2 nm or 3 nm thick alumina layer completely stopped the decay of the enhancement, compared with a loss of 80% of signal enhancement ability for unprotected tips after three weeks using them for one hour a day or 24 hours of continuous operation. Improvement in lifetime for probes was also seen with silica protective coatings, but this improvement was not as good as with alumina. It was found that coatings thicker than 3 nm reduce the intensity of the enhanced field probably because this oxide is not completely homogeneous and can have some optical activity overlapping with the enhanced field. The differences in effectiveness between silica and alumina coatings for effect on the optical properties of the probe could be rationalized on the basis of oxide content. Differences in effectiveness between silica and alumina coating for reduction of mechanical wear can be rationalized by differences in hardness and the character of the metal/oxide interface.

New tip designs and variations of plasmonic structure fabrication were explored as approaches to achieve higher signal enhancements. Greater control over geometry
could be achieved using electron beam induced deposition (EBID). However, for the tip design for which this was tried, a single metal nanopillar, no useful enhancement was found due to contamination from the precursor, a common problem in EBID. The promise of this elegant means of tip structure manufacture still needs further investigation. The second approach involved obtaining highly crystalline dendritic structures. This provided enhancement in certain bands, but greater control of the dendrite growth is needed. The third new approach to tip modification considered was ion sputtering, which provided access to metallized scanning probes with sharper asperities. The signal fluctuations in the Raman bands seen were similar to those observed by others for single molecule surface enhanced Raman spectroscopy (SERS) detection. The origin of the signal blinking is still in debate, but the existence of a very intense signal enhancement, even over short periods of time, represents an exciting opening to real highly sensitive and highly selective chemical imaging.
REFERENCES


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APPENDIX A

GLOSS NUMBERS AND SURFACE ROUGHNESS (RMS) OF SB LATEX FILMS

It has been demonstrated for the SB system that a transition in the morphology on the 10-40 μm length scale occurs at the same concentration at which a sharp change in the macroscopic appearance, as quantified by gloss measurements, is observed. In the case of acrylic formulations, the surface morphology on length scales below 1 μm varied depending on whether fluorosurfactant was used or not, but the value of gloss was not sensitive to the presence of fluorosurfactant.

Transitions in the morphology at the surface of SB latex films are evident from the topography images and seem to be dependent on the type and concentration of fluorosurfactant. So far, the most drastic changes in morphology have been observed when the concentration of short chain fluorosurfactant is increased from 200 ppm to 300 ppm and when the concentration of long chain surfactant is increased from 25 ppm to 50 ppm. Values for RMS surface roughness and gloss measurement for these samples are shown in Table A.1 and Figure A.1, respectively.
Table A.1. RMS roughness of images from dried coatings based on poly (styrene-c-butadiene) containing a short chain (top) or a long chain (bottom) fluorosurfactant.

<table>
<thead>
<tr>
<th>Concentration of Fluorosurfactant (ppm)</th>
<th>RMS Roughness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Short Chain Fluorosurfactant</strong></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>10.0 ± 1.0</td>
</tr>
<tr>
<td>100</td>
<td>11.9 ± 1.0</td>
</tr>
<tr>
<td>200</td>
<td>15.1 ± 3.3</td>
</tr>
<tr>
<td>300</td>
<td>10.0 ± 1.3</td>
</tr>
<tr>
<td>400</td>
<td>10.9 ± 1.2</td>
</tr>
<tr>
<td>600</td>
<td>6.1 ± 0.6</td>
</tr>
<tr>
<td>800</td>
<td>8.3 ± 1.9</td>
</tr>
<tr>
<td><strong>Long Chain Fluorosurfactant</strong></td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>8.0 ± 3.4</td>
</tr>
<tr>
<td>50</td>
<td>6.0 ± 0.6</td>
</tr>
<tr>
<td>200</td>
<td>6.1 ± 1.1</td>
</tr>
<tr>
<td>400</td>
<td>5.1 ± 1.4</td>
</tr>
</tbody>
</table>

Figure A.1. Gardner Gloss at 60 (bottom) and 85 (top) degree angles of observation for SB samples containing different concentrations of short chain fluorosurfactant.
APPENDIX B

CHARACTERIZATION OF ACRYLIC BLOCK COPOLYMERS SYNTHESIZED BY ATOM TRANSFER RADICAL POLYMERIZATION (ATRP)

A PMMA macroinitiator for the diblock copolymer was synthesized by polymerizing methyl methacrylate (MMA) with methyl 2-bromopropionate (MeBrP) in conjunction with copper (I) bromide (CuBr) and 1,1,4,7,7-pentamethylidiethylenetriamine (PMDETA). After purification, the PMMA sample was used as a macroinitiator for the polymerization of the n-butyl acrylate block. Table B.1 presents the molecular weights and polydispersity indices ($M_w/M_n$) of the block copolymers synthesized and Figure B.1 shows the GPC chromatograms for one of the triblock copolymers and its precursor.

Table B.1. Acrylic Block Copolymers and homopolymer prepared using ATRP for adhesion studies.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Polymer</th>
<th>$M_w$ (k)</th>
<th>$M_w/M_n$</th>
<th>$f_{PMMA}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PMMA-$b$-PnBA-$b$-PMMA</td>
<td>13k-61k-13k</td>
<td>1.16</td>
<td>0.30</td>
</tr>
<tr>
<td>2</td>
<td>PMMA-$b$-PnBA-$b$-PMMA</td>
<td>3k-28k-3k</td>
<td>1.09</td>
<td>0.18</td>
</tr>
<tr>
<td>3</td>
<td>PnBA</td>
<td>61k</td>
<td>1.05</td>
<td>0.00</td>
</tr>
</tbody>
</table>
Figure B.1. GPC chromatogram of one all-acrylic triblock copolymer and its precursor.
Blend of high and low molecular weight triblock copolymers

The effect of blending a low M_w (weight average molecular weight) triblock copolymer (additive) on the surface properties of a relatively high M_w polymer triblock copolymer (base polymer) was studied. Force-displacement curves were obtained using contact forces of 49mN or 196mN and contact times of 0.5s or 10s. Pull-off forces and adhesion energies are plotted in Figure C.1 as functions of volume fraction of additive.

The additive in this case was a triblock copolymer of low molecular weight (PMMA-\textit{b}-PBA-\textit{b}-PMMA / 3k-28k-3k). It was expected that addition of this material would increase the tack relative to base polymer due to the lower content of PMMA in the additive. However, in fact, the pull-off force remained about the same or decreased. In particular, at low contact forces and long contact times (49mN, 10s), it appears that the additive is suppressing the tack of the blend. This can be the effect of the short PMMA ends interfering with domain formation by the longer PBA middle blocks of the base polymer.
As expected, the higher pull-off forces were obtained when the contact force and contact times were higher, but the force profiles differed from those of adhesion forces due mainly to differences in shape of the debonding profiles at the fracture stage (right shoulder).

Figure C.1. Pull-off forces and adhesion energies of a blend of 87k triblock copolymer (13k-61k-13k) with 33k PMMA-b-PBA-b-PMMA triblock copolymer (3k-28k-3k) at different concentrations of the lower molecular weight component.

The adhesion energy for pure additive at high contact forces and high contact times was the highest. When blended, even at the lowest volume fraction tested (25%), the adhesion energy dropped very fast. The initial addition of homopolymer to triblock copolymer improves the tack modestly for a short contact time. When a longer contact time is used, a much more marked improvement is obtained by addition of homopolymer.
Blend of high molecular weight triblock copolymer with a poly(butyl acrylate) homopolymer

One way of increasing the tack of a model adhesive made with the base high molecular weight triblock copolymer is by blending with a homopolymer of similar molecular weight to increase the tack of the adhesive film without sacrificing cohesive strength. In this set of experiments the effect of blending the high molecular weight triblock copolymer with a pure homopolymer was studied. The effect of creating a blend of 25vol% homopolymer is shown in the debonding profile in Figure C.2. Addition of homopolymer increased pull-off force and adhesion energy by almost a factor of two.

Figure C.2. Macroscopic force profiles of high molecular weight triblock copolymer (lower curve) and triblock copolymer blended with homopolymer to increase tack (upper curve).

Macroscopic force-displacement curves were obtained at contact forces of 402mN or 980mN and contact times of 1s or 10s. The pull-off forces and adhesion energies obtained from those measurements are shown in Figure C.3.
Improvement in both pull-off force and adhesion energy is seen for all three bonding scenarios tested. For lower contact force and the lower contact time, no further improvement is gained for increasing the volume fraction of homopolymer additive past 0.25. In contrast, when longer contact time or larger force were used, further increases in homopolymer composition proved advantageous. However, for both 980 mN force and 1 sec contact time and 402 nN force with 10 s contact time performance slipped for homopolymer composition above 0.8. The improvements in tack were obtained without decrement of cohesive strength.
APPENDIX D

SURFACE MORPHOLOGY OF FLAT PLASMONIC SUBSTRATES PROTECTED BY SiO$_x$

Figure D.1 shows the 100 nm polystyrene film, the silver structure on the polymer film, and the SiO$_x$ protected silver structure, respectively. The surface morphology was obtained using AFM in tapping mode. The initial spun-coated polystyrene film was very smooth (h=100; RMS=0.3 nm). After the 4.5 nm thick silver islands are deposited, a very rough and highly structured surface is seen (h=4.5; RMS=0.96 nm). Finally, the 5 nm thick SiO$_x$ coating conformally covered the silver islands (h=5.0; RMS=0.94 nm).

Although the data for both samples display some scatter, the overall trend for the sample with the protective coating is a somewhat slower rate of decay of the Raman signal than for the sample with the unprotected silver film. However, even though an improvement was observed with this thin protective coating, the signal still decayed in time and humidity seemed to play an important role - a fact that became more evident after measurements made during the winter, which will be presented below.
The intensity of the benzene ring breathing mode (~1000 cm$^{-1}$) in the Raman spectra of the polystyrene films was followed over time for protected and unprotected films. The samples were not exposed to the 1mW laser light for more than 1h during the experiment. The variations in Raman intensity with time for these samples over a period of 15 days (360 hours) are shown in Figure D.2.

Figure D.1. Morphology of test sample of 100 nm polystyrene film (a) before deposition of any overlayer, (b) after PVD of 4.5 nm of silver, and (c) after additional PVD of 5 nm of SiO$_x$. 

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1.87 nm
6.92 nm
7.83 nm
Figure D.2. Surface enhanced Raman intensity of the benzene ring breathing mode (~1000 cm$^{-1}$) for a 100 nm polystyrene film covered by a 4.5 nm silver film and protected by 5 nm of SiO$_x$ (squares), and a 100 nm PS film covered by a 4.5 nm unprotected silver film (circles) measured during the summer (40%<RH<60%).

It was anticipated that a thicker protective coating would provide better protection and therefore the thickness was increased. A 10 nm thick SiO$_x$ coating was tested next. The normalized intensity data in Figure D.3 demonstrate clearly that the 20 nm thick coating completely stops degradation of the Raman signal enhancement over a period of 19 days (456 hours). This result is very interesting for SERS substrates, but such a thick protective coating would not be as useful for TERS. In order for a signal to be obtained from beneath the tip in TERS, it must be possible to bring the plasmonic structure quite close to the sample.
Figure D.3. Normalized surface enhanced Raman intensity of the benzene ring breathing mode (~1000 cm\(^{-1}\)) for a 100 nm PS film covered by a 4.5 nm silver film protected by thick 10 nm of SiO\(_x\) (squares), and a 100 nm PS film covered by a 4.5 nm unprotected silver film (circles), measured during the summer (40%<RH<60%).

In the general case one may wish to use a layer of silver as a plasmonic structure in another geometry. That is, one might wish to deposit a silver film, protect it with a thin layer of SiO\(_x\) and then deposit the analyte atop the protected silver structure. For this reason, protection of the silver structure with SiO\(_x\) was also tested in another geometry in which the surface of the silver is everywhere in direct contact with the protective SiO\(_x\) layer. This was achieved by depositing the PS film first, then depositing a SiO\(_x\) film atop it by PVD. The polystyrene contacts the SiO\(_x\) layer. This deposition was followed by deposition of Ag and finally by deposition of SiO\(_x\) again.

Figure D.4 shows spectra for three samples. The first is a spectrum from a sample of the previous section for which there was no SiO\(_x\) layer between the PS and the silver. The second spectrum corresponds to the case in which a 2.5 nm thick SiO\(_x\) layer has been placed between the PS and the silver structure. The third spectrum is for a sample with a
5 nm thick intervening SiO$_x$ layer. The intensity of the peak for the benzene ring breathing mode decreases sharply with the imposition of the 2.5 nm film between the analyte and the plasmonic structure. With an increase of the thickness of the layer between the PS and silver to 5 nm the decrease of the signal is even worse. Although using a thickness of 2.5 nm carries a large price in intensity, we were able to consistently create contiguous films at this thickness and we are confident that a film of this thickness provides significant protection.

Figure D.4. Surface enhanced Raman spectra showing the benzene ring breathing mode (arrow) for three 100 nm PS films coated in different ways. The top curve corresponds to a sample with a 4.5 nm silver film directly in contact with the PS and protected at the air interface by a 5 nm thick layer of SiO$_x$ (top). The middle curve corresponds to a sample in which the 4.5 nm thick silver film is separated from the PS by a 2.5 nm thick film of silica. The bottom curve is for a sample with the same geometry as for the middle curve, but with a thicker intervening silica layer of 5 nm thickness.

In summary, the surface morphology of the silver structure is not altered by the deposition of the protective coating. Deposition of a 5 nm thick protective SiO$_x$ layer successfully slows the rate of decay of the enhanced signal intensity from a polystyrene
film. Over a period of 15 days the signal measured on the sample with the protected SERS layer decayed by 20% while that measured on the sample with the unprotected SERS layer decayed by 50%. A 10 nm thick SiO$_x$ layer totally stopped degradation of the signal over time. When the SERS layer was separated from the polymer analyte layer by a 2.5 nm thick SiO$_x$ protective coating underneath it, the signal intensity was strongly decreased by a factor of 6. This suggests that a protective coating of this type on a TERS tip should have a thickness less than 2.5 nm to minimize the impact of the protective coating on intensity.
APPENDIX E
SYNTHESIS OF SILVER-SILICA NANOPARTICLES FOR SERS SUBSTRATES

Raspberry-like structures of silver were synthesized at the surface of silica nanoparticles. These 100 nm “nanoraspberries” were made by the Stöber method from tetraethyl orthosilicate (TEOS) precursor in ethanol, with NH$_3$OH as basic catalyst, at 40°C for 1 hour and followed by the ammonia reduction of silver nitrate at the surface (60°C, 20 hours). These particles were centrifuged and sonicated with fresh ethanol three times before drying. Figure E.1 shows a schematic of a single particle accompanied by a TEM image of a real particle and Figure E.2 shows SEM images of the particles at three different silver nitrite concentrations.

Figure E.1. Single nanoraspberry particle. a) Schematic and b) TEM image.
Figure E.2. TEM images of nanoraspberries. Nanoraspberries were synthesized using a) low, b) intermediate, and c) high concentration of silver precursor during the reduction.

One milliliter of aqueous solution of 1% PEDOT/PSS was sonicated with 10mL of ethanol and 0.1 milligram of dry silver raspberries for 30 minutes. Films of this solution have been prepared either by spin coating (50 nm) or by solution casting (500 nm) on cleaned silicon wafers. The raspberry-like structures seem homogeneously dispersed though the film by AFM imaging. An AFM topography image (left) is shown in Figure E.3 together with a comparison of the spectrum obtained from PEDOT/PSS films without and with the nanoraspberries (right). A 2-D Raman map of the sample tracking the intensity of the strong PEDOT/PSS Raman band at 1450 cm$^{-1}$, shown in Figure E.4, was made after 2 days of annealing at 70°C.
Figure E.3. PEDOT/PSS film containing raspberries. a) AFM topography image and b) Raman spectra.

Figure E.4. Tip enhanced 2-D Raman spectroscopy map of a PEDOT/PSS film containing dispersed nanoraspberries. a) AFM topography image and b) tip enhanced 2-D Raman spectroscopy map. In the TERS image, the intensity of the strong PEDOT/PSS Raman band at 1450 cm$^{-1}$ was measured.