Overview literature on atomic force microscopy (AFM): Basics and its important applications for polymer characterization

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Atomic force microscopy (AFM) is a relatively new technique used for the surface characterization of polymers. It is capable of producing images of a non-conducting polymer surface without any chemical etching or staining. The unique feature of this technique as compared to other microscopy techniques is that we can study the mechanical properties of the polymer surface and it also does not involve the use of electron beam radiation that damages the polymer surface. This paper describes the various applications of atomic force microscopy like evaluation of mechanical properties, determining the chemical composition, studying photo-oxidative degradation of polymers, measuring the surface adhesion forces, studying the thermal phase transitions in polymers and determining the molecular weight and polydispersity index of polymer brushes. These applications have been elucidated with suitable examples.

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The chemical properties and topography of polymer surfaces determine the functionality for a wide range of materials such as adhesives, protective coatings, and thin films for packaging, paints and lubricants. Surface and interface properties are becoming increasingly important. Scanning electron microscopy and transmission electron microscopy are the most frequently used techniques for surface characterization. These techniques use electron beam as the source of irradiation of the polymer sample. There is a possibility of damaging the polymer sample due to electron beam. Moreover, these techniques provide only two-dimensional images of the polymer surface. A new technique known as Atomic Force Microscopy (AFM) for the surface characterization of the polymer surfaces has been developed. This technique is based on the interatomic forces and is a relatively non-destructive technique as compared to scanning electron microscopy and transmission electron microscopy. It is also capable of three-dimensional mapping of the surface.

The development of AFM began since 1981. Researchers at IBM was able to develop scanning tunneling microscope on the basis of Russell Young’s stylus profiler. A major advancement took place in 1986 when Binning and Quate demonstrated the AFM. The first practical demonstration of the vibrating cantilever technique in an atomic force microscope was made by Wickramasinghe in 1987 with an optical interferometer to measure the amplitude of a cantilever’s vibration. Since then, AFM has contributed to ground-breaking research in investigation of DNA, proteins, and cells in biological studies; structure and component distribution in polymer science; mechanical properties in material sciences and pharmaceutical sciences.

AFM has made rapid strides in the field of synthetic polymers, paints and surface coatings and some of its applications with suitable examples have been emphasized in this paper.

Principle and working of AFM

Atomic force microscopy is used in surface science laboratories to obtain images with atomic resolutions of $10^{-10} \text{ m}$ or one tenth of nanometer. This type of microscopy can be effectively applied in the field of polymers to study the surface characteristics of a polymer sample. This method is based on a principle which is illustrated in Fig. 1.

The instrument is based on the principle that when a tip, integrated to the end of a spring cantilever, is brought within the interatomic separation between the tip and sample, interatomic potentials are developed between the atoms of the tip and the atoms of the surface. As the tip moves across the surface, the interatomic potentials, force the cantilever to bounce up and
down with the changes in contours of the surface. Therefore, by measuring the deflection of the cantilever, the topographic features of the surface can be mapped out.

A basic set-up of AFM is shown in Fig. 2. The atomic force between a sample and tip are measured using a laser and a detector to monitor the cantilever motion. The sample holder moves the sample up and down via a piezoelectric scanning tube so as to maintain the interaction force to a preselected level. A three-dimensional image can finally be constructed by recording the cantilever motion in the Z-direction as a function of sample’s X and Y position. Theoretically for any material having certain rigidity, such an instrument is always capable of producing surface images with atomic resolutions. The developments in laser technology have made it possible to detect very minute (atomic level) deflections of the cantilever to be detected easily.

AFM can be subjected to minor modifications to suit particular applications. For example, the set-up for AFM noise analysis of polymer surfaces consists of AFM head, which is fixed to a metal base. The metal base is screwed to three-channel piezoelectric flexure stage for fine approach. The piezo stage has active feedback control with sensors for distance control. A magnetic sample holder is attached to the xyz inertia drive for the coarse approach. This assembly is fixed to the three-channel piezo stage. The set-up is placed in a closed chamber to reduce the thermal drift.

The laser diode of the AFM head is replaced by HeNe laser connected to the AFM head with a single mode optical fiber. This reduces non-thermal noise which affects the stability of the laser diode. The noise power spectra are obtained with a Fourier analyzer. The spectra are on-line fitted with resonance curves. The cantilever chip is glued to the half moon mount which is held to the magnets in the AFM head. This is depicted in Fig. 3. AFM can be operated in three modes:

**Contact mode**

In this mode, the probe is dragged across the surface. During scanning, a constant bend in the cantilever is maintained. A bend in the cantilever corresponds to a displacement of the probe tip equal to $z_t$, relative to an undeflected cantilever in its initial position. The applied normal force is $p = k z_t$, where $k$ is the cantilever spring constant. As the topography of the sample changes, the z-scanner moves the relative position of the tip or the sample to maintain a constant deflection. The motion of the z-scanner is directly proportional to the sample topography. Using this feedback mechanism, the topography of the sample is...
mapped during scanning by assuming that the motion of the cantilever directly corresponds to the sample topography. There are certain drawbacks associated with this mode of operation such as: (i) There is a possibility of contamination of the surface. Damage and deformation of the samples can occur during contact mode imaging in air because significant force has to be applied to overcome the effects of surface contamination (surface moisture)\(^\text{11}\). (ii) Combination of normal force and lateral force created by dragging motion of the probe tip across the sample and small contact areas involved result in high contact stresses that can damage either the sample or the tip or both.

**Non-contact mode**

The cantilever is vibrated near its resonance frequency (about 100 kHz). The tip-sample separation and amplitude are of the order of 1-10 nm. The tip oscillates just above the surface contamination layer. The resonance frequency and amplitude of oscillating cantilever changes as it approaches the surface due to the interactions with weak long-range forces thus essentially imaging the surface. Either the amplitude or the resonance frequency or the amplitude is maintained constant through the feedback loop and the scanner. The motion of the scanner is used to generate the topographic image. The spring constant ‘\(k\)’ is greater than the contact mode to reduce the tendency of the tip to be pulled to the surface by attractive forces. The drawbacks associated with this mode are: (i) Combination of weak interactive van der Waal forces and large spring constants causes the signal to be small, which causes unstable feedback and slower scan speeds. (ii) The lateral resolution is lower than the contact or tapping mode because of the sample tip separation.

**Tapping mode**

This mode is suitable for imaging of soft samples\(^\text{12}\). Although the resolution is similar to contact mode, the applied forces are lower. The cantilever oscillates near its resonance frequency, but the oscillation amplitude is 20-200 nm much greater than the non-contact mode. The tip makes contact with the surface for a very short duration in each oscillation cycle. The tip-sample interaction alters the amplitude, resonance frequency and phase angle of the oscillating lever.

The amplitude of the cantilever is such that the probe maintains enough energy for the tip to tap through and back out of the surface contamination layer.

**Forces acting on the probe**

Forces above the horizontal zero axes are repulsive, and this occurs at separations less, when two atoms are in contact. Forces such as van der Waal forces are attractive, and occur at separations greater\(^\text{11}\). When the force measured is attractive, the imaging mode is said to be non-contact. Non-contact modes involve small forces, and if they are tested at some distance from the surface, long-range forces are involved. The resolution is not as good as the contact modes. Electrostatic charges and the force separation curves can alter real force separation curve\(^\text{13}\).

This extremely simple picture is complicated by three effects. First, there will be a layer of contamination (usually including water) on the sample surface. This layer may be 2-50 nm thick, or may condense in the gap between the tip and the surface even if it is absent elsewhere. As the tip approaches the surface it touches the contamination layer, and the capillary forces pull it towards the surface. These forces can be very much greater than the van der Waal forces, and will depend on the sample and the humidity. At the apparent contact separation, with zero total force, there will be attractive capillary forces around the surface of the probe, and a large repulsive force at the tip. The force distance curve will show a hysteresis when there is a contamination present, as the tip will remain wetted up to larger separations as it is withdrawn from the surface.

The second complication is that the position of the tip is not under direct control. At any point the signal is the deflection (force) for a given position of the cantilever support, not for a given separation between tip and surface. If the slope of the force-separation curve is greater than the value of the cantilever spring constant, and then the deflection will not be stable. As the probe approaches the surface it will suddenly jump towards the surface. There will be a reverse jump at larger separations as the tip is withdrawn from the surface. The tangent lines represent a spring constant (force/distance) of a cantilever and schematically show where this will happen. The jumps occur when the curve becomes vertical, as shown by the arrows. A stiffer spring suppresses the instability but of course the deflections are smaller.

A jump towards the surface is even more likely when the contamination is present, because then the surface and the probe are joined by a liquid layer and surface tension pulls them together. In this case, the probe jumps to the position where there is a net attractive force, but the tip is in repulsive contact with the
surface. Operating the microscope in a good vacuum, in dry gas, or in liquid reduces the effects of surface contamination. Water is often said to be the appropriate liquid, but if there is an oily contamination layer on a hydrophobic surface, iso-propanol or other organic solvents may be better than water.

The third complication is that the measured force-position curve relates to the distance from sample support to the probe support. There are several compliant objects in series here. These are the cantilever, the tip, tip-surface contact region and the rest of the sample. The softest of these objects is the cantilever, and it deforms the most. The sample will also deform under the load applied by the tip. If the sample is soft, its mechanical properties will affect the results. These are elastic properties if the deflections are small, plastic properties if the local forces are small, plastic forces if local forces are large.

**Substrate preparation**

The substrate plays an important role in the successful application of AFM\(^\text{10}\). It is a surface on which the sample rests. An ideal substrate should be chemically inert, easily prepared, relatively in-expensive, readily modified by wide variety of derivatization methods. It should be composed of large, atomically flat domains. The last attribute is important because molecular entities and other types of nanometer sized objects can be easily obscured when a surface with a roughness on the same scale is imaged. Some of the common substrates used are (i) Mica-mica is extremely flat having an average surface roughness of the order of a few angstroms over an area of few square micrometers. It is relatively inexpensive, and can be easily and routinely prepared. (ii) Gold-gold is used as a thin film or bulk material. Though more costly than mica, gold is remarkably inert and can readily be derivatized by sulphur containing compounds (e.g., alkanethiols) to create well ordered architectures of varied compositions, including those with terminal end groups that can serve as coupling agents. Thin film substrates are generally prepared by vapour depositing gold on mica substrates. (iii) Silicon-silicon like gold is remarkably inert. Generally, these surfaces are modified by using silanes, but they have poor reproducibility due to the sensitivity of the silicon precursors to water. (iv) Hydrogen passivated Si surfaces, which are atomically flat and are easily modified.

**Comparison of AFM with other microscopy methods**

A comparison of AFM with other methods is given in Table 1. As compared to SEM (scanning electron microscopy) and TEM (transmission electron microscopy), sample preparation is easy in AFM. The possibility of radiation damage of the sample is almost absent as AFM works on the principle of molecular interactions. Thus, AFM can be considered to be an almost ideal surface characterization technique for polymers.

**Advantages**

(i) AFM produces high-resolution images with a lateral resolution in the range of few nanometers and vertical resolution less than 1 nm. (ii) AFM can be used to produce images from the surface of non-conductors (polymers) without any special preparation to make the sample conducting as required in SEM and TEM. (iii) Simple modification of the AFM allows other properties to be detected. If the sample tip is ferromagnetic, then we can detect the stray magnetic field thus showing the magnetic domain structure of the sample. (iv) AFM gives direct 3-D images of surface structure of polymers. By using lateral force and phase contrast modes, it is possible to differentiate the type of materials at the polymer surface. (v) AFM is well suited for the characterization of nanocomposite materials. (vi) Radiation dam-

<table>
<thead>
<tr>
<th>Technique</th>
<th>Features</th>
<th>Radiation damage</th>
<th>Size range of polymer structure</th>
<th>Best resolution</th>
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<th>Sample preparation</th>
</tr>
</thead>
<tbody>
<tr>
<td>SEM</td>
<td>Surface topography</td>
<td>Rarely serious</td>
<td>10 µm - 0.2 nm</td>
<td>4 nm</td>
<td>20-60000X</td>
<td>Easy</td>
</tr>
<tr>
<td>TEM</td>
<td>Internal morphology, lamellar and crystalline structures</td>
<td>Severe</td>
<td>100 µm-10 nm</td>
<td>0.2 nm</td>
<td>3000-25000X</td>
<td>Difficult and time-consuming</td>
</tr>
<tr>
<td>AFM</td>
<td>Surface topography</td>
<td>None</td>
<td>10 µm - 0.2 nm</td>
<td>0.3 nm</td>
<td>3000-25000X</td>
<td>Easy</td>
</tr>
</tbody>
</table>
The age of the sample as observed in SEM and TEM is avoided. (vii) The best resolution obtained is 0.3 nm which is better than SEM.

Limitations

(i) AFM is complex and susceptible to outside influences like contamination of surfaces and instrumentation control. (ii) In contact mode of AFM imaging, there is a possibility that the soft polymer samples may be damaged.

Applications of AFM

Three types of data can be obtained by operating in tapping mode for AFM. Fig. 4 explains this type of data collection and its usefulness.

Height data

The vertical position of the probe tip is monitored by noting changes in the length of the z-axis on the xyz scanning piezo tube. Input voltage to the scanning piezo tube is proportional to the length of the tube. The change in the z-axis is plotted as a topographical map of the sample surface. Height data is a good measure of the height of surface features but does not show distinct edges of these features.

Phase data

This type of imaging monitors the change in phase offset, or phase angle, of the input drive signal (to the drive piezo) with respect to the phase offset of the oscillating cantilever. The phase of the drive signal (i) is compared to the phase of the cantilever response signal, (ii) on the photo diode detector. As seen in (2) of the above Fig. 4, the phase offset between the two signals is defined as zero for the cantilever oscillating freely in air. As the probe tip engages the sample surface, the phase offset of the oscillating cantilever changes by some angle with respect to the phase offset of the input drive signal. As regions of differing elasticity are encountered on the sample surface, the phase angle between the two signals changes. These changes in phase offset are due to differing amounts of damping experienced by the probe tip as it rasters across the sample surface. These differences are plotted as the so-called 'phase image'.

Amplitude data

The amplitude of the cantilever is monitored by the photo diode detector. The value (rms) of the laser signal on the y-axis of the detector is recorded for each of the 512 segments on a given raster of the probe tip. These values are plotted as an amplitude map of the sample surface. Amplitude images tend to show edges of surface features well.

Figure 5 shows AFM micrographs of freeze fractured styrene-isobutylene-styrene a-b-a block copolymer film.

Nanoindentation of thin polymer films using AFM for measurement of mechanical properties

Recent developments have led to the utilization of the AFM as a nanoindentation device\textsuperscript{14,7}. Nanoindentation is a useful tool that allows the direct measurement of mechanical properties of thin films\textsuperscript{15}, including polymer films\textsuperscript{16,17}.

During operation of the AFM in force mode, the probe tip is first lowered into contact with the sample, then indented into the surface, and finally lifted off the sample surface. Concurrently, a measurement of the probe tip deflection is produced through an optical lever detection system, in which a laser beam is reflected off the top of the probe and onto a segmented photodiode. A plot of this tip deflection signal (force) as a function of the vertical displacement of the piezo scanner is called a force curve (F-d curve). AFM
software has been modified and diamond-tipped stainless steel probes have been developed specifically for indenting and scratching materials with nanoscale spatial resolution. The software modification allows the surface to be imaged in tapping mode immediately before and after indentation, which is particularly important for soft engineering materials that can be damaged easily by contact mode AFM. Thus, we can now image the surface in tapping mode, perhaps utilizing phase contrast imaging, indent (or scratch) at specified points, and then image the residual impressions.

While performing indentation with an AFM cantilever probe, lateral motion of the probe tip occurs as the cantilever bends. This motion causes the tip to deform a larger area of the sample as the tip shifts to the left as depicted in Fig. 6a. Also, a lateral force constraining this motion builds up and produces a moment that bends the cantilever in a direction opposing the bending due to the lateral contact force. To compensate for this effect and create "true" vertical motion of the probe tip, a lateral motion factor is incorporated in the AFM indentation software. This factor is input as an angular measurement in degrees, the tangent of which is equal to the ratio of x-motion to z-motion. Images of the residual impressions left after indenting an epoxy sample using two different types of probes are shown in Fig. 6. In both cases, increasing the amount of compensation (from left to right) produces a smaller indent. The amount of compensation will depend largely on the ratio of tip height to cantilever length, and thus is larger for the diamond-tipped probe.

In practice, complete compensation for the lateral tip motion during indentation is difficult to achieve, so the objective of lateral compensation becomes one of minimizing experimental uncertainties. Other experimental uncertainties that limit the use of the AFM as an indentation device include non-linearity, hysteresis, and creep of the piezoelectric scanners and non-linearity of the photodetector. Despite these technical barriers, achieving quantitative indentation measurements of polymers with nanoscale spatial resolution can be achieved when operational settings are chosen to correctly minimize uncertainties. However, these measurements are generally relative measurements because the probes tip shape and, in some cases, the probe spring constant is typically unknown or known only within large uncertainties. Current research efforts are aimed at overcoming these technical barriers.

Properties like elastic modulus and hardness can be evaluated by the analysis of the force displacement curve. Proper use of this technique allows the mechanical probing of thin films without a significant influence of the underlying substrate.

AFM nanoindentation can be used for studying the mechanical properties of ultra thin polymer films. For example, AFM nanoindentation was used for measuring the elastic modulus and hardness of ultra thin polyelectrolyte multilayer films. This film was made up of weak polyelectrolyte pair poly (allylamine hydrochloride)/poly (acrylic acid). These films find a wide range of applications like drug delivery, photonic structures, electrochemical devices and wear-retarding coatings. The success of these applications is dependent on mechanical properties which refer indirectly to their robustness in various environments. It is difficult to employ conventional methods of characterization in these cases because a small amount of material is available for characterization. Moreover, these polyelectrolyte films are deposited as thin films in the range of 0.5-14 nm per adsorbed bilayer. This increases the influence of underlying substrate on the mechanical properties being measured. This drawback can be overcome by using AFM nanoindentation.

Numerous applications of AFM nanoindentation to polymeric materials can be found, including the identification of phases in polyethylene blends, the characterization of a skin-core phenomenon in a poly-
dimethylsiloxane (PDMS), and elevated-temperature measurements of polymeric composite interphases.

**Phase imaging/Chemical mapping**

A sharp probe is brought into proximity with the specimen surface. The probe is oscillated vertically near its mechanical resonance frequency. As the probe lightly taps the surface, the amplitude of oscillation is reduced and the AFM uses this change in amplitude in order to track the surface topography. In addition to its amplitude, the probe motion can be characterized by its phase relative to a driving oscillator. The phase signal changes when the probe encounters regions of different composition. Phase shifts are registered as bright and dark regions in phase images, comparable to the way height changes are indicated in height images. Fig. 7 elucidates the principle of phase imaging.

Phase images often show extraordinary contrast for many composite surfaces of technological and scientific interest. These include contamination deposits, discontinuous (i.e. defective) thin films, devices built of composite materials (e.g. magnetic recording heads), and cross-sectional specimens of composite materials. Both inorganic and organic materials can be examined. It is found that phase imaging is more convenient and gentler than other methods which are based on contact mode operation. It routinely achieves lateral resolution of 10 nm. As compared to force modulation microscopy which can be used to study the viscoelastic properties, phase detection mode of AFM provides enhanced resolution (better than 10 nm versus 100 nm in force modulation microscopy).

The strong contrast between domains in the images is conspicuous. While the topographic image shows some corresponding features, surface roughness hinders the identification of domains. The phase image allows unambiguous resolution of the different material phases.

For example, AFM was used with phase detection imaging in order to study the surface micro domain morphology of thick films of triblock copolymers. The copolymer studied was poly (methyl methacrylate)-block-polybutadiene-block-poly(methyl methacrylate) copolymer. Bright and dark areas were observed. The darker areas were the soft polybutadiene phase whereas the darker areas were the hard poly (methyl methacrylate) phase. The darker areas correspond to the zero shift phase (the tip interacting with the surface remains in phase with the piezo driver signal) while the brighter areas represent a 180° phase difference, that is, interaction with the surface makes the tip in phase opposition with the piezo signal. When these images are captured simultaneously with the height images, it is seen that the contrast is significantly increased and the surface morphology appears more clearly as compared to height images. A more satisfactory reason for the above phase differences are as follows: Due to the softness of PBD, the tip tends to remain in contact with the material and this leads to a delay in tip motion relative to the piezo signal. In contrast, the interaction with harder PMMA is expected to be shorter and the phase lag should remain close to zero. On this basis, the PBD phase will give rise to the brighter areas while the PMMA phase will appear darker.

Phase imaging was also used to study the phase separation process in thin films of commercial styrene-butadiene-styrene triblock copolymers annealed at high vacuum. It is important to note that the phase image of a homogenous polymer shows no phase contrast.

**Evaluation of elastic and mechanical properties**

Elastic and mechanical properties can be evaluated by using force mode of atomic force microscopy. It gives direct information on the local mechanical properties of various regions on the sample surface. Unlike tapping mode or contact mode, force mode is a non-imaging mode in which the probe tip is moved...
vertically with respect to the sample surface. This mode combines contact mode imaging with a probe tip at a frequency well below resonant frequency. This oscillating force deforms the softer regions more than the harder regions of a heterogenous polymer sample that contrast between these regions are observed. Tip deflection is measured as function of the motion of the piezo scanner in the Z-direction producing a force curve. For example-1 milli Newton force was to distinguish carbon fibers in an epoxy composite with a resolution of 60 nm.

**AFM for evaluating the aging of polymer surfaces by mapping the distribution of adhesion surfaces**

This is feasible by modification of the tip attached to the cantilever. Most commercially available tips have a radius of 30-50 nm and are made from silicon or silicon nitride. These tips have a pyramidal geometry. While important advances have been achieved by coating tips with hard materials such as nanocrystalline diamond, many users are finding that these improvements do not meet their research needs. Fig. 8 shows a modified tip.

The basis for altering the surface composition of a tip recognizes the importance of intermolecular forces on the outermost few angstroms of the tip-sample micro contact in AFM imaging. Most commercially available tips have surfaces that are poorly controlled from a compositional perspective. This lack of control has three potential consequences. First, the surface of silicon based tips has a large number of silanol groups, which results in surface that can be readily altered by the adventitious adsorption of contaminants. This contamination can lead to tips with varied surface contamination. Second, uncoated tips may change shape because of wear under prolonged use. Modification that could reduce wear and thus improve the quantitative repeatability of a characterization would clearly be advantageous. Third, because of an uncoated tip is hydrophilic, the strong adherence of the tip to a delicate, hydrophilic surface may damage the sample.

The most popular method of tip modification is through the immobilization of thiol-based monolayers on gold coated tips\(^{34,35}\). While polymer coatings have been reported, polymer coated tips are chemically and morphologically more heterogenous than those modified with monolayer coatings of thiol on gold. The thiol modification procedure involves the vapour deposition of a thin chromium adhesive surface \(<5 \text{ nm}\) onto a tip followed by deposition of a thicker gold layer \((40-100 \text{ nm})\). The thiol coated tips are then immersed in a dilute solution \((0.1 \text{ mM})\) of thiol which yields a covalently bound monolayer that is thiolate analogue of the thiol precursor. These modified tips are chemically and mechanically stable. Various types of terminal functionalities are commercially available or readily synthesized. A potential disadvantage of this type of modification is that the radius of the tip can significantly increase because of metallization. This may lead to a decrease in lateral resolution.

Organosilanes can also be used for tip modification. Organosilane ad layers which directly couple to the surface silanol groups of a silicon or silicon nitride tip. The formation of the organosilicon films begins with the hydrolysis of the silane precursors and surface silanols result in the formation of two-dimensional lateral network comprised of Si-O-Si bonds. After drying and curing, the silane film is covalently attached to the tip with a concomitant loss of water. This modification changes the tip without the need for metallization. The major disadvantage is the sensitivity of organosilane to moisture as well as the difficulty in controlling the polymerization process and film thickness. Some examples of chemical force microscopy are explained below.

Chemical force microscopy was used to study the aging of polymer surfaces at the submicroscopic scale. Adhesion force mapping using tips modified with methyl and hydroxyl terminated alkanethiols was used to probe the chemical composition of polypropylene surfaces as a function of time. The adhesion force distributions on polypropylene melt pressed films stabilized with antioxidants, process stabilizing agents and UV light stabilizers were measured. These adhesion force distributions were correlated with the additive distribution at the surface. The modifications of the local adhesion properties on the polymer surface due to material aging were also studied.

The additives used were (i) Additive A, i.e., 2-4-bis (1, 1-dimethylethyl) phenol phosphate used as an an-
tioxidant; (ii) Additive B, i.e., benzenepropanoic acid, 3-5-bis(1,1-dimethylethyl)-4-hydroxy-2, 2-bis[3-3, 5-bis(1, 1-dimethylethyl)-4-ydroxyphenyl]-1-oxo-propoxy[methyl]-1,3-propanediy ester] as an antioxidant; and (iii) Additive C, i.e., decanedioic acid, bis[(2,2,6,6-tetramethyl-4-piperidinyl)ester] as a UV stabilizer.

The adhesive interaction between the tip and sample was determined from force versus displacement curves. In these measurements, the deflection is recorded as the probe tip approaches, contacts, and is then withdrawn from the sample. The observed cantilever deflection is converted into force using the nominal cantilever spring constant. AFM force curves provide detailed information regarding the strength of the tip-sample interaction in particular local points, but they lacked the two-dimensionality of AFM mapping. To map the distribution of adhesion forces, the method of ‘force volume imaging’ was used. In this mode the array of force curves can be obtained over the entire scan area. This technique involves taking hundreds or thousands of force curves over the course of a raster scan. Each force curve is measured at a unique x-y position in the area and force curves from an array of x-y points are combined into three-dimensional arrays of force data. Force volume enables the investigation of spatial distribution of the interaction force between the tip and the surface.

The adhesion map has been obtained by using methyl terminated tip in water. This figure shows the lateral distribution of pull-off forces. The majority of the pull-off forces correspond to a low adhesion force, around 1 nN (bright color). This is close to the typical adhesion force measured on additive C (1.8 nN). Small areas present a higher pull-off force (10-20 nN). They can be interpreted as areas where polypropylene or other additives (additive A and additive B) are apparent. The diameter of these areas varies between 300 mm and 1.5 µm. The measure part of the external surface area is thus covered by an external layer of additive C, and the adhesion force measured by AFM corresponds to the adhesion force obtained on pure additive C. A few regions of PP were polypropylene surface are not densely covered by additive C. Bright areas correspond to adhesion forces around 1 nN and dark areas correspond to forces between 10 and 20 nN. The distribution adhesion forces show two maxima around 1 and 16 nN. It elucidates that in this area the surface is made of additive C islands on either pure polypropylene or antioxidants.

Thus, it is also possible to locally detect additives on the surface of polymers like polypropylene by using chemically modified AFM tips.

**Evaluation of changes in nanoscale mechanical properties of polymer composites due to α-radiation**

This application of AFM is explained with the help of following example. The local mechanical properties of silica-reinforced silicone composites were investigated using modified AFM. Elastic modulus measurements (1.5 ± 0.1 MPa) were consistent with bulk measurements (1.9 MPa) and changes in the modulus at the surface of the composite samples (E 4 1.5-3.5 MPa) were observed as a result of α-irradiation (dose 4 1.7 × 10^{10} - 2.0 × 10^{12} /cm^2). The sensitivity of the technique was demonstrated by a detectable change in modulus at even the small dose of 1.7 × 10^{10} /cm^2. The penetration depth of the α-particles into the material, estimated to be 22±2 mm from the sample edge, was determined by cross-section depth profiling; and modeling of the ion penetration depth using transport of ions in matter codes (24.4 ± 0.4 mm) closely matched experimental observations. The polymer matrix used in this study was a random copolymer of dimethyl (90.7 wt.%), diphenyl (9.0 wt. %), and methyl vinyl (0.31 wt. %) siloxanes. This base polymer was compounded into a reinforced composite by milling with a mixture of 21.6 wt.% fumed silica. 4.0 wt.% precipitated silica and 6.8 wt.% ethoxy-endblocked siloxane processing aid.

The silicone matrix is observed along with silica particles embedded at various depths beneath the surface. The elastic modulus of the polymer composite was determined to be approximately 1.5 ± 0.1 MPa, which was consistent with bulk property values. A series of measurements were made across the surface of the silicone samples, and Fig. 9 shows that the surface properties of the material vary considerably due to the presence of embedded silica particles. These particles are known to increase the local elastic modulus of the composite by a factor of two or more. The variations depend upon the depth of penetration of silica particles below the surface, with the deeper more covered particles showing less variation in E (elastic modulus).

**Nanoscale mapping of mechanical properties of polymer surfaces by means of AFM noise analysis**

According to Einstein, the diffusion coefficient of a particle is directly proportional to the viscosity in its environment. Thermal diffusion, by nature, is a gen-
tle process. While it is not strictly guaranteed that thermal diffusion leaves the range of linear response, it is true in most cases of practical interest. Linear response in this context means that the force is directly proportional to the displacement or the speed at all times. Via the Einstein relation the diffusion of the probe particle provides access to the local viscosity. The extension of this approach has been extensively discussed in the context of light scattering\textsuperscript{40} and single particle tracking\textsuperscript{41} on colloidal dispersions. Nanoscale mapping is a conceptually related approach, where the fluctuating object is not a colloidal sphere but rather the cantilever of an atomic force microscope\textsuperscript{42-45}. The analysis of the data is similar to the data in single particle nanorheology. AFM noise analysis differs from nanorheology on the following points. (i) The AFM tip can only access surfaces, whereas the colloidal particles can be located anywhere in the bulk. (ii) The precise positioning of the AFM tip is relatively easy. Colloidal particles have to be positioned by using a optical or a magnetic tweezer. Nanorheology is performed without active positioning of the probe. (iii) The AFM tip is freely suspended, whereas the colloidal particles diffuse freely. In case of AFM, the noise power spectrum is a resonance curve. The surface properties are inferred from the shift of the resonance parameters. (iv) AFM is more sensitive since it is based on optical lever technique.

**Example**

This method was used to study the spatially resolved fibrillation of the latex films\textsuperscript{46}. Polymer latex films were investigated with this instrument perform-
Evaluation of photo-oxidative degradation in polymers by AFM

AFM was used to study the photo-oxidative degradation in polyisoprene by force versus distance analysis and is explained as follows.

**Force versus distance analysis**

Analysis in the force versus distance mode $F-d$ mode probed the changes in the tip to surface adhesion. Adhesion was observed to increase as a result of exposure to UV radiation. Figure 12 shows the typical response of the lever to adhesive interactions in air for a standard film, polyisoprene surface and an exposed polyisoprene surface. The ‘snap on’ feature is different for the three surfaces, indicating that the samples have different surface stiffness or surface chemistry. The standard DLC (diamond like carbon) film has the lowest snap on force of 7 nN. The corresponding values for the polyisoprene and exposed polyisoprene surfaces was 16 nN and 34 nN respectively.

The difference in snap on forces for the polyisoprene and exposed polyisoprene films is associated with the combination of the depth of penetration and the differences in surface chemistry. Such differences will be reflected in the respective surface energies, and thus affect the strength of the adhesive interactions. The likely products of photooxidation lead to an increase in surface energy. The reaction products are more polar, such as $-OH$ and $-COOH$ groups and this leads to an increase in hydrophilicity. The additional wetting due to a thicker layer of adsorbed moisture will give rise to a stronger tip to surface meniscus force, i.e., greater adhesion. Thus, there are three con-
tributions to the differences in response (surface energy, meniscus force and surface stiffness) that could lead to an increase in the size of the snap on feature.

Mechanical properties were also studied by $F-d$ analyses. It is apparent that the increasing exposure resulted in additional softening of the polymer. This is due to the chain scission events on exposure to UV radiation. In the case of unexposed polyisoprene sample the intact polymer chains are stretched by the indenting tip. There is an associated decrease in entropy, giving rise to an elastic restoring force that will counter the force imposed by the lever. There is less entropic change when the comparatively smaller chain lengths are stretched by the indenting tip. These are the qualitative reasons for surface softening. Figure 13 shows tip indentation as a function of applied load for as received and irradiated surfaces, showing the dependence on UV dose.

**Probing surface adhesion forces of Enterococcus Faecalis to medical grade polymers using AFM**

Bacterial adhesion to biomaterials remains a serious clinical problem since it can result in biofilm formation, thereby increasing the probability of infection from medical devices and implants limiting long-term success after implantation. Biofilm infections elicit complications for patients ranging from mild inflammation to subsequent surgeries and potential death, resulting in higher treatment costs. A bacterial biofilm is a complex network of cells protected by extra cellular polymeric substances (EPS).

Bacteria first move towards the surface by physicochemical forces, where they are reversibly attached to the surface. Irreversible binding occurs through molecular and cellular interactions, leading to the aggregation and production of EPS, which permits stronger adhesion and cell-to-cell attachment. The attached cells proliferate to form micro colonies and layers. Since, the initial attachment of bacterial cells on a substrate promotes biofilm development, a more thorough understanding of the mechanisms and the interactions involved in this adhesion stage could aid in delaying or preventing subsequent proliferation and colonization of the surface.

AFM can be used to compare the initial adhesion forces of the uropathogen Enterococcus Faecalis with the medical grade polymers like polyurethane (PU), polyamide (PA) and polytetrafluoroethylene (PTFE). In order to quantify the cell-substrate adhesion forces, a method was developed using atomic force microscopy (AFM) in liquid that allows for the detachment of the individual live cells from a polymeric surface through the application of increasing force using unmodified cantilever tips.

Table 2 represents bacterial properties of polymers before bacterial adhesion as well as the average calculated cell-substrate detachment force. The trend of the unflourinated hydrophobic materials polyurethane requiring higher detachment force than the hydrophilic materials polyamide is consistent with cell-substrate perpendicular interactions. We can infer that, in general the hydrophobic surfaces may be more favorable for the initial attachment of the cells to the substrate and for firmer subsequent adhesion. The results also suggest that chemical composition also plays an important role in bacterial adhesion in addition to both hydrophobic and nanoscale surface roughness, as the PTFE samples required the smallest detachment force while having the greatest roughness and lowest wettability.

The AFM study was carried out by measuring the resonance frequency of each tip by centering the thermal noise envelope using the cantilever tune function in the software. This frequency was used to calculate the spring constant. A force-deflection set point

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Surface roughness (nm)</th>
<th>Water contact angle</th>
<th>Adhesion force (nN)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyurethane (PU)</td>
<td>8±2</td>
<td>106±3</td>
<td>19±4</td>
</tr>
<tr>
<td>Polyamide (PA)</td>
<td>20±7</td>
<td>35±6</td>
<td>6±4</td>
</tr>
<tr>
<td>PTFE</td>
<td>74±15</td>
<td>117±2</td>
<td>0.7±0.3</td>
</tr>
</tbody>
</table>

**Fig. 13**—Tip indentation as a function of applied load for as received and irradiated surfaces, showing the dependence on UV dose.
calibration was generated for each sample over a range sufficient to cover the tip force required for bacterial removal. Tip deflection in nanometers was measured for a series of deflection set points using the AFM software calibration function. The tip force exerted on the sample was then calculated as the product of individual tip spring constant and the measured tip deflection.

AFM images also demonstrated qualitative differences in bacterial adhesion. Polyurethane was covered by clusters of cells with few singlets present, whereas the polyamide was predominantly covered by individual cells. The E. faecalis adhesion to the fluorinated polymer (PTFE) showed different characteristics. Only a few individual cells were found and the bacteria were easily damaged and detached by the tip.

This example demonstrates the utility of AFM for measurement of cell-substrate lateral adhesion forces and contribution these forces make towards understanding the initial stages of bacterial adhesion. It also suggests that initial adhesion can be controlled, through appropriate biomaterial design, to prevent subsequent formation of aggregates and biofilms.

Characterization of wear properties of metallic stent polymer coatings by atomic force microscopy

A fundamental understanding of surface properties of biomaterials on nanoscale is necessary to have a satisfactory knowledge of responses of the tissue to biomaterials thereby minimizing or eliminating tissue trauma on macro-meter scale. There has been a substantial increase in the use of biodegradable or biostable polymers in the last decade. Initially, they were used as carriers for drug-delivery devices, sutures and as a temporary joint spacer. However, the tribological characteristics of these polymers have not been fully investigated and explored. Two aspects can limit the use of such polymers are chemical degradation and/or wear. Chemical degradation starts breaking the long polymer chain into smaller fragments. Some enzymes and ionizing radiation are also capable of attacking polymers. Thus, the polymer may be reduced in molecular weight, increasing its solubility or it may become harder and more brittle due to cross-linking. Relative motion between parts can cause mechanical damage and release of small debris due to wear. The surface of an implanted polymer, such as any other material, is not perfectly smooth on a microscopic scale but rather has small asperity on the surface. Mechanical contact is localized to the asperity. Thus, a relatively low contact pressure for the entire surface can result in very high local pressures relatively to any single asperity. Such localized contact pressures can result in adhesion between asperity of two relatively motion surfaces. After adhesion, subsequent movement can provoke the formation of debris or small fragments. These fragments may react with other chains to form side branches, or react with other chain to form cross-links.

AFM was used for the wear characterization of poly (methyl-methacrylate) (PMMA) and poly (L-lactic acid) (PLLA). PMMA is an amorphous material with good resistance to dilute alkalis and other organic solution. It is known for its exceptional light transparency, wear resistance and biocompatibility. PMMA is used broadly in medical applications such as blood pumps and reservoirs, membranes for blood dialyser. PLLA is a biodegradable polymer widely used in tissue regeneration of cartilage, bone, skin, ligament, bladder and liver. These polymers are two good candidates for coronary metallic stent coatings. It is well known that the implantation of metallic stents is a widely accepted alternative therapy to percutaneous transluminal coronary angioplasty. The applications of stents have shown promising results to prevent acute restenosis. In spite of this advantage, sub-acute restenosis occurs frequently despite of a high antithrombotic pharmaceutical regime. PLLA and PMMA could be good candidates to coat metallic stents rather than traditional polyamide, polyurethane or silicone.

There are different basic factors in providing the efficient wear test, such as type of motion, type of loading, lubrication specimen preparation and environment control. Investigation of the fundamental characteristics of wear at the micro-scale is complicated by few factors that are not critically addressed in the tribology of macro-systems. Since these forces are sensitive to the environment and surface condition of the specimens, it is quite difficult to determine the forces accurately. Quantification of wear is not straightforward since the amount of wear is often too small to be detected by surface-sensitive instruments. Micro-wear measurements have been object of fast development of precise measuring tools followed to the introduction of AFM.

The knowledge of wear mechanisms on micro/nanoscale can help in order to quantify the distribution of material loss during relative motion surfaces. Weighing the sample before and after the test has been the dominant wear quantification technique. A
precision balance typically has a resolution of $10^{-6}$ of the maximum load, which puts a limit to the minimum load possible to be quantified in relation to the total weight of the component. Moreover, the mass of polymers can change due to water absorption. Macro wear on harder materials is 10-1000 times higher than micro-wear, even though the mean contact pressure in the micro-test is higher than in the macro-test.

The smallest wear scars, often only some tens of micrometers in size, require a quantitative technique with a nanometer scale resolution. Formation of debris by biomedical polymers could have serious consequences for human health. Coronary stents are exposed to two main stresses, first one is due to the contact with blood vessel and the second one is the shear stress provoked by the blood flow. Detachement of small wear debris from the polymer coating of metallic stent could stimulate certain complications. This mechanism is not completely understood, for this reason, such as biocompatibility, haemocompatibility and biodegradation. Wear characterization of biomedical polymers could become one important test to define suitable candidates for metallic stent polymer coatings.

The technique for wear testing consisted in using the AFM probing tip to abrade the surface of interest while simultaneously imaging the area where the polymer is progressively damaged by the scanning tip. This technique permitted the following wear properties to be observed both qualitatively and, when possible, quantitatively: (i) formation of ripples on the surface of the polymer; (ii) qualitative evolution of the surface before and after the test; (iii) evaluation of wear volume; (iv) study of adhesion effect and subsequent degradation of probe tip. A δ-Silicon wafer grating is used to test the tip degradation. The measurements are carried out making use of an Auto probe AFM operating in contact mode with normal force varying in the range 1.0-3.0 nN. Images of different areas (typically 256pixels, 256 pixels) are acquired both with a silicon nitride tip (pyramidal shape, nominal probe radius 40 nm, cantilever stiffness 0.03 N/m) and with a silicon tip (conical shape, nominal probe radius of 10 nm, cantilever stiffness 0.24 N/m). The data is treated with the image processing software.

The mechanical contact between the probe tip and the polymer surface is defined by the following parameters: real area of contact, $A$, penetration depth of the probe tip, $z$, and yield stress, $\tau$. These parameters can be approximated by a model which mixes the Hertzian model of elastic contact of a sphere and a flat surface with other models accounting adhesion force contribution and possible high applied load plastic deformation.

$$A = \frac{\pi}{4} \left( \frac{3RF_n}{4E_*} \right)^{2/3} \quad z = A / 2\pi R_t$$

where $R_t$ is the tip radius of curvature and $E_*$ is the reduced Young’s modulus of tip and polymer. The reduced Young’s modulus is the ratio of Young’s moduli of the polymer to that of silicon.

One relevant aspect in AFM study of polymer wear is the formation of ripples. The ripples can be considered a consequence of elastic instability waves. They have been observed on macroscopic length scales for elastically soft materials such as rubber during sliding on hard surfaces. They are produced making use of high load regime contact mode, 100 nN, and then observed on high Young modulus polymeric film. The formation of ripples is commonly considered to be the result of a peeling process operated by the microscope tip on the polymer.

Generally, AFM images of the same area acquired in sequence present lateral and rotational shifts. To be able to subtract accurately two consecutive images, they are aligned almost in x-y dimensions, before the amount of wear can be calculated. The alignment can be carried out making use of a numerical code. In the numerical procedure the images are adjusted by following the steps: first, frames compose by a matrix of pixels is defined for an image.

Then, this frame is searched in a subsequent image making use of the statistical correlation. The application of these two steps was justified by the fact that all observed image shifts comprise translation movements and partially rotational. After undergoing the adjustment procedures, the new surface images were compared quantitatively and the degree of change in wear volume was calculated.

The second step of the wear characterization is regarded the qualitative analysis of polymer mechanical degradation. To highlight this process and possibly quantify it, a zero wear reference is necessary. The zero wear reference is formed covering partially an area of SiO$_2$ with the polymer and then abrading that area at low loads and for a limited number of cycles (maximum of 15 scanning cycles). Under the experimental conditions, only the polymer is exposed to wear due to the significantly higher hardness of SiO$_2$. 
Analogously to the procedure normally used in macro-scale evaluation, the quantitative analysis of wear mechanisms could be carried out using volume change evaluation. The wear volume can be calculated by integrating over the difference of the image data of the total area following the expression \( V = VB - VA \). Where \( VA \) and \( VB \) are two subsequent acquired AFM images after adjustment. Tribological processes are rather complex, involving abrasion, adhesion, plastic deformation and variation of roughness. The behaviours of the volume changes, \( V \) as function of number of cycles show results difficult to be understood in straight manner. Generally, it could be expected that the wear volume tends to decrease as the number of stressing cycles increases due to plastic deformations of polymer. Nevertheless, the possible formation of ripples, as described above, should modify the polymeric surface making the volume changes due to abrasion difficult to observe. Resolution limits and errors in volume calculation could be given by tip geometry, thermal drift and undetected cantilever twist. The first two types of contributions should not be relevant if conical shape probe tip are used and the laboratory is thermally stable. On contrary, undetected cantilever twist could be a source of unexpectedly large errors. Other phenomena like electrical or mechanical noise should not contribute significantly to the error in volume estimation, since volume calculation is an averaging process and the net contribution should therefore be close to zero.

**AFM for studying the thermal phase transitions of polymers**

AFM experiments are usually carried out at room temperature. Very few studies have been reported at higher or lower temperatures. Such studies are important because of strong interest in polymer morphology and the nanostructure changes these polymers undergo during phase changes over a broad temperature range. With this technique it is also possible to study the growth of the individual crystalline lamellae by in situ monitoring of polymer crystallization. This type of information cannot be obtained by any other type of microscopy technique.

In the initial stages of development of this technique for high temperature applications, resistive heaters guided by temperature controllers were placed on the top of the scanner. Studies on phase transitions were carried up to 100°C using contact mode. Contact mode proved to be problematic due to the strong tip-sample interaction. This interaction produced lateral forces which damaged the samples. This problem became more pronounced at elevated temperatures. Therefore, tapping mode is preferred at high temperatures in which the effect of lateral forces was negligible. Studies of phase transitions at low temperatures are carried out by placing the AFM microscope in a thermoelectric chamber and purging it with cold nitrogen.

AFM has been used to investigate the phase transitions of polymers like polydiethylsiloxane (PDES), cyclolinar polysiloxanes, polydipropylsiloxane and syndiotactic polypropylene. Figure 14 depicts the morphology changes which accompany PDES from the mesophase. PDES consists of flexible –Si-O-backbones. It exists not only in crystalline or amorphous phase, but also in partially ordered phase called the mesophase. The monitoring of crystallization below 0°C can be achieved with AFM. Figure 14a demonstrates aggregates of elongated lamellae (each 0.3-0.5 µm wide). These are common in the mesophase. These lamellae are aligned in the rubbing direction (bottom left to upper right). These large lamellae are surrounded by amorphous PDES shown by dark contrast. During crystallization the large lamellae suddenly change their structure by transforming into blocks with linear sub-structures (tens of nanometers wide) shown in Fig. 14b. Figure 14c clearly shows the substructure after crystallization. This phase transition at -4°C occurs only in the mesophase. The amorphous phase remains undisturbed.

**Estimation of molecular weight (M_n) and polydispersity (PDI) index of polymer brushes by AFM**

This is one of the most recent applications of AFM applicable to grafted polymer layers. It is based on the principle of stretching the individual chains away from the grafting surface with an AFM tip. A tethered polymer chain that is adsorbed onto the tip by the free end exhibits a restoring force that varies non-linearly with distance. The attractive force increases with chain extension until the gradient eventually exceeds the spring constant of the cantilever, causing a mechanical instability. The polymer snaps free from

![Fig. 14—Phase transitions of PDES during crystallization.](image-url)
the tip when the elastic restoring force is greater than the adhesion force of the chain to the tip and the deflection signal returns to the base line. The separation at which the polymer ruptures from the tip is used as a measure of the chain contour length \( L_{c,i} \). The molecular weight \( M_i \) of the individual chain is calculated using this contour length. A large number of force curves (\( F-d \) curves) are required to obtain accurate statistical distribution of contour lengths so that average values of \( M_i \) and PDI can be calculated.

Example

AFM was used to estimate the molecular weight, \( M_n \) and polydispersity index, PDI, of densely grafted poly (N-isopropylacrylamide) (PNIPAM) brushes\(^72\).

Copolymer characterization

Characterization of poly(epsilon-caprolactone)-b-poly(ethylene oxide)-b poly(epsilon-caprolactone) (PCL-b-PEO-b-PCL) porous hydrogel by AFM for its lamellar nanostructures\(^73\). Poly(phenylethynylene)-b-poly(phenylenevinylene) (PPE-b-PPV) copolymers used for solar cells were characterized for its morphology of active layer\(^74\). Novel approach of architecturally different components via various techniques were prepared and these copolymers characterized and confirmed their molecular architectural through AFM technique\(^75\).

Conclusions

Atomic force microscopy is a relatively non-destructive technique as compared to conventional scanning electron microscopy and transmission electron microscopy. It also has an additional advantage of 3-dimensional measurements of the surface structure of polymers. The direct visualization of 3-dimensional images of the polymer surfaces is helpful for understanding the effects of changes in processing conditions. The field of nanocomposite is emerging at a rapid rate. Atomic force microscopy can be useful for the characterization of these nanocomposite materials.

The conventional surface characterization techniques provide only pictorial images of the polymer surface. Atomic force microscopy can be exploited to measure the mechanical properties, adhesion forces and structure of the polymer surface by making slight changes in the instrumentation involved. The capability of AFM to delineate the phase transitions of polymers provides us with important insight regarding the factors that are responsible for the peculiar properties exhibited by polymers. Thus, complete characterization of a polymer surface is possible by atomic force microscopy.

References
