

SURFACE MODIFICATION OF BIOMATERIALS BY PULSED LASER ABLATION
DEPOSITION AND PLASMA/GAMMA POLYMERIZATION.

By

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Surface modification of stainless-steel was carried out by two different methods: pulsed laser ablation deposition (PLAD) and a combined plasma/gamma process. A potential application was the surface modification of endovascular stents to enhance biocompatibility. The pulsed laser ablation deposition process, had not been previously reported for modifying stents and represented a unique and potentially important method for surface modification of biomaterials. Polydimethylsiloxane (PDMS) elastomer was studied using the PLAD technique. Cross-linked PDMS was deemed important because of its general use for biomedical implants and devices as well as in other fields. Furthermore, PDMS deposition using PLAD had not been previously studied and any information gained on its ablation characteristics could be important scientifically and technologically.

The studies reported here showed that the deposited silicone film properties had a dependence on the laser energy density incident on the target. Smooth, hydrophobic, silicone-like films were deposited at low energy densities (100-150 mJ/cm²). At high energy

densities ($> 200 \text{ mJ/cm}^2$), the films had an higher oxygen content than PDMS, were hydrophilic and tended to show a more particulate morphology. It was also determined that: 1) the deposited films were stable and extremely adherent to the substrate, 2) silicone deposition exhibited an ‘incubation effect’ which led to the film properties changing with laser pulse number and 3) films deposited under high vacuum were similar to films deposited at low vacuum levels.

The mechanical properties of the PLAD films were determined by nanomechanical measurements which are based on the Atomic Force Microscope (AFM). From these measurements, it was possible to determine the modulus of the films and also study their scratch resistance. Such measurement techniques represent a significant advance over current state-of-the-art thin film characterization methods.

An empirical model for ablation was developed for the 248 nm laser irradiation of silicone. The model demonstrated a good fit to the experimental data and showed that silicone underwent ablation by a thermal mechanism.

In addition to PLAD studies, functionalization of stainless steel was carried out by a combined plasma/gamma method involving deposition of a hexane plasma polymer by RF plasma polymerization, followed by gamma radiation graft polymerization of methacrylic acid. The hydrograft modified surfaces were further modified by chemisorption reactions with poly(ethylene imine) to produce amine-rich surfaces. Bovine serum albumin was then bound via amino groups using glutaraldehyde coupling. A streaming potential cell was also built and used to measure the zeta potential of these ionic surfaces.

CHAPTER 1 INTRODUCTION

Since their introduction in the early 1980s, metallic endovascular stents have revolutionized the treatment of coronary heart disease [1]. When used in conjunction with balloon angioplasty, stenting has a greater than 80% chance of success. The procedure is minimally invasive leading to less patient trauma, faster recovery times and less expense. It involves introducing a stent--an expandable metallic mesh-like tube--mounted on a balloon catheter to the site of vascular disease. The catheter is then blown up, expanding the stent and propping open the blocked blood vessel. Figure 1.1 shows the stent prior to and after expansion.

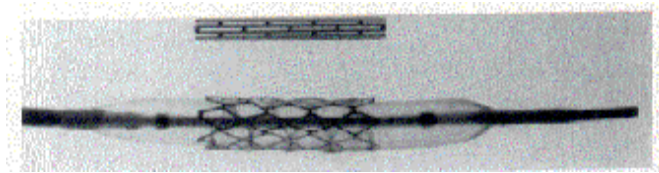


Figure 1.1 Palmaz-Schatz stent prior to and after expansion by a balloon catheter. Ref. [2].

Although significant advances have been made in stent designs, processing and finish, several problems still persist [3]. In the short term, thrombosis or formation of a blood clot is a major concern. The thrombogenicity is caused by the vascular response provoked by the stent's metallic surface. In the long term, cellular ingrowth from underlying smooth muscle cells and other associated events leading to arterial thickening, a phenomenon known as restenosis, remains the major cause for repeat

procedures. This cellular growth is the natural remodeling of the arterial wall in response to the vascular injury elicited by the angioplasty. The restenosis response is quite complex and involves several different growth factors, proteins and cells. Although the use of stents has led to reduced restenosis rates in balloon angioplasty procedures, the figure is still around 15-30% within six months of stenting.

Surface modification of stents with polymer coatings has been seen as one possible solution to these problems. A polymer coated stent could present a less thrombogenic surface to blood and invoke a benign response. Also, with the use of anti-proliferative and anti-inflammatory drugs loaded into polymer coatings it may be possible to mitigate the restenosis response.

Surface modification has been a widely studied technique to improve the performance of biomaterials in a physiological environment [4]. It offers the opportunity to tailor the surface properties for specific applications without compromising the bulk properties of an implant. Surface modification of metals is however challenging. Commonly used techniques like chemical grafting or gamma-radiation initiated grafting are not readily successful due to interfacial bonding problems. High-energy techniques like vapor deposition and ion implantation cannot be applied to produce polymer coatings. The two methods most widely studied are polymer solution coating and radio-frequency plasma treatments.

Polymer solution coating, spray- or dip-coating as it is widely known, is a simple technique wherein a polymer solution is applied to a substrate and dried to produce a coating. This technique, although easy, has disadvantages associated with it. Several processing steps are needed to build up the coating. The coatings produced can have

non-uniform thickness and coverage. The adhesion of the coating to the implant can also be tenuous unless coupling agents are used and the coupling chemistry needs to be tailored for each metal surface.

Radio-frequency plasma treatment is a well-developed technique for modifying metal, ceramic and polymer surfaces. It can produce coatings which are not otherwise obtained by conventional chemical methods. An initiating species is not required and the process usually produces crosslinked polymer films. However, growth rates can be slow and process optimization remains a challenge to date.

Implants such as stents also offer unique problems due to their small size and complex geometry. Apart from developing a coating, assessing the quality and performance of the coating is a challenge. Current methods used for surface modification of stents have usually involved solution coating methods. Apart from the problems noted above with such techniques, polymer webbing between the metal struts may also occur. Surface modification using plasma treatments have been applied only recently to stents and their efficacy is not yet known. Therefore, a method which can apply a coating in a single step, reproducibly and with improved adhesion, would prove beneficial and would also be a significant advance over the current state-of-the-art.

The research reported here investigated the use of pulsed laser ablation deposition (PLAD) of polymers for developing coatings on metal surfaces such as stents. It was hypothesized that the PLAD method could produce coatings by complete transfer of polymer from the target to the steel surface. Thus the desirable properties of the polymer would be reproduced in the coating. The process would use commercially

available polymers for coatings thus obviating the need for monomers, or problematic reagents and conditions. This would be an advantage as compared to solution coating and plasma processes and might provide better control over the coating properties. Stronger film adhesion was also likely due to the energetic nature of the coating process. The PLAD method had not previously been reported for the surface modification of biomedical implants and represented a unique and potentially important new approach for the surface modification of biomaterials.

The polymer primarily investigated here to produce coatings by the PLAD method was polydimethyl siloxane (PDMS), commonly known as silicone. The choice of material was dictated by two reasons. First, the good haemopatibility of silicone has been proven in several studies and this made it a good choice as a material for a blood-contacting stent coating. Crosslinked PDMS can also serve as a drug delivery depot which is a significant advantage. Additionally, the pulsed laser ablation of cross-linked silicone elastomer had not previously been reported and the results would add to our scientific understanding of the polymer ablation and deposition process.

Chapter 2 provides the background and literature review on the topic of stent coatings. The different coatings studied to date are discussed therein. An introduction to the subject of pulsed laser ablation of polymers is also presented. Among the various aspects discussed are the nature and characteristics of the process and applications to surface modification. Further, current methods to produce silicone coatings and thin films are briefly mentioned.

Chapter 3 presents the results of the pulsed laser ablation deposition of silicone on stainless-steel. The variation in surface properties of the deposited silicone films as a

function of the incident energy density is examined in detail. Other aspects examined include the deposition rate, effect of the laser pulse number on the film chemistry, coating stability after solvent immersion and effect of high vacuum during deposition.

The results of nano-indentation and nano-scratch experiments on PLAD silicone films using methods based on the Atomic Force Microscope (AFM) are presented in Chapter 4. These experiments were carried out to determine the mechanical strength and adhesion of the coatings. Nanomechanical testing is a new but promising technique for studying the mechanical properties of thin films. The experiments reported here provide a basis for further investigation of the method for characterizing polymer films and coatings.

Chapter 5 is devoted to the development of a model to explain the ablation characteristics of silicone. This empirical model is applied to experimental results and is seen to give a good fit. Since research on pulsed laser ablation of silicones is limited, this chapter serves to extend current theories of polymer ablation to silicon based polymers.

Immobilization of bioactive molecules is a further important aspect of biomaterial surface modification. The attachment of proteins, peptide sequences and drugs to biomaterial surfaces can lead to an improved outcomes by achieving increased localized bioactivity. However, for stents the challenge has been to attach these biomolecules to metallic implant surfaces. Thus, the second part of this research investigated the surface modification of stainless steel to produce functionalized surfaces. This was done by using a novel plasma/gamma radiation graft method

developed in this laboratory. Biofunctionalization of steel surfaces was achieved by this method by coupling of bovine serum albumin to a modified steel surface.

Chapter 6 presents the results of the surface modification of stainless steel by the plasma/gamma method as well as results for the coupling of bovine serum albumin to the functionalized steel surfaces. The charge on the functionalized, ionic surfaces was measured by a streaming potential cell which was built for this purpose. The design, setup and operation of this cell are given in the appendix.

Chapter 7 presents the conclusions which have been reached from this research and provides recommendations for future research directions.

CHAPTER 2 BACKGROUND

Percutaneous transluminal coronary angioplasty (PTCA) has proven to be a successful technique for treating coronary heart disease. The procedure is minimally invasive and allows patients to regain active function earlier. However a large number of these procedures suffer from the problem of restenosis, a phenomenon in which smooth muscle cells from underlying cell layers proliferate causing gradual thickening of the vessel wall and ultimately occlusion. Stents have been shown to address the problem of restenosis in PTCA procedures successfully. Two recent trials reported that stents reduced the need for revascularization due to restenosis by approximately 30% [5],[6]. Other studies have shown that restenosis rates were reduced from up to 50% for PTCA to 15-30% with stenting in the first 6 months after surgery. Their success has led to the ever increasing use of stenting in PTCA procedures. It was estimated that in 1998 more than 500,000 stent procedures were carried out worldwide on coronary blood vessels [7]. It is expected that stents will be used in 56% of all PTCA procedures worldwide by the year 2001.

However the use of stents in these procedures also has its problems. One of the main problems has been short-term thrombosis or clotting [8],[9]. This is due to the adverse response elicited by the stent surface on implantation. Patients need a longer hospital stay and a rigorous anticoagulant regimen to prevent the acute thrombosis of the stent. Currently all stents on the market are made from stainless-steel, tantalum or a nickel-titanium alloy (i.e. nitinol). These metals are inherently thrombogenic and

induce platelet adhesion and clot formation upon implantation. With current thrombosis rates around 3-5%, up to 20,000 people could experience life-threatening events each year[10].

Research efforts to improve the blood contact properties of stents have concentrated on modifying the outer layer of the stent surface rather than changing the stent material itself. This lets the mechanical properties of the stent remain unaltered while presenting a favorable surface to the blood vessel. Efforts have also been directed at reducing the current restenosis rates to even lower levels. Thus the ideal coating has been viewed to be haemocompatible, thereby not inducing stent thrombosis and non-proliferative thereby reducing restenosis by discouraging cell growth. To this end, stents coated with biocompatible polymers and anticoagulants like heparin have been reported in the literature [11]. The polymer coatings have also been viewed as depots for drug delivery. Thus a number of reports on stent coatings which deliver anti-inflammatory and anti-proliferative agents to the site of vascular injury have also been published.

Currently a number of research groups and stent manufacturers are evaluating the performance of several different kinds of coatings in reducing thrombosis and restenosis. As the use of stents in other anatomic frontiers like carotids, renals and small vessel vascular peripheral disease also increases, producing a stable, biocompatible, drug-eluting coating would be of increasing importance. Indeed, it was recently stated that, "...the potential for application of antiproliferative coatings remains provocative and largely unexplored" [3].

Stent Designs, Materials and Coatings

The ‘stentomania’ of the last decade has influenced manufacturers to introduce a number of new designs. Stent designs usually consist of metallic tubes with a number of slots cut in by lasers, or coil designs which consist of a single wire entwined to form a cylindrical mesh, reinforced at several points [12],[13]. The various mesh designs give the stent different flexibility and handling characteristics and play a role in the thrombosis and restenosis rate [14]. They are usually made of stainless steel although tantalum and nickel-titanium alloy based stents have also been introduced. Table 2.1 gives an overview of some stents with their designs and the coatings being applied. Figure 2.1 shows schematic diagrams of major stent designs. All stent designs require a compromise between scaffolding properties and flexibility to negotiate tortuous vessels. The radio-opacity of the stents also plays a role in stent choice. Thus manufacturers have striven to introduce new designs to improve the stent handling characteristics and radio-opacity. The choice of stent is largely determined by the surgeon’s experience and choice. The Palmaz-Schatz stents have been the most popular choice to date. However failure to innovate has led to a decline in this stent’s popularity. Among the popular choices nowadays are Guidant’s Multilink and Medtronic’s Wiktor stents.

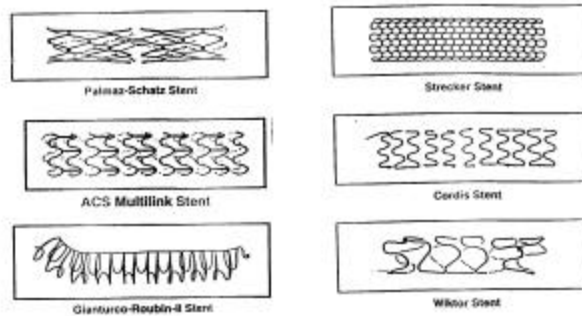


Figure 2.1 Schematic diagrams of several major stent designs in use today.

Table 2.1 Stent specifications and coatings for major designs and manufacturers.

Stent/ Manufacturer	Material	Design	Strut Thicknes smm	Diameter, mm	Length, mm	First Clinical Implantation	Coating/Market Status
Wallstent/Schneider	Inner core platinum; outer core cobalt-based alloy	Wire mesh	0.08-0.1	3.5-6.0	12-42	1986 1991 (less shortening)	-
Palmaz-Schatz/ Johnson & Johnson	316L stainless steel	Slotted tube	0.07	3.0-4.0	15	1988	Heparin/FDA approved 1999
ACS-Multilink/ Guidant	316L stainless steel	Corrugated links connected by multiple links	0.05	3.0-3.5	15	1993	-
Gianturco-Roubin/Cook Inc.	316L stainless steel	Incomplete coil clam- shell loop	0.127	2.5-4.0	20-40	1989 (GR-I) 1995 (GR-II)	Antiplatelet coating (Reopro) Antiproliferative coating (Taxol)
Wiktor/Medtronic	Tantalum	Single wire semi-helical coil	0.127	3.0-4.5	16	1991	Heparin/on market
AVE-Microstent	316L stainless steel	Sinusoidal ring	0.13	2.5-4.0	6-36	1994-95	-
divYsio/Biocompatibles Cardiovascular	316L stainless steel	Interlocking arrowhead	0.15	2.75-4.0	15	1995	Phosphorylcholine
NIR Medinol/Boston Scientific	Stainless steel	Expandable uniform cellular mesh	0.1	2.0-5.0	9-32	1995	Gold

- Adapted from Handbook of Coronary Stents, ed Serruys, PW, Kutryk, MJB, Published by Martin Dunitz Ltd., London, 1997 and Ozaki, Y., *et al.*, Progress in Cardiovascular Disease 39, 2, 129-140, 1996.

Polymer Coated Stents

Research on polymer coated stents was undertaken very early in the evolution of stents. The advantages of a polymer coated stent were seen to be biocompatibility and also its ability to function as a drug reservoir. A majority of the coatings have been produced by dip-coating. However data on the coating thickness, surface analysis and stability is limited in most cases. A review of stent coatings and their performance is given below.

De Scheerder *et al.* have reported on the performance of slotted tube steel stents coated with an amphiphilic polyurethane (PU) [15]. The polyurethane was prepared from an amphiphilic polyester, diphenylmethane-4-4'-diisocyanate and butane diol as a chain extender. It was shown that the polyurethane coating decreased acute thrombotic occlusion in a porcine model. The PU coated stents led to a significantly smaller minimum stented lumen diameter after 6 weeks as compared to controls. Polyorganophosphazene (PP) coated stents were also evaluated in a similar porcine model. The polyphosphazene was selected due to its biodegradability under physiologic conditions. The PP coated stents gave pronounced neointimal proliferation. The degradation products also elicited a severe inflammation response resembling a foreign-body reaction. The authors concluded that PU was promising as a stent coating while PP was not.

Lincoff *et al.* have studied a drug eluting biodegradable polymer coating in a porcine model [16]. A tantalum wire mesh stent coated with a 20-25 μm layer of dexamethasone suspended in a binder namely, poly-L-lactic acid ($M_w = 321,000$ g/mol), was evaluated. Although the dexamethasone did not exhibit reduced neointimal proliferation it was demonstrated that a polymer coated stent could prove to be a means

of effective intravascular drug delivery. The reduced activity of dexamethasone could have been due to the inflammatory response elicited by the degradation products of the poly-L-lactic acid, an aspect which was not examined in the research.

Schwartz *et al.* reported on modifying stents with a fibrin layer by dripping fibrinogen onto it [17]. Subsequent polymerization of the fibrin layer led to the fibrin mass completely encasing the stents. Fibrin was selected since it is a native polymer which deposits at the site of vascular injury. It was hypothesized that a layer of thrombus would form at the site of the injury and fool the body's own response to this event and limit its thrombotic response. The stents were assessed in a porcine coronary model in contrast with polyurethane coated stents. PU-coated stents showed a foreign-body inflammation response with multinucleated cells being present on the surface. In contrast the fibrin-coated stents reduced restenosis rates.

In an effort to mimic the cell-bilayer, phosphorylcholine coatings have been tried by several groups. Zheng *et al.* reported on clinical experience with a phosphorylcholine coated stent [18]. The coated stents were supplied by Biocompatibles Ltd., U.K., and were produced by a proprietary process. The authors found a restenosis rate of 6.1% at 6-month follow-up in 224 patients. The low restenosis rates indicated that the coatings were safe and efficacious in the treatment of coronary lesions. However this study did not compare uncoated stents vs. coated and any conclusions about the performance of the coating are moot. In a more recent study, Whelan *et al.* assessed the biocompatibility of phosphorylcholine coated stents in normal porcine arteries [19]. The coating applied to a *divYsio* stent consisted of a copolymer of methacryloylphosphorylcholine and lauryl methacrylate. The stents were dip-coated from a solution of the polymer in ethanol to

give a coating approximately 50 nm in thickness. In comparing un-coated and coated stents no difference in intimal thickness at 4 and 12 weeks was seen. It was also seen that the phosphorylcholine coating did not elicit an adverse inflammatory response. As a measure of coating stability the authors examined sections of explanted stents, 12 weeks post-implantation by optical microscopy. Although the coating could not be directly seen under the microscope, the authors concluded that the coating was still present based on the staining characteristics of these stents. However, given the tenuous nature of the coating (~ 50 nm) it is highly unlikely that the coating was stable at 12 weeks after implantation. Thus the similar responses of the uncoated and coated stents could be due to the fact that the coatings failed exposing the stent surface.

Van der Giessen *et al.* tested the response of different polymers by deploying them as strips on the circumferential surface of coil wire stents in a porcine coronary model [20]. Five biodegradable polymers namely, polylactic acid-polyglycolic acid (PLGA), polycaprolactone (PCL), polyhydroxybutyrate valerate (PHBV), polyorthoester (POE) and polyethyleneoxide/polybutylene terephthalate (PEO/PBTP), were tested. Three non-biodegradable polymers namely, polyurethane (PU), silicone and polyethylene terephthalate (PET), were also tested. Four weeks after implantation the stent patency was assessed by angiography followed by microscopic examination of the coronary arteries. It was found that all polymers evoked a significant inflammatory and proliferative response. The response was common to biodegradable and non-biodegradable polymers. In all cases the inflammatory response consisted of a chronic inflammatory reaction with an acute component and a persistent foreign-body reaction. The authors speculate that the inflammation response may have been aggravated by the

release of the degradation by-products of the polymers. It should be mentioned that the coated stents were not sterilized prior to implantation which could have contributed to their severe response.

Two studies have examined the efficacy of heparin coated stents in reducing the thrombogenic response. De Scheerder *et al.* studied the thrombogenicity of heparin coated and uncoated stents in a rat arteriovenous model [21]. They found that total clot weight at 30-minute follow-up was significantly lower in the heparin-coated stents compared with bare stents. Subsequently heparin-coated and uncoated stents were implanted in the right coronary artery of 20 domestic pigs. It was shown that heparin-coated stents had no significant difference in luminal area or neointimal hyperplasia compared to uncoated stents. The authors concluded that heparin reduces the thrombogenicity but does not influence neointimal hyperplasia.

Hårdhammar *et al.* studied the thrombogenic response of heparin coated stents in a porcine artery model [22]. The coating was applied by end point coupling of heparin molecules to an underlying polymer matrix. The technique used was a variation of the Carmeda process in which a polyamine layer was deposited on the stent surface, followed by a dextran sulfate layer, followed again by a polyamine layer. Finally the functional amino groups were covalently coupled to aldehyde groups of partially degraded heparin molecules. The activity of the bound heparin was measured by its ability to bind antithrombin-III with high affinity. Since it was determined that heat or ethylene oxide sterilization considerably reduced the antithrombin-III binding activity the stents were coated under clean room conditions but not sterilized. It was shown that the high-activity

heparin coating eliminated subacute thrombosis in porcine coronary arteries. However no reduction in the neointimal layer thickness was observed due to the heparin coating.

Aggarwal *et al.* have studied the response of polymer coated stents eluting platelet glycoprotein IIb/IIIa receptor antibody in a rabbit model [23]. The authors reasoned that using a potent antiplatelet agent eluting from the stent would passivate adherent platelets and reduce thrombus formation after stent deployment. The coating produced by dip-coating consisted of a cellulose polymer applied as a 10% solution with acetone as the solvent. A 30 μm thick coating was produced by this method. The polymer coated stents were immersed in a radio-labeled antibody solution and removed after specified time periods. The activity of the antibody was measured by the radioactivity associated with it. These antibody loaded stents were implanted in rabbits. There was a >50% reduction in platelet deposition 2 hours after stents eluting platelet GP IIb/IIIa antibody were deployed, compared with control stents eluting either irrelevant antibody or no active agents. Furthermore, platelet aggregation in the stent was strikingly inhibited by the eluting GP IIb/IIIa antibody, as evidenced by the almost total abolition of cyclic blood flow variation in these vessels. The authors demonstrated that the surface modification of stents with potent antiplatelet agents can thus enhance the thromboresistance of stents.

It is seen from the above review that surface modification of stents has been done mainly by the dip-coating method. Often data on the success of the surface modification have been sparse or altogether absent. Thus the stability of the coatings cannot be assessed over a long period. The dip-coating method can also present problems like inadequate polymer-metal adhesion, non-uniform and very thin films. It also necessitates

the use of several processing steps. Problems with sterilization have also been noted for some polymer coatings.

Non-Polymeric Coatings

Methods for coating stents using different techniques have also been reported. A silicon-carbide coating of metallic stents has been developed. As a semiconductor SiC is known to have good biocompatibility and it was reasoned that it would modulate the surface charge to reduce thrombogenicity [24]. Therefore a SiC coating was applied by a CVD process and coated stents were evaluated in a closed loop *in vitro* heparinized whole human blood circulation model [25]. Uncoated and heparin coated stents were also compared. The SiC-coated tantalum stent demonstrated a significantly lower GpIIb/IIIa receptor-mediated platelet adhesion at the stent surface compared to all other stents. Also, activated leukocytes demonstrated a significantly lower CD11b receptor-mediated adhesion at the SiC-coated stent than at the stainless-steel stent. The SiC-coated stents were also evaluated in treatment of coronary lesions for high risk patients. The stent thrombosis rate in the high-risk group (3.6%) was not significantly different from that of the low-risk patients (2.1%). The authors concluded that silicon carbide coating on coronary stents may inhibit acute/subacute stent thrombosis even in patients at high risk.

Lahann *et al.* reported on the use of a solvent-less method to produce a polymer coating on stent surfaces [26]. Poly(2-chloroparaxylene) was deposited by a CVD process on steel substrates. A sulfur-dioxide plasma treatment was then carried out on the poly(2-chloroparaxylene) coated metal surfaces to functionalize them. The SO₂ plasma attacked the chloride groups on the polymer to produce (SO₃)⁻ groups on the surface. The polymer films demonstrated high mechanical stability in stent dilation experiments. The

coated surfaces showed a reduction in platelet adhesion as compared to uncoated surfaces.

Radioactive Coatings

Another interesting development in stent coatings has been the use of radiation to control restenosis [27]. Radiation selectively kills proliferating cells independent of the stimulus for cell growth. Since neointimal hyperplasia is a major cause of restenosis, it was reasoned that radiation therapy may reduce restenosis. Radioactive stents have the potential to deliver an appropriate dose of radiation to the area of vascular injury thus reducing restenosis while minimizing the total dose administered. In one method, conventional Palmaz-Schatz stents were bombarded with ions in a cyclotron and subsequently found to emit low-dose β and γ radiation from radioisotopes Co55, 56, 57, Mn52 and Fe55 with half-lives between 17.5 hours and 2.7 years [28]. A dose rate of 0.4 rads/h on the surface results in an integral dose rate of 0.18 Mrads after a period of 100 days. It was found that low-dose radioactive stents markedly inhibited neointimal hyperplasia in rabbits. Endothelialization of the radioactive stents was found to be delayed. Although the degree of neointimal hyperplasia was reduced, it was found, counter-intuitively, that extracellular matrix production increased after stent implantation. A second method used P^{32} -impregnated stents as a means of delivering local radiation. P^{32} is a β emitter with a half-life of 14.3 months. *In-vivo* animal testing in a porcine model showed inhibition of neointimal growth. Currently several clinical trials are underway to assess the performance of radio-emitting stents [29].

Pulsed Laser Ablation of Polymers

In 1982 the use of UV pulsed laser radiation to etch poly(ethylene terephthalate) (PET) was reported for the first time [30]. The attractive features of using pulsed laser radiation were seen to be the degree of control which could be exercised on the etch depth, the lack of detectable thermal damage adjacent to the etch site and the low energy density levels involved. These observations were then confirmed for other polymers at different UV wavelengths. The laser ablation of biological tissue was also reported in 1983 and the application of this technique for surgery was discussed [31]. In the ensuing years a great deal of research was dedicated to studying the laser ablation of a few polymers namely, polyimide (PI) [32], poly(methyl methacrylate) (PMMA) [33], poly(ethylene terephthalate) (PET) [34],[35] and polytetrafluoroethylene (PTFE) [36]. The choice of these polymers is explained by their use in the semiconductor industry. Since lasers had already made forays in the semiconductor industry, their application to etch precise patterns on polymers was logical. Although the potential of using pulsed lasers for thin film synthesis of inorganics had been well recognized early on, this aspect was neglected for polymers till the early 1990s. Thus there is a large phenomenological database on the ablation characteristics of certain polymers but relatively few published studies on thin film synthesis using polymers. However, since an understanding of the laser ablation process is intrinsic to its application in film synthesis, a short review of pulsed laser ablation of polymers is presented here.

Pulsed laser ablation involves two basic elements that interact to give rise to laser ablation. These are the radiation in the form of laser pulses and the polymer which ablates on interacting with the pulse.

Excimer laser. The excimer laser consists of a laser cavity in which a long, narrow discharge tube is set. It is filled with a halogen, a noble gas and a buffer gas to a total pressure of 2 to 3 atm. When a high-voltage discharge (20-30 kV) is fired through this mixture, laser radiation is produced in the UV range. Table 2.2 lists the combination of halogen, noble gas and buffer used to produce various UV wavelengths.

As shown in the table below, a variety of wavelengths can be accessed depending on the choice of excimer. These lasers can be operated with high outputs (1-5 Joules), with short pulsewidths (femtosecond-nanosecond) at repetition rates between 1 to 200 Hz.

The beam dimensions can be well controlled with the use of filters and masks to give an area in the mm^2 to cm^2 range of nearly uniform intensity.

Table 2.2. Operating parameters of different excimer lasers

Active medium	F ₂	ArF	KrCl	KrF	XeCl	N ₂	XeF
Wavelength, nm	157	193	222	248	308	337	351
Helium, mbar	2650	1410	1720	2300		960	2570
Krypton, mbar			200	120			
Argon, mbar		270					
Neon, mbar					2760		
He/F ₂ (5%), mbar	50	120		80			120
He/HCl(5%), mbar			80		80		
Nitrogen, mbar						40	
Total pressure, mbar	2700	1800	2000	2500	2900	1000	2700
Pulse width, ns	19	23	21	34	28	7	30

- Adapted from company brochure, Lambda-Physik, Acton, MA, USA.

Polymer Targets. The second part of the process is the polymer on which the laser pulse is incident. Polymers have UV absorption characteristics which are strongly related to their structure. Polymers like PI and PET absorb strongly in the UV range of the spectrum due to the presence of π bonds, while PE and PTFE are weak absorbers due to the absence of chromophores. Depending on the absorption coefficient the incident UV radiation will penetrate from a fraction of a micron to tens of microns before 95% absorption (optical penetration depth). Absorption of a photon by an organic molecule causes it to rise to an electronically excited state. The first excited state can absorb another photon to give a doubly excited state (i.e. multiphoton excitation). Successive absorption of two such photons by any one chromophore in a polymer will lead to an excited state which may undergo ionization. The efficiency with which the absorption of a single photon can lead to a chemical bond rupture is expressed in terms of a quantum yield. Although quantum yields in the solid-state are far less than unity, secondary reactions following primary bond rupture can lead to an increased yield [37]. Strong absorption, although important is not a necessary condition for polymer ablation since it has been shown that polymers with minimal absorption like PTFE and PE can undergo significant ablation depending on the irradiation conditions.

General Characteristics of Laser Ablation.

The ablation of a polymer surface by a laser pulse is a function of the energy deposited in the solid per unit time, the wavelength of the laser and the time-length of the laser pulse. Depending on these factors, polymer ablation can take place in the μm range. Figure 2.2 gives a general scheme of the process. The ablation is accompanied by light and acoustic emissions, pressure and temperature changes. All of these have been

measured in an effort to understand the ablation process. Based on a number of studies over the past 15 years [32],[38-45], a general curve can be constructed relating the etch rate (thickness of material etched per pulse) to the energy density (laser energy per pulse and unit area) deposited into the polymer.

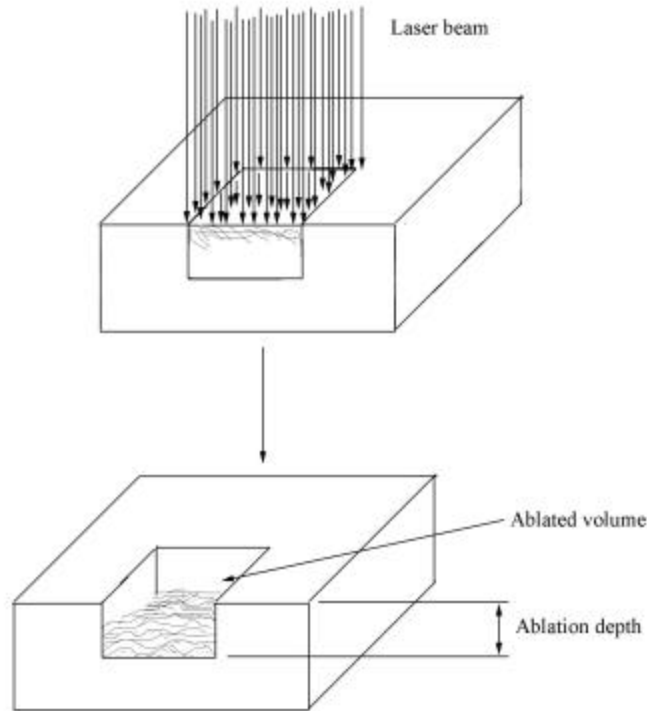


Figure 2.2. Schematic representation of the laser ablation process

As shown in figure 2.3 the plot has three distinct regions. In the low energy density region shown as region I in the figure, (typically $10\text{-}100\text{ mJ/cm}^2$), the etch rate is extremely slow and proceeds in a layer-by-layer fashion. The polymer surface shows minimal change and ablation as characterized by material removal is seen only after a

few hundred pulses. Beyond a certain limit, usually referred to as the threshold energy density, the etch rate rises in a linear fashion with the energy density (shown as region II).

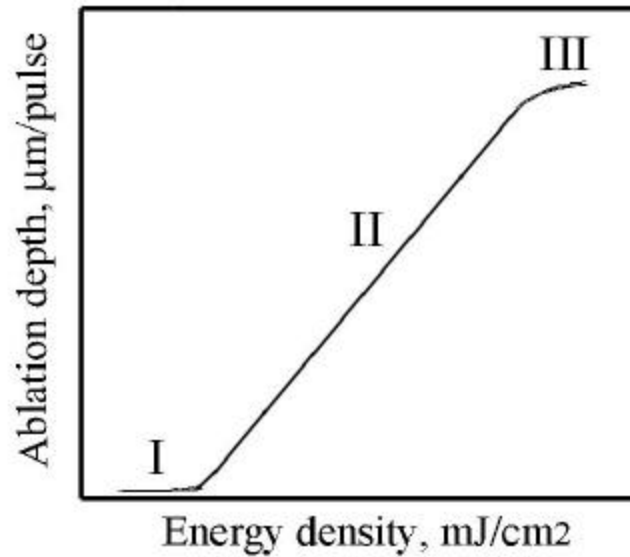


Figure 2.3. Characteristic graph of ablation depth/pulse vs. Energy density for polymers.

Depending on the mode of ablation i.e. photothermal or photochemical, the polymer surface undergoes extensive degradation and material removal. Typical limits for region II are in the $1\text{-}2\text{ J/cm}^2$. In the region III, the etch rate saturates at very high energy densities. The decrease in etch rate can be due to laser pulse attenuation by the ablation plume expanding off the polymer surface or change in the polymer absorption characteristics (optical bleaching). All polymers seem to exhibit the threshold phenomenon and demonstrate two different etch rates above and below the threshold energy density. Many studies [32],[44], have tried to fit the linear region of the plot to a

model based on Beer's law of absorption which takes into account the UV absorption characteristics of the polymer. The fit is based on the following equation:

$$d = \frac{1}{a} \ln \left(\frac{f}{f_o} \right) \quad (1)$$

which relates the ablation depth per pulse, d , to the natural logarithm of the ratio of the incident energy density, ϕ , to the threshold energy density, ϕ_o , with the inverse of the absorption coefficient, α^{-1} as the proportionality constant. However it has been found the slope of this line does not always give the correct value for the absorption coefficient of the given polymer [46]. Also the model can not be applied at extremely low or high energy densities. Thus the ablation behavior can not be modeled by a simple UV absorption model.

Since the dynamics of the ablation process are extremely fast, a knowledge of the different events occurring and their time scales is critical to the understanding of the phenomenon. Koren and Yeh studied the light emission intensity at various distances from a polymer surface after laser irradiation [47],[48]. They concluded that in the etching of polyimide films by ArF pulses (193 nm, 15 ns FWHM), the emission has a fast component which appeared simultaneously with the laser excitation and a slower component which lasted 10 to 100 fold longer than the laser pulse itself. Davis *et al.* carried out a similar study of PMMA and obtained emission signals on the order of the laser pulsewidth [49]. These two studies showed that the polymer could begin to ablate on a time scale that is even shorter than the width of a pulse from a laser beam and the ablation could last on the order of microseconds.

Dyer and Sidhu studied the temperature rise accompanying laser irradiation of a polymer by attaching a thermocouple to a 50 μm polymer film [50]. Temperature increases in excess of 500 K were detected. Gorodetsky *et al.* measured the local temperature rise in a polymer film on laser irradiation by bonding a pyroelectric crystal to a 75 μm thick PI film [51]. It was found that the temperature rise in the irradiated area was directly proportional to the photon energy deposited into the film. These studies demonstrated the high temperatures seen on the polymer surface during laser ablation.

Dyer and Srinivasan found that the local heating produced by a laser pulse below threshold levels causes a stress wave which is sinusoidal in character [52]. The compression wave caused by the heating is rapidly followed by a rarefaction wave caused by the cooling. It was also found that the stress waves generated had large magnitudes. For the ablation of a PI film at 193- and 308 nm peak amplitudes in the 10^5 - 10^7 Pa range were detected. The ablated material is known to be ejected at 2 to 5 times the speed of sound and the pressure generated on the substrate is consistent with these measurements. These stress waves could be detected even at extremely low energy densities at which no significant etching was observed (< 50 nm per pulse). It was calculated that the ablation of < 50 ng of material at a velocity of 2×10^4 cm/s on a 20 ns scale would account for the observed stress wave signal for a PI film irradiated at an energy density of 3 mJ/cm^2 . There also appeared to be a relationship between the chemical structure of a polymer and its stress response upon laser irradiation. PMMA gave a sinusoidal response for a laser pulse of 9 mJ/cm^2 (i.e. compression followed by rarefaction), in contrast to PI which showed a wholly compressive response.

Venugopalan also studied the mechanical response of PI and collagenous tissue to pulsed laser irradiation at 193-, 248- and 308 nm [53]. Results for PI were in agreement with Dyer and showed that stress levels in the GPa range are generated in the polymer. In the ablation of collagenous tissue it was shown that the absorbing chromophore and the characteristic response time of the polymer decided the mode of ablation. At 193 nm, strong absorbance due to CO-NH peptide bonds gave clean ablation with thermal damage localized to a few microns from the ablation site. In the 1064 nm irradiation of tissue, water acted as the main chromophore and the tissue failed due to mechanical fracture caused by water expansion.

Von Gutfeld *et al.* followed the deformation of a film surface on laser irradiation by reflecting a He-Ne laser off the polymer surface and monitoring the reflection with a position-sensitive detector [54]. A laser pulse of 20 ns FWHM and $< 1 \text{ mJ/cm}^2$ energy density caused a deformation in a 125 μm PI film which rose to its maximum in 2 μs . A 50 μm film had the same response time, but the deformation of the surface was fourfold greater. Thus these studies established the large temperature rises and deformation experienced by a polymer surface on laser irradiation.

Dynamics of laser ablation When a laser pulse is incident upon a polymer (or any other material) surface, the etched material is ejected from the surface as a plume. The constituents of the plume are ejected with a certain direction and a great velocity. Plume dynamics has been the subject of much research. The velocity and angular distribution of certain molecules in the plume has been determined for a number of polymers. Srinivasan *et al.* examined the diatomic (C_2) signal during 248 nm laser ablation of PMMA and found its ejection during ablation took place at a supersonic

velocity of 7×10^5 cm/s at energy density levels well below threshold [33]. Velocity measurements on C_2 and CN fragments from the ablation of PI films with 248 nm laser radiation were also undertaken. A Maxwell-Boltzmann fit to the velocity distribution of C_2 showed a maximum at 6×10^5 cm/s. This indicated that the ablation products traveled at supersonic velocities off the polymer surface, a measure of the energy transfer involved in the process.

Chemical composition of ablation fragments. Chemical analysis of the products of ablation have been carried out in a number of studies. Only a limited number of studies have yielded quantitative information correlating the yield of a given product to the mass of polymer that was removed by ablation (i.e. mass balance). The findings for PMMA and PI are summarized below.

PMMA: Srinivasan studied the gaseous species produced during PMMA laser ablation by mass spectrometry [33]. The most stable gas products were carbon monoxide (CO), carbon dioxide (CO_2) and methyl methacrylate (MMA) in the ablation of PMMA by 193 and 248 nm radiation. The MMA yields were 18 and 1% respectively at 193 and 248 nm ablation. MMA oligomers in the mass range of 2500-400 amu were also reported. The morphology of the ablated polymer surface showed significant differences for 193 and 248 nm ablation. The 193 nm laser pulses produced a smooth and debris free etch region, while 248 nm laser pulses showed considerable roughness and bubbling. It was demonstrated that the temperature in the etched volume was greater than the softening point of PMMA (assumed as $150^\circ C$) during 248 nm ablation but not with 193 nm laser pulses. In a similar study Krajnovich reported the ablation products of PMMA by a KrF laser (248 nm, 16 ns FWHM) to be a complicated mix of products [55]. These included

methanol, carbon monoxide, methyl formate, MMA, dimers and fragments from the partially unsaturated polymer backbone. The findings from these two studies are at odds with each other, but the different energy density ranges used could account for that. Srinivasan used energy density levels of 0.5-1.5 J/cm², which was designated as the steady-state ablation regime. Krajnovich's study used a energy density of 0.25 J/cm² for all measurements and found it was possible to ablate PMMA at this level.

PI: A number of studies have found the major products for ablation of PI at 193 and 248 nm to be HCN, CO, H₂, C and H₂O [37]. The presence of higher molecular weight species was not examined. In a report on the formation of surface defects during 248 nm ablation of PI, Krajnovich and Vásquez gave a mass balance for the process based on their observations [56]. They calculated that 1.2×10^{15} monomer units were ablated per second and calculated the volatile molecule production rate at 7.9×10^{15} molecules per second. Thus each monomer could decompose to give 6-7 volatile molecules ($7.9 \times 10^{15} / 1.2 \times 10^{15}$) supporting the production of CO and CN during ablation. One major problem has been the intractability of the polymer which makes molar mass and spectroscopic analysis difficult.

Mechanism of polymer ablation. The mechanisms underlying polymer ablation have been studied in order to provide a theory of polymer ablation. The two modes of ablation are seen as photochemical and photothermal. In photochemical ablation, photon absorption leads to electronic excitation causing bond scission and material ejection off the surface. In photothermal ablation, electronic excitations are transferred to vibrational modes causing material heating and evaporation off the surface. Although many studies

have tried to resolve this issue as yet no clear picture has emerged. In fact the mechanism appears to be dependant on the type of polymer and the kind of laser used.

Pulsed Laser Ablation for Polymer Thin Film Deposition

Although the possibilities of using PLD for thin film synthesis were recognized early on, research on this aspect has made significant progress only recently. Hansen and Robitaille published the earliest report on the use of UV laser ablation for polymer thin film synthesis [36]. They used a variety of polymers in their study namely ; Poly (tetrafluoroethylene) (PTFE), Polyethylene (PE), Poly (methyl methacrylate) (PMMA), Nylon 6,6, Polycarbonate (PC), Poly (ethylene terephthalate) (PET) and Polyimide (PI). The effect of laser wavelengths on polymer film formation was studied by irradiating the polymer targets at wavelengths of 193, 248, 355 and 1064 nm. Laser pulse energy densities ranged from 0.01-2 J/cm². A strong correlation between the deposited film quality and the polymer absorption coefficient at the excitation wavelength was observed. Films deposited using 1064 nm laser pulses were characterized by debris and particulate matter. Films produced by the UV lasers were of higher quality (i.e. particulate free), smooth and homogenous. These films also demonstrated stronger adhesion to the substrate than those produced with the 1064 nm laser. The authors reasoned that since the polymers used were mostly transparent at 1064 nm, the polymer ablated by evaporation causing particles to eject off the surface. At the UV wavelengths, since most polymers had some absorption, the ablation was due to photochemical means causing smaller ions and molecules to eject off the surface.

The laser energy density also had a significant effect on the deposited film quality. As the energy density was increased, the tendency towards particle incorporation

in the film also increased, indicating that the mode of ablation was also energy dependant. The importance of the polymer UV absorbance was demonstrated by the fact that polymers with negligible absorbance (e.g. PTFE, PE) were not deposited as films. It was also found that the growth rates for the polymers which did form films were in the range of 0.2-0.8 Å/pulse, independent of the starting material. Refractive indices (RI) of the deposited films varied from those of bulk polymer values. All the aromatic condensation polymers (i.e. PET, PC and PI) had slightly higher RI values than the bulk polymer. However no other surface analysis of the films was presented.

Size exclusion chromatography (SEC) of PMMA films gave molar masses which depended on the laser wavelength used. As the laser wavelength increased (i.e. lower photon energy), the molar mass of the deposited film increased. The authors concluded that the polymers ablated by a photochemical mechanism at the UV wavelengths. These wavelengths produced substantial but incomplete depolymerization of the target and resulted in the direct transport of small polymer chains. This idea was supported by the observation that all UV absorbing polymers produced films, even those not expected to cleanly depolymerize (e.g. PI). At the longer wavelength (1064 nm), the ablation mechanism was thermal in character. Since a high molar mass was obtained in the PMMA films at this wavelength, the authors reasoned that these species were transported by entrainment following subsurface excitation of absorbing impurities.

Although this study was the first one to demonstrate the use of laser excitation for polymer film deposition, it suffered from several lacunae. First, since the scope of the study was so large (several different polymers and laser wavelengths), no single system was studied in any great detail. Second, only a cursory surface analysis of the deposited

films was presented and since this was the main focus it was a severe shortcoming in the study.

A later report published by the same authors examined the 248 and 1064 nm ablation of polycarbonate in-depth [57]. Measurements of the time-of-arrival (TOA) of ablation products at the substrate indicated that ablation at 248 nm did not involve direct evaporation of small polymer chains. The ablation products were found to travel too fast to have a mass above a few hundred (120 ± 40) a.m.u. IR scans of the deposited film were similar to the starting material. The only difference, as found by gel permeation chromatography was a severe molar mass degradation. In light of these results the authors concluded that the ablation mechanism must involve extensive depolymerization by the laser pulse, transport of the moderate sized fragments and repolymerization on the substrate. However the authors also mentioned that the TOA analysis did not exclude the presence of species heavier than 120 a.m.u, which could also contribute to the repolymerization mechanism.

The above study pointed the way for further research in this field. Research has focussed on addition polymers like PMMA and PTFE for which degradation and repolymerization schemes have been studied.. Condensation polymers like PET, PI and PC although attractive from a thin film standpoint have complex structures and degradation pathways are as yet not well understood.

PTFE. The good mechanical, thermal and chemical stability of PTFE combined with its low surface tension have made it an attractive candidate for use in thin films and surface modification. PLD, along with vacuum sputtering, ion deposition and plasma polymerization have all been investigated as synthesis methods. Blanchet and Shah

reported on the deposition of amorphous fluoropolymers by ablation with 266 nm laser pulses [58]. Amorphous copolymers of PTFE with 2,2-bis(trifluoromethyl)-4,5-difluoro-1,3-dioxole (Telfon AF) were used as target materials. Dioxole contents of 66 and 82% were employed to give copolymers with glass transition temperatures of 160 and 240°C respectively. The films were deposited in argon atmospheres of 50-250 mTorr, with energy densities ranging from 0.4-1.2 J/cm². It was found that the substrate temperature had a great effect on the resultant film quality. Films deposited at room temperature formed a low-density sponge-like structure. In contrast, by maintaining the substrate temperature at or above T_g, films with a smooth morphology were obtained. IR spectra of the films showed a one-to-one correspondence with the starting material. The peak widths for the deposited films were also in the same proportion as the target indicating that all the species were present in the same concentrations as the starting material. This implied that at least a fraction of the complex dioxole structure was not fragmented during the ablation. The authors concluded that the ablation proceeded via a thermal unzipping of PTFE chains and transport of the intact dioxole molecule with CF₂ fragments to the heated substrate, followed by repolymerization.

Blanchet *et al.* also studied the ablation of PTFE at 266 nm [59]. PTFE films were produced at an energy density of 1.5 J/cm² in an argon atmosphere of 250 mTorr. The substrate temperature was kept constant at 320°C. Surface analysis of the films showed them to have an F/C ratio of 2. XRD patterns of the films corresponded to the standard helical configuration of PTFE. The films were estimated to be 50% crystalline from DSC measurements. The mass spectrum of ablation products of PTFE was found to

match that of vacuum pyrolyzed PTFE, leading to the conclusion that the ablation proceeded by a thermal mechanism.

Subsequent to this work, other studies have attempted the laser deposition of PTFE with the goal of producing smooth, adherent, crystalline films with good dielectric properties. Ueno *et al.* studied the PLD of PTFE at 157 nm using an F₂ laser [60]. Since the photon energy at 157 nm is higher than the binding energy of the C-F bond it was expected that unselective bond scission would ensue during the ablation process. Film depositions were carried out in an argon atmosphere at 250 mTorr with energy densities in the range 450-600 mJ/cm². Films were grown at two different substrate temperatures of 300 and 373 K. X-ray photoelectron spectroscopy (XPS) C_{1s} spectra revealed that films with predominantly CF₂ bonding were produced at both the substrate temperatures. The CF₂ contents were 70 and 92% for the substrate temperatures of 300 and 373 K respectively. The film morphology was found to be strongly dependent on the substrate temperature with smooth films being produced at the higher temperature. RI values obtained by ellipsometry were similar to those of PTFE targets. XRD scans showed that films deposited at 300 and 373 K were crystalline in nature. One significant finding of this study was the effect of pressure on the resultant film. Films deposited in 10⁻⁵ Torr were amorphous and XPS C_{1s} spectra exhibited C-F, CC-F bondings. The authors reasoned that the frequent collisions taking place at a higher pressure (200 mTorr) started the repolymerization process resulting in a stoichiometric film, whereas at the lower pressure there would be no plume interactions and the various species would arrive at the substrate as is causing random repolymerization reactions.

Norton *et al.* studied the morphology and crystallinity of PTFE films formed by laser ablation [61]. Films were produced by irradiation of PTFE targets with 248 nm laser pulses, in the energy density range of 3-9 J/cm² at a rate of 30 Hz. The films were deposited in vacuum at base pressures of 10⁻⁶-10⁻⁷ Torr. The primary effect was seen to be due to the substrate temperature. As the substrate temperature increased from 200 to 350 °C the amount of crystalline material in the film increased. At temperatures below 200 °C amorphous films were produced. The authors suggested that the crystallinity of the films changed with the substrate temperature during deposition due to the fact that as the melting point of PTFE is approached, there would be sufficient molecular mobility to allow orientation of the chains into a crystal. TEM images of the films also showed the presence of two kinds of crystalline regions contained in one film. Small crystallites (~ 5 nm diameter) and larger crystalline regions (~ 60 nm diameter) were found. Electron diffraction patterns were consistent for the long chains lying in the film-substrate interface plane. This study thus confirmed earlier data that suggested that substrate temperature controlled the film crystallinity.

Similar results were obtained by two other studies which are only briefly mentioned here. Metal *et al* deposited PTFE films using 248 nm laser pulses, with energy densities of 0.5-3.2 J/cm² at 5 Hz [62]. Argon atmospheres were used to control the pressure between 75-300 mTorr. The substrate temperature ranged from 25-270°C. Based on an optimization study the following conditions were found to give the best films : energy density 2.0 J/cm², pressure 10 Pa, substrate temperature 60°C above the T_g.

Li *et al.* studied the effect of different targets on the film characteristics for the 248 nm ablation of PTFE [63]. It had been suggested that for pressed PTFE targets (vs.

polished PTFE targets) film formation was based on the transport of PTFE grains from the target to the heated substrate surface and the subsequent melting and crystallization of the material. Thus two kinds of PTFE targets were used: polished pellets cut from a PTFE rod stock and pressed PTFE powder pellets. The grain size of the PTFE powder was about 6-9 μm . The deposition conditions used were: energy density 0.5-6 J/cm^2 , repetition rate 1-10 Hz, substrate temperature 300-550°C. Depositions were carried out in an Argon atmosphere at a pressure of 0.1 to 1.0 mbar. The powder targets gave films with superior properties compared to the polished rod targets. Smooth continuous films were formed with the powder targets. Increasing the substrate temperature above 300°C produced films with well defined spherulite morphology. Post-deposition annealing of the powder target films caused an improvement in the morphology and favoured spherulitic growth laterally upto 100 μm . These films exhibited good adhesion to the substrate and passed the Scotch peel test. The rod targets produced rough films with many particulates. In the Scotch peel test, these films exhibited cohesion failure i.e. large particulates would be peeled off the surface. The authors suggest that the laser irradiation of powder PTFE targets caused transfer of complete PTFE grains to the heated substrate, whereon films were formed due to melting and recrystallization. On the other hand the laser irradiation of polished PTFE targets resulted in rapid depolymerization and ejection of low molar mass fragments which repolymerized on the substrate. Since no examination of the targets after laser ablation was carried out, this theory cannot be confirmed. It should be mentioned that the films produced from the powder targets were of remarkable quality and exhibited high crystallinity, excellent dielectric strengths ($1\text{-}3 \times 10^5 \text{ V}/\text{cm}$) and high electric resistivity ($10^{12} \Omega\text{m}$). Also the deposition rates achieved

were higher than those produced by comparable synthesis methods like vacuum evaporation, plasma polymerization and sputtering.

Brannon *et al.* reported an interesting result for the laser ablation of a plasma polymerized fluoropolymer film [43]. It was found that the plasma fluoropolymer underwent efficient ablation at energy density levels which cause very little change in PTFE. The principal difference between this polymer and PTFE was the plasma polymer's much greater absorption coefficient (7×10^4 vs. $\sim 10^2 \text{ cm}^{-1}$). A plot of the ablation depth per pulse versus energy density indicated the threshold for energy density to be 50 mJ/cm^2 . Below the threshold the ablation rate curve could be fit by a single Arrhenius-type exponential suggesting that the ablation process in the low energy density regime was partially governed by a photothermal process. This study demonstrated the importance of the polymer absorption coefficient in defining the ablation conditions.

PMMA. Blanchet produced thin films by ablation of PMMA with a Nd-YAG laser at 266 nm [64]. Energy densities used ranged from $0.2\text{-}0.5 \text{ J/cm}^2$, with a repetition rate of 10 Hz. Films were deposited in an argon atmosphere at 200 mTorr. Examining the effect of substrate temperature on film formation, it was found that film morphology was strongly dependant on the substrate temperature. PMMA films deposited at room temperature appeared hazy and adhered poorly to the substrate. These films appeared to be composed of fairly spherical particles of various sizes forming a loosely packed matrix. In contrast, films deposited at 150°C were dense, clear and exhibited excellent adhesion. Film thickness as a function of the deposition temperature showed a decreasing trend, especially after the substrate exceeded the T_g of PMMA. This was due to the large densification which the films underwent at elevated substrate temperatures.

IR spectra of these films corresponded closely with that of a PMMA reference thus showing that the structure remained the same although the morphology underwent a change due to the deposition temperature. Another important result was the molar mass dependence of the film on the deposition temperature and pressure. Films were deposited from targets with molar masses of 500,000 g/mol and 5820 g/mol at background pressures of 10^{-7} Torr and 250 mTorr and temperatures in the range of -196°C to 250°C . Molar masses of the films were determined by gel permeation chromatography after dissolving them in tetrahydrofuran. At low temperatures molar mass was found to be independent of temperature while it increased linearly above T_g . M_w 's were about 10^4 g/mol for temperatures ranging from -196°C to $+80^{\circ}\text{C}$, increasing linearly to 6×10^4 g/mol at 175°C . Surprisingly, the different targets gave films of similar molar mass under identical conditions. The deposition pressures also caused a change in the molar mass. Using the target with a molar mass of 500,000 g/mol gave a film with molar mass of 325,000 g/mol when deposited 10^{-7} Torr and 175°C . The same target gave a film with a molar mass of 60,000 g/mol when deposited at 250 mTorr and 175°C .

Blanchet explained these results on the basis of changes in radical and chain mobility. Since low molar mass, hazy and low-density films deposited at lower temperatures could be converted to dense clear films by annealing it implied that chain mobility played a role in determining film morphology. As the substrate temperature was increased during deposition, the ablation product molecules arriving onto the substrate would have enough energy to add to the growing chain. Thus high molar mass, dense and clear films could be produced at higher deposition temperatures. Mass spectrum analysis of the ablation products matched closely with those for vacuum pyrolyzed

PMMA. Thus the ablation mainly produced MMA monomer which then proceeded to polymerize via a radical mechanism after arriving on the substrate. Also the threshold energy density for PMMA was estimated as 40 mJ/cm^2 based on the abundance of monomer species detected in the mass spectrometer at that energy density. Blanchet also stated that the energy density had no effect on the kind of films produced. This result is different from an earlier report which showed the formation of a carbon-rich film during ablation of a PMMA target. Since surface analysis of the deposited films was not presented energy density effects could not be commented on.

Based on their results for laser ablation of PMMA and PTFE, Blanchet and Fisher offered the following theory of ablation [65]. Upon laser irradiation of the polymer, photon energy initially absorbed as electronic excitation is converted to vibrational modes, rapidly heating the solid. This intense local heating results in pyrolytic decomposition of the target via rapid unzipping of the polymer chains. An ablation plume consisting of monomer fragments is explosively ejected off the surface. On arriving at the substrate repolymerization occurs to give a polymer film. The similarities between compositions of the ablation plume and pyrolysis products suggested that PTFE and PMMA ablation occurred via the above mechanism. Also for simple addition polymers, which are known to depolymerize by unzipping, the ceiling temperature (T_c) plays an important role in film formation. Since the ceiling temperatures of PMMA and PTFE are 320 and 720°C respectively, the thermolyzed monomer molecules impinge upon the substrate well below T_c . To test this theory, the authors ablated poly (α -methyl styrene) which is known to thermally unzip during pyrolysis. Analysis of the ablation products by mass spectroscopy showed the presence of monomer and dimer species only.

However, films of poly (α -MS) could not be formed by this process. Since the T_c of this polymer is 61°C it was theorized that the ablation products would arrive at the substrate with vibrational energies corresponding to much higher temperatures. Thus there would not be enough driving force for the repolymerization reaction. However this theory was not tested by performing a deposition at a substrate temperature substantially below the T_c . Later reports have since shown the ablation products of PMMA to be much more complex indicating a different ablation pattern than simple unzipping. Thus it is almost certain that the ablation proceeds by mechanisms which are more complex than the simplistic one presented by Blanchet and Fisher.

SI-based polymers. Suzuki *et al.* used PLAD to synthesize silane based polymer films from poly(methyl phenyl silane) (PMPS) [66]. It was found that for the 248 nm irradiation of PMPS, most of the Si-Si bonds in the polymer were converted to Si-C bonds in the deposited films and new bonds like Si-H were also present. The deposited films suffered a molar mass reduction and showed a broader distribution than the starting polymer. The molar mass distribution was also found to be dependant on the energy density.

Natural Polymers and Biomolecules. Several other polymers have also been used for thin film syntheses by laser ablation. These include polyacrylonitrile [67], poly(phenylene sulphide) [68],[69], polythiophene, polyethylene and polyethylene oxide [70]. These studies have demonstrated the feasibility of using this technique for producing polymer thin films.

Due to the interest in producing biocompatible coatings, PLD of collagen and proteins has also been attempted. Conklin and Cotell have reported the PLD of collagen

and apatite/collagen composite thin films [71]. Films were deposited under varying conditions from fibrous collagen targets alone and mixtures of hydroxyapatite (HA) and collagen. An ArF or KrF excimer laser was used in all the depositions in the energy density range of 0.2-1.5 J/cm², in an argon atmosphere. The effect of water in the deposition environment was also assessed by bubbling argon through water before introducing it into the chamber. Surprisingly, it was found that varying the conditions had little effect on the IR spectra of the collagen films. However, the deposition conditions did affect surface morphology with lower energy density levels producing smoother films. Gel electrophoresis and IR results indicated that films were comprised of collagen with an altered secondary structure and possibly shorter chain lengths. XRD analysis revealed a broad amorphous reflection regardless of deposition parameters indicating that the process did not introduce crystallinity in the films. It was also found that water vapor increased the smoothness of the surface while the IR spectra did not show any change. XRD analysis of the HA/collagen composite films revealed that the HA in the deposited film was crystalline. This result was unexpected since the deposition was carried out at room temperature, where amorphous HA is produced. The authors suggest that the presence of collagen in the target causes immobilization of the nucleating calcium species on ablation causing it to crystallize.

Tsuboi *et al.* used PLD for the thin film deposition of a silk fibroin polypeptide[72]. This protein is being investigated for its potential applications in molecular devices and bioelectronics. The PLD method was attractive due to the poor solubility of silk fibroin in many common solvents. The polypeptide target was ablated with an excimer laser at 351 or 248 nm at an energy density level of 700 mJ/cm². IR

spectra of the film deposited at 351 nm showed correspondence with that of the starting polymer. Hence the primary structure of the protein was successfully reproduced in the film. However new absorption bands were seen for films deposited at 248 nm, indicating that part of the structure was destroyed. Atomic force microscopy revealed the deposited film to consist of particles, with smaller particle sizes being produced at 248 nm than at 351 nm.

The above examples of PLD of natural molecules to produce organized structures are certainly thought provoking. As an extension of the idea, Phadke and Agarwal have reported on the PLD of preformed structures of organized molecules [73],[74]. Lasers were used to ablate glucose oxidase dissolved in a sodium dodecyl matrix. The deposited films were shown to retain their enzymatic activity. Similarly, films of Riboflavin were synthesized by this method. It was shown that the native properties such as fluorescence and absorption characteristics remained intact in the films. These examples open the possibility of a solvent free route to produce complex film structures in a desired architecture. The above applications hold particular relevance for device fabrication.

Surface Modification by Laser Ablation

One of the other major application of laser ablation has been for polymer surface sensitization. Laser irradiation can produce surface regions with an altered surface chemistry as compared to the bulk polymer. Furthermore the degree of control which can be exercised using lasers gives modified regions with features on the order of micrometers. Applications of this technique reported in the literature include chemical patterning, metal deposition and surface functionalization.

Metallization of PTFE and other fluoropolymers has offered new applications in the area of electronic packaging. However, due to its chemical inertness, adhesion to PTFE is poor. Latsch *et al.* have studied metal deposition on laser modified PTFE surfaces [75]. PTFE was ablated while immersed in a solution of tetramethylammonium hydroxide (TMAH). It was found that even after ablation at low energy densities (50-120 mJ/cm²) PTFE surfaces turned hydrophilic. XPS spectra of the ablated surface showed the presence of nitrogen and oxygen, indicating that TMAH bonding had occurred. The formation of hydrophilic groups was also accompanied by defluorination. Copper deposited on these modified surfaces exhibited stronger adhesion as compared to copper deposited on virgin PTFE. A similar study has reported on the modification of a fluorocarbon surface by an ArF excimer laser in gaseous N₂H₄ for electroless deposition of copper and nickel.

Copper metallization was attempted using an ArF excimer laser to irradiate a fluoro-copolymer (FEP) film immersed in an aqueous copper sulfate solution [76]. The irradiation of the polymer caused defluorination and copper was nucleated on the ablated regions through the formation of C-O-Cu bonds. The authors suggested that oxygen plays an important role in polymer-metal adhesion. It was also found that energy densities in excess of 25 mJ/cm² gave lower copper nuclei density due to surface roughening. Thus the technique works only due to photochemical reaction and fails when ablation starts to occur.

Niino and Yabe have used laser irradiation to induce dehydrochlorination on a polyvinylidene chloride (PVDC) film to produce conjugated polyene and polyyne structures [77]. Usually chemical reagents such as metal amalgams, potassium

hydroxide, electrochemically activated tert-butanol etc. are used for the dehydrochlorination reaction. However these reactions leave salt of acid or base remains in the modified polymers. KrF excimer laser irradiation of PVDC at a energy density of 30 mJ/cm^2 was found to efficiently produce conjugated carbon bonds without graphitization and crosslinking between main chains. The conjugated structures have applications as materials for nonlinear optical devices.

Song and Netravali used excimer lasers to modify the surface of ultra-high strength molar mass polyethylene (UHSPE) fibers for enhanced adhesion in composites[78]. Using a XeCl excimer laser operating at 308 nm, UHSPE fibers were exposed to a number of laser pulses at energy density levels of 280, 450 and 768 mJ/pulse cm^2 . The number of pulses ranged from 100 to 500. Laser exposure was found to produce surface roughening of the fibers. The degree of roughening depended upon the number of pulses and the energy density level. The fibers became more polar after surface treatment and exhibited an increased oxygen content. The interfacial shear strength increased significantly and this enhancement was attributed to the increased surface roughness and polarity of the fiber. It is worth noting that energy density levels used in this study are much higher as compared to the 3 studies mentioned above. The high energy density levels would cause significant ablation of the polymer surface, in contrast to the low energy densities mentioned earlier which would only cause surface modification.

Another novel application of laser ablation has been in stripping of polymer insulation of metal wires. Brannon and Synder have studied the removal of polyurethane insulation by pulsed laser irradiation [79]. They found that excimer lasers produced

cleaner, higher quality insulation removal as compared to carbon dioxide lasers. The improved performance of the excimer lasers was due to the increased absorption of the ultraviolet radiation by the polymer insulation. They also found that doping the insulation with rhodamine G6, a photosensitizer and irradiating it with a 532 nm frequency doubled Nd:YAG laser produced similar results to the excimer laser irradiation. A dye loading of 10% gave efficient stripping at an incident energy density of 650 mJ/cm^2 , a pulse duration of 12 ns and an exposure of 3-5 s at 10 Hz.

Thus it can be seen that the true potential of laser processing of polymers has been realized only recently. The list of applications which are being targeted is ever increasing and it is expected to be a promising and fruitful area of research [80-82].

Silicone Films and Coatings

Silicone is the generic name for a variety of silicon based polymers which consist of Si-O main chain linkages with organic (methyl or otherwise) groups connected to the Si atoms. Silicone can be synthesized in a number of forms such as fluids, gels, and elastomers. Depending on the desired application, the structure can be tailored to incorporate different chemical groups e.g. phenyl groups for structural rigidity, cyclic siloxanes for higher viscosity, fluorocarbons for low surface energy. The molar mass can also be varied from 500 g/mol to 750,000 g/mol. Polydimethylsiloxane (PDMS) is the most commonly used silicone. The outstanding properties of PDMS arise in part due its structure [83]. The Si-O linkage has a high freedom of rotation which imparts flexibility to the structure. The methyl groups connected to the Si atoms have a large volume of exclusion which imparts chemical inertness and low surface energy to the polymer.

Silicone use in the biomedical field started in the 1950s [84]. The most well-known (and controversial) example of their use has been in silicone gel breast implants. Other applications include catheters, tubing, blood bags, soft tissue implants, intraocular lenses and encapsulation compounds. The haemocompatibility of silicone has also been studied widely. The Cooper group has produced a series of reports evaluating the blood-contact properties of a host of polymeric biomaterials [85-87]. In a recent study, a series of silicone surfaces were systematically modified by siloxane coupling agents with different chemical end-groups like alkyl, amine and fluorocarbon [88]. These surfaces were then evaluated for their blood compatibility in a canine ex-vivo shunt. It was seen that the unmodified silicone surface gave the best haemocompatibility in terms of low platelet adhesion and longer clotting times.

Although silicone has excellent biocompatibility, its poor mechanical properties preclude its use in any structural biomaterial applications like vascular grafts. Thus research efforts have concentrated on producing silicone thin films and coatings. The most common synthesis route is by the plasma polymerization of various siloxane or silazane monomers. Comprehensive reviews on this topic have been published [89],[90]. Plasma polymerization typically produces a cross-linked, branched polymer with molecular structures which are frequently altered compared to the starting monomer. Plasma polymer films may also contain trapped radicals, which can react on exposure to atmosphere, changing the film surface over a period of days or even months. This can lead to a deterioration in the film properties. Also, such films may be under tensile stress leading to cracking or peel-off from the substrate. Therefore the properties of these films can be quite different than those desired of a siloxane polymer.

To overcome some of these limitations, Kwan and Gleason used a pyrolytic process to synthesize silicone thin films [91]. It was seen that the low-pressure thermolysis of octamethyltetrasiloxane (commonly known as D₄) produced films with structures similar to PDMS. Roth *et al.* used excimer lasers to crosslink PDMS copolymers in the liquid phase and also to produce silicone films by the laser-induced chemical vapor deposition from the gas phase [92]. These studies demonstrated that silicone thin films could be produced by methods other than plasma polymerization.

The unique combination of properties of polydimethylsiloxanes (PDMS) has led to their use as coatings in a variety of fields including biomaterials, membranes, optics and dielectrics. Newer applications such as barriers for flame retardancy [93] and passivation of high T_c superconductors[94] have also been reported. Due to their toughness, low surface energy, low and high temperature stability, unique gas permeability and low dielectric constant, it is envisioned that silicone thin films will continue to find new applications and therefore research on synthesizing these films would be a promising area.

The research presented herein explores the use of pulsed laser ablation deposition of silicone for synthesizing thin films. It is believed that this new method would have significant advantages over current methods in synthesizing these films.

CHAPTER 3

PULSED LASER ABLATION DEPOSITION OF SILICONE

Introduction

As previously noted, the pulsed laser ablation deposition (PLAD) of silicone or other cross-linked polymers for that matter had not previously been reported. Thus there was a lack of experimental parameters on which to base these studies. From a study of the literature, it was seen that the energy density (i.e. laser energy per unit area incident on the target surface) was the most important factor which controlled the kind of film produced. Therefore, this study chose to examine in detail the effect of the energy density on the deposited film structure and chemistry. Based on the results of this study, the effect of other parameters like laser pulse number and pressure level on film structure and composition was also examined.

Materials

Targets. Silicone targets were prepared in sheet form by casting and curing a two-part resin system (Shin-Etsu KE 1935 A,B) at 70°C for 24 hours with a platinum catalyst to produce a cross-linked elastomer. Figure 3.1 shows the curing reaction for producing the elastomer. Plaques (2.5 cm dia.) were punched out from the sheets and extracted in chloroform for 48 hours to remove soluble unreacted polymer. The extracted plaques were dried under vacuum (12 hours) and mounted on 1 inch dia. aluminum stubs for use as targets.

Substrates. Silicon wafers or 316L stainless steel (1 cm X 1 cm) were used as the substrates in all the depositions. Silicon wafers were cleaned by sequential sonication in acetone and methanol then dried under nitrogen. Steel substrates were cleaned by sequential sonication in 1,1,1 tri-chloroethane, acetone and methanol then dried under vacuum.

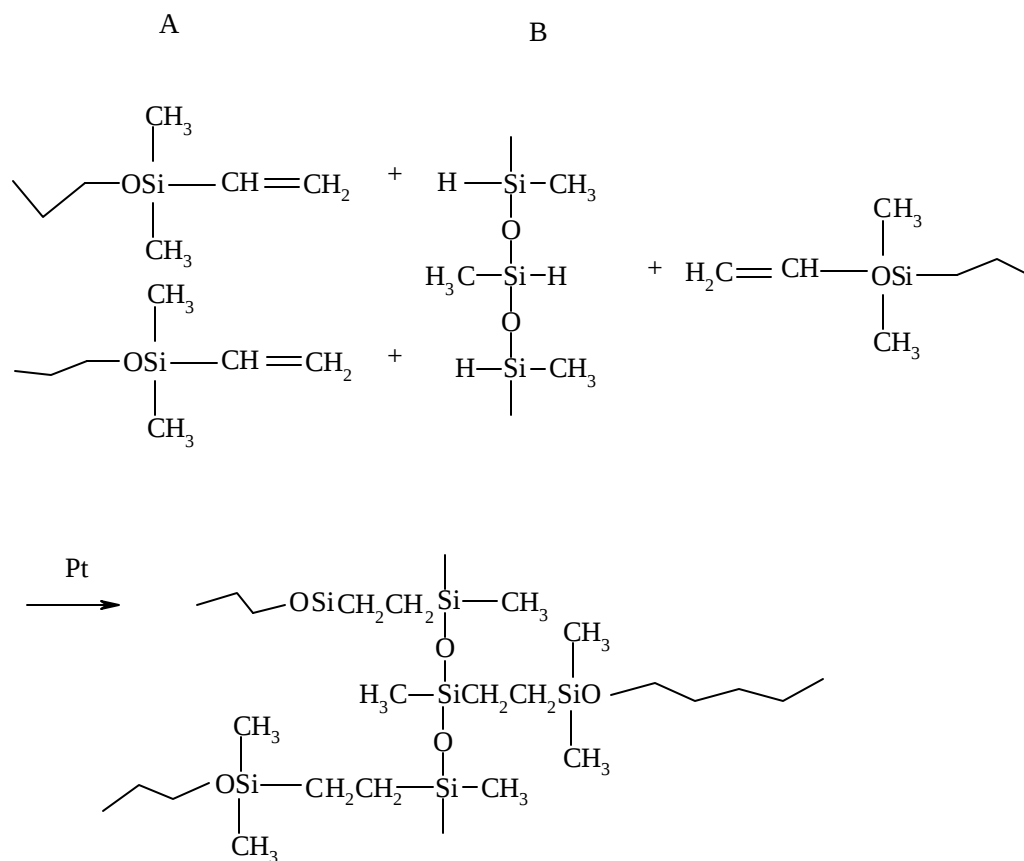


Figure 3.1: Curing reaction for preparing silicone elastomer targets.

Methods

The pulsed laser ablation deposition (PLAD) system consisted of a vacuum chamber which housed the target and substrate. The vacuum chamber was connected to a

mechanical displacement pump allowing the chamber to reach a base pressure of 30 mTorr. The target was mounted on a motor and rotated during each deposition run so as to ensure uniform ablation. A KrF excimer laser (Lambda Physik 301x) operating at 248 nm with a pulse width of 25 ns was used in all the experiments. The laser beam was directed into the chamber by a pair of plane mirrors and a collimating lens. The beam was focussed by a 250 mm focal lens placed at the entrance to the chamber. The laser was operated in the energy range of 100-200 mJ and the energy density was adjusted by moving the focussing lens along a track to get the desired spot size incident on the target. Laser spot size was measured by creating burn areas on thermal paper and measuring the areas with a 10x graduated microscope eyepiece. The eyepiece resolution was 0.1 mm. A joulemeter (Sentec ED 500) was used to measure the incident laser energy inside the chamber. The energy density (also referred to as fluence in the literature) ranged between 75-600 mJ/cm². All depositions were carried out in a Helium atmosphere at a pressure of 100 mTorr and the laser operating at a repetition rate of 5 Hz unless otherwise stated. Figure 3.2 shows a diagram of the experimental setup. Fitz-Gerald [95], provides additional details on the construction and setup of the PLAD chamber.

The procedure for an experimental run was as follows. The substrate and target were mounted in the chamber and the vacuum pump turned on. The chamber was evacuated to < 30 mTorr with two purge fills. The pressure was then adjusted to 100 mTorr by using a helium backfill. After aligning the optics with a He-Ne laser, the excimer was turned on. The target was ablated for the requisite amount of time with the pressure being monitored during ablation. Typically deposition times ranged from 15-20 min, thus giving a laser pulse number range of 4500-6000 (5 pulses/sec x 60 sec x 15-20 min). After the ablation

was complete the chamber was allowed to return to atmosphere by bleeding in helium. The modified substrates were then stored in polystyrene boxes prior to analysis.

Deposition experiments under high vacuum. The chamber setup for the high vacuum chamber was similar to the one described above. The pumping unit included a turbomolecular pump (Pfeiffer TCP 300) backed with a mechanical displacement pump allowing the chamber to reach pressures $< 1 \times 10^{-6}$ Torr. All other arrangements like target and substrate mounts, laser optics, energy density measurements were similar to those described above. The depositions were carried out at a pressure of 1×10^{-4} Torr under a helium atmosphere.

Characterization

Fourier-Transform Infrared Spectroscopy (FTIR). Reflectance absorption FTIR spectra were collected using the microscope stage on a Nicolet Magna 706 FTIR spectrometer. Spectra were collected in the range of $650\text{-}4000\text{ cm}^{-1}$ with a spectral resolution of 4 cm^{-1} , averaging 200 scans per sample. Each spectrum was corrected for carbon dioxide and water absorption since data collection was carried out in laboratory atmosphere. An uncoated steel sample was run as a baseline and used for all baseline corrections. It should be mentioned that attempts at collecting spectra in the Attenuated Total Reflection (ATR) mode of the FTIR failed due to contact problems of the substrate with the ATR crystal.

Contact Angle Goniometry. Static contact angles were measured using the captive air-bubble technique with ultrapure water as the immersion liquid on a Ramé-Hart A-100 goniometer. Measurements were taken on both sides of a $2\text{ }\mu\text{L}$ air bubble with five

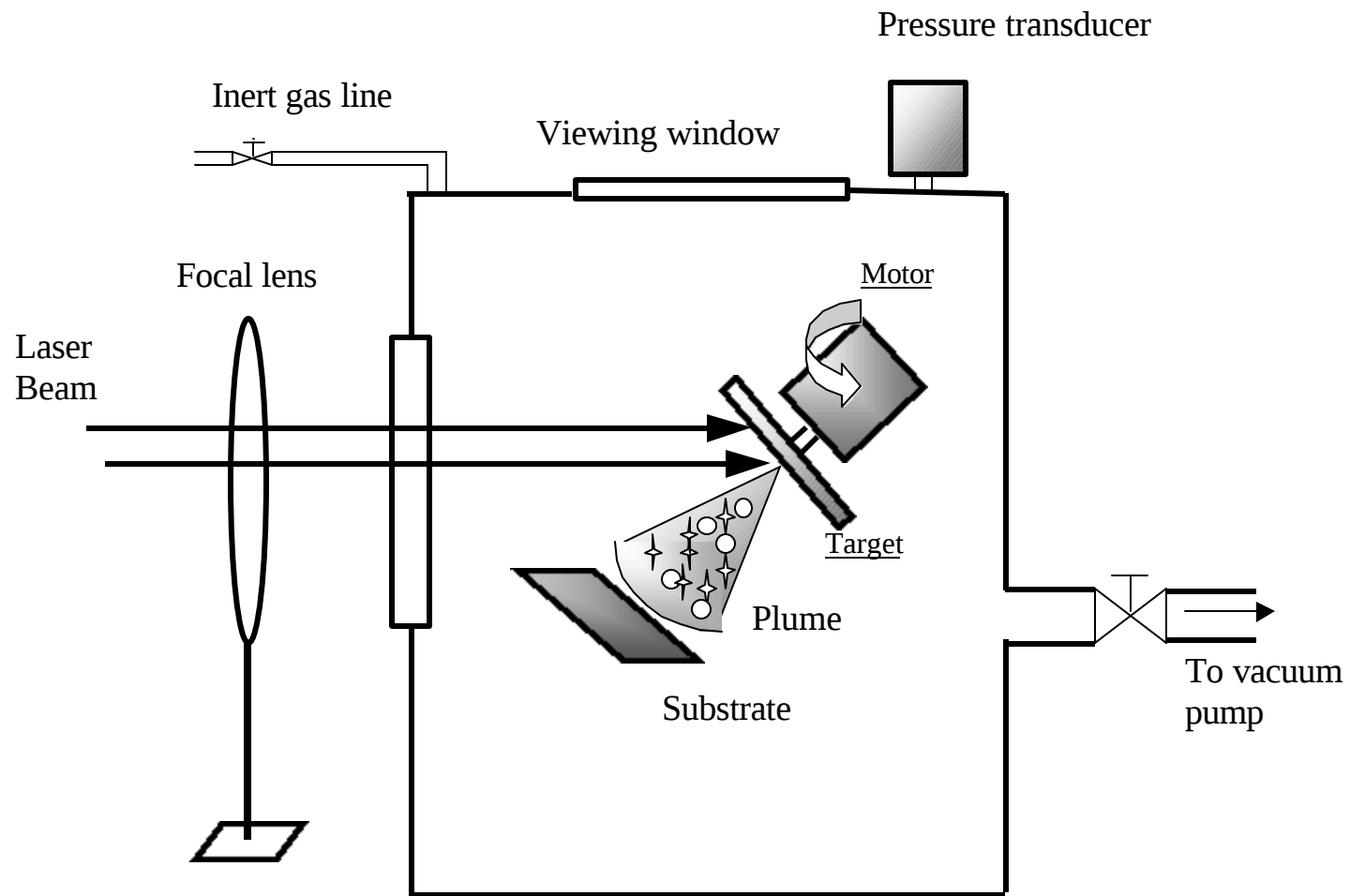


Figure 3.2 Schematic diagram of the vacuum chamber setup for the PLAD process.

bubbles being measured for each sample. Each reported contact angle is an average of these measurements.

X-Ray Photoelectron Spectroscopy (XPS). XPS was performed using a Kratos XSAM 300 spectrometer. This system consists of a Mg K α x-ray source ($h\nu = 1253.6$ eV), a hemispherical analyzer and a multichannel detector. The X-ray source was operated at a power of 108 W. A pass energy of 25 eV was used for spectral collection. All spectra were collected at a photoelectron takeoff angle of 90°. High resolution elemental spectra were used for quantitative analysis. Peak quantification was done by using the peak integration package of the DS800 software.

Scanning Electron Microscopy (SEM). The film morphology was observed with a JOEL 6400 electron microscope, operated at an accelerating voltage of 5 kV, an aperture setting of 2-3 and a condenser lens current range of 8-9 nA. A thin film of Au/Pd was sputtered on all samples prior to examination.

Stylus Profilometry. Film thickness was measured by masking a portion of a silicon wafer with Teflon® tape during deposition and measuring the resulting step height by a stylus profilometer (Tencor Alpha Step 500). The conditions for measurement were: scan length of 500 μm , stylus force of 8.3 mg and scan speed of 50 $\mu\text{m/s}$.

Results

Effect of Energy Density

Films were deposited at different energy densities and analyzed by FTIR, XPS, SEM, Contact angle goniometry and Profilometry.

FTIR. Figure 3.3 shows the FTIR spectra of PLAD films deposited at energy densities of 100-, 250-, and 510 mJ/cm². The three spectra chosen were representative of low, medium and high energy density levels. Table 3.1 lists all the observed absorbance peaks along with literature assignments. A silicone polymer used as a target is shown for comparison in Figure 3.4.

Table 3.1. FTIR absorbance bands observed for PLAD films along with literature assignments.

	Position (cm ⁻¹)	Assignment and mode	Ref.
I	3400 (broad)	H-bonded OH stretching	[83],[96-97]
II	2970-2925	CH _x asymmetric, symmetric stretching	[83],[96-97]
III	2250-2150	SiH stretching	[83],[96-97]
IV	1260	SiMe _x deformation	[83],[96-97]
V	1215-930	SiOSi asymmetric stretching	[83],[96-97]
VI	900-730	Si(CH ₂) ₃ and Si(CH ₂) ₂ rocking	[83],[96-97]

Depending on the energy density, the spectra exhibit several important differences arising from the ablation process. The spectrum of the film deposited at 510 mJ/cm² (Fig. 3.3c), shows two new absorbance bands due to SiH stretching at 2245 cm⁻¹ and OH stretching in the region 3000-3600 cm⁻¹. The OH stretching peak arises from SiOH bonding, since no other peak due to carbonyl or ester groups (i.e. C-O bonds) is manifested in the spectrum. The existence of these peaks suggests that the laser ablation of silicone at this energy density results in large scale degradation and recombination reactions. The presence of SiOH groups maybe attributed to quenching of free radicals by oxygen and water vapor either *in-situ* or on exposure to atmosphere. The position of the SiH stretching peak at 2245 cm⁻¹ indicates that it is bonded to electron withdrawing substituents i.e. trifunctional siloxane units.

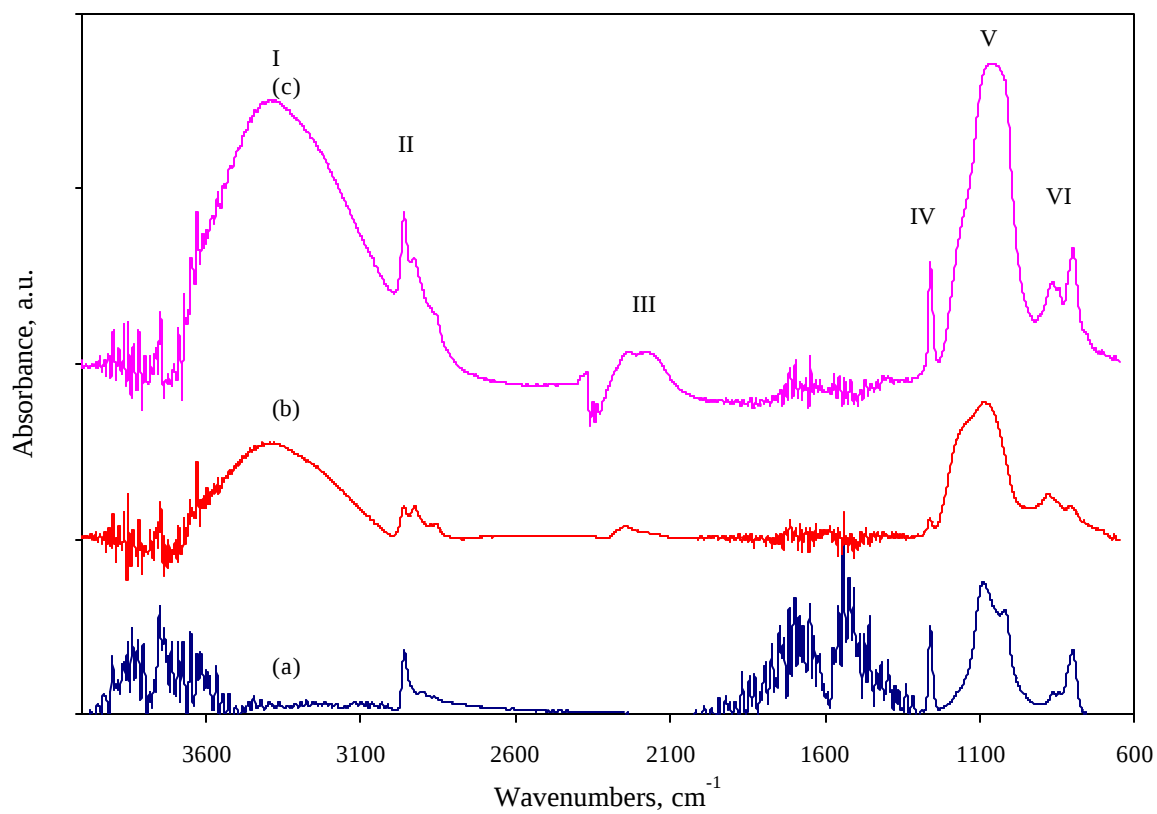


Figure 3.3 Reflectance absorption FTIR spectra of PLAD films deposited at: (a) 100, (b) 250 and (c) 510 mJ/cm².

It is also seen that the Si-O-Si asymmetric stretching peak is broadened which indicates a scrambling in the structure of the Si-O main chain due to distortions, branching and cross-linking reactions. This is seen more clearly in Figure 3.5 which shows an expanded spectrum in the range 700-1400 cm^{-1} . The spectrum for the film deposited at the intermediate energy density of 250 mJ/cm^2 (Fig. 3.3b) shows the same features indicating that the ablation and recombination process is similar at that this energy density level.

On the other hand, the spectrum of the film deposited at 100 mJ/cm^2 (Fig. 3.3a) is substantially different from the preceding examples. The SiH and SiOH peaks seen in the earlier films are absent. Spectral features characteristic of polydimethylsiloxanes including CH stretching peaks at 2925 cm^{-1} , Si-O-Si asymmetric split between 1215-930 cm^{-1} and Si-CH₃ deformation at 1210 cm^{-1} are seen. The peak at 1410 cm^{-1} , indicative of Si-(CH₂)_x-Si bridges is masked due to absorption from water vapor. The Si-O-Si peak (Fig 3.5a) shows clear splitting signifying longer siloxane chains and greater siloxane rings are retained in the film structure. This is also seen by a stronger absorption of the Si(CH₂)₂ peak at 810 cm^{-1} as compared to Si(CH₂)₃ at 875 cm^{-1} , indicating a larger concentration of dimethyl siloxanes compared to trimethyl siloxanes (i.e. chain ends). Figure 3.3a matches the FTIR spectrum shown in Figure 3.4 for the silicone target suggesting that ablation at this energy density level produces a film which is similar to the target polymer.

X-Ray Photoelectron Spectroscopy. Surface elemental compositions of the PLAD films on steel were obtained by high resolution scans for carbon, oxygen and silicon. Iron and chromium peaks from the steel substrate were not seen since the films were thicker than 200 nm.

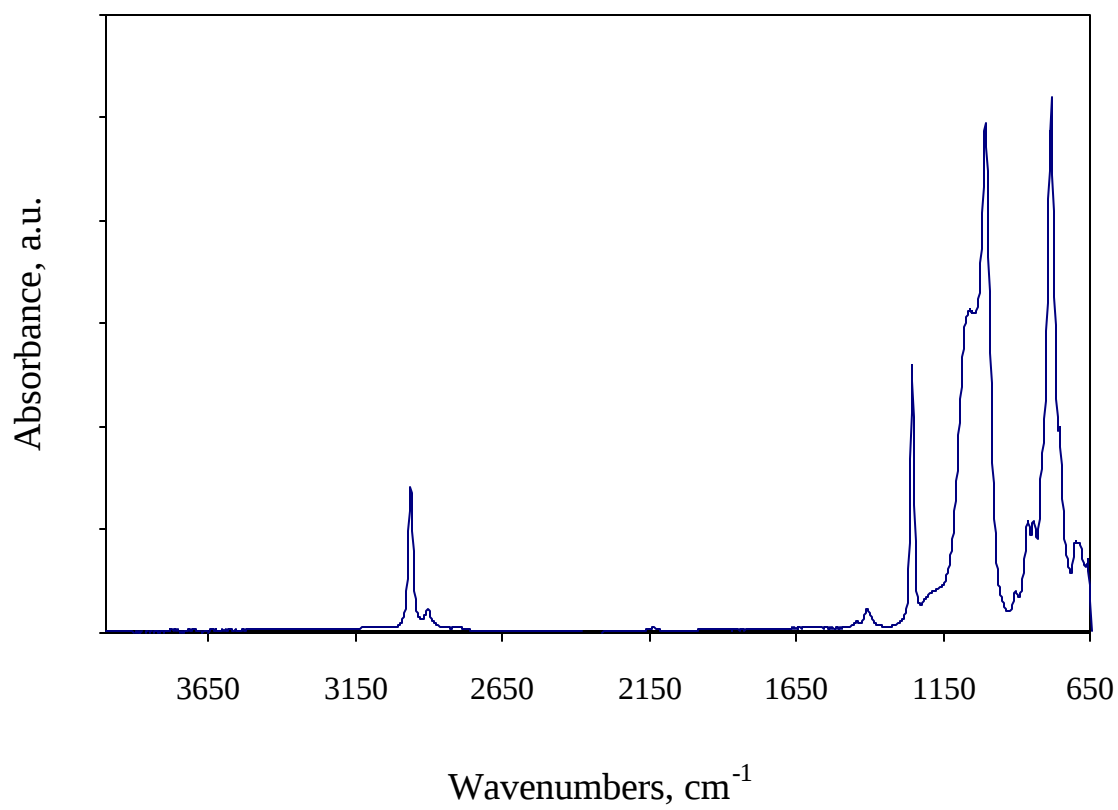


Figure 3.4 Attenuated Total Reflectance –FTIR spectrum of a silicone target.

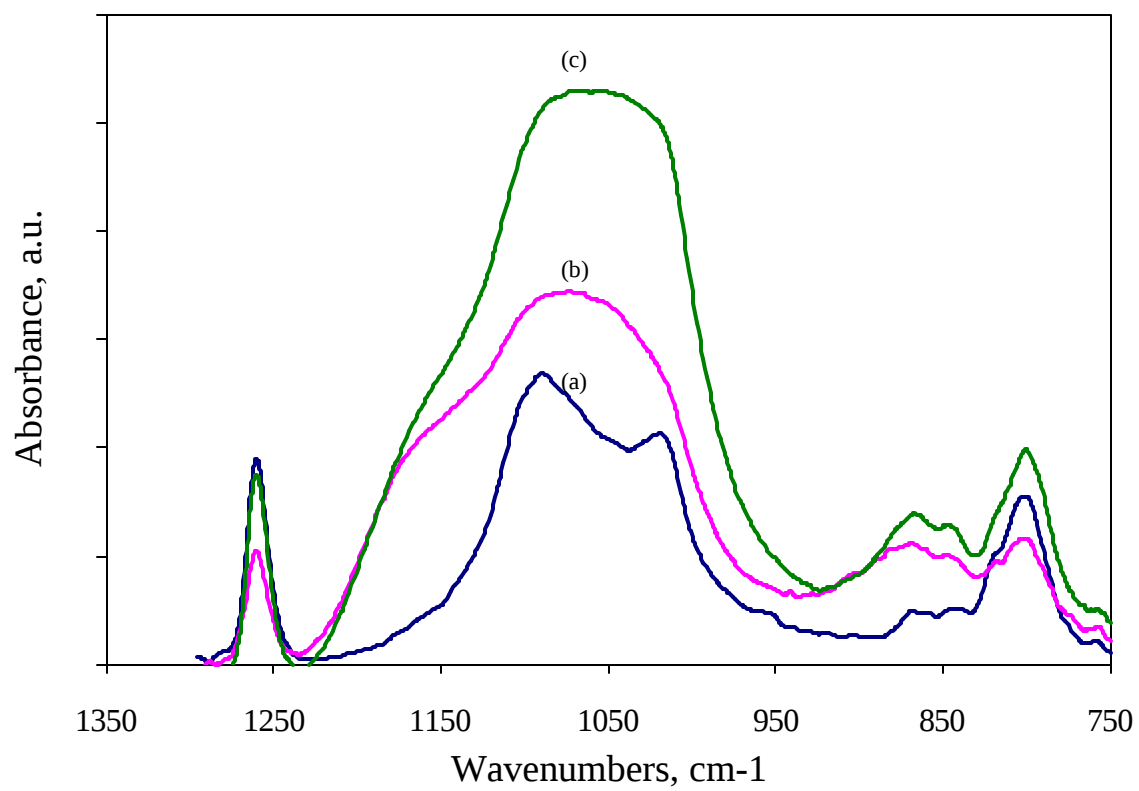


Figure 3.5 Expanded FTIR spectra of PLAD films at different energy densities: (a) 100-, (b) 250- and (c) 510 mJ/cm².

Figure 3.6 shows the % C, % O and % Si values respectively for the PLAD films as a function of energy density. A silicone sample which was used for a target was run as a reference and is shown at zero energy density. The arrow indicates one sample with a very low silicon content, produced at low pulse number. Figure 3.7 shows representative high resolution carbon, oxygen and silicon peaks for the PLAD films. Figure 3.8 shows the high resolution carbon, oxygen and silicon peaks for a silicone sample used as a target.

XPS analyses show that the carbon content of the films decreases while the oxygen content increases with increasing energy density levels. The oxygen levels even at the lowest energy density are higher as compared to the target silicone polymer. This seems to indicate that there is polymer chain scission as a result of the laser irradiation. The chain degradation can lead to free radical generation due to bond-breakage. These radicals can recombine with oxygen in-situ or in atmosphere leading to an increased oxygen content. The radical production can also be due to methyl group abstraction which has been shown to be the primary degradation pathway in plasma polymerization of siloxanes and the thermal degradation of silicone. At low energy density, chain scission and methyl group abstraction may be minimal leading to only a small increase in the oxygen levels. This would mean that longer chains are evaporated off the surface which can then recombine on reaching the substrate. There also seems to be another factor at work at the low energy density level. It is seen that the silicon content is depressed for the films produced at $<150 \text{ mJ/cm}^2$. This seems to indicate that the ablation species produced are depleted in silicon. This could mean that the ablation produces not

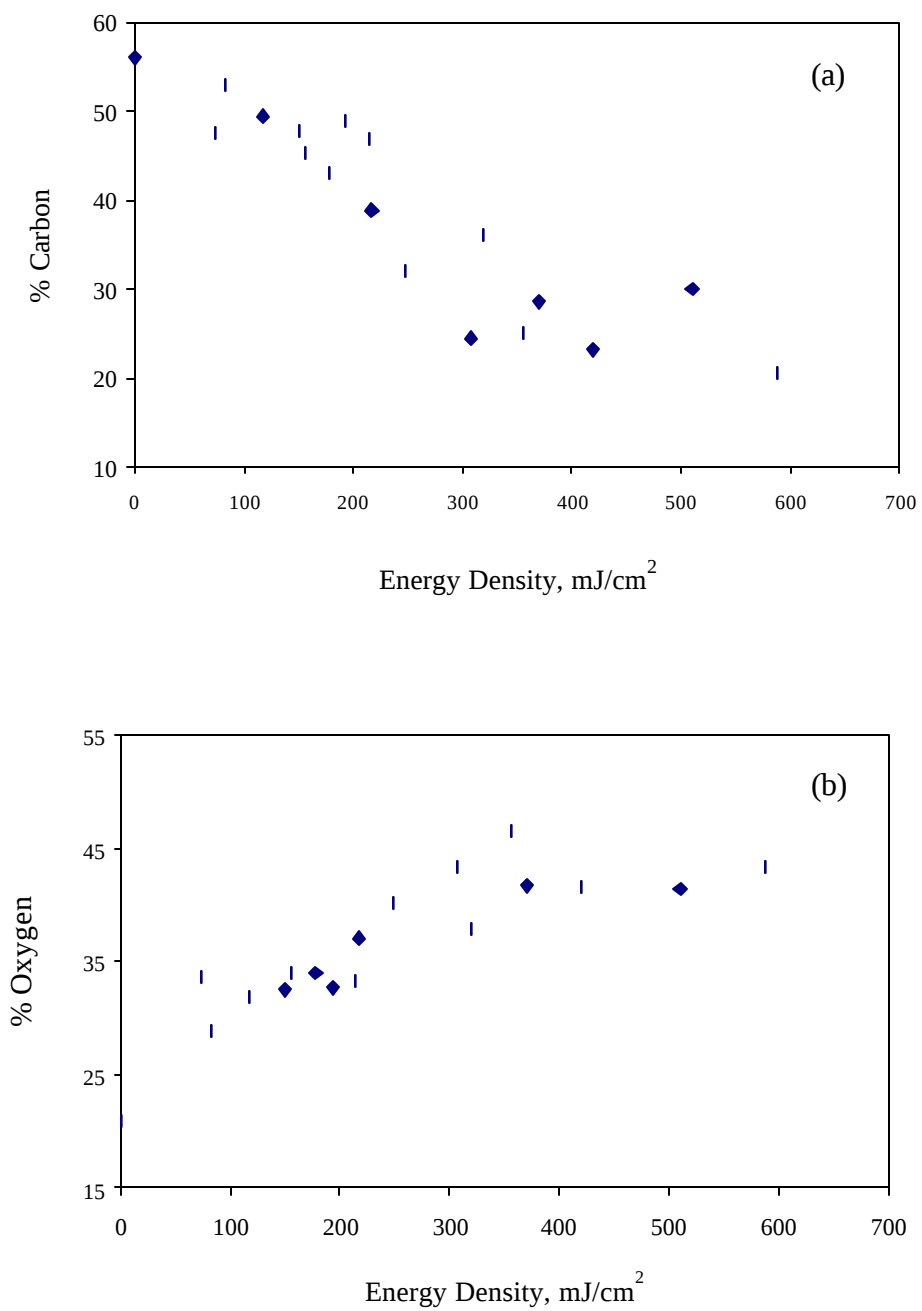


Figure 3.6 Elemental composition of PLAD films as a function of energy density: (a) % Carbon, (b) % Oxygen.

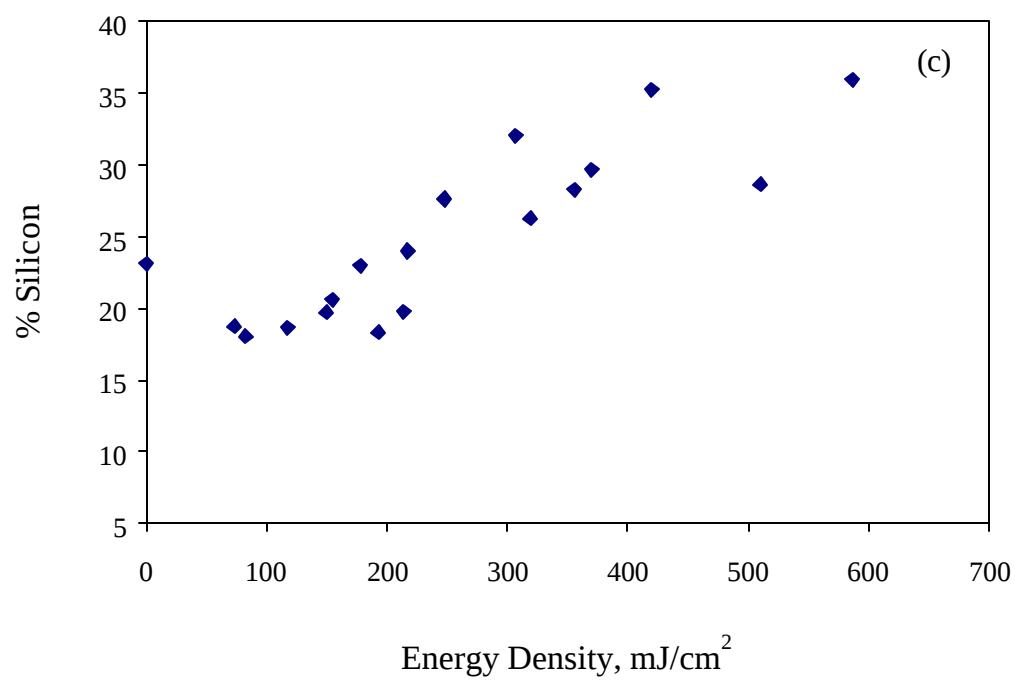


Figure 3.6contd. Elemental composition of PLAD films as a function of energy density: (c) % Silicon.

only polymer chains but also smaller charged molecular and atomic species like *CH_2 and *CH_3 which can get incorporated into the film structure.

Examining the high resolution elemental spectra (Fig. 3.7), it is seen that there is no change in the carbon and oxygen peak shape as a function of energy density. This indicates that no new bonds (e.g. C-O) are formed even after significant fragmentation and recombination. The silicon peak however shows a shift in binding energy depending upon the energy density. The change in the silicon binding energy at different energy densities is plotted in Figure 3.9. A silicone target was also run and the Si2p peak location for this sample is plotted at zero energy density. To minimize the effects of instrument drift these samples were analyzed in a single run in the XPS and the detector was calibrated by setting the carbon 1s peak at 285 eV. Figure 3.9 shows that the Si2p peak shifts to higher binding energy with increasing energy density. This indicates that the binding environment of the silicon atoms is changing [98]. The silicon 2p peak appears at 101.8 eV for silicon polymers and at 103-104 eV for SiO_2 . Thus the shift to higher binding energy in the PLAD films is an indication of the increasing Si-O bonding in the structure.

Contact angle. Figure 3.10 shows the effect of energy density on the contact angle of the deposited films. At low energy densities contact angle is high and approaches that of silicone (shown at zero energy density). As the energy density is increased, the contact angle starts to decrease. A transition is seen in the range of 150-200 mJ/cm^2 , with the films changing from hydrophobic to hydrophilic. Beyond this range all the films exhibit

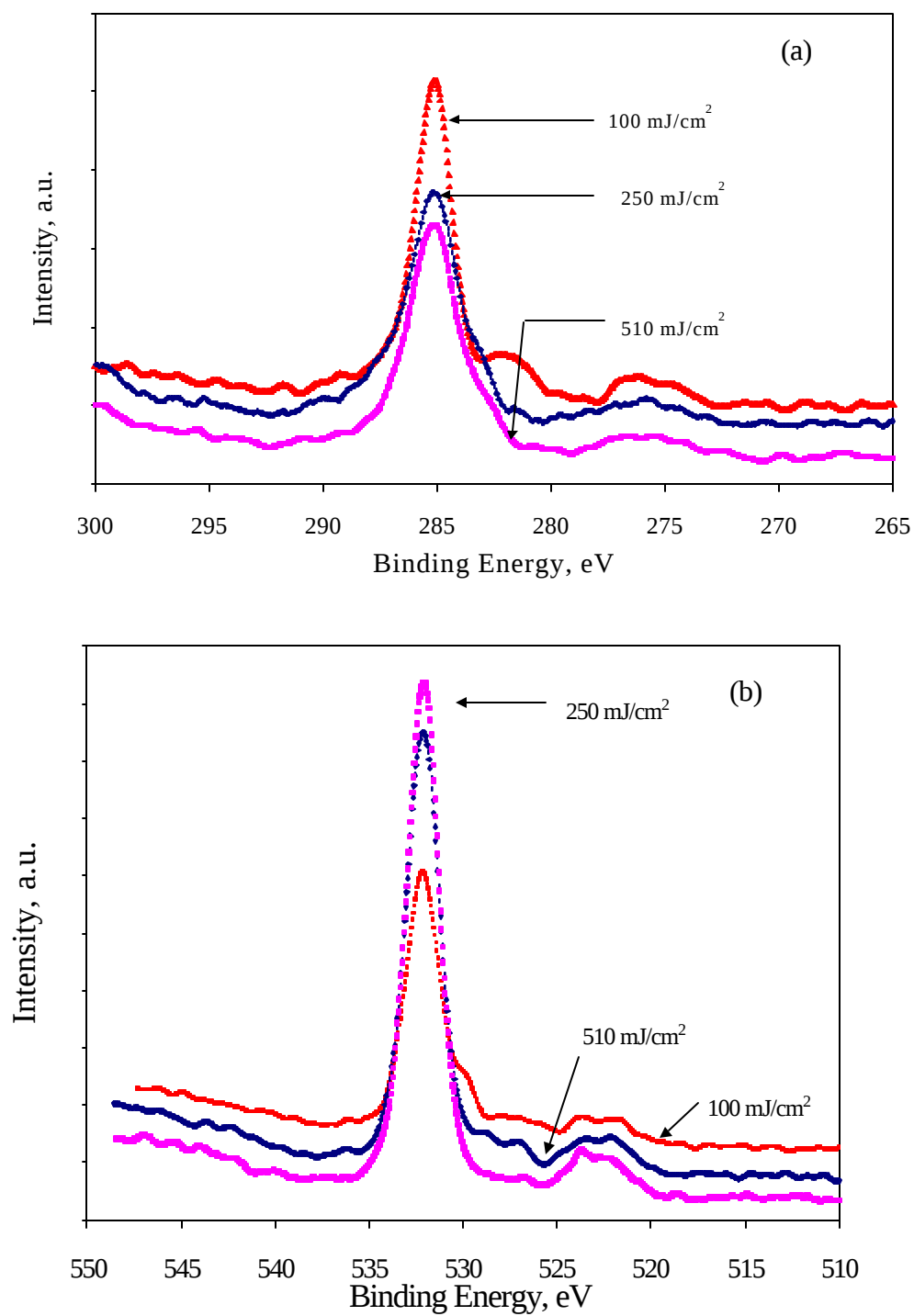


Figure 3.7 High resolution Elemental XPS scans of PLAD films deposited at different energy densities: (a) Carbon 1s, (b) Oxygen 1s.

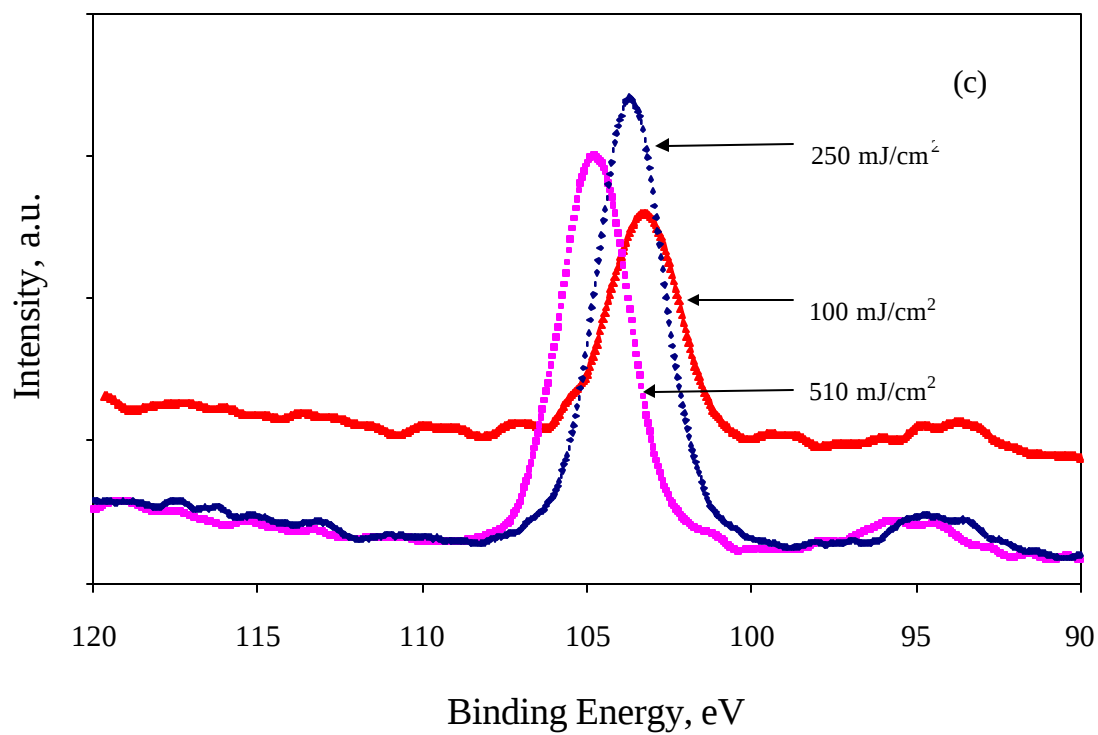


Figure 3.7 High resolution Elemental XPS scans of PLAD films deposited at different energy densities: (c) Silicon 2p.

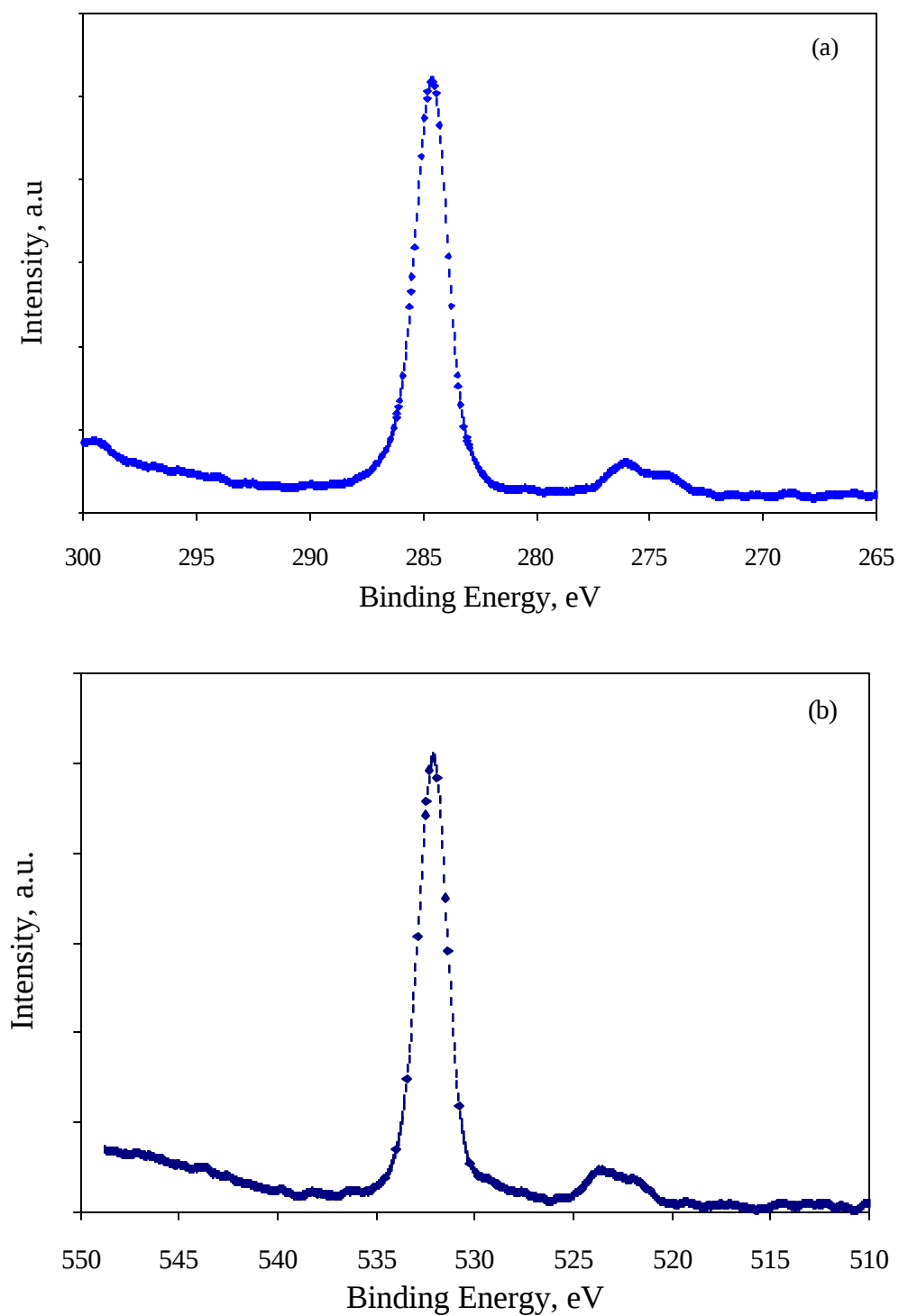


Figure 3.8 High resolution elemental XPS scans for a silicone target: (a) Carbon 1s, (b) Oxygen 1s

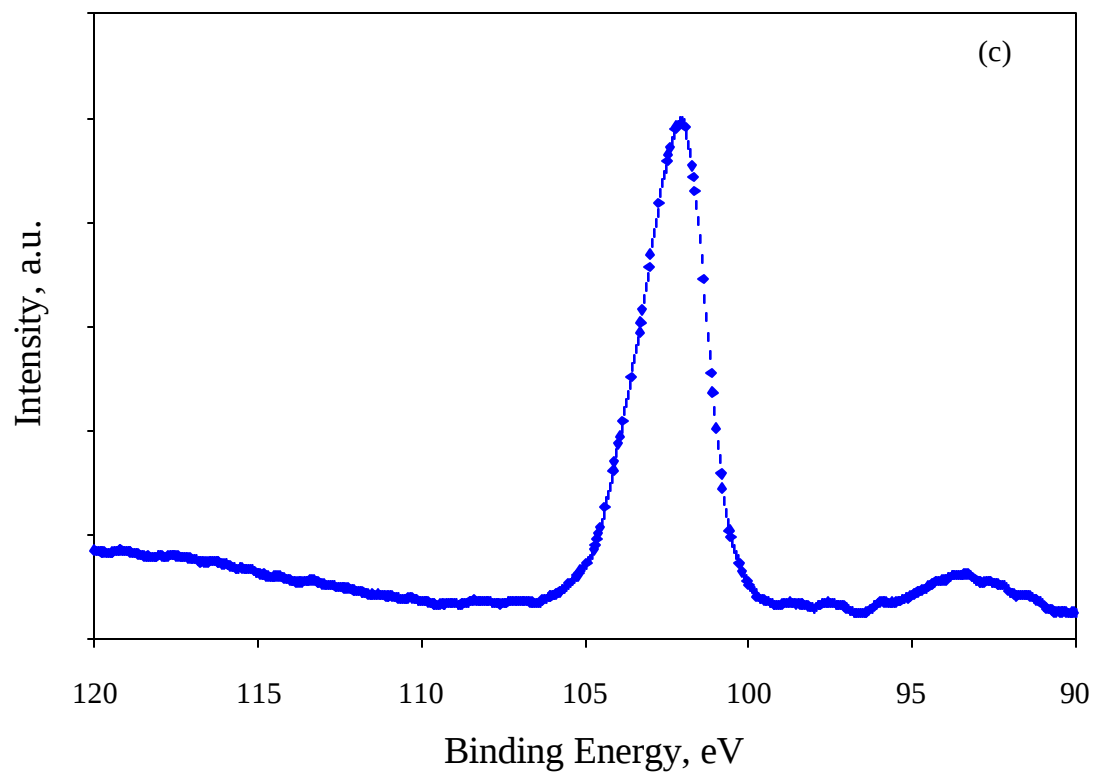


Figure 3.8 contd.
Silicon 2p.

High resolution elemental XPS scans for a silicone target: (c)

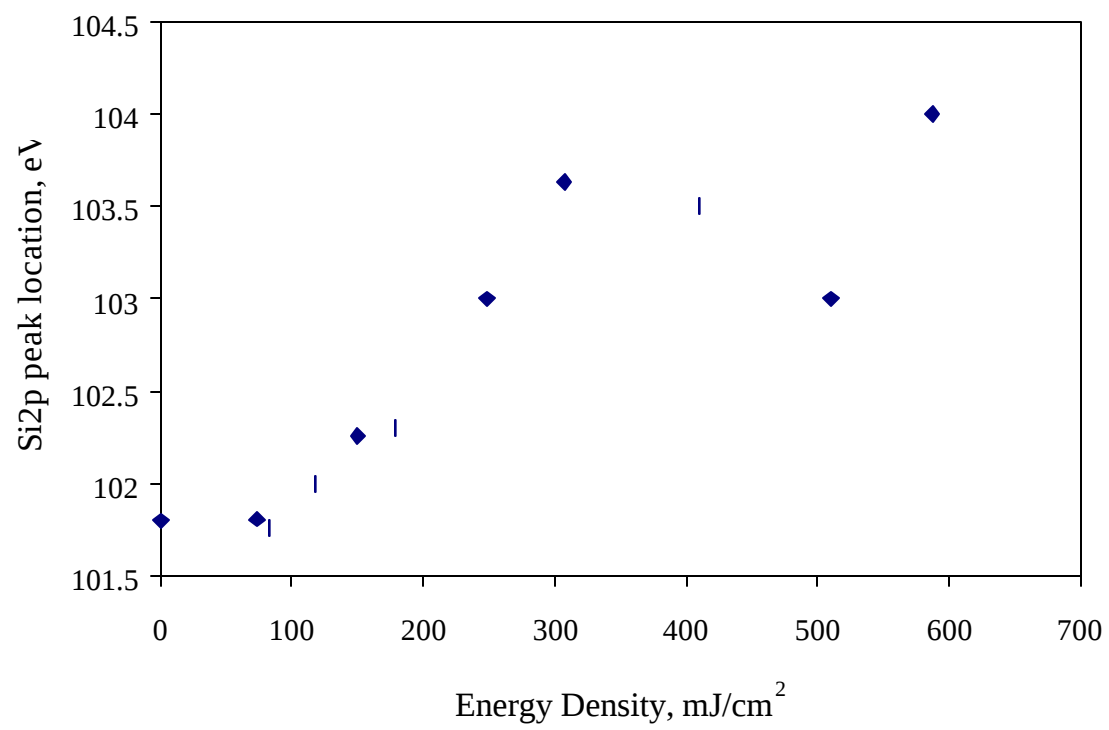


Figure 3.9: Si2p peak location from XPS for PLAD films.

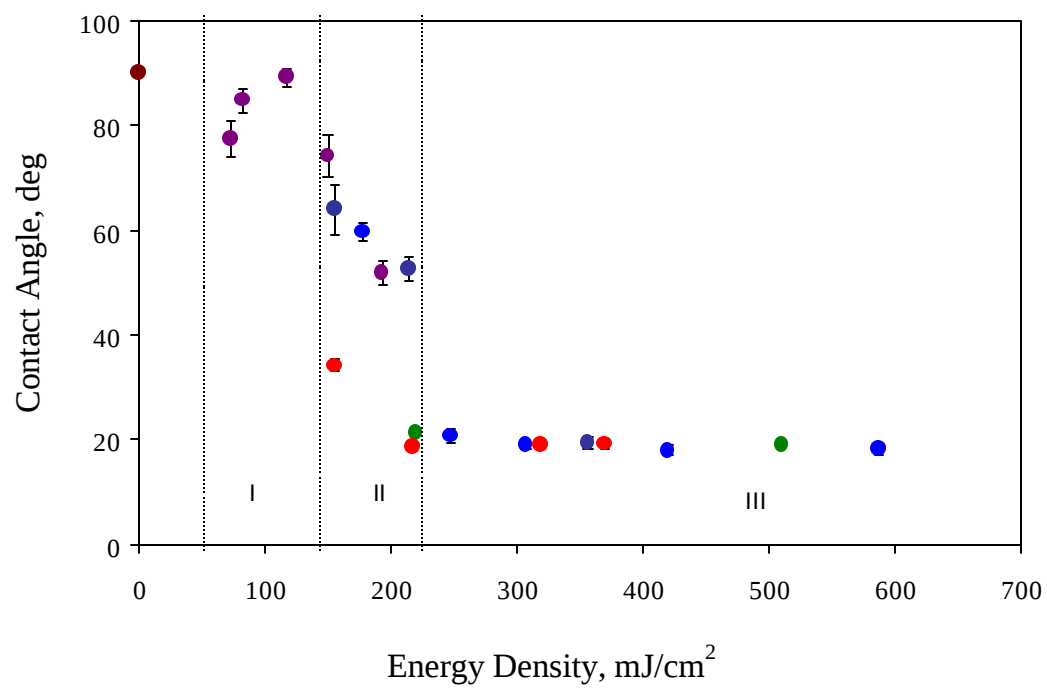


Figure 3.10 Contact angles of PLAD films as a function of energy density.

a low contact angle and are uniformly hydrophilic. The film characteristics give rise to three energy density regimes which are shown in the figure. They are discussed fully in the next section.

Deposition rate. Deposition rate as a function of energy density is plotted in Figure 3.11 for films deposited at 100 mTorr. The deposition rate was calculated per unit time after measuring the film thickness post deposition. As seen in Figure 3.11, the deposition rate starts out low and shows practically no change upto 180 mJ/cm^2 . Beyond this value, the deposition rate increases rapidly with energy density. The effect of pressure during the deposition can be seen in Figure 3.12 for films deposited at 50- and 200 mTorr. Deposition rates were consistently higher for runs carried out at 50 mTorr than those at 200 mTorr. It is known that the plume distribution changes as an effect of the pressure. At lower pressures the ablation plume progresses further, thus increasing the mass flux incident upon the substrate directly in its path leading to higher deposition rates. (Figures 3.11 and 3.12 cannot be compared due to different target-sample orientations).

Film morphology. SEM micrographs for PLAD films deposited at different energy densities are shown in Figure 3.13. Films deposited at energy densities of 100-, 220-, 360-, 420- and 510 mJ/cm^2 are shown. Complete coverage of the substrate was observed at all energy density levels. The films deposited at 100 and 220 mJ/cm^2 (Fig. 3.13 a, b) were smooth. At higher energy densities more debris was seen on the films and the films appear to be composed of particulates. This suggests that at high energy density levels, ablation produced large fragments and clusters which are then deposited on the substrate.

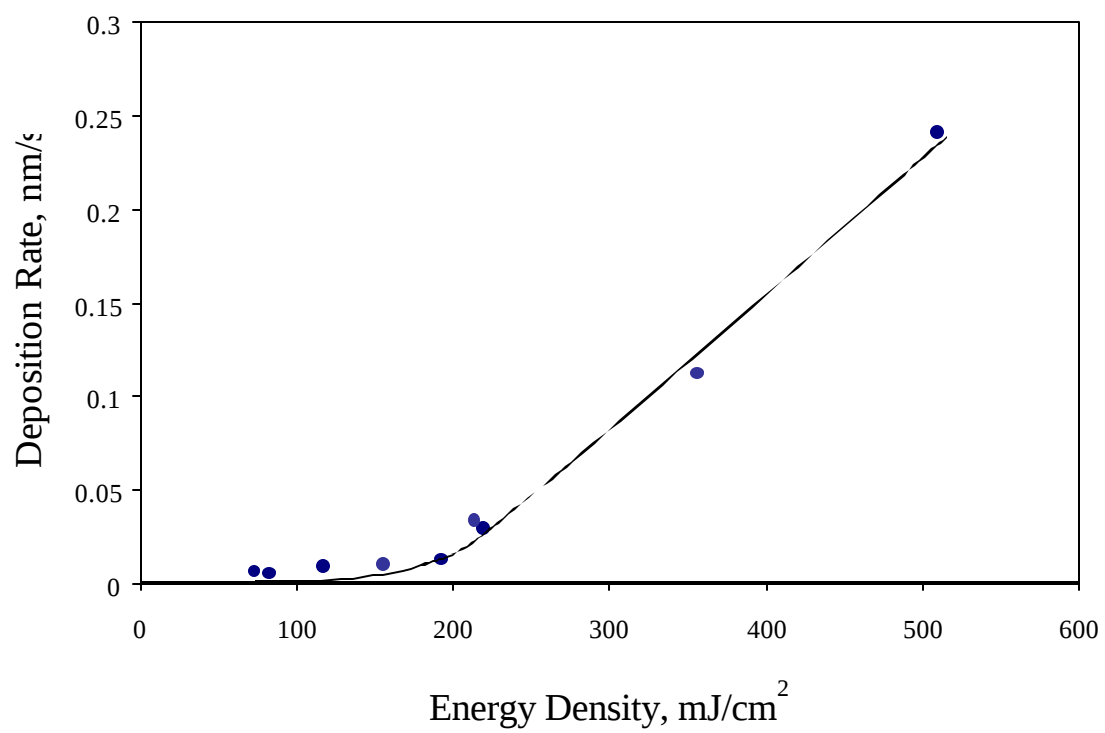


Figure 3.11 Deposition rate as a function of energy density for PLAD films.

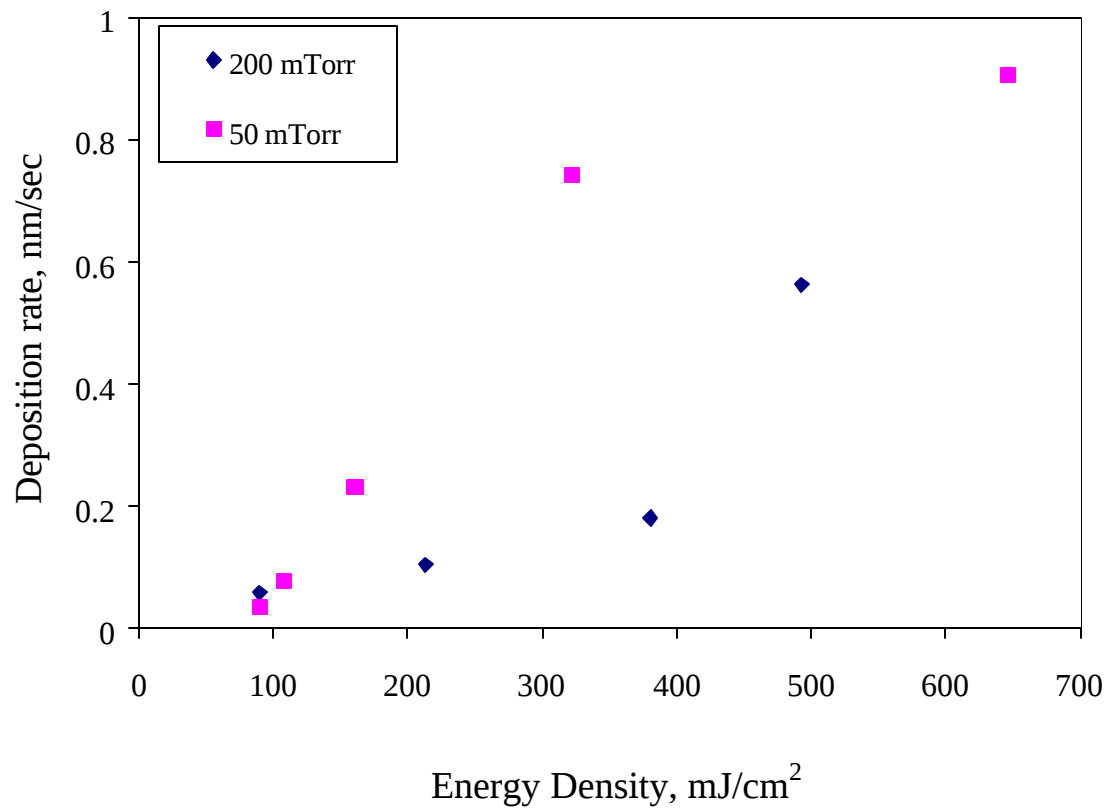


Figure 3.12 Effect of pressure on deposition rate of PLAD films.

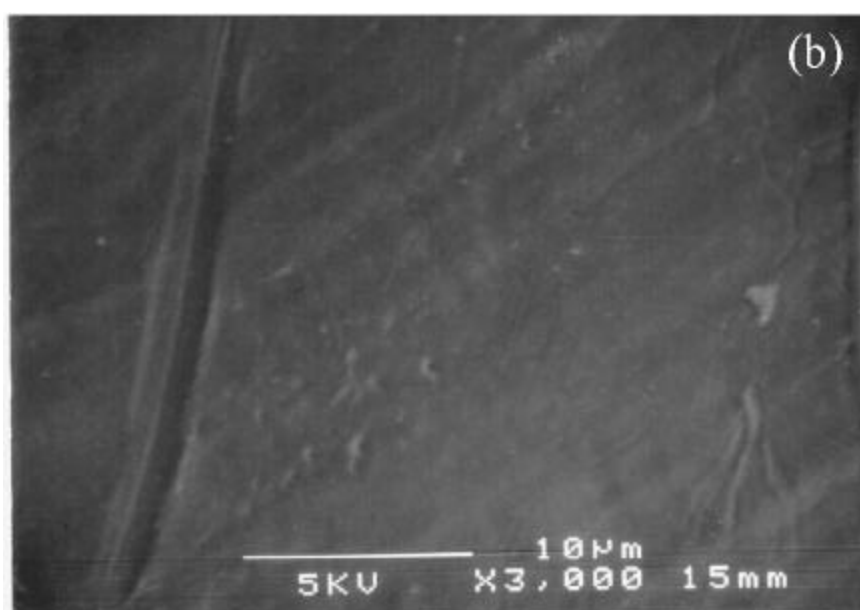


Figure 3.13 Scanning Electron Micrographs of PLAD films deposited at: (a) 100 and (b) 220 mJ/cm².



Figure 3.13 contd Scanning Electron Micrographs of PLAD films deposited at: (c) 420 and (d) 510 mJ/cm²

PLAD Film Stability Testing

The film stability was evaluated by a 24 hour immersion in chloroform followed by XPS and SEM analysis. Figure 3.14 shows the % C, % O and % Si values respectively for the PLAD films, pre-and post-chloroform wash. It is seen that except for the film deposited at 450 mJ/cm^2 , there is very little change in the elemental ratios after the chloroform wash. The film deposited at 450 mJ/cm^2 shows an increase in the %C but a decrease in %O and %Si. However no change in the peak bonding was seen in the XPS spectra. This suggests that there may have been some hydrocarbon contamination on this sample surface. Micrographs of the pre- and post chloroform wash film surfaces are shown in figure 3.15. The films do not show any significant morphological changes after the chloroform wash. Specifically, no areas with debonding or peel-off were seen on any of the samples, indicating that the film-substrate adhesion is good.

Effect of Laser Pulse Number

Literature reports had suggested that the ablation characteristics of a polymer change as a function of the laser pulse number. In weakly absorbing polymers, initial absorption (approx. 100s of pulses) can produce no significant ablation but serve only to increase the temperature on the target surface. Thus the makeup of the ablation fragments changes as a function of laser pulse number. To clarify this effect, PLAD films were prepared by ablating the silicone target for 1000, 2000 and 4500 pulses. The films were then analyzed by XPS to determine the change in composition as a function of pulse number. Table 3.2 gives the elemental compositions of the PLAD film as a function of pulse number and energy density.

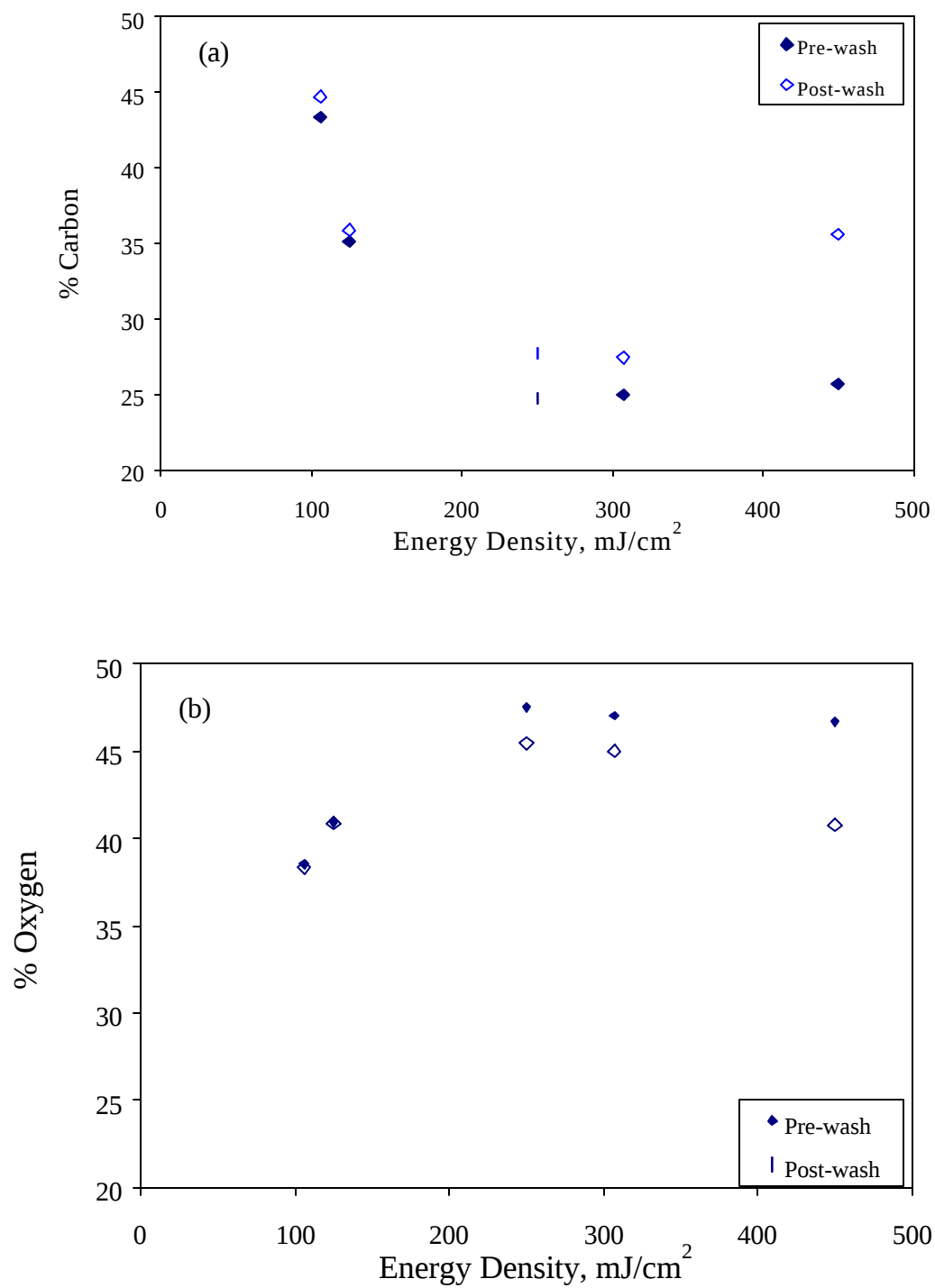


Figure 3.14 XPS elemental % for PLAD films, pre- and post chloroform wash: (a) Carbon, (b) Oxygen.

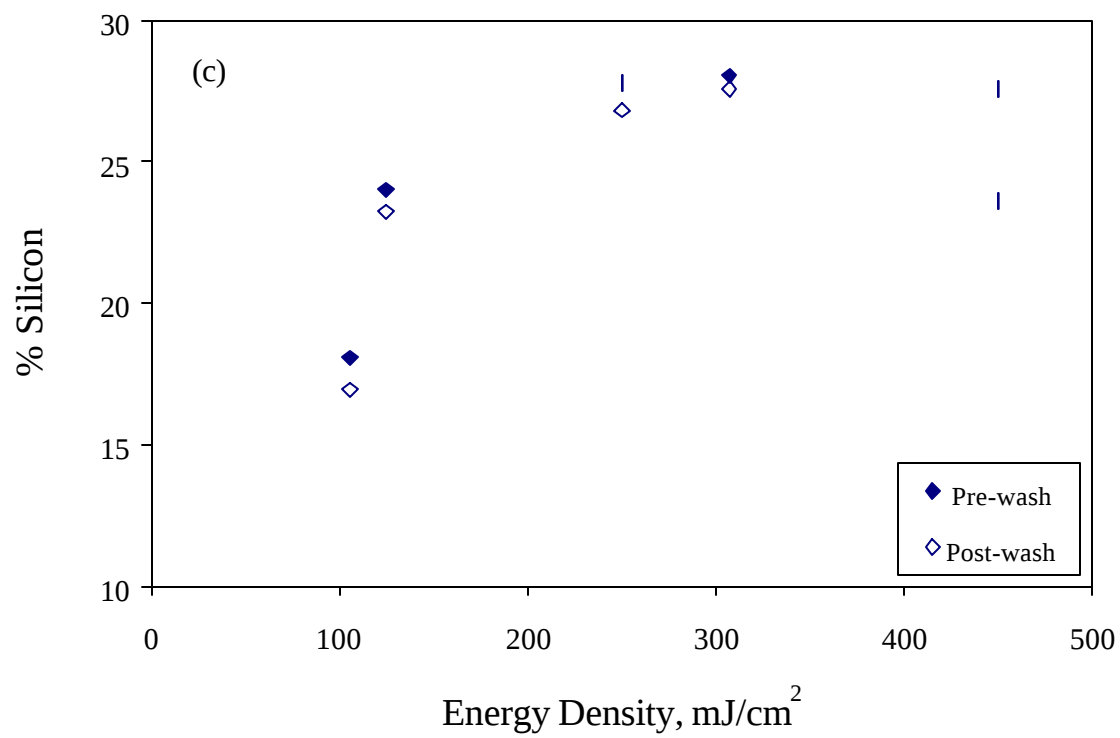


Figure 3.14 contd. XPS elemental % for PLAD films, pre- and post chloroform wash:
(c) Silicon.

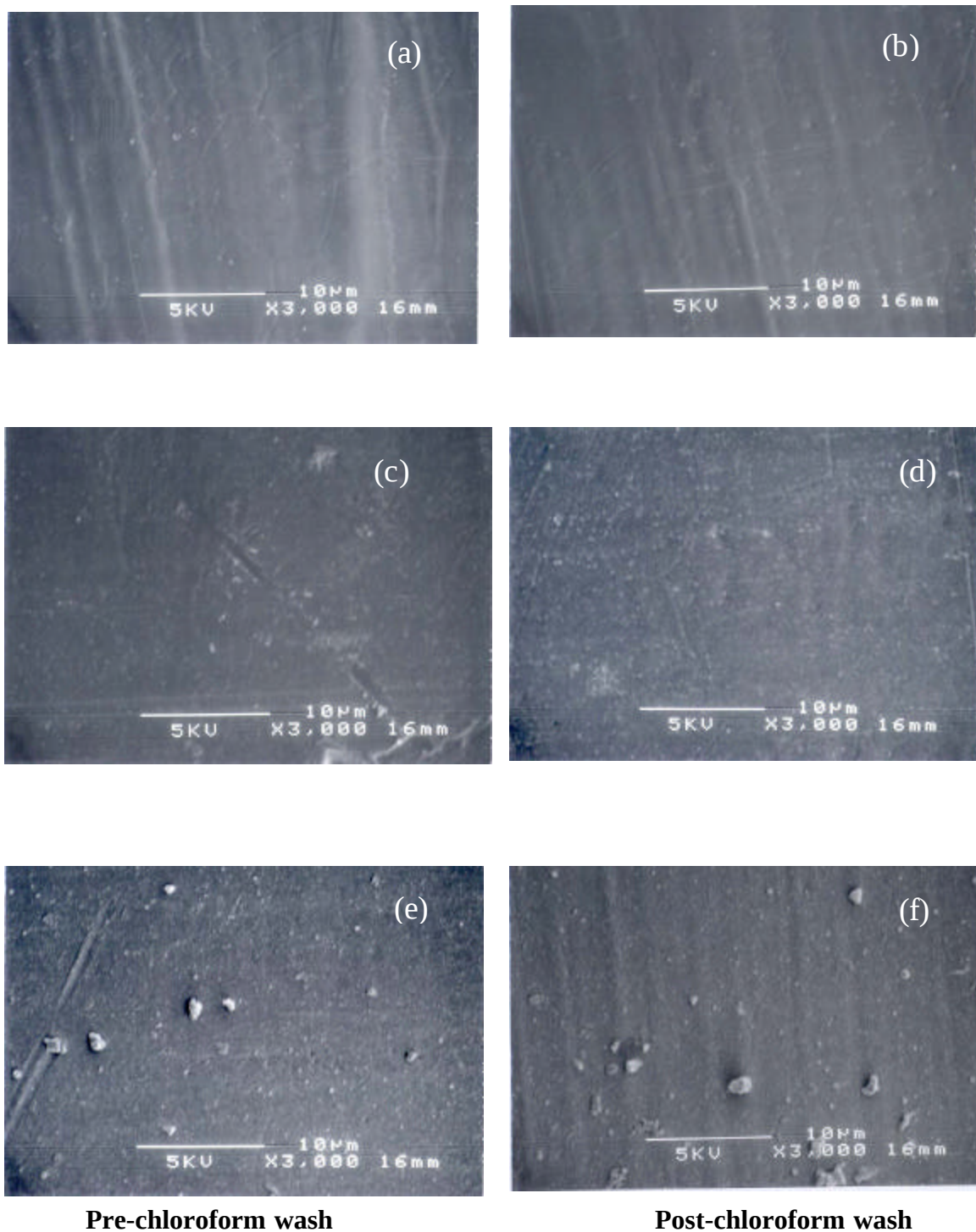


Figure 3.15 Micrographs of PLAD films pre- and post chloroform immersion: (a), (b) 100 mJ/cm²; (c), (d) 125 mJ/cm²; (e), (f) 250 mJ/cm²

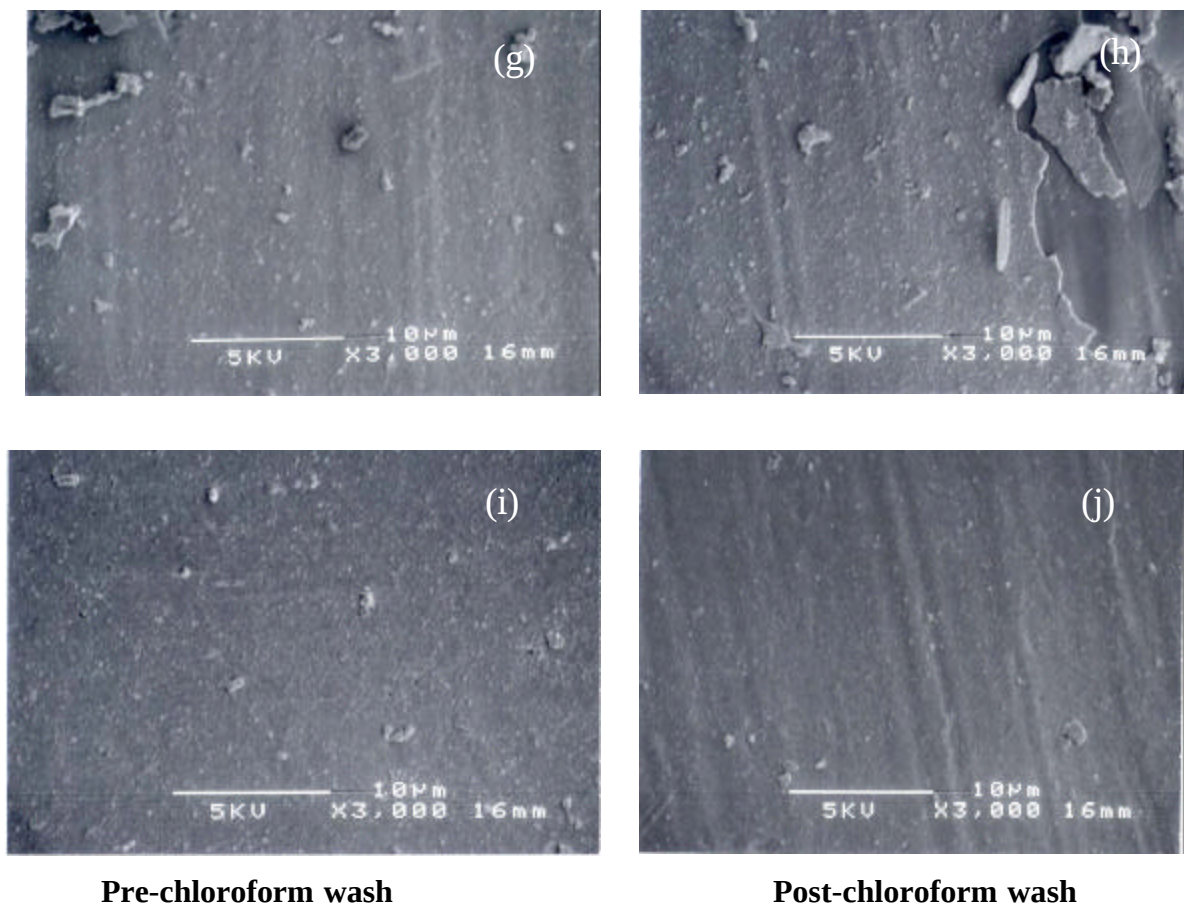


Figure 3.15 contd. Micrographs of PLAD films pre- and post chloroform immersion: (g), (h) 300 mJ/cm²; (i), (j) 450 mJ/cm².

Table 3.2. Elemental compositions for PLAD films deposited at different laser pulse number.

Energy Density mJ/cm ²	Pulse Number	% Carbon	% Oxygen	% Silicon	% Iron
100	1000	44.51	47.25	3.66	4.59
	2000	43.46	46.43	6.66	3.44
	4500	43.40	38.52	18.08	-
250	1000	44.11	38.61	17.28	-
	2000	31.00	45.64	23.36	-
	4500	29.96	47.06	22.98	-
500	1000	26.82	46.67	26.50	-
	2000	26.62	46.58	26.80	-
	4500	27.17	45.89	26.94	-

The XPS analysis showed that the pulse number at a certain energy density did affect the film composition. At 100 mJ/cm², the target irradiated for 1000 and 2000 pulses failed to produce a film. The elemental compositions for these samples were close to that of uncoated steel substrates. The carbon and oxygen XPS peaks also showed a different binding state than ordinarily seen for silicone polymers. The target irradiated for 4500 pulses produced a film with composition similar to those seen earlier at this energy density. As the energy density was increased to 250 mJ/cm², the target started to ablate even at 1000 pulses. However, the film produced was depleted in silicon indicating that the ablation had not reached its steady-state. The films produced at 2000 and 4500 pulses are close in composition demonstrating that the ablation is steady-state. At the highest energy density of 500 mJ/cm², the ablation at all three pulse numbers gave films which were similar in composition to each other. This indicated that ablation started rapidly at this level and attained steady-state in 1000 pulses or less. These results indicated that the ablation of silicone at 248 nm may have a strong thermal component. At low energy density, the temperature needed for ablation processes to start is only

reached after thousands of pulses. As the energy density is increased, ablation may start after a few hundred pulses or even immediately.

Depositions under High Vacuum

The results of the energy density study showed that the deposited films had high oxygen contents. It was thought that this could be due to oxygen attack by elemental oxygen present in the chamber under the mild vacuum conditions (100 mTorr) used to deposit the films. Therefore, experiments were carried out at higher vacuum levels to explore this possibility. Films were deposited at three energy density levels. The XPS and contact angle values for these films are shown in table 3.3. The film thickness was kept low and thus FTIR spectra could not be collected for these films.

Table 3.3. Contact angles and XPS elemental % for PLAD films deposited under high vacuum.

Energy Density, mJ/cm ²	Pressure, Torr	Average contact angle, deg	%C	%O	%Si
100	1 x 10 ⁻⁴	69	48.28	31.57	20.15
220	1 x 10 ⁻⁴	18	30.22	40.02	29.76
400	1 x 10 ⁻⁴	18	23.21	41.55	35.24

The results show that films deposited under high vacuum show similar trends to those deposited under lower vacuum conditions. At low energy density the films are silicone-like and hydrophobic. As the energy density is increased the oxygen content starts to increase and the films are hydrophilic. The film compositions are comparable to

those produced at 100 mTorr. This indicates that the films react with oxygen or water-vapor only on exposure to atmosphere.

Discussion

The results reported here show that the pulsed laser ablation deposition of silicone was successful in producing stable cross-linked films. It was seen that varying the energy density had a profound effect on the film stoichiometry and structure. By controlling this factor, it was possible to deposit silicone films with varying oxygen contents and surface energies. Such behaviour is unique and has not been reported before for linear thermoplastic polymers like PMMA and PTFE.

The surface analysis showed that at low energy densities (approx. $< 150 \text{ mJ/cm}^2$) the deposited films were similar in structure to the target silicone polymer. FTIR spectra of the films (Figs. 3.3a and 3.5a) showed characteristic absorbances including CH stretching, Si-CH₃ deformation and Si-O-Si asymmetric split. The contact angles for these films were close to that of silicone, indicating that the films were hydrophobic. Thus the laser ablation of silicone at these energy density levels seemed to proceed by lift-off and deposition of complete polymer chains on the substrate. Since silicone has no significant UV absorption at 248 nm it is theorized that the laser energy is coupled into the target photo-thermally causing a temperature rise. Optical microscopy examination of the target after ablation revealed the presence of numerous bubbles in the subsurface of the target. This indicated that the energy input was causing local heating and gas generation in the target. The expansion of these bubbles could cause fragmentation of the target and transport of polymer chains. If the heating rate is low enough the target

surface could be removed homogenously in a layer-by-layer evaporation process. Singh has shown that subsurface heating effects can be important in the laser ablation of materials which are poor UV absorbers [99].

However, if this were the only process occurring, the film composition would be similar to that of silicone. As shown by XPS, the film surface chemistry deviated from that of silicone. The films produced at low energy density were depleted in silicon and had higher oxygen contents compared to the target polymer. The preferential etching of methyl (*CH_3) and methylene(*CH_2) groups from the target surface would result in the presence of these species in the ablation plume. These charged species could then recombine with polymer chains in the plume or on the substrate surface. Such a scenario would produce silicone films with methylene bridges or longer alkyl groups hanging off the Si-O-Si main chain. This scenario is partly supported by comparing peak ratios from the FTIR spectra of the PLAD films produced at low energy density (Fig. 3.3a) to the target polymer (Fig. 3.4). The Si-CH₃/Si-O-Si peak ratio is lower for the PLAD film, indicating a loss of methyl groups. However, the CH/Si-O-Si ratio is higher indicating the retention of CH₂ groups in the structure. The higher oxygen content can be attributed to some free radicals on the polymer chain combining with oxygen on exposure to atmosphere. The free radical concentration is low enough for the films to remain hydrophobic.

FTIR spectra (Figs. 3.3b, 3.3c) revealed that at high energy density levels, the films showed absorbances due to OH and SiH groups. Also the Si-O-Si peak broadening (Fig. 3.5b, 3.5c) indicated a variety of distorted structures within the films. Thus increasing the energy density of ablation produced more fragmentation of polymer

chains, leading to smaller chains being present in the plume. These fragments combined in vapor or on the substrate surface to produce organosilicon films. The chain scission also led to free radical production. The trapped radicals in the film could react with oxygen and water vapor upon exposure to atmosphere, producing SiOH groups. The other contributor to free-radical production could be the laser-ablation plume interaction. At high energy density, the ablation product volume can be large enough to absorb a significant portion of the incident laser irradiation. This can also lead to increased radical production through photon absorption. The presence of SiH groups in the FTIR spectra also indicated that H^+ ions were present in the gas phase. It has been shown that the production of H^+ due to methyl group and H abstraction is the preliminary event in the plasma polymerization of siloxane monomers [97]. Thus it is possible that some of the fragmentation and growth mechanisms at high energy densities are similar to plasma polymerization. Increasing methyl group abstraction with an increase in energy density levels would account for the oxygen percentages seen in these films. The high oxygen levels also led to these films being hydrophilic as evidenced by their low contact angles.

The change in the chemistry of the films as a function of energy density is also reflected in the Si2p XPS peak location. Figure 3.9 showed that the Si2p peak location shifted to higher binding energy with increasing energy density. At low energy densities (100-150 mJ/cm²), the Si2p peak is located in the range 101.8-102.5 eV. This indicates that the silicon is bonded to two or more carbon atom. In the energy density range of 200-600 mJ/cm², the Si2p peak is located in the range 102.5-104 eV. This indicates that the silicon is bonded to at least three oxygen atoms.

Suzuki *et al* have reported the use of pulsed lasers for the synthesis of silane based polymeric films from poly(methylphenyl silane) (PMPS) [66]. They found that for 248 nm laser irradiation, most of the Si-Si bonds in the polymer were converted to Si-C in the films and new bonds like Si-H were present. Also the deposited films suffered molar mass reduction and showed a broader distribution than the starting polymer. The molar mass distribution was found to be dependent on the energy density. Although the starting polymer used was different, the trends found in the Suzuki study are similar to what this research reports i.e. increased chain fragmentation with increasing energy densities. It is interesting to note that the PMPS films were found soluble considering the amount of reorganization which was seen in the structure.

Deposition rate measurements and electron micrographs provided a view of the physical nature of the PLAD process. The deposition rate for the PLAD films was low and showed little change upto approx. 180 mJ/cm² (Fig. 3.11). This indicated that there were more molecular (i.e. polymer chains) species involved in film growth and the level of ablation remained relatively constant. As the energy density increased beyond a certain limit, deposition rate showed a sharp linear increase. This led to deposition rates which were quite high when compared with plasma polymerization processes [97],[98]. The deposition rate seemed to indicate the presence of a critical energy density for steady-state ablation. It was also possible to vary the deposition rate by adjusting the vacuum (i.e. pressure) level and substrate-target distance(Fig. 3.12). Such an effect has been noted in the literature for the PLAD of numerous materials. The lower pressure allowed the plume to progress further, increasing the mass flux incident on the substrate. Figures 3.11 and 3.12 also demonstrated the importance of directionality and sample

position in the PLAD process. The deposition rates shown in Fig. 3.11 were measured for samples which were placed away from the plume, leading to lower values. The deposition rates shown in Fig. 3.12 were measured for samples kept directly in the plume path leading to much higher rates of deposition.

The SEM analysis showed that at low energy densities, the PLAD film surfaces were smooth (Fig. 3.13a). As the energy density increased beyond approx. 200 mJ/cm^2 , the films contained more debris and also seemed to be composed of particulates. Thus the deposition rates and SEM analysis indicated that the ablation levels upto approx. 200 mJ/cm^2 were slow and the plume to be composed of smaller molecular species. As the energy density increased beyond this limit, the polymer ablated off as clusters and particles. These then recombined on the substrate to form a film. Thus it seemed that at high energy density, the heating rate is high enough to cause rapid temperature rise and inhomogenous removal of the target surface, while at low energy density, the heating rate is low enough to cause a more uniform ablation of the target surface.

The pulse number study illustrated another important aspect of the nature of silicone ablation. As seen from XPS analysis of films produced at different pulse numbers, the film chemistry undergoes a change dependant on the pulse number. At the lowest energy density of 100 mJ/cm^2 , it was seen that no films were produced after irradiating the target for 1000 or 2000 pulses. Thus the ablation process did not start till after 2000 pulses. During the initial pulses, the temperature rise to allow chain evaporation or gas generation was not achieved. Such a phenomenon is known as incubation and has been shown to occur in the laser ablation of PMMA [100]. On continuing the energy input beyond 2000 pulses, the temperature could increase to a point

where ablation could occur. Thus the film produced with 4500 pulses showed a similar composition to films produced at the same energy density, described earlier in this work.

As the energy density was increased, the incubation phenomenon occurred faster and required a lesser number of pulses. This can be seen by the fact that the target irradiated at 250 mJ/cm^2 produced films comparable to those described earlier after only 2000 pulses. The target irradiated at 500 mJ/cm^2 produced equivalent films after just 1000 pulses. Thus this study indicated that the ablation of silicone had a strong photo-thermal component and that the incubation phenomenon seen for other polymers was also prevalent in silicone.

The above discussion allows us to formulate a theory of silicone ablation at 248 nm based on empirical observations. The ablation behaviour can be divided into three regimes (as shown in Fig. 3.10). In regime I ($75\text{-}150 \text{ mJ/cm}^2$), the ablation proceeds slowly. The initial pulses serve to heat up the polymer and ablation (characterized as polymer removal) starts only after a few 1000 pulses. Long polymer chains are evaporated in a layer-by-layer fashion. There are also some etching and degradation reactions associated with the ablation. An analogy can be drawn between the PLAD process and Matrix Assisted Laser Desorption Ionization (MALDI) mass spectroscopy. In the MALDI process, a laser beam is used to energize the sample consisting of an active matrix and a polymer (or any other molecule of interest). The laser energy is absorbed by the matrix, causing a temperature rise and desorption of the polymer. It has been shown that intact polymer chains can desorb by this method and analyzed in the mass spectrometer.

In regime II (150-220 mJ/cm²), the ablation behaviour stays the same, but there is increased chain scission due to higher energy input. This regime can be characterized as an intermediate one. Although the films produced are silicone-like, they can be hydrophobic or hydrophilic depending on the concentration of free radicals and subsequent level of oxygen incorporation. The contact angles in this regime show poor reproducibility which is an indication of this phenomenon

In regime III, the ablation volume is large due to high heating rates, with the polymer being ablated as clusters and particulates. There is large scale chain scission and CH₃ abstraction, producing films which are particulate and hydrophilic, albeit with a substantial organic content. All the different characterization techniques like XPS, profilometry and SEM seem to indicate that there is a change in the mode of ablation beyond regime II. The critical energy density at which this change occurs can not be accurately determined. Figure 3.16. shows a schematic representation of the above described regimes.

It is believed that when using energy density levels lower than 75 mJ/cm² (i.e. below regime I), the primary mechanism of degradation would be etching rather than true ablation. The low Si levels seen for films deposited in regime I would be further depleted. A similar etching-ablation behaviour has been shown for PTFE laser ablation at 248 nm. It was found that PTFE could be etched (characterized as loss of CF₂ groups) at low energy densities (~ 50 mJ/cm²). However, increasing the energy density beyond a certain limit, it was observed that the etching behaviour decreased and the PTFE started to ablate, (characterized as removal of polymer).

The deposition experiments carried out under high vacuum also served to clarify the ablation and growth mechanisms of this process. One possibility which was thought of was that at the modest vacuum levels (0.1 Torr) used in the experiments discussed above there would be significant oxygen presence inside the chamber. Since oxygen is known to attack free-radicals, it was thought that the high oxygen levels seen in the films were due to oxygen attack *in-situ*. Synthesizing the films under higher vacuum levels would decrease oxygen and water vapor incorporation and allow the free-radicals present in the films time to recombine. Thus the films were deposited under a pressure of 1×10^{-4} Torr which was three orders of magnitude lower than that used earlier. Surface analysis of these films showed that the energy density dependence seen at 0.1 Torr also prevailed at 1×10^{-4} Torr. Films produced at high energy density had a high oxygen content. This indicated that the oxygen and water vapor incorporation did not happen *in-situ* but only on exposure to atmosphere. This also meant that the free radicals had limited mobility indicating a high cross-link density. This aspect of the PLAD process demonstrated some similarities to plasma polymerization. Plasma polymer films are known to have high free-radical concentrations with restricted mobility due to the cross-linked nature of the films. These free-radicals can react over time changing the film chemistry. The PLAD polymer films show similar characteristics, but the free-radical reactions could be faster due to the shorter lifetimes of the Si^* radicals.

In proposing the PLAD process as a coating method, the energetic nature of the process was viewed as an advantage. It was believed that due to the species impacting the substrate, the chances of substrate-coating adhesion would be improved. To test this hypothesis, the film stability was analyzed by a 24 hour chloroform immersion test.

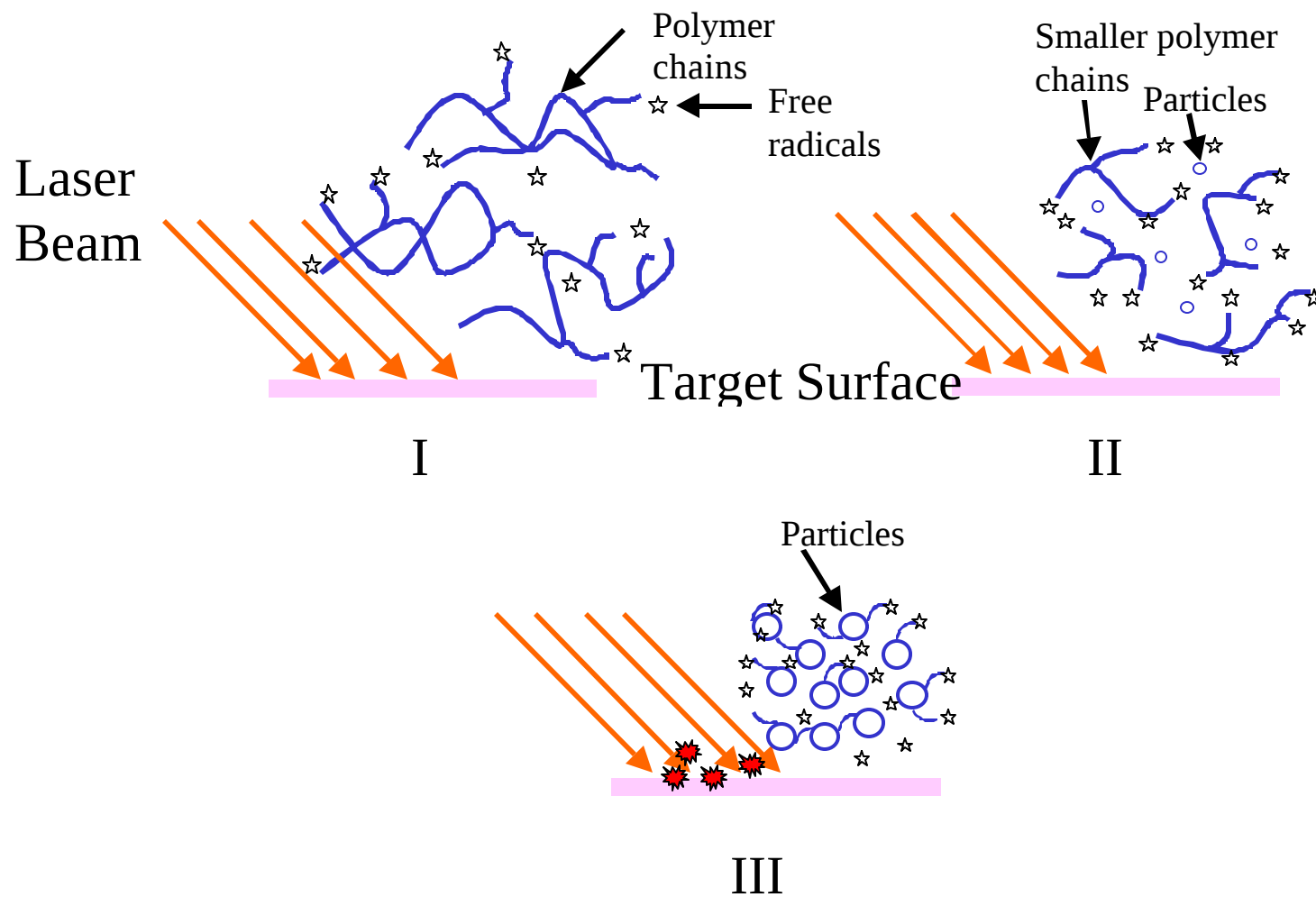


Figure 3.16 Schematic diagram of the different regimes for silicone ablation at 248 nm.

The PLAD films demonstrated remarkable stability, as seen by their resistance to a strong solvent like chloroform. It was expected that the films would swell in chloroform and debond due to the expansive stress. However as shown by XPS and SEM analysis, the films did not undergo any significant change after the chloroform immersion. This meant that the films were highly cross-linked and also strongly adhered to the substrate. This is an attractive property which arises from the PLAD process and leads to an added advantage over other processes like polymer solution coating. (The weight change in the coated steel substrates pre- and post chloroform immersion was on the order of 1 mg which is near the accuracy and resolution limit of the weigh balance and could not be used to characterize loss of soluble polymer species).

Summary

The pulsed laser ablation deposition process was used to synthesize silicone thin films for the first time. A unique energy density dependence was revealed, allowing the synthesis of hydrophobic silicone-like films at low energy density and hydrophilic organosilicon films at high energy density. All films produced were highly cross-linked with a soluble content which was below the measuring sensitivity of the balance. Depositions under high vacuum conditions showed that oxidation reactions on the film surface did not occur in-situ but on exposure to atmosphere. Silicon targets also exhibited an incubation phenomenon, indicating that the ablation may be a thermal process.

Figures 3.17 and 3.18 show a low magnification electron micrograph of a coated steel substrate and a coated stent respectively. A smooth, conformal coating is visible on

both substrates. These two examples demonstrate the feasibility of the PLAD method for coating substrates with complex shapes.

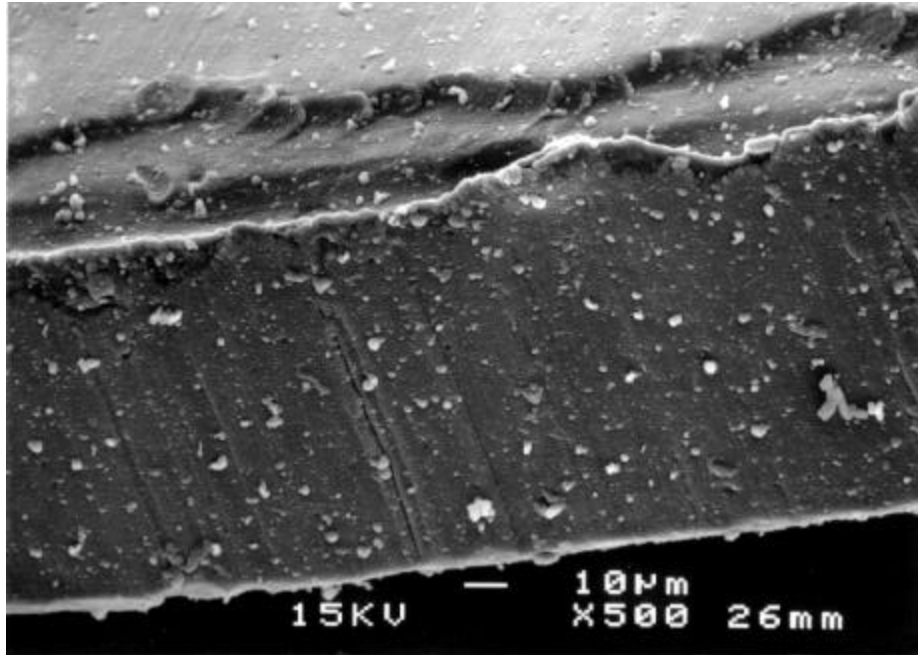


Figure 3.17 Cross-sectional SEM of a PLAD film coated steel substrate. The film was deposited at 400 mJ/cm^2 .

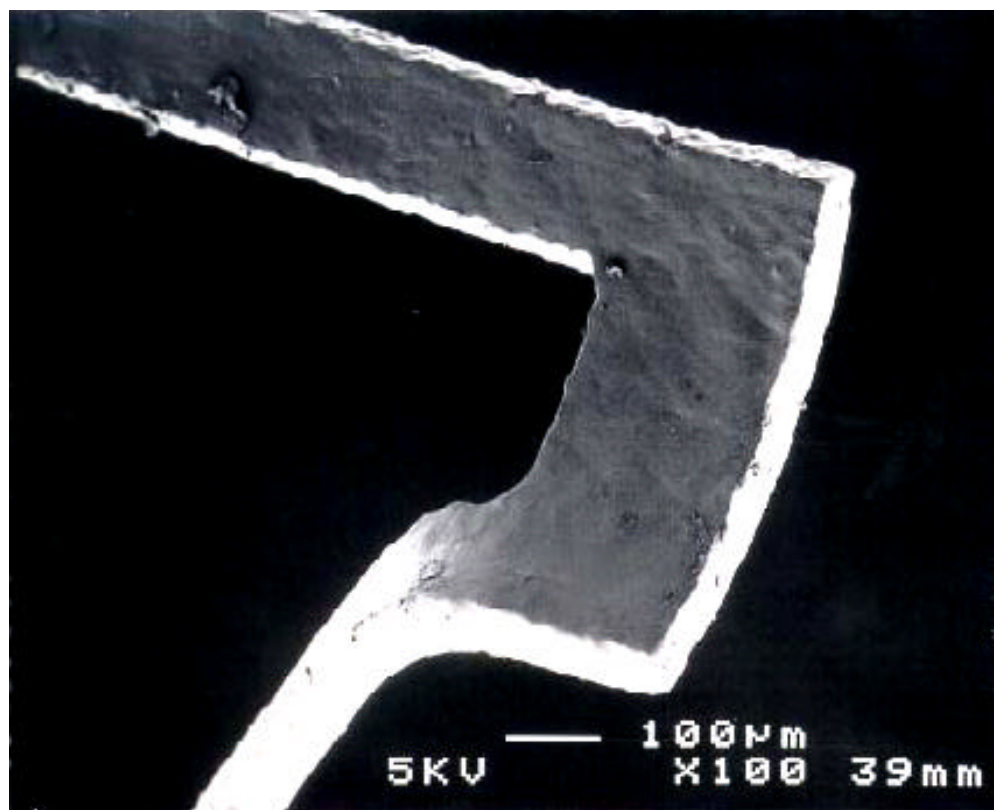


Figure 3.18 Electron Micrograph of a coated stent after expansion.

CHAPTER 4

NANOINDENTION AND NANOSCRATCH MEASUREMENTS ON PLAD FILMS

Introduction

The much heralded age of nano-science and technology has been led by the push towards smaller devices, structures and molecular assemblies in the fields of materials science, chemistry and biology [101]. The invention of the scanning probe microscope (SPM) in the early 1980s was the primary reason for the drive towards the nano-scale. Since then the use of an SPM derivative, namely the Atomic Force Microscope (AFM) for micro- or nano structural studies has led to a better understanding of the morphology of thin films and coatings. In the field of surface modification, the synthesis of films with thickness on the nanometer scale has become easier. The measurement of physical properties like modulus, hardness and adhesion of these films has been viewed critical to their development. Current methods to measure film modulus on the nano-scale rely on the AFM. Other methods to measure film adhesion which include scrape adhesion testing (ASTM D2197) and Scotch-tape testing (ASTM D3359) are woefully inadequate for thin films and coatings.

In synthesizing the PLAD coatings the measurement of the film adhesion was viewed to be of primary importance. PLAD films synthesized at different energy density were subjected to the ASTM Scotch-tape test (D3359). This test involves making defects (i.e. scratches) in the film in a predetermined square pattern. The scotch-tape is then stuck to the sample and peeled off rapidly. The extent of damage to the film is

characterized by the number of damaged squares and the coating adhesion is then assigned a number based on a known scale. This test is extremely qualitative and all the PLAD films passed this test without any damage being inflicted upon them. Other quantitative methods like the peel-test are only applicable to thicker films ($\mu\text{m-mm}$). Thus a better method to measure the mechanical properties of PLAD films was sought. Recently introduced nanomechanical methods derived from the AFM make quantitative measurements feasible under a variety of practical conditions [102],[103]. These methods offer a significant advance over the ASTM standards and it was considered that they could provide valuable information on the mechanical properties of the PLAD films.

Theory

Nanoindentation

In an indentation experiment, a sharp tip is forced into the material being studied while conditions are continuously monitored. This procedure allows the mechanical properties of the material to be evaluated. It can provide an estimation of the material stiffness which allows us to calculate the hardness and Young's modulus. This is done by making the indentation with a well-controlled force, F , while continuously measuring the displacement, h , of the indenter. The indentation depth is related to the force, the area of contact between the indenter and the material under test. A typical force displacement curve showing the loading, holding and unloading steps is shown in figure 4.1 [104]. Under loading, the indentation depth, h_{max} , is the superposition of an elastic component, h_e , and a plastic one, h_p :

$$h_{\text{max}} = h_e + h_p \quad (1)$$

The plastic component, h_p , which corresponds to the residual deformation is the intercept of the unloading curve with the depth axis. This is the value that macro-hardness testing uses to define the hardness of a sample.

The local hardness, H and the Young's modulus, E , of the sample are given by the following equations:

$$H = \frac{F_{\max}}{A_c} \quad (2)$$

$$E_r = \frac{1}{2} \sqrt{\frac{P}{A_c}} \times S \quad (3)$$

where H = Hardness

$F_{\max}$ = maximum force applied

A_c = contact area

and where E_r = reduced modulus

S = contact stiffness (slope of the unloading curve)

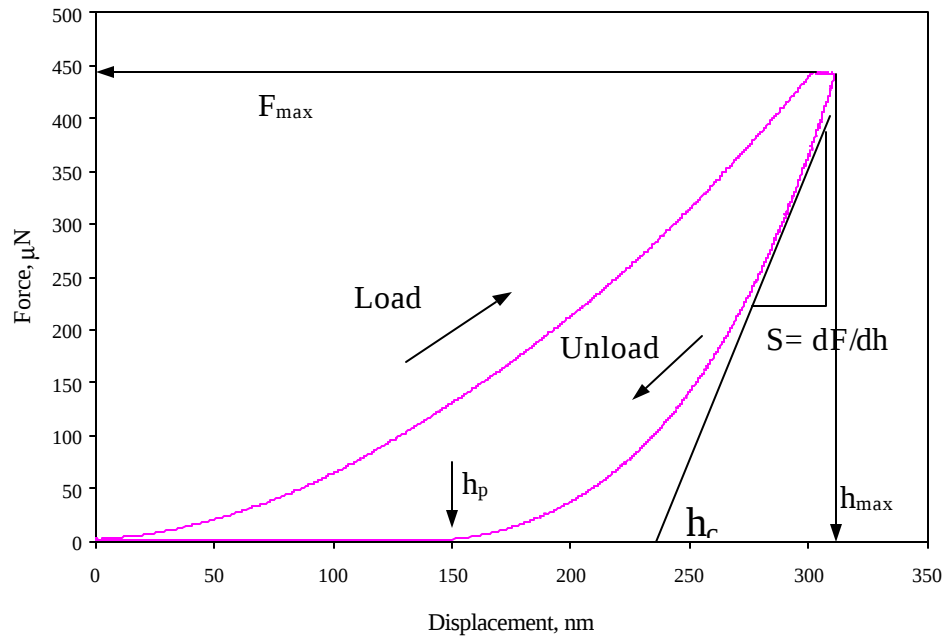


Figure 4.1 Load-displacement curve in a nanoindentation experiment with points of interest.

Figure 4.2 shows the profile of an indentation which indicates physically what some of the values from fig. 4.1 represent.

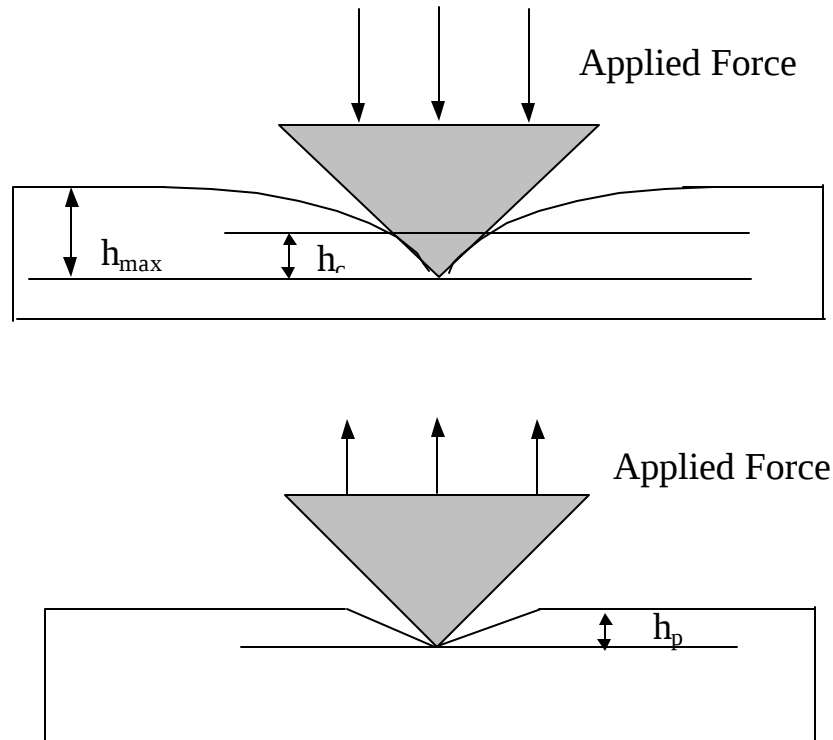


Figure 4.2 Profile of an indentation. The top picture shows the tip in the surface at maximum load. The lower picture is at the end of an indentation cycle. Adapted from ref[104].

Contact area. The contact area of an indentation can be found out from the geometry of the indenter. Since the indenter is a solid body, the contact area can be derived as some function of the contact depth. The standard tip used for nanoindentation is the Berkovich

indenter. The Berkovich shape is a three sided pyramidal indenter with a half angle of 65.35° . For an ideal Berkovich indenter, the area is given as:

$$A = f(h_c) = 24.5h_c^2 \quad (4)$$

Unfortunately, no tip is ideally sharp and has some finite amount of bluntness to it. This amount of bluntness is usually approximated by a sphere and the radius of this sphere is called the 'radius of curvature' of the tip. This results in the contact area deviating from the above equation. However, the contact area needs to be precisely known to determine the Hardness and Young's modulus.

The most common method of finding the area vs. indentation depth relationship or area function as it is known is to make indents into a known sample. Equation (3) can be rewritten as:

$$A_c = \frac{4S^2}{pE_r^2} \quad (5)$$

Since the stiffness value, S , can be found from a load-displacement curve, the contact area of an indentation made in a sample of known modulus can be calculated. The contact depth (h_c) can also be extrapolated from the force-displacement curve. Therefore, if a series of indentations at different contact depths are made in a sample of known modulus, the contact area vs. contact depth can be plotted and an area function can be found. The standard form of the area function is given as:

$$A_c = C_0h_c^2 + C_1h_c + C_2h_c^{\frac{1}{2}} + C_3h_c^{\frac{1}{4}} + C_4h_c^{\frac{1}{8}} + \dots \quad (6)$$

where $C_0 h_c^2$ defines the ideal indenter geometry and the following terms are deviations of the real geometry from the ideal. The area function for the indenter used in these experiments was found out by making a series of indents in a fused quartz sample. The contact area for each indent was found from the stiffness value and the known modulus value for quartz (72.6 GPa). The contact area was then plotted as a function of the contact depth and the area function was derived to provide the best fit to the data. The derived area function with the terms for C_0 - C_2 is shown below. This area function was used in all the Hardness and Young's Modulus calculations.

$$A_c = 30.6h_c^2 + 109h_c + 2406h_c^{\frac{1}{2}} \quad (7)$$

Nanoscratch

In a nanoscratch test, a sharp tip is drawn across the sample under a specified force to create a scratch of desired length. Figure 4.3 shows the different stages in a scratch test along with force-displacement parameters used in the calculation. As can be seen, four such parameters are used to define a nanoscratch test namely: normal force, lateral force, normal displacement and lateral displacement.

The two parameters which are specified at the start of the test are the normal force and the lateral displacement (i.e. scratch length). The loading profile can be either constant force or ramp force. In a constant force scratch, the desired force is applied at the start of the scratch and is kept constant till the end of the test. In a ramp force profile, the force is zero at the start of the scratch and reaches its maximum value at the end of the scratch. This allows us to determine the force at which the film fails. Setting the lateral displacement and the total test time allows us to control the loading rate.

The two quantities which are measured are the lateral force and normal displacement. The lateral force is the resistance which the material offers to the tip. The ratio of the lateral force to the normal force gives the coefficient of friction for the material under test. The normal displacement is the deformation undergone by the material in response to the normal force and is a measure of its scratch resistance. It is also possible to make a qualitative assessment of the material properties by scanning the film surface and looking at features like fracture, delamination, interfacial failure and material pile-up. Figure 4.4 shows a PLAD film surface before and after a 500 μN , 5 μm ramp scratch.

A review of the literature shows that there is no consensus on the definition of film failure. Since most of these tests were originally developed for harder materials, film failure as defined for these materials would not be suitable for polymer films. In the case of a hard film (e.g. diamond-like carbon on magnetic heads), failure is defined to be the point at which the coefficient of friction shows a sharp increase due to the tip scratching the underlying substrate. Polymer films however, do not show these typical failure characteristics. Thus for polymers it can be variously defined as the normal force required to initiate a scratch or normal force required for delamination. Examination of the scratch morphology also reveals important information about the film properties. Thus two types of failure can be defined namely: cohesive failure and adhesive failure.

Cohesive failure or damage is the normal force required to initiate a scratch in the material. Cohesive damage is a measure of the film bulk properties. Adhesive failure is the point at which interfacial failure of the film and substrate occur. It is defined as the

point of break on the normal displacement-normal force curve at the limit of the film thickness. Adhesive failure is a measure of the film interfacial strength.

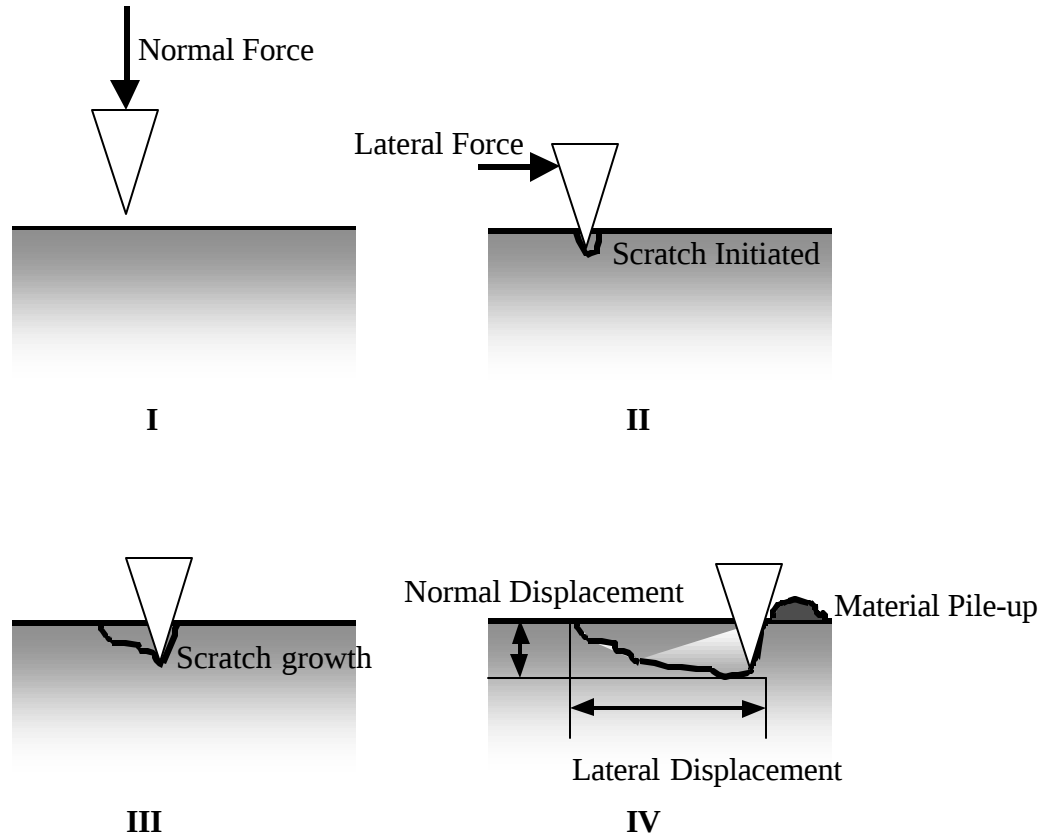


Figure 4.3 Schematic diagram of the stages in a nanoscratch test. A ramp force profile is shown.

Figure 4.4 shows cohesive and adhesive failure along the scratch length, while Figure 4.5 shows the point of adhesive failure on a force-displacement plot. It is seen that in figure 4.5 at the limit of the film thickness, the force-displacement curves become wavy indicating that the film adhesion has failed at the interface leading to rapid tip retraction-extension resulting in a rougher force profile.

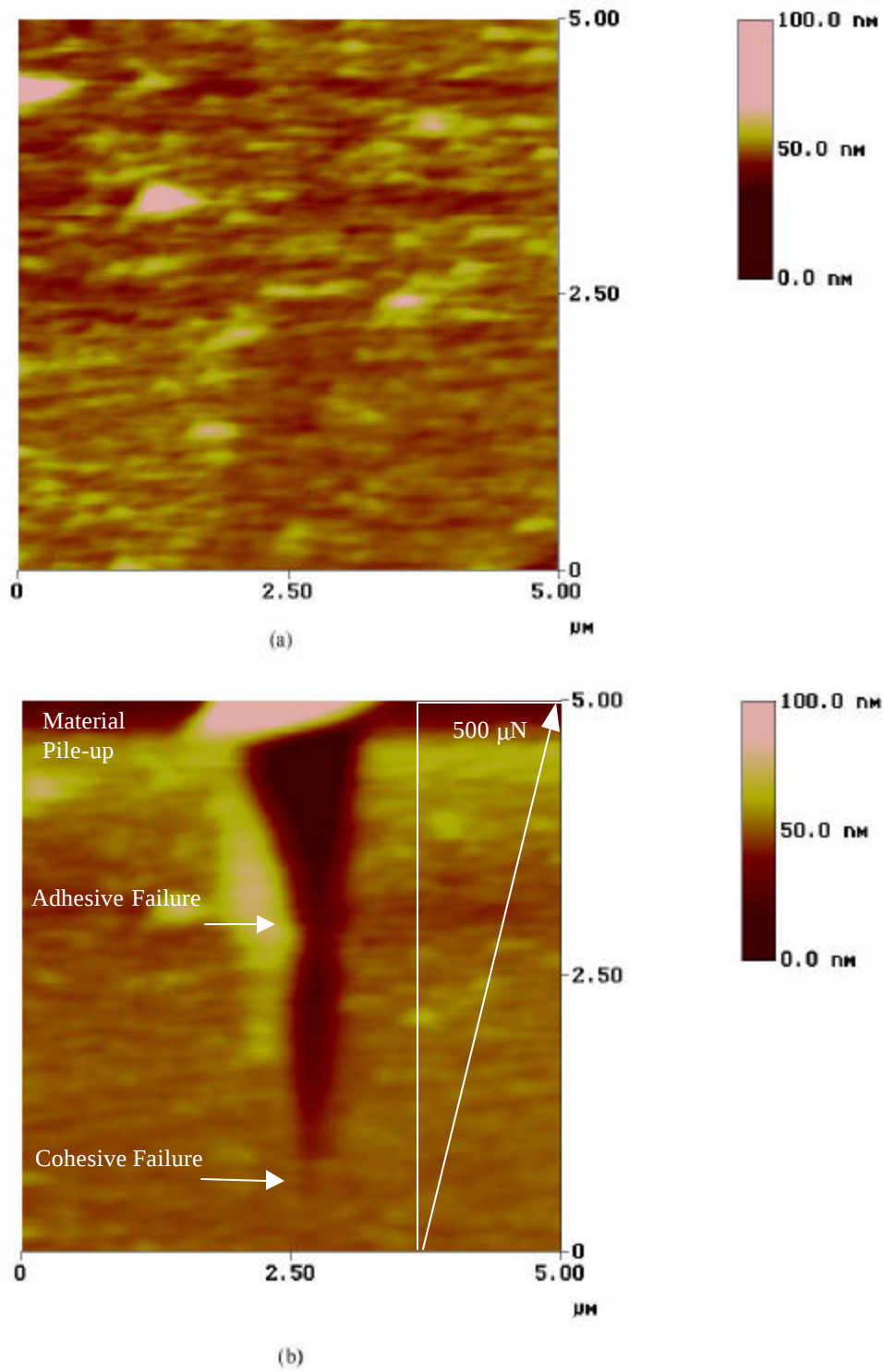


Figure 4.4 AFM scans of a PLAD film surface deposited at 100 mJ/cm^2 (a) pre scratch, (b) post $500 \mu\text{N}$, $5 \mu\text{m}$ ramp scratch.

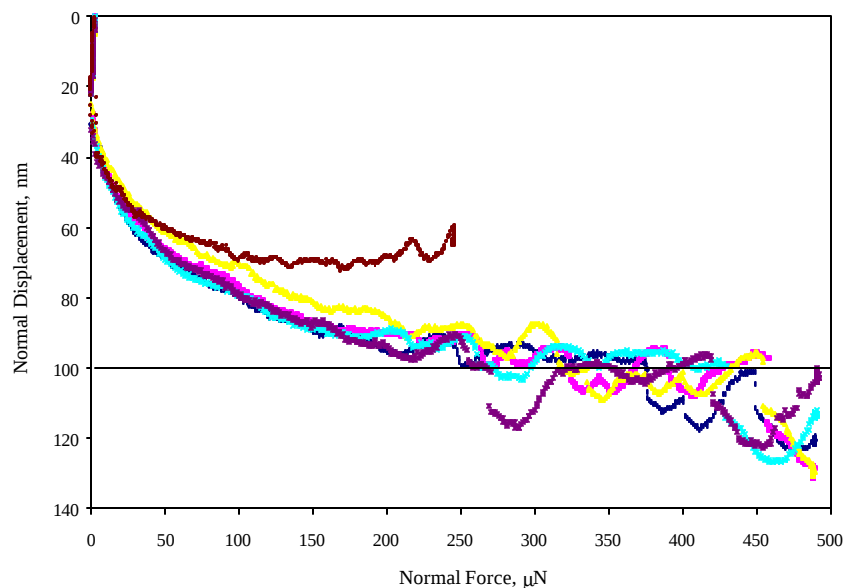


Figure 4.5 Force-displacement curves for the sample shown in fig. 4.4. Adhesive Failure is seen at 100 nm which corresponds to the film thickness. (Shown by the solid line).

Background

Micro- or nano-indentation measurements on polymers have been of interest for a long time, not only due to the small sample size requirements but also due to the possibility of doing time-response testing. This would allow measurement of the creep rate and stress relaxation times of thin polymer films and correlation to their bulk values. Thus, it is possible to study viscoelastic phenomena on a micro- or nanometer scale.

Nanoindentation measurements on the 3 major types of polymers namely; glassy, semicrystalline and elastomeric have been reported. The polymers studied to date include: Polyimide (PI), Polypropylene (PP), Polystyrene (PS), Polydimethyl siloxane (PDMS), Poly(methyl methacrylate) (PMMA), Polyurethane (PU), Poly(vinyl chloride) (PVC) and Poly (tetra fluoroethylene) (PTFE). Table 4.1 gives a summary of these results along with observed effects and model calculations [105-115].

It is seen from table 4.1 that the modulus values for all the polymers were in the range of those reported for bulk measurements. This seemed to indicate the validity of using nanoindentation for measuring the mechanical properties of thin films. Also, the physical nature of these polymers were reflected in their creep or stress relaxation response, i.e. it was possible to see the difference in response of PMMA, a glassy polymer, when compared to PDMS, an elastomeric polymer.

The bulk phenomenon of chain untangling and flow under shear was also seen seen to occur by the creep and stress-relaxation response. Although a 3 element model of a spring in series with a Kelvin-Voigt element has been shown to give good fits to the viscoelastic response of some polymers, a 4-parameter model might be generally useful. The tests were also sensitive to the presence of fillers, with SiO₂ filled PU giving a much higher modulus than rubber filled PU.

However it was also seen that several factors affected the measurement and ultimately the modulus calculation. First, the film thickness played an important role in affecting the modulus values. Thin films gave anomalous high values due to substrate effects. Second, testing conditions also affected the measurement. As one might expect, high loading rates gave stiffer responses. Third, surface inhomogeneity also played a role in the response to nanoindentation. This was shown by the high modulus values seen at very low indentation depths. These unusually high modulus values have been ascribed to surface debris or fillers but it is also possible that there may be a 'skin' effect in such measurements. Fourth, the tip shape was seen to play an important role in determining the response, with flat punch-type indenters giving more representative results.

Table 4.1 Literature results for modulus values from nanoindentation of different polymers.

Polymer/Ref	Coating Method	Film thickness, μm	Modulus, GPa	Model	Observations
PP[105]	Bulk sample	-	2.47-2.72	-	Modulus difference between α and β crystal forms.
PI[106]	Spin-coating	2.2-5.0	2.8+/-0.3	-	Modulus difference for different film thickness.
PMMA[107]	Bulk sample	-	3.3	4-parameter model showed a good fit for PMMA and a borosilicate glass.	-
PDMS[108]	Solvent-free, doctor blade technique	2.0 78.0	90 MPa 10 MPa	3-element model of a spring in series with a Kelvin-Voigt element showed a good fit. Model allowed calculation of shear and elastic modulus values from load relaxation and creep testing.	Thinner films gave higher modulus values due to substrate effects. Values from indentation were in the range of values measured by dynamic mechanical analysis.
PS	Bulk sample	-	1.303		
PU[109]	-	1.0	1.08	3-element model of a spring in series with a Kelvin-Voigt element.	Analytical solutions provided a fundamental basis for interpreting experimental data.
PS	Bulk sample	-	2.19+/-0.08		
PET(Mylar®)[110]	Extruded film	100	2.0-3.0	-	Filler effects were evident with SiO ₂ filled films giving higher modulus values while rubber filled films were weaker. Substrate effects were also seen for displacements > 15% of film thickness
PU(50%v/v SiO ₂ filler)	Solvent-cast	1 μm film on PET	5.5-7.0		
PU(50%v/v rubber filler)	Solvent-cast	1 μm film on PET	1.75-2.0		
Unplasticised PVC[111]	Bulk sample	-	5.1	-	Weathering effects on window grade PVC showed a decrease in hardness values.
PET(Mylar®)[112]	Bulk sample	100	3.12+/-0.34	-	For PMMA, it was found that surface topography, hydrostatic pressure and viscoelastic behavior affected the calculation.
PMMA	Solvent-cast	1 μm film on PET	3.6		
PTFE[113]	Solvent-cast from commercially available nanoemulsion	0.5-15.0	1.2	-	Modulus value was higher than for bulk testing.
Poly(cis-isoprene)[114]	Bulk sample	-	0.37+/-0.01 MPa	-	Dynamic response under sinusoidal load at different frequencies gave storage and loss modulus values comparable to bulk testing
Human artery[115]	Bulk sample	-	34.3 kPa	Standard 3-element model	-

Materials.

A 100 μm Poly(ethylene terephthalate) (PET) (Mylar[®], Dupont) film was used as a reference to check the validity of the measurements. A cross-linked silicone film, prepared similar to a silicone target, as described in Chapter 3 was used for baseline measurements. Silicone specimens for tensile testing were punched out from a cross-linked silicone sheet using a die per ASTM specifications. PLAD films were deposited, according to procedures described in chapter 3, at the following energy densities: 100, 250 and 500 mJ/cm^2 . These films were used as samples for the nanoindentation and nanoscratch testing. The film thickness was in the range of 2.0–2.5 μm for nanoindentation and 0.37-0.5 μm for nanoscratch. All samples were mounted on 1cm dia. AFM pucks with superglue prior to testing.

Methods.

Nanoindentation. The Triboscope[®] Nanomechanical testing system (Hysitron Inc., Minneapolis, Minnesota) was used for these experiments. This system incorporates a patented three plate capacitive transducer with sharp diamond tips[104]. Due to the small size of the transducer the Triboscope[®] can be adapted to an existing Scanning Probe Microscope. This allows *in-situ* imaging of the sample which lets the user precisely place indentations on nanometer scale features on samples. During testing a trapezoidal force-profile was applied to the sample. The profile consisted of 3 sections namely: loading, holding and unloading. The loading and unloading rate was kept constant at 10 $\mu\text{N}/\text{s}$, while the hold period was constant at 5 seconds. Thus a maximum

force of 500 μN would require a load time of 50 sec, giving a total test time of 105 sec (load, hold and unload).

Nanoscratch. The samples were subjected to a ramp force profile with a maximum force of 500 μN and a scratch length of 5 μm . The normal force and lateral displacement profiles are shown in figure 4.6. The lateral displacement is the distance traveled by the scratch tip on the sample surface during testing. The load was applied over 50 sec. giving a loading rate of 10 $\mu\text{N}/\text{sec}$. Each sample was tested multiple times, and the plot of normal displacement vs. normal force was used to characterize film adhesion. As a second indicator of the film's scratch resistance, the ratio of the lateral force to normal force was also plotted as a function of time. This ratio is the coefficient of friction of the film and is another important indicator of the stresses experienced by the film during the scratch test.

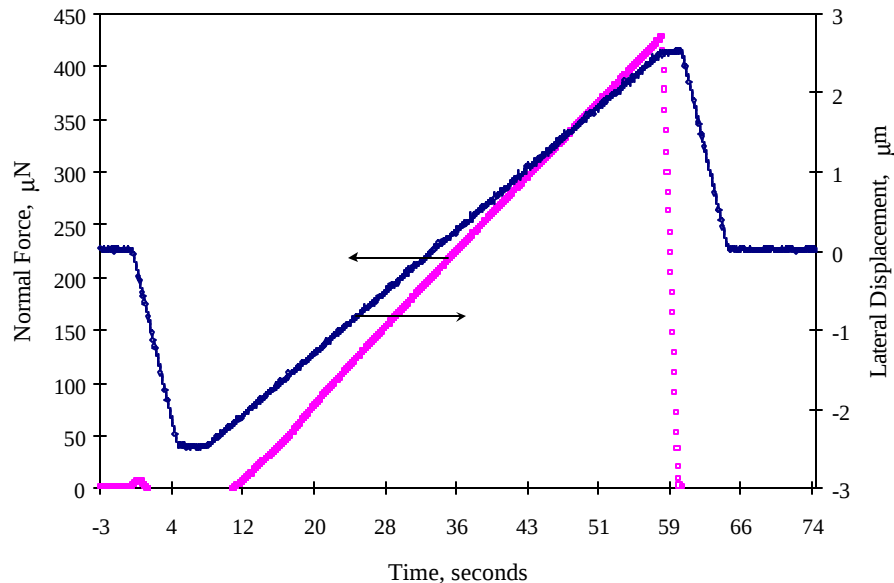


Figure 4.6 Normal force and lateral displacement profiles as a function of time used for the nanoscratch testing.

Results.

Nanoindentation. The results of nanoindentation testing on the PET film are shown in figure 4.7. It is seen that the modulus decreases with increasing contact depth and plateaus out to a near constant value. This phenomenon has been reported in the literature and it is speculated that it occurs due to skin effects, tip shape or debris present on the surface. The average PET modulus value measured by nanoindentation was 4.38 ± 0.56 GPa ($n=22$). This value is higher than literature values because it is weighted towards the modulus values at low contact depths. The standard procedure is to only include values in the plateau region of the modulus-contact depth graph. Including only such values for the above graph gives an average modulus value of 3.96 ± 0.254 GPa ($n=10$). This value is closer to literature values [112],[108] and indicates the validity of the Triboscope[®] results. Figure 4.8 shows the force-displacement curves for the PET sample at three different loading levels. The figure shows that the PET film undergoes the same deformation pattern at different maximum forces.

As a second reference, a $100\text{ }\mu\text{m}$ cross-linked silicone film prepared similar to a silicone target used in the PLAD experiments was tested. The results of the tests are shown in figure 4.9. It is seen that the modulus overestimation at low contact depths seen for the PET sample is over-accentuated for the silicone sample. The modulus at low contact depths is in the range of 80-130 MPa. Only at deep indentations does the modulus approach reasonable values (~ 1 -10 MPa). The average modulus value for the silicone sample in the plateau region is 3.72 ± 1.64 MPa ($n=11$). The reason for the high modulus values at low contact depths could be debris, fillers or other surface effects.

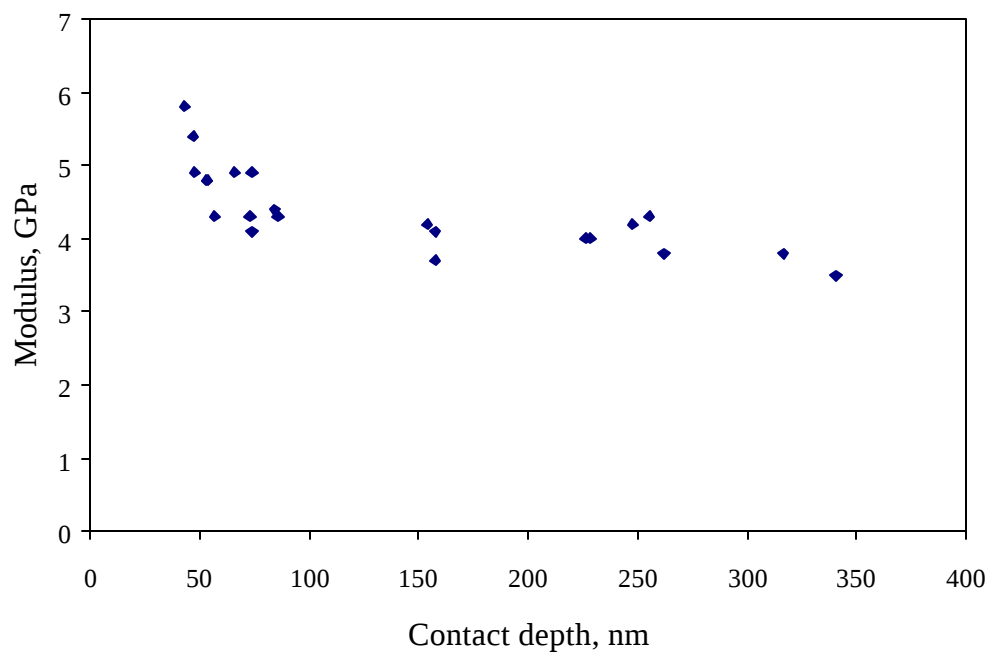


Figure 4.7 Modulus vs. contact depth for a 100 μm PET film.

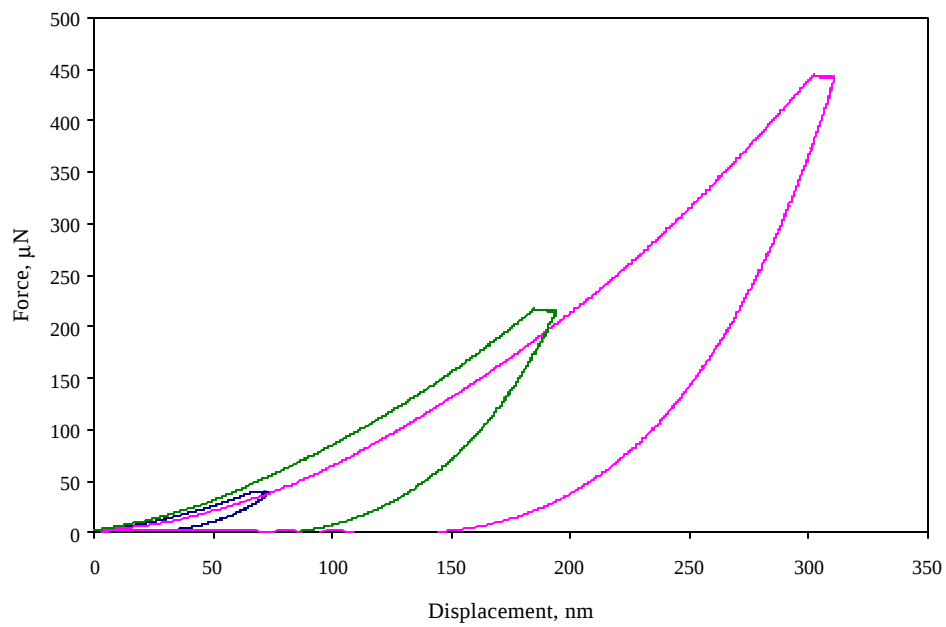


Figure 4.8 Force-displacement curves for a 100 μm PET film.

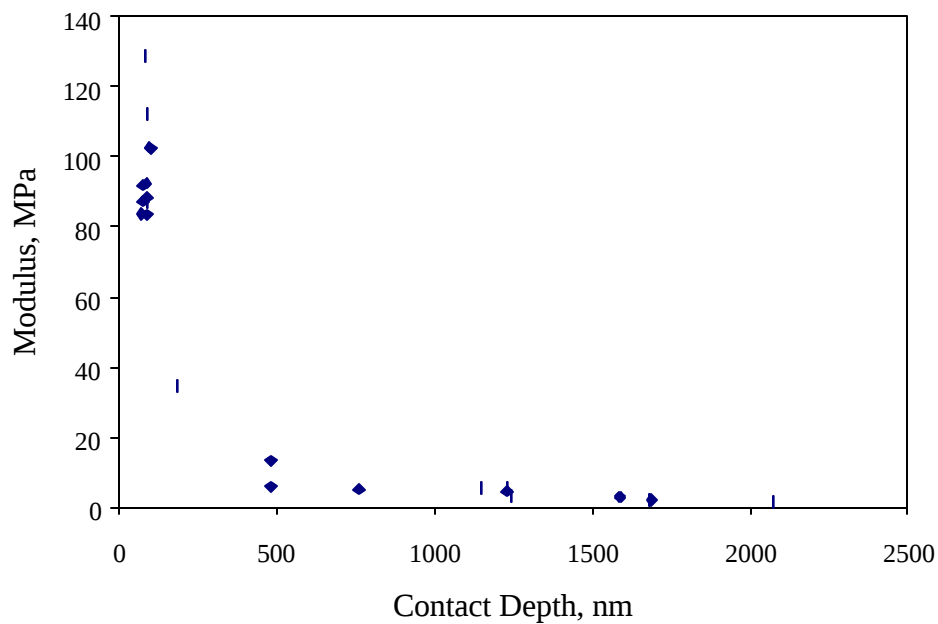


Figure 4.8 Modulus vs. contact depth for a 100 μm cross-linked silicone film.

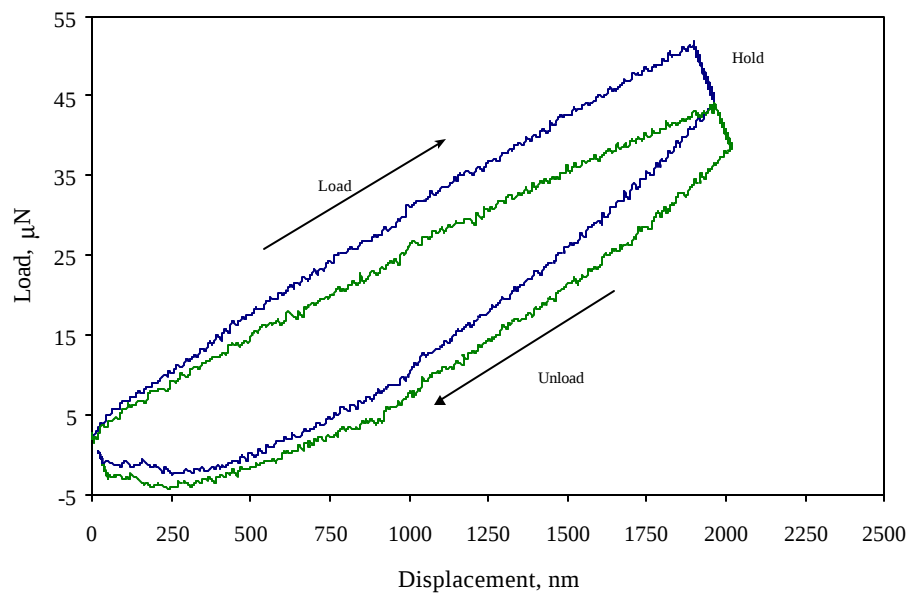


Figure 4.9 Force vs. displacement curves for a 100 μm silicone film. (Compare scale with figure 4.5).

Figure 4.9 shows the force-displacement curves for the silicone sample. It is seen that the silicone has a very 'weak' response. Even at extremely low forces (50 μN) the silicone film displacement is on the order of 2 μm . The PET and Silicone responses seem typical of a semicrystalline and elastomeric polymer respectively. The results indicated the importance of contact depth in calculating modulus.

Cross-linked silicone samples which were tested per ASTM D412-92 specifications gave a modulus value of 8.65 $\pm$ 2.65 MPa (n=7). Thus the values obtained from tensile testing and nanoindentation were in agreement indicating the validity of the measurements. (The tensile testing was done in collaboration with Dr. Chris Widenhouse).

The PLAD film samples were analyzed similar to the PET and silicone samples. Figures 4.10-4.12 show representative force-displacement curves at three loading levels for PLAD films deposited at different energy densities. It is seen that all the samples give different displacement responses at the same force. This indicates a change in the films' mechanical properties with energy density. In particular, figure 4.12 shows the wide variability in response for the film deposited at 500 mJ/cm^2 . This film demonstrated an elastomeric response for some force profiles.

The modulus dependence on contact depth seen earlier for the PET and silicone films was also exhibited by the PLAD films. As seen in figure 4.13 at low contact depths, modulus values are higher and only begin to plateau out as the contact depth increases. As stated before, the reason for this phenomenon is not completely known and can only be theorized. It is possible that the topmost layer of the PLAD films have a higher crosslink density than the deeper layers.

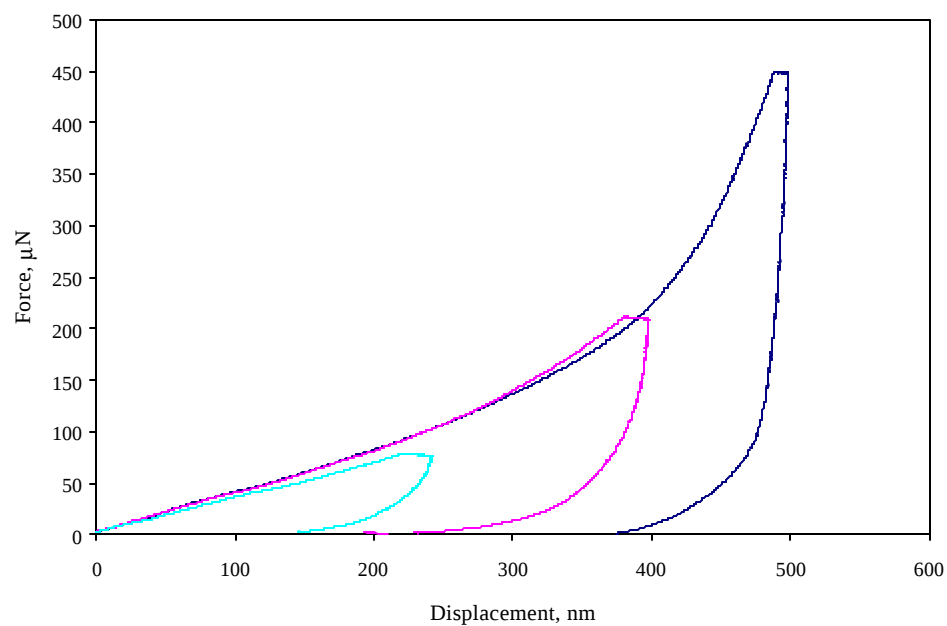


Figure 4.10 Force-displacement curves for a PLAD film deposited at 100 mJ/cm^2 .

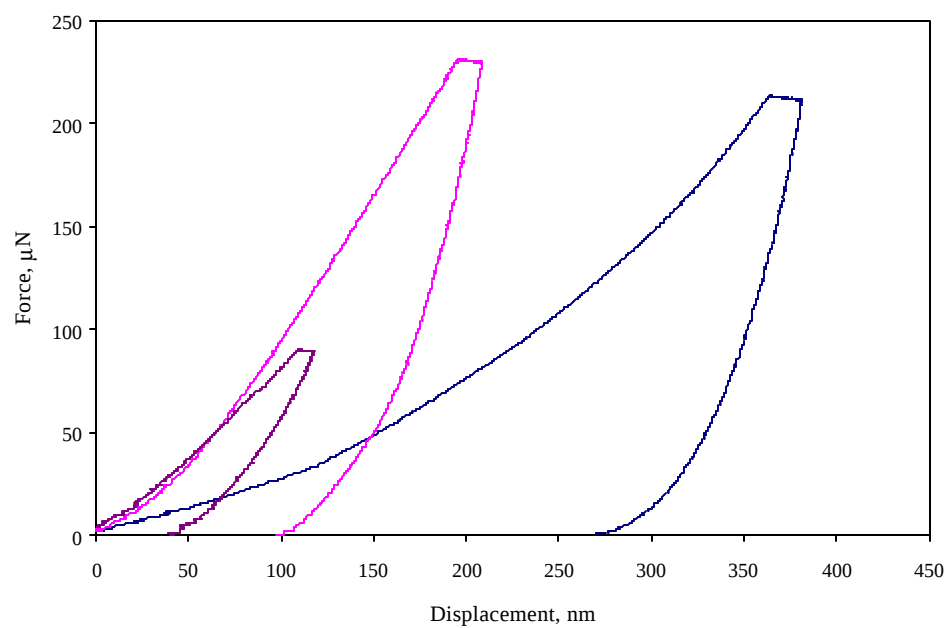


Figure 4.11 Force-displacement curves for a PLAD film deposited at 250 mJ/cm^2 .

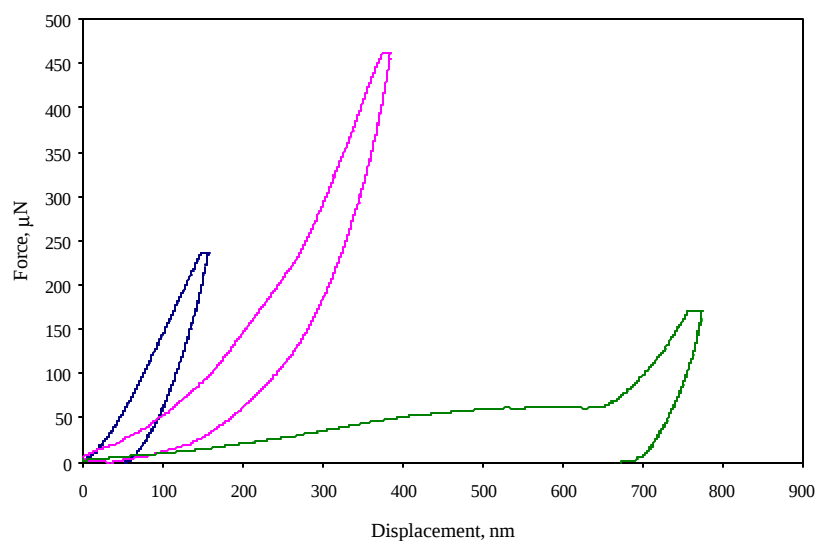


Figure 4.12 Force-displacement curves for a PLAD film deposited at 500 mJ/cm^2 .

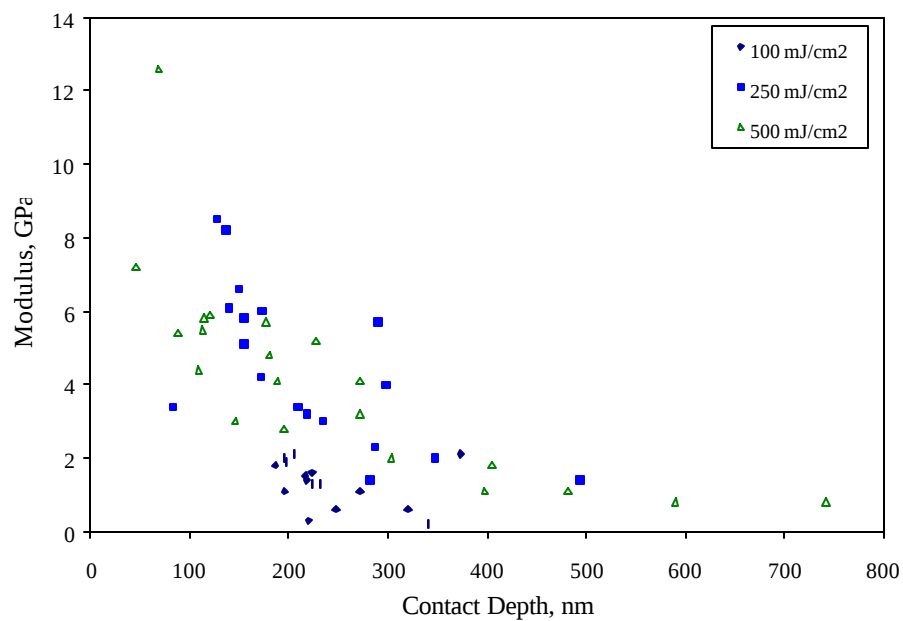


Figure 4.13 Modulus vs. contact depth for PLAD films synthesized at different energy densities.

Figure 4.14 shows the time-displacement response of a PLAD film deposited at 100 mJ/cm^2 . The representation of displacement vs. time allows differentiation of the various components of the response. During loading, an elastic and viscous response can be detected on the displacement. The polymer exhibits significant creep during the hold period. As the film is unloaded it again demonstrates elastic and viscous components. Finally, the permanent deformation can be clearly seen at the end of unloading. This representation shows that the film undergoes a 'classic' viscoelastic response as a function of time indicating that even though the PLAD process may cause significant rearrangement in the structure, the film retains its polymeric character.

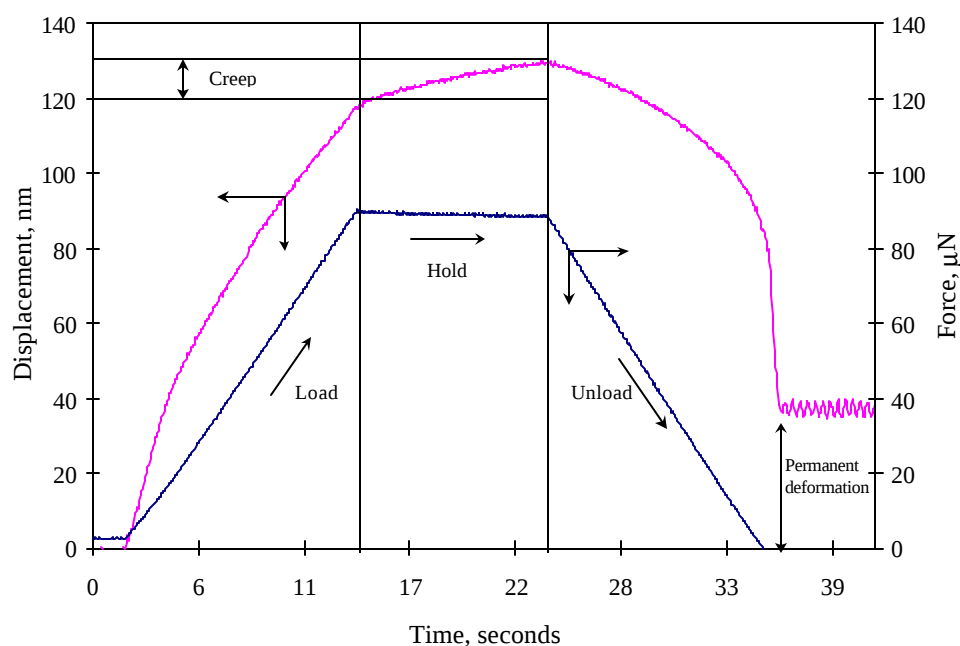


Figure 4.14 Time response of a PLAD film deposited at 100 mJ/cm^2 .

The combined results of the modulus values from the force-displacement curves are shown in figure 4.15. Only the modulus values in the plateau region for all the samples were included in the analysis. A minimum of 10 data points per sample were

taken for the calculation of the average modulus. It is seen that the average modulus shows a change with respect to the energy density. At 100 mJ/cm^2 , the deposited film is weaker and shows failure (characterized as permanent deformation) at lower force. Consequently the average modulus value is also low. It was also seen that this film gave reproducible measurements as compared to films deposited at higher energy densities.

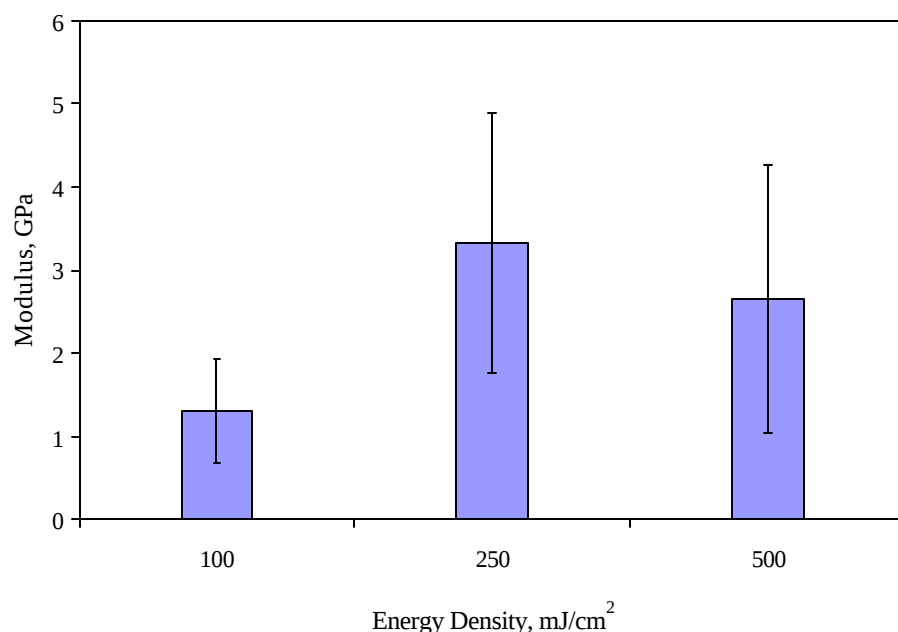


Figure 4.15 Average modulus values for PLAD films deposited at different energy densities.

At 250- and 500- mJ/cm^2 , the modulus values are higher but also show greater variability. This indicates the inhomogeneity of the film surface at high energy densities. The inhomogeneity could be caused by the particulate nature of the ablation products resulting in a film which has areas of high and low crosslink density. The film deposited at 500 mJ/cm^2 also showed soft spots with an elastomeric response. This indicated that the ablation products could contain discrete silicone particles ablated off the surface. If

these particles are incorporated in the film as is it would result in the kind of response seen in this film.

All the modulus values were much higher (approx. three orders of magnitude) than those seen for the target silicone sample. Modulus values in the GPa range seem inconceivable for silicone films. The high modulus values could be due to high cross-link density caused by the PLAD process. The other possibility is substrate effects. In the case of a soft film on a hard substrate, the substrate properties will dominate beyond a certain film thickness. If the substrate contributes to the deformation response, it would result in artificially high modulus values. It is also possible that the tip shape contributed to the measurement. The Berkovich tip shape is a sharp indenter which can cause severe damage to soft samples.

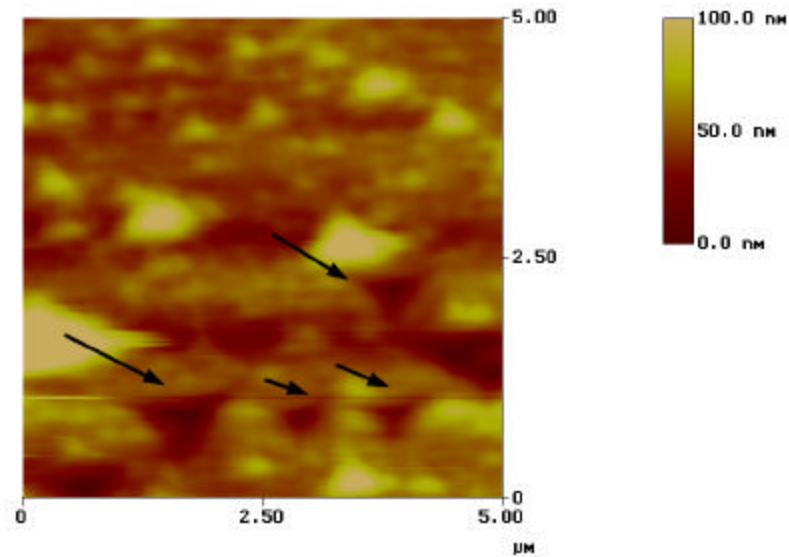


Figure 4.16 AFM scan of a PLAD surface. Arrows indicate indent sites.

There are conflicting reports in the literature on the maximum displacement to which a film can be indented without seeing substrate effects. A conservative estimate is

to let the maximum displacement be <10% of the total film thickness. Others have reported that in the case of an elastomeric film it is possible to deform the film to the extent of its thickness without seeing any substrate effects (Lance Kuhn, Hysitron Inc., Minneapolis, MN, Personal communication, 2000). For the PLAD films it was seen that deep indents gave the same modulus values as shallow indents in the plateau region. Thus it is possible that the higher modulus values seen for the PLAD films arise due to their higher cross-link density and not from the underlying substrate.

The above results are an improvement of several orders of magnitude in sensitivity as compared to macro-hardness testing. The modulus results also show that nanoindentation can be used to measure small changes in surface properties.

Nanoscratch. PLAD films synthesized at 100, 250 and 500 mJ/cm² were subjected to a ramp force scratch of 500 μ N with a scratch length of 5 μ m. Film thickness for all the samples was in the range of 0.37-0.56 μ m. Thin films were used so that the interfacial adhesion could be measured. All the samples showed certain general scratch characteristics. The scratch morphology for all the films appeared to be similar, with an approximately triangular shape which increased in size as the ramp force increased. The typical force for scratch initiation was within 50 μ N for all samples. As the tip penetrated deeper into the sample, material pile-up was seen, although no areas of drastic failure as characterized by delamination or fracture were observed. Only four force-displacement curves are shown per sample, although each sample was subjected to at least ten scratches. The curves shown were selected to include the wide range of responses which were measured.

Figure 4.17 shows the force-displacement curves for a PLAD film synthesized at 100 mJ/cm^2 . It was seen that this sample gave reproducible results for all the scratch tests. The film response can be characterized as weak based on the small force needed for scratch initiation. It was also seen that the test never reached its maximum set value of $500 \text{ }\mu\text{N}$, indicating that the film was flowing causing the ramp force to stay constant. Figure 4.18 shows force profile and lateral/force/normal force response vs. time for a single test. It is seen that the force reaches a maximum and then stays constant. The ratio of the lateral force/normal force is the coefficient of friction for the film. It is seen that this value starts around 0.4 and then starts decreasing as the test progresses, ultimately plateauing out below 0.1. Since silicone is known for its lubricating properties, a low coefficient of friction could indicate that the material in the vicinity of the indenter is flowing. Figure 4.19 shows the AFM scan of a representative scratch.

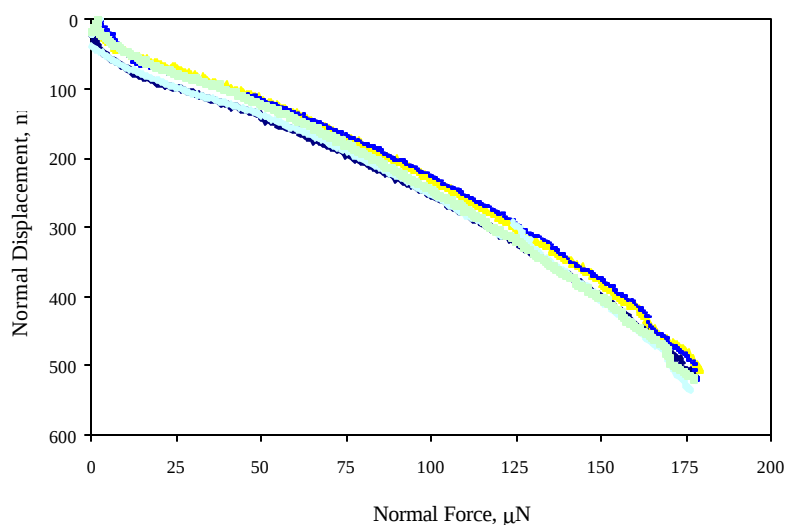


Figure 4.17 Normal displacement of a PLAD film deposited at 100 mJ/cm^2 , subjected to a ramp force scratch of $500 \text{ }\mu\text{N}$. The graph shows four scratch profiles.

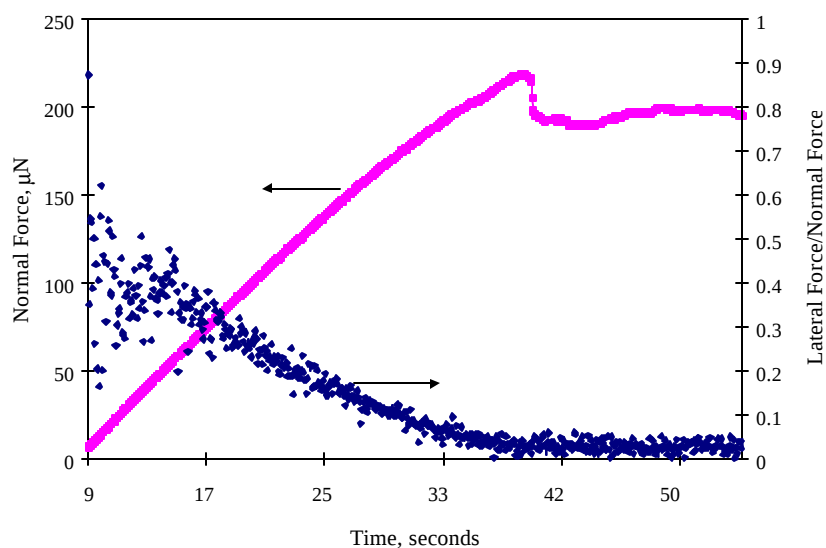


Figure 4.18 Time profiles of Normal force and lateral force/normal force for a PLAD film synthesized at 100 mJ/cm^2 . A yield point is seen on the normal force profile.

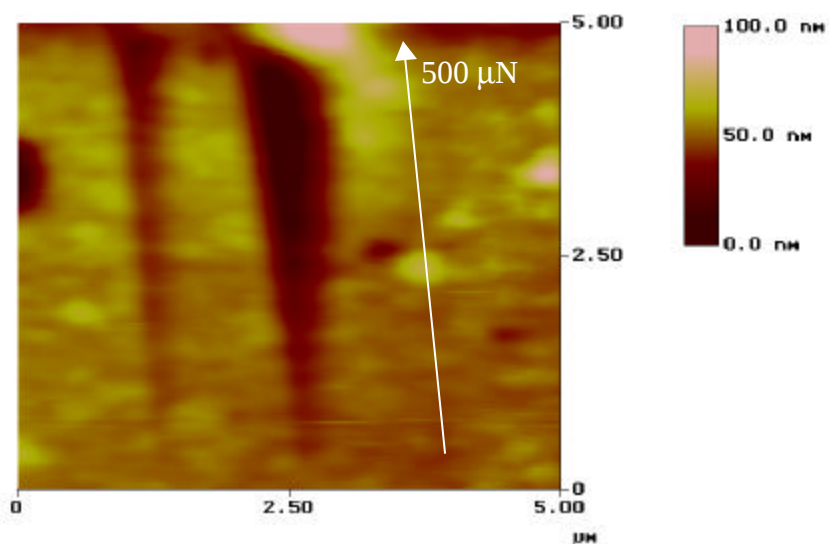


Figure 4.19 Atomic Force Microscope (AFM) scan of a PLAD film surface deposited at 100 mJ/cm^2 , with a 500 μN , 5 μm scratch. A 250 μN ramp scratch is seen to the left of the main scratch.

Figure 4.20 shows the force-displacement plots for a PLAD film synthesized at 250 mJ/cm^2 . It was seen that this sample gave a variety of responses, some of which are shown in the figure. All the other scratch tests gave curves which fell within this range. Comparing the curves in figure 4.20 to each other it is evident that at some spots on the sample a weak response is elicited as characterized by a large displacement at small forces while at other spots the film showed a strong response characterized by a small displacement at large forces. This indicated the inhomogenous nature of the film giving rise to different mechanical properties at different spots.

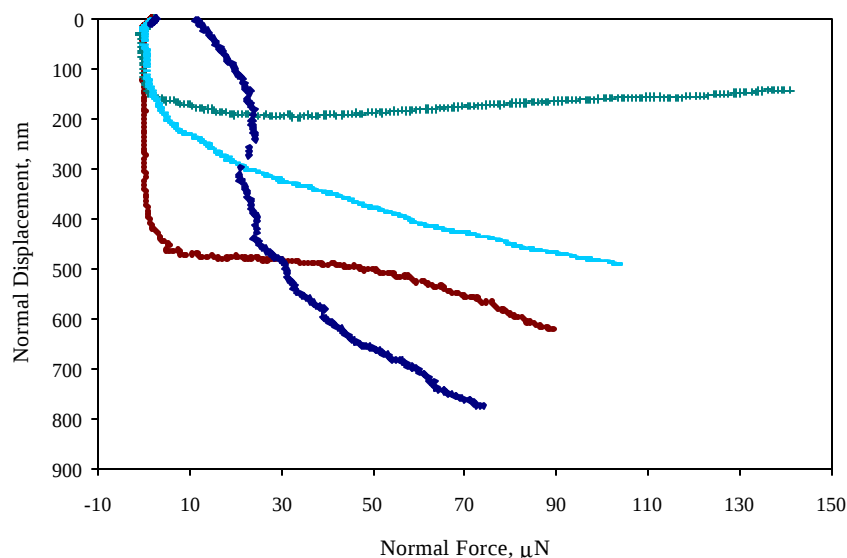


Figure 4.20 Normal displacement of a PLAD film deposited at 250 mJ/cm^2 , subjected to a ramp force scratch of $500 \mu\text{N}$. The graph shows four scratch profiles which show a variety of responses.

Figure 4.21 shows the normal force and lateral force/normal force response vs. time for a single test. As the ramp force increases, the coefficient of friction initially increases and then starts to decrease. Figure 4.22 shows the AFM scan of the film surface after a scratch.

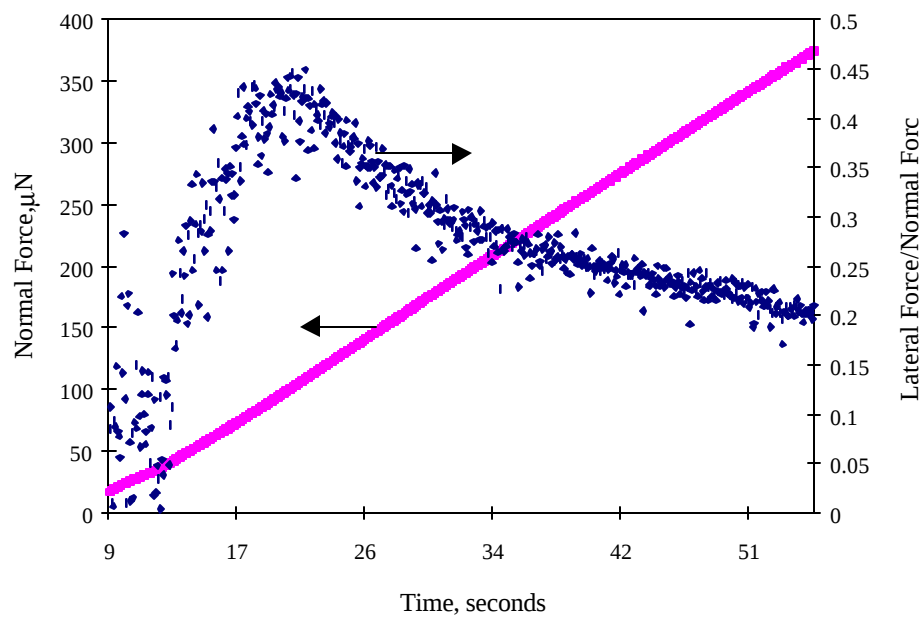


Figure 4.21 Time profiles of normal force and lateral force/normal force for a PLAD film synthesized at 250 mJ/cm^2 .

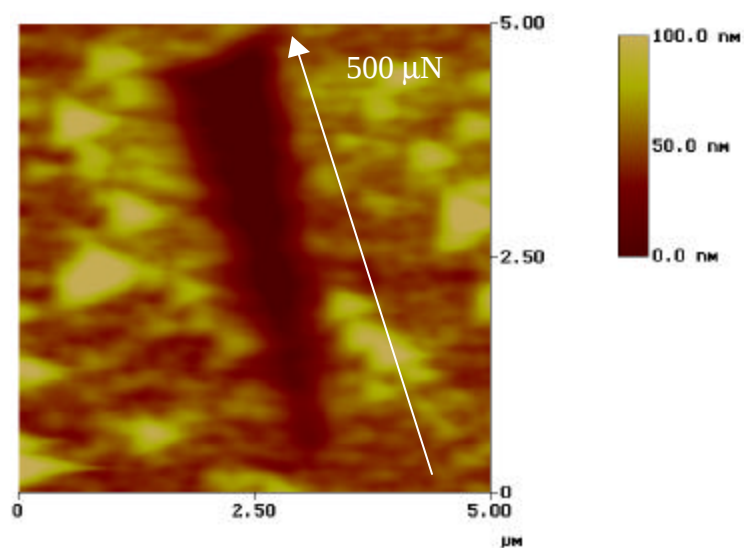


Figure 4.22 Atomic Force Microscope (AFM) scan of a PLAD film surface deposited at 250 mJ/cm^2 , with a 500 μN , 5 μm scratch.

Figure 4.23 shows the force-displacement plots for a PLAD film synthesized at 500 mJ/cm^2 . Similar to the earlier example, this sample also gave a variety of responses. Several scratches showed breaks in the force-displacement profile which indicated that the film could be delaminating at this point. These break points did not always occur at the same film thickness which could be due to the inhomogenous makeup of the film.

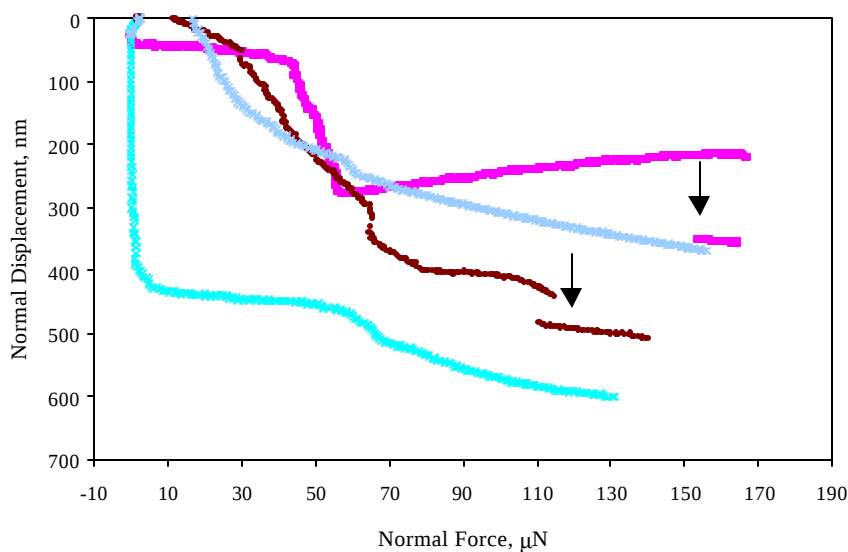


Figure 4.23 Normal displacement of a PLAD film deposited at 500 mJ/cm^2 , subjected to a ramp force scratch of 500 μN . The graph shows four scratch profiles which show a variety of responses with the arrows indicating points of film failure.

Figure 4.24 shows that normal force and lateral force/normal force vs. time response for a single scratch test. Similar to the earlier samples, as the ramp force increases, the coefficient of friction starts out high and then decreases as the test progresses. Figure 4. 25 shows the AFM scan of the film surface after a 500 μN scratch.

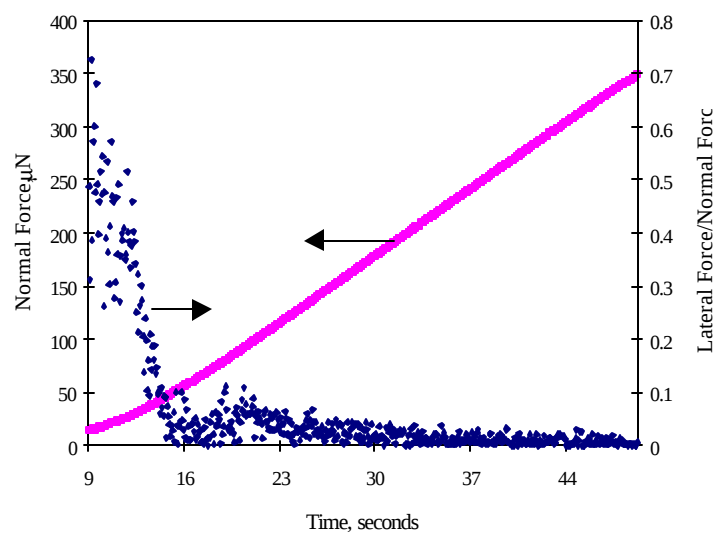


Figure 4.24 Time profiles of normal force and lateral force/normal force for a PLAD film synthesized at 500 mJ/cm^2 .

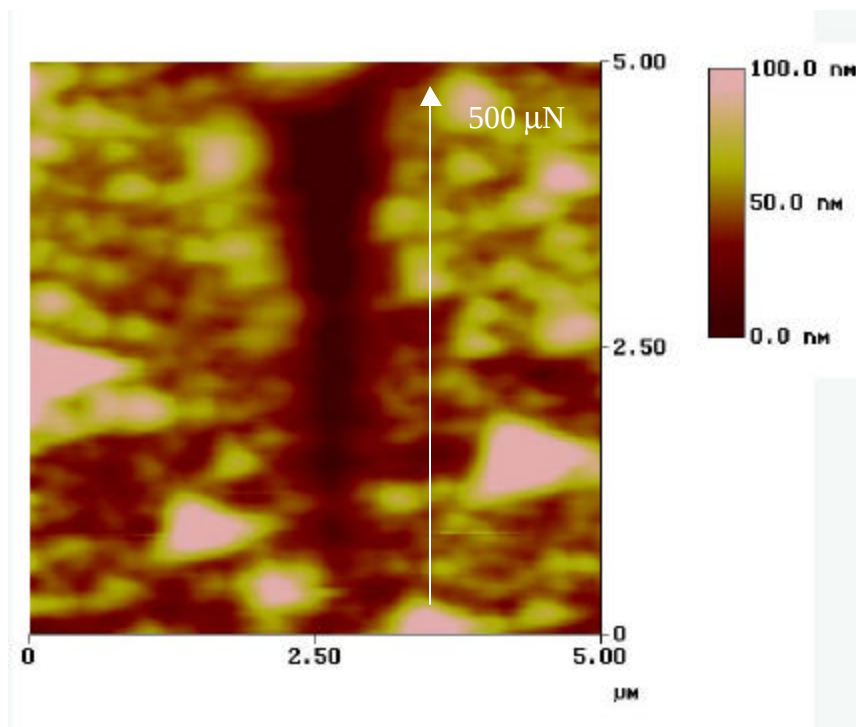


Figure 4.25 Atomic Force Microscope (AFM) scan of a PLAD film surface synthesized at 500 mJ/cm^2 , with a $500 \mu\text{N}$, $5 \mu\text{m}$ scratch.

Finally, figure 4.26 shows the force-displacement curves for a cross-linked silicone film subjected to a 500 μN , 5 μm scratch test. The silicone film failed easily in comparison to the PLAD films. (Compare scale for figures 4. 17, 4.20, 4.23 and 4.26). Figure 4.27 shows the normal force and lateral force/normal force vs. time response for the silicone film. The coefficient of friction did not develop in the same fashion as the PLAD films. The initial decrease at the start of the test is followed by a small increase before plateauing out at approximately 1.2. The silicone film scratch morphology is not shown since attempts to scan the film surface post-scratch testing were not successful.

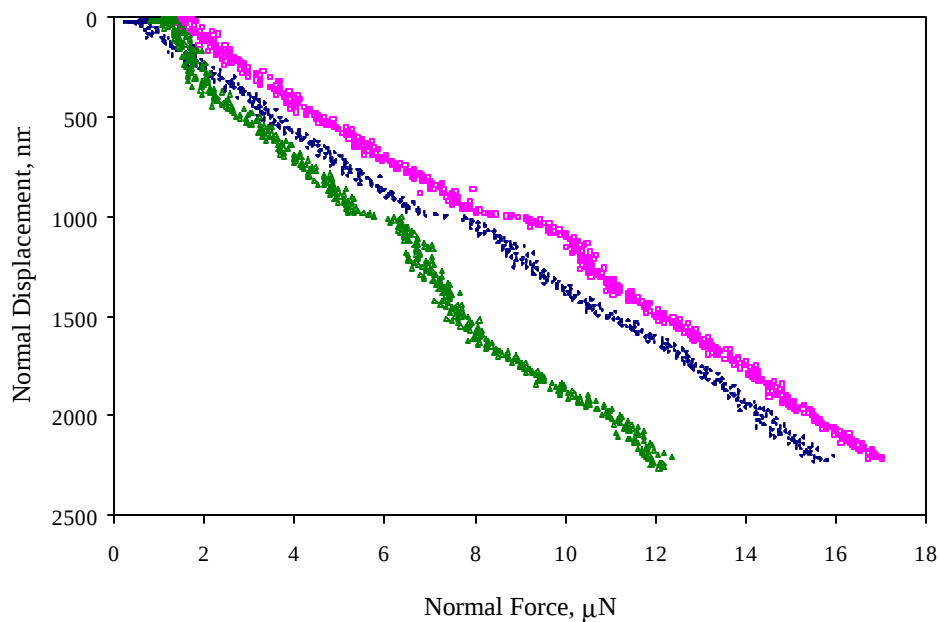


Figure 4.26 Normal displacement plots for a cross-linked silicone film subjected to a 500 μN , 5 μm scratch test.

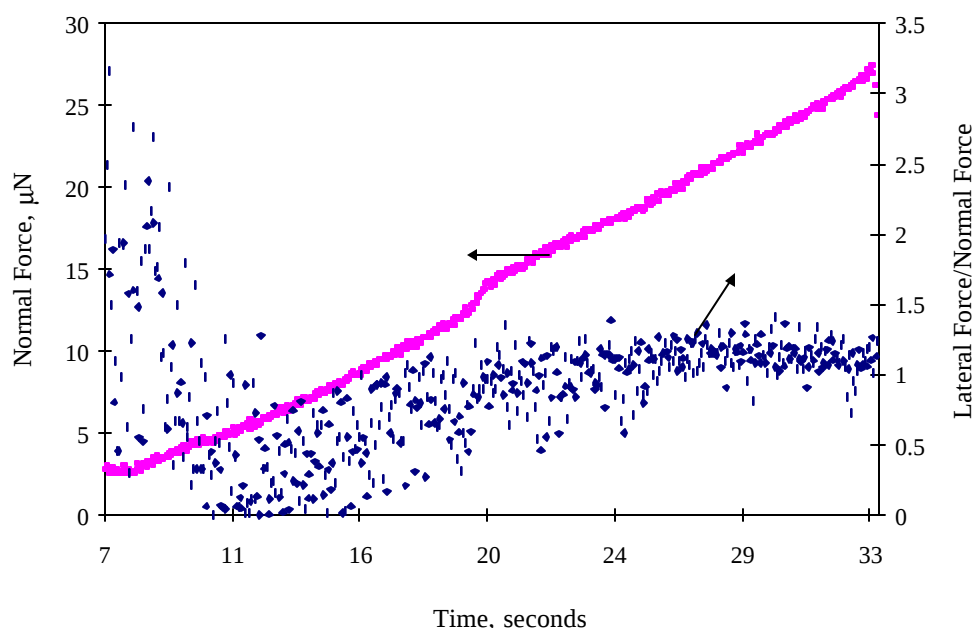


Figure 4.27 Normal force and lateral force/normal force vs. time profile for a single scratch test for a cross-linked silicone film.

Discussion

The nanoindentation testing on the PET and cross-linked silicone films gave modulus values which were in agreement with literature results. This indicated that nanoindentation was a valid method to measure thin film mechanical properties. However, it was also seen that the contact depth played a significant role in determining the modulus values for a particular polymer. Higher modulus values were observed for both PET and silicone. The reason for this phenomenon is as yet unknown although some speculation can be made. The PET film surface could experience different cooling rates during processing causing a skin formation with a higher crystalline content, similar to that known to exist in PET fibres. The high modulus values for the silicone sample are intriguing since this polymer is known to be extremely mobile in the bulk. The higher

values could be due to the presence of a skin which is structurally different than the bulk or due to preferential segregation of nanophase silica filler at the surface. This aspect needs further investigation and it is possible that nanoindentation measurements may yield insights into the surface structure of silicone which could prove useful in the surface modification of silicone and also its use as a lubricant.

The nanoindentation results for the PLAD films indicated that the change in film properties as a function of energy density could be followed by this method. The film synthesized at 100 mJ/cm^2 gave reproducible results indicating that the deposition process at this energy level was gradual giving rise to a homogenous film. Increasing the energy density produced films which gave a variety of responses from elastomeric to tough. This result seemed to be due to the film formation processes occurring at the higher energy densities. As shown in chapter 3, ablation at high energy densities (approx. $>200 \text{ mJ/cm}^2$) produced films with a particulate nature. Thus the film could contain discrete silicone particles which were ablated off the target and also inorganic particles due to oxidation. In addition, the deposited film could contain areas of low and high cross-link density. All these effects could give rise to a film wherein the mechanical properties differ at different areas.

The average modulus value for the PLAD films was approx. three orders of magnitude higher than that measured for the cross-linked silicone film. The film synthesized at 100 mJ/cm^2 had the lowest modulus value among all the PLAD films indicating that it may have a larger content of silicone-like polymer. As stated before, the higher modulus values for the PLAD films could be due to substrate effects affecting the indentation measurement. It was seen that deep indents gave the same modulus values as

shallow indents in the plateau region. This effect does require further study to determine the exact cause of the stiffer responses of the PLAD films. However, although no absolute modulus values can be conclusively assigned to the PLAD films, the nanoindentation measurements can be used to detect relative changes in film properties based on synthesis conditions.

The nanoscratch results showed a similar trend to the nanoindentation tests. The PLAD film synthesized at 100 mJ/cm^2 gave reproducible results while those synthesized at 250- and 500 mJ/cm^2 gave a variety of responses. All PLAD films demonstrated better scratch resistance than the cross-linked silicone sample. This was in agreement with the nanoindentation results which seemed to indicate that the films had better mechanical properties than the target. Although it was believed that nanoscratch testing would provide an exact measure of the film-substrate adhesion, a sharp break in the force-displacement curve was not always seen. Thus a quantitative value for the film's adhesion strength could not be assigned. However important information on the film's scratch resistance could be gathered by monitoring the coefficient of friction and also by examining the scratch morphology. The film adhesive failure did not seem to occur by delamination or fracture but seemed to be a gradual, progressive process dependent on the force of the scratch. All the PLAD films demonstrated a low coefficient of friction, in comparison to the cross-linked silicone sample. The scratch morphology did not show any film fracture or other signs of drastic failure.

Summary

Newly introduced nanomechanical methods were used to characterize the mechanical properties of PLAD films. The validity of the test method was checked by

measuring the modulus of PET and cross-linked silicone films. It was seen that these values were in agreement with literature results. PLAD films gave modulus values which were much higher than the cross-linked silicone targets. Although substrate effects could affect the measurement, the exact cause of the higher modulus was not apparent. Further testing would be needed to determine this. Nanoscratch testing showed the PLAD films to have better scratch resistance than the cross-linked silicone sample.

CHAPTER 5

EMPIRICAL MODEL FOR ABLATION OF SILICONE AT 248nm

Introduction

Laser ablation has been shown to be an efficient route for etching polymers to produce structured surfaces. The numerous literature reports on the use of laser ablation in the fields of microelectronics and ophthalmic surgery have attested to the success of this technique. It can be seen from these studies that two general conditions are required for efficient photoablation to occur. First, the polymer needs strong optical absorption at the laser wavelength of interest. Second, the light (laser) intensity needs to exceed a threshold value for significant ablation to occur. Providing these conditions are met, etch pits with structured features and a debris-free surface can result after laser ablation.

The first condition decides the mode of ablation. When the polymer is not a strong absorber of laser radiation, the quality of ablation is poor. This is typically seen in the ablation of PTFE which absorbs weakly in the UV and produces a ragged, disrupted surface when irradiated at 248 nm. Another example is the 1064 nm irradiation of collagenous tissue which produces etch pits with ragged edges and a large zone of injury to the surrounding tissue.

On the other hand when the polymer strongly absorbs the laser radiation, efficient photoablation results. Typically etch pits which show little debris and smooth features

are produced with minimal damage to the surrounding surfaces. The effect of radiation confinement is especially important in the laser irradiation of tissue. It is also seen that lower intensities are required to produce ablation in these polymers. Ablation of PMMA at 193 nm is an example of this type of photoablation.

The second condition of laser intensity decides the efficiency of ablation. It has been seen from literature reports that all polymers exhibit a threshold energy density below which ablation proceeds at a very slow rate. Above the threshold the ablation rate increases linearly to a limiting value beyond which the ablation rate starts to saturate. Weakly absorbing polymers have a higher threshold as compared to strong absorbers. This has been elegantly illustrated in a report by Brannon *et al.* in which they ablated a plasma polymerized fluorocarbon film by 30 ns , 248 nm laser pulses [43]. The plasma polymer exhibited efficient ablation at 100 mJ/cm^2 as compared to PTFE which did not ablate at this energy density level. The plasma polymerized fluorocarbon had a higher absorption coefficient (7×10^4 vs. 10^2 cm^{-1}) due to the presence of conjugated double bonds in the structure causing it to undergo ablation at lower energy density levels than PTFE.

Attempts have also been made to convert weak absorbers into strong ones. Three methods have been reported that allow efficient ablation of weakly absorbing materials. Chuang *et al.* [116], and Srinivasan and Braren [117] have demonstrated success in ablating polymers by incorporating UV absorbing dyes into the polymer matrix. Küper and Stuke [118], and Srinivasan *et al.* [119] have used 300 femtosecond laser pulses to produce ablation in weakly absorbing polymers. The shorter pulsewidths correspond to higher intensity (energy density/pulsewidth) levels which then allow ablation. Yet

another approach to this method has been the use of deep UV lasers (193 nm and lower) which cause absorption in all polymers.

The above discussion highlights several factors which contribute to polymer ablation. These factors can be absorption coefficient at the incident wavelength, incident energy density and laser pulsewidth operating alone or in concert. Since it was observed that the mode of ablation was dependent on the experimental conditions attempts to arrive at a single theory of polymer ablation have been unsuccessful thus far. Two mechanisms have been theorized to account for the observed behaviour namely; photochemical and photo-thermal ablation. In photochemical ablation, photon absorption leads to electronic excitation causing bond scission and material ejection off the surface. In photo-thermal ablation, electronic excitations are transferred to vibrational modes causing material heating and evaporation or pyrolysis off the surface. When photochemical processes determine the ablation then the absorption coefficient becomes a significant factor. When thermal processes dominate then factors like thermal diffusivity and degradation temperature become important. The rate of ablation is then generally determined by a rate constant with an Arrhenius type dependence on temperature and an activation energy. In many cases both processes can occur simultaneously during ablation and their relative contribution is decided by the energy density, laser wavelength and pulsewidth.

The earliest efforts by Jellinek and Srinivasan [120] to model the ablation behavior concentrated on describing it as a photochemical process wherein the etch (or ablation) rate was described as:

$$d = \frac{1}{a} \times \ln \left(\frac{I}{I_{th}} \right) \quad (1)$$

where d = etch depth per pulse (m/pulse)
 α = absorption coefficient (m^{-1})
 I = incident intensity (W/m^2)
 I_{th} = threshold intensity (W/m^2)

A more common practice is to use the energy density (energy per unit area) instead of the intensity in the above expression. It was found that the experimental etch depth vs. energy density curve often showed deviation from this ideal case. Some curvature in the low and high energy density region was observed for most polymers. It was also seen that the slope in the linear region of the curve did not always equal $1/\alpha$ [121]. These discrepancies led to several modifications to the original treatment. One approach was to separate the ablation mechanism into photothermal and photochemical components. This model was purely phenomenological and successfully described the etching behavior of PI at 193 nm [46]. However it was thought that a simple additive rule accounting for photothermal and photochemical processes was not valid.

Further modifications to the ideal case have been proposed by Küper, Modaressi and Stuke (KMS) [122]. Their model suggested that deviations from equation (1) occurred due to the need for incubation steps. Incubation is the phenomena wherein the initial laser pulses incident upon a polymer surface alter the absorption cross-section due to chemical structural changes making the polymer a strong absorber. Thus the KMS model took into account the absorption dynamics of the process. The nature of the thermal distribution in the low energy density regime led to the development of a thermal diffusion model by Furzikov [123]. This model accounts for the deviation from ideality through a modified absorption coefficient α_{eff} . The modified absorption coefficient takes into account the heat diffusion per pulse duration from the surface into the volume. Other

models developed include those by Cain *et al.* [121], which was fashioned similar to Furzikov's and interpreted ablation purely in terms of temperature rise and thermal decomposition of the polymer. Such an approach was found to be consistent with available data for the laser ablation of PI.

The above discussion detailed the different approaches which have been used to model polymer ablation. It was seen that earlier models assumed a substantial photochemical component contributing to the ablation. Thus many models required knowledge of the UV behavior of the polymer ie. values for the optical absorption coefficient needed to be accurately measured at the wavelength of interest. Most researchers have neglected the effect of temperature in the ablation mechanism. Furzikov's thermal model successfully described the ablation behavior of PI, PET and PC at 193 nm. Cain *et al.* also proposed a model which took into account the thermal diffusivity and heat transfer effects of the ablation process. D'Couto simplified this treatment to describe the ablation of PI at 193 nm successfully [46]. D'Couto's model did not require any assigned values for the absorption coefficient. Based on the data presented below it was believed that a purely thermal model fashioned after that of Cain and D'Couto could describe the ablation behavior of silicone. The model development and prediction are described in detail in the ensuing pages.

Results and Discussion

In order to understand the mode of ablation in silicone, SEM analysis of polymer target surfaces post ablation was undertaken. Silicone targets, prepared as per the procedure given in chapter 3, were ablated at three different energy density levels for a

set number of pulses. Figures 5.1-5.5 show the effect of energy density and pulse number on the ablated surfaces.

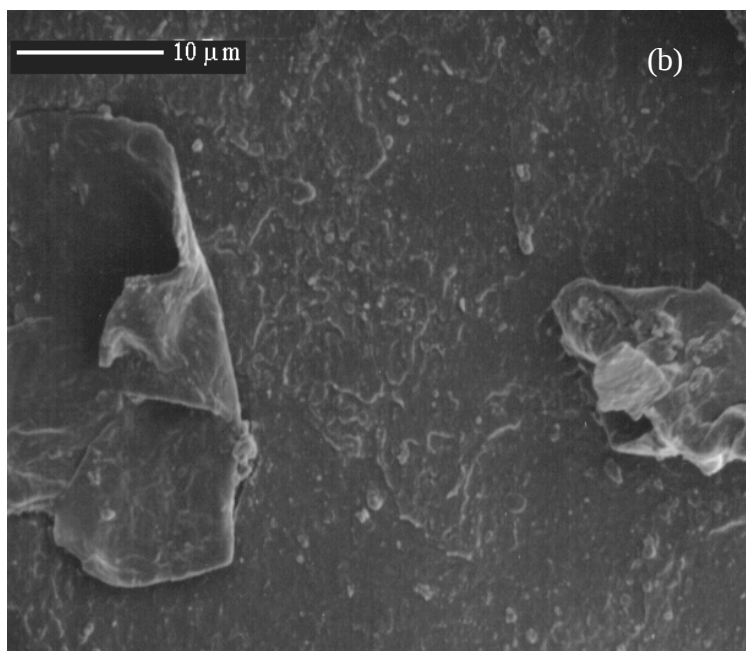
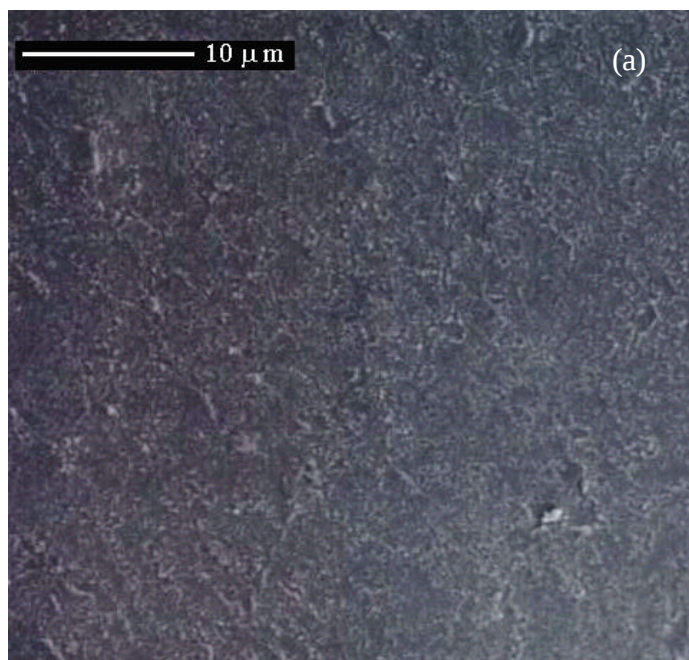


Figure 5.1 Scanning Electron Micrographs of silicone target surfaces ablated at 100 mJ/cm² (5kV, x2000) (a): 100 pulses, (b): 5000 pulses.

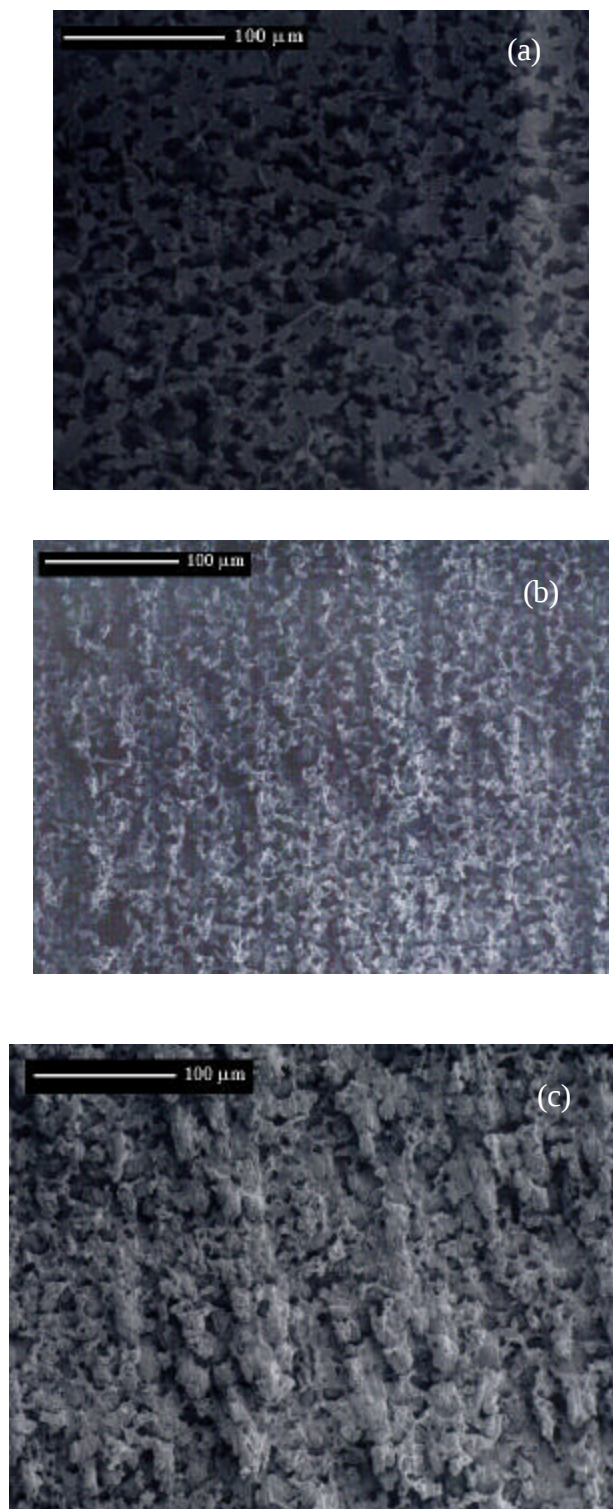


Figure 5.2 Scanning Electron Micrographs of silicone target surfaces ablated at 250 mJ/cm² (5kV, 500x) (a) 100 pulses, (b) 2000 pulses, (c) 5000 pulses.

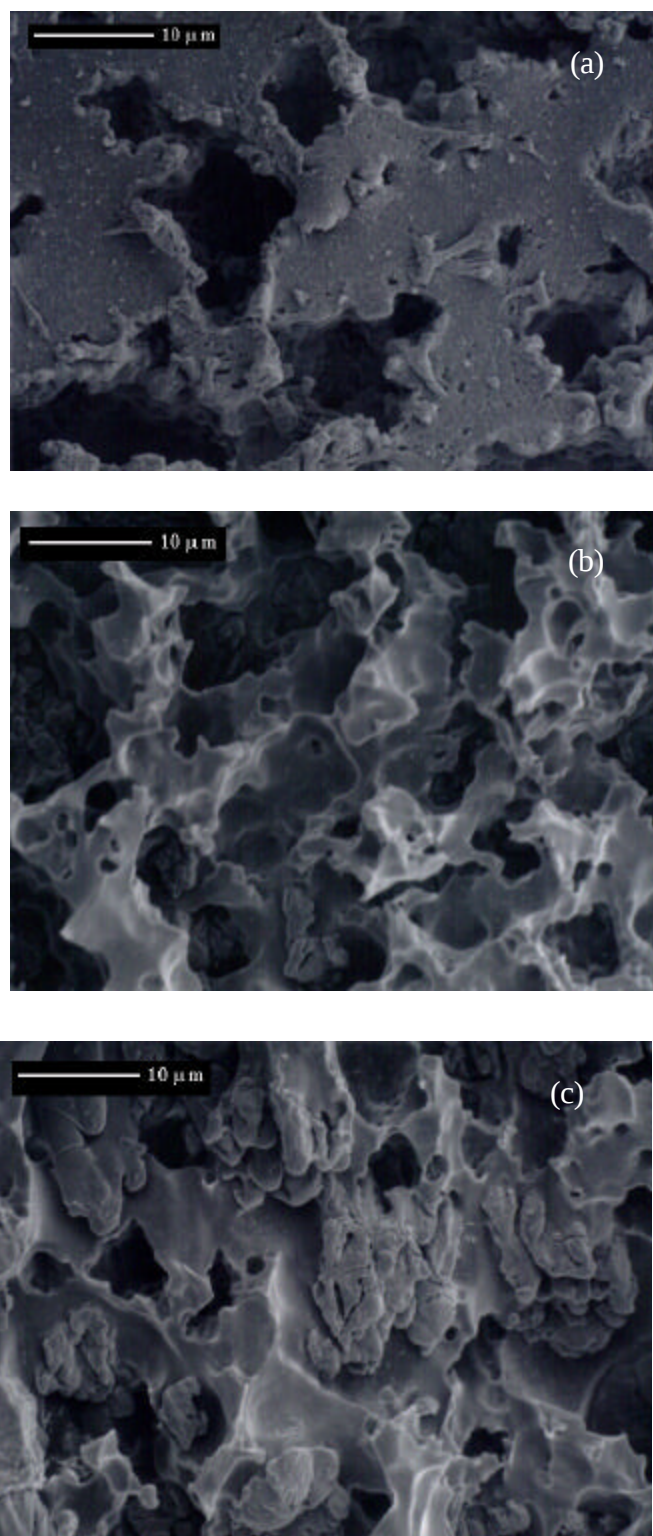


Figure 5.3 Scanning Electron Micrographs of silicone target surfaces ablated at 250 mJ/cm² (5kV, x2000) (a) 100 pulses, (b) 2000 pulses, (c) 5000 pulses.

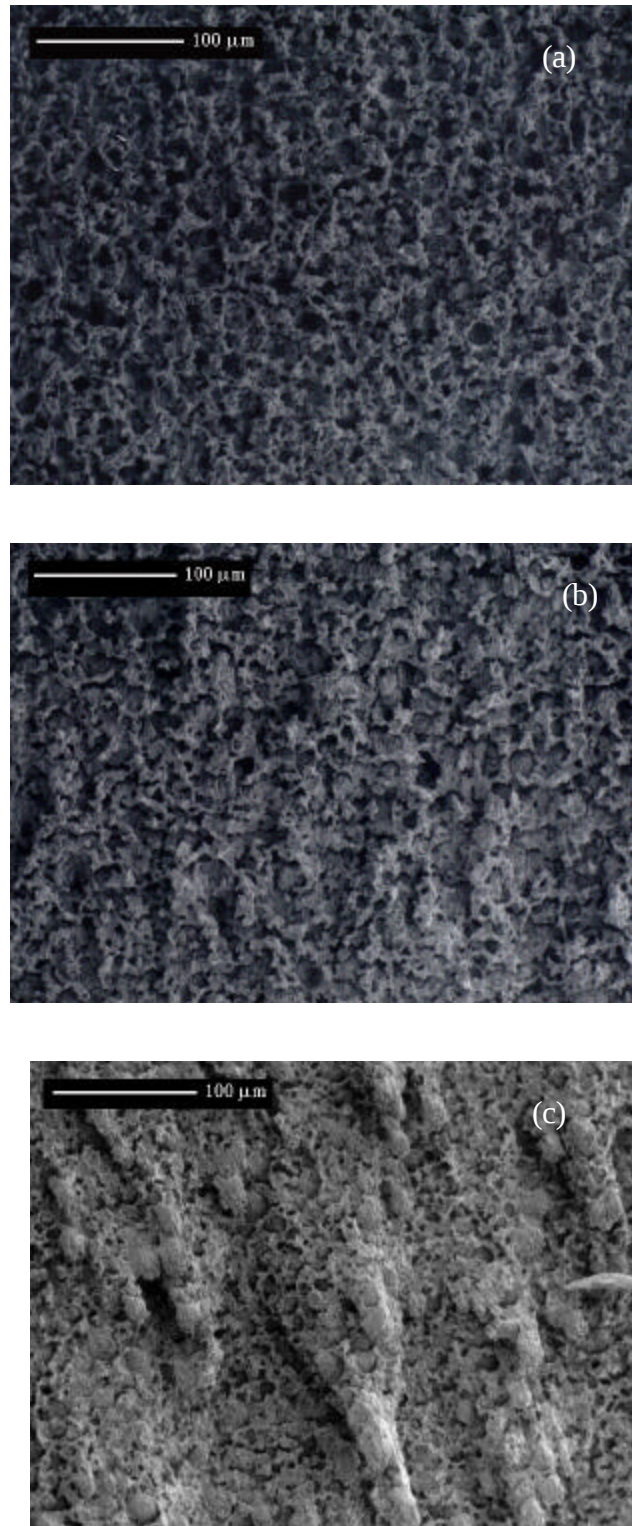


Figure 5.4 Scanning Electron Micrographs of silicone target surfaces ablated at 420 mJ/cm² (5kV, x500) (a) 100 pulses, (b) 2000 pulses, (c) 5000 pulses).

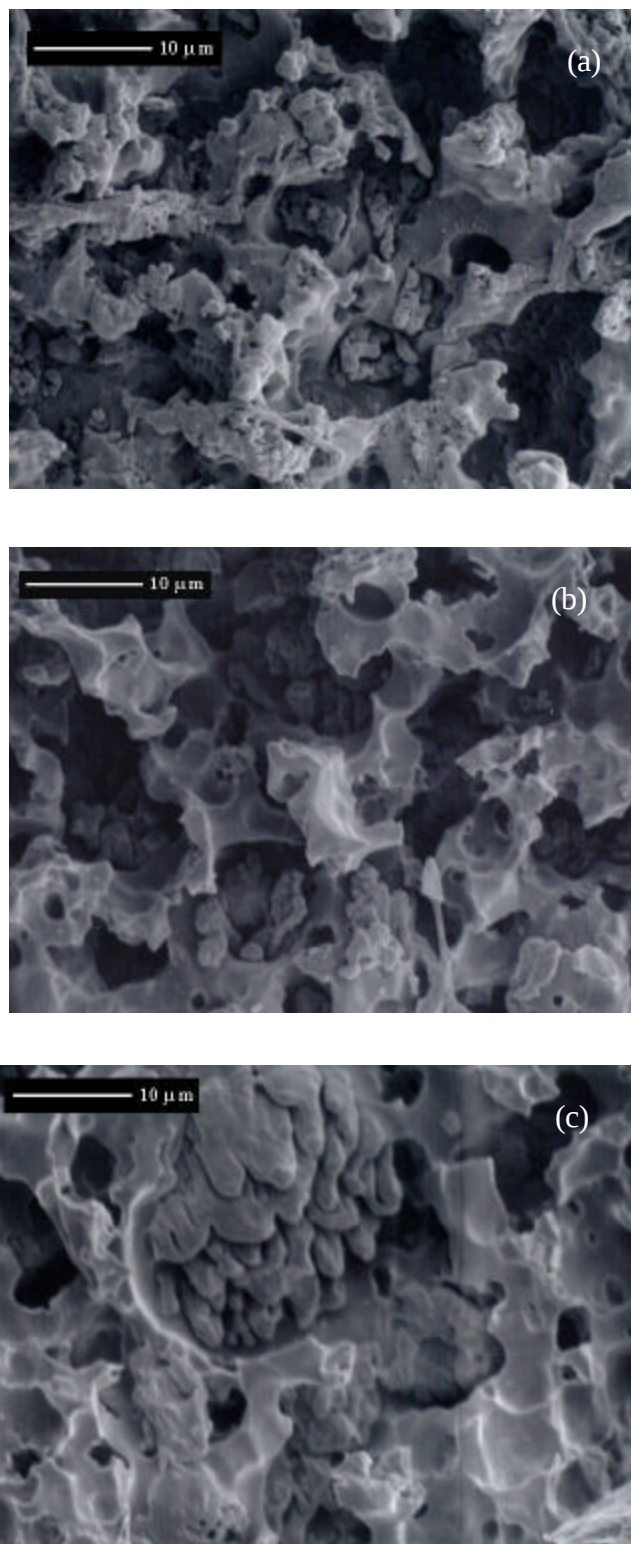


Figure 5.5 Scanning Electron Micrographs of silicone target surfaces ablated at 420 mJ/cm² (5kV, x2000) (a) 100 pulses, (b) 2000 pulses, (c) 5000 pulses.

At the lowest energy density of 100 mJ/cm^2 , damage to the surface is minimal even after 5000 pulses (Figs. 5.1 a, b). The smooth target surface indicates that ablation could be occurring in a layer-by-layer fashion. Although the level of ablation seems to be minimal, it was shown in the previous chapter that material removal and film formation can occur at this energy density.

As the energy density is increased to 250 mJ/cm^2 , the target surface shows significant damage and degradation (Figs. 5.2 a,b,c). The ablation proceeds mainly by removal of large polymer clusters from the surface as seen in the progression for a surface ablated with 100 pulses to 5000 pulses. Examining the ablated surface under higher magnification (Figs. 5.3 a,b,c) this progression is seen more clearly.

Increasing the energy density from 250- to 450 mJ/cm^2 (Figs. 5.4 a,b,c and 5.5 a,b,c) does not change the ablation mode significantly and similar ablation features are presented at the higher energy density. Another interesting feature which was seen for the target surfaces ablated at high energy density levels was the presence of microcracks around the ablated area. Figure 5.6 shows the edge of an ablated region and the microcracks which emanate from it into the unablated target region.

Thus the above analysis showed that the energy density was critical in deciding the level of ablation in silicone. At low energy density levels, the ablation rate was slow and produced minimal visible damage to the target even after 5000 pulses. At high energy density levels, the target surface showed considerable damage even at 100 pulses. The ablation seemed to proceed mainly through the expulsion of polymer clusters off the surface. Also the ablation was not confined to the surface but extended for a considerable distance (μm) into the bulk. The presence of microcracks at high energy density levels

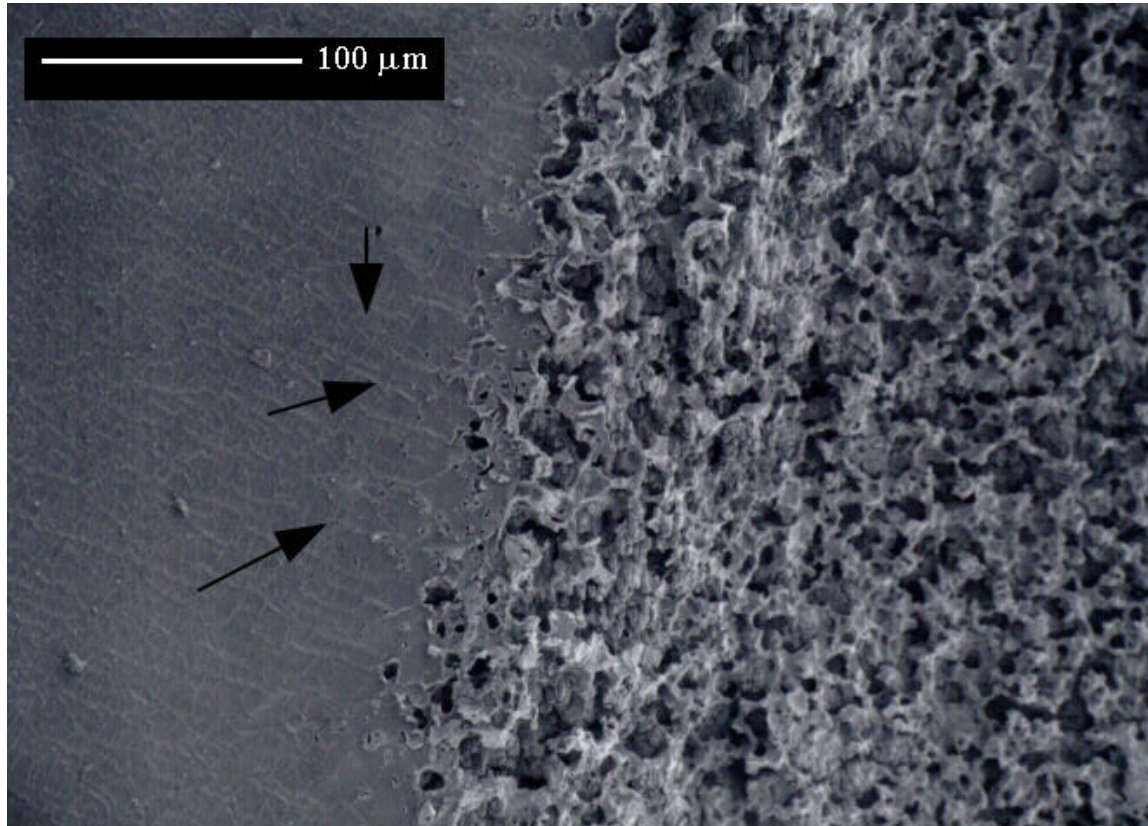


Figure 5.6 Scanning Electron Micrograph (5kV, x500) of a silicone target showing the edge of the ablated area. Arrows indicate the presence of microcracks.

also indicated that the target experienced considerable mechanical shock during ablation. The microcracks could be produced due to compression and expansion of the surface under the action of the laser pulse.

The existence of a threshold energy density also seemed to be indicated from this study. At or below the threshold ablation proceeded in a layer-by-layer fashion. Above the threshold, substantial polymer degradation occurred and the ablation proceeded in an uncontrolled fashion. The kind of damage produced i.e. jagged edges, debris etc. seemed consistent with a thermal ablation mechanism. Observation of the target surface under an optical microscope also revealed the presence of a large number of bubbles in the target bulk. These bubbles were observed under ablation at all energy density levels. Bubble production is linked to target heating, vaporization and gas generation due to degradation reactions under the action of laser pulses, another indicator to the thermal nature of the ablation.

Based on the above analysis, an ablation rate study was undertaken to elucidate the mechanism of ablation. Silicone target surfaces were ablated at a set energy density and pulse number. The ablation area on the target surface was measured with a 10x graduated microscope eyepiece for the energy density calculation. Laser energy incident on the target was measured with a joulemeter (Sentec 200ED). The incident energy was changed by changing the laser charging voltage. The etch pits created were measured by cross-section analysis in the SEM. Figure 5.7 shows an etch pit on the target surface while figure 5.8 shows a typical cross-section of an etch pit.

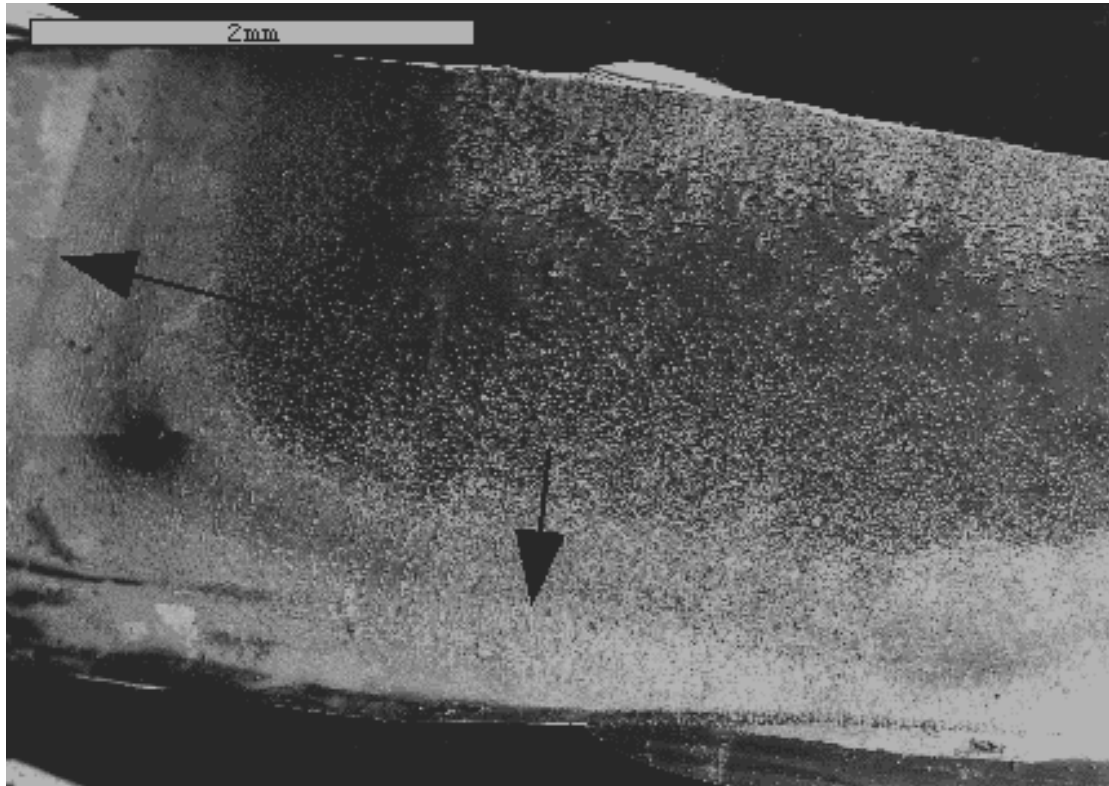


Figure 5.7 Scanning Electron Micrograph of an ablated region on a silicone target showing the resultant etch-pit. The arrows indicate the edges of the pit. (Scale bar = 2 mm).

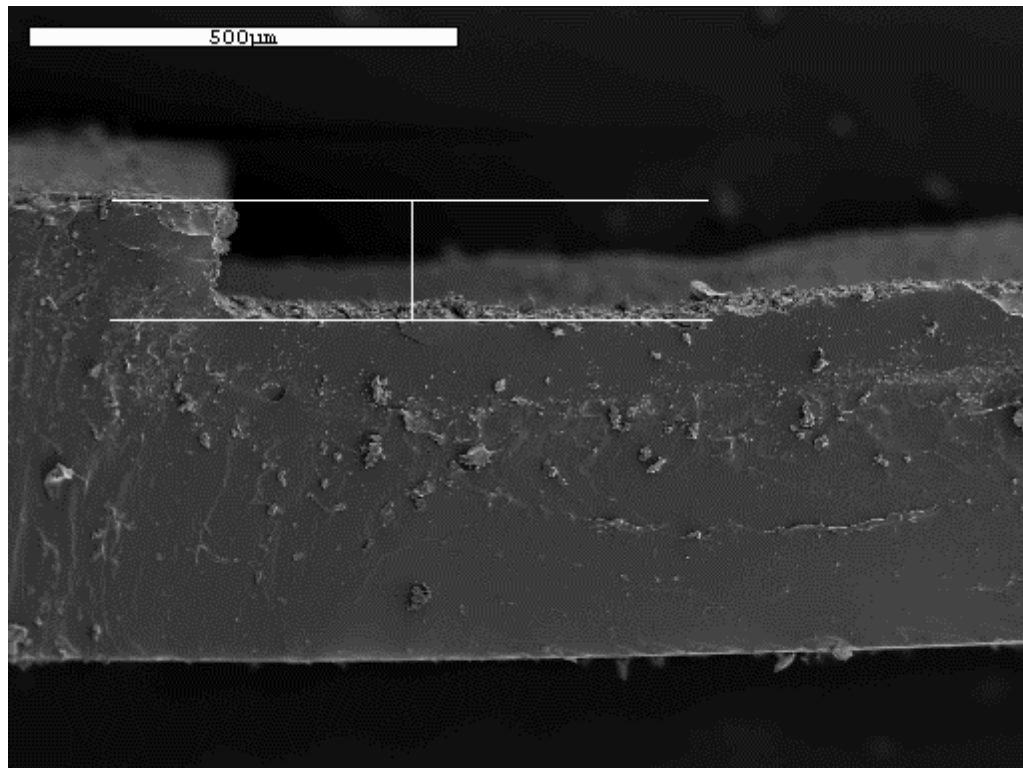


Figure 5.8 Scanning Electron Micrograph (5 kV, x100) showing the cross-section of an etch pit. The lines indicate the depth of the pit.

Figure 5.9 shows the results of this study. The etch rate is described by an S-shaped curve, starting at very low rates and increasing with the incident energy density before saturating at high energy density levels. At low energy density levels, the polymer ablation can be described as a laser induced thermal desorption process (LITD). In LITD, a pulsed laser is used to heat a surface and cause thermally activated desorption of a species—a process which is controlled by a frequency factor and an activation energy (i.e. an Arrhenius relationship). This description is consistent with the surface morphology exhibited by the target at these energy density levels. The energy density level is low enough to effect uniform heating and desorption off the target surface.

The LITD process proceeds only up-to a certain energy density level. Beyond this limit the energy input is high enough to cause rapid heating and vaporization of the polymer. Optical microscopy also revealed that vaporization can occur deep in the polymer bulk. The vapor generation and expansion leads to ablation of polymer clusters in the form of particles. The ablation rate is also extremely large and shows a steady increase in this region of the etch rate curve. At high energy density levels the mass flux expanding off the target surface is high enough to generate a large plume. The decrease in the etch rate at high energy density levels could be due to beam attenuation caused by absorption of part of the laser pulse by the plume expanding off the target. Other factors could be change in the absorption cross-section of the polymer leading to bleaching effects.

The exponential fit to the data is quite good, suggesting that a thermal mechanism of ablation. Another factor which bears consideration is the absence of a clear threshold

energy density in the ablation rate curve. Thus the energy density level where an LITD type process is taken over by steady-state ablation cannot be clearly assigned.

The above results indicated that the ablation of silicone under the action of laser pulses had a considerable thermal component. Consequently a thermal ablation model was proposed for the ablation of silicone at 248 nm. This model has been adapted from those proposed by Cain *et al.* and D'Couto. Based on the data, a position dependant temperature profile was calculated by assuming one-dimensional heat flow into the polymer target. Such an analysis had been originally developed for pulsed laser heating of metals. D'Couto also used a similar treatment for his model and found good agreement with data for the 248- and 308 nm ablation of PTFE and PI doped PTFE.

Cain *et al.* employed several assumptions for their model. First, it was assumed that the electronic states excited by the absorbed light decay rapidly to the ground state, with the absorbed energy being deposited into vibrational modes. Second, the distribution of vibrational energy was assumed to be Boltzmann allowing a temperature profile to be developed. Third, the absorption and ablation were treated as separate processes. Fourth, a pseudo-zeroth-order rate law was assumed. The analysis is shown below.

Assuming a pseudo-zeroth order rate law the ablation rate is described as:

$$d = k_0 e^{-E/RT} \quad (2)$$

d = etch rate, m/s

k_0 = Arrhenius pre-exponential factor, m/s

E = activation energy, J/mol

R = molar gas constant, J/mol °K

T = temperature averaged over the irradiated region, °K

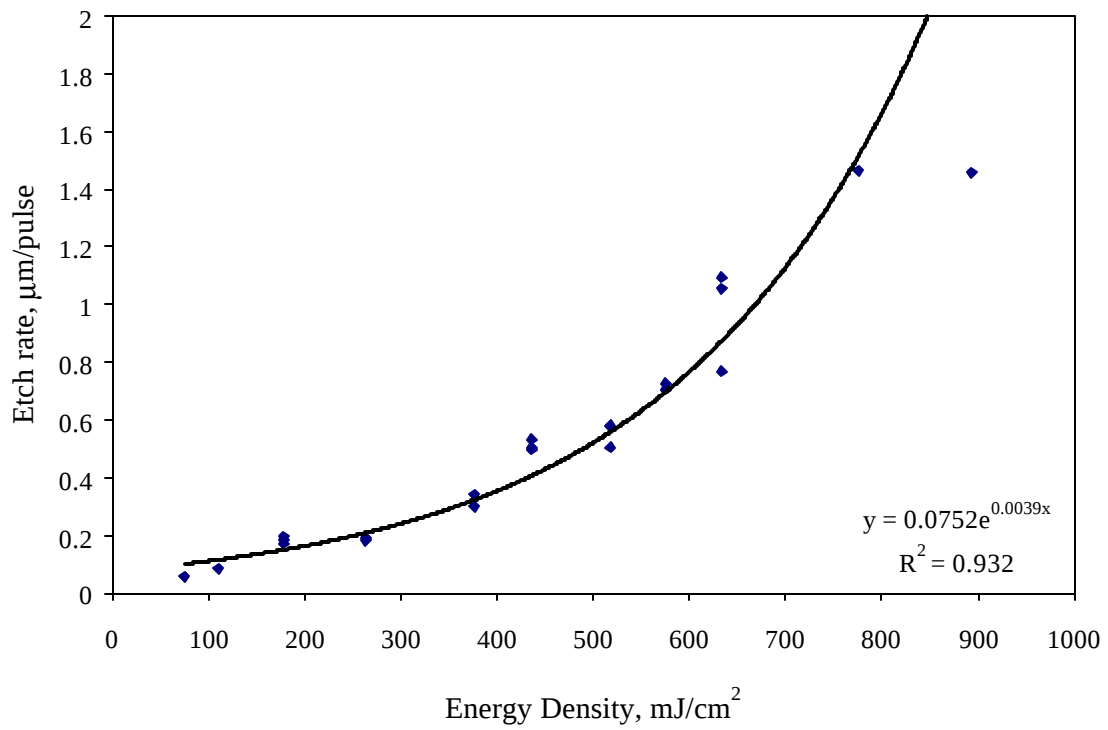


Figure 5.9 Plot of the ablation rate vs. incident fluence.

Temperature is time and position dependant. Assuming a one-dimensional heat flow temperature is calculated as per ref.[121] :

$$T_x = \frac{a_{eff} F e^{-a_{eff} x}}{C_p} \quad (3)$$

α_{eff} = effective absorption coefficient, m^{-1}

F = incident energy density, J/m^2

C_p = heat capacity per unit volume, $J/m^3 \text{ } ^\circ K$

x = position measured from the moving surface of the ablating polymer, m

Temperature is calculated from the known energy distribution within the polymer target surface. Thus a temperature profile can be generated throughout the optical penetration depth (OPD). The OPD is given by a relationship based on Beer's Law:

$$d_p = \frac{1}{a_{eff}} \ln \left(\frac{F}{F_{th}} \right) \quad (4)$$

F_{th} = threshold energy density for steady-state ablation, J/m^2

Integrating equation (3) , we obtain an average temperature over the irradiated volume from the surface ($x = 0$), to the penetration depth ($x = d_p$)

$$T_{avg} \propto \frac{a_{eff} F}{C_p d_p} \int_0^{d_p} e^{-a_{eff} x} dx \quad (5)$$

Performing the above integration and substituting for d_p from equation (4), T_{avg} can be calculated.

$$T_{avg} \propto \frac{a_{eff} (F - F_{th})}{\ln(F / F_{th})} \quad (6)$$

The assumption of an average temperature throughout the ablation volume was used by D'Couto to model the ablation behavior of PTFE and PI doped PTFE with good results. The reasons for the above assumption are explained later.

Substituting equation (6) into (2), we obtain the etch rate as:

$$d = k_0 e^{(-E' \ln F / F_{th}) / \alpha_{eff} (F - F_{th})} \quad (7)$$

where $E' \hat{=} EC_p/R$

Assuming α_{eff} is constant throughout the duration of the irradiation, we have :

$$\ln d = \ln k_0 - \frac{E'}{\alpha_{eff}} \times \frac{\ln(F / F_{th})}{(F - F_{th})} \quad (8)$$

Thus plotting $\ln d$ vs. $\ln(F/F_{th})/(F-F_{th})$ should yield a straight line with a slope of $-E'/\alpha_{eff}$ and an intercept of $\ln k_0$

The advantage of this model is that it does not assume the values of E' and α_{eff} *a priori*. However a value for F_{th} does need to be assigned and from an examination of the data the threshold is not immediately apparent. A threshold energy density of 180 mJ/cm² which was the inflection point on the deposition rate curve (Figure 3.11) in Chapter 3 was assumed and based on this value, the relationship in equation (8) was plotted. The result is shown in figure 5.10.

It is seen that the data is relatively linear considering the error involved in etch depth measurement and the variation in incident energy density.

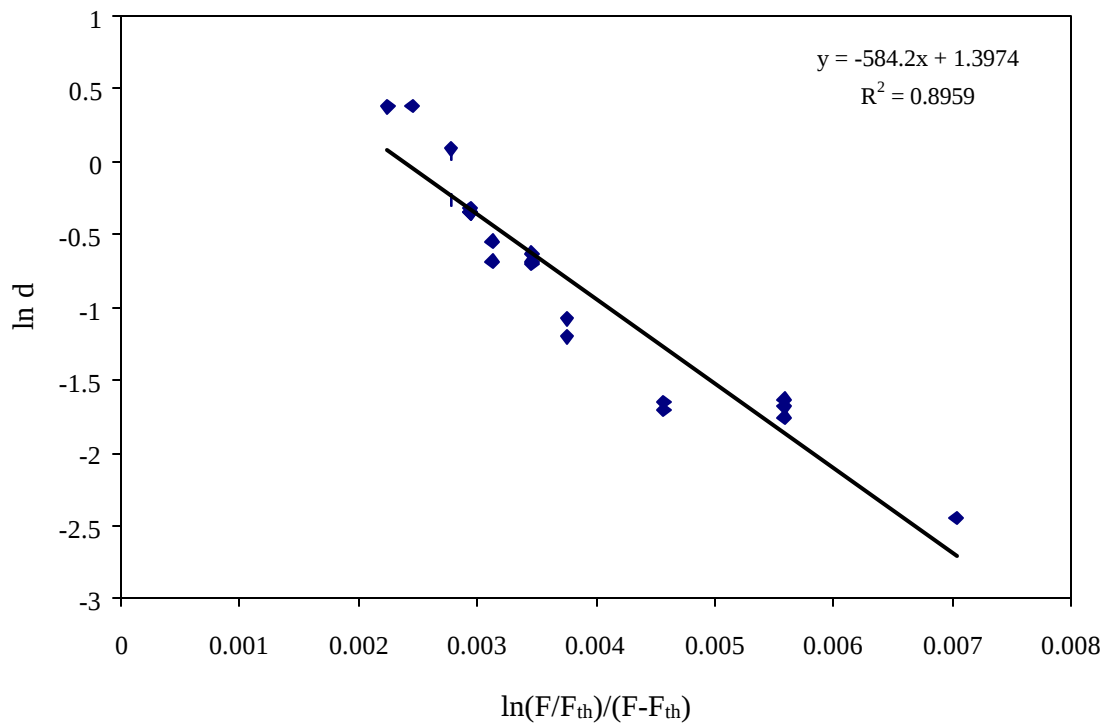


Figure 5.10 Data from figure 5.9 plotted according to equation 8. The line represents the best fit.

The model is effective because the assumption of an average temperature inside the ablation volume appears to be valid. The assumption is based on two facts. First, the thermal diffusivity of silicone is low, therefore the laser energy is confined in a small area. Second, the polymer ablation proceeds on a longer timescale (μsec - msec) than the laser pulse (psec) thus making it likely that the heat generated by the laser energy absorption diffuses into the polymer, making the temperature more uniform at the end of the laser pulse. This has been seen in the case of PMMA [124]. The model fit to the data suggests that the temperature averaging mechanism though simple is quite effective. Thus even though the model is purely phenomenological it has its application in describing the ablation rate of silicone quite successfully. The model can be further refined by accurate measurement of the low intensity absorption coefficient of silicone at 248 nm and assuming that the activation energy (E_{act}) corresponds to the bond energy of either Si-CH₃ or Si-O.

Finally it should also be mentioned that the above study suffers from some limitations. First, the method of measuring the etch pit depth through cross-sectional SEM analysis is not the most accurate one. A better method would be to use a silicone film mounted on a quartz crystal microbalance (QCM) as a target. A QCM would provide information on mass loss, rather than etch volume, with a sensitivity in the μg - mg range. Second, the variation in laser energy during an ablation experiment can cause uncertainty in the incident energy density calculation. It is estimated that a 10% error is inherent in the energy density measurement. Third, the model gives a time-averaged picture of the ablation mechanism and not a dynamic one. Thus effects like incubation, changes in absorption cross-section are ignored.

Summary

Literature survey revealed the existence of many different models for describing polymer ablation under the action of laser pulses. Earlier models explained the phenomena as a photochemical process, while recent models have considered photo-thermal processes an important part of ablation. Examining silicone target surfaces after irradiation with 248 nm laser pulses made it apparent that the ablation had a large photo-thermal component. At low energy density levels the ablation proceeded at a slow rate and could be described as a laser desorption process. As the energy density level increased, heating effects caused vaporization and expulsion of polymer clusters off the target. The ablation rate was linear in this region. At higher energy density levels the ablation rate saturated. The ablation behavior was adequately described by modified photothermal models such as those of Cain and D'Couto.

CHAPTER 6

FUNCTIONALIZATION OF STAINLESS-STEEL BY A COMBINED PLASMA/GAMMA PROCESS

Introduction

Plasma Polymerization

Plasma polymerized thin films have a number of industrial applications due to their interesting chemical, physical, mechanical and electrical properties [125],[126]. Their use in diverse fields like optics, microelectronics, sensors and biomaterials have been reported in the literature. It had been recognized early on that surfaces exposed to a glow discharge in an organic phase (vapor or gas) are covered with oily deposits. (The first report dates to 1863) [126]. These early reports regarded the deposits, which we now recognize as plasma polymers, as a nuisance. Plasma polymerization of hydrocarbon monomers for the express purpose of depositing thin films was not reported until the 1960s. Since then a variety of monomers have been successfully polymerized by this technique.

The general characteristics of the process involve introducing a monomer species into a reactor under vacuum where it is energized by an electromagnetic impulse. The monomer is dissociated, producing electrons, ions and neutral fragments. Gas-phase reactions between charged species cause the formation of polymeric fragments which are deposited on the substrate. These fragments can couple with each other and the substrate to form a film. Subsequent growth reactions can occur by burying of the initial layer with newer layers. Usually radio-frequency glow discharges are employed for this

technique, but plasma polymers have also been produced by other kinds of discharges including AC, DC, microwave and pyrolytic chemical vapor deposition.

General classes of monomers used for synthesis include hydrocarbons (saturated, unsaturated, aromatic etc.), fluorocarbons, silicon-containing monomers (siloxanes and silazanes), vinyls and metal-containing monomers. These monomers are used because of the interesting and desirable properties of the resultant polymers. In addition, functional monomers with charged groups like pendant amines, alcohols, esters etc. have also been used for synthesis. Interestingly, monomers which cannot be polymerized by chemical initiation methods are readily polymerized by this method. Thus reports on the synthesis of polymers from molecules like acetone [127], toluene [128] etc. are also seen in the literature.

Among the many advantages associated with this process are: smooth, conformal insoluble films, no substrate geometric restriction, wide range of chemistries possible and clean processing due to vacuum [129]. However, plasma polymers also suffer from some disadvantages. The end polymers lack structural correspondence with their monomers and often films with widely differing structures can be produced depending on the deposition conditions. Plasma polymers also contain trapped free-radicals which react on exposure to atmosphere changing the film chemistry over a period of days or months [130]. Further, the films produced can be under stress leading to debonding or peel-off from the substrate [131]. The large number of variables affecting the synthesis in a complex fashion also makes process optimization difficult. The multitude of reactor designs and system configurations have also led to the lack of any laboratory or industry standard on reference conditions. This has led to a concomitant delay in the widespread

adoption of this technology for industrial applications. Lately, with the advent of pulsed plasma systems greater control can be exercised on the process leading to tailored film properties [132]. Also, the application of statistical design of experiments has led to advancements in process optimization [133].

Surface Modification of Stainless steel

Plasma glow-discharges have been applied to the modification of polymer, metal and ceramic surfaces. Two general methods of modification have been seen in the literature. The first method involves activation of the substrate surface in a reactive plasma. Reactive plasmas include non-polymer forming species like water-vapor, oxygen etc. which impact the surface producing peroxides and free-radical species. The activated surface is then reacted with a monomer solution via chemical or thermal initiation. The free-radicals and peroxides on the surface can initiate polymerization causing chain growth off the surface. Yahiaoui reported the use of a combined plasma/gamma method for the surface modification of polymers [134]. This involved activating the substrate through the use of an RF water-vapor or oxygen plasma to produce peroxides on the surface. The activated substrate was then introduced into a monomer solution which was polymerized by gamma radiation initiation. The peroxides dissociated under the action of the gamma rays producing radicals on the substrate surface, allowing the monomer to polymerize on this surface. Yahiaoui successfully used this method to modify Poly(methyl methacrylate) (PMMA) and Polydimethylsiloxane (PDMS) with N-vinyl pyrrolidone (NVP). This method has also been used as an adhesion promoter in the metallization of polymers. Grace *et al.* reported increased

adhesion strength of sputtered silver films on poly(ethylene terephthalate) (PET) after activation of the PET surface in an nitrogen plasma [135].

The second and more common method involves direct deposition of a plasma polymer on the substrate. This method is attractive for modifying metals [136],[137] and ceramics which do not produce charged species in abundance as do polymers upon plasma activation. In this research group, methods to modify steel surfaces by plasma polymers for vascular applications are under investigation. It has been known that anionic surfaces have lower thrombogenicity in a vascular environment. Thus modifying steel implants with functional polymers to produce hydrophilic, anionic surfaces was hypothesized to be of benefit in improving the function of these implants. Biagtan [138] and Amery [139] used Yahiaoui's plasma/gamma method for surface modification of stainless-steel. The first step involved depositing a hexane plasma polymer film onto steel. This was followed by the gamma radiation initiated grafting of NVP and sulfopropyl acrylate, potassium salt (KSPA) onto the steel. The idea was to use the hexane plasma polymer as a hydrocarbon base layer for further modification since activation of the steel by a water-vapor or oxygen plasma did not prove as successful. Biagtan reported a reduction in mean-platelet count for the modified steel surfaces compared to unmodified steel in a canine *ex-vivo* shunt experiment. This proved the effectiveness of the method. Biagtan and Amery also suggested the use of these functional surfaces for coupling bioactive molecules like proteins or anti-inflammatory drugs for sustained release. This idea is explored in the research *vide infra*.

Materials

Chemicals. The monomer used for the plasma polymerization was 99% n-hexane (Fisher Scientific). The monomer used for the gamma radiation initiated polymerization was methacrylic acid (Aldrich Chemicals). The methacrylic acid was distilled under vacuum (30 in. Hg) at 65°C, prior to use. Polyethylene imine (PEI) (Polysciences) (Mw = 30,000 g/mol), Bovine Serum Albumin (Sigma) and glutaraldehyde (25% v/v aq.) (Sigma) were used as received. The structure of PEI is shown in Figure 6.1. It consists of primary, secondary and tertiary amines in the ratio 1:3:1 coupled to a ethylene backbone.

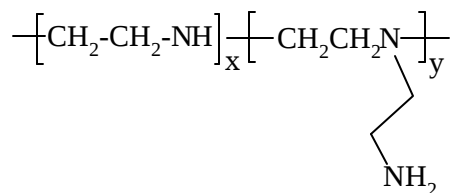


Figure 6.1 Chemical structure of Poly(ethylene imine)

Substrates. 316L stainless steel (1 x 1 cm²) slabs and silicon wafers were used as substrates. The steel substrates were cleaned by sequential sonication in 1, 1, 1 tri-chloroethane, acetone and methanol then dried under vacuum for 12 hours. The silicon wafers were sonicated in acetone and methanol and dried under argon gas flow.

Methods

Plasma Polymerization of Hexane

The setup consisted of a bell-jar reactor which was connected to a vacuum pump via a cold trap. Two gas lines were introduced into the top of the reactor for inert-gas

flow. The monomer inlet was in the main body of the reactor, for reasons explained later. Monomer flow rate was controlled by a needle valve. Inert gas flow was controlled by a mass flow controller. The plasma was ignited by a RF generator coupled to a matching network. The matching network transferred the field to a copper coil wound around the neck of the reactor. Upon the introduction of a monomer, the plasma was ignited inductively. Figure 6.2 shows a schematic diagram of the plasma reactor.

The procedure for a plasma polymerization was as follows. Clean substrates were placed on a stand and introduced into the reactor. The vacuum pump was turned on and the reactor was evacuated. The pressure was allowed to reach <40 mtorr after 3 argon purge-fills. The argon line was then opened and the gas flow was adjusted till the pressure reached 50 mTorr. The RF generator was then turned on and the substrate was ablated under an argon plasma for 15 minutes. After this cleaning step, the plasma was turned off and the monomer line was opened. The monomer flow rate was adjusted till the pressure was at 50 mTorr. The monomer was 99% n-hexane which had previously been purged with argon. The generator was then turned on which ignited a hexane plasma. The polymerization was allowed to proceed for a suitable time. The end-point was usually determined visually by observing a change in color on the substrate surface indicating the presence of a plasma polymer film. The plasma generator was then turned off, the hexane line was shut off and the reactor was again purged with argon. The reactor was then isolated from the vacuum line and allowed to return to atmosphere under the argon flush. The substrates were stored in polystyrene boxes for analysis or used as is for further modification.

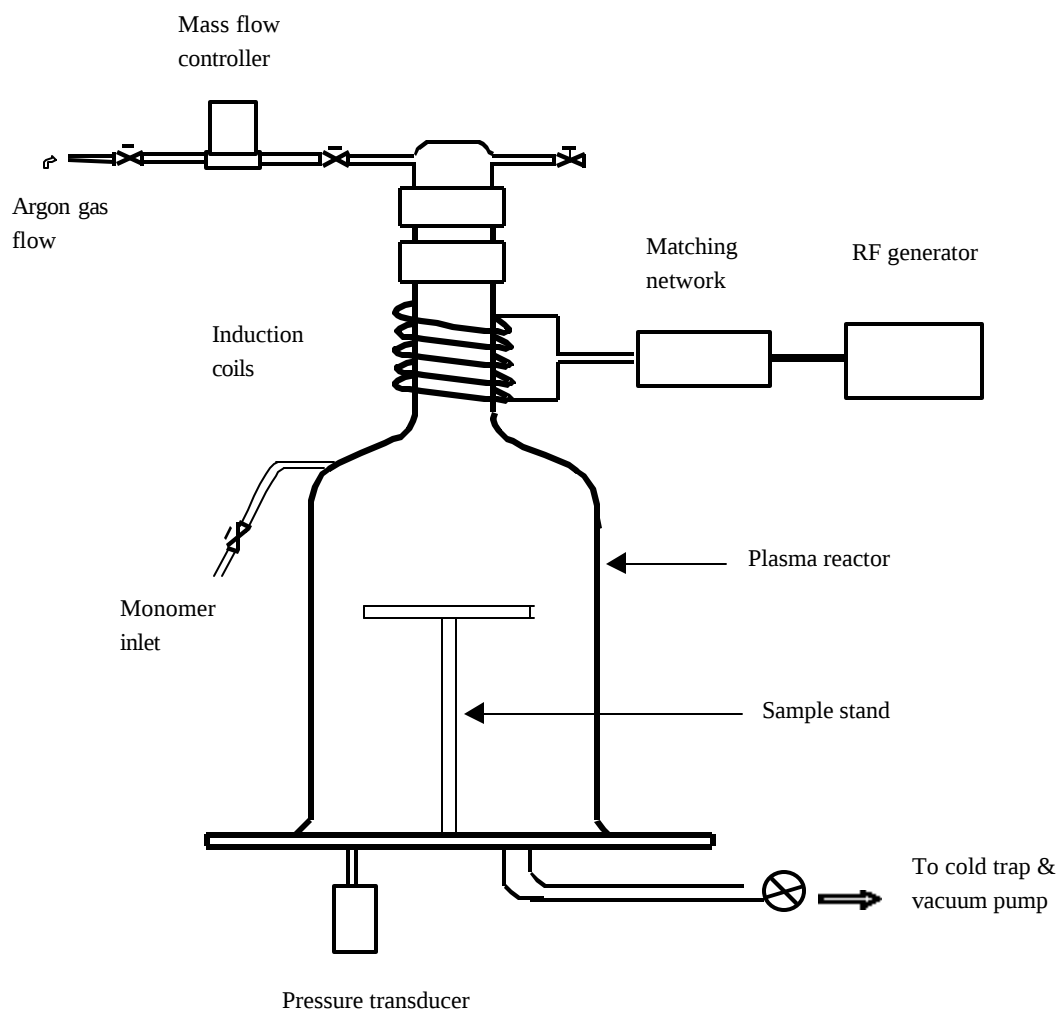


Figure 6.2. Schematic diagram of the plasma reactor and accompanying instrumentation.

Gamma Radiation Initiated Grafting of Methacrylic Acid

The hexane plasma polymer coated substrates were placed in a 5%(v/v) aqueous methacrylic acid (MA) solution and introduced into the ^{60}Co source where they were irradiated for a dose of 0.05 Mrad. The monomer solution was purged with argon before its introduction into the gamma source. The dose rate over the course of these experiments ranged from 290- to 370 rads/min. At the end of the irradiation the modified

substrates were washed with an ultrapure water spray. The substrates were then kept immersed in ultrapure water with the wash water being changed twice daily. The wash routine was continued for two days at the end of which the wash water was analyzed in a UV-VIS spectrometer (Perkin-Elmer Lambda 3) for the presence of organics. After a negative result from the spectrometer the substrates were used for further modification or analyzed after drying under vacuum for 12 hours.

Chemisorption with Polyethylene imine (PEI)

The plasma/gamma coated samples produced by the above method were used as the substrates in this step. The substrates were immersed in a 1%(w/v) aqueous solution of PEI for 12 hours.. After the chemisorption the substrates were washed with ultrapure water to remove non-specifically adsorbed PEI and kept immersed in same for further modification. Samples for analysis were dried under vacuum for 12 hours.

Bovine Serum Albumin (BSA) Grafting

The PEI chemisorbed samples were used as the substrates in this step. The substrates were exposed to a 25%(v/v) glutaraldehyde solution for 90 minutes. The substrates were then washed and immersed in a 1% (w/v) aqueous BSA solution and incubated for 12 hours. The BSA solutions usually turned brown due to cross-linking reactions from the glutaraldehyde. At the end of the reaction the samples were washed with ultrapure water and the wash routine outlined above was followed. The substrates were then dried under vacuum. Figure 6.3 shows a schematic diagram of the modification process with all the associated steps.

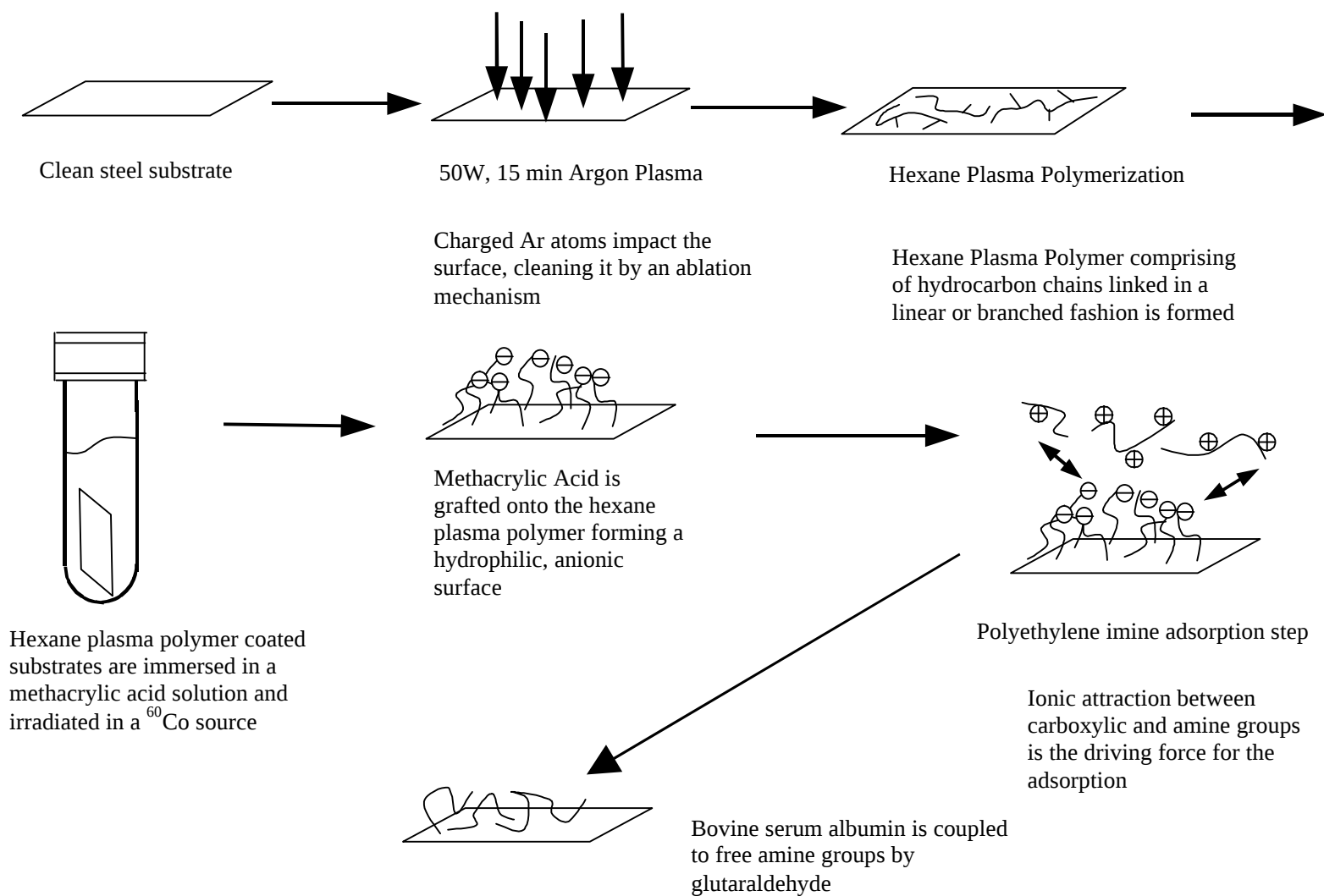


Figure 6.3. Schematic diagram of the surface functionalization process for stainless steel.

Characterization

Surface characterization was done by FTIR, XPS, Contact angle goniometry, Stylus profilometry and SEM similar to methods described in Chapter 3.

Results

Surface Characterization of Hexane Plasma Polymer

Fourier Transform Infrared Spectroscopy. Figure 6.4 shows the FTIR spectrum window from 2700 to 3100 cm^{-1} for 3 hexane plasma polymer films produced at input powers of 25-, 50- and 100 W. All three films show peak absorbances at 2960- and 2850 cm^{-1} indicative of CH symmetric and asymmetric stretching modes. The input power does not appear to change the bonding in the plasma polymer. It is of interest to note that no absorbances above 3000 cm^{-1} which would indicate the presence of aromatic structures in the film were seen. The introduction of the monomer after the plasma glow region ensures that monomer dissociation is minimized forming long chains.

X-Ray Photoelectron Spectroscopy. Table 6.1 shows the XPS results for hexane plasma polymers produced at 25-, 50- and 100 W along with unmodified steel and argon plasma etched steel. The low resolution survey scans for unmodified steel and a hexane plasma polymer synthesized at 50W can be seen in figure 6.5. The XPS analysis showed that the argon plasma etch produced a reduction in the carbon content on the steel surface and an increase in the oxygen content. This is due to the cleaning effect of the argon plasma and exposure of the oxide layer of the steel. Iron and chromium contents are also elevated as compared to unmodified steel.

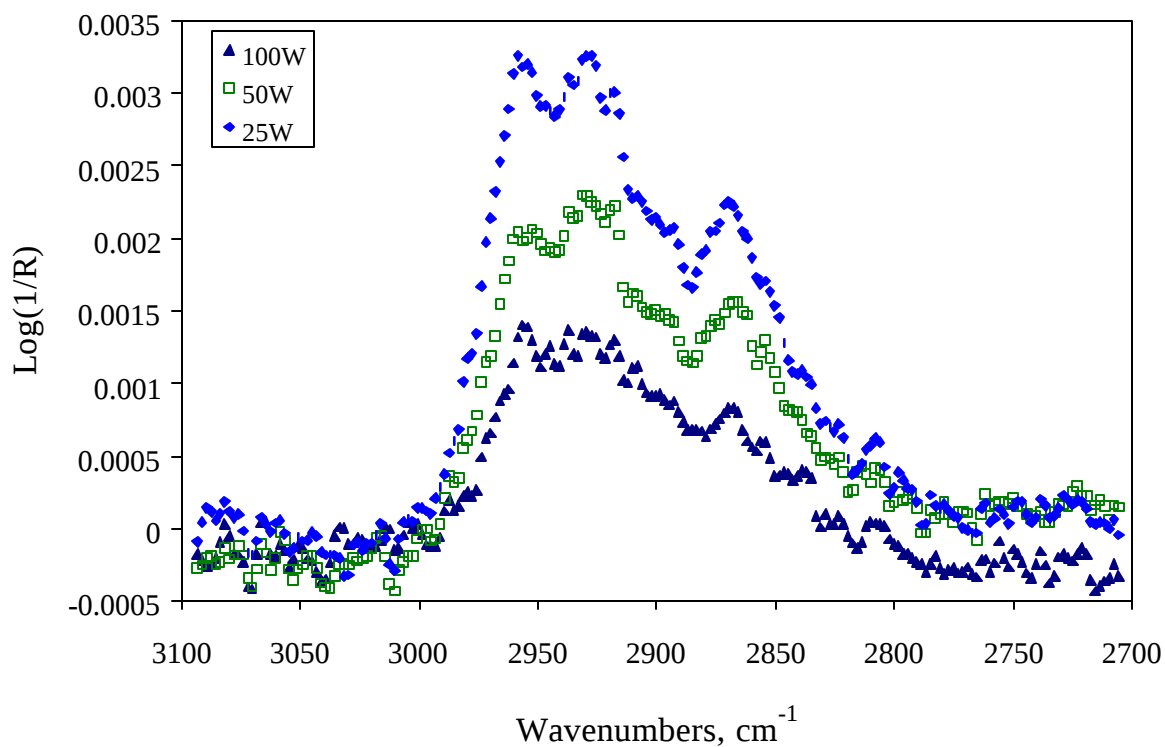


Figure 6.4 Reflectance absorption IR spectra of hexane plasma polymers synthesized at different input power.

The surface also shows the presence of nitrogen and it is thought that this is due to nitrogen impurity in the argon gas. Literature reports have also shown similar nitrogen levels on the surface after argon plasma treatment. The hexane plasma treatment produces a surface which is carbon rich. It is seen that the carbon content of the hexane plasma polymers is between 85-90%. It is also seen that the input power does not affect the carbon percentage significantly.

Table 6.1. XPS analysis of plasma polymers synthesized at different input power.

Surface	%C	%O	%N	%Fe	%Cr
Steel, unmodified	48.51+/- 5.33	45.90+/- 4.22	-	4.54+/- 0.92	1.04+/- 0.24
Steel, argon plasma etched	36.73+/- 4.44	52.37+/- 3.47	4.01+/- 1.29	5.20+/- 0.55	1.71+/- 0.41
Hexane plasma polymer coated steel, 25W i/p power	85.18+/- 1.06	14.82+/- 1.05	-	-	-
Hexane plasma polymer coated steel, 50W i/p power	88.19+/- 1.53	11.81+/- 1.53	-	-	-
Hexane plasma polymer coated steel, 100W i/p power	89.28+/- 2.38	10.72+/- 2.38	-	-	-

*Note: 5 samples were analyzed for each modification step.

The small amount of oxygen seen could be due to oxidation reactions occurring at the surface from trapped free radicals in the film. Figure 6.6 compares the high resolution C1s and O1s peaks for a hexane plasma polymer coated steel surface and an unmodified steel surface. The unmodified steel surface shows evidence of C-O bonding at the surface. The hexane plasma polymer on the other hand shows a single carbon peak with no shoulder indicative only of C-C and C-H bonds being present in the structure. The O1s peak also undergoes a change as seen in figure 6.6(b) with the dual bonding states for the unmodified sample changing into a single bonding state for the hexane plasma polymer. Figure 6.7(a) shows the C1s peaks for hexane plasma polymer films states for the unmodified sample changing into a single bonding state for the hexane plasma polymer. Figure 6.7(a) shows the C1s peaks for hexane plasma polymer films produced at input powers of 25-, 50- and 100W. The peak shapes remain unaltered for all three power inputs and show only C-C and C-H type bonding. The lack of a $\pi-\pi^*$ shake-up peak at 290 eV indicates the absence of any aromatic structures in the film verifying the structures seen in the FTIR spectra. Figure 6.7(b) shows the O1s peak for

hexane plasma polymers synthesized at different input power. The O1s peak also remained unaltered for all three power inputs.

Contact angle goniometry. Table 6.2 presents the average contact angle for hexane plasma polymers synthesized at 25-, 50- and 100 W along with appropriate controls. The results show that the steel substrates undergo a change in contact angle after each modification step. The argon plasma etch step produces a hydrophilic surface as seen by the contact angle value of 19°. The hexane plasma polymer films were hydrophobic with contact angles between 78-80°. The input power did not affect the contact angle of the hexane plasma polymers. (Note: 3 samples were analyzed for each modification step).

Table 6.2. Average contact angles for hexane plasma polymers.

Surface	Avg. Contact Angle (deg)
Steel, unmodified	56
Steel, argon plasma etched	19
Hexane plasma polymer coated steel, 25W i/p power	78+/- 2.5
Hexane plasma polymer coated steel, 50W i/p power	80+/- 2.6
Hexane plasma polymer coated steel, 100W i/p power	78+/- 2.6

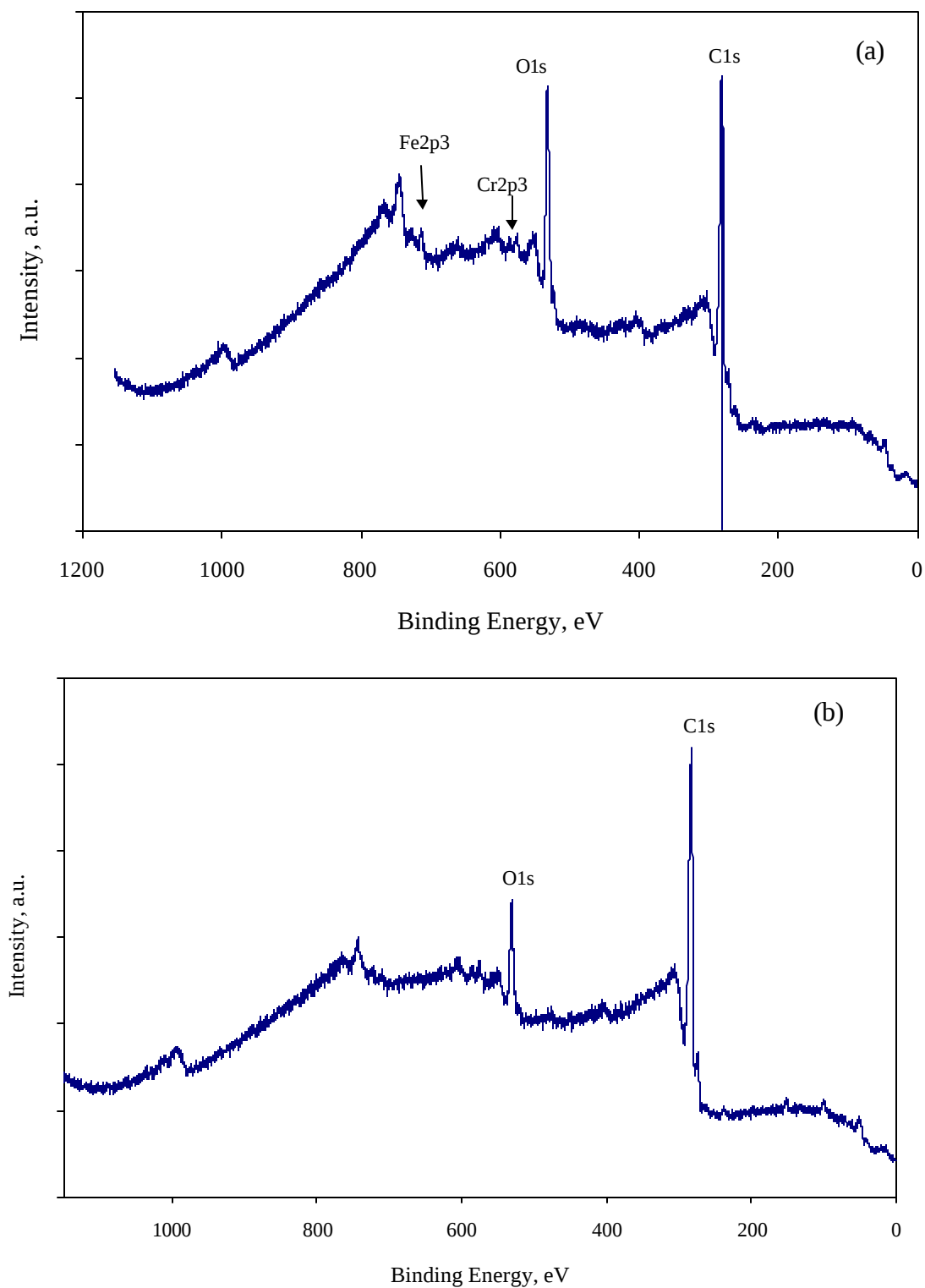


Figure 6.5. Low resolution XPS survey spectra of steel surfaces (a) unmodified and (b) hexane plasma polymer coated.

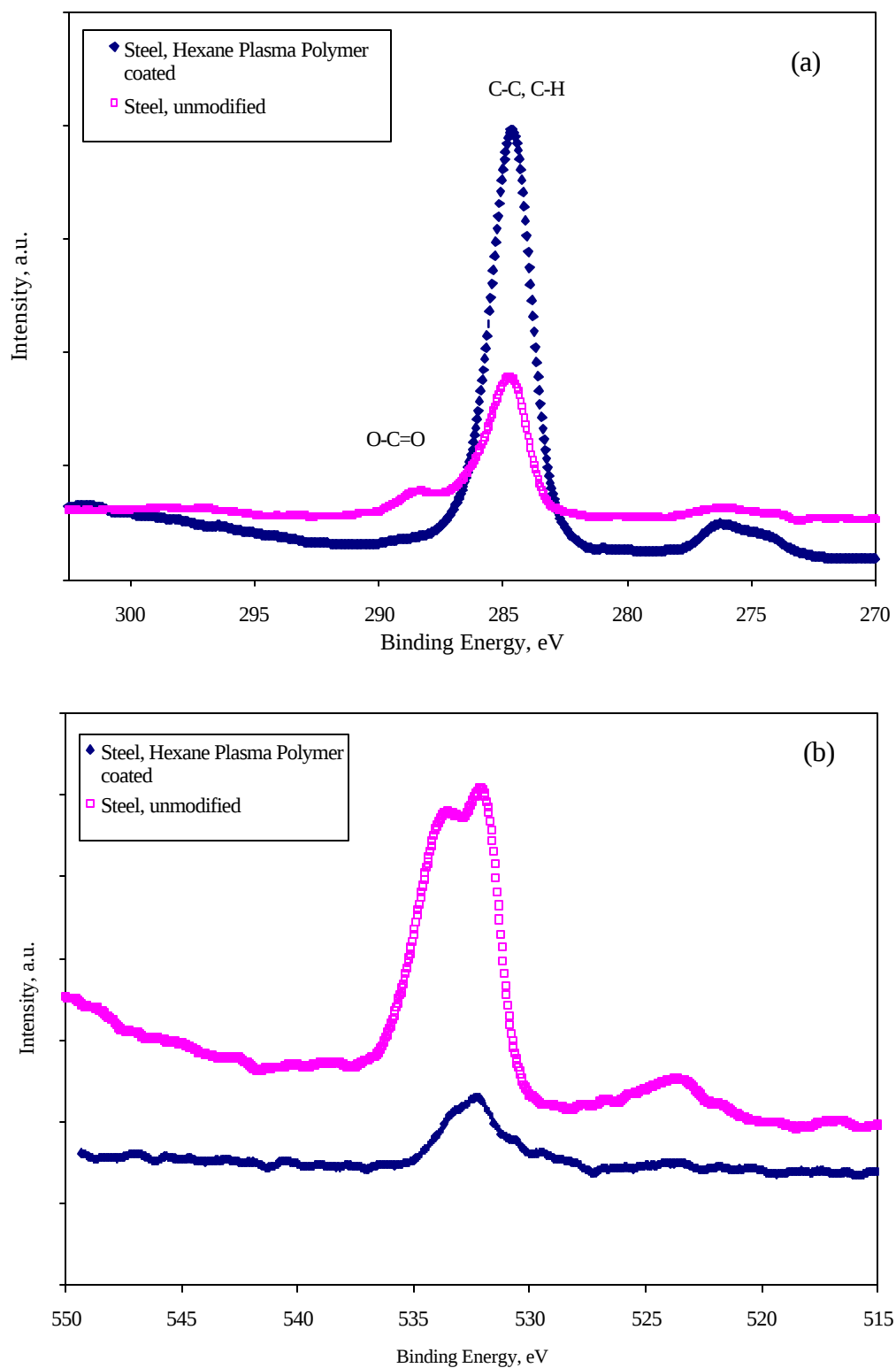


Figure 6.6. High resolution XPS spectra of unmodified steel and a hexane plasma polymer coated steel surface (50W power input) (a) C1s and (b) O1s.

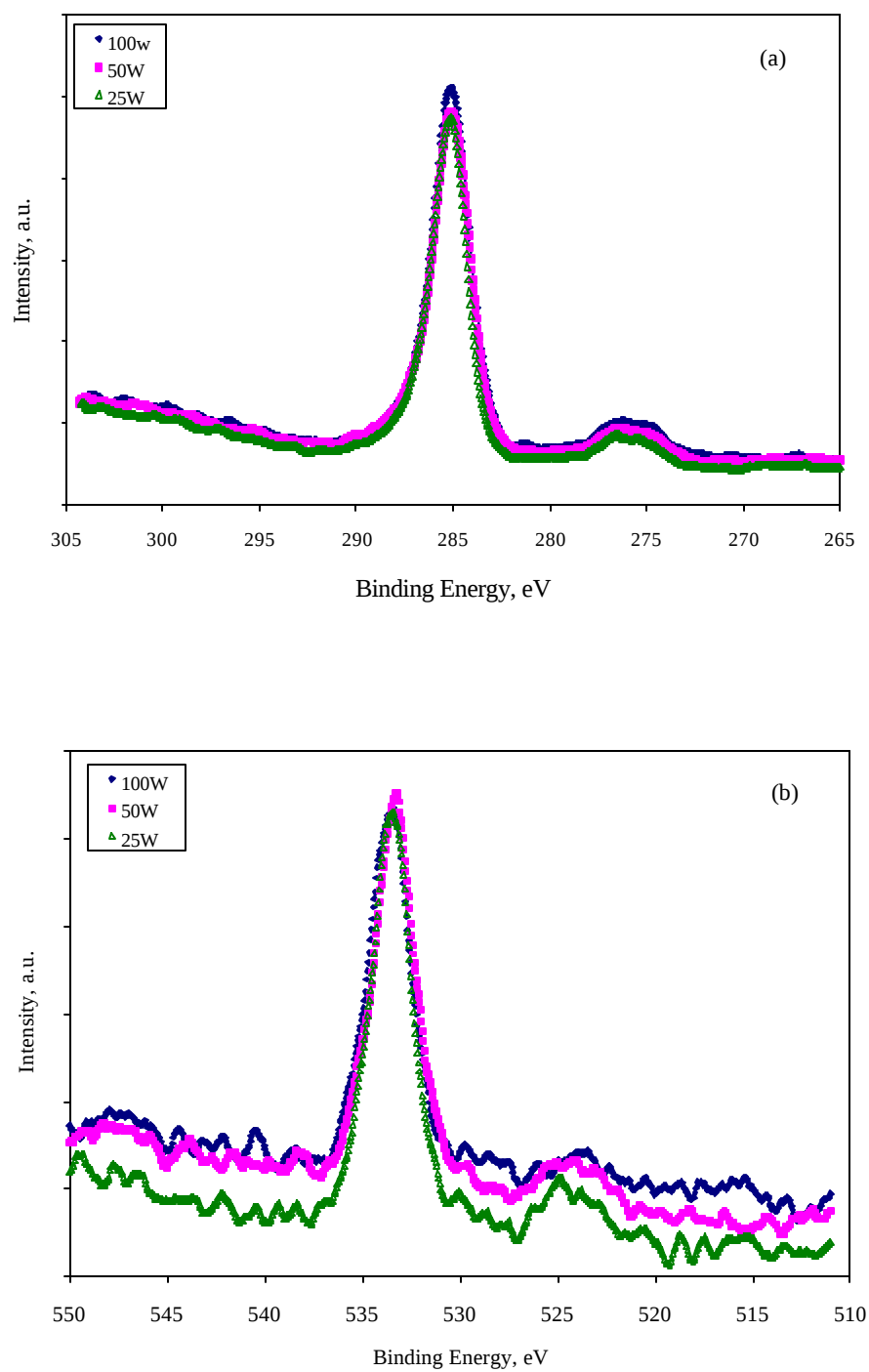


Figure 6.7. High resolution scans of hexane plasma polymers synthesized at 25-, 50- and 100 W (a) C1s and (b) O1s.

Profilometry. Deposition rates were measured by profilometry after depositing hexane plasma polymers onto masked silicon wafers. Table 6.3 shows the results of these measurements for films deposited at 25-, 50- and 100 W. The deposition rate at all three conditions was low. Surprisingly, the deposition rate at the intermediate power level of 50W was the highest. Large variations in film thickness (as shown by the standard deviations) were seen based on the sample position inside the reactor. This indicated that the plasma field inside the reactor was not uniform leading to different growth rates in different regions. The deposition rates also demonstrated that film growth was a slow process.

Table 6.3. Deposition rates for hexane plasma polymers at different input power.

Input power, Watt	Deposition rate, nm/min
25	1.38+/-0.43
50	4.05+/-1.57
100	1.88+/-0.68

*Note: 3 samples were analyzed for each modification step.

Scanning electron microscopy. Scanning electron microscopy was carried out to reveal the morphology of the hexane plasma polymers. Figure 6.8 shows the micrographs of hexane plasma polymers synthesized at 25-, 50- and 100W. The films produced were extremely smooth with little or no surface features. No pin-holes were observed on the films indicating complete substrate coverage during plasma polymerization. The power input also did not appear to affect the film morphology to any great extent.

Surface Characterization of Functionalized Steel Surfaces.

Fourier Transform Infrared Spectroscopy. Figure 6.9 shows the FTIR spectral window from 2700- to 3500- cm^{-1} for functionalized steel surfaces. The plasma/gamma MA modified surfaces only exhibited CH stretching peaks. Chemisorbing PEI onto this surface caused a change in the absorbance with new peaks at 2832 and 2930 cm^{-1} corresponding to C-N bonding. The broad hump centered around 3310 cm^{-1} was also indicative of a PEI layer. After reacting this surface with BSA, the surface bonding again underwent a change to reflect C-C and C-N bonding. The BSA grafted surface also showed a broad peak in the 3000-3300 cm^{-1} region indicative of carboxylic acid and amide groups. Surprisingly a similar feature (i.e. absorbance at 3300 cm^{-1}) was missing on the MA grafted surfaces and could be an indication of the low concentration of carboxylic groups. It could also be that the MA layer is thin enough to cause most of the absorbance to come from the underlying hexane plasma polymer. Since the data collection took place in laboratory atmosphere the spectral region around 1740 cm^{-1} which shows absorbances from carbonyl bonds could not be examined due to interference from water peaks.

X-Ray Photoelectron Spectroscopy. All samples which were examined in the XPS were dried under vacuum overnight before being mounted on the sample stubs. Figure 6.10 shows the low resolution survey spectra for MA, PEI and BSA modified steel surfaces. The spectra reflect the change in the surface after each modification step. The MA modified surface shows an increased oxygen content (compare with figure 6.5 for the hexane plasma polymer surface). The PEI and BSA modified surfaces (Figures 6.10b,c) show nitrogen peaks. A small sulfur peak can also be seen on the BSA modified surface.

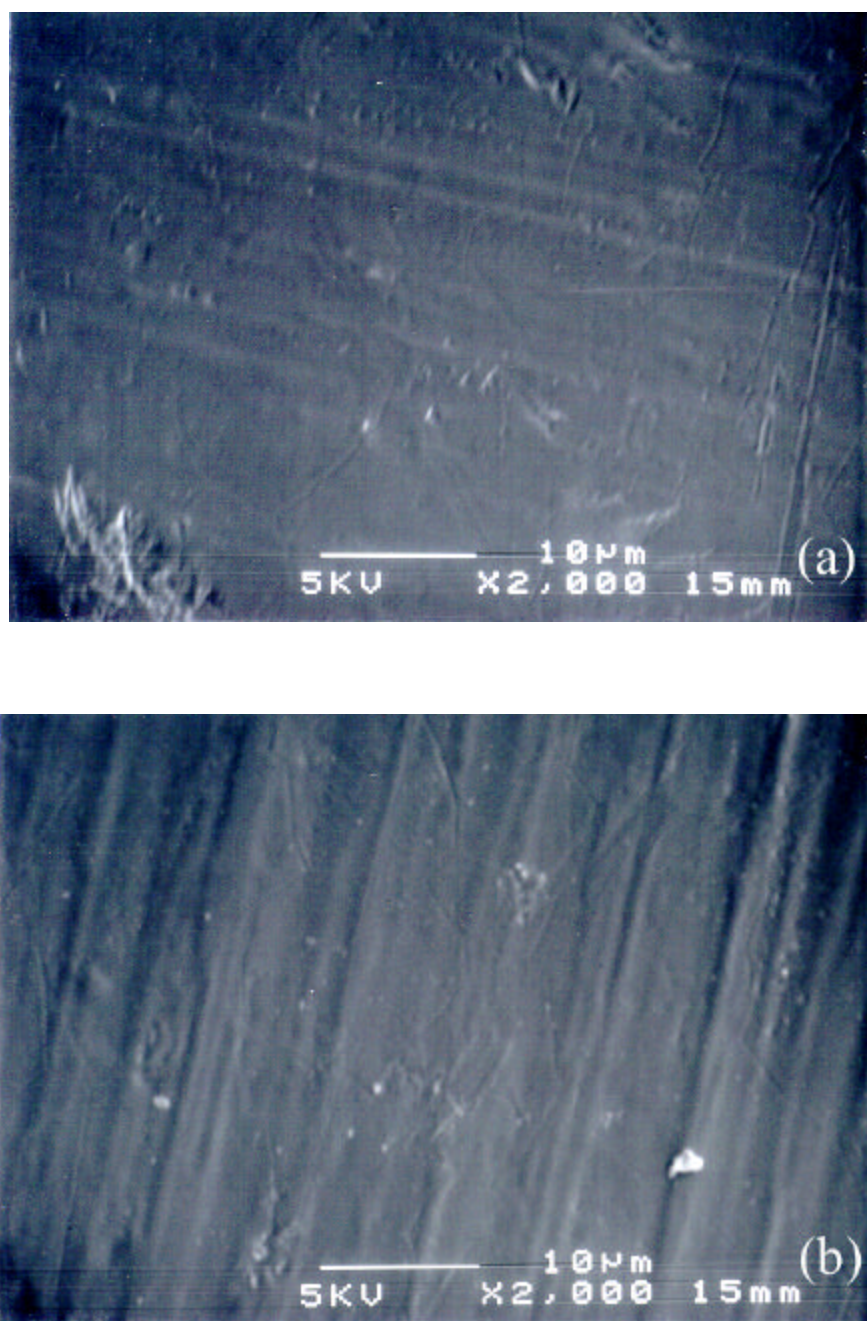


Figure 6.8. Scanning electron micrographs of steel surfaces coated with hexane plasma polymers synthesized at different input power: (a) 25 W and (b) 50W.

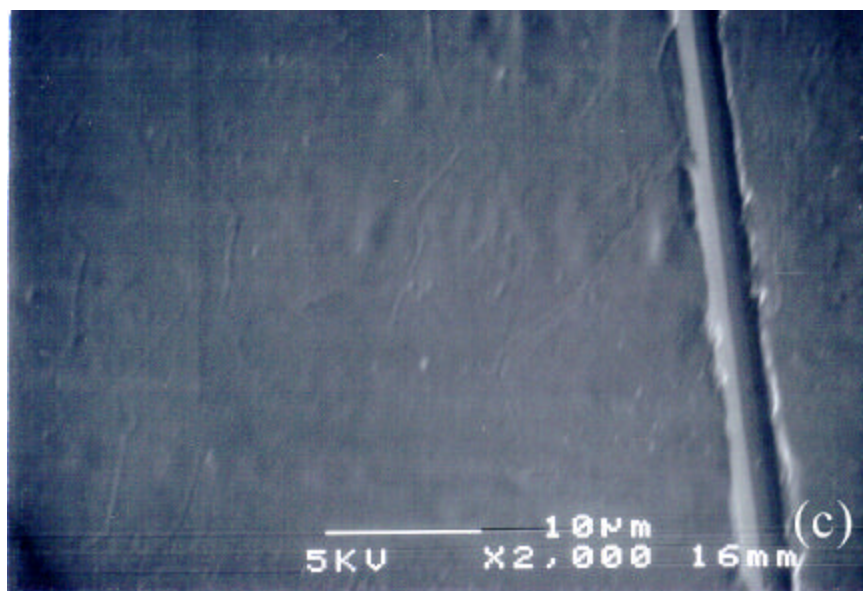


Figure 6.8 contd. Scanning electron micrographs of steel surfaces coated with hexane plasma polymers synthesized at different input power: (c) 100 W.

The elemental analysis was carried out after quantifying high resolution peaks for all the surfaces and is presented in table 6.4. At least three samples were analyzed at each modification step.

Table 6.4: XPS results for functionalized steel surfaces

Surface	%C	%O	%N	%S	%Fe	%Cr
Steel, hexane plasma polymer coated, 50W input power	88.19+/- 1.53	11.81+/- 1.53	-	-	-	-
Steel, plasma/gamma modified with MA	74.77+/- 0.93	25.07+/- 0.91	-	-	-	0.78+/- 0.0
Steel, post chemisorption with PEI	73.16+/- 1.14	12.20+/- 0.7	14.63+/- 1.06	-	-	-
Steel, hexane plasma polymer coated, PEI adsorbed	77.53+/- 0.86	14.61+/- 0.6	7.86+/- 0.076	-	-	-
Steel, post reaction with BSA	68.40+/- 0.31	18.66+/- 0.95	12.72+/- 0.96	0.22+/- 0.049	-	-

As noted above, the plasma/gamma grafting with methacrylic acid caused an increase in the oxygen with a corresponding decrease in the carbon content. Also the carbon peak for this surface as seen in figure 6.11(a) showed a characteristic shoulder on the high eV side in addition to the main carbon peak which indicated the presence of C=O and C-O groups on the surface. The O1s peak (shown in figure 6.11(b)) showed a clear splitting due of the dual binding states of the oxygen atoms. After chemi-sorption with PEI the surface showed an increase in nitrogen content to approx. 15%. Surprisingly, the PEI surface also showed an oxygen content of 12%, which could indicate incomplete or patchy coverage of the PEI over the underlying polymethacrylic acid layer. Post BSA grafting the surface showed a decrease in the nitrogen content and also showed a small sulfur peak which could be only due to the presence of BSA on the surface.

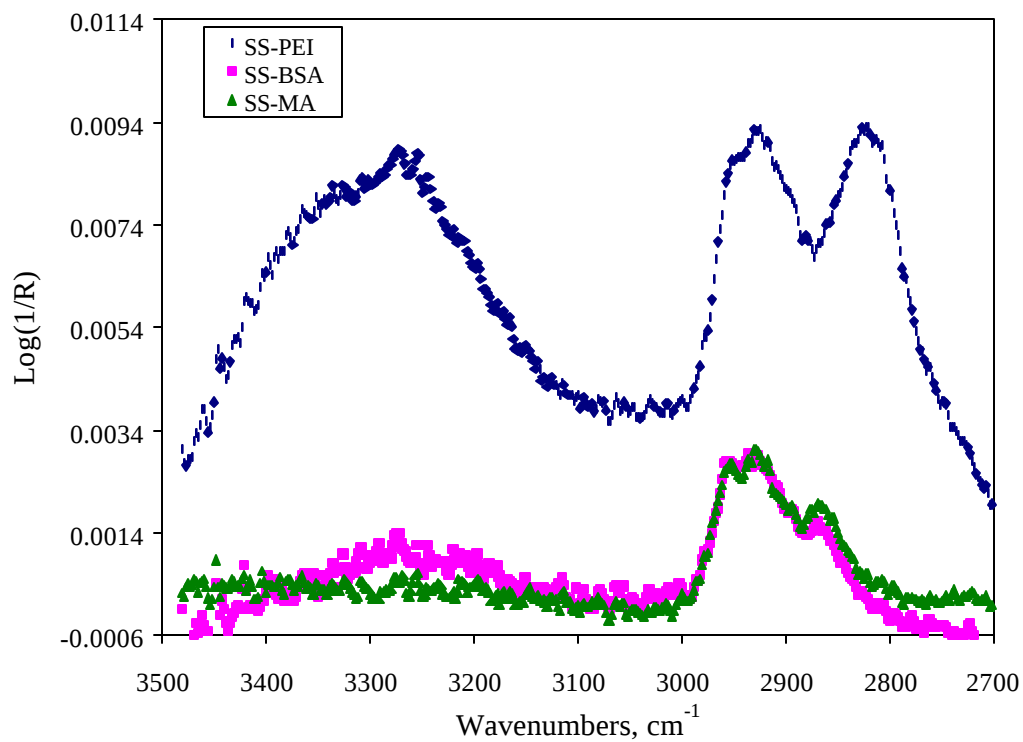


Figure 6.9. Reflectance absorption IR spectra of steel surfaces after successive modifications with methacrylic acid, polyethylene imine and bovine serum albumin..

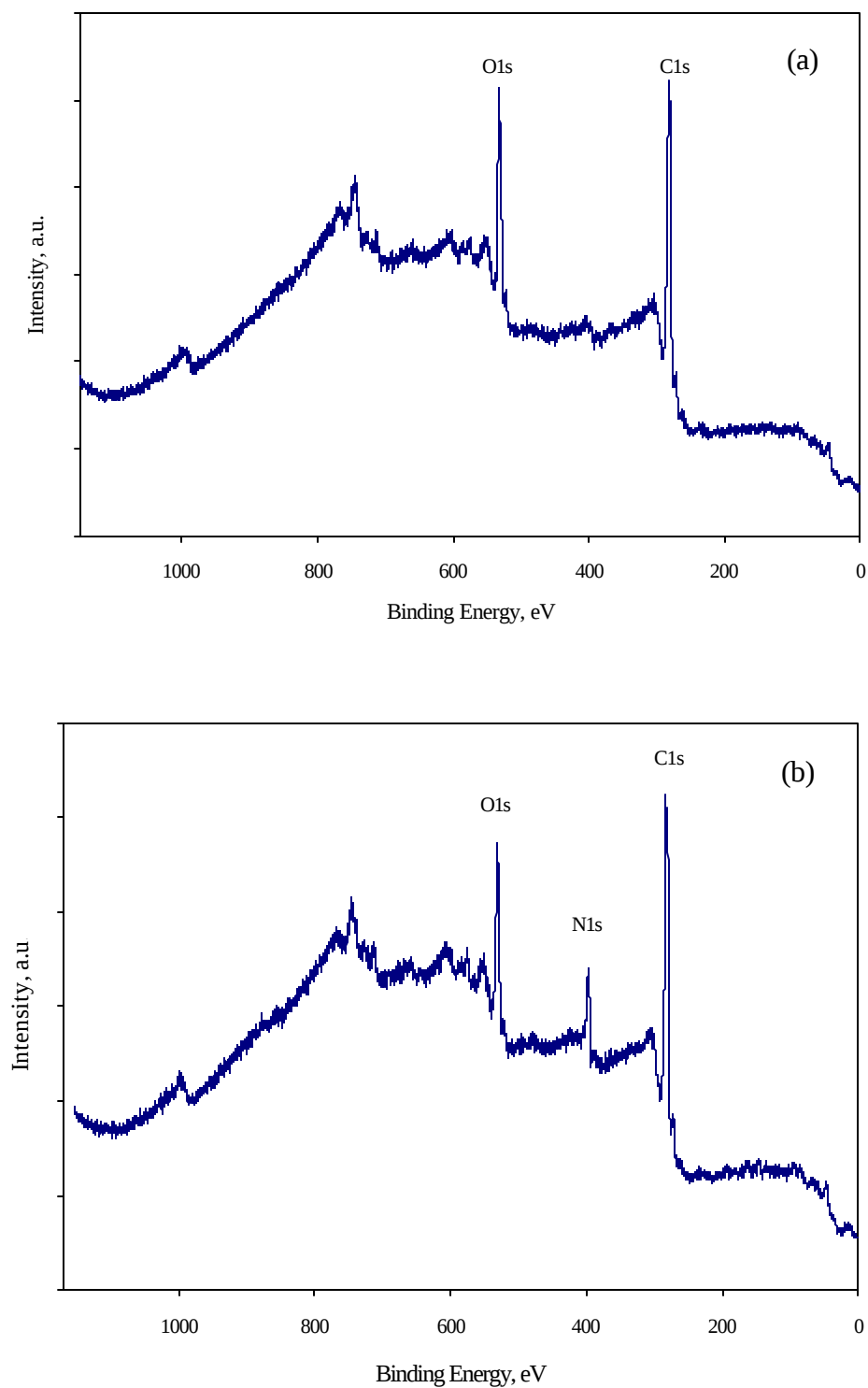


Figure 6.10. Low resolution XPS survey spectra of steel surfaces, (a) methacrylic acid plasma/gamma modified, (b) polyethylene imine chemisorbed.

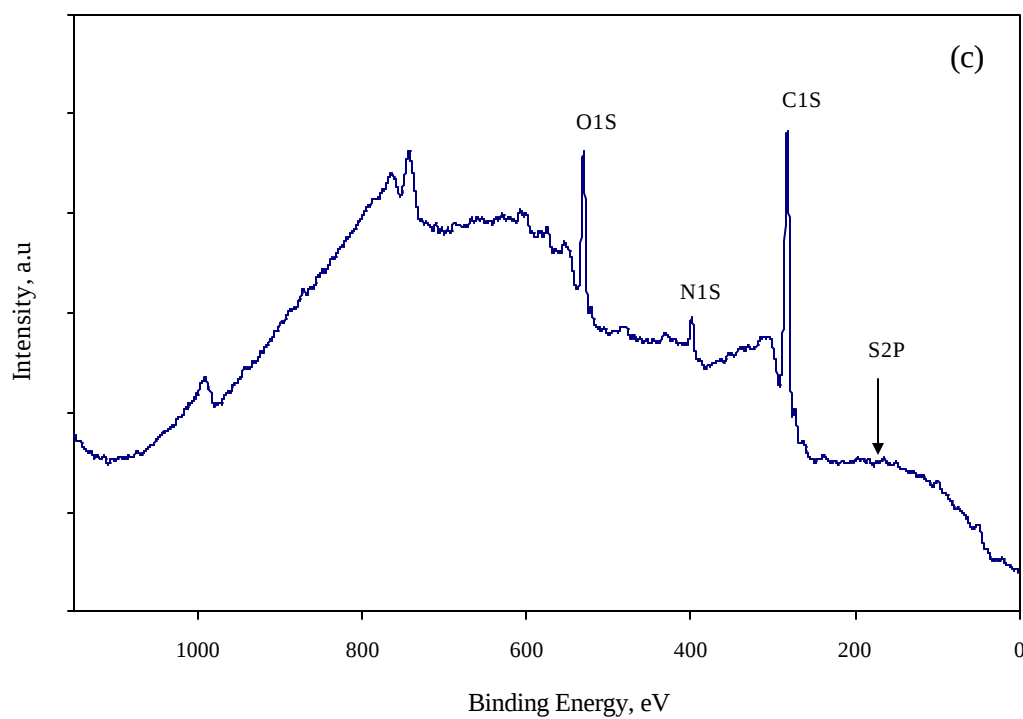


Figure 6.10 contd. Low resolution XPS survey spectra of steel surfaces, (c) bovine serum albumin reacted.

Figure 6.12 compares the high resolution C1s, O1s and N1s peaks for the PEI and BSA surfaces. All three elemental peak shapes reflect the change in the surface chemistry for the PEI and BSA modified surfaces. The carbon peaks exhibit only C-C and C-N bonding for the PEI surface, while the BSA surfaces show amide and carbonyl bonding in addition to C-C bonds. The BSA surface shows 2 types of nitrogen bonding, while the PEI surface shows three types of nitrogen bonding corresponding to the primary, secondary and tertiary amines which are present in the polymer. The S2p peak for a BSA modified steel surface is shown in figure 6.13.

Control experiments of PEI adsorption on hexane plasma polymer coated steel were also carried out and the results are reported in table 6.4. It is seen that these surfaces exhibit a lower nitrogen content, indicating that the amount of PEI adsorbed on the surface is less as compared to a MA plasma/gamma modified steel surface. This indicates that the chemical attraction between the carboxylic and amine groups of the two polyelectrolytes is the driving force for the adsorption.

Contact angle goniometry. The contact angles measured for the different steel surfaces are shown below in table 6.5. Each measurement is an average of 3 bubbles on 3 samples for each kind of surface (i.e. a total of 9 bubbles per surface). The deviations for each surface were well $\pm 2^\circ$ of the average.

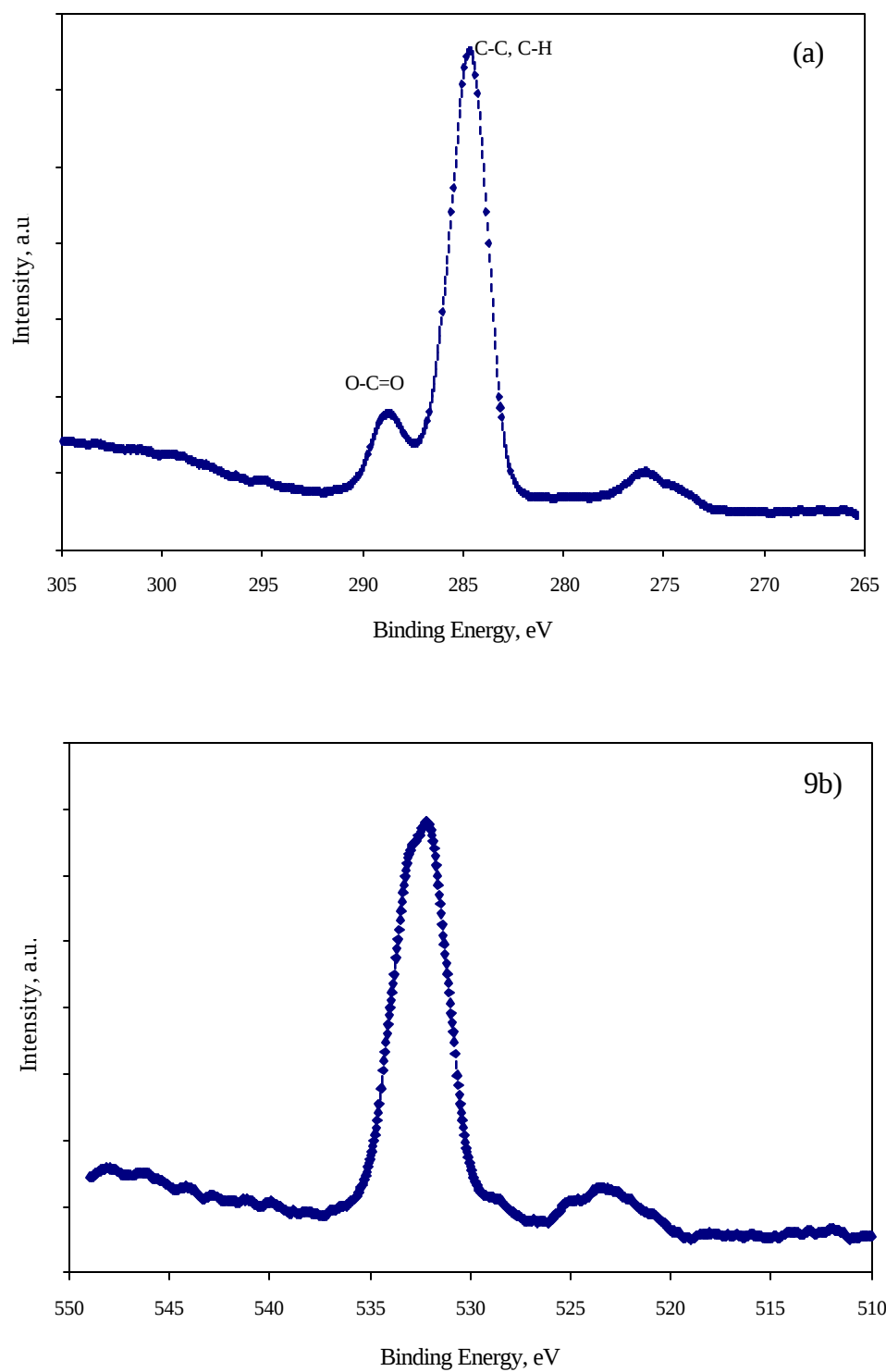


Figure 6.11. High resolution XPS spectra of a methacrylic acid modified steel surface, (a) C1s and (b) O1s.

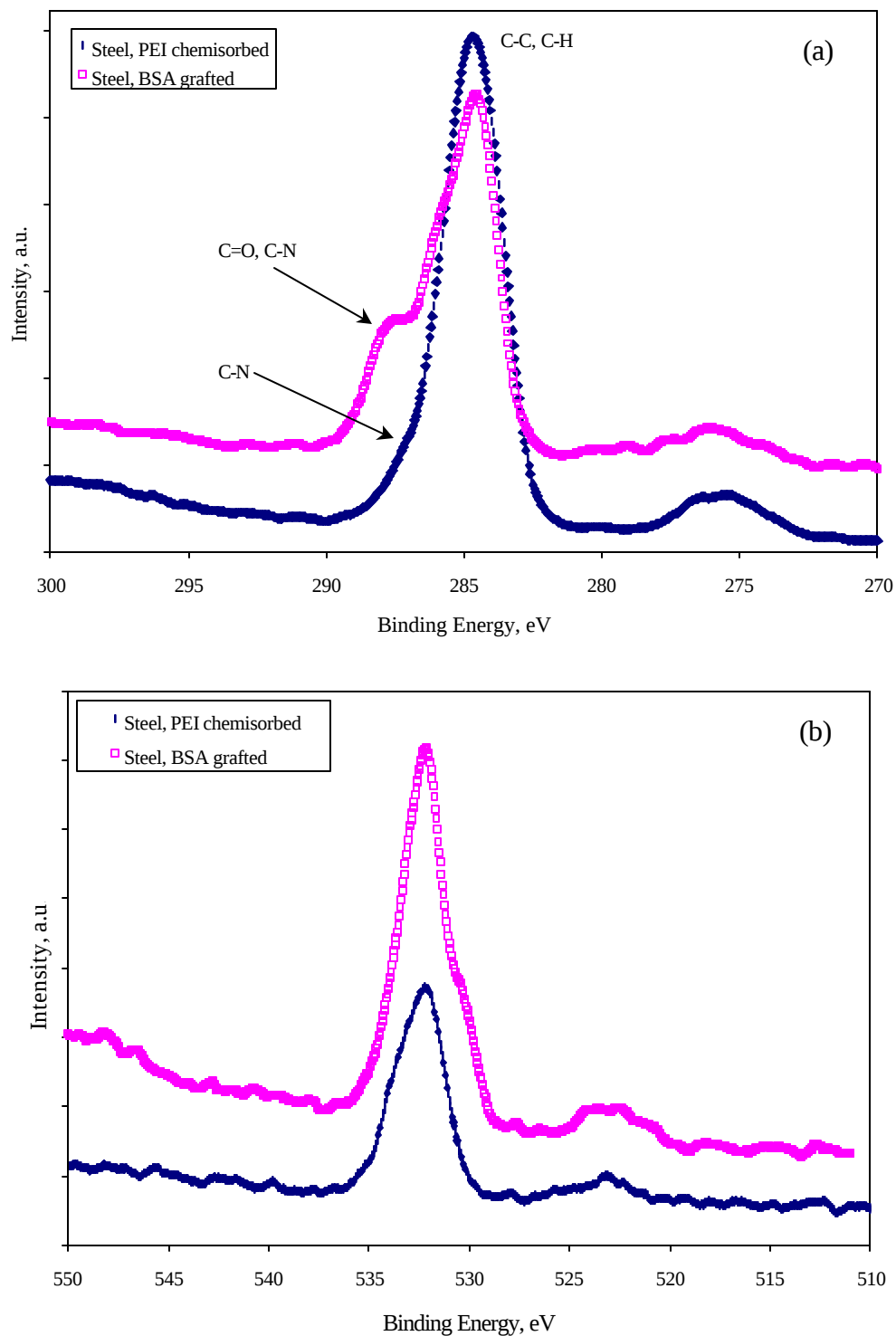


Figure 6.12. High resolution XPS spectra of polyethylene imine and bovine serum albumin modified steel surfaces, (a) C1s and (b) O1s

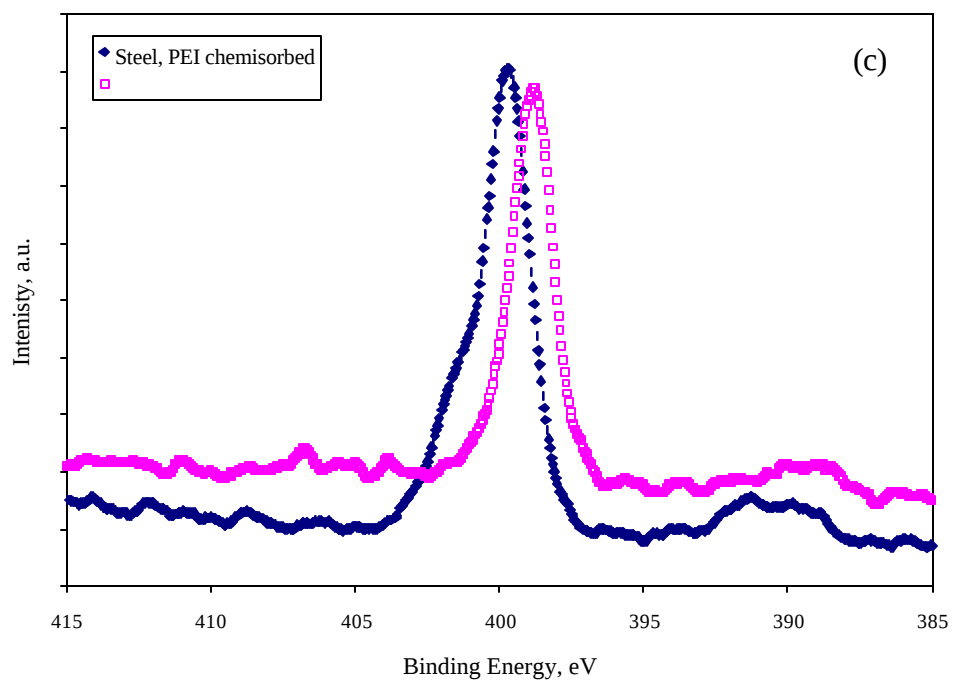


Figure 6.12 contd. High resolution XPS spectra of polyethylene imine and bovine serum albumin modified steel surfaces, (c) N1s.

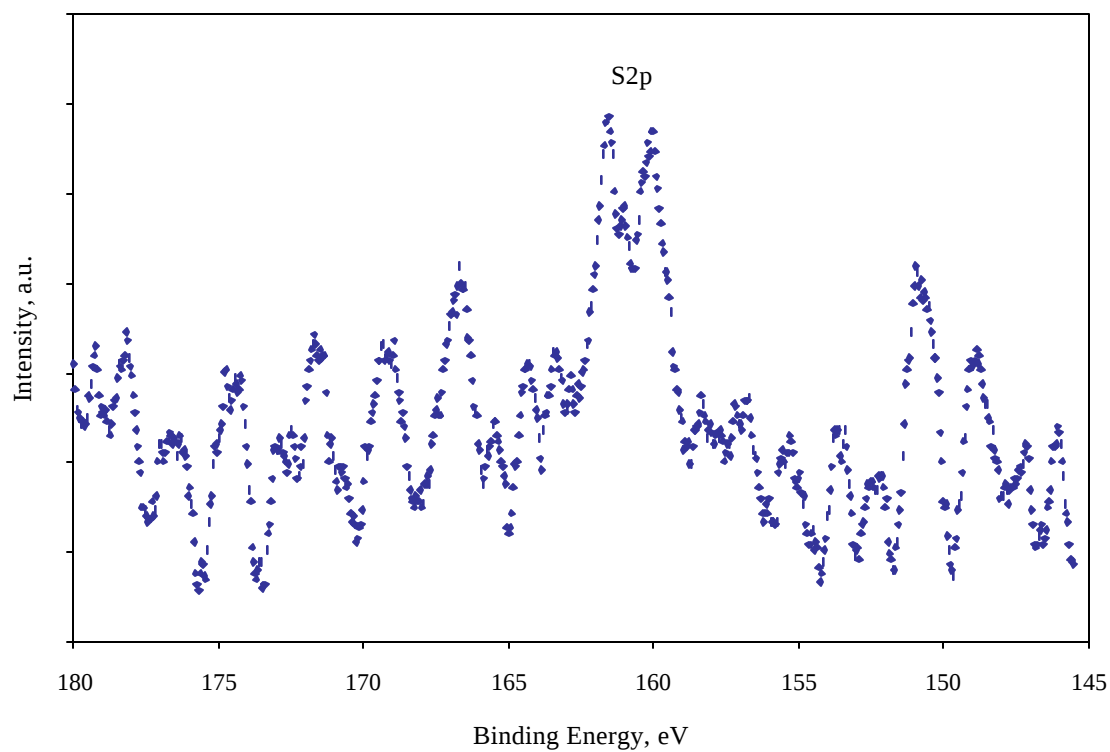


Figure 6.13. High resolution XPS spectrum of the S2p peak for a bovine serum albumin modified steel surface.

Table 6.5 : Average contact angle values for different steel surfaces

Surface	Average Contact Angle (deg)
Steel, plasma/gamma modified with MA	18
Steel, post chemisorption with PEI	18
Steel, post binding reaction with BSA	24

The MA modification produced a hydrophilic surface as shown by the contact angle value of 18°. Subsequent modifications with PEI and BSA did not change the surface hydrophilicity significantly as reflected by the low contact angle values for these surfaces.

Streaming potential measurements. Zeta potential values for the different surfaces calculated at two pHs are presented in table 6.6. Streaming potential values were measured in a specially designed cell for flat surfaces and used for the zeta-potential calculations. The design, set-up and calibration of this instrument is given in Appendix A. The streaming solution used was 1×10^{-3} M KCl.

Table 6.6: Zeta potentials of different steel surfaces

Surface	Zeta potential, mV (pH 4.4)	Zeta potential, mV (pH 7.0)
Steel, unmodified	10.14	-25.21
Steel, hexane plasma polymer (i/p=50W)	21.67	-15.14
Steel, plasma/gamma modified with MA	-8.47	-26.31
Steel, post chemi-sorption with PEI	15.6	-18.63
Steel, post grafting with BSA	~ 0	-29.83

The hexane plasma modified surface showed a strong charge which is surprising considering the high carbon content and hydrophobicity of this surface. It has been shown that hydrophobic surfaces like polytetrafluoroethylene can possess a strong charge under

similar streaming conditions [140]. It is also possible that the radicals present on the surface caused a charge to build up on the surface. The plasma/gamma MA modified steel surfaces were strongly negatively charged even at low pH. This was due to the presence of -COOH groups on the surface. Chemisorption with PEI produced a positively charged surface at low pH due to the presence of amine groups. The BSA grafted surface was electro-neutral at low pH. As the pH was increased to 7.0 all the surfaces became negatively charged. It was also seen that except for the hexane plasma polymer surface and the PEI chemisorbed surface, all zeta potential values were in the range of -25 to -30 mV. The negative charge on the PEI surface was surprising as XPS and FTIR analysis had indicated a large number of amine groups on this surface and literature reports have shown that these surfaces can be positively charged at pH 7.0. However the XPS analysis had also revealed the presence of oxygen on this surface indicating incomplete coverage. The carboxylic groups from the polymethacrylic acid layer could affect the streaming potential measurement, leading to an increase in the zeta-potential at high pH.

Scanning electron microscopy. The morphology of the steel surfaces after different modification steps was examined by SEM. The samples were air-dried and sputtered with a thin gold-palladium coating before examination. Figures 6.14, 6.15 and 6.16 show the steel surfaces after modification with methacrylic acid, polyethylene imine and bovine serum albumin respectively. Large scale peel-off effects which exposed the hexane plasma polymer could be seen in all three figures.

Discussion

Hydrocarbons were among the first monomers polymerized by glow-discharge methods. Stille *et al.* [141] studied the polymerization of benzene by rf plasmas in the 1960s. Kobayashi *et al.* [142] polymerized a series of alkanes and alkenes and produced plasma polymers from all of the starting monomers. Their results revealed that saturated alkanes polymerize much slower than their unsaturated analogues. Specific conditions under which polyethylene-like films could be produced were also reported. Elemental analysis indicated that such plasma-PE films were hydrogen deficient suggesting a high degree of cross-linking.

The surface analysis of hexane plasma polymers synthesized in this research indicated that these plasma polymers had structures similar to literature reports. The effect of input power on the structure of hexane plasma polymers was examined by FTIR, XPS and contact angle goniometry. The analysis revealed that the power levels used in the above experiments did not affect the structure of the plasma polymer in a significant fashion. The FTIR and XPS spectra showed that the plasma polymers were largely composed of C-C bonds linked together. Thus the surface could be thought of as a polyethylene-like structure with linear and branched chains. The oxidation evident on the surface was thought to be due to trapped free-radicals reacting on exposure to atmosphere.

Typically all plasma polymers are highly cross-linked which leads to a loss of chain mobility and a high free-radical concentration. These free-radicals can react on exposure to atmosphere and change the polymer surface over a period of days or months. Such an effect was also seen for the hexane plasma polymers. Table 6.7 shows the elemental percentages for a hexane plasma polymer synthesized at 50W and analyzed at

different times. It was seen that initially the film had a carbon content of approx. 95%. Upon storage for two months, the carbon content dropped to 87%. The oxygen content showed an opposing trend. Radiation damage from the x-ray source of the XPS can be discounted as a source of free-radical formation since samples analyzed multiple times at short intervals did not show any change.

Table 6.7. Effect of storage time on elemental composition of a hexane plasma polymer film.

Time of analysis	%C	%O
After synthesis	94.67	5.33
After 2 months storage	87.29	12.71

In characterizing plasma polymerization Yasuda defined the composite parameter W/FM where W is the input power in watts, F is the monomer flow rate in cm^3 (STP)/min and M is the molecular weight of the monomer. The parameter can be thought of as the energy input per unit mass of monomer. Based on this parameter plasma polymerization can be classified into two regimes, power deficient or flow rate deficient. In the power deficient regime, the input power is the rate determining step in the process. This means that the plasma glow is confined to one area of the reactor due to the quenching effect of abundant monomer species and inadequate power. In the flow rate deficient regime, the flow rate is the rate determining step. The power input is above a critical value so that polymerization can occur. Since there is ample power to sustain polymerization the plasma glow can grow to cover a large area in the reactor and the rate of polymerization (or deposition) is governed by the monomer flow rate.

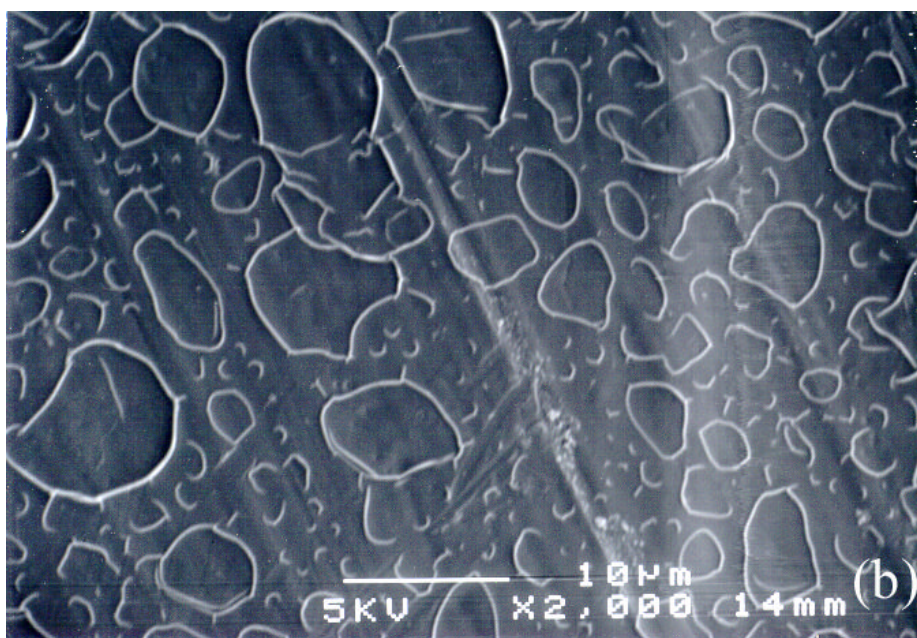
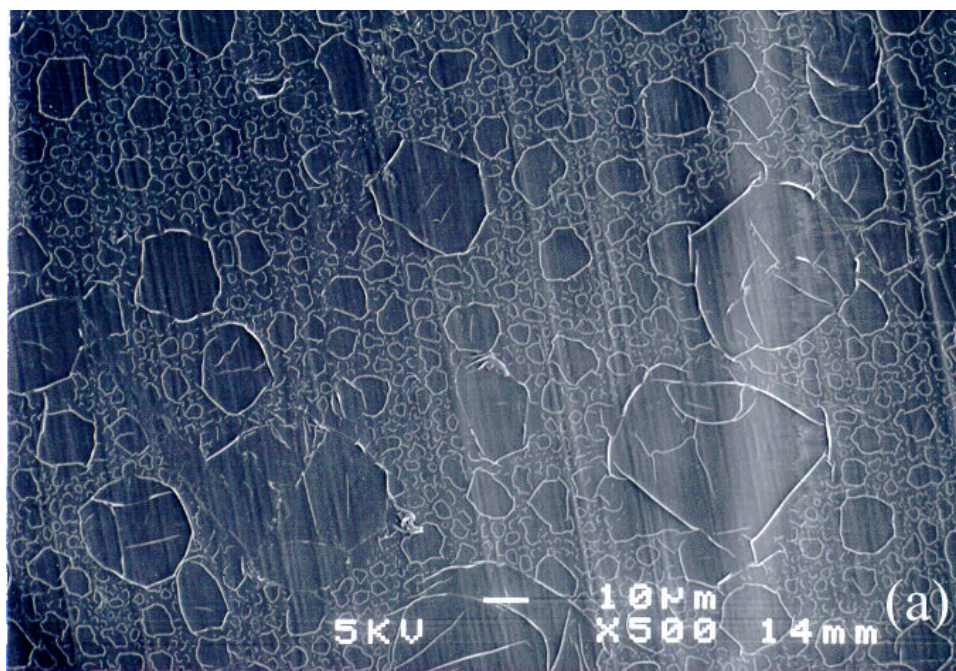


Figure 6.14. Scanning electron micrographs of methacrylic acid plasma/gamma modified steel surfaces at (a) x500 and (b) x2000.

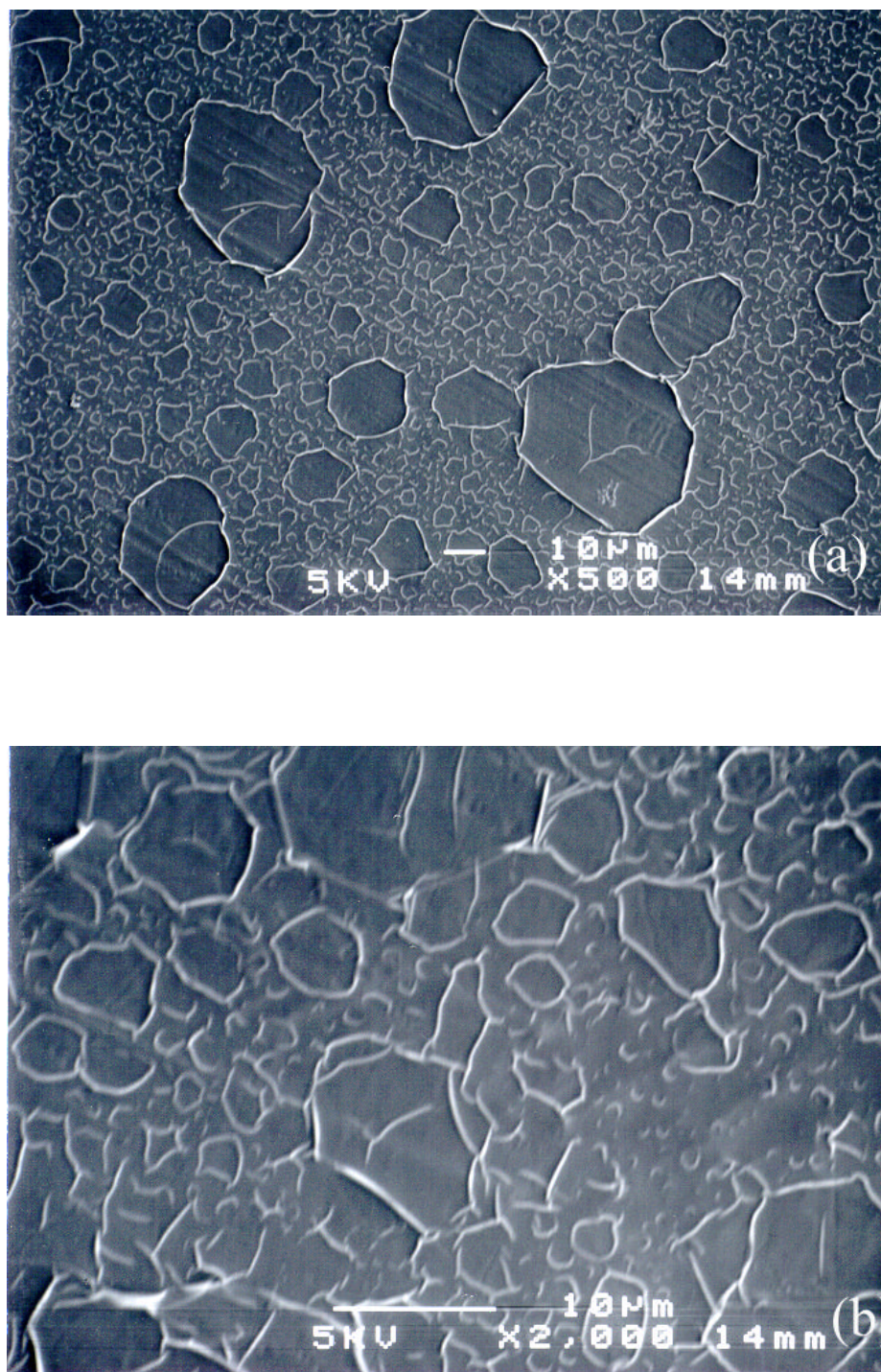


Figure 6.15. Scanning electron micrographs of polyethylene imine chemisorbed steel surfaces at (a) x500 and (b) x2000.

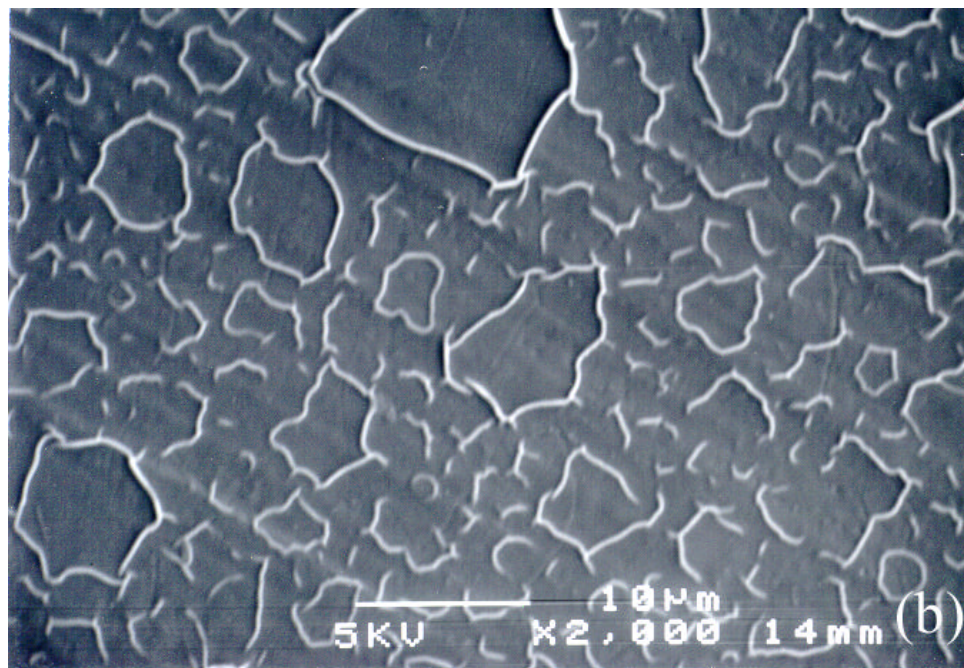
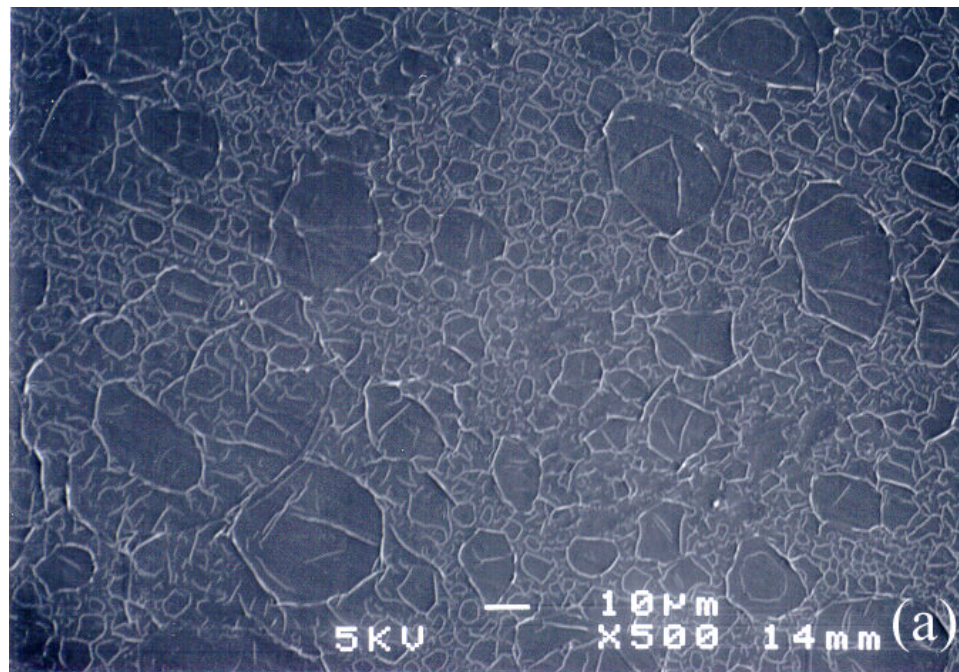


Figure 6.16. Scanning electron micrographs of bovine serum albumin modified steel surfaces at (a) x500 and (b) x2000.

To determine the regime in which the hexane plasma polymerizations occurred the W/FM value was measured as follows. After evacuating the reactor and allowing the pressure to reach its base value (<10 mTorr), the monomer inlet valve was opened and the pressure was stabilized at 50 mTorr. The outlet valve was then closed and the pressure increase in the reactor was measured as a function of time. The flow rate was calculated using the following equation derived from the ideal gas law [130]:

$$F = \frac{dp}{dt} \times 16172 \times \frac{V}{T}$$

where F = flow rate (cm³(STP)/min); p = pressure (mbar); t = time (s); V = volume of the plasma reactor, = 2 L; T = temperature, = 293 K. The flow rate at 50 mTorr was calculated to be 1.55 cm³(STP)/min. Thus the W/FM value ranged from 0.187 to 0.747 W min mol/g cm³(STP) for an input power range of 25-100 W.

As defined by Yasuda for n-hexane, this meant that at 25 W the input power was below the critical value required for sustained polymerization. It was seen that at 25W the plasma glow did not fill the complete reactor which was another indicator of the W/FM factor being below its critical value. As the power was increased to 50 W, the plasma glow grew to fill the whole reactor. Thus at 25W the polymerization was in the power-deficient regime while at 50- and 100W the polymerization was in the flow rate deficient regime. However, as shown by the surface analysis, the polymerization regime did not affect the structure of the plasma polymer. The theory predicted that the major impact of the polymerization regime would be on the growth or deposition rate of the polymer. However, this effect of the composite parameter (W/FM) on the deposition rate was hard to clarify since the deposition rates showed poor repeatability. The only

conclusion which could be drawn based on the average deposition rate values was that the polymerization process was a slow one. SEM analysis showed that all films were extremely smooth with little defects. Complete coverage was also effected on all samples with no bare sites.

From the above discussion it is clear that plasma polymerization of hexane produced films with C-C bonds linked in a linear or branched fashion. The films also showed evidence of some oxidation and trapped free-radicals. The trapped free radicals served as oxidation sites and increased the oxygen content of the films over a period of time.

These plasma polymer surfaces served as a convenient base for further modification. The viability of this idea was proven by the fact that steel surfaces which were not coated with a hexane plasma polymer could not be modified by the gamma grafting method. The ability of gamma rays to generate radicals in hydrocarbon polymers is well-known and this property was utilized for the grafting reaction. It is speculated that the trapped free-radicals in the polymer also proved advantageous during the grafting step by acting as initiation sites.

The gamma radiation grafting of methacrylic acid was carried out at low concentration and radiation dose. Fox and Alexander studied the x-ray initiated polymerization of methacrylic acid in aqueous solutions [143]. They found that since methacrylic acid is a precipitant for its polymer, whereas water readily dissolves the latter, the rate of polymerization decreased as a function of monomer concentration. Polymers with high molar mass were obtained at dilute monomer concentration. The MA gamma polymerization conditions used in the stainless-steel modifications were based on

these results. It was found that these conditions successfully produced a surface which was hydrophilic and negatively charged. It was also found that using a concentration higher than 7.5% (w/w) caused a gel to form which made the sample difficult to extract. The radiation dose used in this study is also much lower than any previously reported. It is believed that using this low dose can produce the same modification effect produced in studies using higher doses. SEM of these plasma/gamma modified steel surfaces revealed that the MA layer was not uniform and showed signs of peel-off. It was believed that the vacuum drying process caused the widespread peel-off effect seen on these surfaces since polymethacrylic acid can absorb large amounts of water. However SEM examination after freeze-drying of hydrated surfaces showed no change in the morphology. Thus it is probable that the methacrylic acid grafting did not fully cover up the hexane plasma polymer layer. This could be due to the fact that the methacrylic acid initiation only took place at free radical sites on the hexane plasma polymer. However even though the surface coverage was incomplete as shown by SEM, this surface was negatively charged even at low pH. This indicated the presence of a large concentration of carboxylic groups.

Such a functionalized surface was useful for binding biomolecules to the surface by two different methods. First, the carboxylic acid groups on the surface could be used for coupling proteins or drugs through carbodiimide coupling. Second, and the more facile method was to employ a polyelectrolyte deposition process to attach a polymer with amine groups on the surface. Amine groups are more amenable to coupling reactions through the use of glutaraldehyde. Decher *et al.* [144],[145] developed the alternate polyelectrolyte method to prepare organic thin films on glass slides and silicon substrates.

They had demonstrated that films consisting of 60 layers of oppositely charged polyelectrolytes can be built up by this method. Using the above process methodology, polyethylene imine was deposited onto the MA grafted steel surfaces. PEI is a commonly used coupling agent in bioconjugate chemistry. The ionic attraction between the MA carboxylic groups and the PEI amine groups was the driving force for the reaction. The success of this reaction was demonstrated by FTIR and XPS. The control experiments on hexane plasma polymer coated steel showed that smaller amounts of PEI were deposited as compared to the plasma/gamma modified steel. The ionic attraction between MA and PEI caused a higher amount of PEI to be adsorbed. SEM analysis revealed that the surface of the PEI chemisorbed steel showed the peel-off effect seen earlier on the MA grafted surfaces. It is probable that the PEI deposited only on areas with polymethacrylic acid causing it to follow the contours of this layer. The PEI chemisorbed surface also provided an abundance of free amine groups for further modification.

Bovine serum albumin was used as a model molecule for the coupling reaction. In a vascular environment the deposition of serum albumin on the implant surface has been shown to be the primary event. Thus mimicking such a surface would provide a beneficial effect for any vascular implant [146]. The BSA was reacted with the PEI chemisorbed steel through the use of glutaraldehyde. It was seen that this reaction was successful in binding large quantities of BSA. XPS scans showed the change in C1s and N1s peaks for PEI and BSA modified surfaces. The BSA modified surface also showed the presence of sulfur in the XPS. The % sulfur in BSA is around 1.96% [148], thus the fact this small amount can be seen in the XPS indicates that a large amount of BSA is

bound to the surface. Interestingly, the SEM results for the BSA modified steel were similar to the MA and PEI modified surfaces. This indicated that non-specific adsorption of BSA was minimal and the reaction occurred only in the areas where PEI is present. This result is surprising considering the large size of this molecule and also since BSA is known to bind to both hydrophilic and hydrophobic surfaces.

The streaming potential experiments made it possible to assess surface charge of the modified substrates. The importance of zeta-potential measurements in vascular environments was demonstrated in pioneering experiments by Sawyer *et al* [148]. It was shown that electropositive surfaces like those seen on some metals elicit a greater thrombogenic response in canines as compared to electronegative surfaces. The electric potential at cell bilayers was also measured and found to be in the range of -70 to -90 mV. The modified steel surfaces showed comparatively smaller zeta-potentials at close to physiological pH. At pH 7.0 all the surfaces had a negative zeta potential with low values (-10 to -30 mV). It is believed that the PEI chemisorbed surface was also negatively charged due to incomplete coverage of this polymer over the polymethacrylic acid layer. The zeta-potential was thus affected in a complex fashion due to the interaction of these oppositely charged surfaces resulting in a negative value. The BSA coupled surface showed zeta potential trends similar to literature. The isoelectric (IEP) point for this protein is 4.75 (± 0.1) [149], and it was seen that at pH 4.4 (close to the IEP) the zeta potential for the BSA coupled surface was approximately zero. This indicated the formation of a stable, thick protein layer on the functionalized steel surface.

It is not known how the zeta potentials of the modified steel surfaces would affect their behavior in a vascular environment. Streaming potential measurements were carried

out under 'ideal' conditions since the Smolouchowski equation requires the use of dilute electrolyte concentrations. Under physiological conditions the ionic concentration is much higher and multi-valent ions and proteins are also present. These ions can affect the zeta potential of a surface in a complex fashion. Thus the behavior of the modified steel surface would need to be assessed in *in-vivo* experiments. However, zeta potential measurements in surface modification can serve the important function of assigning a numerical value to the number of functional groups on the surface [150]. Thus it can determine the adhesion of the modification layer under flow conditions and serve as a tool in ensuring repeatability between experimental runs.

Summary

Stainless steel surfaces were modified by a combination of plasma/gamma and chemical attachment processes to obtain surfaces with functional groups. Hexane plasma polymerizations produced hydrocarbon based films with some oxidation. These coated surfaces proved useful as a base for further modifications. The plasma/gamma process produced a surface with carboxylic groups on it. PEI was coupled to this surface by chemisorption. The surface was thus changed to an amine rich one. BSA was chosen as a model biomolecule and coupled to the amine groups by glutaraldehyde proving the utility and ease of this modification concept. Zeta potential measurements of these surfaces provided important information on the surface charge and level of ionicity of such modifications

CHAPTER 7 CONCLUSIONS AND FUTURE WORK

Pulsed Laser Ablation Deposition

Thin films were synthesized by pulsed laser ablation deposition of cross-linked silicone for the first time. Films were produced at a variety of experimental conditions and it was found that small changes affected the film properties to a great extent. Specifically, as shown in chapter 3, the energy density was found to have a profound effect on the deposited film structure and chemistry. At low energy densities ($< 150 \text{ mJ/cm}^2$), smooth, hydrophobic films which resembled silicone were deposited. At high energy densities ($> 150 \text{ mJ/cm}^2$), hydrophilic films with increased oxygen content were deposited. The film structures had some similarity to siloxane films synthesized by plasma polymerization, indicating that the growth mechanisms for both these processes might be similar. These films also had a particulate nature due to the production of particles and clusters upon ablation. Such an energy density dependence has not been reported before for the PLAD of any other polymer and represents a potentially important method to make tailored film properties.

All films were found to be strongly adhered to the substrate even after a 24 hour chloroform immersion. This is an important property which arises from the use of the PLAD process. Laser pulse number and deposition rate studies revealed that the laser ablation of silicone has a strong thermal component.

Chapter 4 presented the results of the mechanical property analysis of the PLAD films. Nanoindentation and nanoscratch measurements were carried out to measure modulus and strength of adhesion of the films. Nanoindentation measurements of the films revealed that the modulus values were in the range usually seen for glassy polymers. These values were approximately 3 orders of magnitude higher than those measured for the silicone target. It is not known yet whether this was due to the underlying substrate or an inherent property of the films. However, from the time-displacement response of the films it was evident that the films were viscoelastic. This meant that the PLAD process, although quite destructive to the target still produced films which were polymeric. Nanoscratch measurements quantified the force required to initiate a scratch and cause adhesive failure. It was shown that the force required to initiate a scratch was approximately the same for films synthesized at different energy densities. However the force required to cause adhesive (interfacial) failure was different, indicating a greater degree of interfacial bonding for films synthesized at higher energy densities.

Chapter 5 presented an empirical model for the ablation of silicone at 248 nm. The model was developed for photothermal ablation and gave a good fit to the data for ablation depth of silicone as a function of energy density. The model represented an important step in understanding the ablation processes for silicone.

The PLAD research presented here raises provocative questions which deserve to be investigated. First, the energy dependence of silicone was investigated in a relatively narrow range. It is not known whether using much higher energy densities ($1\text{--}2\text{ J/cm}^2$) would produce a different effect. Therefore a study investigating the PLAD of silicone in

this range would need to be done. Second, since several parameters like energy density, pressure, substrate-target distance and repetition rate affected the film thickness and morphology, a statistically designed study would need to be done to find out the most important factor and all the interactions. Third, current surface characterization techniques like FTIR and XPS can only provide limited information on larger molecules or chain systems. Therefore, it would be important to do mass spectroscopy using Matrix Assisted Laser Desorption Ionization (MALDI). MALDI would provide greater structural information on larger molecules and chains which would help in understanding the film growth processes. Fourth, silicone coatings are unique because they can serve as drug-delivery surfaces. Widenhouse has shown that dexamethasone loaded silicone coatings can be effective in a vascular environment. Thus, a dexamethasone releasing film produced by the PLAD of a dexamethasone loaded silicone target would be worth investigating. Fifth, and possibly the most immediate step would be a canine *ex-vivo* shunt study to test the biocompatibility of the PLAD coatings. In addition, the nanoindentation and nanoscratch studies presented here though promising are very preliminary. Further work is needed to qualify the validity of the nanoindentation measurements and also to figure out a measure for adhesion strength of the film from nanoscratch measurements.

Finally, the research presented here would need to be extended to other classes of polymers including cross-linked elastomers, hydrogels, polyesters and polycarbonates. Developing thin films from these polymers could prove important in several applications.

Functionalization of Stainless-steel by Plasma/Gamma Processes

The plasma polymerization of hexane was studied in-depth. It was found that varying the power input did not affect the film chemistry and structure to a great extent. All experimental conditions produced a highly crosslinked, branched film with low surface energy. The gamma polymerization on the plasma hexane films was effective in creating a hydrophilic, anionic surface. Chemisorption with PEI proved to be a facile method for producing an amine-rich surface. The unique feature of this process was the ionic attraction between the carboxylic groups of the poly (methacrylic acid) and PEI causing increased adsorption of the PEI. This surface was seen to be extremely stable and also proved to be amenable to glutaraldehyde coupling chemistry, as shown by the BSA binding reaction.

Process optimization has always been a problem with plasma systems. Therefore, a optimization study which would determine the conditions for producing a plasma polymer film with known thickness reproducibly would need to be done. Newer systems like pulsed plasmas offer better control during the polymerization process and it would prove useful to shift to such a system. The gamma radiation initiated polymerization of methacrylic acid onto the plasma polymer of hexane needs to be optimized. Particularly, conditions which give complete grafting coverage of the plasma polymer need to be found out. The polyelectrolyte deposition process would also gain by being automated. This would produce thin films reproducibly and with better features morphologically. The coupling process should also be tried out with a variety of biologically active molecules to produce biofunctional surfaces. Some candidates for biofunctionalization could be salicylic acid, phosphorylcholine or its reactive analog, RGD peptide residues and dexamethasone.

APPENDIX DESIGN, SETUP AND CALIBRATION OF A STREAMING POTENTIAL CELL

Introduction

The charge at a surface known as the zeta potential can be determined by measuring the streaming potential associated with that surface. Streaming potential is the potential generated when a fluid is forced through a capillary [151]. The streaming potential across a capillary can be measured as a function of pressure by a high impedance electrometer. The potential is plotted as a function of pressure and the zeta potential is calculated by inserting the slope of the regression line in the Smoluchowski equation. The equation is given below:

$$z = \frac{4\rho h}{k} \times \frac{\Delta E_s}{\Delta P} \times r \quad (1)$$

where ζ is the zeta potential, η is the viscosity, ρ the specific conductivity of the electrolyte, $\Delta E_s/\Delta P$ is the slope of the streaming potential vs. pressure plot and κ is the dielectric constant of the fluid.

The streaming potential of flat plates and films can be measured by creating a small flow channel in which the length and width of the channel are far greater than its height. This creates the conditions necessary for the measurement of the streaming potential associated with the surface. The design and setup of such a flow cell is given below.

Streaming Cell Design and Setup

The design of the streaming cell was based on several models which had been published [152],[153]. The streaming potential cell was machined out of poly(methyl methacrylate) (PMMA). The cell consisted of two rectangular blocks with inlet and outlet ports in the upper half for electrolyte flow. Slots with the dimensions of standard microscope glass slides (75 cm x 25 cm x 0.1 cm) were made to accommodate samples. Figures A.1 and A.2 give the dimensions and features of the cell. Cavities for mounting electrodes were also machined into the upper half. Standard Ag/AgCl electrodes were used. A 120 μm thick poly (tetrafluoro ethylene) (PTFE) gasket was used to create a seal. The gasket also served to create a rectangular capillary between the two sample pieces for electrolyte flow . The inlet and outlet ports were connected via polyethylene (PE) tubing to electrolyte reservoirs. The electrolyte was directed under inert gas (Argon) pressure into the cell and the direction of flow was controlled by a four way valve. Connections from the reservoir tubing were fed to a differential pressure transducer with a real time output read via a computer. Streaming potentials were measured using a high input impedance electrometer (Keithly Instruments). The cell was electrically isolated within a grounded Faraday cage to negate the effects of stray currents. Figure A.3 shows a schematic of the streaming potential cell setup while figure A.4 shows a schematic of the sample and cell assembly. The electrolyte was 1×10^{-3} M KCl prepared with de-ionized ultrapure water (resistivity $> 15 \text{ M}\Omega \text{ cm}$). The pH was adjusted to the desired value by adding 0.01 N HCl or KOH. The electrolyte pH and conductivity was measured before and after every experiment. The constants used in the zeta potential calculation are given in table A.1.

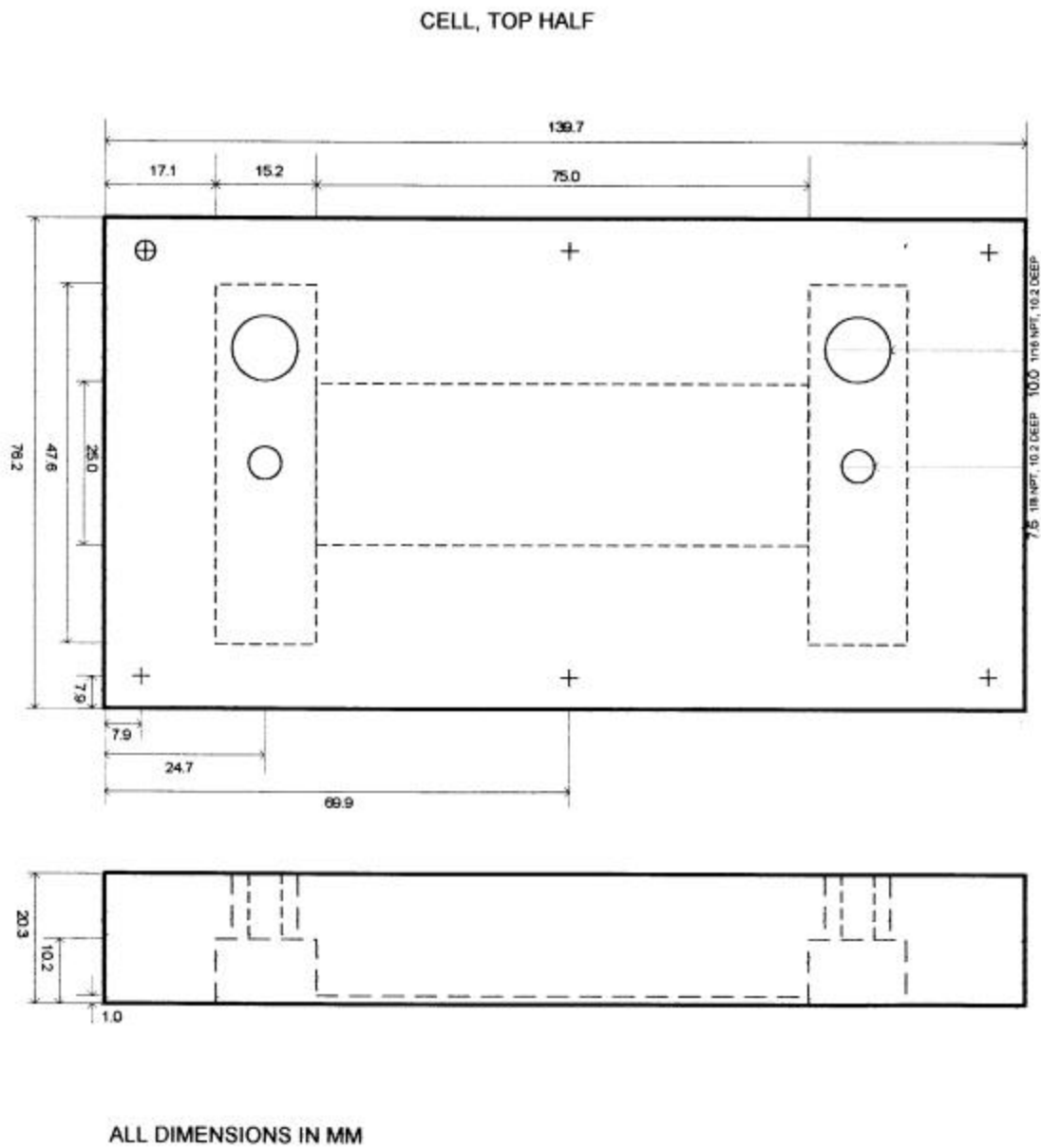


Figure A.1. Top block of the streaming cell showing the associated features.

CELL, BOTTOM HALF

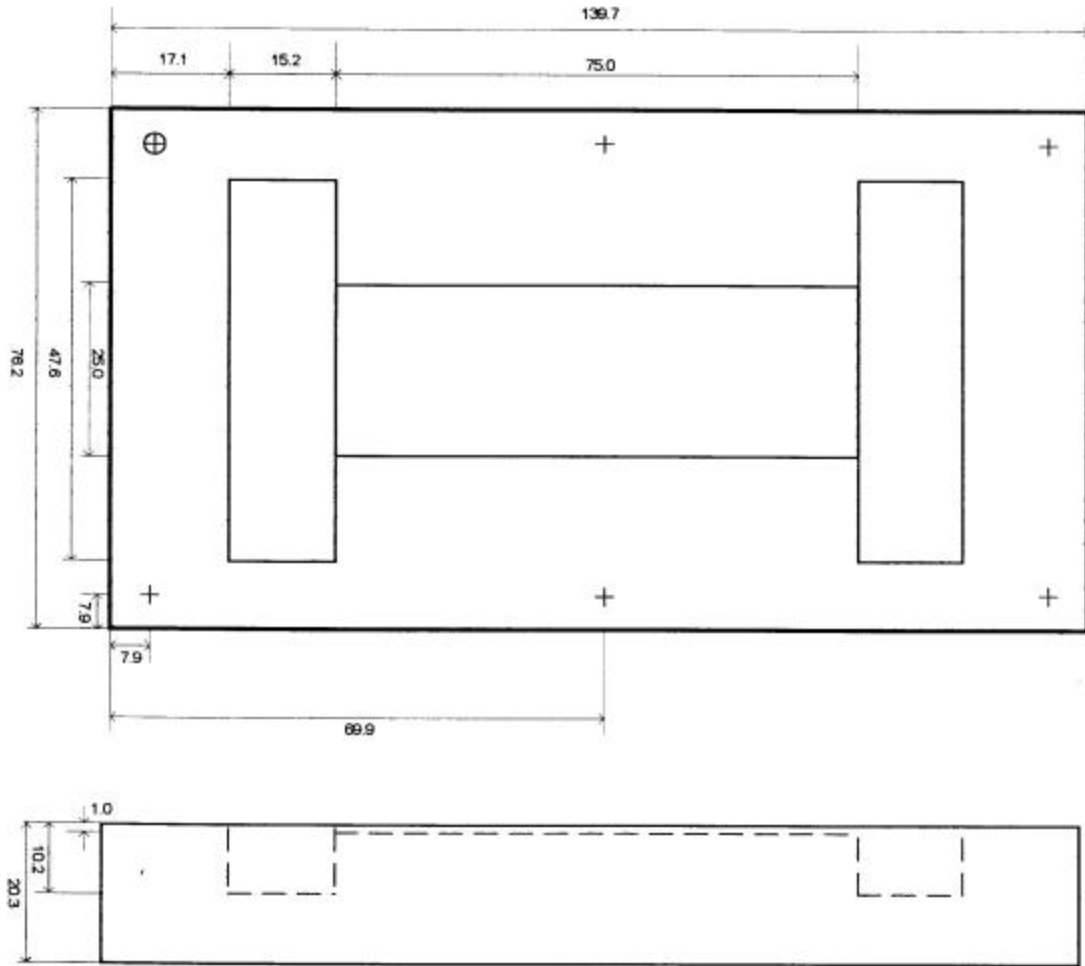


Figure A.2. Bottom block of streaming cell.

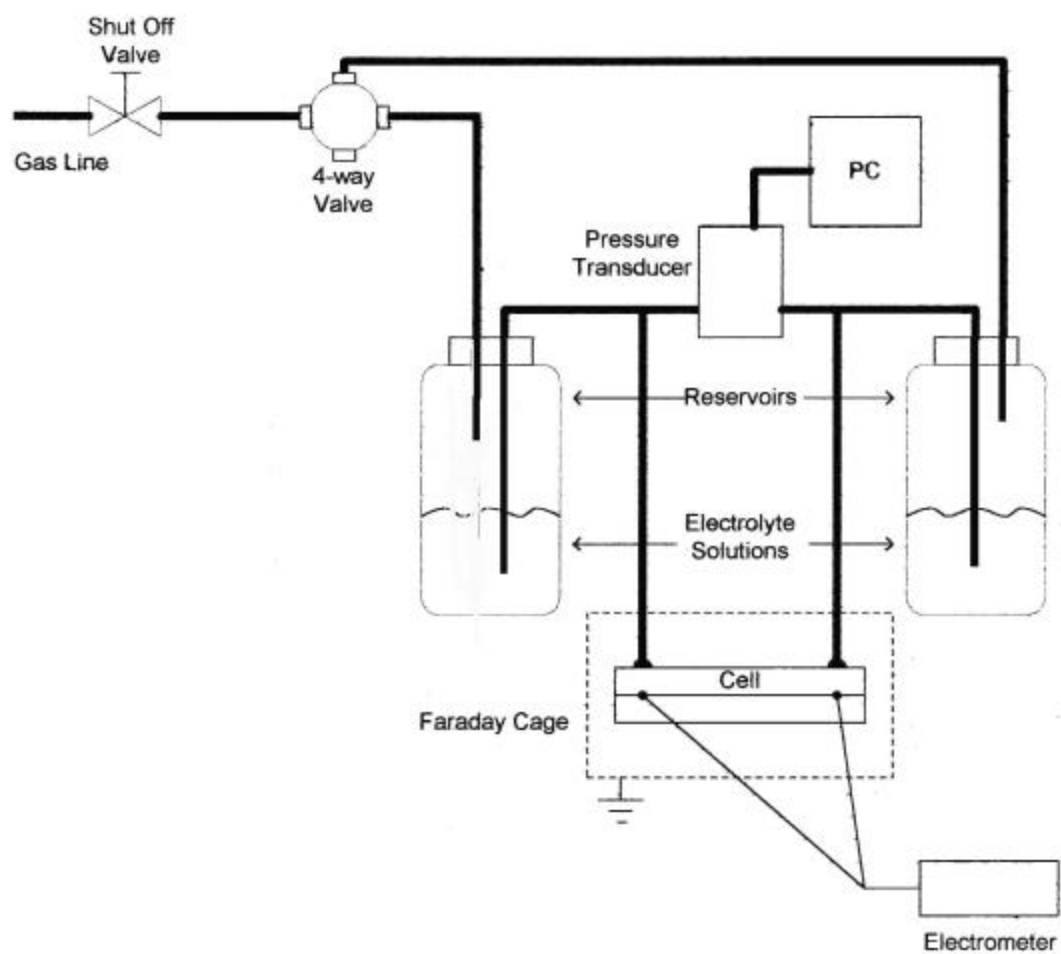


Figure A.3. Schematic of the experimental setup for measuring streaming potential.

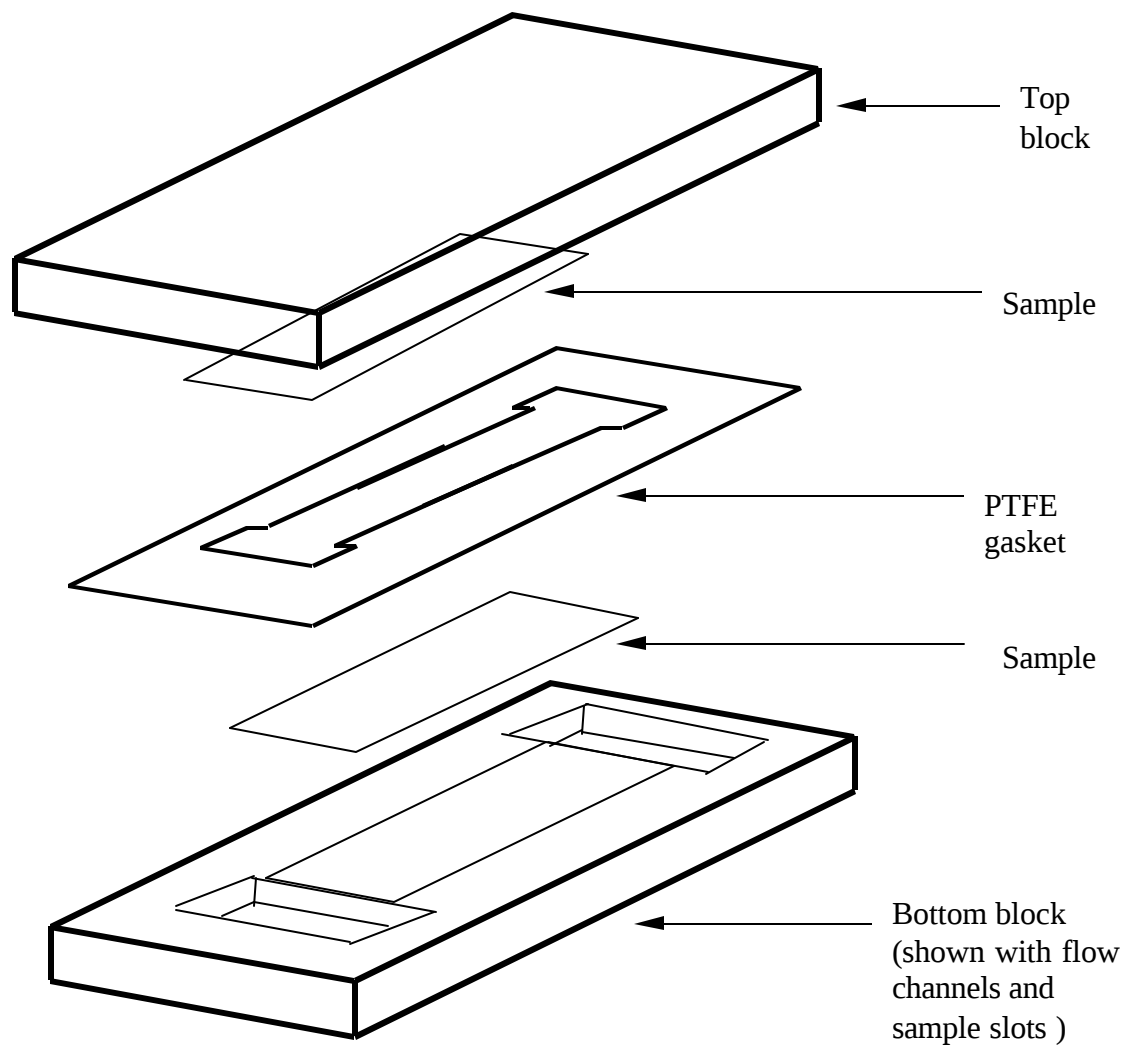


Figure A.4. Cell block, sample and gasket assembly for the streaming potential cell.

Table A.1. Physical parameters along with units used in the zeta potential calculation

Quantity	Symbol	Value	Units
Viscosity	η	0.000105	Pa.s
Dielectric constant	κ	72.4	-
Fluid Density	ρ	1000	Kg/m ³
Specific conductivity	ρ	Variable	$\mu/\Omega\text{cm}$

The procedure for any experiment was as follows. The streaming cell and all associated glassware were cleaned by copious washings with de-ionized water. The samples were then mounted in the cell and the gasket was placed between the two cell halves. The whole assembly was then clamped together to provide a water tight seal. The inlet and outlet electrolyte lines were connected. Ag/AgCl electrodes were mounted in the cell after equilibration for 30 minutes in 1×10^{-3} M KCl. The electrolyte flow was started and all bubbles trapped in the cell were removed by frequent flow reversals. The pressure transducer was then zeroed out. The electrometer was connected to the electrodes and the Faraday cage was placed on top of the cell. The flow was then started at a set pressure and the streaming potential reading from the electrometer was noted. After 30 seconds the pressure was increased and the new reading was noted. This process was continued till at least 8 measurements were made. The data set of pressure and streaming potential was then plotted and a linear regression was fitted to the points. The line fit was assessed by its intercept (ideally = zero) and the R^2 value. If the intercept was smaller than 5% of the maximum streaming potential value obtained the fit was accepted. Usually a good fit to the data was obtained for all the samples tested with deviations usually being associated with drift in the electrodes. The slope of the line was then used to calculate the zeta potential.

Flow Analysis of the Streaming Potential Cell

The zeta potential equation for flow through a rectangular capillary is based on the flow between two parallel plates [152]. The flow system consists of two parallel plates (as shown in Figure A.5) of length L , width w , separated by a distance $2h$ where $L \gg w \gg 2h$. The analysis is based on the assumption of Poiseuille conditions i.e. the flow is steady, incompressible, laminar and established.

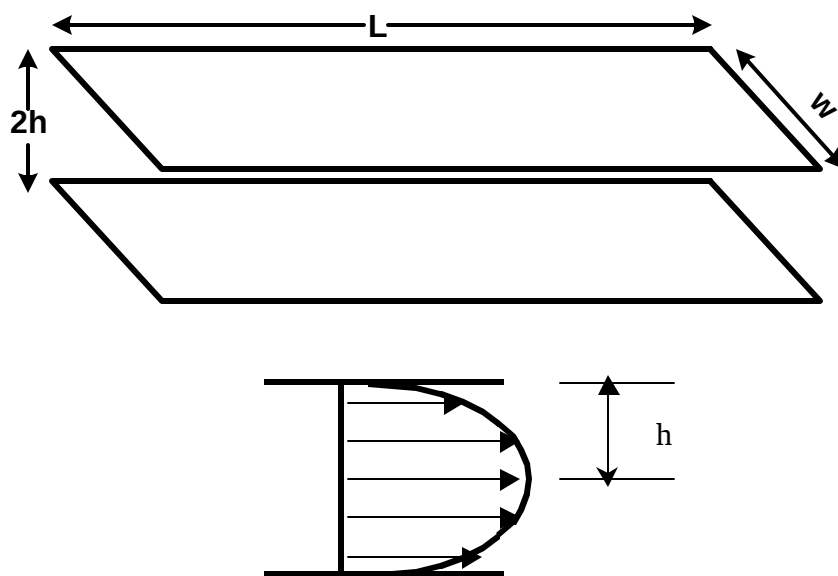


Figure A.5. Schematic representation of the parallel plate flow system and the velocity profile.

The Reynolds number for a rectangular capillary is then calculated using the equation

$$Re = r \times \frac{Q}{(w + 2h)h} \quad (2)$$

where Q is the volumetric flow rate, ρ is the fluid density, η is the dynamic viscosity, w is the width of the flow channel and h is half the distance between the parallel plates.

The flow rate was measured by collecting the electrolyte volume flowing through the outlet port of the cell in 30 sec at a set pressure. Figure A.6 shows the plot of pressure vs. flow rate. As can be seen in the figure the flow rate linearly increases with pressure.

The Reynold's number is plotted in figure A.7 by using equation 2. The plot shows that Re reaches a maximum of 757 for the highest flow rate achieved. Since the Re limit for laminar flow is 2300, every experimental pressure used produced laminar flow. van Wagenen and Andrade [152], and Bowen [154] have also suggested the need to have established as well as laminar flow. Fluid flow requires a minimum length to develop an equilibrium flow profile. It has been shown that if this entrance length (L_e) is greater than 10% of the total capillary length L , the measured value of the streaming potential will be lower than its true value. The equation given below was used to calculate the entrance length.

$$Le = 0.026 \times h \times Re \quad (3)$$

Figure A.8 shows the plot of L_e vs. Re . It is seen that at its highest value L_e is only 7.5% of L (0.075 m). Thus from the above analysis, the pressure range which produced laminar, established flow was found. This pressure range was adhered to in all the experiments reported.

Streaming Cell Calibration

Fused silica slides were used for calibrating the streaming cell. Fused silica is a widely used material in colloid science for zeta potential measurements. Zeta potentials

for this surface have been reported by different techniques including electrophoresis, streaming potential and titration.

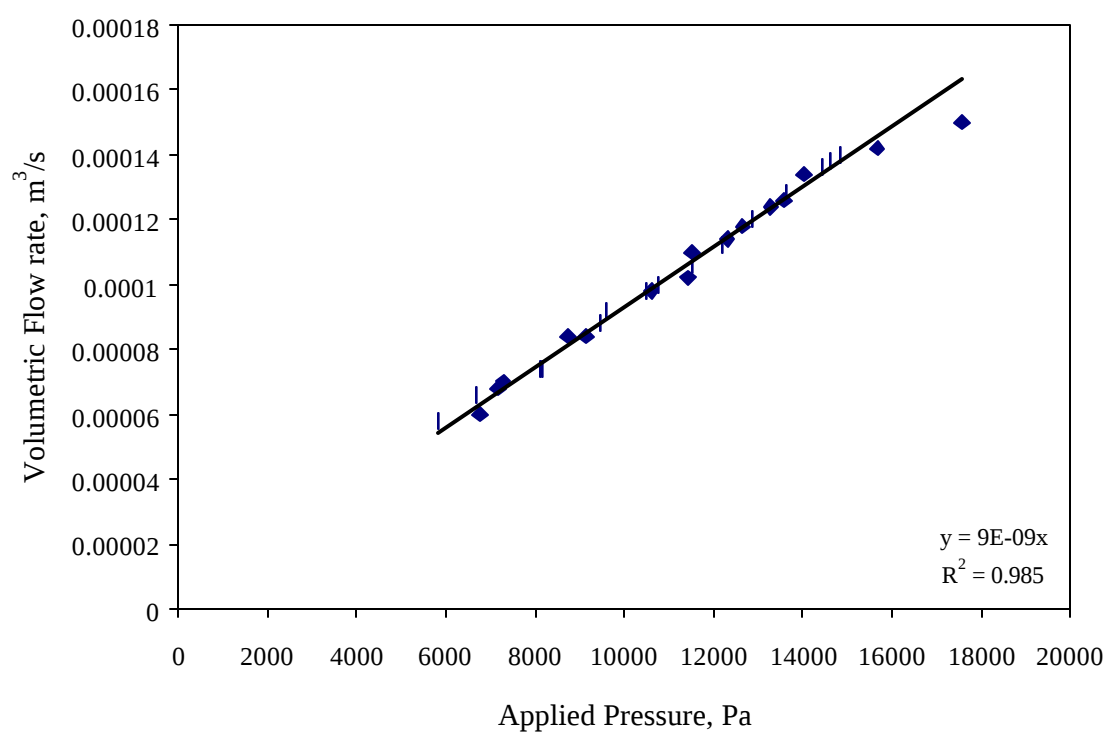


Figure A.6. Volumetric flow rate as a function of driving pressure for the streaming

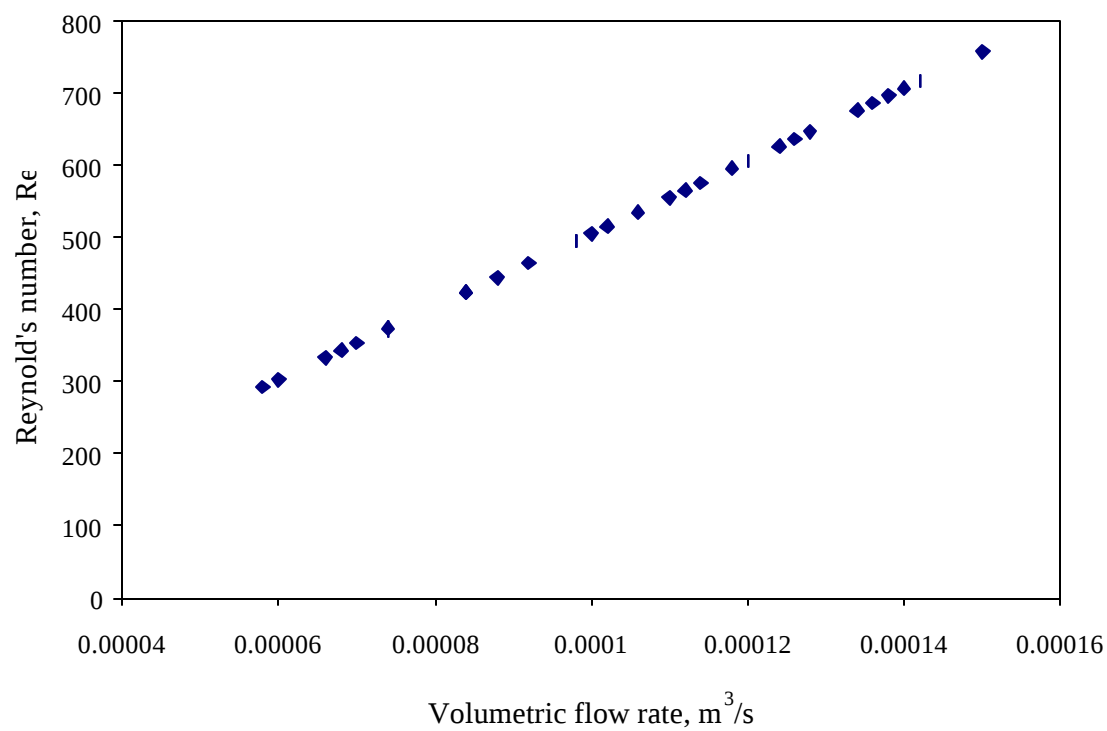


Figure A.7. Reynold's number as calculated from equation 2 for the streaming potential cell indicating that the flow is laminar under all experimental conditions.

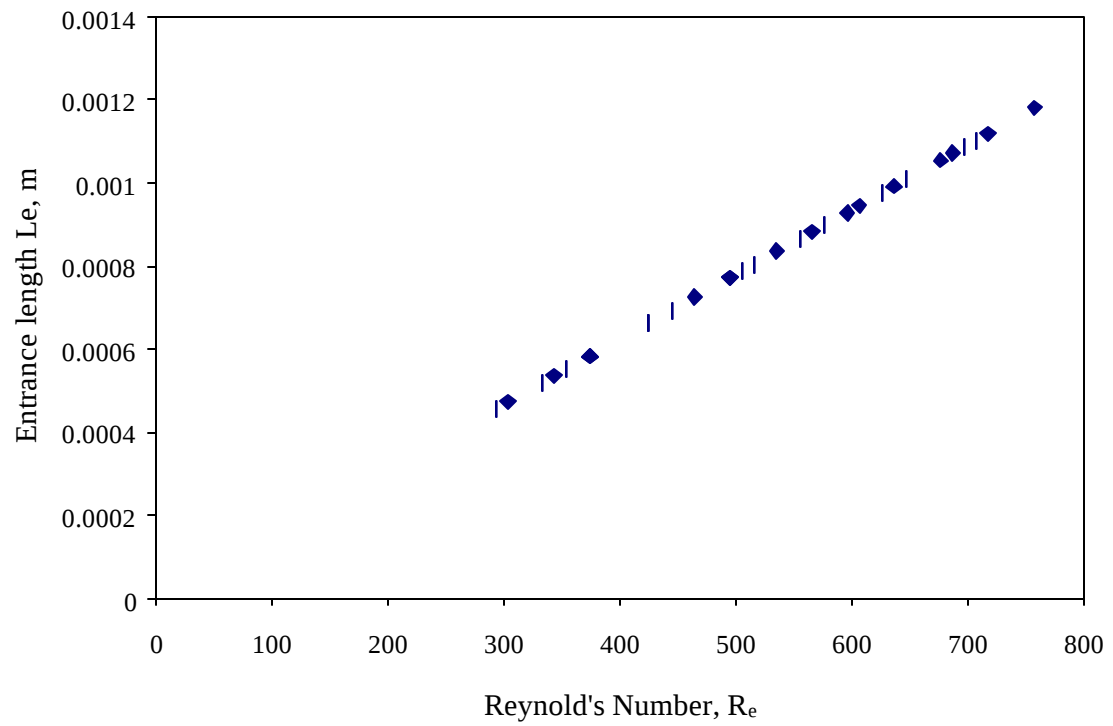


Figure A.8. Entrance length as a function of Re as calculated from equation 3.

The streaming cell was tested over a large pH range and the results compared to literature values. Figure A.9 shows the zeta potential vs. pH trend for fused silica at 1×10^{-3} M KCl as measured by two different operators over a 6 month timespan. The trend seen in the figure has been reported by other workers in this field i.e. the zeta potential increases in the negative direction with increasing pH. However absolute values of zeta potential at a certain pH are different than literature values. Scales *et al.* [153] published much higher values (-120 mV at pH 9) for silica in a streaming cell setup similar to the one used here. Habeger has reported a value of -22 mV at pH 5.7 for quartz using a similar streaming cell setup [155]. Habeger also reported a value of -16 mV at pH 6.8 for the same quartz material using a Brookhaven Instruments commercial streaming potential analyzer. Both these values are lower than those measured in the above setup. Thus examining the literature values for fused silica, it is believed that the values obtained using the above streaming cell are valid.

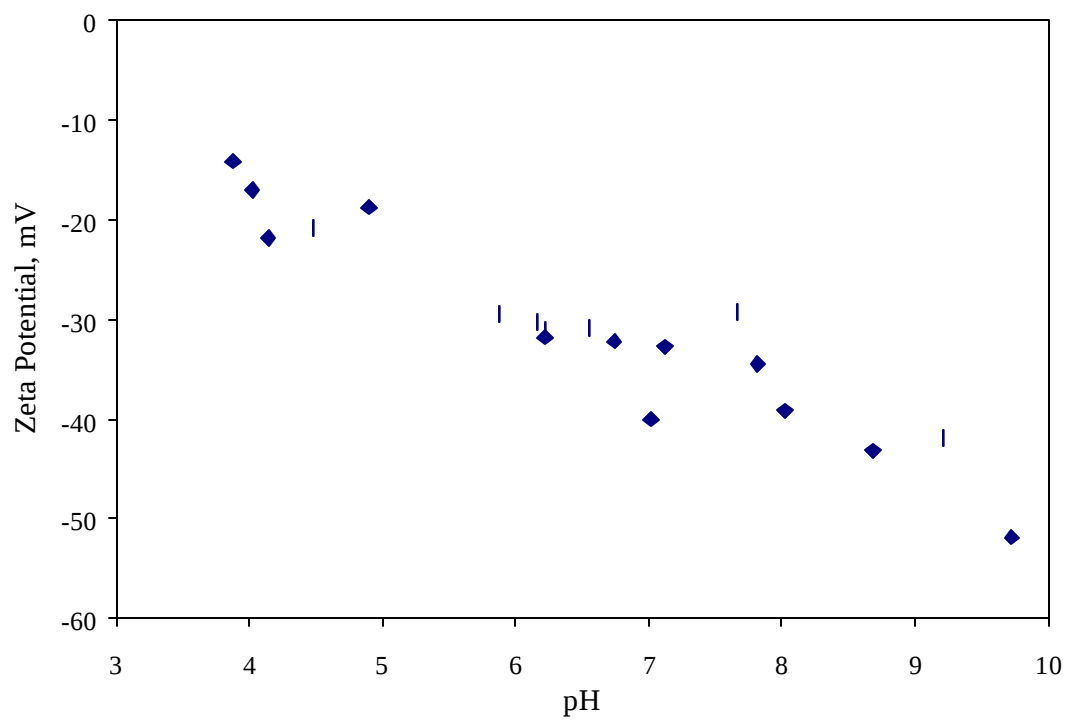


Figure A.9. Zeta potential vs. pH trend for fused silica substrates.

LIST OF REFERENCES

1. Zollikofer CL, Antonucci F, Stuckmann G, Mattias P, Salomonowitz EK: Historical overview on the development and characteristics of stents and future outlooks. *Cardiovasc Intervent Radiol* 1992; 15(5): 272-8.
2. Schatz RA, Palmaz JC, Tio FO, Garcia F, Garcia O, Reuter SR: Balloon-expandable intracoronary stents in the adult dog. *Circulation* 1987; 76(2): 450-7.
3. Oesterle SN, Whitbourn R, Fitzgerald PJ, et al.: The stent decade: 1987 to 1997. Stanford Stent Summit. *Am Heart J* 1998; 136(4 Pt 1): 578-99.
4. Ratner BD, Hoffman AS: Thin Films, Grafts and Coatings. In: Ratner BD, Hoffman AS, Schoen FJ, et al., eds. *Biomaterials Science, An Introduction to Materials In Medicine*. London, UK: Academic Press, 1996; p105.
5. Serruys PW, de Jaegere P, Kiemeneij F, et al.: A comparison of balloon-expandable-stent implantation with balloon angioplasty in patients with coronary artery disease. Benestent Study Group [see comments]. *N Engl J Med* 1994; 331(8): 489-95.
6. Fischman DL, Leon MB, Baim DS, et al.: A randomized comparison of coronary-stent placement and balloon angioplasty in the treatment of coronary artery disease. Stent Restenosis Study Investigators [see comments]. *N Engl J Med* 1994; 331(8): 496-501.
7. Topol EJ, Investigators fE: Randomised placebo-controlled and balloon-angioplasty-controlled trial to assess safety of coronary stenting with use of platelet glycoprotein-IIb/IIIa blockade. *Lancet* 1998; 352: 87-92.
8. Nath FC, Muller DW, Ellis SG, et al.: Thrombosis of a flexible coil coronary stent: frequency, predictors and clinical outcome. *J Am Coll Cardiol* 1993; 21(3): 622-7.
9. Makkar RR, Litvack F, Eigler NL, et al.: Effects of GP IIb/IIIa receptor monoclonal antibody (7E3), heparin, and aspirin in an ex vivo canine arteriovenous shunt model of stent thrombosis. *Circulation* 1997; 95(4): 1015-21.
10. Kottke-Marchant K: Thrombosis and Restenosis with Intracoronary Stents: In-vitro, In-vivo and Explant Perspectives. Society for Biomaterials, Annual Meeting, San Diego, 1998.
11. Peng T, Gibula P, Yao KD, Goosen MF: Role of polymers in improving the results of stenting in coronary arteries. *Biomaterials* 1996; 17(7): 685-94.

- 12.** Ozaki Y, Violaris AG, Serruys PW: New stent technologies. *Prog Cardiovasc Dis* 1996; 39(2): 129-40.
- 13.** Popma JJ, Lansky AJ, Ito S, Mintz GS, Leon MB: Contemporary stent designs: technical considerations, complications, role of intravascular ultrasound, and anticoagulation therapy. *Prog Cardiovasc Dis* 1996; 39(2): 111-28.
- 14.** Rogers C, Edelman ER: Endovascular stent design dictates experimental restenosis and thrombosis. *Circulation* 1995; 91(12): 2995-3001.
- 15.** De Scheerder IK, Wilczek KL, Verbeken EV, et al.: Biocompatibility of biodegradable and nonbiodegradable polymer-coated stents implanted in porcine peripheral arteries. *Cardiovasc Intervent Radiol* 1995; 18(4): 227-32.
- 16.** Lincoff AM, Furst JG, Ellis SG, Tuch RJ, Topol EJ: Sustained local delivery of dexamethasone by a novel intravascular eluting stent to prevent restenosis in the porcine coronary injury model. *J Am Coll Cardiol* 1997; 29(4): 808-16.
- 17.** Schwartz RS, Huber KC, Edwards WD: Native fibrin film as a biocompatible, absorbable material for intracoronary stent implant and drug delivery. *J. Am. Coll. Cardiol.* 1992; 19: 171A.
- 18.** Zheng H, Barragan P, Corcos T, et al.: Clinical experience with a new biocompatible phosphorylcholine-coated coronary stent. *J Invasive Cardiol* 1999; 11(10): 608-614.
- 19.** Whelan DM, van der Giessen WJ, Krabbendam SC, et al.: Biocompatibility of phosphorylcholine coated stents in normal porcine coronary arteries. *Heart* 2000; 83(3): 338-45.
- 20.** van der Giessen WJ, Lincoff AM, Schwartz RS, et al.: Marked inflammatory sequelae to implantation of biodegradable and nonbiodegradable polymers in porcine coronary arteries [see comments]. *Circulation* 1996; 94(7): 1690-7.
- 21.** De Scheerder I, Wang K, Wilczek K, et al.: Experimental study of thrombogenicity and foreign body reaction induced by heparin-coated coronary stents. *Circulation* 1997; 95(6): 1549-53.
- 22.** Hardhammar PA, van Beusekom HM, Emanuelsson HU, et al.: Reduction in thrombotic events with heparin-coated Palmaz-Schatz stents in normal porcine coronary arteries. *Circulation* 1996; 93(3): 423-30.
- 23.** Aggarwal RK, Ireland DC, Azrin MA, Ezekowitz MD, de Bono DP, Gershlick AH: Antithrombotic potential of polymer-coated stents eluting platelet glycoprotein IIb/IIIa receptor antibody. *Circulation* 1996; 94(12): 3311-7.

- 24.** Heublein B, Pethig K, Elsayed AM: Silicon Carbide Coating: A semiconducting hybrid design of coronary stents: A feasibility study. *J Invasive Cardiol* 1998; 10(5): 255-262.
- 25.** Heublein B, Ozbek C, Pethig K: Silicon carbide-coated stents: clinical experience in coronary lesions with increased thrombotic risk. *J Endovasc Surg* 1998; 5(1): 32-6.
- 26.** Lahann J, Klee D, thelen H, Bienert H, Vorwerk D, Hocker H: Improvement of haemocompatibility of metallic stents by polymer coating. *J Mater Sci: Materials in Medicine* 1999; 10(7): 443-448.
- 27.** Fischell TA, Hehrlein C: The radioisotope stent for the prevention of restenosis. *Herz* 1998; 23(6): 373-9.
- 28.** Hehrlein C, Kubler W: Advantages and limitations of radioactive stents. *Semin Interv Cardiol* 1997; 2(2): 109-13.
- 29.** Durairaj A, Faxon DP: The ARTISTIC and ARREST Trials. *J Invasive Cardiol* 2000; 12(1): 44-49.
- 30.** Srinivasan R, Leigh WJ: Ablative photodecomposition: Action of the far-ultraviolet (193 nm) laser radiation on poly(ethylene terephthalate) films. *J Am Chem Soc* 1982; 104: 6784-6785.
- 31.** Srinivasan R: Ablation of polymers and biological tissue by ultraviolet lasers. *Science* 1986; 234: 559-565.
- 32.** Andrew JE, Dyer PE, Key PH: Direct etching of polymeric materials using a XeCl laser. *Appl Phys Lett* 1983; 43(8): 717-719.
- 33.** Srinivasan R, Braren B, Seeger DE, Dreyfus RW: Photochemical cleavage of a polymeric solid: Details of the ultraviolet laser ablation of poly(methyl methacrylate) at 193 and 248 nm. *Macromolecules* 1986; 19: 916-921.
- 34.** Srinivasan R, Mayne-Barton V: Self-developing photoetching of poly(ethylene terephthalate) films by far-UV excimer laser radiation. *Appl Phys Lett* 1982; 41(6): 576-578.
- 35.** Heitz J, Arenholz E, Bauerle D, Hibst H, Hagemeyer A, Cox G: Dendritic surface structures on excimer-laser irradiated PET foils. *Appl Phys A* 1993; 56: 329-333.
- 36.** Hansen SG, Robitaille TE: Formation of polymer films by pulsed laser evaporation. *Appl Phys Lett* 1988; 52(1): 81-83.

- 37.** Srinivasan R, Braren B: Ablative Photodecomposition of Polymers by UV Laser Radiation. In: Fouassier J-P, Rabek JF, eds. *Lasers in Polymer Science and Technology : Applications*, vol 3. Boca-Raton, Florida, USA: CRC Press, 1990; 134-179.
- 38.** Lazare S, Granier V: Excimer laser light induced ablation and reaction at polymer surfaces measured with a quartz-crystal microbalance. *J Appl Phys* 1988; 63(6): 2110-2115.
- 39.** Dyer PE, Oldershaw GA, Schudel D: XeCl laser ablation of polyetheretherketone. *Appl Phys B* 1990; 51: 314-316.
- 40.** Costelo A, Garcia-Moreno I, Florido F, et al.: Laser ablation of polymeric materials at 157 nm. *J Appl Phys* 1995; 77(6): 2343-2349.
- 41.** Chirila TV, van Saarloos PP: Ablation of poly(2-hydroxyethyl methacrylate) by 193-nm excimer laser radiation. *J Appl Polym Sci* 1992; 44: 1355-1363.
- 42.** Burns FC, Cain SR: The effect of pulse repetition rate on laser ablation of polyimide and polymethylmethacrylate based polymers. *J Phys D: Appl Phys* 1995; 1349-1355.
- 43.** Brannon JH, Scholl D, Kay E: Ultraviolet Photoablation of a Plasma-Synthesized Fluorocarbon Polymer. *Appl Phys A* 1990; A52: 160-166.
- 44.** Itaya A, Kurahashi A, Masuhara H: Fluorescence characterization of ablated polymeric materials: Poly(methyl methacrylate) doped with 1-ethylpyrene. *J Appl Phys* 1990; 67(5): 2240-2244.
- 45.** Kalontarov LI: Mechanism of laser-induced ablation of polymeric solids. *Phil Mag Lett* 1991; 63(5): 289-294.
- 46.** D'Couto GC: Experimental and Theoretical Investigation of The Excimer Laser Ablation Process [PhD]. Clarkson University; 1993.
- 47.** Koren G, Yeh JTC: Emission spectra, surface quality and mechanism of excimer laser etching of polyimide films. *Appl Phys Lett* 1984; 44: 1112.
- 48.** Koren G, Yeh JTC: Emission spectra and etching of polymers and graphite irradiated by excimer lasers. *J Appl Phys* 1984; 56: 2120.
- 49.** Davis GM, Gower MC, Fotakis C, Efthimiopoulos T, Argyrakis P: Spectroscopic studies of ArF laser photoablation of PMMA. *Appl Phys Lett* 1985; 46: 828.
- 50.** Dyer PE, Sidhu J: Excimer laser ablation and thermal coupling efficiency to polymer films. *J Appl Phys* 1985; 57: 1420.

- 51.** Gorodetsky G, Kazyaka TG, Mecher RL, Srinivasan R: Calorimetric and acoustic study of ultraviolet laser ablation of polymers. *Appl Phys Lett* 1985; 46: 828.
- 52.** Dyer PE, Srinivasan R: Nanosecond photoacoustic studies on ultraviolet laser ablation of organic polymers. *Appl Phys Lett* 1986; 48: 445.
- 53.** Venugopalan V: The thermodynamic response of polymers and biological tissues to pulsed laser irradiation [PhD]. Massachusetts Institute of Technology; 1994.
- 54.** von Gutfield RJ, McDonald FA, Deyfus RW: Surface deformation measurements following excimer laser irradiation of insulators. *Appl Phys Lett* 1986; 49: 1059.
- 55.** Krajnovich DJ: Incubation and photoablation of poly(methyl methacrylate) at 248 nm. New insight into the reaction mechanism using photofragment translational spectroscopy. *J Phys Chem* 1997; 101: 2033-2039.
- 56.** Krajnovich DJ, Vazquez JE: Formation of "intrinsic" surface defects during 248 nm photoablation of polyimide. *J Appl Phys* 1993; 73(6): 3001-3008.
- 57.** Hansen SG, Robitaille TE: Arrival time measurements of films formed by pulsed laser evaporation of polycarbonate and selenium. *J Appl Phys* 1988; 64(4): 2122-2129.
- 58.** Blanchet GB: Deposition of amorphous fluoropolymers thin films by laser ablation. *Appl Phys Lett* 1993; 62(5): 479-481.
- 59.** Blanchet GB, Fincher Jr. CR, Jackson CL, Shah SI, Gardner KH: Laser ablation and the production of polymer films. *Science* 1993; 262: 719-721.
- 60.** Ueno Y, Fujii T, Kannari F: Deposition of fluoropolymer thin films by vacuum-ultraviolet laser ablation. *Appl Phys Lett* 1994; 65(11): 1370-1372.
- 61.** Norton MG, Jiang W, Dickinson JT: The morphology of polytetrafluoroethylene (PTFE) thin films formed by pulsed-laser deposition. *Materials Research Society Symposium Proceedings*, 1995.
- 62.** Metal M, Myslik V, Jelinek M: Deposition of thin polymer films by pulsed excimer laser ablation. *Proceedings of SPIE*, 1995.
- 63.** Li ST, Heitz AJ, Bauerle D: Pulsed-laser deposition of crystalline Teflon (PTFE) films. *Appl Surf Sci* 1998; 125: 17-22.
- 64.** Blanchet GB: Deposition of poly(methyl methacrylate) films by UV laser ablation. *Macromolecules* 1995; 28: 4603-4607.
- 65.** Blanchet GB, Fincher J, C. R.: Thin-film fabrication by laser ablation of addition polymers. *Adv Mater* 1994; 6(11): 881-887.

- 66.** Suzuki M, Nakata Y, Nagai H, Goto K, Nishimura O, Okutani T: Synthesis of silicon-based polymer films by UV laser ablation deposition of poly(methylphenylsilane). *Mater Sci Eng* 1998; A 246: 36-44.
- 67.** Nishio S, Chiba T, Matsuzaki A, Sato H: Preparation of polymer films by laser ablation of polyacrylonitrile: significant dependence on ablation wavelengths. *Appl Surf Sci* 1996; 106: 132-136.
- 68.** Kale S, B. OS, Jog JP, Nadkarni VM: Deposition of polyphenylene sulphide (PPS) polymer by pulsed excimer laser ablation. *Mater Lett* 1992; 15: 260-263.
- 69.** Das A, Bera S, Joseph M, Sivakumar N, Patnaik A: Deposition and characterization of laser ablated poly(p-phenylene sulfide) thin films. *Appl Surf Sci* 1998; 135: 37-45.
- 70.** Manoravi P, Joseph M, Sivakumar N: Pulsed laser ablation-thin film deposition of polyethylene oxide. *J Phys Chem of Solids* 1998; 59(8): 1271-1277.
- 71.** Conklin JA, Cotell CM: Pulsed laser deposition of collagen and apatite/collagen composite biocompatible thin films. *Advances in Coating Technologies for Surface Engineering*, Orlando, FL, 1997.
- 72.** Tsuboi Y, Goto M, Itaya A: Thin film formation of a protein by laser ablation deposition technique. *Chem Lett* 1998: 521-522.
- 73.** Phadke RS, Agarwal G: Laser-assisted deposition of preformed mesoscopic systems. *Mater Sci Eng* 1998; C 5: 237-241.
- 74.** Agarwal G, Phadke RS: Laser assisted deposition of supramolecular organizes on solid surfaces. *Mater Sci Eng* 1998; C 6: 13-17.
- 75.** Latsch S, Hiraoka H, Bargon J: Metal deposition on laser modified teflon surfaces. *Materials Research Society Symposium Proceedings*, 1995.
- 76.** Okoshi M, Murahara M: Area-selective nucleation of copper on fluorocarbon-resin surface using ArF excimer laser-induced chemical modification. *Appl Phys Lett* 1998; 72: 2616-2618.
- 77.** Niino H, Yabe A: Formation of conjugated polyene and polyyne structure by KrF excimer laser-induced dehydrochlorination on polyvinylidene chloride film. *J Polym Sci: Part A: Polym Chem* 1998; 36: 2483-2487.
- 78.** Song Q, Netravali AN: Excimer laser surface modification of ultra-high strength polyethylene fibers for enhanced adhesion with epoxy resins. Part 1. Effect of laser operating parameters. *J Adhesion Sci Tech* 1998; 12(9): 957-982.

- 79.** Brannon J, Snyder C: Pulsed 532 nm laser wirestripping : Removal of dye-doped polyurethane insulation. *Appl Phys A* 1994; A59: 73-78.
- 80.** Brannon J: Excimer Laser Ablation and Etching. *IEEE Circuits and Devices* 1997; 13(2): 11-18.
- 81.** Ozdemir M, Sadikoglu H: A new and emerging technology: Laser-induced surface modification of polymers. *Trends in Food Sci Technol* 1998; 9: 159-167.
- 82.** Hiraoka H, Sendova M, Lee C-H, et al.: Pulsed UV-Laser applications for surface science : Nano-structure fabrication to diamond deposition. *Laser Techniques for Surface Science II* San Diego, CA, USA 19950712-19950714, San Diego , California, 12-14 July , 1995, 1995.
- 83.** Kendrick TC, Parbhoo B, White JW: Siloxane Polymers and Copolymers. In: Patai S, Rappaport Z, eds. *The Chemistry of Organic Silicon Compounds*: John Wiley and Sons, 1989; 1289-1361.
- 84.** Tiffany JS, Petraitis DJ: Silicone Biomaterials. In: Wise DL, Trantolo DJ, Altobelli DE, et al., eds. *Encyclopedic Handbook of Biomaterials and Bioengineering , Part A: Materials*, vol 1: Marcel Dekker, Inc., 1995; 1675-1691.
- 85.** Hergenrother RW, Yu XH, Cooper SL: Blood-contacting properties of polydimethylsiloxane polyurea-urethanes. *Biomaterials* 1994; 15(8): 635-40.
- 86.** Lin JC, Cooper SL: Surface characterization and ex vivo blood compatibility study of plasma-modified small diameter tubing: effect of sulphur dioxide and hexamethyldisiloxane plasmas. *Biomaterials* 1995; 16(13): 1017-23.
- 87.** Silver JH, Hergenrother RW, Lin JC, et al.: Surface and blood-contacting properties of alkylsiloxane monolayers supported on silicone rubber. *J Biomed Mater Res* 1995; 29(4): 535-48.
- 88.** Silver JH, Lin JC, Lim F, Tegoulia VA, Chaudhury MK, Cooper SL: Surface properties and hemocompatibility of alkyl-siloxane monolayers supported on silicone rubber: effect of alkyl chain length and ionic functionality. *Biomaterials* 1999; 20(17): 1533-43.
- 89.** Wrobel AM, Wertheimer MR: Plasma-Polymerized Organosilicones and Organometallics. In: D'Agostino R, ed. *Plasma Deposition, Treatment and Etching of Polymers*. Bari, Italy: Academic Press, 1990; 163-268.
- 90.** Wertheimer MR, Klemberg-Sapieha JE, Schreiber HP: Advances in basic and applied aspects of microwave plasma polymerization. *Thin Solid Films* 1984; 115: 109-124.

- 91.** Kwan CM, Gleason KK: Pyrolytic CVD of Poly(organosiloxane) Thin Films. *Chem Vpr Dep* 1997; 3(6): 299-301.
- 92.** Roth W, Hoffmann KW, Kurz W: Laser-induced generation of thin silicone layers with high chemical and spectral purity. *J Polym Sci: Part A: Polym Chem* 1994; 32: 1893-1898.
- 93.** Bourbigot S, Jama C, Le Bras M, Delobel R, Dessaux O, Goudmand P: New approach to flame retardancy using plasma assisted surface polymerisation techniques. *Polym Degrad Stab* 1999; 66(1): 153-155.
- 94.** Nakamura T: Passivation effects of plasma polymerized films from organosilicon compounds on ceramic high temperature superconductors. *Kobunshi Ronbunshu/Jpn J Polym Sci Technol* 1995; 52(5): 249-257.
- 95.** Fitz-Gerald JM: Synthesis and characterization of engineered particulates with controlled surface architecture. [PhD]. University of Florida; 1998.
- 96.** Noll W: *Chemistry and Technology of Silicones*. New York: Academic Press, 1968.
- 97.** Rau C, Kulisch W: Mechanisms of plasma polymerization of various silico-organic monomers. *Thin Solid Films* 1994; 249: 28-37.
- 98.** Morra M, Occiello E, Garbassi F: The effect of plasma-deposited siloxane coatings on the barrier properties of HDPE. *J Appl Polym Sci* 1993; 43: 1331-1340.
- 99.** Singh RK: Target ablation characteristics during pulsed laser deposition of thin films. *J Non-Cryst Solids* 1994; 178: 199-209.
- 100.** Srinivasan R, Braren B, Casey KG: Nature of the "incubation pulses" in the ultraviolet laser ablation of polymethyl methacrylate. *J Appl Phys* 1990; 68(4): 1842-1847.
- 101.** Schulz W: Nanotechnology: The Next Big Thing. *Chem Eng News* 2000; 78(18): 41-47.
- 102.** Whitehead AJ, Page TF: Nanoindentation studies of thin film coated systems. *Thin Solid Films* 1992; 220: 277-283.
- 103.** Lawson NS, Ion RH, Pollock HM, Hourston DJ, Reading M: Characterising polymer surfaces-nanoindentation, surface force data, calorimetric microscopy. *Physica Scripta* 1994; T55: 199-205.
- 104.** Kuhn L: *The Triboscope Nanomechanical Testing System*. Company Manual, Hysitron Inc., Minneapolis, MN, 1999.

- 105.** Labour T, Ferry L, Gauthier C, Hajji P, Vigier G: α - and β -crystalline forms of Isotactic Polypropylene Investigated by Nanoindentation. *J Appl Polym Sci* 1999; 74: 195-200.
- 106.** Poilane C, Delobelle P, Bornier L, Mounaix P, Melique X, Lippens D: Determination of the mechanical properties of thin polyimide films deposited on a GaAs substrate by bulging and nanoindentation tests. *Mater Sci Eng A* 1999; 262: 101-106.
- 107.** Grau P, Meinhard H, Mosch S: Nanoindentation experiments on glass and polymers at different loading rates and the power law analysis. *Fundamentals of Nanoindentation and Nanotribology*, San Francisco, CA, USA, 1998.
- 108.** Strony A, Gerberich WW: Experimental analysis of viscoelastic behavior in nanoindentation. *Fundamentals of Nanoindentation and Nanotribology*, San Francisco, CA, USA, 1998.
- 109.** Cheng L, Scriven LE, Gerberich WW: Viscoelastic analysis of micro- and nanoindentation. *Fundamentals of Nanoindentation and Nanotribology*, San Francisco, CA, USA, 1998.
- 110.** Xia X, Strony A, Scriven LE, Gerberich WW, Tsou A, Anderson CC: Constitutive property evaluation of polymeric coatings using nanomechanical methods. *Fundamentals of Nanoindentation and Nanotribology*, San Francisco, CA, USA, 1998.
- 111.** Turnbull A, White D: Nanoindentation and microindentation of weathered unplasticised poly-vinyl chloride (UPVC). *J Mater Sci* 1996; 31(16): 4189-4198.
- 112.** Strojny A, Xia X, Tsou A, Gerberich WW: Techniques and considerations for nanoindentation measurements of polymer thin films constitutive properties. *J Adhesion Sci Technol* 1998; 12(12): 1299-1321.
- 113.** Lucas BN, Rosenmayer CT, Oliver WC: Mechanical characterization of sub-micron polytetrafluoroethylene (PTFE) thin films. *Thin Films-Stresses and Mechanical Properties VII*, Boston, MA, USA, 1997.
- 114.** Asif SAS, Pethica JB: Nano-scale viscoelastic properties of polymer materials. *Thin Films-Stresses and Mechanical Properties VII*, Boston, MA, USA, 1998.
- 115.** Lundkvist A, Lilleodden E, Siekhaus W, Kinney J, Pruitt L, Balooch M: Viscoelastic properties of healthy human artery measured in saline solution by AFM-based Indentation technique. *Thin Films: Stresses and Mechanical Properties VI*, San Francisco, CA, USA, 1997.
- 116.** Chuang TJ, Hiraoka H, Modl A: Laser-photoetching characteristics of polymers with dopants. *Appl Phys A* 1988; A45(4): 277-288.

- 117.** Srinivasan R, Braren B: Ultraviolet laser ablation and etching of polymethyl methacrylate sensitized with an organic dopant. *Appl Phys A* 1988; A45(4): 289-292.
- 118.** Kuper S, Stuke M: Femtosecond UV excimer laser ablation. *Appl Phys Lett* 1989; 54: 4.
- 119.** Srinivasan R, Sutcliffe E, Braren B: Dynamics of ultraviolet laser ablation of polymer surfaces. *Appl Phys Lett* 1987; 51: 1285.
- 120.** Jellinek HHG, Srinivasan R: Theory of etching of polymers by far-ultraviolet, high-intensity pulsed laser and long term irradiation. *J Phys Chem* 1984; 88: 3048-3051.
- 121.** Cain SR, Burns FC, Otis CE: On single-photon ablation of polymeric materials. *J Appl Phys* 1992; 71(9): 4107-4117.
- 122.** Kuper S, Modaressi S, Stuke M: Photofragmentation pathways of a PMMA model compound under UV excimer laser ablation conditions. *J Phys Chem* 1990; 94: 7514.
- 123.** Furzikov NP: Approximate theory of highly absorbing polymer ablation by nanosecond laser pulses. *Appl Phys Lett* 1990; 56(17): 1638-1640.
- 124.** Srinivasan R, Braren B, Casey KG, Yeh M: Ultrafast imaging of ultraviolet-laser ablation and etching of polymethylmethacrylate. *Appl Phys Lett* 1989; 55: 2790.
- 125.** Yasuda H: *Plasma Polymerization*. Orlando, FL: Academic Press, 1985.
- 126.** Beiderman H: Polymer films prepared by plasma polymerization and their potential application. *Vacuum* 1987; 37(3-4): 367-373.
- 127.** Lopez GP, Ratner BD: Substrate temperature effects on film chemistry in plasma deposition of organics. I. Nonpolymerizable precursors. *Langmuir* 1991; 7: 766-773.
- 128.** Kaplan S, Dilks A: Characterization of plasma-polymerized materials by modern spectroscopic techniques. *J Appl Polym Sci.* 1984; 38: 105.
- 129.** Ratner BD, Johnston EE: Surface characterization of plasma deposited organic thin films. *J. Elec. Spec. Rel. Phenom.* 1996; 81(3): 303-317.
- 130.** Gengenbach TR, Griesser HJ: Deposition conditions influence the postdeposition oxidation of methyl methacrylate plasma polymer films. *J Polym Sci: Part A: Polym Chem* 1998; 36: 985-1000.
- 131.** Zuri L, Narkis M, Silverstein MS: Film formation and crack development in plasma polymerized hexamethydisiloxane. *Polym Eng Sci* 1997; 37(7): 1188-1194.

- 132.** Mackie NM, Castner DG, Fisher ER: Characterization of pulsed-plasma-polymerized aromatic films. *Langmuir* 1998; 14(5): 1227-1235.
- 133.** Vickie Pan Y, Barrios EZ, Denton DD: In situ FTIR investigation of MMA plasmas, plasma-polymerized films, and reaction mechanisms. *J Polym Sci: Part A: Polym Chem* 1998; 36: 587-602.
- 134.** Yahiaoui A: Surface modification of intraocular lens polymers by hydrophilic graft polymerization for improved ocular implant biocompatibility [PhD]. University of Florida; 1990.
- 135.** Grace JM, Freeman DR, Corts R, Kosel W: Scale-up of a nitrogen glow-discharge process for silver-PET adhesion. *Proceedings of the 1996 39th Annual Technical Conference Philadelphia, PA, USA, 1996.*
- 136.** Wang TF, Yasuda HK: Modification of wettability of a stainless-steel plate by cathodic plasma polymerization of trimethylsilane-oxygen mixtures. *J Appl Polym Sci* 1995; 55: 903-909.
- 137.** van Ooij WJ, Sabata A, Zeik DB, Taylor CE, Boerio FJ, Clarson SJ: Metal surface preparation by plasma-polymerized films. *J Testing and Evaluation* 1995; 23(1): 33-40.
- 138.** Biagtan E: Effects of gamma radiation on polymer degradation and surface graft polymerization [PhD]. University of Florida; 1995.
- 139.** Amery DP: Hydrophilic surface modification of polymer vascular prostheses and metal endoluminal stents [PhD]. University of Florida; 1997.
- 140.** Sperling C, Koenig U, Hermel G, et al.: Immobilization of human thrombomodulin onto PTFE. *Journal of Materials Science: Mater in Med* 1997; 8(12): 789-791.
- 141.** Stille JK, Sung RL, Kooi V: The reaction of benzene in a radiofrequency glow discharge. *J Org Chem* 1965; 30: 3116-3119.
- 142.** Kobayashi H, Bell AT, Shen M: Plasma polymerization of saturated and unsaturated hydrocarbons. *Macromolecules* 1974; 3: 272.
- 143.** Chapiro A: Radiation Polymerization of Vinyl Monomers. *Radiation Chemistry of Polymeric Systems*. London, UK: John Wiley and Sons, 1962; 331.
- 144.** Decher G, Hong JD: Build-up of ultrathin multilayer films by a self-assembly process. 1. Consecutive adsorption of anionic and cationic bipolar amphiphiles on charged surfaces. *Makromol Chem, Makromol Symp* 1991; 46: 321.

- 145.** Hong JD, Lowack K, Schmitt J, Decher G: Layer-by-layer deposited multilayer assemblies of polyelectrolytes and proteins: from ultra thin films to protein arrays. *Prog Coll Polym Sci* 1993; 93: 98-102.
- 146.** Mueller-Schulte D, Horster FA: Radiation grafted polyethylene as carrier for protein immobilization- 1. Covalent immobilization of human serum albumin. *Polym Bull* 1982; 7(2-3): 77-81.
- 147.** Peters T: All About Albumin. London: Academic Press, 1996.
- 148.** Sawyer PN, Stanczewski B, Lucas TR, Srinivasan S, Ramasamy N, Kirschenbaum D: Physical Chemistry of the Vascular Interface. In: Sawyer PN, Kaplitt MJ, eds. *Vascular Grafts*. New York, NY: Appleton-Century-Crofts, 1977; 53-75.
- 149.** Krajewski A, Malavolti R, Piancastelli A: Albumin adhesion on some biological and non-biological glasses and connection with their Z-potentials. *Biomaterials* 1996; 17: 53-60.
- 150.** Schurz J, Erk G, Schempp W, Ribitsch V: Zeta potential as an analytical tool for graft copolymers and for polymer surfaces. *J Macromol Sci* 1990; A27(13-14): 1673-1692.
- 151.** Hunter RJ: Measuring surface charge and potential. *Introduction to Colloid Science*. Oxford, UK: Oxford University Press, 1993; p249.
- 152.** van Wagenen RA, Andrade JD: Flat plate streaming potential investigations: Hydrodynamics and electrokinetic equivalency. *J Coll Interface Sci* 1980; 76(2): 305-314.
- 153.** Scales PJ: Electrokinetics of the silica-solution interface. *Langmuir* 1992; 8(9): -974.
- 154.** Bowen JD: Streaming potential in the hydrodynamic entrance region of cylindrical and rectangular capillaries. *J Coll Interface Sci* 1985; 106: 367.
- 155.** Habeger CF: Measurement of adhesion between calcium oxalate monohydrate and model surfaces using a dynamic wet cell [PhD]. University of Florida; 1997.

BIOGRAPHICAL SKETCH

The author was born in the city of Pune, India. After completing his bachelor's degree in polymer engineering at the Maharashtra Institute of Technology he came to the United States for his master's degree. After discussions with and advice from Drs. Goldberg and Brennan, he switched to the doctoral program (a decision he has yet to regret). Upon the completion of his degree the author hopes to use his newfound knowledge and skills for the solution of urgent engineering problems, be they biomedical, polymeric or otherwise.

During his spare time the author enjoyed the usual graduate student activities of drinking beer (always), canoeing and hiking (sometimes). He hopes to continue these activities in the future with the addition of some new ones like learning a musical instrument or a foreign language. Always an avid reader, with a partiality to scientific fiction (as opposed to science fiction), he also someday hopes to write a novel.